To: all Reviewers of the ECOFRAM Aquatic Report.

From: Paul Hendley and Jeff Giddings.

May 4, 1999

This report is being sent out in Adobe™ PDF format to ensure that all pagination and diagrams remain consistent across platforms and software. In your reviews, please reference any comments by page number and line number and, if any more written material is issued (see below), by the version name from the header (in this case Aqex_ecofram_Peer01_may499.doc).

This report is being issued today in order to give you all a reasonable chance to get through such a long report before the June deadlines. However, as you will see, there are a few areas highlighted to indicate that more effort/material is needed from one of the authors. We apologize that the report is still a "work in progress" but do not believe that these minor incompletions are fundamental to your comprehension of the thinking behind ECOFRAM. If any significant new material is developed in the next 4 weeks, we will send you the information as a courtesy but would not expect you to review the material unless you wished.

As the senior editors, Jeff and I accept the responsibility for all errors and omissions but would like to acknowledge the hard work of the rest of the ECOFRAM aquatic workgroup members. Please do not hesitate to contact Jeff or I by email or phone to discuss questions that may occur to you.

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Thank you again for your willingness to review this package. We are looking forward to meeting you all in June.

Sincerely

Paul and Jeff.

ECOFRAM Aquatic Workgroup Co-chairs

ECOFRAM Aquatic Report

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2. ECOFRAM Aquatic Risk Assessment Process

This chapter provides an overview of the output from the ECOFRAM Aquatic Workgroups. Chapters 3 and 4 provide greater detail on the deliberations specific to the Aquatic Exposure and Aquatic Effects Workgroups respectively.

2.1. ECOFRAM History, Purpose, and Structure

The FIFRA Scientific Advisory Panel (SAP) met for three days, May 29-31, 1996, to address several scientific issues regarding the US Environmental Protection Agency (EPA) Office of Pesticide Programs' (OPP) ecological risk assessments and guidelines. One of the major topics explored with the Panel was OPP's ecological risk assessment methods and procedures. OPP provided two ecological assessment case studies for review and requested the Panel to comment on how OPP could improve the methods and procedures used in these case studies.

While recognizing and generally reaffirming the utility of the current assessment process and methods for screening, the Panel indicated that OPP's methods were deterministic for assessing the effects of pesticides and suggested moving to probabilistic assessments for the chemicals of concern. The Panel strongly encouraged OPP to develop and validate tools and methodologies to conduct probabilistic assessments of ecological risk. In addition, the Panel also identified several areas in the assessments that could be expanded to present a more complete characterization of the potential environmental risk for the pesticides examined. They also strongly encouraged field research to validate models used in the assessment process and to support any new models or methodologies that are developed.

To address the recommendations of the SAP and build on the work of earlier projects that had addressed aquatic risk assessment issues such as the 1994 Aquatic Risk Assessment and Mitigation Dialogue Group (SETAC 1994) and the 1992 Aquatic Effects Dialogue Group (RESOLVE 1992), the Environmental Fate and Effects Division (EFED) within OPP began a new initiative in 1997 to develop and validate tools and methodologies to conduct probabilistic assessments to address terrestrial and aquatic risk.

In recognition of the importance of involving stakeholders in redesigning its ecological risk assessment process, OPP EFED initiated several channels for external involvement in this initiative. This led to the formation of the Ecological Committee on FIFRA Risk Assessment Methods (ECOFRAM) which was charged specifically with conducting a primary review of the current assessment process and developing new tools and methodologies. The ECOFRAM was also asked to identify additional methods as well as developmental and validation needs to ensure that the assessment process supports environmental decisions that are scientifically defensible.

The ECOFRAM is divided into two workgroups: one for terrestrial assessment and one for aquatic. These workgroups are further divided into exposure and effects sub-groups. The ECOFRAM members are experts drawn from government agencies, academia, environmental groups, industry, and other stakeholders. Participants were selected based on expertise,

affiliation, availability and other relevant information to ensure that the appropriate disciplines are represented along with a cross-section of affiliations. A full list of participants in the two Aquatic Workgroups is shown in Appendix 2-1.

This report details the joint findings of the two Aquatic Workgroups.

2.2. Background

2.2.1. Earlier Recommendations for Improving Aquatic Risk Assessments

During the last few years, a number of initiatives have developed risk recommendations related to aquatic risk assessment. Probably the most significant amongst these was the Aquatic Risk Assessment and Mitigation Dialog Group (ARAMDG) which integrated the thinking of earlier groups and published a final report through SETAC in 1994 (SETAC 1994). The full recommendations from ARAMDG were extensive. Those most significant for risk assessment were:

a) Integrated probabilistic risk assessment approaches that include both the probability of exposure and magnitude of effects should be implemented within the OPP.

b) Improved capabilities for predictive risk assessments through tiered modeling and focused laboratory studies should be encouraged and, when conducted, should be included as part of the refined risk assessment.

c) Mitigation must provide meaningful ecological risk reduction, be pragmatic and achievable, and consider the need for timely decisions and cost-effective utilization of financial and human resources. In addition, mitigation should be consistent with other federal, regional, and state resource protection and pollution prevention initiatives.

d) The general trend whereby EPA is moving toward watershed/holistic approaches for risk assessment and risk management suggests a need for the incorporation of "landscape factors," via probabilistic risk assessments, into risk management decisions.

e) Risk managers must focus on developing a better understanding of the scientific principles governing risk assessment. The ability to make appropriate risk management decisions requires a basic understanding of the scientific components of risk assessment.

Clearly, many of these recommendations were highly relevant to the ECOFRAM process.

2.2.2. Rationale for Probabilistic Risk Assessment

Prior to the meeting with the SAP, OPP EFED had already begun to work toward probabilistic assessments. In addition to participating in the initiatives described in section 2.2.1, EFED had internal efforts as well. The first probabilistic aquatic exposure assessment using mechanistic environmental fate models was completed in 1991 (Jones and Hetrick 1991). This assessment used GLEAMS and PRZM along with additional thermodynamic modeling to estimate the exposure profile. It also included a sensitivity analysis to uncertainty in the Koc, an assessment of different management practices, and a comparison of exposures in lentic and lotic environments.

In 1992, the issues related to estimating exposure probability in aquatic environments were outlined (Parker 1992). In this memo, modeling uncertainty, defining "worst case," frequency of occurrence of adverse events, scale and variability, and site selection were discussed.

In 1993, several probabilistic assessments for pyrethroids using PRZM and EXAMS were conducted with annual maximum series for several different exposure durations, though full documentation for these simulations was lacking. A fully documented Tier 2 EEC was completed in August 1993 (Jones 1993).

During the course of these efforts, as well as those described in section 2.2.1, many of the comments provided by the SAP were made. As a result, OPP EFED began this initiative to continue these efforts and to provide a response to the SAP.

As indicated in section 2.1, the SAP made several suggestions regarding the methods and procedures OPP EFED uses in its ecological assessments. These comments may be summarized under four general topic areas.

Topic Area #1: Probabilistic Assessments

A major area of discussion for the SAP was that OPP was "trapped" in the deterministic mode of assessing effects of pesticides (hazard assessments) to non-target organisms because of data gaps. The Panel suggested that the current test methodologies and specific endpoints used by OPP in its model assessments were designed to support the relative simplistic process of hazard assessment, not risk assessment. The Panel indicated that the current approach has a number of limitations, and its utility in risk assessments is of questionable value. They also pointed out that gaps in the current methodologies must be filled to accomplish effective and comprehensive risk assessments. As a result, they strongly urged OPP EFED to conduct probabilistic assessments (risk assessments) to evaluate the ecological impacts from pesticides. Although they acknowledged that the available data are inadequate to support such an approach, they did not address the amount and type of data needed to conduct probabilistic assessments.

Topic Area #2: Extrapolation and Validation

Several steps in the assessment process involve extrapolations, and the Panel indicated that these extrapolations need to be addressed to reduce the uncertainty. They include extrapolations from laboratory data, both for effects and exposure, to the field. They also include extrapolations of field effects data, field exposure data or exposure modeling results from one crop to another, one formulation to another, one application method to another, and one region of the country to another. The validity and scope of these extrapolations have not been adequately investigated to date, and little real world data have been collected to validate the model predictions.

Topic Area #3: Risk Characterization

While not specifically addressing the issue of risk characterization, a number of the issues the Panel raised appear to roughly fall under this heading. The Panel in several of their comments suggested that further use of the available data

could be made to provide better insight into the potential environmental effects for the chemicals reviewed. A prominent point of discussion appeared to be the integration and use of environmental fate data in the selection of exposure levels. For aquatic exposure determinations, point estimates for exposure are selected from a temporal distribution of values for use in the exposure portion of aquatic assessments. However, they indicated that additional refinements are needed, such as tools for spatial probabilistic exposure assessment.

The Panel also stressed the need to report and incorporate the slopes of concentration-response curves in the assessments, which are easily calculated from the results of the basic toxicity tests. They indicated that the shallowness or steepness of these curves can provide significant insight into the potential effects of a chemical and needs to be factored into the weight of the evidence.

The SAP further suggested that the assessments need to be expanded to more completely address important parts of the food chain such as reptiles, amphibians, and critical forage insects. They also raised a concern about mortality as the major input used in the assessment process. They stated that the cost of this convenience may be immense in establishing risks and embarking on mitigation, especially when the goal is to proceed from individual toxicity measurements to an understanding of population effects. Parameters such as biomarkers (e.g., cholinesterase, P450 levels, hormone levels, reproductive indices or birth abnormalities) should also be used as endpoints.

The SAP implied that “rough probabilistic statements” (interpreted to mean risk characterization) could be developed based on current fate, exposure and effects data, overcoming some of the problems inherent in assessments based solely on quotients calculated from point estimates. The Panel further implied, that even considering the shortcomings of the current databases and conceptual assumptions, further elaboration and description of “risks” based on the potential environmental fate of the chemicals could be made in the assessments.

The Panel also suggested expanding the scope of the data requirements to include additional toxicity testing, life-stages, species and chemical formulations.

Topic Area #4: Guideline Field Testing and Research

The fourth major issue raised by the Panel was field studies. The Panel addressed two issues:

1) the reinstatement of field studies to support registration and reregistration; and
2) field studies that need to be designed to validate the assessment models that are used.

The Panel emphasized that for pesticides used on corn and other field crops, work is needed to clarify exposure, validate toxicities, and establish site-specific and benchmark data for species critical to the regulatory decision-making process. Therefore, they urged “the Agency to reinstate critical field testing and related mesocosm studies for chemicals to monitor chemical use, test paradigms and modeling algorithms and to obtain base line data on the interactions between chemicals, habitats and toxicities to birds, small mammals, aquatic organisms and other appropriate wildlife.”

The recommendation to reinstate field tests to monitor chemical use addresses the need for field studies to support registration and reregistration, while the latter part of the recommendation (to reinstate field studies to test paradigms and modeling algorithms and obtain baseline information) addresses the validation issue.

In reference to the validation issue, the Panel implied that the uncertainties associated with OPP's present methods must be considered if improvements are to be made in assessment methods. There is a great need to better understand the functional relationship between the tools used to estimate effects, and exposure estimates, and actual effects under field conditions. These relationships most likely would be the foundation for any model, deterministic or probabilistic. Therefore, if advances are to be made, they need to be better defined. In the absence of this research, which the Panel suggested is long over due, the questions associated with present methodologies will persist even if more sophisticated methodologies are developed**.**

2.3. ECOFRAM Aquatic Risk Assessment Process

Underpinning all of the findings and recommendations of the ECOFRAM Aquatic Workgroups is a revised tier system for assessing pesticide risk within the FIFRA regulatory process.

2.3.1. Overview of the proposed ECOFRAM tiered process

A tiered or phased approach has been recommended as a rational procedure for assessing the risks of toxicants or other stressors by many authors and regulatory authorities (ASTM 1979; Urban and Cook 1986; European Union 1991; Suter 1993; SETAC 1994; OECD 1995; Environment Canada 1997; EPA 1998). The purpose of a tiered process is to provide a logical progression of tests and risk assessment approaches to address the potential risks of toxicants to aquatic systems. The common feature of all tiered regulatory processes is a progression beginning with conservative assumptions and moving toward more realistic estimates. Tiered processes tend to be cost effective in that they ensure that resources are expended on pesticide products/issues meriting attention

For pesticides, the ECOFRAM Aquatic Workgroups propose a process consisting of four tiers, each structured similarly, with a Problem Formulation phase, Analysis phase, and Risk Characterization phase (Figures 2-1, 2-2 and 2-3). Tiers are differentiated primarily by the data likely to be available at that stage in the risk assessment process and the relative cost of achieving risk refinement appropriate for that tier of analysis. The tier process amounts to a cost-benefit balance in which additional resources are expended with progressive tiers to reduce uncertainty and address variability in risk assessment and characterization. For example, early tiers can be performed relatively rapidly from data generated under standard core studies conducted under § 158, although the process is designed to be conservative to compensate for uncertainty in the risk assessment. Higher tiers involve progressively more resources with respect to data and interpretation in order to achieve more realistic evaluation of risk and a more comprehensive risk characterization. While a tiered approach provides necessary structure and organization, defines a progression for refined assessments, and allows

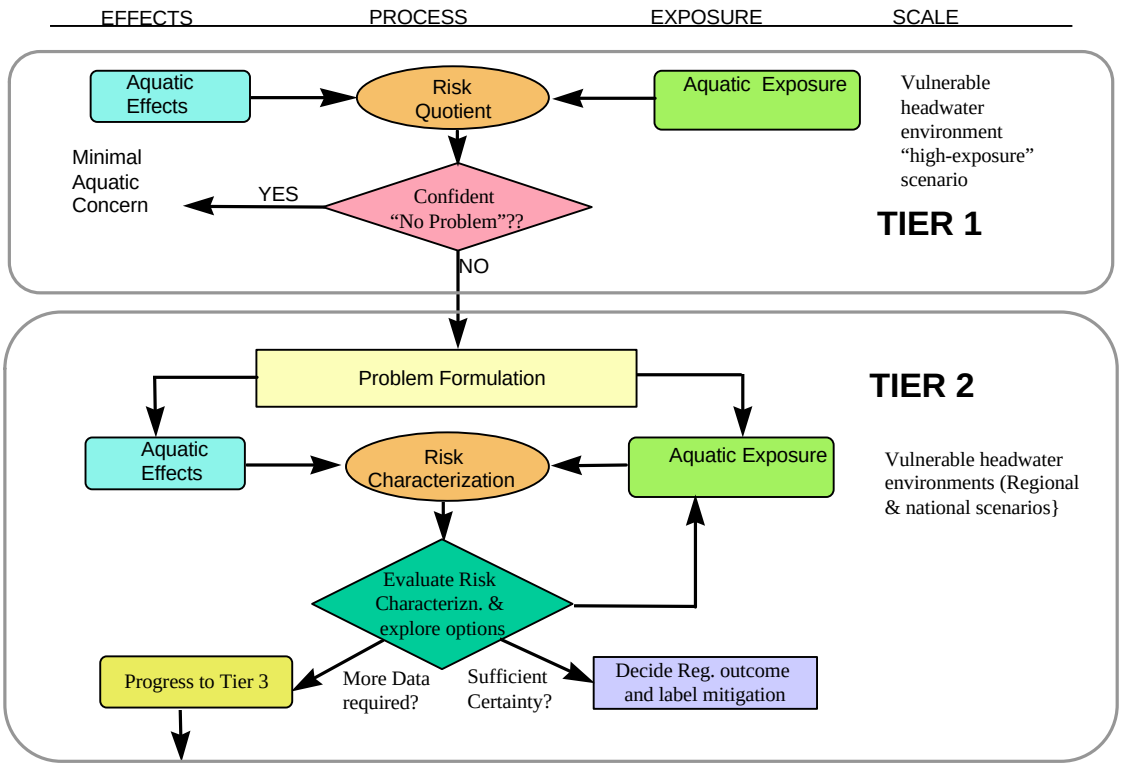
regulatory decision points, the separation between the tiers **is not intended to be rigid**. It is recognized that to the extent possible, all relevant data should be utilized and that valid effects and exposure comparisons may cross tier boundaries. For example, higher tiered effects data, if available, may be compared with exposure estimates generated at lower tiers (or vice versa). The four tiers are described in the following sections.

2.3.1.1. Tier 1 - Screening

The objectives of Tier 1 are to:

- Identify those pesticide products which a risk assessment indicates with high confidence to have minimal environmental/ecological concerns (e.g. minimal aquatic ecological risks);
- Focus any higher tier risk assessment work on combinations of use patterns and sensitive taxa (e.g. invertebrates, fish or aquatic plants) most likely to be of concern;
- Prioritize the use patterns for a product in terms of potential environmental exposures;
- Provide an assessment of whether acute or chronic concentrations may be of concern.
- Determine the potential need to consider sediment toxicity impacts. While it is currently not possible to evaluate sediment and pore water exposure using the standard Tier 1 exposure model, this functionality is recommended to be built into the next generation of exposure models.

Figure 2 -1. ECOFRAM Risk Assessment Process - Tier 1 and 2 -Screening and basic temporal and spatial risk characterization



Tier 1 generates a simple deterministic risk quotient based on the standard battery of FIFRA aquatic toxicity data [acute and chronic tests including 4 to 7 freshwater species (2 fish, 1 invertebrate and 1 to 4 algae) with 3 marine species where relevant] and a simple and conservative edge-of-field scenario. The exposure scenario is selected to represent a defined exposure "severity" set by regulators such that a Tier 1 indication of "no risk" is protective at the defined level of concern. The output of Tier 1 EITHER provides a decision that the risk assessor is confident that there is minimal aquatic ecological concern associated with the product/use pattern, OR the tier indicates progression to Tier 2 is essential.

2.3.1.2. Tier 2 - Basic temporal and spatial risk characterization

The objectives of Tier 2 are to:

- Provide probabilistic expressions for potential risk associated with use patterns/taxa combinations identified in Tier 1;
- Confirm that risk predicted in Tier 1 still applies when physico-chemical processes and environmental fate parameters are better represented;
- Provide an estimate of the variation of risk temporally, regionally and seasonally across a wide range of conditions characteristic of product use;
- Permit preliminary evaluation of basic mitigation and management options, provided that there is sufficient understanding of the ecological risk; and
- Provide guidance on which Tier 3 options to consider.

Tier 2 provides a probabilistic assessment of potential risk using complete dose response relationships derived from the standard battery of toxicity test data from Tier 1combined with a multi-regional exposure assessment that provides the distribution of concentration in surface water adjacent to treated fields. At Tier 2, the environmental fate behavior data generated as part of the standard FIFRA battery of laboratory and field studies is incorporated into the exposure assessment modeling. Currently, in many cases, compounds entering Tier 2 also require some form of Tier 3 assessment.

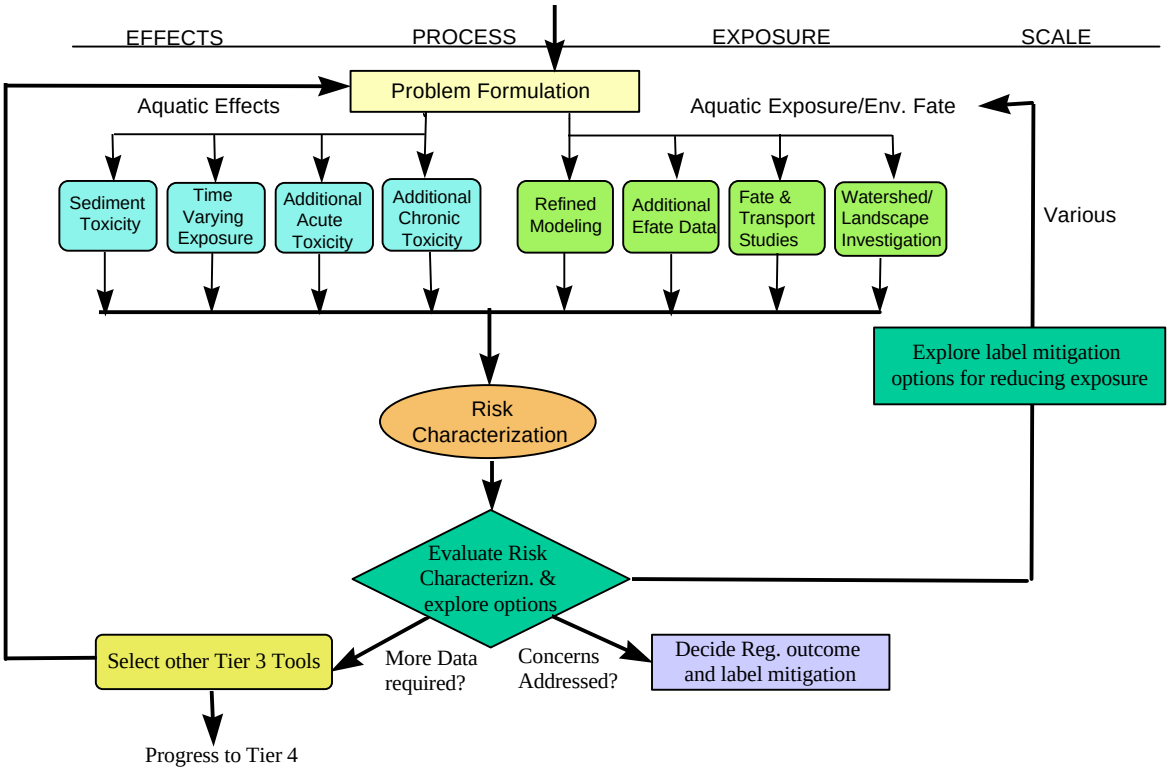
The assessment step (diamond) identified as "Evaluate Risk Characterization. & Explore Options" in the Tier 2 section of Figure 2-1 represents a process common to Tiers 2, 3, and 4. It is a multi-step process for the risk assessor to decide whether the uncertainty around the risk characterization is sufficiently well understood to permit any further evaluation and, if so, the process then involves a more detailed exploration of the output. This process is described in more detail in section 2.3.1.5. KEVIN RAISED THE QUESTION OF WHETHER MORE DETAIL WAS NEEDED HERE - MY JUDGEMENT SAYS NO

2.3.1.3. Tier 3: Refining estimates of risk and uncertainty

The objective of Tier 3 (Figure 2-2) is to provide a probabilistic assessment of potential risk using similar approaches to Tier 2, but *refined by additional data or information derived from relevant studies selected from the following types*.

- Acute toxicity studies with additional species;
- Investigations of the toxicity associated with time-varying or repeated exposure;
- Chronic toxicity studies;
- Sediment toxicity studies;
- Additional laboratory or pseudo field environmental fate studies;
- More sophisticated exposure modeling approaches;
- The inclusion of a more realistic scenarios representing the relevant agricultural landscape using GIS and/or spatial modeling approaches;
- More detailed evaluation of mitigation and management options, provided there is a sufficient understanding of the ecological risk.

Figure 2-2. Tier 3 - "Toolbox" approach, refining estimates of risk and uncertainty.



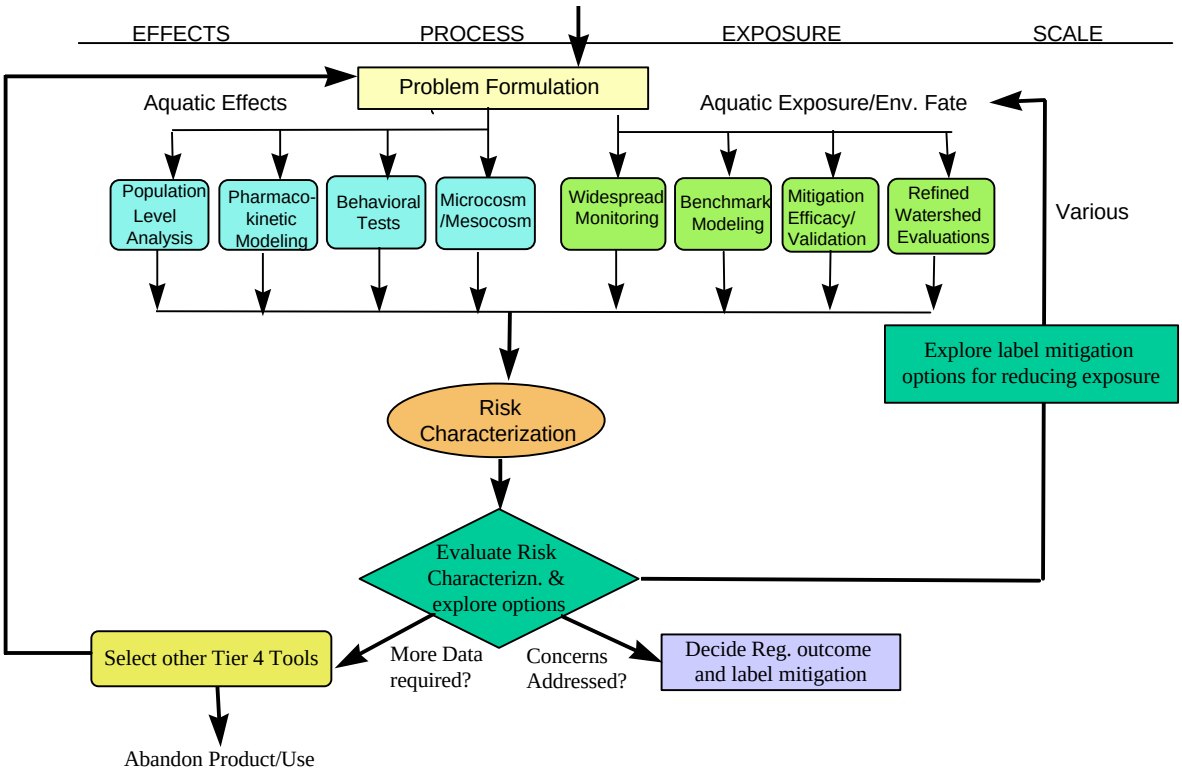
The selection of one or more of the Tier 3 options is based on expert judgement. The concept to consider is one of identifying the most appropriate tool or tools from a well equipped "toolbox." Assuming clear generic guidance on the tier system is defined, it is likely that much of the work encompassed by Tiers 1 to 3 can be conducted by the registrant prior to discussion with OPP EFED. Nevertheless, discussion between risk managers and risk assessors may often be helpful to share information on likely issues associated with a product/use pattern and to benefit from expert Agency opinion at any point in this risk assessment process..

2.3.1.4. Tier 4: Major programs, sophisticated modeling or mitigation validation studies

Tier 4 (Figure 2-3) generally involves broad reaching experimental or monitoring programs designed to definitively characterize key aspects of the toxicity or exposure profiles. Examples of Tier 4 programs include::

- Widespread monitoring;
- Detailed investigation of the efficacy of mitigation;
- Highly refined watershed evaluations and modeling;
- Benchmark modeling relative to existing chemical data;
- Modeling of population or ecosystem dynamics;
- Microcosm or mesocosm studies.

Figure 2-3. Tier 4 - Major programs, sophisticated modeling or model validation studies.



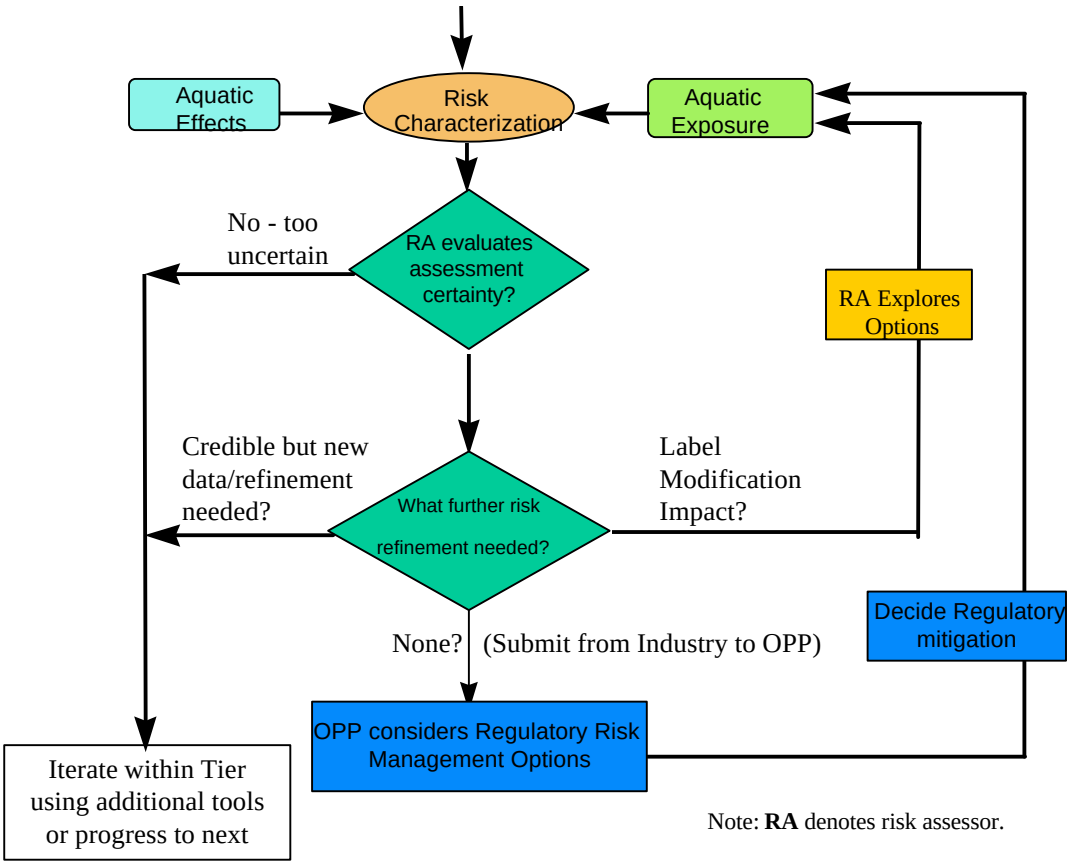
Which options are selected at Tier 4 depends entirely on the risk assessment issues that remained after Tier 3. Both Tiers 3 and 4 are intended to be highly flexible. Consultation between registrants and regulators is essential at this stage because of the extraordinary cost associated with the programs

2.3.1.5. Risk characterization evaluation process.

Whether conducted by a registrant or a regulator, at the conclusion of each tier, the information generated is evaluated and the options for a next step are evaluated. [Note that Tier 1 is an exception to this as it provides only two options - EITHER there is confidence that there is “no problem” and aquatic concerns are minimal OR the product risk assessment progresses to Tier 2.]

Figure 2-4 provides insight into some of the detail of the evaluation process at the conclusion of iterations of Tiers 2 or3, . (The acronym RA refers to the Risk Assessor). At Tier 4, the final outcome differs somewhat as the final outcome can no longer include progression to a further risk refinement step.

Figure 2-4. The risk characterization process common to Tiers 2 and 3 (and Tier 4 to some extent)



Note: **RA** denotes risk assessor.

The first step is for the risk assessor to critically examine the risk characterization output to address the question, "Is the uncertainty within this ecological risk assessment sufficiently well understood to support the consideration of risk management options?" This question must be addressed by both industry scientists performing risk assessments prior to submission to EPA and also by EPA risk assessors performing internal assessments. If the answer is that the uncertainty surrounding the risk assessment is too high, the need for more work is triggered.

If, however, the risk characterization is sufficient to justify considering risk mitigation options and discussion between risk assessors and risk managers, the next step is to more fully explore the output of the risk characterization and, where necessary, evaluate risk mitigation options and their impact on reducing ecological risk. Unless the initial assessment indicates acceptable risk directly, this exploration may involve reiterations with the same input data to investigate regulatory options associated with making label modifications (e.g. reducing application rate or frequency or adding a drift buffer). Other work performed at this review point might be to examine the sensitivity of the characterization output to various key usage or landscape/weather factors. This work will often be conducted initially in industry prior to any submission to the Agency; it will also be repeated in OPP EFED after a risk assessment is submitted or during Agency evaluation of products. At this stage, the may be two conclusions:

Conclusion 1:

To decide that although the Tier 2 risk assessment adequately characterizes risk and uncertainty, the risk appears to be unacceptable given the label mitigation options considered. Further assessment related work is needed to better

understand the impact of risk mitigation measures or risk reduction; alternatively, the product/use may be restricted or abandoned.:

Actions resulting from conclusion 1:

a) If within Tier 2, progress to Tier 3;
b) If within Tier 3, progress to Tier 4 or use another "tool" from Tier 3 to refine the Tier 2/Tier 3 risk assessment and/ot the impact of risk mitigation /risk reduction options;
c) If within Tier 4, use another "tool" from tier 3 or Tier 4 to refine the Tier 2/Tier 3 risk assessment and/ot the impact of risk mitigation /risk reduction options.

Conclusion 2:

The concerns are addressed with adequate certainty.

Actions resulting from conclusion 2:

a) If the evaluation has been conducted by the registrant, submit the risk assessment to OPP for evaluation by OPP risk assessors and scientists
b) If the evaluation has been conducted and/or reviewed by OPP scientists, submit the risk assessment to OPP risk managers for consideration of the regulatory options and decision making (including necessary mitigation as needed).

2.3.1.6. Risk management options

Both EPA OPP EFED and Registrants routinely have to consider risk management options during a pesticide's development and registration. Some of these decisions are made internally by the registrant or Agency to determine the next steps in their internal investigations while official regulatory risk management decisions can only be made by OPP EFED when a registration action is made.

Registrants will frequently make risk management decisions during the development of a product prior to a submission to OPP. The following table illustrates typical actions that may result from various specific risk management decisions. ;

Risk Management Decision	Registrant Action
Ecological risk to aquatic systems considered and understood to be minimal and acceptable.	No further risk assessment or consideration of risk mitigation measures required.
Risk considered and understood to be unacceptable but mitigation options exist that may reduce risk to acceptable levels.	Registrant performs risk assessment incorporating mitigation options.
Risk considered and understood to be unacceptable and mitigation options that appear to effectively reduce risk are not available or not acceptable to the registrant; additional data are needed to reduce uncertainty and refine approximations used in assessment or evaluation of the impacts of risk mitigation options.	If registrant believes additional work is worthwhile, further risk assessment at a higher tier will be undertaken.
Risk is considered and understood to be unacceptable, the potential effects of mitigation options are well understood and viewed as insufficient to reduce risk to acceptable levels, and/or costs for further assessment are not justifiable for registrant.	Product/use abandoned or discontinued.

Table 2-1. Typical Registrant actions arising from various risk management decisions.

The OPP risk assessors and managers are the only source of formal regulatory risk assessment and mitigation decisions. Once EPA/registrant negotiations are completed after a risk assessment submission, the options in table 2-1 still apply.

2.3.1.7. The importance of the problem formulation step to the tiered process

Every risk assessment should be focused on selected assessment endpoints. An assessment endpoint is defined as "a quantitative or quantifiable expression of the environmental value considered to be at risk in a risk assessment" (Suter 1993). For example, an assessment endpoint might be the maintenance of sustained populations of fish species. Because assessment endpoints cannot usually be measured directly, one or more measurement endpoints are used to make inferences about the assessment endpoint. A measurement endpoint is defined as "a quantitative summary of the results of a toxicity test, a biological monitoring study, or other activity intended to reveal the effects of a substance" (Suter 1993). For example, a measurement endpoint might be mortality of fish in an acute toxicity test. (EPA 1998 refers to measurement endpoints as "measures of effects.") The relationships between assessment and measurement endpoints should be clearly defined for each risk assessment.

Although each tier is a risk evaluation by itself, it is important that, if testing proceeds to higher levels, the assessment endpoints established from the original Tier 1 assessment are carried forward to provide continuity in the risk assessment among tiers. The measurement endpoints employed may change as the ecological risk assessment progresses to higher tiers; however, the initial assessment endpoints should remain the same. For example, if the assessment endpoint is

sustainability of a fish population, one measurement endpoint in Tiers 1 and 2 would be acute toxicity data on fathead minnows. However, in Tier 3, the selected measurement endpoint might be population time to recovery analysis at various concentrations.

The problem formulation phase preceding each tier is intended to focus the assessment by specifying the critical question(s) and helps clearly identify the endpoints, testing needs, and decision points. Data collected in the analysis phase of each tier are evaluated and a decision is then made concerning the degree of risk for each endpoint being evaluated. If it is judged that additional testing could provide data that would confirm or reduce the concern, endpoints for which the risk remains high may be carried forward to higher tiers. The purpose of higher tiers is to reduce uncertainty in the risk characterization and/or, by generating additional data, to replace the conservative assumptions with increasingly representative values. The tiered approach is used because generally the costs and complexity of generating higher tier estimates of toxicity and exposure are greater (sometimes much greater) than those involved in using conservative assumptions.

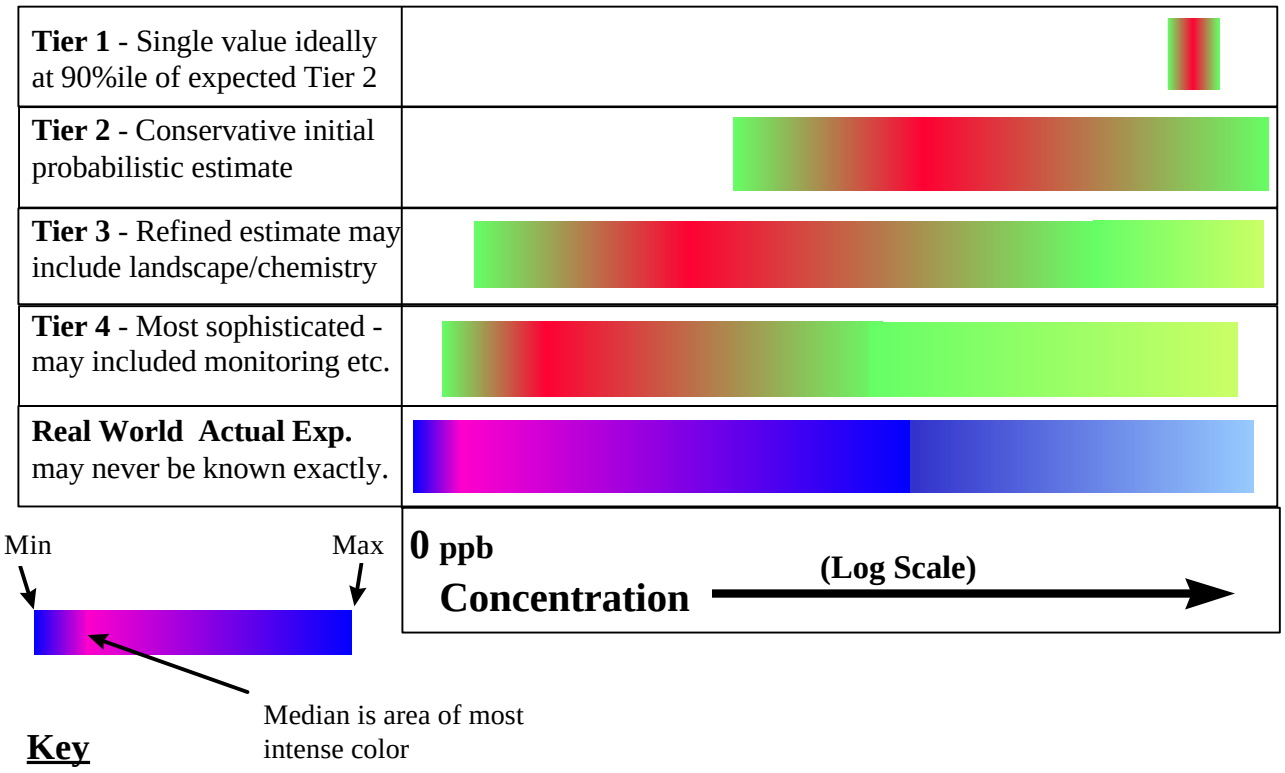
2.3.2. Concepts Behind the Aquatic Exposure Refinement Process

The goal as a risk assessment progresses through the tiers is to refine the understanding of exposures so that:

- the probability distribution of exposures of a given magnitude is better understood.
- the exposure magnitude and duration are predicted more accurately and realistically;
- the spatial variation of potential exposure becomes clearer in terms of;
    - ◊ variation within a water body,
    - ◊ between water body types,
    - ◊ within a watershed, and/or
    - ◊ by region
- the temporal variation of exposure becomes clearer in terms of;
    - ◊ duration,
    - ◊ frequency above a certain magnitude,
    - ◊ intervals between “events”,
    - ◊ seasonal differences,
- the potential for exposure to be mitigated by various measures is more clearly defined

Figure 2-5 depicts the conceptual relationship between tiers. Tier 1 is a tight distribution (and in most cases a single value) that exceeds the actual or “true” concentration profile because of conservative assumptions used in the exposure estimate. This level of conservatism is necessary because of the uncertainty that exists in the understanding of physicochemical processes under varying environmental conditions. The succeeding tiers enhance exposure characterization by improving the representation of physicochemical processes and incorporating additional “real-world” factors until, ultimately, the predicted distribution approaches that which would occur in nature.

Figure 2-5. Representation of the conceptual relationship between Tiers.



The fact that the progressive tiering process typically serves to decrease the mean estimate exposure is often misrepresented as a manipulation of the system to ease pressure on regulators and improve the position for industry. In fact, the progression toward higher tiers only takes place on an "as-needed" basis because the cost of progressively higher tier studies increase somewhat exponentially to both the registrant (in terms of conducting the studies) and to OPP (in terms of reviewing, discussing, and approving the studies). In an ideal world, the early tier models would be able to provide an accurate representation of reality. Given the current state of aquatic exposure modeling, the progressive tiering system will be the only viable approach for some time.

2.3.3. Concepts Behind the Aquatic Effects Refinement Process

The starting point for analysis of potential aquatic effects is a set of standard acute and chronic toxicity tests with well-studied species. Such studies are routinely conducted by registrants early in the development of an active ingredient. Results of these studies—i.e., acute LC_{50} values and chronic EC_x values—are readily compared with other pesticides and with estimates of exposure concentrations. Although data from the set of standard tests are indicative, rather than

predictive, they are essential for establishing a basic toxicity profile, determining which types of organisms (fish, invertebrates, or plants) are sensitive, and inferring the range of exposure concentrations that might cause toxic effects.

Depending on the results of this initial analysis, refinement of the effects assessment may require further investigation of:

- the responses of organisms under exposure conditions that more closely reflect actual pesticide use (which in turn requires an understanding of exposure patterns under different scenarios of interest);
- the toxicity of the pesticide to other species; and
- the ecological significance of expected effects.

The need for such investigations is determined only after the exposure assessment has undergone a first level of refinement for two reasons. First, risk characterization based on the initial effects analysis and the refined exposure analysis may be sufficient to estimate ecological risk within the desired bounds of uncertainty, so further refinement of the effects analysis is not needed. Second, experimental and analytical techniques for refining the effects assessment are less standardized than the initial set of toxicity tests, and more complete information about exposure is necessary to guide the design of the higher-tier effects studies if they are needed.

If the risk assessment does proceed to Tier 3, a variety of tools are available for refining the effects analysis in the three areas listed above. To reduce the uncertainty that results from differences between actual exposure scenarios and the exposure conditions used in standard acute and chronic toxicity tests, laboratory studies incorporating more realistic exposure regimes can be undertaken. These may include time varying exposure followed by pesticide dissipation, repeated exposures, or testing in the presence of sediment to allow sediment-water partitioning to take place (with organisms exposed in either the sediment or the water, or both). To reduce the uncertainty due to differences in sensitivity among species, additional species may be tested and the results used to determine the distribution of species sensitivity. To enable an evaluation of the ecological significance of effects, techniques for population analysis can be applied to extrapolate from effects on individuals (such as are measured in laboratory toxicity tests) to effects on the abundance and persistence of populations. A variety of laboratory and field experimental designs (including microcosms and mesocosms) are also available to measure the effects of pesticides on populations and communities.

Most of these tools for higher-tier aquatic effects analysis are not probabilistic, and do not address stochastic uncertainty as do many of the techniques for refined exposure analysis. However, they are effective in reducing other kinds of uncertainty, especially uncertainty that results from incomplete knowledge of processes and relationships.

2.3.4. Uncertainty in the Aquatic Risk Assessment Process

The ECOFRAM Aquatic Workgroups spent much of the first few meetings dealing with identifying the sources of uncertainty in the effects and exposure characterizations. KEVIN SUGGESTS WE ADD EXAMPLES HERE The results of these analyses are included in the separate sections associated with each discipline.

It is important to note that approaches to blending uncertainty into probabilistic risk assessments for terrestrial organisms such as birds and aquatic organisms are likely to differ substantially for technical reasons.

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2.3.5. Tier 1 Risk Assessments

Tier 1 is designed to be protective and not predictive. Tier 1 of the aquatic risk assessment is a deterministic analysis that involves the calculation of a risk quotient (generated by dividing the Estimated Environmental Concentration (EEC) by an appropriate effects measurement endpoint). The objectives of the Tier 1 assessment are to:

- Identify those pesticide products which a risk assessment indicates with high confidence to have minimal environmental/ecological concerns (e.g. minimal aquatic ecological risks);
- Focus any higher tier risk assessment work on combinations of use patterns and sensitive taxa (e.g. invertebrates, fish or aquatic plants) most likely to be of concern;
- Prioritize the use patterns for a product in terms of potential environmental exposures;
- Provide an assessment of whether acute or chronic concentrations may be of concern.
- Determine the potential need to consider sediment toxicity impacts. While it is currently not possible to evaluate sediment and pore water exposure using the standard Tier 1 exposure model, this functionality is recommended to be built into the next generation of exposure models.

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2.3.5.1. Problem Formulation at Tier 1

The FIFRA statute and regulations require that no unreasonable adverse effects will result from the use of a pesticide. In ecological risk assessment, a standard battery of aquatic toxicity tests with surrogate species is used to represent the organisms potentially exposed to pesticides under field conditions. At Tier 1, these tests measure ecologically relevant endpoints on sensitive life stages, which are compared to conservative exposure scenarios to assess the potential risk to nontarget organisms. Relevant assessment endpoints may include the sustainability and propagation of populations of organisms.

2.3.5.2. Exposure Characterization at Tier 1

Conceptually, an ideal Tier 1 exposure model will generate a conservative exposure assessment of likely concentrations in aquatic systems arising from pesticide runoff, erosion or spray drift entry in surface water immediately adjacent to treated areas. The estimate will be generated using a single simulation model which will comprise a “user friendly” shell making

use of approved surface water exposure models (either as a version with simplified inputs or via "meta-data" from pre-run model output).

The tool will use scenarios representing a wide range of crops and use patterns (either as relevant groups of crops or as individual scenarios). Ideally, there will be an opportunity to incorporate different types of water bodies but all will be directly adjacent to the treated area. Of particular importance is the need to be able to define the relative "severity" of the scenario in terms of a probability of aquatic exposure. The chosen Tier 1 "scenario severity" will be at a conservative return frequency set by regulatory policy makers relative to the expected Tier 2 model predictions (in terms of some standard output parameters such as water runoff volume, sediment yield and wind speed). For example, the scenario severity might be the 90th percentile of the 10 year return frequency of exposure. It is important to note that because this value is set **relative** to the Tier 2 output rather than to real world exposures, it represents a much more conservative option when compared with the real world distribution of residues.

The output from model runs would ideally provide water column instantaneous and various time interval concentrations for a static pond and a flowing water scenario and should include a simple error estimate. Ideally, sediment and sediment pore water concentrations would also be provided. Additionally, it would be useful for the model to provide an estimate of the general shape of the time course of pesticide exposure in the receiving bodies.

This tier provides exposure estimates that allow a deterministic risk assessment of risk by the quotient method.

Currently (Fall 1998), Tier 1 estimates are generally made using GENEEC version 1.2 or 1.3 (see section 3.4.4.1.1.) and the selected site severity is based on approximately the 90th percentile Tier 2 site for cotton agriculture (ranked by erosion potential). For technical reasons (see section 3.7.3.3.2), in a few defined circumstances, GENEEC is not an appropriate model and a simple form of PRZM3/EXAMS should be employed. As a result of the primary use of the GENEEC model, the key variables for calculating aquatic EECs are application frequency and rate, partition coefficients, along with degradation rate constants measured in aerobic aquatic, abiotic hydrolysis and/or aquatic photolysis laboratory degradation studies.

The model output obtained currently includes the initial peak, 96h, 21d and 60d time-weighted-average water column concentrations. Sediment concentrations are only available from the use of PRZM3/EXAMS. More complete discussions of the current and proposed methodology for generating Tier 1 exposure estimates are given in section 3.7.3.

2.3.5.3. Effects Characterization at Tier 1

Tier 1 effects characterization is based on a set of standard acute and chronic toxicity tests with fish, invertebrates, and algae. The set of tests recommended by ECOFRAM is generally consistent with those currently required under FIFRA (40 CFR 158). These include acute toxicity tests with one invertebrate (*Daphnia magna*), two species of fish (warm water and cold water), and one or more species of algae or higher aquatic plant. If there is a potential for estuarine exposure, acute

toxicity tests are also recommended for an estuarine fish, an arthropod, and a mollusk, although freshwater species can usually be considered as surrogates for marine species at Tier 1. Chronic studies including alife cycle study with a freshwater invertebrate (*Daphnia magna*) or marine invertebrate (*Mysidopsis bahia*) and one or more early life-stage (ELS) studies with warmwater, coldwater or estuarine fish are also recommended for Tier 1. While these chronic studies are currently only conditionally required under FIFRA, ECOFRAM considers that they should be included in Tier 1 for a more thorough assessment and to reduce the time required to reach a registration decision.

When acute toxicity tests are conducted, mortality is reported at 24-h intervals (at least), and the LC_{50} (with 95% confidence limits) and slope for each observation time should be reported. Specific endpoints measured include: *Daphnia magna* 48-h EC_{50} and 21-d EC_x (where x represents a defined percent reduction of survival or reproduction), warm water and cold water fish 96-h LC_{50}, fish ELS EC_x (where x represents a defined percent reduction of survival or growth), and algae 96-h EC_{50}. Time-to-event analysis generally provides a better estimate of acute LC_{50} values than conventional probit analysis (see section 4.3). For chronic studies ECOFRAM recommends the regression-based point estimates (e.g., EC_x) over the ANOVA-based NOEC approach because of well documented problems with the latter (see section 4.8). Based on expert opinion, ECOFRAM recommends the use of an EC_{10}. A NOEC should only be used if a study is technically acceptable but the data do not support regression analysis.

2.3.5.4. Risk Characterization at Tier 1

For acute effects, peak EEC's are compared to the EC_{50}s and LC_{50}s to calculate risk quotients for the species of invertebrate and fish tested. The risk quotient (RQ) is determined by dividing the EEC by the measurement endpoint (LC_{50} or EC_{50}).

For chronic studies, the peak EEC is divided by the chronic endpoint (EC_x or NOEC) to calculate a chronic risk quotient. This risk quotient is very conservative, because the chronic endpoint is measured after prolonged continuous (or, less often, semi-continuous) exposure, whereas the peak EEC reflects an instantaneous maximum concentration. If chronic data are not available for the species that was most sensitive in the acute tests, then an acute-to-chronic ratio derived for another species may be used to estimate the chronic endpoint for the most sensitive species.

The ECOFRAM Aquatic Workgroups discussed whether the chronic risk quotient should be based on the peak EEC or a time-weighted average. Quantal endpoints such as mortality or hatching may reflect the effects of short-term exposure at critical stages in the life cycle. Continuous variables such as growth generally reflect the effects of cumulative exposure, and a time-weighted average EEC may be more appropriate than the peak EEC for characterizing risk. However, because Tier 1 is intended to be protective, it may be advisable to avoid assumptions about cumulative vs. short-term effects; unless relevant information is available in a particular case, the chronic risk quotient should therefore be based on the peak EEC.

The calculated acute and chronic risk quotients are compared with levels of concern (i.e. risk criteria) established by regulatory risk managers to reflect current policies and concerns. Table 2-2 shows the values current in Fall 1998. If the risk criteria are not exceeded, it is concluded that there will be minimal ecological concern from the proposed use of the product and the aquatic risk assessment process is judged complete. If the risk criteria are exceeded, the risk assessment process advances to Tier 2 analysis, but only for those taxa and/or application scenarios that have been indicated to be of potential concern.

Thus the decisions made at this tier are either:

- Conservatively estimated concentrations for use pattern "X" indicate that in static waters, no ecological hazard above the level of concern is likely to result from use of the product to taxa A, B, or C; OR
- The predicted conservative exposure value when compared with a standard battery of toxicity test results suggests that the possibility of an adverse impact to taxa A, B or C exists. It is therefore necessary to progress to Tier 2 to refine the risk estimate.

Table 2-2. Criteria used for risk characterization in Tier 1 (modified from Urban and Cook 1986).

TAXA[A]	EEC	MEASUREMENT ENDPOINT	LEVEL OF CONCERN[E] (RISK CRITERIA)
Invertebrate – acute	Peak[C]	48-h EC_{50} (daphnia), 48 to 96-h EC_{50} (mollusk)[D], 96-h EC_{50} (mysid) [D]	0.05 / 0.1 / 0.5 0.05 / 0.1 / 0.5 0.05 / 0.1 / 0.5
Invertebrate – chronic	Peak[C]	21-d EC_{10} [B] 28-d EC_{10} (mysid)[BD]	1.0 1.0
Fish – acute	Peak[F]	96-h LC_{50}	0.05 / 0.1 / 0.5
Fish- chronic	Peak[F]	35-d EC_{10} [B] 90-d EC_{10} [B]	1.0 1.0
Algae or Macrophyte	Peak[F]	96-h EC_{50} (algae) 14-d EC_{50} (duckweed)	1.0 1.0

[A] The measurement endpoint of the most sensitive species should be used to calculate the risk quotient.

[B] Use NOEC if study is technically acceptable but data do not support regression analysis.

[C] EEC for pore water, if available, can be used for sediment risk assessment.

[D] Estuarine testing.

[E] 0.05 Level of Concern is applied for endangered species, 0.1 indicates a risk that may be mitigated by restricted use, and 0.5 or greater indicates a higher risk category.

[F] The comparison of peak exposure values with chronic toxicity data is highly conservative for most endpoints and may be expected to "pass on" more pesticide products/use patterns to higher tier assessments.

2.3.6. Tier 2 Risk Assessments

Tier 2 of the aquatic risk assessment process is designed to provide a basic understanding of the ecological risks associated with a particular pesticide use pattern. Tier 2 provides a preliminary probabilistic assessment of potential risk using complete dose response relationships derived from the same standard battery of toxicity test data used in Tier 1, combined with a multi-regional exposure assessment providing the distribution of concentration in surface water adjacent to treated fields.

The objectives of Tier 2 are to:

- Characterize spatio-temporal variations in risk to headwater/static aquatic ecosystems using monthly, seasonal and annual exposure frequency distributions derived from modeling based on a better representation of physico-chemical processes and environmental fate parameters;
- Confirm that risk predicted in Tier 1 still applies when physico-chemical processes and environmental fate parameters are better represented;
- Refine the analysis of potential effects through more complete use of the rsults of Tier 1 toxicity tests;
- Extend the interpretation of potential effets through simple, generic population level analysis;
- Provide probabilistic expressions of potential risk associated with use patterns/taxa combinations identified as concerns in Tier 1;
- Further refine the understanding of which regional cropping / use patterns merit more detailed attention at Tier 3 and which are of no further concern;
- Permit preliminary evaluation of basic risk mitigation and management options;
- Provide guidance on which Tier 3 approaches may be appropriate for refinement of exposure and effects characterization.

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2.3.6.1. Problem Formulation at Tier 2

The Tier 2 effects analysis focuses on the tested taxa for which the risk criteria have been exceeded in the Tier 1 assessment. While no further toxicity testing is conducted in Tier 2, the Tier 1 results are extended through use of complete concentration-response relationships and through simple extrapolations to population-level endpoints. The probabilistic exposure characterization is developed for those use scenarios that exceeded the risk criteria in Tier 1, and is expressed as maximum and/or time-weighted average concentrations for annual, seasonal, or monthly periods. These time scales provide a range of probabilistic exposure data from which an appropriate selection can be made to address the population recovery times for fish, invertebrates or algae. The exposure data developed for Tier 2 are also analyzed in various ways to provide data on exposure duration and times between exposures as well as magnitude of exposure. Through the process of refining the exposure assessment and reevaluating the effects data, uncertainty in the risk assessment is reduced.

2.3.6.2. Exposure Characterization at Tier 2

Conceptually, an ideal Tier 2 will be an automated process with user input limited to chemical-specific properties that include the crop of interest; geographical restrictions that may exist because of pest/disease pressures or other market reasons; rates, frequencies, and methods of application; and chemical properties that dictate mobility and persistence.

Tier 2 would generate standardized scenarios to allow chemicals to be evaluated under uniform and consistent procedures. Scenarios would represent realistic conditions under which the crop is grown and the pesticide is used. Scenarios would be designed on a watershed basis using GIS approaches and grouped by region to reflect regional characteristics; these would be defined to address both federal and state regulatory needs. Each region would contain an appropriate lentic and lotic system capable of addressing different aquatic species and hydraulic residence times; for each water body, a range of soil and climate conditions would be automatically generated appropriate for the use pattern.

The important processes that govern chemical fate and transport would be represented and models would appropriately allocate the applied pesticide to foliage, within the soil, or directly to the adjacent water body as a result of direct application or drift. For most analyses, simulations would be conducted under variable weather conditions. Weather records having at least 35 years of data are recommended. The ideal Tier 2 model would permit reasonably specific analyses of the potential for various mitigation options to reduce exposure.

Ideally, Tier 2 would be constructed using modular (object-oriented) technology with respect to data bases and predictive algorithms so that the operational software could remain flexible in its ability to adapt as data sources, model technology, and risk assessment end points evolve.

Output would be layered to address a hierarchy of analysis. One level of output would contain cumulative area-weighted probability curves (nationally and by region) for standard exposure duration concentrations in both tabular and graphical format. The probability curves would include instantaneous peak concentrations, 24-hour, 48-hour, 96-hour, 21-day, 60-day, and 90-day durations for monthly, seasonal, and annual maximum series. Included in this level would be thematic maps indicating where soil/climate combinations are most likely to occur at different risk end-point levels. Additional levels of effort would provide frequency distribution curves for each individual scenario and summary information related to mass loadings (e.g., drift, runoff, erosion) for the scenarios closest to the assessment end-point criteria to help outline potential mitigation alternatives. KEVIN WOULD LIKE TO SEE NEW TEXT ADDED HERE

In addition, the ECOFRAM Aquatic Exposure Workgroup has developed a post processor tool (Risk Assessment Tool to Evaluate Duration and Recovery - RADAR) for performing more detailed analyses of the daily output series developed by existing (EXAMS) or future models. RADAR examines the output in terms of “events” during which the concentration exceeds a threshold designated by the risk assessor (for example, a fraction of the LC50). For each event the program determines the maximum concentration, the average concentration, the duration of exposure, and the time before the next

event occurs. This aspect of exposure characterization is of value for interpreting population recovery potential and designing pulsed dose toxicity studies where appropriate.

Currently (Fall 1998), Tier 2 exposure prediction involves the use of PRZM3/EXAMS simulations on a single site, or multiple single sites, covering climate/soil/cropping scenarios estimated to represent a high-end exposure scenario for the crop of interest. The scenario or scenarios chosen are professional best judgement sites expected to produce runoff greater than would be expected at 90% (assumed) of the sites where the appropriate crop is grown. The aquatic system modeled is a static farm pond adjacent to the treated crop. The exposure should be modeled for an extended period (e.g. 36 to 50 years) to provide a meaningful distribution of predicted concentrations. A recently developed modeling tool (MUSCRAT) is gaining acceptance and this provides similar output across a wider range of scenarios characteristic of the regional and national distribution of the crop of interest

Currently, for each set of model output, the exposure is characterized as the distribution of annual maxima for a given exposure duration. The annual maximum series represents the maximum concentrations for each year of simulation determined from a rolling average evaluation for the year for that exposure duration. Analyses are performed on the instantaneous maximum, 96-hour, 21-day, and “longer-term” durations.

Full discussions of the current and proposed Tier 2 exposure characterization procedures are given in section 3.7.4.

2.3.6.3. Effects Characterization at Tier 2

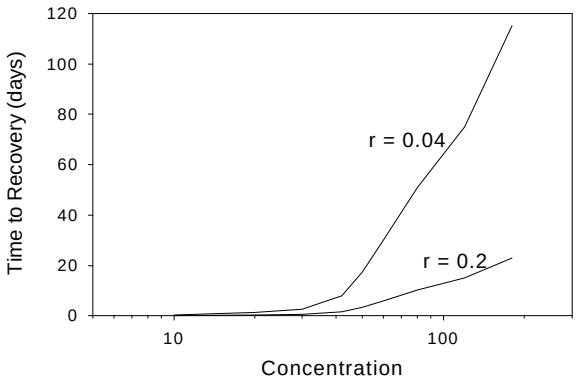
Effects characterization at Tier 2 is based on the results of the same acute and chronic toxicity tests used in Tier 1—that is, no additional laboratory tests are conducted. However, the data are used more comprehensively, and are coupled with interpretive tools (population level analysis) that address some of the sources of uncertainty inherent in the Tier 1 effects characterization, as explained below.

At Tier 1, effects are characterized by point estimates of acute and chronic toxicity (e.g., LC_{50} and EC_x). These measurement endpoints do not indicate variability in sensitivity among individuals. However, information on individual sensitivity is embodied in the concentration-response relationships that are determined in standard acute and chronic toxicity tests. Effects characterization in Tier 2 makes use of the full concentration-response relationship for each test species, and thereby addresses uncertainty resulting from intra-specific variation in sensitivity.

The endpoints measured in acute and chronic toxicity tests refer to pesticide effects on individuals. However, except in the special case of protected species, the environmental entity to be protected—the assessment endpoint—is not the individual but the population. Tools for population level analysis exist by which acute and chronic test data can be extrapolated to estimation of population-level parameters such as reductions in population density, time to population recovery, and likelihood of local extinction. These tools, described in detail in Section 4.4, enable the Tier 2 effects characterization to begin to bridge the gap between measurement endpoints and assessment endpoints.

Predicting the dynamics of a particular population at a particular site requires sophisticated models and a great deal of specific data, and is not attempted at Tier 2. Instead, Tier 2 uses simple tools to analyze hypothetical populations representing common life history strategies—for example, species with rapid reproductive rates and short generation times (e.g., *Daphnia magna*), or longer-lived, more slowly reproducing species (e.g., rainbow trout). The result of the analysis is a different type of concentration-response relationship, in which the response (the effect) refers to a population instead of an individual (see Figure 2-6).

Figure 2-6. Concentration-effect curve for time to population recovery for two populations with different intrinsic rates of increase, r (see Section 4.2.2.2).



Effects characterization at Tier 2 still leaves important sources of uncertainty unresolved. In particular, it does not account for differences in sensitivity among species, nor does it address the discrepancy between the effects of time-varying exposure (typical of many pesticide use scenarios) and constant exposure (as in standard toxicity tests). Options for investigating these factors are incorporated into Tier 3.

2.3.6.4. Risk Characterization at Tier 2

ECOFRAM's approach to characterizing risk at Tier 2 is to define the relationship between the magnitude of effect and the probability of occurrence for that effect. This approach uses the distribution of estimated exposures described in section 3.7.4 (Tier 2 exposure) for either annual or monthly series depending upon the life cycle of the species of concern. Normally the distribution of time-weighted average EEC's will be used to correspond with the toxicity endpoint concerned; however, the choice of using maximum or time-weighted average EEC's can be made independently for each endpoint after considering the relationship between LC_{50} or EC_x and exposure, the mechanism of action, and information on related compounds.

Risk characterization at Tier 2 is based on full concentration-response relationships rather than just point estimates of toxicity. The concentration-response relationship may apply to effects on individuals as measured directly in toxicity tests, or to extrapolated population endpoints as described in section 4.2.2.2. In either case, the frequency distribution of exposure concentrations is integrated with the concentration-response relationship to create a Joint Probability Curve. The Joint Probability Curve depicts the probability that an effect (response) exceeding any given magnitude will occur under the range of exposure scenarios used to generate the EEC distribution. The procedure for constructing a Joint Probability Curve is described in section 4.2.2.3.

An example of the use of Joint Probability Curves is presented below. Figure 2-7 shows the distribution of EEC values as a cumulative exceedance curve. For each concentration on the horizontal axis, this curve indicates the frequency that the concentration is exceeded. For example, the exposure distribution might represent the distribution of 90th percentiles (i.e. 1-in-10-year return concentrations) for the annual maximum concentration at each of 25 sites representing a particular use pattern in a particular region (e.g. corn in the Midwest). Plotted against the same horizontal concentration axis in Figure 2-7 is a concentration-response curve for mortality of *Daphnia magna*, derived from an acute toxicity test. Each concentration on the horizontal axis can thus be related to a probability of exceedance and a magnitude of effect. The pair of points (probability and magnitude) associated with each concentration are plotted as a Joint Probability Curve shown in Figure 2-8. This curve shows, for example, that in 20% of the Midwest corn use sites modeled, a concentration causing 58% mortality is exceeded one year in ten. The risk assessment could now proceed to a consideration of the consequences to a *Daphnia* population of a 58% mortality event occurring on average one year in ten (or any other combination of magnitude and frequency).

Figure 2-7.

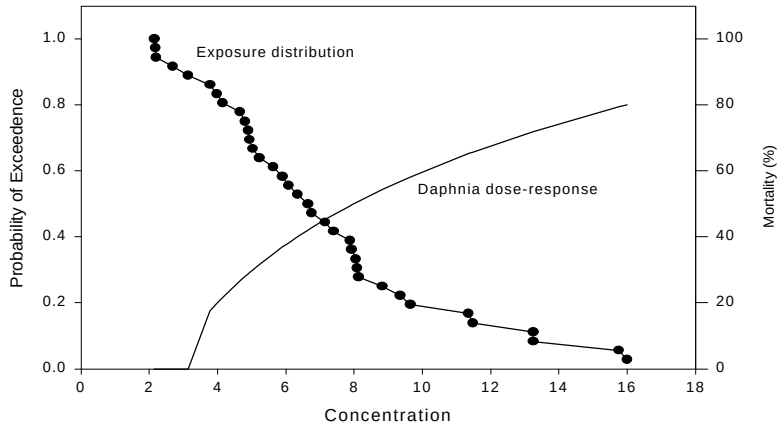
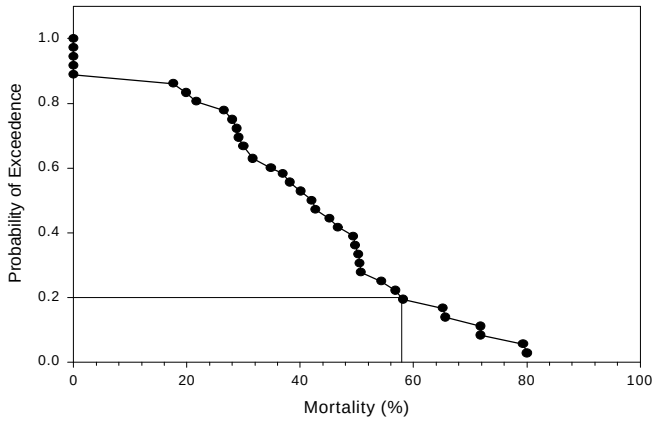


Figure 2-8.

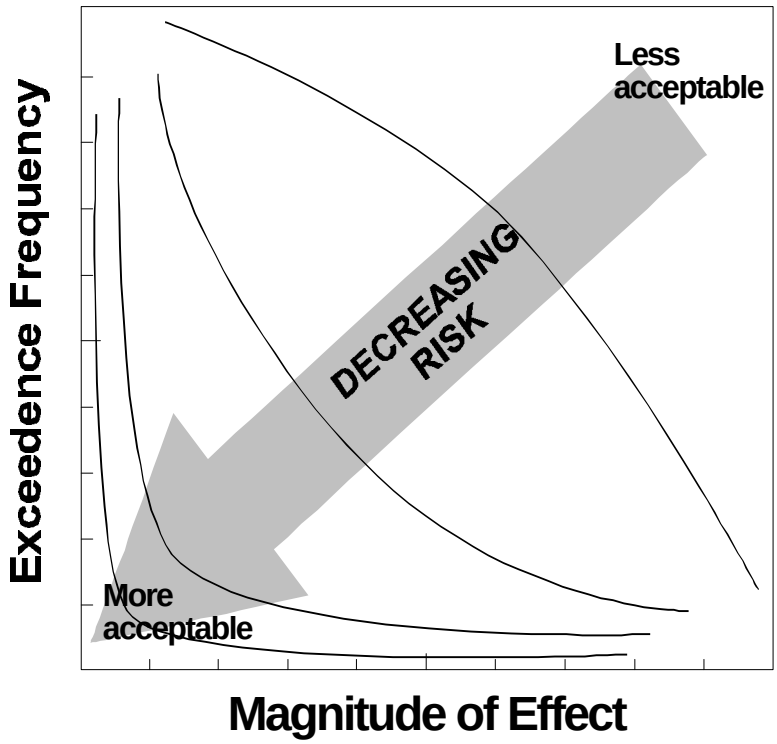


2.3.6.5. Risk Management and Mitigation Decisions where Risk Characterization is Judged "Adequate" at Tier 2

Following the initial risk characterization, an assessor/risk manager collaboration may result in the exposure models being re-run to identify the impact of mitigation options such as label rate reduction, formulation change, area restrictions, appropriate buffers, and application frequency on reducing the risk. Potential mitigation options may be defined after this "risk mitigation feedback loop" for each site scenario.

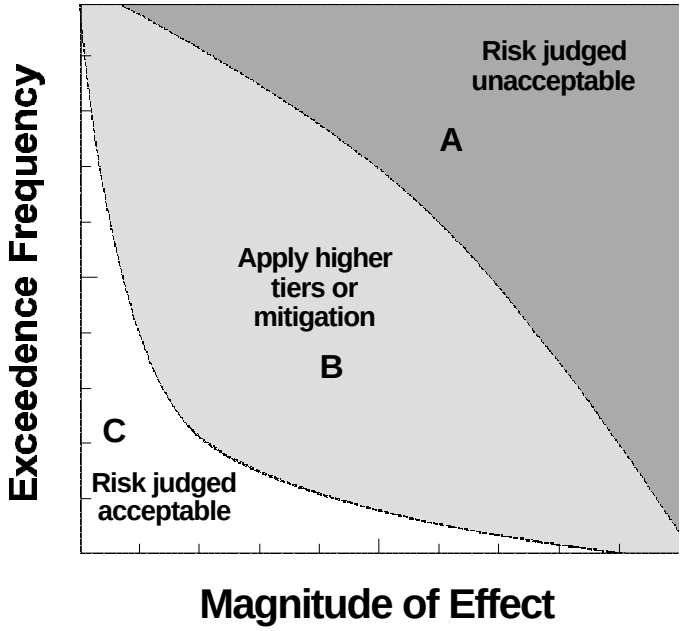
Risk management decisions at the end of Tier 2 are based on evaluation of Joint Probability Curves for different exposure estimates (e.g., distributions of 50^{th} percentile, 80^{th} percentile, 90^{th} percentile, and 95^{th} percentile annual maximum EEC's), pesticide use scenarios, mitigation options, and assessment endpoints. The closer a Joint Probability Curve comes to the axes, the lower the probability of effects of a given magnitude, and hence the lower the concern about adverse ecological effects. The farther the Joint Probability Curve lies from the axes, the higher the ecological concern, as shown in the family of curves in Figure 2-9.

Figure 2-9.



A dialog between risk assessors, risk managers, and other stakeholders may result in agreement on the boundary between acceptable risk, uncertain risk, and unacceptable risk (conceptualized in Figure 2-10). The positioning of lines defining "acceptable" and "unacceptable" is, of course, a policy matter for final determination by the Agency. If the Joint Probability Curve lies between the acceptable risk boundary and the axes, the risk is judged to be minimal. If the Joint Probability Curve lies outside the unacceptable risk boundary, the risk is judged to be high. If the Joint Probability Curve lies between these two boundaries, more information is required to characterize the risk. The assessment should not proceed to Tier 3 if the risk is judged to be minimal, or if the risk is so great that the registrant decides that mitigation options are unlikely to provide a label that is commercially viable and agrees with the Agency that the registration process should be stopped due to ecological concerns. If the risk is high or if significant uncertainty prevents a complete risk characterization, the risk assessment proceeds to Tier 3. The Tier 3 risk assessment will focus on those sites/scenarios where the risk to the aquatic environment is highest or where more information is required to characterize the risk.

Figure 2-10.



The rationale for presenting the risk characterization in the form of a Joint Probability Curve; or, more accurately, a family of curves reflecting the uncertainties in the analysis, is that it provides a better basis for decision making than a simple quotient. However, because so much more information is conveyed, informed judgement must be applied to the interpretation of the risk characterization. The following are examples of considerations that may come into play in evaluating Joint Probability Curves at Tier 2:

- If exposure analysis shows that exposure duration is typically shorter than the test duration, risk characterization based on a distribution of peak concentrations (rather than maximum time-weighted averages) may have overestimated the magnitude of effect;
- If exposure analysis shows that multiple exposures occur within one year for fish, or within 30 days for invertebrates and algae, then risk characterization based on peak or maximum time-weighted averages may underestimate the magnitude of effect.

Two examples—one sophisticated and one simple—of the types of information that could ideally be obtained from a Tier 2 assessment are given below.

1) "A preliminary assessment of product X use on corn to control corn borer suggested that potential water column concentrations in adjacent water bodies might impact aquatic invertebrate populations. Accordingly, a Tier 2 probabilistic evaluation of aquatic exposure was conducted using [current preferred primary regulatory model (e.g. PRZM-EXAMS (version 1.97) for ponds adjacent to corn fields in the Midwest following two aerial applications of product X at 1.1 pounds ai per acre using medium spray droplet quality applications with a 10 day interval in the early summer. This usage represents the maximum labeled use rate for the product across the region in which 90 percent of this use pattern occurs (Doane's research 1998)."

"By reference to the standard aquatic toxicity laboratory study data, a probabilistic analysis of the predicted exposures indicate that in 15% of 30 day periods (uncertainty range 10 to 25%), it is expected that more than one water column exposure "event" will exceed the 48 hour *Daphnia* LC_{50} value for more than 48 hours without a recovery period of at least 21 days."

"An assessment of the resulting probability of impacting the populations of aquatic invertebrates indicates that approximately one year in five, the population of *Daphnia* would be reduced for two to three 30-day periods. This value carries a relatively high uncertainty but is most unlikely to happen more than two years in five."

2) "Comparison of the 90^{th} percentile concentrations predicted for static and/or surface waters representing high exposure scenarios from an annual/30 day maximum series derived for use pattern "X" in region(s) "y" with the laboratory data developed in the standard package for acute and chronic toxicity for invertebrates and fishes indicates that short term impacts on fish species might be seen approximately 1 year in 10."

In either case, three types of risk management decisions are possible as shown:

- Ecological risks to aquatic organisms are determined to be minimal and the registration process may continue;
- Label modifications reducing application rate/frequency (or no more than two applications per season, or imposing a 50-ft untreated buffer adjacent to ponds, etc.) are required to ensure that ecological impacts will be minimal; or
- The risk assessment needs further refinement to reduce uncertainty and demonstrate that the concentrations predicted to be of concern are unlikely to occur in practice. Progression to Tier 3 is therefore necessary.

In practice, many compounds that reach Tier 2 will proceed to Tier 3. This is the result of some of the highly conservative assumptions still inherent in the exposure assessment process.

2.3.7. Tier 3 Risk Assessments

Tier 3 of the aquatic risk assessment process is essentially a probabilistic assessment designed to focus on those sites/scenarios and assessment endpoints identified in Tier 2 as requiring a refined risk assessment. Tier 3 is designed to reduce uncertainty in the assessment and better understand the nature of the risk and/or the potential impact of various mitigation options. Tier 3 uses similar approaches to Tier 2 but the process *builds on Tier 2* by incorporating new data or analyses such as the following:

- Acute toxicity studies with additional species;
- Investigations of the toxicity associated with time-varying or repeated exposure;
- Chronic toxicity studies;
- Sediment toxicity studies;
- Additional laboratory or pseudo field environmental fate studies;
- More sophisticated exposure modeling approaches;

- The inclusion of a more realistic scenarios representing the relevant agricultural landscape using GIS and/or spatial modeling approaches;
- More detailed evaluation of mitigation and management options.

The concept is one of identifying the most appropriate tool or tools from a well equipped "toolbox".

2.3.7.1. Problem Formulation at Tier 3

The previous tiers in the risk assessment process have determined the taxa and scenarios for which the risk criteria have been exceeded, and thus which require a refined assessment. Therefore the problem formulation phase in Tier 3 is dependent on the chemical and the use pattern, and the selection of one or more of the Tier 3 "tools" is based on expert judgement.

The Tier 3 problem formulation process requires that the risk assessor closely consider the basic information developed at Tier 2 to decide which issues are driving the predicted ecological risk and where, in the Tier 2 process, the conservative simplifying assumptions resulted in unrealistic output. Once the key factors are identified, a classic problem formulation analysis to define the specific question(s) to be addressed is possible. The resulting problem definition will allow the assessor to make a judgement call on which Tier 3 approaches should be investigated.

2.3.7.2. Exposure Characterization at Tier 3

Conceptually, Tier 3 begins with output from Tier 2 probabilistic modeling in hand. This may also include estimates of the impact of simple mitigation options on the exposure predictions. Some indication of the temporal distribution of the residues may be available as RADAR output. Figure 2-2 shows four examples of the types of Tier 3 exposure refinement that can be undertaken.

It is important to realize that there is no set process or "required" studies at Tier 3. On a case by case basis, the assessor must determine the most appropriate "tool" or 'tools" to refine the understanding of exposure. Since Tier 3 exposure refinements will often be focussed, at least in part, on understanding the impacts of mitigation alternatives, this may be an important factor to consider when selecting appropriate tools.

Refinements to Tier 2 modeling

This approach is normally adopted to help define uncertainty, to introduce additional factors and/or variation or to develop an understanding of exposure output sensitivity to various parameters. Options include:

- Use of additional or revised environmental fate parameters;
- More careful determination of the regional differences in predicted exposure with the intention of modifying label/mitigation on regional grounds;
- Use of"typical case" parameters as opposed to more conservative assumptions to better understand sensitive variables;

- Development of enhanced understanding of the impact of potential mitigation options (e.g. longer application intervals, more specific soil slope restrictions);
- Use of customized scenarios to address a wider range of water bodies (e.g. wetlands or estuaries) or temporal/spatial resolutions (e.g. hourly time steps for products that degrade rapidly in water or soil);
- Use of Monte Carlo approaches to investigate the likely range of exposure estimates associated with the distributions of environmental fate parameter measurements derived from laboratory studies;
- Use of AgDrift to evaluate sophisticated options for reducing drift entry to aquatic bodies and generate revised input for incorporation into revised Tier 2 model runs;
- Use of "secondary" models designed to deal with unique agronomic conditions or physico-chemical processes that are not specifically addressed in primary regulatory models. (e.g. RICEWQ);
- Comparison of model output with existing monitoring data for closely related chemicals.

Develop additional environmental fate (lab or field) data

This option would be selected to help reduce uncertainty, permit the replacement of default(often conservative) modeling assumptions or refine Tier 2 options or to incorporate a better understanding of the uncertainties around specific chemical parameters. Options include:

- Measurement of laboratory soil degradation rates and/or adsorption/desorption parameters across a wider range of soils;
- Measurement of foliar degradation and/or wash off rates (although ECOFRAM recommends this should ideally be part of basic data requirements for a foliar applied compound);
- Determine compound specific soil behavior data (e.g. dependency of degradation rate on moisture or adsorption behavior with aging);
- Other studies on a chemical specific basis.

Conduct fate and transport studies to better represent important processes.

This option would typically be selected to refine Tier 2 input values as above, to increase confidence in model prediction, help understand the relative importance of "real world" processes or whether the model algorithm is "missing" some important factor. Examples of the types of study to be considered include:

- Conduct a "Fate-o-Cosm" study (radiolabeled fate study in some sort of microcosm) to better measure physico-chemical processes acting in aquatic bodies and determine if important processes are not accounted for in the surface water model. This study also provides additional information that helps refine inputs used for Tier 2 modeling.
- Conduct small scale runoff studies (probably with simulated rainfall) to investigate relative runoff and/or confirm modeled runoff values.
- Conduct field soil metabolism studies to confirm which processes are most important under "real world" conditions.

Investigate actual landscape configuration for model scenarios.

This option would be selected in order to refine the scenario assumptions used for Tier 2 to:

- reflect relevant conditions;
- characterize the Tier 2 scenarios relative to typical use conditions;
- reduce spatial uncertainty;
- otherwise better understand the regional or crop specific landscape.

Options include the use of remotely sensed imagery and Geographic Information systems (GIS's) as well as marketing and USDA data to generate information to refine Tier 2 model scenarios to account for the issues such as:

- Typical occurrence of the crop of interest within watersheds in the region of concern;
- Extent of adoption of the compound of concern in the region of concern;
- Typical usage of the chemical by region (as opposed to modeling the maximum permitted usage);
- Proximity of the crop to water bodies;
- Soil/slope distribution for the crop of interest in watersheds at risk;
- Directional inter-relationship between water bodies and crop of interest;
- Existence of physical buffers (e.g. tall dense stands of trees) or vegetative filter strips which may reduce drift or sediment entry;
- Assess the spatial variability of soil/slope combinations or agronomy across the region of interest.

Any of the above work leads to new sets of model output and, possibly, additional post-processed datasets using RADAR.

2.3.7.3. Effects Characterization at Tier 3

The aquatic effects characterization can now become more focused and refined as needed. Depending on the uncertainties remaining after Tier 2 (as defined during the Tier 3 problem formulation), the effects analysis can follow a number of different paths including investigation of time-varying exposure, additional acute toxicity studies, additional chronic toxicity studies, or sediment toxicity testing.

Analysis of time-varying or repeated exposure

The decision to focus on analysis of time-varying or repeated exposure (see section 4.6) would depend upon the output of the exposure characterization. If it was predicted that water bodies of significance within a region or otherwise associated with a particular use pattern will experience multiple inputs of a pesticide, or that the pesticide concentration will vary significantly over time periods comparable to those used in toxicity tests, then an investigation of the effects of time-varying and/or repeated exposure should be considered.

Standard acute and chronic aquatic toxicity tests are designed to measure the effects of exposure to constant chemical concentrations. However, pesticide concentrations under field conditions typically vary over time. Also, organisms in the field often experience repeated exposures due to repeated pesticide applications or runoff events. Effects of time-varying and repeated exposure may differ from those of constant exposure in various ways.:

- Time-to-effect - Shorter exposure may have less effect than an exposure of standard duration.

- Selection - Previous pulses could select against the weakest individuals in the population, so subsequent pulses would affect fewer individuals.
- Cumulative damage - Previous pulses could weaken the survivors, so subsequent pulses would have greater impact.
- Acclimation - Previous pulses could strengthen the survivors, so subsequent pulses would have less impact.
- Delayed effects - Effects could occur after the exposure ends.

To examine these possibilities, the results of the exposure event analysis (via RADAR) can be used to help design laboratory toxicity studies simulating the exposures sensitive taxa would experience under actual field conditions. For example, if exposure analysis shows that exposure duration is typically shorter than the laboratory test duration, laboratory test methods can be modified to determine the relationship between exposure duration, concentration, and magnitude of effect. If exposure analysis shows that multiple exposures occur within one year for fish, or within one month for invertebrates and algae, laboratory tests can be designed (or tissue concentration and population level analysis can be used) to show how the magnitude of effect varies with exposure duration, concentration, and the interval between events.

The measurement endpoints generated from these studies replace those generated from the standard (constant exposure) toxicity studies used in Tiers 1 and 2.

Additional acute toxicity studies to determine sensitivity distributions

Development of acute toxicity data for additional species (see Section 4.5) is recommended if:

- acute toxicity concerns are not alleviated in the previous tiers; or
- substantial variability in sensitivity among taxa is demonstrated in previous tiers or expected based on the pesticide's mode of action.

Additional species in the most sensitive taxonomic groups (as determined in previous tiers) may be tested in order to 1) reduce the uncertainty associated with interspecies differences in sensitivity, 2) support a distributional analysis of species sensitivity, allowing estimation of the fraction of species affected at different exposure levels (Figure 2-11), or 3) generate more ecological information for site-specific analysis in Tier 4. Information generated in the exposure analysis will be used to determine the appropriate exposure duration for tests with additional species.

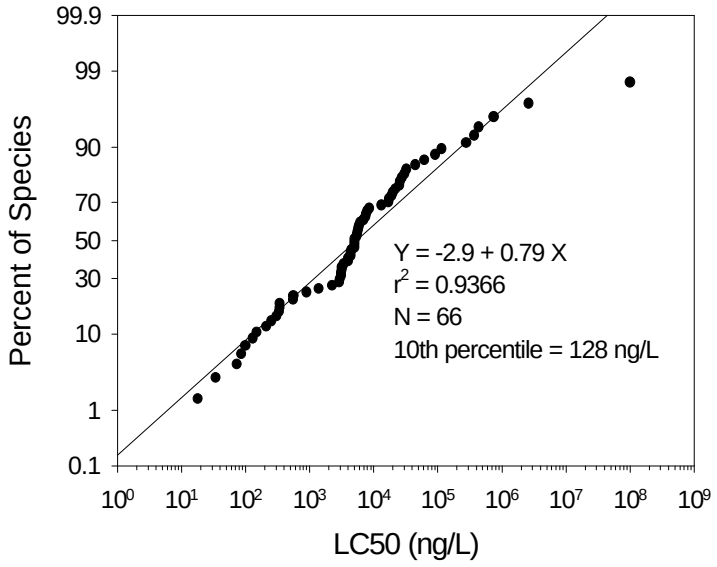


Figure 2-11. Distribution of LC50s for permethrin for all species tested.

Additional chronic toxicity studies

Development of chronic toxicity data for additional species is recommended if:

- chronic risk is demonstrated in lower tiers;
- significant prolonged or repeated exposure is expected;
- the compound has a potential for bioconcentration (high K_{ow} or measured bioconcentration factor);
- the mode of action or other data (e.g., reproductive effects in other organisms) suggests that chronic effects may occur.

A fish full life-cycle study may be triggered at this stage. Additional chronic studies on aquatic invertebrates may be useful to allow a distributional analysis (see section 4.5). The appropriate exposure regime would be determined based on information generated in the exposure analysis.

Sediment toxicity

A decision to focus the assessment on sediment toxicity (see section 4.??xxx) would be based on acute and chronic risk characterization using pore water concentrations (as determined by an exposure model such as PRZM/EXAMS) and the invertebrate toxicity tests from Tiers 1 and 2. The prediction of pore water concentrations takes into account the factors influencing partitioning of the pesticide between sediment particles and water, such as the pesticide's octanol-water partition coefficient (K_{ow}) and the organic content of the sediment. If the risk criteria shown in Table 2-2 are exceeded,

acute or chronic sediment toxicity test with a sediment-dwelling aquatic invertebrate may be triggered. A sediment chronic test may also be triggered by results of a sediment acute test.

If sediment toxicity is found to differ substantially from that expected based on pore water concentrations, unknown factors may be influencing bioavailability. In such cases, predicted pore water concentrations are not reliable indicators of sediment toxicity, and tests with additional sediment types may be needed.

If the sensitivity of benthic species is found to be comparable to that of pelagic species already tested, data for pelagic species can be used to estimate the distribution of species sensitivity for benthic organisms. If benthic species are judged to be substantially more or less sensitive than pelagic species, it may be useful to test additional benthic species to estimate the distribution of benthic species sensitivity.

2.3.7.4. Risk Characterization at Tier 3

After the exposure and effects risk characterization phases of Tier 3, refined exposure model output essentially similar to that already produced for Tier 2 will be available. In addition, there may be new toxicity results. Generally, the same approaches will be used for risk characterization as have already been described for Tier 2. A few comments are appropriate where new data have been generated in the course of the Tier 3 effects characterization.

Effects of time-varying exposure

The Tier 3 risk characterization uses the exposure assessment (e.g., RADAR output, with an event threshold defined in relation to acute or chronic toxicity concentrations) to estimate the concentrations for different time periods, their duration, and their return frequencies (the interval between events). The relationships between these parameters and magnitude of effect are used to predict the magnitude of effect associated with each exposure event. The distribution of exposure events generated by RADAR may then be compared to the distribution of effect magnitudes to generate a Joint Probability Curve as in Tier 2 (see section 2.3.6.4.). Alternatively, age-structured population models can be used to extrapolate the acute or chronic measurement endpoints (depending on which path is followed) to population effects (see section 4.4).

Sensitivity distributions

The cumulative distribution of species sensitivities (e.g., Figure 2-11) is a type of concentration-response relationship, and as such can be used to construct a Joint Probability Curve for a given exposure scenario or set of scenarios. Such a Joint Probability Curve indicates the probability, within the range of scenarios used in the exposure analysis, of exceeding a given toxicity threshold (usually the $LC_{50,}$) but another point estimate could be used instead) for a specified percentage of aquatic species.

2.3.7.5. Risk Management and Mitigation Decisions at Tier 3

The decision options applicable following Tier 3 risk characterization are essentially similar to Tier 2. The decision may be one of the following:

- Aquatic ecological risks are determined to be acceptable and the registration process may continue;
- Label modifications to reduce exposure are required to ensure that ecological impacts will be within acceptable limits; or
- The risk assessment needs further refinement to reduce uncertainty and demonstrate that unacceptable effects are unlikely to occur in practice. Progression to Tier 4 is therefore necessary.

In practical terms, many compounds that are indicated as needing further evaluation at Tier 1 will reach this point in the aquatic risk assessment. As a result of the practicalities of registering pesticides, it is likely that in many cases with new pesticidal active ingredients, the registrant will have conducted work to this level before any significant discussions with Agency regulators have taken place. Accordingly, the ECOFRAM aquatic groups strongly recommend that OPP EFED develops stringent standards for reporting model runs accurately and succinctly with clear descriptions of the input variables and standard expressions of the outputs. This will ensure that when registrants submit exposure estimates they do so in a format that meets EPA standards and can serve as an vehicle for permitting efficient OPP EFED decision making and focusing registrant/Agency discussion on risk management options. The associated electronic files must be readily available to EPA OPP EFED scientists so that they can verify that the modeling and selection of input parameters and scenarios meets current standards and properly addresses the science and regulatory issues. It is equally useful to submit effects data electronically. As with all other studies submitted by registrants to EPA under FIFRA, the regulators will have the task of approving or rejecting the submission or requesting additional information.

2.3.8. Tier 4 Risk Assessments

If the outcome of a Tier 3 risk assessment indicates that there is still uncertainty about the potential for aquatic ecological impacts and feasible mitigation options have been judged not to be acceptable and/or effective, the only options are to abandon further work on the product or to progress to the more complex studies involved in Tier 4. Progression to Tier 4 is only likely to occur after the outcome of Tier 2 and 3 risk assessments have been discussed with EPA and a joint problem formulation meeting between EPA and the registrants has identified specific goals. One underlying reason for this is the high cost and commitment involved in many of the Tier 4 activities; this level of investment should only be considered when a clear regulatory consensus has been forged.

Tier 4 generally involves broad reaching experimental, field monitoring or mitigation validation programs designed to definitively characterize key aspects of the toxicity or exposure profiles. Tier 4 assessments are only conducted on a case-by-case basis and are very tightly focused on a specific question. The purpose of a Tier 4 assessment is often to validate predictions resulting from the Tier 3 assessment (though, in certain circumstances, a registrant might decide to conduct a Tier 4 program without conducting Tier 3 evaluations) and to further reduce uncertainties.

2.3.8.1. Problem Formulation at Tier 4

The problem formulation step for Tier 4 is very similar to that of Tier 3. It is based upon a detailed review of the output from Tiers 2 and 3 and normally focuses on highly specific scenarios or uses indicated in Tier 3 as still being of concern. Tier 4 is distinguished from Tier 3 because this problem formulation step will most likely involve discussion between registrants and regulators. Another driver may be the need to demonstrate and/or validate model predictions including the impact of agreed mitigation measures.

2.3.8.2. Exposure Characterization at Tier 4

Conceptually, Tier 4 exposure characterization study design is founded upon a sound understanding of the key risk factors associated with a use pattern/exposure scenario. The problem to be addressed is often very specific but rarely easy to address since the obvious "tools" will already have been applied in Tier 3. Figure 2-3 shows four examples of the types of Tier 4 exposure refinement that can be undertaken. As with Tier 3, there is no set process or "required" studies; the assessor must determine the most sensible approach to cost-effectively answer the regulatory questions.

Examples of what might be involved in addressing each of the four "types" of Tier 4 exposure study are given below. However, the typical case will be to design a specific experiment to address a particular issue.

Widespread monitoring

Increasingly commonly under the pressures imposed by the Food Quality Protection Act (FQPA), it may be necessary to perform widespread monitoring of water residues associated with the use of a pesticide. This is generally only an option for compounds with a well established position in the market place. The monitoring data have the potential to provide confirmation that model-based estimates of exposure, even at Tier 3, still exaggerated the actual residues found in the "real world" because many conservative assumptions are still included amongst the model inputs.

The ECOFRAM Aquatic Exposure Workgroup strongly recommends that widespread monitoring be carefully utilized and that the results from monitoring studies should not be given undue emphasis. Unlike predictive modeling they only represent one scenario in one season and thus can prove misleading (for example if there is a "one-in-a-hundred-year" runoff event or if a particular area never sees an extreme storm in two or three seasons). Widespread modeling is included only at the Tier 4 level because the workgroup members feel that compound specific monitoring should only be set in place when relatively sophisticated modeling has indicated key issues and regional differences. When used in concert, modeling and monitoring can make a powerful combination; used alone either can prove misleading given the uncertainty associated with model predictions and monitoring only reflecting a few unique sets of circumstances unless continued for many years across many sites.

Detailed investigation of the efficacy of mitigation

Perhaps more appropriate for a novel active ingredient that will not achieve full market share for several seasons are post-registration field studies specifically designed to investigate the efficiency of agreed mitigation measures at reducing potential transport. These studies must be designed on a case-by-case basis. They would most often involve strategically designed monitoring studies in fully characterized and instrumented watersheds where meaningful comparative data on the impact of various mitigation approaches can be generated. It is worth noting that it may take more than one season of monitoring within a specific watershed to establish improvements of baseline parameters resulting from mitigation steps.

Highly refined watershed evaluations and modeling

The team envisage that in some exceptional cases, it might be necessary to use highly complex watershed scale models to address larger receiving water bodies and the accompanying landscape features. This might be needed to place the results of widespread monitoring studies in context.

Benchmark modeling relative to existing chemical data

Another option for a product which is novel or not widely used, is to use a "benchmarking" approach based on results of ambient monitoring of a chemical with relatively similar environmental fate and application characteristics.

By a combination of comparative modeling using the chemical under review and the "benchmark" product and extrapolation to the monitoring data for the benchmark, more realistic and justifiable estimates of the concentration of the chemical under review may be created.

2.3.8.3. Effects Characterization at Tier 4

Effects characterization could follow a number of different paths depending on the questions to be answered. As with exposure characterization at Tier 4, the types of problem to be addressed are often very specific but rarely easy to address. Figure 2-3 shows four examples of the types of refined effects characterization that can be undertaken in Tier 4. Examples of what might be involved each of these effects characterizations are given below. However, the typical case will be to design a specific experiment to address a particular issue.

The ECOFRAM Aquatic Effects Workgroup considered the following tools for Tier 4: population level analysis, pharmacokinetic or toxicokinetic modeling, behavioral tests, and microcosms/mesocosms. Each of these is discussed in more detail in Chapter 4.

Population level analysis

Methods for population analysis in Tier 4 assessments would be highly species- or environment-specific. Individual-based models, meta-population models, or spatially-explicit population models could be used (see section 4.4). The analysis would be specifically designed to address the uncertainties (regional variability, effects on endangered species, indirect effects, unusual modes of action, etc.) that trigger a Tier 4 assessment.

Pharmacokinetic or toxicokinetic models

Physiologically-based pharmacokinetic (PBPK) or toxicokinetic (PBTK) models are used to describe absorption, distribution, metabolism, and excretion of chemicals in biota (see section 4.6). The principal application of these models is the prediction of a dose to a target tissue, a body burden for a parent chemical or transformation product or chemical concentrations over a period of time in specific tissues and organs. By coupling these models with critical body residues (CBRs), effects of time-varying or repeated exposures can be estimated. This concept can also be applied to other cases where exposure-response relationships are complex, such as exposure via sediments or diet. PBPK models can be used to reduce uncertainty associated with conventional concentration-response analysis.

Behavioral tests

Behavior is a manifestation of physiological and biochemical processes, and as such can act as a sensitive indicator of exposure to a toxicant or of a change in conditions (see section 4.7). Behavioral tests could be designed to answer an ecologically relevant question with an interpretable response. For instance, avoidance of a toxicant may decrease exposure to the toxicant, but does this avoidance have implications due to the displacement of the organism from beneficial habitat?

Microcosms/mesocosms

Microcosms and mesocosms (model ecosystems) allow the following advantages when attempting to determine the risks associated with the use of a pesticide:

- quasi-realistic exposure including pesticide partitioning and dissipation;
- measurement of the responses of many taxa;
- observation of population, community, and ecosystem responses; and
- observation of ecological recovery.

The limitations of mesocosm/microcosm studies are that they are expensive to conduct, produce complex results which may be difficult to interpret, and can have very high variability. These studies may be very useful, however, to address the "what if?" and "so what?" questions posed by risk managers. The mesocosm tests must be focused on a particular question and designed to test a specific hypothesis (see section 4.9).

2.3.8.4. Risk Characterization at Tier 4

The approach to risk characterization in Tier 4 depends entirely on the site-specific or chemical-specific concerns that remained after Tier 3. Results of the specialized studies conducted in Tier 4 are used to refine or validate the predictions resulting from Tier 2 and 3 risk characterizations. For example, analysis of a time varying exposure and the resulting magnitude of effect could be further refined using exposure and/or effects monitoring, higher level population or pharmacokinetic modeling, or microcosm/mesocosm studies. Professional judgement and a weight of evidence approach would be used to define the aquatic risk and mitigation required.

2.4. Expression of Probabilities and Reporting of Risk

2.4.1. Expressing Exposure

Pesticide concentrations in aquatic environments are variable and transient because of application frequency (residue availability), physicochemical properties that dictate mobility and persistence, and stochastic forces (e.g. rainfall or wind speed) that drive the hydrodynamic response of the receiving water system. Moreover, care must be taken to consider how much of the **absolute** measured or predicted concentration is bio-available to the organisms of concern. This is critical because the concept of exposure describes contact between the bio-available fraction of the compound of interest with the target organism of concern.

Fortunately, aquatic exposure assessment may be considered simpler than terrestrial pesticide exposure estimation due to a pair of over-riding assumptions which were used by the ECOFRAM Aquatic Workgroups:

- that the water concentrations are homogenous within the movement range of the organisms being considered; and
- that the dominant route of exposure for an organism is via experiencing the concentration present in the water column and therefore that dietary or behavioral factors can be ignored under all but the most complex analyses.

Once these assumptions are adopted, it becomes clear that because of the innate temporal variability of water body concentrations, potential exposure should be described with great care. For example, in terms of a concentration across some specified time period such as a time weighted average (e.g. annual mean concentration) or a maximum/minimum in a given time period (e.g. maximum daily value) or as a duration when the exposure concentration exceeds a specific threshold value (e.g. concentration exceeded *Daphnia* LC_{50} for 2 days).

The latter case is particularly instructive and has been termed an “exposure event profile” since it starts to describe the time dependent nature of the exposure that organisms may experience and offers greater opportunities for understanding associated risks. Exposure event profiles are derived from analysis of a complete measured or predicted time series based on the minimum time step resolution available (e.g. daily predicted water column concentrations from a 36 year PRZM-EXAMS output file). The exposure event profiles attempt to describe the instances of exposure exceedance relevant to the endpoint specified in the problem formulation statement. Examination of the entire time series allows a probability analysis of key aspects of such event profiles such as duration of exposure above the threshold, the intervals between significant events and their frequency of occurrence. It was for this purpose that the RADAR tool was developed by the ECOFRAM Aquatic Exposure Workgroup.

MAY PUT IN SOME GRAPHIC EXAMPLES OF EXPOSURE PROFILES ACROSS TIERS HERE AFTER PEER REVIEW

2.4.2. Expressing Effects Characterization

To be added.

2.4.3. Expressing Risk Characterization

Effective communication between the risk assessor and the risk manager can be cultivated by adopting relatively standard formats.. While the exact format of this may be a matter of EPA policy, the details of what needs to be defined to adequately describe the information is a matter of science. While the scope of the information to be communicated obviously will increase with progression through the tiers, the concepts involved do not change. The examples below are not comprehensive but serve to illustrate the concepts.

Ideally, a series of statements along the following lines is needed. In this paragraph "variables" to be included are shown italicized and enclose din square brackets *[example]* and then some more specific examples are given in the following sections.

A sentence is needed to summarize the "problem formulation" that generated the risk assessment:

> "An initial assessment of the use of *[product X]* on *[crop]* with *[use pattern]* suggested that the potential *[exposure metric]* might impact *[endpoint]* for *[type of organism]*; as a result, a risk assessment has been conducted."

A description of the effects and exposure characterization needs to follow:

> "A tier *[number] [evaluation type]* evaluation of aquatic exposure was conducted using *[model, approach]* for *[potential receiving water system] [proximity]* to *[crop]* fields in *[region]* following *[numbers of treatments] [application method]* with *[product]* at *[use rate]* using *[additional use pattern info]* (e.g. intervals, incorporation etc). This use pattern reflects the *[representativeness]* usage by farmers in the *[regions (give reference)]* ."

If the effects characterization goes beyond the standard data set, additional descriptive material specifying the endpoints used would be needed here.

A description of the risk characterization follows:

> "Consideration of the exposure information described above with the *[standard aquatic toxicity study data and/or additional test results]* indicated that in *[percentage]* of *[period description]* with *[+/- percentage uncertainty]*, the *[medium (e.g. water column/sediment]* concentration will exceed the *[threshold]* for *[taxa/species]* for [*duration]* with *a [recovery period description]*."

If joint probability curves linking the effects dose response data and probability of exposure have been prepared, the following type of description can be added:

> "An assessment of the probability of impacting the *[problem formulation endpoint]* indicates that in *[probability]* of *[time units (e.g. seasons, 30 day periods or years)]* the impact on *[problem formulation endpoint]* will be *[describe]*. The uncertainty around this value is believed to vary between *[variability]."*

Note that these idealized expressions of the results of exposure, effects and risk characterizations will rarely be completely achieved. Nevertheless, the ECOFRAM groups believe that this should represent the goal to which risk assessor should aspire. In all cases, risk assessors must be prepared to justify the assumptions they have made and, moreover, where information is NOT available for key parameters, they should be in a position to explain why. Probabilistic risk assessments are complex and only through precise explanations of the underlying data and findings can clarity be achieved.

The ECOFRAM team developed a simple table (2-3) to indicate the range of variables likely to be covered in these statements.

Table 2-3 Key Variables associated with each step of the ECOFRAM proposed Tier Process for Aquatic risk assessments.

Parameter	Tier 1	Tier 2	Tiers 3 and 4
Evaluation type	Deterministic	Probabilistic	Probabilistic
Model	Ideal Tier 1 model (GENEEC)	MUSCRAT 2 (PRZM-EXAMS)	Refined Ideal Tier 2 - describe refinement/approaches
Potential receiving water body	Pond	Pond, Headwater stream	Pond, Headwater stream, river, reservoir
Proximity	Adjacent to treated fields	Adjacent to treated fields	Varying degrees of removal from edge - includes buffers or mitigation
Crop	"Row crop", cranberry, rights of way, forestry or rice (ideally crop specific)	Crop specific	Crop specific (perhaps regional)
Region	High exposure scenario	National or relevant regional	National, relevant regional and more specific scenarios
No. of treatments/ application methods	Closest approximation in Tier 1	Specific details from worst case	Worst case and options
Representativeness	Worst label case	Worst case and/or "typical case" and /or mitigated cases	Worst case and/or "typical case" and /or mitigated cases
Toxicity study data	Standard study suite	Standard study suite	Standard studies plus additional work as available
Occurrence % of periods	Currently not applicable	Indicated by RADAR or direct from PRZM-EXAMS output	Indicated by RADAR or direct from PRZM-EXAMS output
Periods	Annual return frequency	pre-specified for taxa, annual, 30 day or seasonal by life cycle	pre-specified for taxa, annual, 30 day or seasonal by life cycle

Parameter	Tier 1	Tier 2	Tiers 3 and 4
% uncertainty	Currently not applicable	Probability of exposure available from PRZM-EXAMS	Other information as available
Medium	Water col. (sediment desired)	Water col., sediment	Water, sediment, other water body compartments
Censoring threshold	None	Standard toxicity values and/or LOEC/NOEL	Various
Taxa/species	Fish/Aquatic Invert	warm/cold water fish, benthic invert, water col. Invert, marine fish/invert, non-target aquat. plant	Warm/cold water fish, benthic invert, water col. Invert, marine fish/invert, non-target aquat. plant
Duration	Instantaneous, 21, 60 or 90day	Instant, 24, 48, 96 hr, 21, 60, 90 d	Tier 2 plus intervals as needed
Recovery period	Ignored	from RADAR	from RADAR

The ECOFRAM Aquatic Workgroups strongly recommend that EPA and industry risk assessors adopt the approach described above to improve precise reporting of risk assessments. A small workgroup should be set up to develop improved and agreed lists of the key parameters to be included in the risk characterization statement.

2.4.3.1. Example

The following paragraphs provide a more concrete example of the type of idealized information that might be expected by a risk manager.

A preliminary assessment of product X use on corn to control corn borer suggested that potential water column concentrations in adjacent water bodies might impact aquatic invertebrate populations. Accordingly, a Tier 2 probabilistic evaluation of aquatic exposure was conducted using PRZM-EXAMS (version 1.97) for ponds adjacent to corn fields in the Midwest following two aerial applications of product X at 1.1 pounds ai per acre using medium spray droplet quality applications with a 10 day interval in the early summer. This usage represents the maximum labeled use rate for the product across the region in which 90 percent of this use pattern occurs (Doane's research 1998).

By reference to the standard aquatic toxicity laboratory study data, a probabilistic analysis of the predicted exposures indicate that in 15% of monthly periods (uncertainty range 10 - 25%), it is expected that more than one water column exposure event will exceed the 48 hour Daphnia LC_{50} value for longer than 48 hours without a recovery period of greater than 21 days.

An assessment of the resulting probability of impacting the populations of aquatic invertebrates indicates that approximately one year in five, the population of daphnia would be reduced for two to three thirty day periods. This value carries a relatively high uncertainty but is most unlikely to happen more that 2 years in 5."

2.5. Risk Management and Mitigation

Ecological risk assessment in pesticide regulatory operations is best viewed as the application of regulatory science in a risk management context. This view is supported by emerging risk-based approaches to environmental regulations (Thomas, 1987; Science Advisory Board, 1990a, b, c, d), which promote increased integration of societal values, science, and risk mitigation practices for environmental decision making (Maciorowski,1998). The integrated decision-making process involves the following three interactive phases:

1. **Ecological risk assessment** is a science-based activity that integrates exposure and effects (the interaction of stressors and ecological receptors). Risk characterization estimates the risk and summarizes the strengths, limitations, assumptions, and major uncertainties.
2. **Risk mitigation** involves remediation or mitigation measures to reduce or eliminate source contamination and hence reduce exposure and adverse environmental impacts.
3. **Risk management** is a policy-based activity that defines risk assessment questions and endpoints to protect human health and the environment. It takes the scientific information provided in the risk assessment and incorporates social, economic, technical, political, and legal factors that impinge or influence the final decision and selects regulatory actions.

The underlying principles behind risk reduction and integrated decision making are detailed in the strategic initiatives and guiding principles recently released by U.S. EPA, (USEPA, 1994) and include ecosystem protection, pollution prevention, strong science and data, partnerships, and environmental accountability. In essence, the emerging policies are directed toward greater participation in environmental problem solving and decision making, including parties affected by the decision (regulated community, user groups, public interest groups, general public, and scientists).

2.5.1. Risk Assessment Interface

Risk assessors are generally concerned with performing risk assessments in the most scientifically credible manner and identifying additional data or research to better characterize risk. This perspective is appropriate in that risk assessment is a tool to evaluate and communicate scientific information. As such, it must retain scientific independence and rigor to ensure that risk characterizations provide an objective evaluation of the available data and information. Once a risk characterization is used to reach a decision, the risk assessor rarely has an opportunity to request more data or information on which to base opinions or recommendations. Indeed, there is longstanding precedent for separating risk assessment and risk management to ensure that scientific integrity is maintained in decision making (NRC, 1983, 1993; Thomas, 1987; U.S. EPA, 1998). However, separation does not imply an absence of communication or a failure to understand risk managers processes and needs (Maciorowski, 1998).

Effective communication of risk assessment results to managers is a perennial issue. Better communication of risk assessment results enhances the role the risk assessor can have in the risk management arena. Communication of

probabilistic data is particularly problematic., Figure 2-10 is a conceptual diagram presenting risk assessment information using a gradient of ecological acceptability. Assessors must decide on a policy basis the qualitative or quantitative boundaries for "less and more acceptable". The area (or "gray zone") between these boundaries might be established on a compound or region specific basis. Once policies are established, risk managers could balance other management factors, evaluate decision options, and negotiate within agreed upon areas of the gradient.

Recognizing that the conceptual risk assessment framework is purely numerical, the risk manager and assessor need to consider the social and ecological value of species to groups of organisms that may be affected, even when the exceedance probabilities are low. This requires that the risk assessor and manager be cognizant of the biological and social significance of the species in the potentially affected ecosystem.

2.5.2. Mitigation and Risk Reduction

Once an ecological risk characterization is passed to a risk manager, additional communication and discussion is necessary. The risk assessor will often be asked to analyze and the risk manager to judge the effect of proposed risk mitigation on the originally assessed risk. This does not change the original risk assessment, which serves a baseline estimate, but the analysis may determine as to whether management actions such as mitigation will reduce risk to acceptable levels.

Presented with a scientific evaluation of risk, the risk manager may want additional information or study, or may need to act on the information in hand regardless of its scientific strengths or shortcomings. Rather than refine the risk assessment, a risk manager or registrant may opt to adopt mitigation to reduce the risk, even in the face of uncertainty that the mitigation will be effective. When such situations occur, risk assessors must clearly and succinctly summarize risk, uncertainties, and options for the benefit of risk managers, stakeholders, and the public at large. Furthermore, risk assessors must be willing to evaluate the relative merits of risk mitigation even in the absence of data. **Risk reduction or risk mitigation activities are defined as actions to reduce or eliminate adverse human health or environmental effects.** In the ecological area, they are becoming increasingly important risk management tools. In the case of pesticides, these are usually manifested as changes or restrictions for specific uses, resulting from label changes (Maciorowski, 1998).

The risk reduction/mitigation process can begin any time during the process of reviewing a pesticide for the purpose of registration or reregistration. The environmental fate and effects of the pesticide are evaluated using the required studies and available incident data for terrestrial and aquatic systems. If an ecological concern is suggested at any stage in the process, then either further risk refinement or risk mitigation or a combination of these approaches can be initiated. Risk mitigation alternatives are tools used in discussions between risk assessors and managers to evaluate whether the exposure or effects of a pesticide can be reduced to result in a level of risk below the concern. Mitigation options were reviewed by

the Aquatic Risk Assessment and Mitigation Dialogue Group (SETAC 1994), and they made the following recommendations to promote a fuller consideration of mitigation alternatives in the decision making process.

1. Mitigation must provide meaningful ecological risk reduction, be pragmatic and achievable, and consider the need for timely decisions and cost-effective use of financial and human resources.
2. A phased approach for evaluating the efficacy of mitigation measures should be adopted via the appropriate regulatory channels as the current working guideline.
3. Collaborative efforts among registrants, government, and academia should be encouraged when addressing mitigation verification issues.
4. Risk managers must focus on developing a better understanding of the scientific principles governing risk assessment.

The ECOFRAM Aquatic Workgroups have considered mitigation in more detail.

2.5.2.1. Overview of Approaches for Mitigating and Managing Perceived Risk

When a potential for ecological risk is shown to exist, there are various options open to the EPA OPP and registrants to meet their mutual goals. These range from cancellation (existing chemicals) or non-registration (new agricultural chemicals) to approval in recognition of the fact that the risk is not judged significant in the context of FIFRA. Most often, however, the agreed way forward involves applying various risk management and mitigation options to modify the product use pattern to reduce or manage the risk such that the FIFRA risk benefit assessment becomes acceptable to OPP. Although occasionally there are opportunities to reduce the effective toxicity of the formulation (e.g. micro-encapsulation, retentive granules) it is more usual for risk reduction strategies to reduce the predicted exposure. There is a hierarchy of approaches to achieve this:

1) The most effective method is to reduce the amount of chemical applied since this instantly reduces risk in a highly quantifiable fashion. This input "reduction" can take several approaches.
   a) Reduction of required application rate on the product label for some or all uses.
   b) Reduction of permitted application frequency and/or season; possibly on a regional basis.
   c) Spatial restrictions (e.g. avoiding estuarine areas, avoiding endangered species habitats).
2) The second type of approach is to modify the application methods to reduce potential transport. For example, if the risk assessment shows that drift from aerial applications is significant then requirements to ensure that drift is reduced or eliminated (e.g. buffer zones, boom/nozzle configuration, droplet size and meteorological restrictions) can be effective. Similarly, where runoff appears the dominant transport mechanism, incorporation of the chemical can significantly reduce potential exposure
3) Thirdly, efforts may be made to minimize transport from the treated fields, normally focusing on runoff. Within this category, there is again a hierarchy.
   a) Ideally, the chemical in runoff is trapped within the field before reaching the edge. Examples of this approach include construction of terraces to hold up runoff and permit settling of sediment and the use

of conservation tillage and/or vegetative strips within the field as alternatives to minimize runoff in the field.

b) Failing this, various approaches (e.g. edge of field buffers) can be employed to reduce the amount of sediment and chemical reaching aquatic systems near the edges of fields.

2.5.2.2. Selecting Mitigation Practices

Many factors interact to determine transport of pesticides from agricultural fields. These factors and their interactions need to be understood before appropriate decisions on potential mitigation options can be made. These factors can be categorized into:

1) Pesticide properties:
   - The major factors determining concentrations of pesticides in runoff from cropland are persistence, adsorption to soil. and solubility
2) Pesticide transport process:
   - Runoff Entry: The major factors are hydrologic; including the intensity and duration of precipitation and the rate of infiltration as affected by soil factors and conditions.
   - Drift Entry: The major factors are the wind speed / direction and the relative humidity in combination with the application method and the impact of the boom/nozzle/volume /pressure combination selected as it affects droplet size distribution.
3) Landscape
   - The major factors are the extent of occurrence of the crop of interest within the watershed, the area treated, the existence of natural or managed untreated buffers and presence of various soil/slope combinations.
4) Application and management practices:
   - The major management factors to reduce field transport of pesticides are the rate, method, timing, and choice of applied pesticides; cropping sequence (in time and space); water management; and tillage or soil management systems. Field-to-stream transport of pesticides may be managed using mechanical structures, such as terraces, and use of landscape reconfiguration such as wetlands or buffer strips.

To determine the best combination of mitigation practices to reduce pesticide transport by runoff, mechanisms of loss and pesticide interactions with the soil and mitigation practices must be considered. Depending on soil adsorption in relation to other factors, pesticides can be mostly lost with surface runoff water, sediment, or water percolating out of the root zone (water which may return to the surface through base flow or artificial subsurface drainage). Erosion control is a good mitigation practice for strongly adsorbed pesticides. For moderately adsorbed pesticides, soil incorporation is a good mitigation practice that reduces the amount of pesticide in the thin surface soil "mixing zone" and thereby decreases surface runoff transport. Other practices that enhance infiltration can also reduce surface runoff but with a concomitant increase in leaching. The route of infiltration (e.g., through "macropores") can allow pesticides to percolate through the root zone more quickly than normally expected, resulting in "concentration spikes" that may be of ecological concern if a field has tile drains. However, for moderately to strongly adsorbed pesticides, leaching transport is usually much less

significant than movement in surface runoff. For weakly or non-adsorbed pesticides, increased infiltration reduces runoff but may enhance leaching. Appendix 2-2 provides further details of runoff mitigation factors and practices recommended by the ARAMDG report (ARAMDG, 1994). USDA and others are starting various education programs to promote the importance of landscape management approaches for reducing pesticide and , more importantly, sediment transport in runoff (USDA Grassed Buffer promotion programs). EPA OPP EFED is collaborating with Industry to develop specific guidance documentation to standardize approaches of particular value for pesticide issues (EPA, in press). Unfortunately, the existing methodology for modeling pesticide runoff does not yet have proven tools for accurately predicting the impact of runoff mitigation practices.

Where drift entry of a pesticide into aquatic systems appears to provide the most cause for ecological concern, different mitigation options apply. The Spray Drift Task Force (SDTF) has developed extensive documentation after conducting a wide ranging and comprehensive program of field studies. The field data has been analyzed to develop a suite of tiered models covering atomization as well as pesticide drift arising from aerial, air-blast and ground hydraulic applications. These validated models provide the necessary tools for calculating the potential impact of various options for mitigating drift including nozzle types (as evidenced in spray quality), boom configurations, swath offsets, avoidance of stronger winds and volume/pressure combinations. The SDTF has also prepared various guidance materials and training programs to educate applicators in measures for drift reduction (e.g. SDTF, 1998a, 1998b, 1998c and 1998d).

The proposed ECOFRAM Aquatic tiered risk assessment approach permits the examination of the potential impact of very simple mitigation options (e.g. removing certain regions, reduction of rate, numbers and/or frequency of applications) at Tier 2. More sophisticated evaluation and modeling of mitigation options is one of the risk refinement 'tool box" options at Tier 3. At this point, the information developed can be presented to risk managers and interested parties to clearly present the strong and weak points of the various alternatives.

2.5.3. Communication of Mitigation Alternatives to the Risk Manager

Risk managers must be carefully informed of the output of revised risk characterizations resulting from characterizing the anticipated output from mitigation alternatives scenarios. In many ways, the communication challenge is even greater at this step since in addition to the science based issues associated with the Tier 2/3 risk assessments, the inclusion of the anticipated impacts of field scale mitigation measures will often add considerable uncertainty to the process. The proposal for a mitigation option requires evaluation of human, societal and economic factors likely to influence the adoption of the measures as well as a consideration of how adherence to the process can be enforced and/or monitored.

Mitigation alternatives and their impact on assessment endpoints could occur in a complex variety of ways. For example:

- A single alternative and a single response (*e.g*. effects of reduced applications per season on small mouth bass populations);
- A single alternative and multiple responses (*e.g*. effects of reduced application amounts on aquatic

invertebrate species and the ensuing secondary effects to aquatic ecosystem health);

- Multiple alternatives and a single response (*e.g.* effects of buffer zones, reduced application number and the resulting reduced water column concentration on lake trout populations);
- Multiple alternatives and multiple responses (*e.g.* effects of buffer zones, reduced application number and resulting reduced concentration on species diversity and fish population time to recovery).

In view of the high uncertainties associated with several of the options for mitigating aquatic exposure, validation of the effectiveness of mitigation alternatives may be required. Once mitigation measures have been identified and implemented, focussed field experiments or monitoring may be required to verify the efficacy of the risk mitigation measures. Because of the inherent variability of weather parameters relative to the chemical application date, quantifiable verification of effectiveness of the mitigation may take many years of monitoring and therefore, in some cases, managed field experiments can validate the potential for a mitigation approach to work. Building upon some of the ideas of SETAC (1994); discussions within ECOFRAM have resulted in a multi-phase approach to the verification of mitigation effectiveness.

- Steps investigated largely during Tier 3 (and to a limited extent in Tier 2):
  - Simulation models to establish effectiveness (not yet feasible);
  - use of professional judgment and inference to evaluate effectiveness;
  - evaluation of acceptability and practicality in the agricultural community
- If ecological concerns are not alleviated, then consider in Tier 3 and/or Tier 4:
  - additional mitigation measures and/or develop greater user acceptance/training; and/or
  - agree protocols for site-specific managed field studies to demonstrate the potential efficacy of the approach.
- Ultimately, exposure monitoring and/or cause-effect field studies may prove essential where the uncertainty and/or the potential impacts are still sufficiently high as to merit confirmatory validation

2.6. Recommendations for Improving Aquatic Risk Assessment and Characterization

The fundamental recommendation of the ECOFRAM Aquatic Workgroups is that a flexible, tiered process for Aquatic risk assessment be agreed and published so that registrants and OPP EFED are using to facilitate common framework for discussion and submission of assessments. The following recommendations address more detailed aspects of Risk Assessment and Characterization. Specific recommendations relating to aquatic exposure and effects studies or issues are documented in Chapters 3 and 4, respectively.

2.6.1. Recommendations to Improve the Overall Assessment Process

1) Where possible, aquatic risk assessment methodologies should be harmonized both internationally and between State and Federal organizations within the USA. While risk management and risk mitigation decisions can and should be

made on a more local basis depending on the socio-political and physico-geographical circumstances, it is wasteful of resource to have competing approaches and ecotoxicological and exposure related study requirements. The important step is to agree a common framework and then include scenarios that reflect local needs.

2) In order to ensure that a consistent message describes the ECOFRAM process whenever its findings are communicated within EPA, industry, and academia in public fora or in scientific presentations, an agreed "simple" and "detailed" set of presentation materials should be developed.

3) EPA OPP EFED should rapidly assess the ECOFRAM reports and evaluate the proposed tools and approaches. EFED should accept or refine the ECOFRAM recommendations, and share the distilled output with the original SAP who suggested the ECOFRAM process along with a clear plan for implementation. Once the SAP has commented on the OPP EFED ECOFRAM-related processes and plan, definitive public documentation of OPP EFED's plans to build probabilistic approaches into ecological risk assessment should be placed on the record to ensure that there is a common understanding of goals and timelines.

4) Indications from working within the relatively expert group of ECOFRAM scientists is that probabilistic risk assessments require very precise explanation and careful use of terminology to avoid confusion. To ensure clear messages when EPA and/or industry probabilistic assessments are communicated to the public effectively, some guidance on communicating probabilistic assessments is essential. It is therefore recommended that EPA and industry risk assessors and risk managers convene a meeting/workshop to consider optimal ways of educating regulators and the public and of communicating risk issues using probabilistic techniques.

2.6.2. Recommendations to Improve Risk Characterization

1) The ECOFRAM aquatic group recommends that clearer definition be provided by EPA OPP EFED risk managers on what bodies of water are truly the primary focus of protection within the risk/benefit context of FIFRA. A better understanding of whether a particular product is of more concern for estuaries, reservoirs, continental rivers, lakes, mid-size rivers, ponds, streams, headwater ditches/streams or runoff drainage-ways would permit potential spatial or regional label mitigation options to be prescribed.

2) A generic list of achievable measurement endpoints that correspond to potential aquatic risk assessment endpoints at each of the proposed tiers should be developed.

3) In a number of areas, the ECOFRAM Aquatic Workgroups have described the value of additional or improved eco-toxicity and environmental fate studies. In a few cases, it has been suggested that such studies should be added as requirements. However, to ensure that options remain open for registrants, it is recommended that the majority of the recommended study package enhancements be expressed in the following manner:

> *"Registrants should understand that where the potential for ecological impacts on aquatic systems exists, additional data on [study objective] will often be valuable for reducing the uncertainty of the exposure/toxicity assessment. Accordingly, registrants may choose to submit additional [study objective] data - typically [guidance number] additional studies will cost effectively provide a suitable understanding of the associated uncertainty. In the absence of additional studies, EPA*

OPP EFED will make a conservative assumption of [describe] to account for the undefined uncertainty .”

4) The EPA OPP EFED should urgently re-evaluate the tests required under FIFRA relating to aquatic toxicity and exposure prediction in the light of recommendations suggested by ECOFRAM. Ideally and in time, a revision to FIFRA should be prepared codifying improvements in the process but, in the meantime, as ECOFRAM recommendations important for ecological risk assessment are accepted, guidance on what OPP EFED would prefer to see should be developed and made public via a process such as a PR Notice.

5) The ECOFRAM aquatic groups also recommend that EPA OPP EFED develops and maintains a web page carrying up to date details of recommended models, databases and approaches for handling exposure or toxicology data. This would be an important part of the process for informing the public about ecological risk assessment of agrochemicals as well as providing a vehicle for rapid dissemination of new regulatory tools and information to the regulated community.

6) The ECOFRAM aquatic groups strongly recommend that OPP EFED develops stringent standards for reporting exposure model output accurately and succinctly with clear descriptions of the input variables and standard expressions of the outputs. The rationale for selection of each input variable should also be given. This will ensure that when registrants submit exposure estimates they do so in a format that meets EPA standards and can serve as an vehicle for permitting efficient EFED decision making and focusing registrant/Agency discussion on risk management options.

7) The ECOFRAM aquatic groups recommend that EPA OPP encourages general efforts throughout EPA and other government agencies to support the generation and reporting of data and the regulation of aquatic issues on the basis of physiographic, geologic, ecological and climatic “regionalization” (e.g. via hydrologic units, land resource areas, ecoregions) rather than according to geo-political boundaries (states and counties). There is already an encouraging trend in this area (e.g. EPA “surf your watershed” (http://www.epa.gov/surf/) and the EPA Office of water model BASINS). Efforts must be made to continue this.

8) Given the limited resources available for pesticide risk assessment and the development of approaches for exposure estimation, a clear recommendation from the group is that, where possible, approaches to aquatic exposure estimation should be harmonized to minimize duplication of effort. This refers to initiatives being developed to address ECOFRAM recommendations, to understand FQPA exposure issues, to address Safer Drinking Water Act and Clean Water Act mandates, NAWQA, USDA buffer evaluation and similar programs. In particular, within OPP EFED, ECOFRAM recommends that scientists involved in developing approaches to Ecological and FQPA related exposure issues be encouraged to communicate frequently to develop common tools where possible.

9) On a general basis, the ECOFRAM work groups recommend that widespread monitoring be carefully utilized and that results from this monitoring should not be given undue emphasis. Since they only represent a small “window” across a few seasons, they can only be understood when allied with model predictions.

2.6.3. Recommendations to Improve Risk Management and Mitigation

1) All risk assessments should be presented to risk managers in a format that ensures the underlying exposure, effects and risk characterizations are precisely described in order to:
   - ensure that the risk manager is able to readily compare risk assessments;
   - ensure that there is minimal confusion about the components of the risk assessment being considered;
   - help focus thinking on the key elements; and
   - provide a framework from which omissions, additional factors and unique issues will be readily identifiable.

   The ECOFRAM aquatic groups have presented a suggested standard for reporting that offers a place from which OPP EFED can start to develop guidance of reporting probabilistic risk assessment output. A small work group should be set up to develop improved and agreed lists of the key parameters to be specified in risk characterization statements.
2) A compilation of mitigation alternatives should be prepared with the aid of relevant experts (e.g. USDA NRCS specialists) and agreed between EPA OPP and Industry to be used as a unified standard "mitigation reference book" for guidance on the development of label restrictions and mitigation alternatives. To be effective, the suggested practices need to be relevant at the field level and supported and understood by local USDA/extension personnel.
3) Additional research is needed to enhance the understanding of the impacts of various runoff mitigation alternatives to reduce transport of agricultural chemical residues in sediment and water. A phased approach for evaluating the efficacy of mitigation measures should be developed between registrants and the Agency. This work should be conducted in concert with model development to permit the inclusion of the impacts of mitigation approaches within the recommended regulatory exposure estimation models.
4) In addition and as a short term measure, data already available on the impact of mitigation approaches to reduce sediment, water and pesticide transport should be collated and converted to simple nomographs.
5) The Spray Drift Task Force (SDTF) has already developed an extensive body of data that enables an understanding and simulation modeling of the impact of various aerial drift mitigation options. Clear guidance should be compiled on drift mitigation options (e.g. Buffers, swath offsets and droplet size management) and their effectiveness agreed between Industry and EPA OPP. In addition, the SDTF and surface water model developers should be charged with introducing a tool for predicting the probability of drift by region and season so that this data can be combined with the existing probabilistic data for weather related runoff entry. Only then will the true impact of drift buffers be understood in context.
6) Improvements in pesticide application methodology should be encouraged by EPA and USDA, since they are often very effective mitigation measures.

2.7. Aquatic Risk Assessment Issues Not Addressed by ECOFRAM

The issues listed below are aspects of risk assessment and characterization that were recognized by ECOFRAM but not specifically addressed. Additional issues associated directly with aquatic effects or aquatic exposure disciplines are listed in the separate workgroup reports.

1) A major issue that was not within the remit of the ECOFRAM Aquatic Workgroups to address was how regulators, the regulated community and society at large can better understand which "types" of water bodies should be protected and to what degree. Clarification of this is an important recommendation from ECOFRAM and would help focus efforts on the development of appropriate modeling scenarios at the various tiers of risk assessment proposed by ECOFRAM.
2) Year to year chemical accumulation and or biological memory can complicate assessments and require case by case consideration. Further consideration has not been given to this issue.
3) The ECOFRAM Aquatic Workgroups have based their thinking on the assumption that species of concern are independent of the type/region of water body modeled. Again, if this assumption could be refined, additional spatial and/or regional mitigation options might be available. It is recommended that EPA considers the creation of "bio-geographic" databases describing the spatial occurrence of organisms.
4) Neither the Aquatic Effects nor the Exposure workgroups have considered the impact of metabolite formation and decline, except in so far as effects of metabolites are incorporated into microcosm studies.
5) The ECOFRAM Aquatic Workgroups did not deeply consider the potential importance of seasonally variable sensitivity and other "life cycle" related or behavioral biological factors. Currently, implementing the ECOFRAM recommendations is already breaking much new ground but at some point in the future, the consideration of such factors may offer important insight where a risk assessment moves into the "Tier 3" area (e.g. the relative timing of spawning behavior opposite likely exposure event occurrence).
6) The possibility that synergy might occur between multiple stressors (either separate agricultural chemicals or combinations of "parent" products and metabolites in aquatic systems) was frequently touched upon but was outside the scope of the workgroup's charge.
7) The ECPFRAM Aquatic Workgroups did not consider the impact of secondary stressors combined with pesticide residues. For example, the residues associated with erosive runoff events are always associated with high sediments loads.

3. ECOFRAM Aquatic Exposure Workgroup Report

3.1. Summary and Recommendations

3.1.1. Summary

The ECOFRAM Aquatic Exposure Workgroup was comprised of personnel with a considerable range of technical and regulatory expertise and viewpoints from industry, academia, state and federal organizations. Activities of the Workgroup included a critical evaluation of the current exposure assessment process and an evaluation of the tools and data used currently employed by the Agency for exposure characterization. The Workgroup also identified additional existing tools and data sources that can be utilized to reduce uncertainty in the risk assessment process. Limitations in technology and data were identified as research recommendations.

For the purposes of ECOFRAM, two important definitions were established. "Exposure" was defined as the contact between the bio-available fraction of the compound of interest and the organism of concern. The "exposure profile" was defined as exposure exceedance relevant to a specific assessment endpoint.

The Workgroup endorses the use of a tiered approach to characterize exposure and recommends a revised Tiering scheme. The tier progression is based on resource optimization with respect to cost and time. Early tiers makes use of standard environmental fate data generated under FIFRA §158. Conservative assumptions are employed to account for uncertainty in the understanding of physicochemical properties and their interaction in the environment. Subsequent tiers incorporate additional information to refine the understanding of physicochemical processes, address variability in usage environments toward the goal of achieving probabilistic estimates of exposure, and otherwise reduce uncertainty in exposure estimation.

Tier 1. provides an upper bound point estimate of exposure for a vulnerable headwater environment based on conservative assumptions in environmental fate properties, processes, and environmental conditions. Tools employed to conduct this analysis would be similar in purpose to the GENEEC model currently employed by the Agency with recommendations to address a larger variety of crop/usage conditions. Two decisions points are possible pending the output of Tier 1:

1) that the risk assessor is confident that there is minimal aquatic ecological concern associated with the product/use pattern; or
2) that progression to Tier 2 is essential.

Tier 2. provides probabilistic estimates of exposure for vulnerable headwater environments (temporally, regionally, and seasonally) across a wide range of geographical conditions appropriate for product use. Tools

employed to conduct this analysis would be similar in purpose to the MUSCRAT model designed by the FIFRA Exposure Modeling Work Group and under development by American Cyanamid. Tier 2 would continue to use standard environmental fate laboratory data generated under FIFRA §158, but contain a better representation of physicochemical processes. Preliminary evaluations of basic mitigation and management options may be addressed provided that there is sufficient understanding of ecological risk. Failure at Tier 2 indicates that a further refinement of risk characterization is required before uses could be allowed for those environmental conditions identified as having potential concern.

Tier 3 consist of a range of study options (i.e., tool box) that could be employed on a case-by-case or issue-specific basis. The tool employed would be used to refine the exposure profile generated under earlier tiers for those specific use patterns and environmental conditions identified as being a potential concern. Tools can include additional laboratory studies to better understand the variability in chemical degradation, modeling studies to evaluate mitigation options, modeling of less vulnerable environments to assist in risk characterization, or customized modeling of unique chemical-specific physicochemical processes or agronomic conditions. The selection of one or more of the Tier 3 options is based on expert judgement. Decision points could include cancellation, label mitigation, or progression to Tier 4.

Tier 4. Tier 4 also consists of a tool box, but is differentiated from Tier 3 primarily based on having substantially higher costs and turn around time to achieve results. Tools at this stage or more directed toward validation, and may include widespread monitoring studies; detailed investigations of the efficacy of mitigation; highly refined watershed evaluations and modeling (i.e., incorporation of more “real-world” factors); and benchmark modeling relative to existing chemical data. Given the costs associated with Tier 4, consultation between registrants and regulators is essential.

Simulation modeling has been identified as an important tool for exposure characterization based on the ability to predict exposure concentrations prior to introduction of a crop protection chemicals into the environment and the ability to generate probabilistic exposure profiles. Many of the recommendations identified by the Workgroup, as outlined below, are geared toward developing better modeling input data for models, establishing and advancing the predictive capabilities of regulatory models, and improving the modeling process with respect to standardization and automation.

Field monitoring will continue to play role in risk assessments through extrapolation of existing data and the generation of new data. However, owing to its costs and the difficulty of obtaining a comprehensive dataset, compound specific monitoring should only be used as a Tier 4 option in concert with modeling to help put the monitoring data into context. A more attractive option is to use ongoing monitoring programs such as NAWQA covering existing products as a source of surrogate data to link with model estimates for the new product.

Detailed recommendations have been developed by the group.

3.1.2. Recommendations

The underlying recommendation of the ECOFRAM Aquatic Workgroups is that a flexible, tiered process for Aquatic risk assessment be agreed and published so that registrants and OPP EFED are using to facilitate common framework for discussion and submission of assessments. However, while the tiers are useful for conceptually organizing the process, it should be recognized that distinctions between tiers are not necessarily rigid. That is, appropriate combinations of toxicity values and estimates of aquatic exposure may exist across tier levels, depending upon compound specific information. Additionally, it may sometimes be appropriate to "jump" tiers or perform additional studies on a compound specific basis.

To implement these recommendations, OPP EFED should work closely with other groups such as ACPA, USGS and USDA to ensure that cost effective approaches utilizing all available expertise are developed. Groups such as the FIFRA Exposure modeling work group (FIFRA EMWG) could provide useful fora for discussion of more complex issues. In the light of international moves to harmonize on pesticide risk assessment approaches (probably under the aegis of OECD), it would be valuable to share experiences and plans with the European FOCUS surface water group during the process of finalizing the OPP EFED view on the ECOFRAM Aquatic risk assessment report.

The following recommendations are specific for Aquatic Exposure assessment and modeling; the suggestions strive to avoid reference to specific models in order to "future proof" the recommendations. Specific recommendations relating to Risk Assessment/Characterization Issues and Aquatic Effects are documented in Chapters 2 and 4 respectively..

3.1.2.1. Recommendations to Improve Aquatic Exposure Assessment:

3.1.2.1.1.Improvements To The Studies Required Under FIFRA §158

1) EPA OPP EFED should consider introducing tiers into FIFRA part 158 to provide a logical and tiered sequence for study conduct that matches the proposed ECOFRAM risk assessment process. In particular, clarification of the studies that are "required" and those that should be optionally performed where needed would be useful (see recommendations in section 2.6.2 above). Studies that are not used at all in risk assessment should also be made optional and/or considered for removal from FIFRA. Until these changes are made part of FIFRA, interim guidance should be made available to the public.
2) Changes should be made to the FIFRA part 158 guidance as recommended in detail in the ECOFRAM report. These changes should be implemented before OECD harmonization takes place and, where feasible, the improved guidance should be incorporated into the OECD guidance as well as FIFRA. In particular, changes (or specific guidance where none currently exists) are recommended in the following studies:
    - Obtaining Rate Constants For Degradate Formation And Decline
    - Obtaining Hydrolysis Rate Constants As A Function Of Temperature

- Determining Quantum Yields
- Selection Of Multiple Soils For Soil Aerobic Dissipation Studies
- Enhancing Batch Equilibrium Study Design and Analysis
- Conducting Aquatic Metabolism Studies Where Runoff Is Likely To Be Significant
- Conducting Foliar Dissipation And Washoff Studies For Foliar Pesticides
- Focusing Anaerobic Soil Metabolism Studies on Degradation in Subsoil Horizons and Aquifers.
- Potential Of Uptake from Soil into Plants

3) When the studies in subpart N are revised, the group strongly recommends that each study be prefaced by a clear section describing the OBJECTIVE of the study, the PURPOSE for which the resulting data will be used and appropriate information on how the magnitude of the study might depend upon the use pattern being examined (e.g. For a minor use crop, only two soils may be required to define laboratory degradation rate while for widespread use on corn, studies on upwards of four soils may be required). These introductions should clearly explain the possible implications to the uncertainties associated with a risk assessment if the registrants supply a greater or fewer number of studies.

4) The new guidance should clarify that if registrants believe their compound is dissipated as a result of processes not normally accounted for by FIFRA studies, it is their responsibility to provide sufficient data to describe the occurrence and quantify the rate of the additional process. In the absence of this information , it is likely that EPA OPP EFED risk assessors will make a conservative assumption in the absence of data. In most cases, this assumption will be that the dissipation process is not occurring.

3.1.2.1.2.Improving The Reporting Of Environmental Fate And Exposure Modeling Data

So much data is included in a submission of agrochemical data under FIFRA that it is sometimes difficult for reviewers to identify key information needed for risk assessments. It is recommended that registrants submit various types of summaries of their data along with official reports. The action rests with EPA OPP EFED to formally propose a format and system for submission, however, the ECOFRAM Aquatic Exposure Workgroup recommends three potential data dissemination methods.

1) Inclusion of study specific summary tables at the front of each report.
   - EPA OPP, perhaps working together with ACPA, should develop a study specific one page summary table for inclusion at the beginning of each submitted report providing a “minimum data set”. As a move towards international harmonization (perhaps under the auspices of OECD), it might be sensible to ensure that any EPA recommendations should not be rigid as to format and should also encompass the minimum requirements of the EU Level 1 summaries

2) Submitting a full summary of all data relevant to each submitted risk assessment
   - it is recommended that registrants include a full summary of data relevant to aquatic exposure modeling when they submit a risk assessment or are aware that Agency scientists are conducting an assessment. This recommendation is also being endorsed by the Fifra Exposure Modeling Task Force (FEMVTF). Ideally, a

"tool" should be developed to enter this data into a simple electronic file (e.g. a commonly used spreadsheet) such that the source of every value is clearly documented and also so that the input values can automatically be read into the user friendly "modeling shells" being recommended by ECOFRAM.

3) Making the data more generally available through the ARS PPDB and EPA "one-liners"
   - ECOFRAM recommends that the pesticide industry and USDA jointly support ongoing maintenance of the USDA ARS PPDB. Alternatively an alternative reliable long term repository for data useful for pesticide exposure modeling should be developed and maintained. Ultimately, the EPA and USDA PPDB databases should be combined into a unified pesticide environmental fate regulatory database
   - Registrants should submit data to the PPDB firstly as soon as a registration is achieved and thereafter as soon as studies are approved by EPA
   - ECOFRAM recommends that the EPA issue an up to date version of the one-liner database as soon as possible.

3.1.2.1.3.Clarification Of Handling And Reporting FIFRA Study Data And Obtaining and Developing Model Inputs

1) EPA OPP EFED should work together with a group of academic and industry experts, to develop and agree a flexible guidance document based on consensus to specify an approach for calculating rate constants from FIFRA environmental study data in order to standardize comparative risk assessments and simplify Agency review of studies. In the interim, a definitive statement from EFED specifying an approach that would address current EFED concerns would avoid duplication of effort.
2) EPA OPP EFED should provide clear guidance on how to select appropriate values for any model input parameters and also how best to express the variation around the single value initially selected. Sources of data suitable for generating each parameter should be specified but the guidance should be flexible and provide the modeler an option to use other estimation approaches provided that a sound rationale for not following the guidance is provided in the submission. This guidance should be disseminated openly to the public (e.g. via PR notice and on an EPA web page)
3) EPA OPP EFED (in concert with other interested groups (e.g. ACPA, USDA NRCS, USGS NAWQA, etc)) should set up and maintain a FIFRA Risk Assessment web page providing access to approved models, databases and GIS coverages and associated meta-data to help standardize risk assessment technology version control etc.
4) EPA OPP EFED should work together with registrants to prepare a list of recommended sources of data on key non-chemical data required as model inputs. In particular, special efforts should be made to obtain spatially distributed information useful for regional and national exposure modeling and spatial risk assessments. For example, various agronomic practices (e.g. tillage) by region and crop, regional information on typical ratios of land areas and water body volumes, typical watershed cropping ratios by region.

   This effort should be completed as soon as possible to identify "deficient" datasets and recommend measures to prepare comprehensive, spatially referenced datasets.

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3.1.2.1.4.Expressing Exposure Estimates and Reporting Exposure Characterizations

The ECOFRAM Aquatic exposure group recognizes that the expression of exposure is fundamental to the proper communication of risk characterization. Accordingly the following recommendations apply.

1) ALL exposure estimates (whether deterministic or probabilistic) passed to risk assessors or used in text summaries etc should precisely specify:

- Tiering level
- Models and version used
- Region simulated
- The weather record period used (and location)
- Type of water body modeled
- Adjacency to field (i.e. directly adjacent or separated by a buffer)
- Cropping, agronomic and tillage practices simulated
- Application information (i.e. use pattern details)
- Scenario name (if standard) or details
- The exposure endpoint(s) reported
- The probabilistic context of the value(s)/distributions reported

Examples of suitable ways of expressing exposure in risk characterizations are provided in the body of the report. Although the idealized expression of exposure will not always be completely achievable, they represent a goal to aim for and, where information is missing, risk assessors should be prepared to explain the reason for the discrepancy.

3.1.2.2. Recommendations to Improve Aquatic Exposure Modeling

The ECOFRAM Aquatic Exposure Workgroup identified several areas where useful improvements in models and the underlying data could be beneficial.

3.1.2.2.1.General Modeling Issues

1) Developing sound statistical approaches to quantifying uncertainty around exposure profiles is an essential goal to support all ECOFRAM approaches.
2) It is critical for the future of aquatic exposure modeling that a suite of modeling tools be developed that utilizes modern and well documented coding and offers the capability of adding “modules” as improved approaches and/or algorithms are developed. Ideally, the model suite should handle leaching, runoff and foliar degradative and dissipation processes and the same model (driven by different scenarios and "complexity levels") should handle at least Tiers 1, 2 and 3. It would also be ideal if the model suite dealt with volatilization and plant uptake as well as providing enhanced capabilities for handling compounds with extended soil persistence. The objective of including as many processes as possible in one model is to approach the goal of accounting for mass balance. Additionally, the models should be carefully integrated to facilitate automated use and they should automatically produce reports in an EPA approved format that fully documents input parameters and output appropriate to the tier of modeling being

conducted.

This "modern" model suite should be well managed and guaranteed of support and adequate manpower to perform improvements, "bug fixes" and longer term development as needed. Ideally, such a model would be internationally applicable with national distinctions being made as needed by selection of country specific scenarios and weather data and "process" modules.

3) More sophisticated models like WEPP, RZWQM and EPIC should be evaluated to see if they contain code that could help address ECOFRAM recommendations and/or would be suitable for inclusion in the "modern" model.

4) All scientifically sound data should be considered valid for inclusion in modeling. However, it should only be used under a scheme that carefully controls potential misuse:

- Initial exposure model runs should be made with the recommended input values:
- Comparisons of predictions with "real world data" may then be made and , where necessary, used to explain why additional SCIENTIFICALLY valid data are needed to refine the exposure assessment;
- Additional exposure model runs may then be conducted using the additional data;
- The output from these "refined dataset" runs must be reported alongside the data prepared using "standard" assumptions along with a clear rationale justification for use of additional data.

5) Correlated environmental fate and landscape data should be kept together in model simulations (especially Monte Carlo type approaches)- e.g. Soil texture with Slope with OM % dependent on landform position or chemical adsorption behavior and chemical half life.

6) Guidance for the selection of "standard" distributions for Monte Carlo modeling to account for variation of chemical parameters should be produced. A review of available information on the "shape" of the typical distributions of chemical and environmental factors should be conducted and published via a peer review process in order to establish some baseline default distributional information.

7) ECOFRAM recommends that data is needed to support model development and validation in many areas, some include

- There is a need for a clearer understanding of the spatial variability associated with field soil degradation and related properties at both the micro and macro spatial scales;
- There is a need to better describe the effects of water content, aeration, and microbial activity on chemical degradation in a way which can be routinely parameterized for use in modeling;
- There is a need for a compilation of literature data on the extent to which oxygen and organic carbon are transported to subsoils in infiltrating water and an assessment of how this relates to subsoil degradation;
- Information is needed on the relative importance of volatilization from leaf surfaces. If this information shows that this can be a significant route of dissipation, a laboratory study will need to be developed that can describe how foliar volatilization occurs. Also, guidance on when to require the study will also need to be developed. Methods to quantify foliar volatilization will also be needed for use in conjunction with guideline field dissipation studies.
- Data on variation of residues within a water body is needed to improve surface water models

- Develop additional data to support model developments to better account for the occurrence of multiple soils within a watershed/field
- Prepare a comprehensive regional water body database categorized by
    - Depth, volume
    - drainage area/volume ratio
    - slope
- Data available on the impact of mitigation to reduce sediment, water and pesticide transport should be collated and ideally used to help validate more sophisticated "mitigation impact" aquatic exposure modeling modules.

8) ECOFRAM recommends that major improvements be made to models

- Dilution in flowing waters should be included in a surface water model
- Models should account for water body volume variation
- Models should be able to incorporate the impact of mitigation techniques
- Mass transfer between sediment and water compartments needs better handling
- New surface water models should have the capability of accounting for variation of concentration WITHIN a water body with time
- Mechanisms to obtain weather sequences longer than 36 - 50 year model runs should be developed where the extreme portion of the exposure distribution is under examination. Combined with this, multiple runs varying the application date within the same weather data set may be useful to better understand the "tails" of the distributions.
- Better input parameter entry, documentation and reporting modules with readily readable input and output files are required
- Improved models need the capability to deal with higher order degradation kinetics where simple first order equations fail to adequately describe the behavior of the compound of concern.
- Easy tools for incorporating "within field" variation of key parameters such as degradation rate and hydrology factors should be incorporated.
- The range of storm hydrographs available should be regionally and seasonally selectable
- Models need the capability to deal with long rainfall events (covering multiple days)
- Conversely, future runoff models need to enhance the flexibility to use shorter time steps
- Improved surface water models should include the capability of "spreading the runoff input" across a range of time equivalent to that generated by PRZM.
- Improvements are needed on how to express the changing concentration across time in each daily reporting unit.

3.1.2.2.2.Recommendations related to the CURRENT Tier 1 process

1) GENEEC should continue to be used at present as a Tier 1 model (especially for row crops) provided its limitations are clearly specified.

2) GENEEC must be considered to be a simple "trigger" in Tier 1, the exposure estimates stemming from GENEEC should only be used for simple "pass" or "Do more detailed exposure estimation" decisions.

3) It is not appropriate to try to "tweak" GENEEC parameters on a compound specific basis.

4) EPA should do some "validation" or "confidence building" for the risk managers in EPA and industry; particularly in regard to the relationship of its out put to Tier 2 predictions for a range of crops.

5) Comparisons should also be made to confirm that GENEEC does represent around the 95th percentile of a MUSCRAT simulation for a range of crops

6) Comparison of Tier 1 GENEEC and PRZM/EXAMS simulations should be conducted for a range of pesticide products and crops to confirm the validity of the proposed Tier 1 PRZM/EXAMS input parameter selection guidance

7) GENEEC should be made an official EPA model and must be made available from official EPA web sites along with full documentation

8) The group recommends that a "EURO-GENEEC" be developed using a similar background to US GENEEC but using different assumptions appropriate to EU conditions

9) GENEEC should be re-examined (and re-coded as needed) using latest PRZM and EXAMS code after the FIFRA Exposure Model Validation task Force (FEMVTF) has fed back initial results and any modifications to Przm have been made

10) While it is recognized that the current additional scenarios (rice, cranberry and rights of way) will not be meta models of validated and approved regulatory tools; GENEEC (or its successor) is an appropriate vehicle to use for Tier 1 exposure estimates for these uses. Therefore further development and validations of these modules in the very short term is essential and worthwhile.

11) Additionally, and following the same logic, specific turf and muck soil modules should be developed and validated

3.1.2.2.3.Recommendations For Longer Term Improvements To A Tier 1 Exposure Assessment Process

1) A single Tier 1 model that addresses the needs of the idealized Tier 1 model (above) should be developed. Key parameters of a successful Tier 1 model include:

- A range of national and regional scenarios that represent the 95th percentile of Tier 2 modeling in terms of water/sediment transport
- Separate "scenarios" to represent the 95th percentile for major crop groups (in terms of some combination of water runoff volume and sediment transport)
- Fast run time on a mid range PC

- Small executable file
- Does not require expert modeling knowledge to run
- Limited weather data input file requirements
- automatically produces reports in regulatory format
- Sediment and water column concentration outputs
- Indication of the typical "shape" of pesticide dissipation in a receiving body

2) The ECOFRAM workgroup recommends that as soon as possible after an agreed "ideal" Tier 2 model is available, a series of Tier 1 "scenarios/meta-models" should be derived for major crop groups/agronomic situations to represent the 95th percentile of the Tier 2 distribution expected across the national distribution of the crop. Clearly, actual distributions will be dependent on the combination of chemical properties, and thus it is recommended that for convenience the 95th percentile scenario should be based on some combination of estimated runoff volume and sediment movement predictions.

3.1.2.2.4.Recommendations related to the CURRENT Tier 2 process

1) The current Tier 2 process is dependent on a relatively few crop specific scenarios that are presently anecdotal and not available centrally. This Tier 2 single site scenario information should be collected, annotated with explanatory text and justifications and made available through a publicly available system. They should be put into some context of "severity" by comparing with MUSCRAT runs
2) Documentation should be prepared describing of the status of validation of EXAMS code in terms of Pesticide endpoints and, if necessary the latest version of EXAMS should be re-run using the original validation datasets. A group should assess the need for a more detailed validation of EXAMS.
3) A group of experienced aquatic exposure modelers should work with the AgDrift Model developers to investigate how best to develop probabilistic estimates of drift and incorporate these estimates with PRZM inputs to provide probabilistic surface water exposure estimates using the current system.
4) It is necessary to generate a more comprehensive regionalized set of wind speed and direction data to provide the necessary drivers for probabilistic analyses of drift.

3.1.2.2.5.Recommendations for longer term Development of a Tier 2 Exposure Assessment Process

1) The ECOFRAM Aquatic group has prepared detailed recommendations for an idealized Tier 2 aquatic exposure. A joint group of EPA and ACPA scientists should be asked to draw together a plan for how best to implement this plan.
2) Another group should investigate the approaches suggested by ECOFRAM for the definition of more appropriate scenarios for Tier 2 exposure models. The goal is a series of scenarios for each crop that will represent national and regionalized distributions but also States should be constructed to identify special local needs that they have for highly localized combinations of factors (e.g. Floridian canals passing through agricultural areas).

3) The ECOFRAM aquatic group strongly recommends that the RADAR tool is finalized and made publicly available via an EPA sponsored web site as soon as possible. A manual needs to be written and a user- feedback mechanism established to garner recommendations to help drive future improvements.

4) Early efforts should be made to incorporate elements of AgDrift into the surface water component of the model and to

3.1.2.2.6.Recommendations Relating to Tier 3 and Beyond

1) The MUSCRAT tool currently used as Tier 3 should be refined and issued formally via an EPA sponsored web site. Documentation to help users install the program reliably should be prepared. An evaluation should be conducted of the conditions under which MUSCRAT is likely to provide higher estimates of exposure than the current site specific Tier 2 models.

   Among the refinements to MUSCRAT that should be considered are

   - a soil pore water/sediment concentration module
   - a mechanism for introducing a distribution of variable (e.g. OM%)
   - a link to the National Resources Inventory for better data on the association of crops with specific soil types

3.1.2.3. Aquatic Exposure Modeling and Assessment Issues Not Addressed by ECOFRAM

The issues listed below are aspects of Aquatic exposure assessment that were recognized by ECOFRAM but not specifically addressed. Additional issues associated directly with Aquatic Effects or Risk Assessment and Characterization fields are listed in the separate parts of the report.

1) What truly constitutes "model validation"?? This issue ranges between classical mechanistic formal validation and "improving the level of confidence in the model". It is expected that the report of the FIFRA Exposure Model Validation Task Force will help to clarify some of these issues.
2) When monitoring, is it better to measure concentrations more often at one place or less often at more places?? I.e. are we interested in focussing the investigation on variation within time or variation within space
3) Development of scenarios to cover specific exposure scenarios representing significant local needs is important if a common and harmonized exposure and risk assessment process is to be used by Federal and State pesticide regulatory bodies- e.g. FL sugar cane.
4) During the meetings, the suggestion was made that a field by field classification of vulnerabilities on which label restrictions may be based should be created. For example, a series of factors such as proximity to water bodies of concern, erosion and water soluble runoff, leaching potential, presence of engineering such as buffers or terraces, presence of ditches, presence of tile lines, weather risk potential could be prepared and ranked for each field and then label statements could refer to mitigations necessary on a field with a leaching risk rank of 3 or a runoff risk ranking of 2. This suggestion is merely an extension of the current process to identify as "highly erodible" all fields containing more than 30% of soil with an erodibility index of 8 or greater.

5) The issue of parent and/or metabolite modeling and/or monitoring was NOT addressed.

Application of Ag Drift as a tool for generating probabilistic estimates of drift entry to water bodies was not considered in depth. The initial implementations of Agdrift offer simple deterministic output at the lower tiers and imply that the only way to mitigate drift entry to water bodies is by direct imposition of a buffer. Efforts are needed to put drift entry into the same context as runoff entry and for the mitigation of risk associated with Drift entry to be considered by the same tiered risk refinement process as is recommended by ECOFRAM for runoff entry.

3.2. Introduction

The ECOFRAM process was set up in response to suggestions made by an EPA Scientific Advisory Panel (SAP) as described in section 2.1. This section of the Report describes the detailed findings of the Aquatic Exposure Workgroup.

3.2.1. Team Members and Affiliations

The ECOFRAM process was initiated by an organizing committee charged *inter alia* with inviting workgroup participants representing a wide range of disciplines. The Aquatic Exposure Workgroup composition reflects a wide range of technical and regulatory experience and backgrounds. Participants are listed below and full details are provided in Aquatic Exposure Appendix 2-1

James Baker, Iowa State University, Ames, IA.
Lawrence Burns, US EPA-ORD/NERL, Athens, GA.
David Farrar, US EPA-OPP, Environmental Fate and Effects Division, Washington D.C. (part-time)
Paul Hendley, Zeneca Ag. Products, Richmond, CA.
Alan Hosmer, Novartis, Ecological Toxicology, Greensboro, NC.
David Jones, US EPA-OPP, Environmental Fate and Effects Division, Washington, D.C
Walton Low, USGS, Reston, VA.
Mark Russell, DuPont Ag. Products, Wilmington, DE.
Mari Stavanja, Florida Department of Agriculture and Consumer Services, Bureau of Pesticides, Tallahassee, FL
Martin Williams, Waterborne Environmental Inc., Leesburg, VA
James Wolf, US EPA-OPP, Environmental Fate and Effects Division, Washington, D.C.

The composition of the team remained unchanged throughout the process. However, a few others contributed in part; these included Ron Parker, Henry Nelson and Paul Mastrodone (EPA OPP EFED) and Dennis Laskowski (Dow Agro).

The group met around ten times in a 15 month period to address the charges from EPA. In addition, work and development of alternative approaches was conducted by group members between meetings.

3.2.2. Initial Workgroup Objectives and Scope

During its original meeting, the ECOFRAM Aquatic Exposure Workgroup developed some specific goals:

- Developing a conceptual framework for the assessment of potential exposure in aquatic systems. This was to be used as an underlying "base-map" against which the desired tools can be scoped out, assessed and qualified;
- Developing a tiering system and/or decision tree designed to ensure that the majority of risk managers or assessors would follow a similar path to investigate the potential aquatic exposure arising from a particular pesticide use-pattern;
- Prescribing the use of "tools" in the tiering system that either exist presently or need to be developed. The group would recommend success criteria and specifications for the tools and processes by which they might be developed;
- Developing a list of issues that need to be addressed to help define or characterize the tools and the uncertainty associated with their use.

During the process to address these goals, the group decided that the related factors and issues below should be considered:

- Aquatic exposure estimates design to improve the Ecological Risk Assessment process may also help address concerns raised under the FQPA statute;
- Tools to be designed for estimating exposure should, where appropriate, include the ability to help design exposure mitigation options of value for regulatory decision making;
- There are many valuable initiatives, workgroups, tools and insights ongoing within the US and International Aquatic Exposure science communities. These should be incorporated/used where appropriate to maximize the efficiency of the ECOFRAM tools;
- While a large number of studies currently form part of the FIFRA part 158 regulatory requirements for pesticides, the group should consider if these are the most appropriate studies to support the desired aquatic exposure tools and make recommendations where necessary on the organization and content of the existing studies or suggest additional studies where needed.

3.3. A Brief History of Aquatic Risk Assessment Under FIFRA

Aquatic exposure assessment under FIFRA was first documented in June, 1986 in **Hazard Evaluation Division Standard Evaluation Procedure: Ecological Risk Assessment** by Doug Urban and Norm Cook. This document describes a tiered system for assessment with acute toxicological data at the first tier, chronic, estuarine toxicological data and bioaccumulation data at the second tier, the fish full life cycle study at the third tier, and field studies of population effects such as a mesocosm study at the fourth tier. Aquatic exposure assessment is described with "levels" rather than tiers. The first level has a full application being dissolved in a 6 inch deep water body. There is no guidance given for multiple

applications. The second level indicates that routes of loading should be considered but not other routes of dissipation. It notes that 10% of the application rate appeared to be an appropriate estimate for spray drift loading. Runoff estimation was to consider chemical and site specific parameters such as field size, pond size and depth and runoff percentage. No guidance is given for estimating runoff percentage. The third level was to use computer models such as EPA-SWRRB and EXAMS and considered other routes of dissipation. This version of SWRRB is an unpublished version of SWRRB developed with Office of Pesticide Programs and supported through the EPA Athens lab. The scenario was a 1 ha pond, 2 m deep and a field size of 13 ha. The flow through the pond was not defined. Sixteen standard scenarios were available from Georgia, Ohio, and Mississippi. Simulations were apparently done for 50 days in one year. Only the peak concentrations of the pesticide in the water body were considered. In practice, these third level EEC's were infrequently employed in the risk assessment process.

Prior to 1991, an aquatic exposure assessment method, known as the "back of the envelope" had been developed by Richard Lee of OPP and was in common use. The method is documented as the initial screening calculation to be done in Aquatic Effects Dialog Group, 1992. The loading to the pond is based on solubility of the pesticide in water. If the solubility was greater than 100 mg/L then the 5 per cent of the application rate was used, if the solubility was between 1 and 100 mg/L then 2% of the application rate was used. If the solubility was less than 1 but greater than .001 mg/L then the runoff per cent was one. Below 0.001 mg/L, the runoff per cent was 0.1%. These values were developed from 8 year EPA-SWRRB simulations on the Mississippi site mentioned above for amitraz, lambda-cyhalothrin and malathion. Five per cent of the application rate was used for spray drift. The majority of aquatic exposure assessments done between the late 1980's and 1995 were done using this method with no refined assessment completed even when the risk criteria were exceeded.

The Aquatic Effects Dialogue Group (AEDG) was convened in 1990 to make recommendations for improving aquatic risk assessment in the Pesticide Program (Aquatic Effects Dialogue Group 1992). Aside from documenting the current practices, the AEDG recommended that a defined scheme for refined exposure assessment be developed and documented and that guidance for monitoring and runoff field studies be developed, at least in part, to calibrate and validate the models. Of particular interest for ECOFRAM, the AEDG discussed the usefulness of probabilistic modeling in a regulatory framework. They did not, however, specifically recommend that probabilistic tools be developed or adopted. In addition the probability of exposure at different sites was described, but temporal variability was not addressed, nor were the issues of acute versus chronic exposure.

The first probabilistic aquatic exposure assessment done in the pesticide program was completed in October, 1991 by Jones and Hetrick to support the Copper Reregistration Eligibility Document which has yet to be issued. This assessment used GLEAMS rather than PRZM as the runoff model and used annual total loadings for each loading to the pond. The first Tier 2 assessments similar to those being done presently were completed by Ron Parker in mid-1992. The first fully documented Tier 2 EEC's were completed to support the Methiocarb RED (1993) in late 1992 by David Jones. Those EEC's are not substantially different than those done now, consisting of multiple years at a single high exposure site. The

site is intended to represent a site which has aquatic exposure greater than 90% of the sites in the use pattern. However, the selection of the site was (and still is) based on best professional judgment, so the accuracy of the actual site severity is open to question. In addition, mean EEC's reflecting the length of exposure were calculated so that the nature of chronic exposure could be better characterized. Maximum annual four-day, 21-day, 60 day, and 90 day EEC's were estimated as well as the annual peaks. These were obtained by calculating a running a average of each duration through each year and then finding the day in the year when the running average was its maximum. The annual maximums for each year were then used to generate an exceedance probability distribution. The value with a one in ten year annual exceedance was selected from the distribution for use in the deterministic risk assessment. It is worth noting that OPP had at this point abandoned the paradigm of regulating based on worst case scenarios by explicitly using defined frequencies in time and space.

In March, 1992, the Aquatic Risk Assessment and Mitigation Dialog Group was convened under the auspices of Society of Environmental Toxicology and Chemistry (SETAC) as a second effort to improve aquatic risk assessment. The report, *Aquatic Dialogue Group Report: Pesticide Risk Assessment and Mitigation,* issued in 1994 and described in considerably more detail an aquatic exposure assessment regime. The first two tiers described had in fact been implemented by the time of the publication's release. The Aquatic Dialog Group recommended two higher tiers for exposure assessment. The third tier consisted of modeling over multiple sites and multiple years. The fourth tier was based on either site specific EEC's of pulsed exposures (This was not explicitly defined as to how it differed from the lower tiers which were capable of generating pulsed exposures) or landscape modeling. The Aquatic Dialog Group also recommended that the focus of field studies be shifted to support model validation, and that the Agency develop a long-term strategy to support models and the necessary databases.

Concurrently with these other efforts, an advisory work group, the FIFRA Environmental Modeling Work Group (EMWG) was formed. This group provided a forum for the Agency, registrants, and consultants to discuss issues relevant to the use of models in the regulatory setting, particularly aquatic exposure assessment. Four particularly useful outcomes of the EMWG were a Good Modeling Practices Standard Operating Procedure (Estes et al., 1994), an evaluation of models potentially usable in regulatory assessments, the development work to support the Tier 3 modeling efforts (the credit for intiaiting and supporting this largely belongs to American Cyanamid Corporation and Dow AgroSciences who provided the background supercomputer runs and underlying database technologies respectively), and the initiation of efforts to validate the agricultural field models in the way they are used in the pesticide regulatory framework.

This last task has been undertaken by the FIFRA Environmental Mode Validation Task Force (FEMVTF - see below). The task force is a consortium of pesticide registrants who, with guidance from Agency personnel, have undertaken to validate the agricultural field models for both runoff and leaching of pesticides. While a number of models were initially considered, the focus has been primarily on PRZM. This effort has included a comprehensive literature review, identification and selection of field data sets, development of protocols for input parameter selection, simulation of the various field sites, and statistical assessment of the level of agreement between the field data and the model simulations.

Three types of assessment have been proposed, the first level does the input parameter selection the same way the data is selected by the Agency. The second level uses more site specific criteria including field dissipation half-lives used for degradation rate inputs for PRZM. The third level uses the distributions of input parameters rather than single values. Most of this work has been completed and the final reports will be published in 1999.

3.4. Background

As discussed in section 2.1, there have been several initiatives that have addressed potential improvements to Aquatic Risk Assessment. Traditionally, risk refinement has centered on modification of exposure estimates and this was reflected in the findings of these earlier efforts. The recommendations from those earlier groups were considered by the ECOFRAM Aquatic Exposure Workgroup. In addition, several workgroup participants have worked on other aquatic exposure related committees and programs and brought a deep awareness of the factors being considered in these other fora. Some background on these related areas is given below.

3.4.1. Status/Activities of Aquatic Exposure Monitoring Initiatives

There is increasing interest in the monitoring and simulation modeling of pesticide exposures in surface water and it is useful to describe a few of the key programs that are underway. Aspects of several of these are suggested for incorporation or validation of ECOFRAM outputs.

3.4.1.1. The National Water-Quality Assessment Program (NAWQA)

The National Water-Quality Assessment Program of the U.S. Geological Survey is designed to assess the status of and trends in the quality of the Nation's ground and surface water resources and to link the status and trends with an understanding of the natural and human factors that affect the quality of water. The study design balances the unique assessment requirements of individual hydrologic systems with a nationally consistent design structure that incorporates a multi-scale, interdisciplinary approach. The building blocks of the program are Study-Unit Investigations in 60 major hydrologic basins (Study Units) of the Nation; work on these study units is phased in a cyclic pattern to permit efficient use of resources. Sampling surface water involves temporal and flow driven strategies and over 80 analytes are routinely analyzed.

Data from NAWQA investigations is beginning to become available and exemplifies the trend of increasing availability of important environmental monitoring data over the Internet. The results from the program are expected to provide the most comprehensive organized monitoring program including pesticides. Some more background is given in Appendix 3-1x which also includes key web sites which provide results and also access to lists of published references on the program.

3.4.1.2. Mid-Continent Monitoring Project

The occurrence, transport, and fate of agricultural chemicals is being studied in a 12-State area in the upper Midwest as part of the U.S. Geological Survey Midcontinent Herbicide Project. Scientists are identifying factors that affect dispersal of these chemicals in surface and groundwaters from point of application and are evaluating the resulting effects in small streams and large rivers, at reservoir outfalls, in shallow groundwater, and in precipitation. The goal is to provide the general scientific basis needed to develop agricultural management practices that protect the quality of the region's water resources. Further details are provided in Appendix 3-2.

3.4.1.3. Heidelberg College Monitoring Studies

In 1983, the Water Quality Laboratory at Heidelberg College (Tiffin, OH) initiated a monitoring program for agricultural chemicals in eight Lake Erie tributaries draining agricultural watersheds (Richards and Baker, 1993; Baker 1993). Sampling stations have been in operation since 1983 for the majority of the watersheds, which range in size from 11 to 16,000 km^2. Pesticide analyses have included alachlor, metolachlor, atrazine, cyanazine, metribuzin, linuron, terbufos, butylate, chlorpyrifos, EPTC, phorate, fonofos, and simazine. Other water constituents include suspended sediment, total and soluble phosphorus, nitrate plus nitrite nitrogen, nitrite nitrogen, ammonia nitrogen, total Kjeldahl nitrogen, chloride, sulfate, silica, and conductivity. Each watershed is subtended by USGS stream gauging station. Sampling frequency and pattern have varied from year to year and from station to station, but in general, three samples per day are collected between April 15 and August 15 (the pesticide runoff season). All samples from runoff events during this season are analyzed, whereas two samples per week are analyzed during low-flow periods. A minimum of two samples per month are collected and analyzed at other times of the year. The monitoring program was designed to characterize day-to-day, season-to-season, and year-to-year variability in water in order address effects on stream biota, drinking water, and evaluate best-management practices.

3.4.1.4. USDA Management Systems Evaluation Areas (MSEA's)

The Management Systems Evaluation Area (MSEA) Program is part of an interagency initiative to evaluate the effects of farm management systems on water quality. The cooperating agencies of the MSEA Program are the U.S. Department of Agriculture's Agricultural Research Service (ARS) and Cooperative State Research Service (CSRS), the U.S. Environmental Protection Agency, the U.S. Geological Survey, and other Federal and State agencies.

The general goal of the MSEA Program is to reduce the effect of agriculture on the environment through the use of improved farm management practices. The cooperating agencies are collaborating on research ranging from laboratory experiments to 50 square kilometer watersheds. The research objectives are to (1) measure the effects of prevailing and modified farming systems on ground- and surface water quality, (2) understand the processes and factors affecting the fate of selected agricultural chemicals on ecosystems, (3) assess the effects of selected agricultural chemicals on ecosystems, (4) assess the projected benefits to water quality of implementing modified farming systems, (5) evaluate the

socioeconomic impacts of using modified farming systems in the Midwest, and (6) transfer appropriate agricultural technology to farmers.

Five MSEA's were selected to represent the principal hydrogeologic settings and geographic diversity of prevailing farming systems in the Midwest. MSEA's in sand and gravel settings are located in Minnesota, Nebraska, and Ohio; those in loess and till settings are located in Iowa and Missouri. Research focuses on processes that affect groundwater quality at all MSEA's, but processes that affect surface water quality are also a major consideration at the Iowa and Missouri MSEA's. Several additional MSEA sites have also been created more recently (e.g. Mississippi Delta MSEA (www.sedlab.olemiss.edu/msea.html)). More detail on the MSEA programs is provided in Appendix 3-3..

MSEA data is gradually being published. Provided the underlying data is comprehensively reported, the data for each of the sites will represent some of the best site specific information focussed on particular issues.

3.4.1.5. Four Mile Creek, Iowa.

Data on the field-to-stream transport of sediment and chemicals from an intensively farmed agricultural watershed were collected in a five-year study (1976-1980). Measurements were made for small (~ 6 ha) corn, soybean, and pasture fields; for two larger mixed cover watersheds, and at three stream sites (largest 5055 ha). Data on land use, chemical inputs and runoff analyses are available accompanied by additional data aimed at supporting model validation. More details are given in Appendix 3-4

3.4.1.6. Pesticide Specific Surface Water Monitoring Programs

Over the last few years, EPA OPP EFED has required various pesticide manufacturers to design and conduct compound specific monitoring studies. While some focussed on groundwater (e.g. The National Alachlor Well Water Survey (NAWWS,)) others have been directed towards surface and drinking waters.

One example is the program required by OPP EFED for the new herbicide acetochlor which included retrospective and prospective groundwater monitoring as well as a drinking water specific surface water monitoring requirement . To meet this surface water requirement, manufacturers of the product (the Acetochlor Registration Partnership (ARP)) set up a 5 year program encompassing 175 community water systems across 12 states. Samples have been taken biweekly across the spring and summer months and intermittently across the remainder of the year. The samples are analyzed for acetochlor, atrazine and alachlor and two other corn herbicides. Data is reported to EPA, the states, and other interested parties. For more details, visit http://www.arpinfo.com/ or http://www.epa.gov/oppefed1/aceto/

Similarly, Novartis has performed monitoring for atrazine in surface water (Solomon et al, 1996) and it seems likely that under the new FQPA legislation, there will be increased requirements for surface water pesticide residue monitoring programs to validate simulation modeling predictions.

3.4.1.7. State Pesticide Monitoring Efforts.

Many states are developing databases to report and/or support pesticide surface water monitoring efforts. Increasingly this data is available over the Internet. Examples are given below.

3.4.1.7.1. Missouri

The state of Missouri maintains a data file of pesticides in surface water, predominantly herbicides including atrazine, alachlor, metolochlor, cyanazine, metribuzin, and simazine. This data base represents information from different studies and analytical data generated by many laboratories with different detection limits. It is recommended that this data base be used carefully. Questions concerning the data base should be referred to John Ford, Water Pollution Control Program, Missouri Department of Natural Resources, PO. Box 176, Jefferson City, MO 65102 or call at 573-751-7024.

3.4.1.7.2. Illinois

The EPA Illinois samples for pesticides from a station subnetwork of the Ambient Water Quality Monitoring Network. Samples are collected twice in the spring, twice in the summer, once in the fall, and once in the winter. The samples are analyzed for herbicides including atrazine, and cyanazine; insecticides and fungicides. The pesticides are selected based on the estimated quantity of use in Illinois and their estimated runoff potential in addition to physical chemical characteristics, and estimated leaching potential. Most data is available from STORET or NAWQA

3.4.1.7.3. California

The Department of Pesticide Regulation monitors pesticides in air, water, soil, or vegetation to determine if there is contamination and its extent, and to evaluate the likelihood of exposure to workers and to people near treated fields. Data is used to support further studies, to develop or modify mitigation practices, or to develop new pesticide use regulations. California centralizes monitoring results from various government agencies that sample wells for pesticides residues such as bentazon, bromacil, diuron, prometon, simazine, atrazine, etc. For more information contact Candace Miller at 916-324-4188 or cmiller@cdpr.ca.gov.

3.4.1.7.4. Florida

In addition to state-wide pesticide and nutrient monitoring activities, Florida is notable for the quality of the spatial and monitoring data recorded by some Water Management Districts. For example, the South Florida Water Management District (SFWMD) has a data base of hydro-meteorological monitoring within the District. The data have been used in the evaluation of water resources, ecosystem research, basin planning activities, and information for engineering design. The data base include records from most of the 16 counties and information on rainfall, weather, stream discharge, canals and more than 215 water control structures. As well as this, the data base has information on water level stages at several sites on streams, lakes, and 1500 miles of the primary canal system. For more information, contact the SFWMD at 1-800-432-2045, ext. 6514.

3.4.1.7.5.The STORET database

STORET is a historical database containing data on tens of thousands of analyses and pesticides are included among the analytes. Each record may contain many details including the spatial location of the sampling point, analytical details (including LOD) and date of sampling information. Unfortunately, STORET records are of variable quality and represent no defined sampling plan. Thus reports of a positive detection from STORET is difficult to place in context and may merely be used as part of a weight of evidence argument.

3.4.2. Status/Activities of Aquatic Exposure Simulation Modeling Initiatives

Complementing the practical agricultural chemical monitoring efforts described above, there are a number of initiatives under way to improve and/or validate exposure simulation modeling both in the USA and in the European Union (EU). These initiatives are working on similar timelines to ECOFRAM and the ECOFRAM aquatic exposure working group believes it is critical to try to coordinate these activities where possible. Given the limited resources available for pesticide risk assessment and the development of approaches for exposure estimation, a clear recommendation from the group is that, where possible, approaches to aquatic exposure estimation should be harmonized to minimize duplication of effort.

3.4.2.1. FIFRA Exposure Model Validation Task Force (FEMVTF)

To provide increased confidence in regulatory modeling, an exposure model validation task force has undertaken a multiyear project to compare the results obtained from the Pesticide Root Zone Model (PRZM, Version 3.12) with an extensive set of field studies of pesticide leaching and runoff. The task force was funded by a consortium of 13 agricultural chemical companies with technical and/or advisory participation by members of the USEPA/OPP, NRCS, academia and the agricultural chemical industry.

Three types of exposure modeling runs were conducted for comparison with the appropriate field data:

Level 1: Modeling with reasonable worst-case input parameters for chemical properties and standardized procedures for selecting soil and agronomic inputs, representing typical regulatory modeling performed by the USEPA.

Level 2: Modeling with best estimates of input values for chemical, soil and agronomic inputs, following a Standard Operating Procedure developed by the task force.

Level 3: Modeling which has been calibrated to the results of the field studies by modification of the most sensitive input parameters within justifiable value ranges.

The first type of modeling is intended to compare the results from current regulatory modeling following USEPA guidance with actual field results to determine the extent of conservatism resulting from selection of worst-case input values. The second type of modeling uses best estimates of chemical properties and provides insight into how well this type of "database" modeling compares with actual field results. The final type of modeling involves calibration of both the hydrology and transport processes in the model, as necessary, and provides increased understanding of the sensitivity of the predicted results to specific model inputs as well and the possible extent of agreement between the model and field data. The results of calibrated modeling can also be used to identify potential deficiencies in the model or the experimental data in representing specific processes.

Specific products of this project include comparisons of predicted and experimental data for groundwater and surface water studies, development of standardized procedures (SOP's) for selecting appropriate input values for Level 1 and Level 2 modeling and development of a sensitivity analysis tool to determine the most important input parameters in a specific simulation and to evaluate the impact of varying these parameters within appropriate ranges.

Several tentative conclusions have been drawn from this project already:

1) For leaching assessments, PRZM generally provides a good representation of the overall hydrology of a specific site. The model can also provide reasonable estimates of chemical transport due to leaching if adequate environmental fate data is available for the chemical (e.g. degradation rate with depth and sorption as function of organic carbon, texture and pH).
2) For runoff assessments, PRZM provides reasonable estimates of runoff and erosion for most of the sites evaluated. The agreement between the predicted and experimental runoff and erosion losses from the edge of a treated field is generally within an order of magnitude and is frequently within a factor of 2-3X.

3) The greatest source of variability in environmental fate modeling is the judgment of the individual modeler in selecting appropriate values for the input parameters. In response to this observation, standard procedures have been developed by the USEPA and the FEMVTF to guide selection of parameter input values used for modeling.

The FEMVTF project is currently ongoing with completion anticipated in early 1999 and publication of results expected in mid/late 1999. Details of progress and findings may be found on http://www.femvtf.com.

3.4.2.2. FIFRA Exposure Modeling Work Group (FIFRA EMWG)

The FIFRA EMWG first met in January 1993 as an open forum for academics, EPA OPP EFED and other government and Industry modelers to discuss issues & address the following goals:

- To develop guidelines for use of screening, scenario-based and probabilistic simulation models to predict environmental aquatic exposure to pesticide residues;

- To design appropriate experimental studies to support models to improve accuracy of exposure assessments and facilitate regulatory decision making;
- To coordinate activities with other USA & international organizations concerned with exposure modeling.

The workgroup has successfully addressed many specific objectives (Hendley et al, 1994; Estes, 1995) and its achievements include documentation on the use of lysimeters (FIFRA EMWG, 1994), recommendations for improving EPA Environmental Fate study guidelines (Hendley et al, 1994; Nelson, 1994), guidance for good modeling practices (Estes and Coody, 1994) as well as updated guidance on models recommended for regulatory purposes (FIFRA EMWG, 1998 and Estes, 1995).

Some recent efforts on behalf of the group have included:

- The conception, gestation and implementation of the FIFRA Model Validation Task Force (FEMVTF - see section 3.4.2.1 above);
- The ongoing revision of the recommended primary and secondary model tables (FIFRA EMWG, 1998 - see section 3.4.3);
- The peer review of developments to PRZM & GENEEC;
- The provision of guidance and review for the development of the Multiple Scenario Risk Assessment. Tool - MUSCRAT (American Cyanamid, 1997 and see section 3.4.4.3);
- The unification of efforts to coordinate Industry, USDA ARS and EPA databases of chemical parameters;
- The fostering of cooperation between industry, USDA and EPA OPP to develop guidance on mitigation approaches.

The FIFRA EMWG continues to address pesticide exposure modeling issues and may be an effective vehicle to help implement several ECOFRAM Aquatic Exposure Workgroup recommendations

3.4.2.3. European Union Exposure Modeling Activities - the FOCUS and COST66 groups

To provide guidance for regulatory modeling of groundwater and surface water in the EU, a comprehensive set of representative scenarios are being generated by two independent FOCUS working groups.

These scenarios provide detailed guidance on the parameterization of acceptable regulatory models to estimate Predicted Environmental Concentrations (PECs) in groundwater and surface water for use in risk assessment. Each scenario specifies the crop, soil, agronomic and climatic input parameters necessary to run a specific model. The only remaining inputs required are the parameters used to characterize the properties and application characteristics of the pesticide being evaluated.

Acceptable regulatory leaching models in the EU include PELMO, PRZM, MACRO and PESTLA. Current recommended runoff models include PELMO and PRZM. MACRO and PESTLA are recommended for use in estimating

tile drainage and discharge to surface waters while EXAMS and TOXSWA are recommended to evaluate the environmental fate of pesticides in receiving water bodies.

Approximately 10 surface water and 10 groundwater scenarios are being defined, representing a distribution of environmental scenarios across the agricultural landscape of Europe. For each scenario, a weather set of 20 or more years has been obtained for use in modeling to permit simulation over extended periods of time. For most situations, FOCUS will recommend that an average weather year be used to evaluate the leaching and runoff potential of the pesticide in a specific scenario. To provide a regulatory evaluation of Predicted Environmental Concentrations in surface water (PECsw) or groundwater (PECgw) for a pesticide on a specific crop, only those scenarios appropriate for the crop need to be simulated. This project is ongoing with final reports scheduled for issue in late 1999.

The COST66 working group will publish its findings in 1999 XXXXX MARK - please can you add text

3.4.2.4. Food Quality Protection Act (FQPA)

The Food Quality Protection Act (FQPA), passed by Congress in August of 1996 made substantial changes in how the Agency assesses risk to human health. These changes have had some indirect impact on ecological risk assessment as well. The majority of the changes wrought under FQPA affect the eligibility for tolerances**1** under the Federal Food Drug and Cosmetic Act (FFDCA) rather the registration under FIFRA. The biggest impact was that the standard for food safety was changed to "a reasonable certainty of no harm" based on an assessment of "all reliable data". In addition, the risk was to be assessed against the aggregate of all routes of dietary and residential exposure (this does not include risk from worker exposure which is still assessed under the FIFRA risk-benefit standard). This has led to the use of a "risk cup" metaphor for describing the risk. The exposure from different routes are added together and compared to the regulatory level of concern based on the toxicity of the compound, the uncertainty in the data, and an additional safety factor if there is an unaddressed concern for children. If the aggregate exposure exceeds the level of concern, or "the risk cup has overflowed" and tolerances cannot be granted. In addition to aggregate exposure, if several different pesticides have a common mechanism of toxic action, then they all share the same risk cup. In Agency jargon, this is the "common mode" issue. While FIFRA does not require that the aggregate exposure and common mode be considered in ecological risk assessment, it certainly does not preclude them either and it would be expected that these issues will eventually have to be dealt with during the ecological risk assessment of pesticides.

1A tolerance is the maximum concentration of a pesticide that would be expected to occur on a food item from a legal application of a pesticide to a crop. They are used primarily for enforcement and are granted under the Federal Food, Drug and Cosmetic Act (FFDCA) rather than FIFRA. Prior to FQPA, the tolerance level was used in dietary risk assessment, but the decision whether to grant the tolerance was not necessarily tied to the results of the risk assessment. Under FQPA, the tolerance cannot be granted unless the aggregate risk from dietary and other residential routes of exposure are below the regulatory level of concern.

Perhaps the largest impact of FQPA on ecological risk assessment has been that FQPA now requires that drinking water be considered. Because the tools for aquatic exposure assessment were already in place and the estimate produced by them would be, in general, greater than that which would be expected in drinking water, they were adopted on an interim basis to assess risk in drinking water. Consequently, the number of refined assessments needed has been increased substantially as the need for refinement can be generated to address an exceedance in either the ecorisk or human health risk assessment. In the longer term, it will be necessary to develop basin scale tools to adequately address drinking water exposure. This is because, a basin of at least several hundred acres, but more normally tens to hundreds of square miles, is needed to assure and adequate supply of water throughout the year. Thus there is currently a fairly strong drive to develop a basin scale modeling capability to support the drinking water assessment effort. Aquatic exposure assessment will benefit from this effort as basin scale modeling offers the opportunity for improvements in this area as well. However, the nature of the refinement provided by basin scale modeling differs for drinking water exposure and aquatic exposure is different. For drinking water exposure, the estimate of the magnitude of the exposure is improved. This is because the intakes for drinking water facilities are usually near the lower end of the basin and basin scale modeling allows for a better estimate of the concentration profile flowing past the intake. For ecorisk, basin scale modeling allows for a better estimate of the areal extent of risk. Current Tier 2 modeling (single high exposure site per crop, multiple years) gives an estimate for a position high in the watershed. These estimates are intended tobe reasonably accurate for that environment and make suitable screens; if the regulatory level of concern is not exceeded, then there is likely to be at most, only occasional aquatic effects from the chemical in a limited area. If however, the exposure at Tier 2 exceeds the level of concern, we do not how far down the watershed the risk may extend. This question can be addressed with basin scale modeling tools by looking at the concentration profile at different points extending down the basin

3.4.3. Overview and Comparison of Current Aquatic Exposure Models

In order to understand the direction that the ECOFRAM Aquatic Exposure Work group has taken, it is important to understand the current status of aquatic exposure simulation modeling within the pesticide regulatory process.

3.4.3.1. Comparative Table of Available Models

The FIFRA EMWG developed a table to compare Agricultural Chemical Exposure models of potential significance - this can be accessed over the Internet at http//:www.acpa.org/public/science_reg /misc/em-model.html.

3.4.3.2. Recommended Models for Ecological Risk Assessment

The FIFRA Exposure Modeling Work Group has identified three categories of models to address environmental exposure issues related to pesticide residues in groundwater and surface water (FIFRA EMWG, 1995). Models currently recommended by the EMWG for regulatory pesticide aquatic exposure estimation are listed in Table 3-1.

Screening models. Screening models are used to provide a rapid examination of the environmental fate of a compound

and typically involve either simple algorithms to describe the environmental fate of a chemical or more sophisticated algorithms employing several "default" parameters. Regulatory officials must approach screening models with the understanding that the accuracy of model results is often unknown and that results are more appropriately interpreted as qualitative as opposed to quantitative. Example applications of screening models for pesticide registration include: (1) evaluating the relative impact that different soil conditions have on chemical behavior to determine potential sensitive usage environments (e.g., to assist in field study-site selection or label restrictions), and (2) comparing the environmental fate of a chemical relative to a group of other chemicals (e.g., evaluating potential environmental concerns in response to a "Section 18" emergency use request).

Primary models. Primary models are recommended in order to provide a standardized approach, where possible, to characterize pesticide behavior. Primary models enable a more rapid review of modeling submissions to USEPA, provide a focus for continued support and development of existing models, and help ensure consistent regulatory decisions on pesticide registration. Specific models have been selected based on familiarity by industry and USEPA scientists and the capabilities of the models in representing predominant environmental fate processes for many typical pesticide conditions. The primary runoff, soil erosion, and leaching model currently used for regulatory submission is PRZM3. The primary receiving water model is EXAMSII.

Secondary models. Secondary models are appropriate for chemical- and site-specific concerns that cannot be adequately addressed through primary models. As an example, RICEWQ is included as a secondary model based on its ability to simulate pesticide releases from rice paddies resulting from the unique water balance associated with rice production. These processes cannot be simulated by PRZM3.

TABLE 3-1: Recommended Models for USA Pesticide Registration (FIFRA EMWG, 1998)

Model Type	**Leaching Models**	**Runoff Models**	**Spray Drift Models** (See note 2)	**Surface Water Receiving Models**	**Surface Water Watershed Models**	**Groundwater Receiving Models**
Screening	CHEMRANK CMLS (AF/RF) PATRIOT SCIGROW (See note 3)	GENEEC	AgDRIFT - Tier I (same code is in GENEEC)	GENEEC	???	(See note 1)
Primary	PRZM3	PRZM3	AGDRIFT	EXAMS	SWAT (prov.) EXAMS (See note 5)	(See note 1)
Secondary (see note 4)	LEACHM/ LEACHP GLEAMS MACRO	EPICWQ RICEWQ GLEAMS	FSCBG AGDISP	WASP5 RIVWQ	SWRRBWQ HSPF	(See note 1)

1 The FIFRA EMWG has decided to invest no further efforts to investigate groundwater receiving models. Depending upon the outcome of Phase II of the FIFRA Model validation Task Force, this decision may be reconsidered.

2 The Spray Drift Task Force (SDTF) modeling group is still evaluating these models and official release is also pending EPA review of the SDTF data submissions.

3 This model is currently being designed to serve as a Tier 1 model to estimate groundwater concentrations for FQPA considerations.

4 In view of recent reorganizations and increasing pressure of work in EPA, it is important for registrants to realize that exposure modeling using secondary models is currently less likely to be reviewed/ accepted by EPA than was the case in 1993/1994. In circumstances where primary models are not relevant to particular compounds/use patterns/situations, it is recommended that registrants consult with EPA before investing effort in a secondary model.

5 Note that EXMAS has been added here by the ECOFRAM team using information available in September 1998.

3.4.3.3. EPA Review of Basin Scale Surface Water Simulation Models for FQPA

An EPA team reviewed the available large watershed Basin scale models for a Scientific Advisory panel held in July 1998. A detailed report is available on the EPA OPP web pages (http://www.epa.gov/pesticides/SAP/July).

3.4.4. Current Exposure Assessment Process

In order to understand the significance of the proposals made by the ECOFRAM Aquatic Exposure Workgroup, it is necessary to understand the approaches presently used to estimate pesticide concentrations in the aquatic environment. The Environmental Fate and Effects Division (EFED) of the U.S. Environmental Protection Agency's (US EPA) Office of Pesticide Programs (OPP) has been using a multi-tiered aquatic risk assessment approach for several years. A four-tiered system of environmental fate computer modeling was suggested to minimize the amount of analysis required to assess the potential risk associated by a given chemical (Parker et al., 1997; Nelson et al., 1997). The higher the Tier, the greater the implied potential for ecological effects and thus the more detailed assessment. Currently, only Tiers 1 and 2 have been developed and are regularly utilized by the Agency. Tier 1 generally uses the screening model, EFED's GENEEC. Tier 2 generally uses the USEPA PRZM and EXAMS models. Tier 3 uses (informally) the recently developed MUSKRAT model. Tier 4 has been referred to in passing, but never actually formalized. The models currently (GENEEC, PRZM, EXAMS) used in Tiers 1 and 2 are described in the following subsections.

3.4.4.1. Current Tier 1 Assessment

Tier 1 is intended to be a coarse screen to determine whether a pesticide poses sufficient risk to require a higher level assessment. The screen only considers a few basic chemical properties, the application rate, number, and methods. If application rates or methods vary substantially by crop, several crops may be considered. The scenario is designed to represent a high exposure condition and is thus deliberately conservative. Consequently, under this high exposure scenario, if the level of concern (i.e., RQ) is not exceeded, it is likely that the pesticide has low risk and no additional assessment is conducted. However, when the level of concern is exceeded, it is possible that the risk is overestimated because of the conservative assumptions rather than because the actual risk is above the level of concern; therefore, additional exposure assessment is conducted by making improved estimates of exposure (environmental concentrations) using more information (e.g., additional data, more sophisticated models, monitoring data). The new estimates, or refined estimates, will have less uncertainty associated with them than the initial assessment. This reassessment may require additional data from the registrant. The level of effort therefore required to conduct the risk assessment increases as the tiered process progresses. However, as the information considered and the assessment becomes more detailed, the associated uncertainty would decrease or at least be better defined.

3.4.4.1.1. The GENEEC model

In the current regulatory tiered process for aquatic risk assessment the GENEEC (**GEN**eric **E**stimated **E**nvironmental **C**oncentration) computer model (a meta-model of PRZM-EXAMS output) is used as the regulatory touchstone to estimate environmental concentrations (EEC's) for a pesticide in an edge-of-field water body for comparison with aquatic toxicity benchmarks to determine whether further risk characterization effort is warranted. GENEEC was developed in EFED by Parker et al. (1995; 1997) to provide screening level EEC for pesticides in an aquatic environment. Thus, it was intended to provide an upper-bound concentration value which might be found in ecologically sensitive areas because of pesticide

use. The estimates are thought to be conservative because the pond has a constant volume with no outlet, uses a site that is representative of vulnerable (high) runoff, the entire contributing area is assumed to be treated with the maximum pesticide application, and foliar degradation is not considered.

GENEEC was specifically designed to mimic PRZM (Carsel et al, 1984) and EXAMS (Burns, 1991) programs, which are the more complex computer models used in current Tier 2 assessments. GENEEC is a single runoff event model, which can account for spray drift from multiple applications. Outputs presently provide a maximum peak, a 4-day average, a 21-day, and a 56-day mean EEC's, using a few readily available environmental fate properties: soil/water partition coefficient and degradation half-lives to estimate runoff from a 10 hectare field into a one hectare by two meter deep farm pond with no outlet. GENEEC is generic with respect that it does not consider differences in climate, soils, topography, and crop. Currently, it only is capable of simulating crops that can be grown in something similar to a typical agricultural field: row crops, orchards, and turf. A prototype version GENEEC (Parker et al., 1997) has been developed to include rice, cranberries, and ditch-banks/rights-of-way, but its use has not been formalized by OPP EFED. The output concentrations in the standard pond are compared against a specified endpoint (e.g.., 2-day or 4-day LC50).

GENEEC's primary virtues are its ease and speed of use, and the minimal data requirements. Thirty or forty GENEEC runs can be done in an hour which allows the screening of a large number of uses for a chemical. All the data used in GENEEC is available early in the registration process. This allows for preliminary assessment even at the Experimental Use Permit stage in many cases.

3.4.4.1.2. Inherent Assumptions in GENEEC

A detailed discussion of GENEEC is available elsewhere (Parker et al. 1995, 1997). Key assumptions that drive GENEEC are listed below:

- GENEEC output is intended to represent a one in ten year EEC at a 90^{th} percentile for cotton. This is expected to be a larger EEC than for most (but not all) other crops in the United States. Certain crops grown dominantly in the southeast such as citrus and sugarcane may have higher EEC's because growing conditions favor greater runoff;
- The runoff event transports a maximum of 10% of the pesticide remaining and available in the top 2.5 cm at the time specified above. This value is based on an review of empirical data (Wauchope, 1979), not on PRZM modeling;
- The nature of relationship between pesticide transport to the pond and K_{oc} was estimated by using multiple runs of PRZM 1. These were done with a Loring silt loam soil with an organic carbon content of 1.61% on a cotton field in Yazoo County, Mississippi. The runoff was generated with a single 10 cm storm;
- Pesticides enter the pond in solution **or** attached to eroded sediment **or** via spray drift;
- One or more applications can be simulated and these may be applied/incorporated in various ways (broadcast, disked in after broadcast, chisel plowed after broadcast, surface banded, banded-incorporated, T-banded, in-furrow, and by aerial or ground spray);

- Application efficiency is 95% for aerial and spray blast, 99% for ground sprays and 100% for granular applications with the remainder drifting off site. Five per cent of the application rate is loaded to the pond for each aerial or spray blast application and 1% of each ground spray application;
- Degradation of pesticides entering the pond via drift begins immediately upon entry;
- Pesticide degrades in soil via aerobic metabolic processes following a first order decay;
- Degradation starts at the first application and occurs between multiple applications;
- Runoff to the pond occurs two days after a single application or on the day of the last application of a multiple application series;
- For pesticides which are watered in, the pesticide runoff into the pond occurs on the same day it is applied;
- GENEEC EEC's are based on the concentration of pesticide in the water column. This is dependent upon the compound's K_{oc} value with the solubility controlling the upper limit of the water column concentration;
- Adsorption in the pond occurs simultaneously with chemical and biological degradation until binding equilibrium is reached (as a function of K_{oc});
- Degradation occurs separately in water and sediment phases after initial partitioning. The meta model provides pesticide concentration values as a function of $K_{oc;}$
- Degradation in the pond represents a combination of first order rates for aerobic aquatic metabolism, abiotic hydrolysis and aqueous photolysis (modified by pond depth);
- 100% of the watershed is cropped and treated with the pesticide.

3.4.4.1.3.Limitations of GENEEC

The inherent limitations of GENEEC in estimating aquatic exposures relate largely to the assumptions inherent in the meta-model and are listed below:

- Degradates are not considered;
- Only edge of field risks are considered;
- Foliar interception and dissipation are not considered;
- Volatilization is not considered;
- Only considers a single rainfall event occurring after a specified time, depending upon number of pesticide applications and method;
- Farm pond has a constant volume;
- Spray drift is only a function of application rate;
- Generic site based on MS cotton site specific properties;
- Maximum rates and applications and shortest application intervals are considered;
- Assumes first-order degradation (aerobic soil metabolism rate) after each application;
- Pesticide partitioning is described using an empirical relationship of PRZM Koc for the Yazoo, MS cotton site (1.6% soil organic carbon);

- Microbial-mediated degradation is considered as the a total (lumped) first-order degradation process (including hydrolysis);
- GENEEC has never been formally validated;
- It is not known how closely GENEEC approximates the 90th percentile of a Tier 2 run.

3.4.4.1.4.Input requirements of GENEEC

The input requirements of GENEEC are summarized in Table 3-2 and the current EPA criteria used to select values are listed under comments.

Table 3-2. Input Parameters for GENEEC

MODEL INPUT VARIABLE	**COMMENTS**
Application Rate (lbs ai/A)	Current label maximum
Maximum No. of Applications	Current label maximum
Koc	Mean value provided a correlation is demonstrated between OC & Kd
Kd	Lowest "non-sand" value
Aerobic Soil Metabolic Half-life (days)	Maximum value
Is the pesticide wetted-in?	Yes or No
Depth of Incorporation (in.)	Current label minimum
Spray Drift	Aerial = 5%; Ground = 1%; Granular = 0%
Solubility (mg/L)	Registrant submitted data
Aerobic Aquatic Metabolic Half-life (days)	Maximum. If stable, use 0.
pH 7 Hydrolysis Half-life (days)	Maximum. If stable, use 0.
Photolysis Half-life (days)	Maximum. If stable, use 0.

Note: Hydrolysis half-life is entered only when a zero is entered for the aerobic aquatic metabolism half-life.

3.4.4.1.5.Input combinations that lead to under-prediction of aquatic exposure

In certain circumstances, GENEEC will under-predict aquatic exposure such that a Tier 2 modeling run using PRZM-EXAMS would estimate higher concentrations of compound of interest than the GENEEC estimate.

EPA EFED have carefully examined this finding and have identified it is likely to occur where the following circumstances ALL occur:

- The compound of interest is relatively long lived in the environment (lab half life greater than 26 weeks);
- The compound of interest has moderate to high Kd (e.g. > 2);
- Multiple applications are made within a season and the application interval is less than 4 times the lab soil half life.

GENEEC will also underestimate the exposure when degradates are also toxic and can occur at significant concentration relative to the parent.

3.4.4.1.6.Additional GENEEC Scenarios

There are a number of pesticide application scenarios that are not well represented by the agricultural field-pond scenario now used in GENEEC and PRZM/EXAMS. Scenarios and hydrology have been proposed for four of these scenarios and been developed at the beta test stage in GENEEC for first tier assessment; these were included in a version of GENEEC (version 1.3) that has received some limited circulation but which is not yet (Spring 1999) approved for regulatory use. The four scenarios are cranberries, forestry, rice, and rights-of-way.

The cranberry scenario is represented by a direct application to 30 cm of water. Degradation in the water proceeds at the aerobic aquatic metabolism rate. The water is held for a specified period of time and then drained. Different holding times are used for the four different primary growing regions: Massachusetts, New Jersey, Oregon, and Wisconsin. The drainage water is mixed with an equal volume of water in the receiving water body to estimate the EEC.

Forestry is represented by direct application to a 15 cm deep water body. The loading is reduced from the application rate by half to represent the removal by filtering in the canopy. Degradation occurs at the aerobic aquatic metabolism rate.

Rice is represented by a 10 cm deep water body that either receives a direct application of the pesticide, or the application is made to the field and then the field is flooded. The pesticide degrades at the aerobic soil metabolism rate in the field prior to flooding and at the aerobic aquatic metabolism rate after flooding. The water is held 15 days and then a storm overflows the paddy. The storm volume is set for three different scenarios (Gulf Coast, Arkansas, and California) to the 1 in 10 year storm event in that location. The water released is mixed with an equal volume of water in the receiving water body to estimate the final EEC.

Rights of Way are similar to forestry except that the filtering parameter can be set values other than 50%. However, the 50% value is recommended for this scenario as well.

These are proposed scenarios, it is not clear how well these scenarios represent high exposure scenarios suitable for regulatory purposes. These scenarios have not yet received even minimal validation and no timetable had been set for their implementation by early 1999.

3.4.4.1.7.Workgroup Views on GENEEC

During the ECOFRAM process, the Aquatic Exposure Subgroup decided that GENEEC was a valid first tier model and could serve in the new system as proposed by ECOFRAM provided the limitations described above are recognized. It was thought that ideally, a Tier 1 exposure model would be more flexible and would include additional measures (e.g.

sediment concentration estimates) and perhaps some more useful aquatic residue time course information. However, GENEEC version 1.2 is a satisfactory tool - especially for row crops. The key message is that any Tier 1 model should specifically reflect a known percentile of a Tier 2 run.

Key points from the discussion are highlighted below:

- GENEEC is a "meta-model" of PRZM2-EXAMS which are both approved regulatory models;
- GENEEC uses conservative assumptions that will either predict the same or higher than is found in the Tier 2 models in most cases (see discussion above);
- There is a general level of comfort using this for row crops at Tier 1 as described;
- This comfort level does not apply to rice, cranberries and rights-of-way since the scenarios have not been tested/validated and there is no tested and applicable Tier 2 model;
- The group does not see replacing GENEEC as Tier 1 as a high priority but, when possible, an improved Tier 1 model will be welcome;
- GENEEC must be considered to be a simple "trigger" in Tier 1, the exposure estimates stemming from GENEEC should only be used for simple "pass" or "Do more detailed exposure estimation" decisions. It is not appropriate to try to "tweak" GENEEC input parameters on a compound specific basis.

3.4.4.2. Current Tier 2 Assessment

The Tier 2 EEC assessment CURRENTLY uses a single site (or multiple single sites) which represents a high-end exposure scenario from pesticide use on a particular crop or non-crop use site for multiple years (typically 36 yrs, but range 20 - 40 years). The scenario or scenarios chosen are professional best judgement sites expected to produce runoff greater than would be expected at 90% (assumed) of the sites where the appropriate crop is grown.

EPA OPP EFED currently uses linked PRZM and EXAMS models for a refined (Tier 2) estimation of pesticide concentrations in surface waters and aquatic exposure assessments. The refined estimate of Tier 2 is intended to remove some of the uncertainty associated with Tier 1 assessments. PRZM3 (Carsel et al., 1998) which simulates the erosion and runoff from an agricultural field and EXAMS 2.97.5 (Burns, 1997) simulates the fate in a surface water body.

3.4.4.2.1. The Pesticide Root Zone Model (PRZM)

The Pesticide Root Zone Model (PRZM) was developed through the U.S. Environmental Research Laboratory in Athens, Georgia by a number of EPA staff members and subcontractors who contributed to the development of various portions of the model's code. The first version of PRZM (PRZM-1) model was released in 1984, with the accompanying user's manual written by Carsel et al. 1984. PRZM-1 was upgraded to PRZM-2. The second version (PRZM-2) linked two models together: PRZM and VADOFT (Mullins et al., 1993). PRZM-2 contains not only the processes (some may have been improved) found in PRZM-1, but additional algorithms were added to PRZM-2 to simulate soil temperature,

volatilization and vapor phase transport in soils, the addition of irrigation, microbial transformation, and a method (MOC algorithm) to reduce numerical dispersion. Several of these components were excerpted from the RUSTIC model (Dean et al., 1989). The VADOFT model (Mullins et al., 1993) simulates one-dimensional water flow in the unsaturated zone using Richards' equation. Release number 2.0 (PRZM-2) became the official version of PRZM in the early 1990's (Mullins et al., 1993).

Prior to the release of PRZM-3, a number of enhancements were made which resulted in several intermediate releases of PRZM-2. Applications of PRZM-2 included linking PRZM-2 with HSPF, WASP, and PATRIOT modeling systems, and linking PRZM-2 with the Watershed Data Management (WDM) database structure (Lumb et al., 1990) and modifications to the soil moisture depth for runoff and surface water mixing zone calculations (Donigian et al., 1994). PRZM-2.2, included a nonuniform extraction algorithm for estimating pesticide runoff; bi-phase transformation of parent compound and metabolites; the ability to transform a parent compound from a sorbed phase to metabolites; metabolite loading transfer into EXAMS-2.97; enhanced flexibility in chemical applications and improved output features. These modifications are more fully covered in the User's Manual for PRZM-3 (Carsel et al, 1998).

PRZM-2 became PRZM-3 when a septic system module and algorithms were added for modeling the fate and transport of soil nitrogen. Ultimately, the third release of PRZM (PRZM-3) resulted from the efforts of fifteen years of focused model development (Carsel et al., 1998). The current User's Manual (Carsel et al., 1998) is interim user's manual for PRZM-3 pending formal release of the final documentation by US EPA..

3.4.4.2.1.1.The PRZM model

The Pesticide Root Zone Model (PRZM) manual describes PRZM as an one-dimensional, dynamic, compartmental model that can be used to simulate chemical movement in unsaturated soil systems within and immediately below the plant root zone. PRZM was designed to provide a deterministic simulation of the fate of pesticides, applied for agricultural purposes, both in the crop root zone and the underlying vadose zone. The model is capable of simulating multiple pesticides or parent/daughter relationships and is also capable of estimating probabilities of concentrations or fluxes in or from various media for the purpose of performing exposure assessments. Predictions are made on a daily basis. Output can be summarized for a daily, monthly, or annual period. Daily time series values of various fluxes or storage can be written to sequential files during program execution for subsequent analysis or as input (pesticide loading) for the EXAMS model.

PRZM simulates two major processes, hydrology and chemical transport. The hydrologic component partitions precipitation into runoff and infiltration. The runoff and erosion is based on the Soil Conservation Service (SCS) curve number (CN) technique and the Universal Soil Loss Equation (USLE). Evapotranspiration (ET) is estimated either directly from pan evaporation data, or based on an empirical formula and is divided among evaporation from crop interception, evaporation from soil, and transpiration by the crop. Water movement in the soil is simulated by the use of generalized soil parameters, field capacity, wilting point, and saturation water contents. (Carsel et al., 1998) and is often

referred to as the "tipping bucket" method. The aquatic exposure assessment is concerned with the pesticides "leaving the area" in either runoff water or entrained sediment.

PRZM3 links two models: PRZM and VADOFT. Two options were considered by the model developers when linking the two models. The first involved only PRZM. For this configuration, PRZM would be used to simulate both the root zone and the vadose zone. This option was rejected by the developers because the assumptions of the elementary soil hydraulics in PRZM (i.e., drainage of the entire soil column to field capacity in 1 day) were considered inadequate for simulating flow in a thick vadose zone. The second option involved PRZM linked to an unsaturated zone model. In this configuration, the enhanced version of PRZM3, PRZM is linked to a one-dimensional vadose zone flow and transport model. Both the vadose and PRZM models simulate water flow and solute transport. New model code (VADOFT) was written to perform the flow and transport simulation in the vadose zone. It is not, however, required to run VADOFT when running PRZM. Since it is considered a separate component it can be turned on and off.

The pesticide transport component can simulate pesticide application on the soil or on the plant foliage. Two options are available to solve the transport equations: (1) the original backwards-difference implicit scheme that may be affected by excessive numerical dispersion at high Peclet numbers, or (2) the method of characteristics algorithm that eliminates numerical dispersion while slightly increasing model execution time. Biodegradation can also be considered in the root zone. Dissolved, adsorbed, and vapor-phase concentrations in the soil can be estimated by simultaneously considering the processes of pesticide uptake by plants, surface runoff, erosion, decay, volatilization, foliar washoff, advection, dispersion, and retardation. Many of these dissipation pathways available in PRZM require data, or parameters, that are generally not available. Therefore, either the pathway is not considered or a default or an assumed values are used. PRZM3 produces time series of pesticide loadings (output files) in sediment and runoff water leaving a field (or area) which are written to input files for use with the EXAMS models.

PRZM has the capability to simulate multiple zones. This allows PRZM/VADOFT to combine different root zone and vadose zone characteristics into a single simulation. Zones can be visualized as multiple land segments joined together in a horizontal manner. Three reasons cited by Carsel et al. (1998) that a user may choose for implementing multiple zones: (1) to simulate heterogenous PRZM root zones with a homogeneous vadose zone, (2) to simulate a homogeneous root zone with heterogenous vadose zones, and(3) to simulate multiple homogeneous root zones with multiple homogeneous vadose zones. Multiple zones are not generally used in Tier 2 scenarios.

3.4.4.2.1.2.Inherent Assumptions in PRZM

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3.4.4.2.1.3.Limitations of PRZM

Hydrologic and hydraulic computations are performed in PRZM on a daily time step even though, for some of the processes involved (evaporation, runoff, erosion, infiltration), finer time steps would be more greater accuracy and better

reflect reality. For example, simulation of erosion by runoff depends upon the peak runoff rate, which is in turn dependent upon the time base of the runoff hydrograph. This depends to some extent upon the duration of the precipitation event. PRZM uses daily time step primarily because of the relative availability of daily versus shorter time step meteorological data. This limitation can partially be mitigated by enhanced parameter guidance within PRZM input selection.

Soil drainage through unsaturated flow is also important in as much as it influences the soil water balance, and therefore, antecedent soil water content which not only influences runoff, but also pesticide transport away from the soil surface. In PRZM, the soil hydraulics are simple. All drainage to field capacity water content is assumed to occur within 1 day. The 1-day drainage assumption has an effect, especially on deeper soils, of inducing a greater-than-anticipated movement of chemical through the profile. Although this representation of soil hydraulics remains in PRZM, the user has the option of linking PRZM to VADOFT. PRZM is then used to represent the root zone, while VADOFT, with a more rigorous representation (Richards equation) of unsaturated flow, is used to simulate the thicker vadose zone. The VADOFT model can be reviewed in more detail by consulting the PRZM manual (Carsels et al., 1998).

PRZM does not consider subsurface lateral water flow which could contribute to pesticide loads reaching surface water bodies. A number of limitations of the pesticide leaching pathway are noted in the PRZM manual (Carsels et al., 1998), and are not repeated here.

Many of the dissipation pathways available in PRZM (Carsel et al., 1998) also require data, or parameters, that are generally not available. Therefore, either the pathway is not considered or a default or an assumed values are used. Additionally, not all simulated dissipation pathways have been validated.

The algorithms which simulate volatilization also identifies another limitation of the soil hydraulics of PRZM. PRZM simulates only advective, downward movement of water and does not account for diffusive movement due to soil water gradients. Thus PRZM is unable to simulate the upward movement of water in response to gradients induced by evapotranspiration. This process has been identified as important in simulating volatilization. However, the process would seem less likely to impact the movement of chemicals with high vapor pressures. For these chemicals, vapor diffusion would be a major process for renewing the chemical concentration in the surface soil.

Other limitations:

- PRZM is dependant upon site specific properties (e.g., curve numbers and precipitation event relative to pesticide application);
- PRZM can not address spatial and temporal variability;
- High runoff soils are considered (Hydrologic C and D);
- Assumes 100% of the watershed is treated with pesticide;
- Maximum rates and applications and shortest application intervals considered;

- Scenario represents "edge of field" exposure;
- Does not consider hydrology at watershed or basin scale;
- Degradation of a pesticide in or on soil may be due to such processes as hydrolysis, photolysis, and microbial decay. If these processes follow pseudo first-order kinetics, the rate coefficients may be combined into a single decay coefficient. Assuming the same rate constants for the solid and dissolved phases;
- The foliarly applied pesticide is subjected to degradation (as a lumped first-order foliar degradation rate), transformation to metabolites and losses through volatilization;
- Adsorption and desorption are treated as instantaneous, linear, and reversible processes;
- Foliar interception/dissipation is considered, but rate data are rarely available;
- PRZM uses first-order degradation in soil pore water and on the soil surface;

- Scenario assumption rather than PRZM. Assumes that 1% and 5% of each application for ground and aerial spray applications, respectively, are directly deposited into the pond.

Further discussion concerning limitations and assumptions for PRZM are given in Carsel et al. (1998).

3.4.4.2.2.The Exposure Analysis Modeling System (EXAMS)

The Exposure Analysis Modeling System (EXAMS) was developed at the U.S. Environmental Protection Agency Office of Research and Development's (ORD) research laboratory in Athens, Georgia to rapidly screen and identify synthetic organic chemicals likely to adversely impact aquatic systems (Burns, 1997).

3.4.4.2.2.1.The EXAMS model

EXAMS estimates exposure, fate, and persistence following release of an organic chemical into an aquatic ecosystem. For the estimation of pesticide concentrations in surface water for aquatic risk assessments, the pesticide is loaded into the water body in response to precipitation events and spray drift from files created by PRZM.

EXAMS consists of a number process modules that link fundamental chemical properties to the limnological parameters that control the kinetics of fate and transport in aquatic systems (Burns, 1997). The chemical properties are measured by conventional laboratory methods, which are required under various regulatory data requirements (Burns, 1997). EXAMS provides facilities for long-term (steady-state) analysis of chronic chemical discharges, initial-value approaches for study of short-term chemical releases, and full kinetic simulations that allow for monthly variation in mean climatological parameters and alteration of chemical loadings on daily time scales. Since EXAMS is a "steady-state" model it does not accurately characterize the transient nature of water flow and pesticide influx. EXAMS was written in a generalized (N-dimensional) form in its implementation of the algorithms representing spatial detail and chemical degradation pathways.

The environment in EXAMS is represented through long-term average values of the forcing functions that control the behavior of chemicals. EXAMS is capable of considering steady state input loadings, pulse loads, and coupling to the output of the PRZM model, which can provide a lengthy time-series of contamination events due to runoff and erosion of sediments from agricultural lands.

When a pesticide reaches an aquatic system, the entire array of transport and transformation processes begins at once to act on the chemical. The processes are combined into mathematical descriptions of their total effect on the rate of change of chemical concentration in the system. To use numerical techniques, the system is divided into a grid of spatially discrete elements, which are continuously varying in space and time. These elements are also referred to as "grid points" or as "compartments". The compartments are assumed to be "well-mixed", that is, the reaction processes are not slowed by delays in transporting the compound from less reactive to more reactive zones in the volume element.
The transport of a chemical from a loading point into the bulk of the system takes place by advected flows and by turbulent dispersion. The physical space of the system is broken down into a series of physically homogeneous elements (compartments) connected by advective and dispersive fluxes. Each compartment is a particular volume element of the system, containing water, sediments, biota, dissolved and sorbed chemicals, etc. Pesticide loadings and exports are represented as mass fluxes across the boundaries of the volume elements; reactive properties are treated as point processes within each compartment.

EXAMS provides analyses of:

- Exposure: the expected environmental concentrations (EECs) resulting from a particular pattern of chemical loadings;
- Fate: the distribution of the chemical in the system and the fraction of the loadings consumed by each transport and transformation process; and
- Persistence: the time required for purification of the system (via export/transformation processes) should the chemical loadings cease.

3.4.4.2.2.2.Inherent Assumptions in EXAMS TO BE BULLETIZED

EXAMS was designed to evaluate the consequences of longer-term, primarily time-averaged chemical loadings that ultimately result in trace-level contamination of aquatic systems (Burns, 1997). EXAMS generates a steady-state, average flow field (long-term or monthly) for the ecosystem. EXAMS thus cannot fully evaluate the transient, concentrated EECs that arise, for example, from chemical spills. This limitation derives from two factors. First, a steady flow field is not always appropriate for evaluating the spread and decay of a major pulse (spill) input. Second, an assumption of trace-level EECs, which can be violated by spills, has been used to design the process equations used in exams.

The following assumptions were incorporated into EXAMS (Burns, 1997). The pesticide is assumed not to radically change the environmental variables that drive its transformations. Thus, for example, an organic acid or base is assumed not to change the pH of the water body; the compound is assumed not to itself absorb a significant fraction of the light

entering the system; bacterial populations do not significantly increase (or decline) in response to the presence of the chemical.

EXAMS uses linear sorption isotherms, and second-order (rather than Michaelis-Menten-Monod) expressions for biotransformation kinetics (Burns, 1997). This approach is known to be valid for low concentrations of pollutants but its validity at high concentrations is less certain (after Burn, 1998). EXAMS controls its computational range to ensure that the assumption of trace-level concentrations is not grossly violated. This control is keyed to aqueous-phase (dissolved) residual concentrations of the compound: EXAMS aborts any analysis generating EECs that exceed (the lesser of) 50% of the compound's aqueous solubility or 10 micromolar (10^{-5} M) concentrations of a dissolved unionized molecular species. This restraint incidentally allows the program to ignore precipitation of the compound from solution and precludes inputs of solid particles of the chemical. Although solid precipitates have occasionally been treated as a separate, non-reactive phase in continuous equilibrium with dissolved forms, the efficacy of this formulation has never been adequately evaluated, and the effect of saturated concentrations on the linearity of sorption isotherms would introduce several problematic complexities to the simulations.

Sorption is treated as a thermodynamic or constitutive property of each segment of the system, that is, sorption/desorption kinetics are assumed to be rapid compared to other processes (Burns, 1997). The adequacy of this assumption is partially controlled by properties of the chemical and system being evaluated. Experience with the program has indicated, however, that strongly sorbed chemicals tend to be captured by benthic sediments, where they are released to the water column is controlled by their availability to benthic exchange processes. This phenomenon overwhelms any accentuation of the speed of processes in the water column that may be caused by the assumption of local equilibrium.

3.4.4.2.2.3.Limitations of EXAMS TO BE BULLETIZED

EXAMS is primarily limited because it is a steady-state model and cannot accurately characterize the dynamic nature of water flow. A model with dynamic hydrology would more accurately reflect concentration changes due pond overflow and evaporation. Thus, the estimates derived from the current model simulates a closed-system, because the pond has no outlets, flowing water, or turnover. It is also assumed the inflow from runoff is exactly balanced by evaporative losses.

Currently, OPP EFED is using a standard water body which is maintained at a constant volume (20,000 L). The contributing area is also always assume to be the same (10 ha). The physicochemical properties of this small water body are characteristic of a farm pond in Georgia.

Daily edge-of-field loadings of pesticides dissolved in runoff waters and sorbed to entrained sediment, as predicted by PRZM, are discharged into the standard small water body simulated by the EXAMS model. Pesticide loading, through spray drift, is assumed to be a fixed percentage of the pesticide application rate, which is dependant upon method of application.

The EXAMS can account for volatilization, sorption, hydrolysis, biodegradation, and photolysis of the pesticide within the water body. Although, EXAMS considers many possible routes of dissipation, the environmental fate properties such as aerobic and anaerobic aquatic half-lives (or degradation rates) are often lacking for inclusion as inputs into EXAMS. Fate data for degradates are also often not available.

Aborting the generation of EECs when the concentration exceed (the lesser of) 50% of the compound's aqueous solubility or 10 micromolar (10^{-5} M) concentrations of a dissolved unionized molecular species.

Further discussion concerning limitations and assumptions for PRZM are given in Carsel et al. (1998) and for EXAMS in Burns (1997).

3.4.4.2.3.Tier 2 Assessment Scenarios

Having considered the two key models in detail, it is important to discuss how they are used together in the current Tier 2 risk assessment process.

3.4.4.2.3.1.An example PRZM3-EXAMS scenario to be bulletized

The standard PRZM3-EXAMS runoff modeling scenario for Tier 2 assessment is based on a 100% cropped and treated 10 ha field draining into a 1 ha by 2 meter deep small, stagnant body, with no outlet. This scenario represents a watershed drainage area/water volume ratio of 5 m^2/m^3. Each PRZM modeling scenario represents a unique combination of climatic conditions (*e.g.*, rainfall), crop specific management practices, soil specific properties, site specific hydrology, and pesticide specific application and dissipation processes. Each PRZM simulation is conducted for multiple years (typically 36 years but can be as much as 40 years) to provide a probabilistic exposure characterization for a single site. Pesticide concentrations in the water column are extracted from the simulation as the annual daily peak, maximum annual 96-hour average, maximum annual 21-day average, maximum annual 60-day average, and annual average. The upper 10^{th} percentile concentrations (except annual average) are used to compare against ecotoxicological and human health levels of concern (LOC).

Spray drift is determined by method of pesticide application (5% for aerial spray; 1% for ground spray, 0% for granular or soil incorporated applications). PRZM simulations are generally made with both with the recommended and maximum application rates, maximum number of yearly applications, and the shortest recommended application interval.

For information, the model input parameters for a standard scenario (Yazoo) are given in Appendix 3-5.

3.4.4.2.3.2.Limitations of Tier 2 Aquatic Exposure Assessment to be bulletized

A single 10 hectare field with a 1 hectare pond does not accurately reflect the dynamics in a watershed or basin. The entire basin or watershed would also probably not be planted completely to a single crop nor be completely treated with a pesticide. Additionally, treatment with the pesticide would likely occur over several days or weeks, rather than all on a single day. This would reduce the magnitude of the concentration peaks, but also make them broader, reducing the acute exposure but perhaps increasing the chronic exposure.

The scenario or scenarios that are selected for use in Tier 2 assessments are ones that are likely to produce high concentrations in aquatic environments. The scenarios were intended to represent sites that actually exist and are likely to be treated with a pesticide. These sites should be extreme enough to provide a conservative estimate of the EEC, but not so extreme that the model cannot properly simulate the fate and transport processes at the site. Currently, sites are chosen by best professional judgement to represent sites which generally produce EECs larger than 90% of all sites used for that crop. The EECs in this analysis are accurate only to the extent that the sites represent the hypothetical high exposure sites. The most limiting aspect of the site selection is the use of the "standard pond" which has no outlet. It also should be noted that the standard pond scenario used here would be expected to generate higher EECs than most water bodies; although, some water bodies would likely have higher concentrations (e.g., a shallow water bodies near agriculture fields that receive direct runoff from the treated field.

The quality of the analysis is also directly related to the quality of the chemical and fate parameters available for a given pesticide. Available data maybe acceptable, but it is usually rather limited. Data were not available for degradates and the aquatic aerobic metabolism rate are often not known, but estimated or not considered. The measured aerobic soil metabolism data lacked sufficient range (sample size) to accurately establish the half-life. However, the use of a range of data (mean times an uncertainty factor-3) may be sufficient to capture the probable estimated environmental concentration in a manner similar to when only a single measured value is available. Knowledge concerning agronomic practices (method of pesticide application) and usage information (amount, number, rate of application, acres treated) is also needed.

Aerial spray drift reaching the pond is assumed to be 5 percent of the application rate. Another limitation is the lack of field data to validate the predicted pesticide runoff. Although, several of the algorithms (volume of runoff water, eroded sediment mass) are validated and understood, the estimates of pesticide transport by PRZM3 have not yet been fully validated. From limited analysis it appears that PRZM3 may generate pesticide loadings that are higher than really occur. This would result in conservative EEC estimates. Other limitations of the models are the inability to handle within site variation (spatial variability), crop growth, and the overly simple soil water balance. Another limitation is that only 36 years of weather data was available for the analysis. Consequently there is only a 1 in 36 chance that the true 10% exceedance EECs are larger than the maximum EEC in the analysis. If the number of years of weather data were increased, it would increase the level of confidence that the estimated value for the 10% exceedance EEC was close to the true value.

3.4.4.2.3.3.Additional TIER 2 Scenarios

EPA OPP EFED has developed a number of standard scenarios for different crops: i.e., alfalfa, almonds, apples, beans, berries, broccoli, cabbage, cherries, citrus, corn, cotton, cucurbits, filberts, golf course, grapes, kiwi, lettuce, peaches, peanuts, pears, pecans, plums, potatoes, sorghum soybeans, strawberries, sugar beets, sugar cane, sun flowers, tobacco, turf, walnuts, wheat, and grass/pasture/hay.

Scenarios are selected by identifying "high use areas (e.g., county) for a crop from USDA Agricultural Census data. A soil with a soil hydrologic group of C or D from the identified high use area is selected. Soils data from the specific soil can is obtained from the SCS (NRCS) or PIC database (Bird et al., 1992).

Currently, many of these scenarios are anecdotal; until a revised Tier 2 is available, the current standard scenarios should be collected, annotated (with justifications) and published via an EPA Internet site.

3.4.4.3. Current Tier 3 Assessment

Currently the exposure modeling conducted to provide Tier 3 estimates of pesticide exposure involves the use of PRZM/EXAMS runs conducted with the aid of a "shell" program (MUSCRAT) that conveniently provides for multiple runs of the programs across relatively large numbers of scenarios based on crops and regions. The MUSCRAT model was conceived and drafted between 1996 and 1997 and, although it is being used for some risk assessments, at the time of writing, this shell program has still not been officially approved by EPA OPP EFED via the EPA ORD laboratories. It should therefore be regarded as an indication of the concepts behind Tier 3 thinking prior to ECOFRAM. However, it is not always the most appropriate tool and sometimes registrants move to other approaches (loosely defined as Tier 4)

3.4.4.3.1.MUSCRAT background

The Multiple Scenario Risk Assessment Tool, MUSCRAT, is a Windows application program developed to standardize and automate Tier 3 ecological risk assessments under FIFRA. MUSCRAT links chemical, crop, soil, and climate data bases; facilitates the creation of PRZM-3 and EXAMSII input files; batch processes multiple model simulations; and performs statistical analyses on predicted exposure concentrations (Figure 3-1).

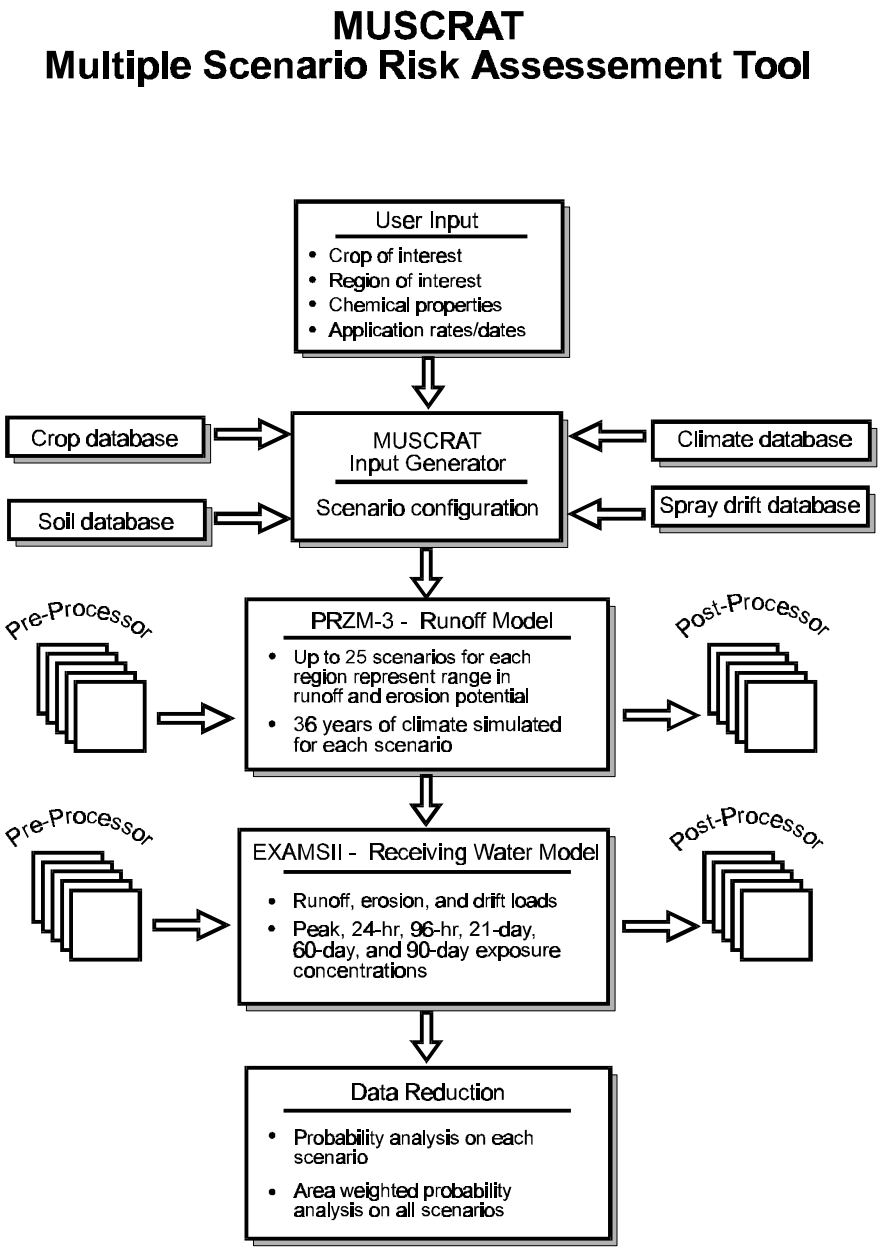


Figure 3-1. MUSCRAT Process Diagram

MUSCRAT evolved under the auspices of the FIFRA Exposure Modeling Work Group. Technical work was directed by Gary Mangels (American Cyanamid) with help from Ron Parker (USPEA), and Pat Havens (Dow Agro Sciences). American Cyanamid provided the majority of the funding for the project with some assistance by the Rh^ne-Poulenc Ag Company. The model scenario selection process was based on a pilot study designed by Dow Agro Sciences. Data base processing for various aspects of this project was performed by the San Diego Supercomputer Center, American Cyanamid, Texas A&M University, Waterborne Environmental, Inc. and Compliance Services International. Code development was performed by Waterborne Environmental, Inc.

MUSCRAT is a regional risk assessment tool whereby the United States is divided into 11 regions (Figure 3-2)

Figure3- 2. MUSCRAT Regions

Each region is subdivided into 25 runoff/erosion categories or "bins" yielding 275 bins for the entire U.S.. All agricultural soils within a region are allocated to a bin based on their respective runoff/erosion potential. This is done using a data set generated on the San Diego supercomputer for each STATSGO soil polygon using local weather station data. Runoff/erosion potential was determined from annual water runoff and sediment yield predicted 30-year model simulations for each soil/weather combination. This dataset offers potential for other approaches to scenario definition (see section 3.7.4.4). Each bin is represented by a specific scenario (i.e., meteorological station and soil series). Acreage within each bin is tabulated by crop based on "crop suitability" as determined by the U.S. Department of Agriculture for those soils associated with the respective bin.

A Tier 3 analysis involves selecting a crop and a region of interest from which a subset of scenarios is determined. For example, selecting cotton for all regions would result in 102 scenarios in 6 regions. Selecting a minor crop would result in substantially smaller number of regions and scenarios. MUSCRAT lists 23 crops for which 19 are currently active.

A scenario represents a 10-hectare field draining to a 1-ha pond, as patterned after EPA's standard pond scenario for Tier 2 ecological risk assessments. Chemical loadings to the pond are simulated for 36 consecutive years of pesticide application with a corresponding 36-year climate record. Chemical loadings include dissolved residues in runoff water, sorbed residues in eroded sediment, and drift. Dissolved and eroded loads result from storm events and are predicted using PRZM-3. Drift loads are based on USEPA drift figures for the day of application as a function of the application method and the user can change these values based on data available to them. Future versions of MUSCRAT may link AgDrift to calculate drift loads to the pond. Dissipation in the pond is simulated by EXAMSII.

For each scenario, a normal probability analysis is performed on the annual maximum series of predicted exposure concentrations for a given exposure duration. The annual maximum series represents the maximum concentrations for each year of simulation determined from a rolling average evaluation for the year for a given exposure duration (per ARAMDG). Analyses are performed on the instantaneous maximum, 96-hour, 21-day, 60-day, 90-day, and "long-term" durations. Other exposure durations may eventually be included in the analyses. Values associated with the year closest to the 10th percentile are reported (10-year return period).

A second probability analysis is performed on the data set consisting of the 10th percentile concentrations for all scenarios within the region. Each scenario receives an area-weighting based on the total acreage for that crop in the scenarios bin for that region. Acreage is based on crop suitability as defined by USDA as opposed to crop production. Area-weighted probability curves are produced for each exposure duration (Figure 3-3).

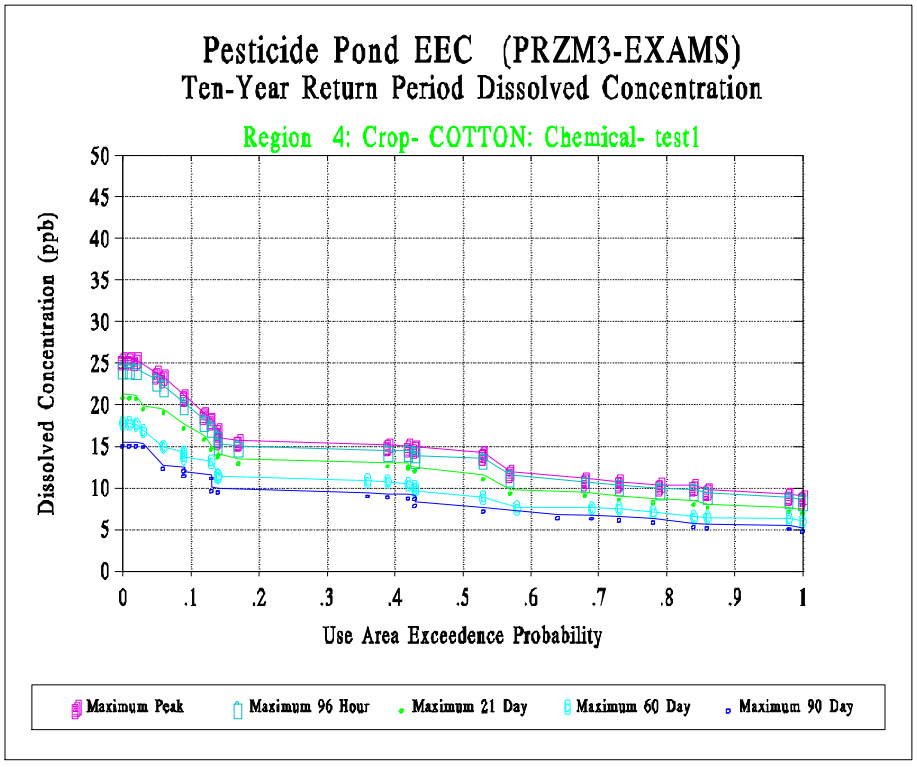


Figure 3-3. MUSCRAT Area-Weighted probability curve

The strengths of MUSCRAT as currently implemented, include the following:

- It automates and standardizes the Tier 3 ecological risk assessment process.
- The tool is built around the primary models used for pesticide evaluations under FIFRA.
- The program uses object-oriented (modular) technology so that future versions of PRZM, EXAMS, AgDrift or alternate environmental fate models could be substituted.

- The underlying data generated by the San Diego supercomputer consisting of runoff estimates for water and sediment from each agricultural soil in each region is of potentially great value for the preparation of spatially explicit relative runoff maps.
- MUSCRAT produces a distribution of exposure values across entire regions or use areas and thus embodies a great deal more data of value to the risk assessment process.

3.4.4.3.2.Inherent Assumptions and limitations of MUSCRAT

The following bullets represent key assumptions leading to limitations in MUSCRAT

- Risk characterization only reflects the variability associated with soil and weather for an index pond scenario.
- Chemical applications are assumed to occur on the same day of the month for every year of simulation and do not reflect weather variability or other stochastic components.
- Chemical degradation is neither climate nor soil dependent.
- Constant drift factors do not reflect the variability that occurs with weather, application equipment, formulations, and other factors.
- Temporal and spatial variability in other factors, including watershed size and receiving water body volume, hydrodynamics, and environmental chemistry, are not considered
- The crop suitability assessment from STATSGO does not necessarily represent "real world" cropping practice
- The crop acres value used does not typically represent acreage treated.
- MUSCRAT does not presently provide a "national" set of scenarios for widely used crops.
- Because many of EPA's current 'standard" scenarios are "tuned" on the basis of local erosion and detailed soil data, MUSCRAT can provide HIGHER values than some Tier 2 runs

DO WE NEED A SECTION ON DESIRED IMPROVEMENTS TO MUSCRAT TO GIVE THE DESIRED TIER 2 MODEL??

Examples include the need to retain "correlated variables" on a regional basis (e.g. watershed area to pond size/depth/volume, adsorption characteristics with half life, soil textures and slopes, soil characteristics and Kd's

3.4.4.4. Recent Tier 4 Approaches - an Example

Currently "Tier 4" is not defined and can encompass many types of study ranging from mitigation investigations to mesocosms studies to large scale monitoring programs. A different approach was applied for the pyrethroid insecticides by the Pyrethroid Working Group (PWG - an association of the 6 US pyrethroid manufacturing companies). The problem to be addressed was that the use of EPA's Tier 2 aquatic exposure assessment procedures for the use of pyrethroids on cotton resulted in anticipated pond concentrations exceeding the LOC for aquatic invertebrates. The application of MUSCRAT resulted in comparable exposure values; however, even then, the predicted exposures, decline curves and LOC exceedance produce predictions that were not congruent with the experience of several years sales or chemical fate results found in the

extensive series of mesocosms run by the PWG companies in the late 1980's. As a result, the PWG decided to investigate the validity of some of the assumptions inherent in the existing Tier 2/3 models and developed a study design that can be considered as an example of a Tier 4 study.

Essentially, the landscape analysis approach identified key assumptions associated with Tier 2/3 and used satellite imagery and other data to better define the cotton agricultural landscape in Yazoo County Mississippi. Cotton was identified from the imagery and the compositions of the landscape was defined. The proximity of cotton to water bodies of various types was investigated as was the spatial placement of cotton fields around water bodies (to investigated sensitivity of deposition to wind direction. Soil and slope information for the cotton producing fields was also investigated. Finally high resolution imagery and classification provided information on the physical nature of the "buffer' area between agricultural fields and water bodies.

A fraction of the resulting measured data was combined with Tier 2 modeling to provide a reassessment of the potential exposure to each of the ponds in the county. The resulting estimate of the expected concentration in a 90th percentile pond in a 90th percentile weather year was between 12 and 15 times lower than the original Tier 2 estimate and, being based on measured values, reduced the uncertainty associated with the predictions. Many additional factors describing the cotton landscape in Mississippi could have been incorporated such the estimated values remained demonstrably highly conservative.

This approach is examined in considerable depth later in the report (section 3.7.5.5) when the landscape assessment approach is recommended as a useful tool for refining predicted risk to aquatic ecosystems and reducing the associated uncertainty.

3.5. Conceptual Models of Key Components of the Agricultural Landscape

Before developing approaches for improving the current process, it was necessary to develop an understanding of the key processes operating across the agricultural landscape to influence the potential exposure of aquatic systems to pesticides.

3.5.1. Introduction/scope

Conceptual models are a product of the first, or "problem formulation" phase of ecological risk assessment (*Framework for Ecological Risk Assessment* (EPA/630/R-92/001, February 1992)). The problem formulation phase sets the objectives for risk assessment. Because pesticides constitute a patent toxicological hazard, the need for careful evaluation of potential dangers to food safety and ecological health has been a recurrent theme in American public policy debates. The current "problem formulation" has developed as incremental improvements derived from an *ad hoc* process of negotiation among producers, environmental groups, chemical companies, public health advocates, and the regulatory community as required to satisfy the spirit of the "risk/benefit" provisions of FIFRA. Because it is important that the logic and technical basis of risk assessment be accessible to public scrutiny, the Agency has periodically documented the basis for its risk assessments

– most notably in OPP's *Hazard Evaluation Division Standard Evaluation Procedure – Ecological Risk Assessment* (EPA-540/9-85-007, June 1985), and in the series of documents released by the Risk Assessment Council of the Office of Research and Development (ORD), culminating in the *Proposed Guidelines for Ecological Risk Assessment* (EPA/630/R-95/002B, September 1996.) The *Guidelines* emphasize problem formulation as a critical stage in ensuring the success of a risk assessment – suggesting that pesticide risk assessment could benefit from a systematic review of its assumptions and scope within that formalized framework. The conceptual models presented here are a step along that path.

The *Guidelines* document defines a "conceptual model" as "a written description and visual representation of predicted responses by ecological entities to stressors to which they are exposed. ...exposure scenarios may qualitatively link land-use activities to sources and their stressors, may describe ... exposure pathways, and may describe co-occurrence between exposure pathways, ecological effects, and ecological receptors." In recognition of the reality that scientific knowledge is always tentative or conditional, i.e., subject to revision in the light of further investigation, the *Guidelines* characterize conceptual models as collections of "risk hypotheses" – "assumptions made in order to evaluate logical or empirical consequences." Conceptual models are further defined as consisting of two principal products:

- A set of risk hypotheses that describe predicted relationships between stressor, exposure, and assessment endpoint response, along with the rationale for their selection
- A diagram that illustrates the relationships presented in the risk hypotheses.

Here we present a set of conceptual models of pesticide aquatic exposure at the scale of regions, landscapes, and ecosystems. These models helped to focus discussions and to characterize the capabilities of the models currently in use by OPP. They also served to highlight issues in need of vigorous discussion and analysis by the technical community. Chief among these is perhaps the issue of "what we are trying to protect," especially as we pass from general statements of ecological value and a stewardship ethic to the level of detail necessary to put finished assessment tools into the hands of practitioners. The spatial scale needed for the analysis is an important determinant of the inferential tools (general statistical correlations or "empirical models," process-based models based in chemical, physical, toxicological and ecological fundamentals, etc.), databases, and integrative techniques (stratified sampling methods, statistical characterization of uncertainty, Bayesian inference, etc.) needed in the risk assessment.

For example, OPP EFED uses the "constructed farm pond" as its primary ecosystem focus for evaluating aquatic exposure. This stratification of the entire universe of aquatic ecosystems is justified on the basis of proximity to treated areas, the ubiquity of these systems (their number probably exceeds 1,000,000 nation-wide), and their multiple uses – constructed farm ponds are used for stock watering, as a source of irrigation water, for water-contact recreation and angling by farm families and, in many cases, by the public, and they are a habitat resource for both migratory and resident wildlife. They may not, however, be the best model for drinking water concerns, damage to endangered anadromous fishes, or broader-scale impacts of the more volatile of the pesticidal chemicals. For example, although farm ponds may be a source of recharge water to a few farmstead wells, most small water supply reservoirs are found in watersheds that include a variety of cropping systems and land uses – in which case a conceptual model of potential water quality impacts of pesticides must encompass the attenuation of farm sources by water flows from forested, urbanized, and industrial sources, and must

accommodate analysis of the aggregate effect of multiple products used across the entire watershed – for residential and industrial as well as for agricultural purposes.

3.5.1.1. Regional Scale Concepts

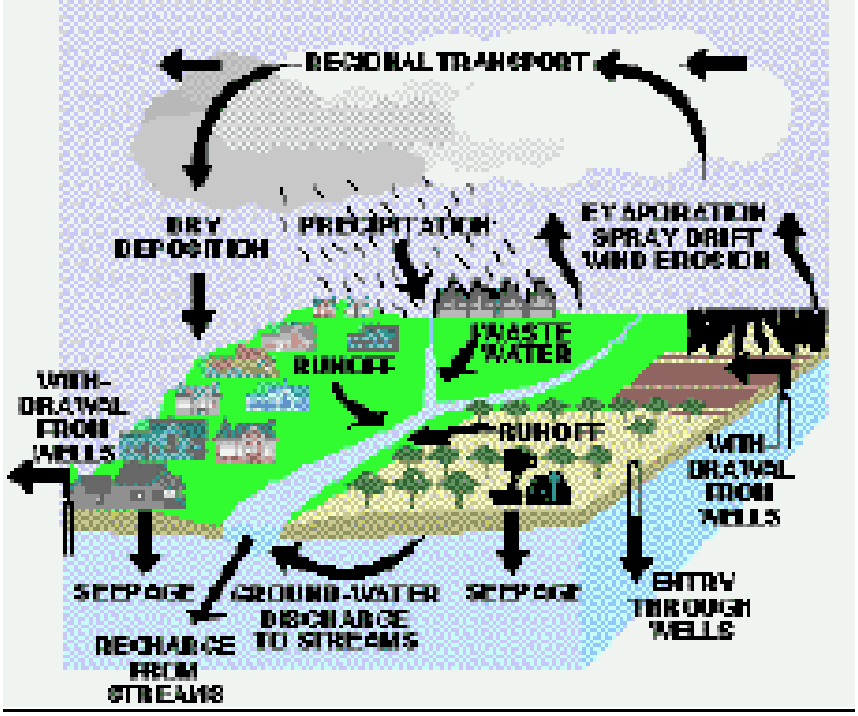


Figure 3-4: A regional scale view of potential routes of pesticide transport

Agricultural chemicals are essential for effective food production but may pose potential risks to humans and the environment; EPA OPP has the responsibility to address this dilemma under the FIFRA statute. While it is often assumed that pesticide contamination is a phenomena associated with agricultural areas, recent research shows that urban areas can contribute extensively to pesticide residues in urban streams. Therefore an assessment of the probabilities of non-target aquatic exposure to pesticides must take a wide view of pesticide use.

Figure 3-4 (courtesy of USGS NAWQA) takes a broad view of potential pesticide transport routes. Once the pesticide has been applied, one of the most significant routes for potential risk to non-target organisms, ecosystems and humans, is via subsequent contamination of the hydrologic system.

- Possible atmospheric transport routes are via spray drift, volatilization or wind erosion and subsequent dry fall or deposition in rain
- Possible aquatic transport mechanisms are via leaching (seepage) and/or surface runoff.
- Movement to natural surface water can be via runoff and/or groundwater discharge

The ECOFRAM Aquatic Workgroup concentrated mostly on refining an understanding of the impact of spray drift and runoff routes of entry on the probabilities of aquatic exposure in non-target water bodies.

A major issue that the ECOFRAM process has not been able to address is how regulators, the regulated community and society at large can better understand which water bodies need to be protected and to what degree. One corollary to that debate is the recommendation of appropriate modeling scenarios (e.g. edge of field concentrations, concentrations in farm ponds or reservoir residues) for the various "tiers" of an aquatic risk assessment.

3.5.1.2. Routes of transport to aquatic systems at different scales

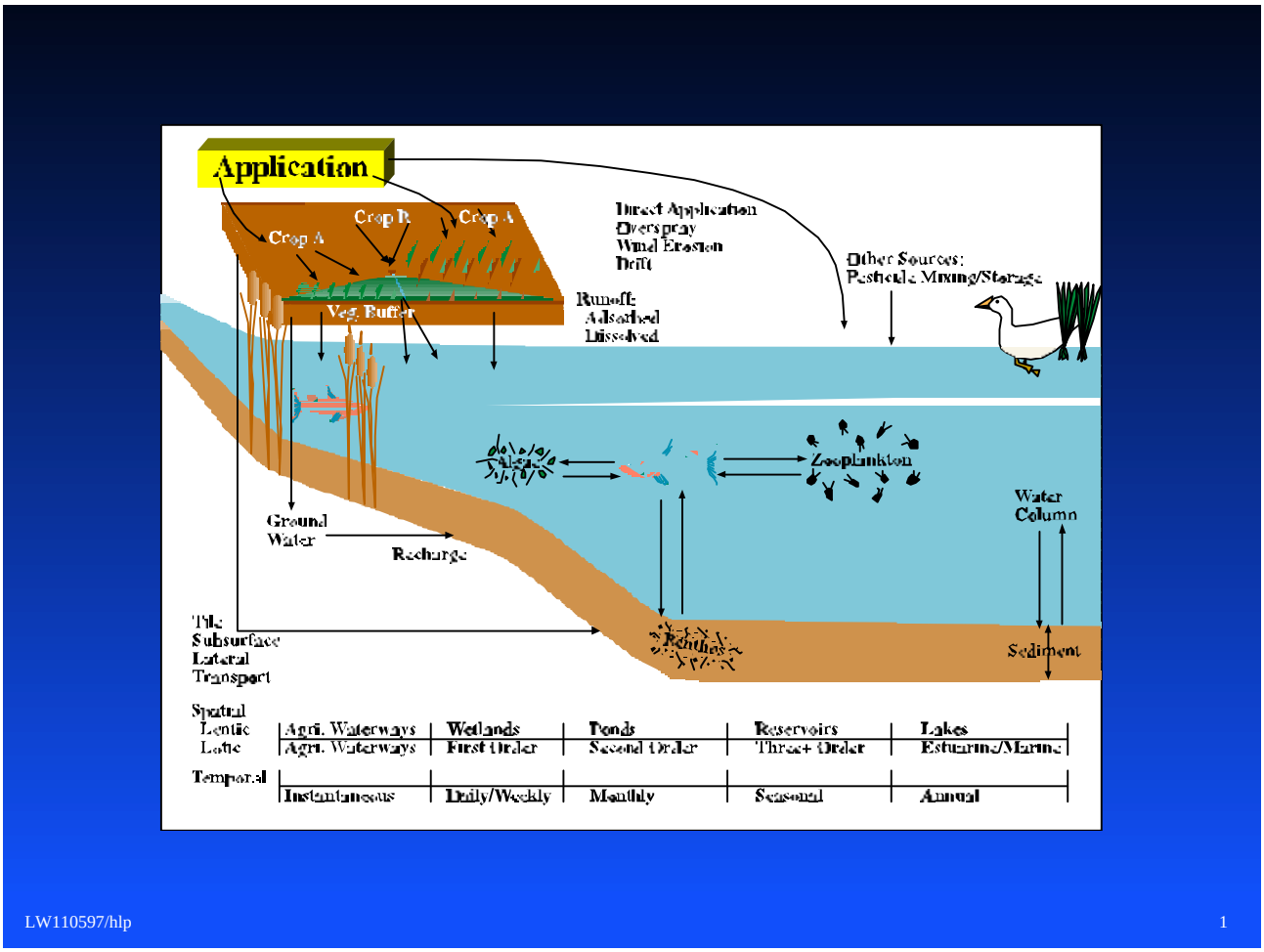


Figure 3-5: Details of the interfaces where transfer can occur between aquatic systems and Agriculture

Figure 3-5 is a simplified model of potential fate pathways from the point of pesticide application to aquatic habitats and relevant areas in the hydrologic system. Surface runoff and aerial exposure, governed by many environmental factors, make the most significant contribution to pesticide loading. Exposure of aquatic organisms and animals in the food chain associated with aquatic habitats is a factor of the complex pathways within the system, including flux of chemicals between sediment and associated benthos and interactions among water column organisms. The dynamics of different water bodies on a spatial scale (e.g. size and water flow), as well as temporal input and distribution, also greatly influence pesticide concentration and duration of exposure.

Most aquatic pesticide exposures originate from applications to crops adjacent to surface water. Although direct entry of chemicals may occur during application, aerial deposition and runoff are primary pathways for entry of pesticides into a water body. Aerial deposition occurs via wind erosion or drift, while surface runoff (adsorbed onto soil and related particles or dissolved in an aqueous medium) may enter directly from site of application or as input from areas, including vegetative buffers, between the crop and the aquatic system. Recharge from groundwater, tile drainage, or subsurface lateral transport are minor pathways of pesticide entry into aquatic systems.

Once a pesticide(s) enters a water body, complex interactions control distribution within the ecosystem. Varying environmental conditions may create periodic flux or release of some compounds between sediment, aquatic vegetation, and overlying water, thereby affecting availability to organisms occupying different niches within the system. Furthermore, residues may be metabolized, accumulated and/or transferred between organisms (e.g. phytoplankton, zooplankton and benthic invertebrates or higher vertebrates, such as fish and waterfowl).

Key elements of aquatic exposure depicted in Figure 3-5 are the range of spatial scales involved for both lentic and lotic aquatic systems and the relationships which generally exists between spatial scale and the various durations of exposure. As one moves from left to right on the scales, exposure concentrations typically decrease while duration may increase and a greater range of landscape features must be considered such as water volume and flow, dilution, composition/land cover of the watershed, the dynamics of chemical fate. For example, as one moves from wetlands to ponds to lakes, depth and flow typically increase while the percentage of the watershed in agricultural production typically declines. In the case of spray drift as one moves to progressively larger water bodies the chance for even and high level spray drift entry in more than a few waterbody margins tends to decrease.

3.5.1.3. The Agricultural Landscape:

Figure 3-6 represents the factors in the Agricultural Landscape that need to be included in detailed assessments of aquatic exposure arising from pesticide use. For example, the percentage of the crop of interest in the watershed, the proximity of that crop to the water itself, the percentage of the crop that is treated and the spatial relationship of the crop and water body are all critical determinants of the potential exposure. Many of these factors are discussed in more detail in the example of a Landscape Analysis given in section 3.7.5.5. **A fundamental cornerstone of the analysis of the probability of aquatic exposure is that risk factors must co-occur in time and space to contribute to overall potential exposure**.

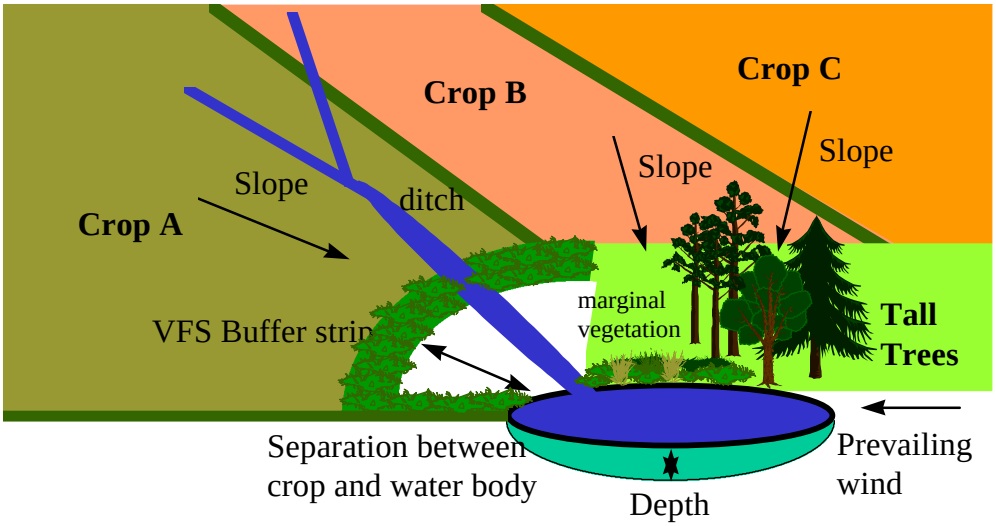


Figure3-6: Conceptual factors important to understand the interaction between agriculture and water GRAPHIC TO BE REPLACED

3.5.2. Fate and Transport of Agricultural Chemicals in the Field

This section examines the important factors that influence the fate and transport of the pesticides in the field prior to entry into Aquatic systems. The fate of a pesticide applied in the environment is governed by the complex interactions of numerous factors (Table 3-3), including:

- physicochemical characteristics of the pesticide
- hydrologic factors
- climatic parameters that affect the timing and volumes of runoff and leaching transport water
- management practices related to the production of the crop
- management practices related to the use of the pesticide product

The effects of these factors are combined in mathematical models to estimate field scale pesticide losses due to spray drift, drainage and erosion from treated agricultural fields.

Table 3-3: Processes Incorporated in Current Models

Processes	**Tier 1: GENEEC**	**Tier 2: PRZM/EXAMS**	**Tier 3: MUSCRAT**	**Tier 4: Modeling**
Infiltration	no	yes	yes	yes
Evapotranspiration	no	yes	yes	yes
Soil Moisture Content	no	yes	yes	yes
Surface Runoff	no	yes	yes	yes

Processes	Tier 1: GENEEC	Tier 2: PRZM/EXAMS	Tier 3: MUSCRAT	Tier 4: Modeling
Erosion	no	yes	yes	yes
Leaching	no	yes	yes	yes
Subsurface / Tile Drainage	no	no	yes	yes
Spray Drift	yes	yes	yes	yes
Canopy Development / Washoff	no	yes	yes	yes
Volatilization	no	yes	yes	yes
Effective Depth Of Mixing Zone	no	yes	yes	yes
Rill Flow And Erosion	no	no	no	no
Time Step Shorter Than One Day	no	no	no	no
Time-Variant Pesticide Properties	no	yes	yes	yes
Depth-Variant Pesticide Properties	no	yes	yes	yes
Preferential Flow	no	no	no	no
Sediment Enrichment	no	yes*	yes*	yes*

* Constant Enrichment Value Used For All Management Practices

3.5.2.1. Overview of Processes

A schematic diagram of the major processes involved in environmental fate modeling is shown in Figure 3-7. Each spatial compartment in the soil profile has specific processes which combine to represent the overall environmental fate of the pesticide in soil. The hydrologic response of soil to water inputs (precipitation and/or irrigation) is a function of both time-variant and time-invariant factors which combine to determine the timing and volumes of runoff, evapotranspiration, percolation and change in water storage in the soil profile. The transport of pesticides in soil is a function of pesticide application parameters, washoff from crop canopies, degradation kinetics, sorption and dispersion. The availability of pesticide for runoff and erosion is primarily controlled by sorption and distribution in the soil surface ("mixing zone") while pesticide leaching is determined primarily by a combination of degradation rate, sorption and dispersion.

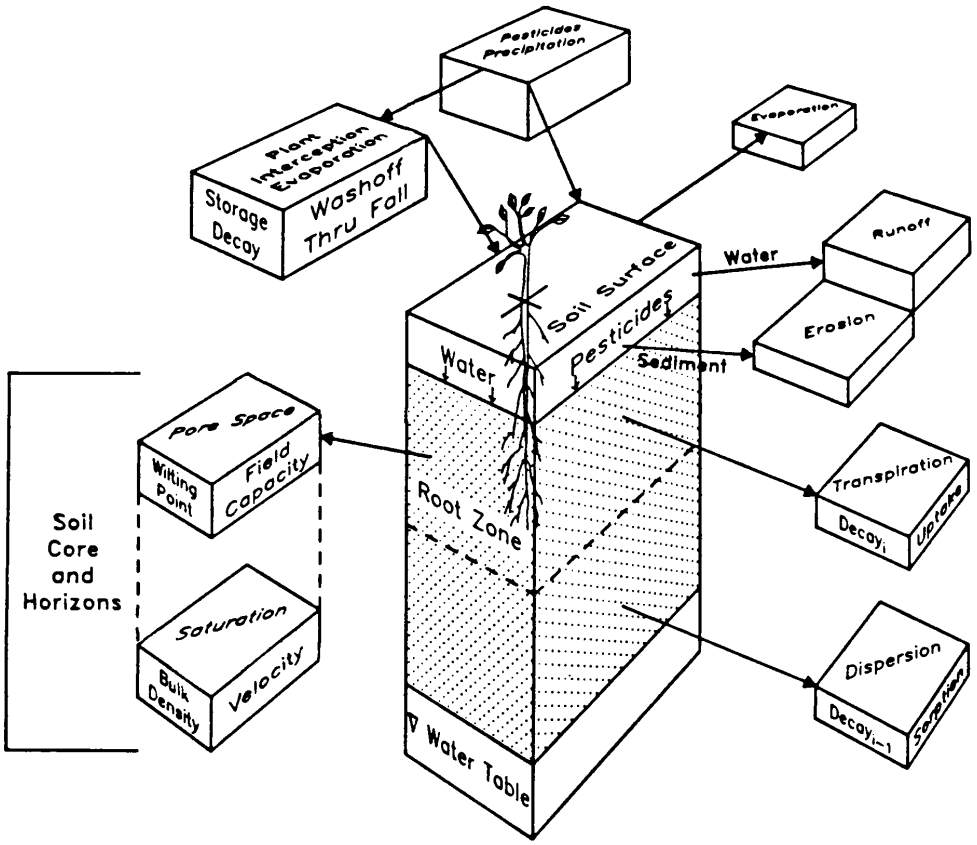


Figure 2-7: Schematic of key processes operating to influence pesticide transport behavior in the field

3.5.2.2. Key Factors

In modeling the fate and transport of a pesticide, the dominant processes are:

- **Sorption**

  The degree of interaction between the pesticide and the soil is primarily determined by the adsorption properties of the pesticide and the composition of the soil, primarily the organic matter and clay contents.

- **Dissipation**

  The rate of dissipation of the pesticide is a function of both its overall transformation rate due to microbial degradation, hydrolysis and photolysis as well as loss mechanisms such as volatilization, runoff, erosion and leaching.

- **Hydrology**

  The hydrologic response of a field to precipitation/irrigation is a complex function of soil characteristics, cropping parameters, tillage practices and time-variant factors such as antecedent moisture content.

- **Management Practices**

  In-field management practices include the pesticide use pattern (e.g rate, method and timing of application) and cropping, tillage and conservation practices. Off-site management practices include vegetative filter/buffer strips and constructed/ reconstructed wetlands.

A complete listing of the various factors that are typically involved in estimating the environmental fate of pesticides WITHIN THE FIELD is presented in Table 3-4.

Table 3-4: Analysis of Factors Involved in Estimating Edge-of-Field Chemical Runoff and Erosion from Treated Agricultural Fields

	Tier 1: GENEEC	Tier 2: PRZM/EXAMS	Tier 3: MUSCRAT	Tier 4:
Chemical Factors				
Chemical / Physical				
Molecular Weight	no	yes (for metabolites)	yes (for metabolites)	yes (for metabolites)
Solubility	yes	yes	yes	yes
Pka	no	yes	yes	yes
Vapor Pressure	no	yes	yes	yes
Mobility				
K_D	yes	yes	yes	yes
Transformation				
Hydrolysis half-life	yes	yes	yes	yes
Aqueous Photolysis half-life	yes	yes	yes	yes
Soil Photolysis half-life	no	yes	yes	yes
Aerobic Soil Degradation half-life	yes	yes	yes	yes
Anaerobic Soil Degradation half-life	no	yes (as a limit)	yes (as a limit)	yes (as a limit)
Field Soil Degradation half-life	yes	yes	yes	yes
Canopy Volatilization half-life	no	yes	yes	yes
Canopy Degradation Half-Life	no	yes	yes	yes
Canopy Washoff Rate	no	yes	yes	yes
Hydrologic Factors				
Soil				
Time-Invariant Factors				
Organic Matter	no	yes	yes	yes
pH	no	yes (indirect)	yes (indirect)	yes (indirect)
texture	no	yes (indirect)	yes (indirect)	yes (indirect)
hydrologic group	no	yes	yes	yes
field capacity	no	yes	yes	yes
wilt point				
Time-Variant Factors				

	Tier 1: GENEEC	Tier 2: PRZM/EXAMS	Tier 3: MUSCRAT	Tier 4:
Bulk Density / Compaction	no	yes / no	yes / no	yes / no
Surface Sealing / Infiltration	no	no	no	no
Landscape				
Field Slope And Length	no	yes	yes	yes
Structure Of Complex Slopes	no	no	no	no
Distribution/Fraction Of Treated Fields	no	no	no	yes
Distribution/Composition Of Untreated Area	no	no	no	yes
Climatic Parameters				
Precipitation	no	yes	yes	yes
Air Temperature	no	yes	yes	yes
Relative Humidity	no	yes	yes	yes
Wind Speed	no	yes	yes	yes
Solar Radiation	no	yes	yes	yes
Management Practice				
In-field				
Crop Type	yes	yes	yes	yes
Rotational Pattern	no	no	no	yes
Tillage Practices	no	yes	yes	yes
Terraces	no	yes	yes	yes
Contouring	no	yes	yes	yes
Application				
Method	no	yes	yes	yes
Incorporation Depth	yes	yes	yes	yes
Rate	yes	yes	yes	yes
Timing	no	yes	yes	yes
Formulation	no	no	no	yes?
Spray Drift Control	no	yes (external)	yes (external)	???
Irrigation	no	no	no	???
Subsurface Drainage	no	no	no	???
Off-Site				
Constructed Wetlands	no	no	no	???
Vegetated Filter/Buffer Strips	no	no	no	???

3.5.2.3. Relative Ranking of Factors

In most modeling of edge-of-field runoff and erosion, there are two sets of important factors: hydrologic factors and transport factors. The hydrologic response of a specific site is an integration of the characteristics of crop, soil and landscape combined with the effects of climate. The potential movement of pesticide residues from a treated field to adjacent surface water bodies is a function of the driving forces of runoff and erosion as well as spray drift during application. In general, surface water impacts from pesticide use are greatest when a high proportion of the landscape is in agricultural production, a high proportion of this acreage is chemically treated, the soil has a relatively low infiltration rate, the landscape is sloping, surface water is immediately adjacent to treated land and the surface water has a low flow rate.

Fortunately, this combination of factors does not occur frequently. Areas which have intensive crop production typically involve low to moderate slopes. More steeply sloping lands are generally managed to help control soil losses through use of terraces, contouring and conservation tillage or are placed in conservation reserve programs. Locations with a high proportion of moderately to steeply sloping land are generally drained by numerous small streams with relatively rapid flow rates. Finally, most agricultural fields have some type of natural or created filter strips between the edge of the field and adjacent surface water. As a result of these natural attenuation factors, the calculation of potential aquatic exposures resulting from field scale runoff, erosion and drift directly entering a quiescent water body represents a conservative estimate of the pesticide residues typically detected in surface water monitoring studies.

Numerous evaluations of the relative significance of specific combinations of pesticide and environmental parameters have been published (e.g. FEMVTF, 1999 and Fontaine et al., 1992). ANY MORE WE WANT TO INCLUDE

3.5.2.4. Subsurface flow and Drainage influence Hydrology and Pesticide Aquatic Concentrations

Pesticide mass loading of surface water resources takes place via a combination of chemical dissolved in runoff water as well as that adsorbed to sediment transported in overland flow, as well as that present in water leaching from the bottom of the root zone and that returning to the surface through either base flow or artificial subsurface drainage. Transport via leaching is highly attenuated by adsorption by soil, sub-soil, and aquifer materials; and by other physical, chemical, and biological processes that can take place in the time it takes to reach the point of surface discharge. As such, attenuation is dependent on the properties of both pesticide and earthen materials; on the proximity of the treated field to the surface water resource and the existence, or lack thereof, of artificial subsurface drainage; and the climatic conditions which determine the volume and timing of subsurface flow. In areas where subsurface drainage is needed and used, volumes of subsurface flow and surface runoff can be similar.

Although pesticides are sometimes detected in base flow and subsurface drainage, they are usually products with more extensive use; at most, moderate adsorption, and longer persistence, such as atrazine. However, even for those products,

concentrations in leaching water from treated fields, when quantifiable, are usually in the ppb or sub-ppb range, as contrasted to concentrations in surface runoff water which can exceed 1 ppm (1000 ppb) in runoff from a treated field shortly after application. When annual losses are calculated, surface runoff losses of products such as atrazine are usually in the 1 to 5% of applied range, whereas that lost with leaching water is often ten to one hundred times less, usually being less than 0.1% of that applied.

Numerous investigators have assessed pesticides in tile drain effluent. Recent investigations by Soenksen (1996) and Fenelon and Moore (1998) assessed nutrients and pesticides in tile drain effluent and flow and transport processes. Soenksen (1996) determined atrazine transport losses for three types of runoff ranged from 0.3 to 20 percent of atrazine applied and 0.1 to 2.9 percent of metolachlor. Specifically for tile drains, 0.3 percent atrazine and metolachlor loss rates were noted in a small watershed near Ames Iowa. Fenelon and Moore (1998) found atrazine concentrations increased from trace levels to more than 20 micrograms per liter in tile drain effluent in a small central Indiana watershed. Increases in atrazine concentrations in surface water are correlated with increased atrazine concentrations and discharge of tile drain effluent. Tile drains were shown to be important pathways for migration of pesticides and nutrients from agricultural lands to surface water.

3.5.3. Fate and Behavior in Water Bodies

3.5.3.1. Aquatic Exposure Conceptual Process

Figure 3-8 depicts exposure of aquatic ecosystems to pesticides, using the ecological circuit language of H. T. Odum (1983). The diagram is not, however, an ecological model *per se*; it is rather a model of pesticide transport, fate, and exposure pathways. Thus, for example, the “phytoplankton” block in Figure 3-8 represents *pesticide* in the phytoplankton rather than the ecology of the plant community itself; the arrows represent metabolism of the pesticide (arrow to ground) and transfers between the phytoplankton and other elements of the ecosystem. The building blocks used for this diagram are defined in Figure 3-9. In the conceptual model itself (Figure 3-8) double-headed arrows and “control action” blocks are used to depict exchange processes; irreversible transfer pathways are shown as uni-directional arrows and control blocks. The arrows to ground represent transformation processes; the “tank” and ecological community symbols represent storage compartments.

Figure 3-8.

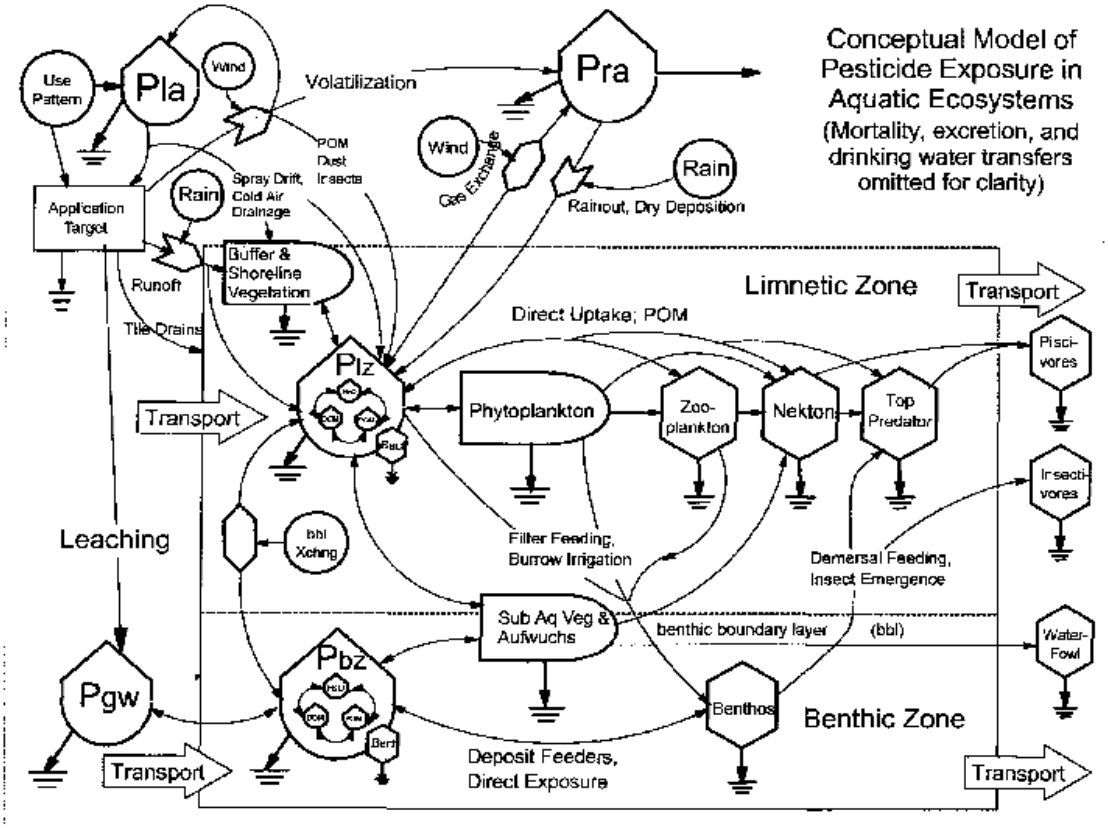
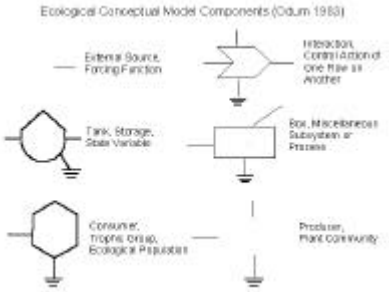


Figure 3-9.



The intended use pattern of the pesticide determines its initial environmental distribution, whether it be used for agricultural, industrial, residential, forestry, or public health purposes. Pesticides migrate away from their immediate target by drift of spray material during application, followed by evaporation, wind erosion of contaminated particles, and by seepage into the groundwater. Pesticides move to natural water courses via groundwater discharges and surface runoff, and once in the regional atmosphere are redeposited by dry fall and with rain. Pesticide in the local atmosphere (Pla), the regional atmosphere (Pra), and in ground water (Pgw) are depicted as state variables in this diagram; aquatic system analysis and simulation can be conducted either by describing their dynamics to the aquatic model (as is the current practice), or by a full-scale multi-media model.

Upon reaching aquatic ecosystems, pesticides have a variable lifetime, depending on the speed of transport and transformation processes in that system. The model is structured to represent both lotic (flowing rivers and streams) and lentic (ponds, reservoirs, lakes) ecosystems, although spatial detail (both vertical, as from thermal stratification, and

horizontal, as in depth zonation) has been omitted for clarity. The fundamental division between the limnetic zone (and its pesticide content, Plz) and the benthic zone (Pbz) is, however, retained.

Uncontaminated water, solid materials, including sediments (sand, silt, clay) and organic detritus, here summarized as "POM" (particulate organic matter), and "dissolved" organic matter (DOM, or its functional equivalent, "dissolved organic carbon" (DOC)) enter the system (at the left border in the diagram) through hydraulics and via "bed-load" transport in the benthic zone. Once in the system, they act as diluent and as a medium for subsequent removal from the system, depicted here as the transport arrows on the right-hand border representing down-stream flows leaving the system. If sufficient sediments enter the system, longer term removal may take place by burial below the active benthic zone; the benthic zone transport arrow thus representing both down-stream bed-load transport and burial.

Sorption processes maintain a dynamic quasi-equilibrium among pesticide dissolved in the aqueous phase (the bulk phase of the water column; the pore water of benthic sediments), that complexed with DOM, and that sorbed to the sands, silts, and clays of the abiotic particulate fraction (POM, which includes much material ultimately of organic origin). Exchange of pesticide across the benthic boundary layer (bbl) is a complex phenomenon driven by physical (turbulent momentum transfer, groundwater discharge), chemical (sorption from the water column to surficial sediment layers), and biological (disturbance by demersal and benthic organisms) processes. A substantial literature exists describing individual components of this exchange, including sediment deposition and resuspension in turbulent flows, sediment "bursting" in response to momentum transfer, biological disturbance and irrigation of sediments, and clearance of particulate matter from the water column by filter feeding organisms. Because of its inherent complexity, the models in use today use an empirical "mass transfer" or "dispersion coefficient" approach, either alone or in combination with a more physical or biological description of some contributing elements of the exchange process.

Transformation processes in both the water column and the benthic zone break down the parent material, usually resulting in the elimination of toxicity. These are summarized in the Figure with the uni-directional arrows to the dissipative ground symbol. Metabolism processes of the plankton, nekton, and benthos are seldom of significance to an exposure analysis – if only because of the relatively slight mass of pesticide in these components of the system – although metabolic detoxification is often important in effects evaluations.

Purely chemical processes are represented here as dissipation from the bulk phases of the system (Plz and Pbz), with the proviso that sorption has profound effects on reactivity. Chemical transformation is sometimes crudely represented in general water-quality models as a time- and space-invariant "first-order" process. Models specifically designed for pesticide studies make use of process-based mechanistic models of aquatic photochemistry, hydrolysis, and oxidation/reduction which ally chemical with limnological knowledge to tailor the behavior of the pesticide to its climatological, hydrologic, and water quality setting.

The biological dissipation of pesticides by the bacterioplankton and the benthic microbial community are depicted separately, in intimate contact with bulk-phase pesticide. Despite detailed laboratory studies of the fundamental enzymatic kinetics and metabolic responses of bacteria to pesticides, this, perhaps the most important dissipative process in aquatic ecosystems, remains one of the least understood. The fundamental Michaelis-Menten-Monod models of bacterial enzyme kinetics and growth, under the condition of trace-level contamination typical of pesticide problems, simplify to a "second-order" model in which transformation flux is dependent on the availability of pesticide and the size of the degrader populations. The latter factor is known in only the coarsest detail, however, so empirical "first-order" models derived from laboratory tests are often used to approximate biolytic dissipation of pesticides in the aquatic milieu.

In competition with the dissolved and particulate non-living matter in the system, organisms absorb pesticides from the aqueous medium; herbicides may have a direct impact on phytoplankton and rooted aquatic macrophytes. Hydrophobic compounds can be sequestered in benthic sediments and can contaminate both the planktonic and benthic food chains. Benthic organisms are also exposed to contaminants in the water column by burrow irrigation and, in the case of filter-feeding mollusks, by direct ingestion of food items. Piscivores—which may include birds such as kingfishers, herons, and eagles, as well as mammals from mink to man—feed on the nektonic fishes and the game fish often found as top carnivores. During insect emergence, pesticide is transferred from the benthic zone to predatory fishes, and to insectivorous birds, including many passerines. Waterfowl (e.g., swans, geese, dabbling ducks) are exposed to pesticides contaminating the aquatic vegetation and associated sediments.

3.5.3.2. Key Factors

Modeling pesticide behavior in aquatic systems requires attention to key issues analogous to the key factors of the "within field" environments (section 3.5.2. above)

- **Sorption**

  Association of pesticide with abiotic materials has profound effects on both transport and fate. Complexation with DOC can facilitate transport, e.g., through the bed to contaminate alluvial aquifers. Sorption to suspended and bed sands, silts, and clays removes pesticides from reactive sites of transformation processes, and can result in protracted contamination of the benthic zone.

- **Dissipation**

  Aquatic transformations include bacterial biolysis, photochemical processes, hydrolysis, eukaryotic metabolism, and water-borne export and volatilization.

- **Hydrology**

  The hydrology of a water system develops from a prolonged interaction of landscape, climate, and bio-geography. Regular seasonal changes in discharge volumes and water quality often have profound effects on ecological processes and pesticide persistence.

Factors most often considered in estimating the aquatic fate of pesticides are listed in Table 3-5 below.

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Table 3-5: Analysis of Factors Involved in Estimating Chemical Exposure in Aquatic Ecosystems

Processes and Parameters	**Tier 1: GENEEC**	**Tier 2: PRZM/EXAMS**	**Tier 3: MUSCRAT**
Chemical Factors			
Chemical / Physical			
Molecular Weight	no	yes	yes
Solubility	yes	yes	yes
pKa	no	yes	yes
Vapor Pressure	no	yes	yes
Henry's Law constant		yes	yes
Mobility			
Kow		yes	yes
Koc	yes	yes	yes
Kd		yes	yes
Bioconcentration Factor		yes	yes
Transformation Process Kinetics			
Hydrolysis	yes	yes	yes
Direct Photolysis	yes	yes	yes
Indirect Photolysis	no	yes	yes
Bacterioplankton Biolysis	yes	yes	yes
Benthic Microbial Biolysis	no	yes	yes
Oxidation/Reduction	no	yes	yes
Product Yields	no	yes	yes
Hydrologic Factors			
Water Quality Parameters			
Time-Varying Chemical Factors			
Sediment Organic Content	no	yes	yes
pH, pOH	no	yes	yes
Dissolved Oxygen	no	yes	yes
Dissolved Organic Carbon	no	yes	yes
Ion Exchange Capacity	no	yes	yes
Reducing Agents	no	yes	yes
Time-Varying Biological Factors			
Bacterioplankton Population	no	yes	yes
Benthic Bacteria Population	no	yes	yes
Benthic Biomass	no	yes	yes
Chlorophyll & Pheophytins	no	yes	yes
Plankton Biomass	no	yes	yes
Macrophyte & Aufwuchs Biomass	no	no	no
Hydrography			
Plan Area/Shape	yes/no	yes	yes
Volume	yes	yes	yes
Depth	yes	yes	yes
Stream Width	no	yes	yes

Processes and Parameters	**Tier 1: GENEEC**	**Tier 2: PRZM/EXAMS**	**Tier 3: MUSCRAT**
Stream Length	no	yes	yes
Stream Cross-section	no	yes	yes
Stream Velocity/Discharge	no	yes (indirect)	yes (indirect)
Base Flow/Suspended Sediment	no	yes	yes
NPS Flows/Sediment Loads	no	yes	yes
Groundwater Discharge/Recharge	no	yes	yes
Bed Load Transport	no	yes	yes
Bed Armoring	no	no	no
Biotic Structuring of Benthic Zone	no	no	no
Bed Form Evolution/Consolidation	no	no	no
Bed Bulk Density	no	yes	yes
Bed Water Content	no	yes	yes
Bed Slope & Friction	no	no	no
Vertical (thermal) Stratification	no	yes	yes
Horizontal Dispersion	no	yes	yes
Benthic Exchange	yes	yes	yes
Net Sediment Deposition & Burial	no	yes	yes
Reservoir Discharge Schedules	no	no	no
Bank Storage/Alluvial Aquifers	no	no	no
Complex Hydrodynamics/Routing	no	seldom	seldom
Climate & Geography			
Precipitation	no	yes	yes
Evaporation	no	yes	yes
Water Temperature	no	yes	yes
Relative Humidity	no	yes	yes
Wind Speed	no	yes	yes
Solar Radiation	no	yes	yes
Air Mass Type	no	yes	yes
Cloud Cover	no	yes	yes
Stratospheric Ozone	no	yes	yes
Atmospheric Turbidity	no	yes	yes
Latitude	no	yes	yes
Elevation	no	yes	yes

3.5.3.3. Relative Ranking of Factors

The importance of the factors is very strongly system-dependent, and the dependence varies with the physico-chemical properties of the pesticide. In general, strongly sorbed chemicals tend to be captured in the benthic subsystem, where they are shielded from photochemical processes and significantly protected from biolysis and alkaline hydrolysis. Dissipation may then be largely dependent on bed transport and burial, or on slow anaerobic biodegradation. Volatilization, for any individual compound, will be both more rapid and more effective in dissipating pesticides from flowing waters than in

lentic ecosystems. In less turbid waters, photochemistry can dominate dissipation, both by direct transformation of pesticides and by (indirect) reaction with singlet oxygen and photochemically generated peroxy radicals.

The more soluble compounds are thus usually the more easily dissipated, at least in the sense that they are removed from the immediate locality of the contaminant source. This can be a mixed blessing, as hydrologic transport then acts to spread the contamination far beyond the original site, perhaps converting (or combining) an intensive acute exposure to an extensive chronic exposure, as with the Spring flush of corn herbicides from the Mississippi basin to the Gulf of Mexico. The probability of degradation or dilution below toxicologically significant levels is least likely for the very strongly sorbed chemicals, especially those with hydrophobic sorption mechanisms, as they tend to contaminate benthic systems over long periods, and tend to accumulate in the lipid of living organisms as well.

3.5.4. How the Agricultural Landscape Influences Potential Aquatic Exposure

3.5.4.1. Overview:

This section considers the impacts that "real world" agricultural practices, topography and spatial relationships between water bodies and agriculture can have on the potential exposure of aquatic bodies to agricultural chemicals. A practical example of the application of these factors is given later (section 3.7.5.5). Figures 3-25, 3-26 and 3-27 provide relevant examples of some of the issues that need to be considered. In the current state of aquatic exposure modeling, many of these factors are ignored in designing scenarios and thus become additional "safety factors" making conventional Tier 2/3 estimates more conservative.

There is no reason why key "landscape variables" should not be incorporated in basic scenarios used for Tier 3 models since they can have a very substantial effect on the expected concentrations. For example, in early efforts to address surface water concentration prediction, EPA found it necessary to incorporate estimates of the extent of the crop of interest present in a watershed to obtain realistic but conservative estimates of exposure.

3.5.4.2. Key Landscape Factors

Table 3-6 depicts key factors for consideration. The workgroup divided these into general "classes" and then further evaluated each factor in terms of whether is should be considered at all levels or only in intermediate (designated "mid" in table) and/or at the most sophisticated (designated "high" in table) tiering levels. The considerations here involved the current and ready availability of relevant data and the potential ease of building these parameters into the model scenarios. It can be seen that there are a wide range of identified factors that the workgroup believed could and should be incorporated into the more standard modeling scenarios. Perhaps paramount among these is regional information on the ratios between land and water areas, the likely area of the scenario watershed expected to be cropped to the crop of interest and the proportion of that crop likely to be receiving any or all of the maximum permitted number of applications in a

season. Table 3-6 also seeks to list the expected uncertainty around estimating any of these factors and their relative importance. In addition, some comments are added where relevant to help explain the significance of the item.

The ECOFRAM Aquatic Exposure Workgroup recommends that researchers looking to improve the quality of aquatic exposure estimation should consider each of these factors carefully and consider whether each can be incorporated on an as needed basis. More importantly, several of these factors should be taken and built directly into the existing Tier I and Tier 2 scenarios sets and, where needed, steps must be taken to ensure necessary data is gathered at a suitable resolution (for example, the use of given pesticides by crop by region)

Table 3-6: List of key factors associated with the agricultural landscape that may influence the fate of pesticides and their transport to aquatic bodies

Class	Factors/Issues	Tier	Uncertainty	Importance	Comments
Physical	Land area	All	L	L	
	Land area/water area	All	H	H	Regional, ,varies by water body type
	Basin Scale	Mid/High	L	M	Has impact on model parameterization
	Basin Geometry	High	H	M	impacts travel time, peak flow and sedimentation
	Range of distances from treated land to water	High	M	H	Different for Drift and runoff entry
	Homogeneity of soil textures	Mid	M	L/H	Only matters if big discontinuity
	Homogeneity of soil OM%, pH etc etc	Mid	M	L/H	Only matters if big discontinuity
	Range of slopes	High	H	M	Too site specific for easy application but generic issue should be accounted for
	Uniformity of slopes within watershed	High	H	H	Too site specific for easy application but generic issue should be accounted for
	Complexity of slopes and related depressions within fields (micro-relief)	High	H	H	Too site specific for easy application but generic issue should be accounted for
	Presence of ditches or rills to transport runoff	High	M/H	H	Can be key route, MITIGATION potential
	Complexity of drainage network [if scale medium to large]	Mid	L	M	Model complexity issue
Agronomic	Area in agriculture, urban development etc.	All	M/L	H	Can be incorporated into generic scenarios
	Area in crop of interest	All	M/L	H	Can be incorporated into generic scenarios
	Ag area/water area	Mid	H	H	Requires remote sensing or crop rot assumptions
	Crop area/water area	Mid	H	H	Requires remote sensing or crop rot assumptions
	Presence and width of Buffers	High	H	H	Requires remote sensing or crop rot assumptions
	Composition of buffers	High	M	H	Grass or trees will mitigate drift and runoff differently
	Requirement for & width of set backs	High	L	M	
	Extent of “pesticide of interest" usage	All	L/H	H	Can be incorporated into generic scenarios
	Use of same pesticide for other use patterns (e.g. urban	All/FQPA	L/H	M/H	A risk cup issue

Class	Factors/Issues	Tier	Uncertainty	Importance	Comments
	lawns)				
	Adoption of conservation tillage practices	High	H	M/H	Difficult to quantify
	Presence of "engineering controls" (e.g. terracing)	High	H	M/H	Easier to quantify
	Extent of channelization in rills and waterbody entry points	High	H	M	Very difficult to get information unless evaluation is field specific
	Presence of tile drainage	High	H	??	????? depends on water body importance??
	Irrigation Method	High	M	M	May influence leaching and hence return flow
	Relative spatial positioning of crop and water body (e.g. relative to wind)	High	M	H	
	Crop vigor and density	High	M	M	
	Crop planting date & growth rate	All	M	M	
Water body	Area	Mid/High	M	H	Many of these focus in on issue of what are we trying to protect??
	Depth	High	H	H	Raises many worrying issues such as mixing, sedimentation, stratification, refugia, organism behavior
	Volume	Mid	M	H	The real variable associated with area/depth
	Shape	High	M	M	Can affect impact of drift and runoff
	Flow in/out (controls)	High	M	M	should be a modeling issue - we need to account for wash-through and finite system volume
	Return flow	Mid	H	L	same issue as tiles drainage - probably only matters for the most sensitive resources
	Bank Storage	High	M	L	Probably more of a human impact/DW issue
	No of RO entry points	Mid/High	M	H	Can be critical opposite loading and whether RO comes from same or different sources
	Representativeness within region	All	H	H	CRITICAL for risk assessment
	Marginal vegetation	High	H	M	Can strongly influence drift
	Natural or man-made pond, lake or reservoir	All	M	L/H	Depends on how we judge significance

Class	Factors/Issues	Tier	Uncertainty	Importance	Comments
	Self sustaining or manipulated (catfish pond)	High	L	M	Depends on how we judge significance
	Range of species represented	Mid	M	H	Should be incorporated into basic tiers structure
	Stream order/pond class	Mid	M	L/H	Should be incorporated into basic tiers structure
	Tile drainage entry??	High	H	L	See return flow
Weather	Prevailing wind direction and speed	High	L	H	Key for drift entry
	Range of wind speeds and directions	Mid	M	M	
	Storm frequency	High	L	H	Key for runoff entry - can be regionalized
	Storm intensity	All/mid	M	H	To some extent, this is already incorporated in PRZM 3
	Storm hyetograph (typical hydrograph)	All/mid	M	H	As above
	Temperature change with time				Affects snow melt, degradation kinetics
Spatial factors	Relative positioning of crop of interest and water body	Mid/High	M	L/H	Requires RS, key for drift - maybe needs to be built into standard scenario
	Do all entries deliver from treated areas?	High	H	M	A scaling issue???
	Extent of differences between regions	Mid/High	H	M/H	Tiering and Probabilistic issues
Model	Suitability of watershed/waterbody for existing models (SWAT, SWRRB or HSPF)	All	H	H	Model selection first or scenario selection??
General	What is the water system we are trying to protect	All	!!!!!	H	Key issue to establish in problem formulation
	Define the assessment endpoints carefully before selecting final scenario for waterbody type	All	H	H	Requires input from risk managers
	Presence of other contamination sources (mixer loader points, agricultural drainage wells…)	???	M/H	M/H	Depends if we are doing monitoring or using monitoring data??
	Look for validation information	All	H	H	Depends if we are doing monitoring or using monitoring data??

Class	Factors/Issues	Tier	Uncertainty	Importance	Comments
	Societal value attributed to water bodies	All		H	Requires consideration by risk managers
	Acceptability of temporal changes	All		H	Requires consideration by risk managers
	Extent to which water bodies are challenged by alternative stressors	All		H	Requires consideration by risk managers

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3.6. General Findings of ECOFRAM Aquatic Exposure Workgroup

This section concentrates on some of the findings of the workgroup in addition to the main work which focussed on the development of an improved tiering process. Amongst the areas the group agreed were important were:

- Ensuring that the data generated on Pesticide Environmental Fate and Properties under FIFRA is applicable for risk assessment and optimized for exposure simulation modeling.
- Simplifying the reporting of FIFRA pesticide Environmental Fate and Properties data
- Clarifying methods for calculating values with significance for exposure assessment modeling (e.g. laboratory soil aerobic half lives) from study data
- Starting to prepare a list of recommended Geographic and Environmental data sources of potential value for exposure modeling and spatial risk assessments
- Providing clear guidance on reporting environmental fate and exposure simulation modeling study results
- Providing guidance on how best to express aquatic exposure estimates
- Providing guidance to help clarify the roles of monitoring and modeling

3.6.1. Chemical Data Generation for Exposure Estimation

3.6.1.1. Submitted Regulatory Studies under FIFRA Part 158

Table 3-7 provides a list of some of the required studies that are either required or conditionally required under FIFRA Part 158. The listed guidelines are judged by the ECOFRAM Aquatic group as generating data of potential value for modeling aquatic exposure. The table includes the guideline number, study title, the useful parameter measured, an indication of whether the study is frequently required and, finally, whether the ECOFRAM group is proposing a change.

THIS TABLE STILL NEEDS CHECKING FOR ACCURACY OF GUIDELINE NUMBERS AND FILLING IN ANY MISSING ONES - ANY CHANCE YOU CAN HANDLE THIS PLEASE MARI??

Table 3-7: List of Studies currently required or conditionally required to establish the environmental fate and transport properties of pesticides

Old Guide-line No.	New Guide-line No.	Study Name	Potential value	Comments	Often Done	To be Changed ?
63-5		Melting Point	Temperature dependence of volatility??	Easy to do	Yes	No
63-6		Boiling Point	Temperature dependence of	Easy to do	Yes	No

Old Guide-line No.	New Guide-line No.	Study Name	Potential value	Comments	Often Done	To be Changed ?
			volatility????			
63-8		Solubility		Solubility value	Yes	No
63-9		Vapor Pressure		Indicator of issues	Yes	No
63-10		Dissociation Constant		Indicator of issues	Yes	No
63-11		Octanol-Water partition Coefficient		Indicator	Yes	No
161-1		Hydrolysis		Input value	Yes	Yes
161-2		Photodegradation in water		Input value	Yes	Yes
161-3		Photodegradation in soil		Indicator of issues	Yes	No
161-4		Photodegradation in air		Experimental problems	No	No
162-1		Aerobic Soil Metabolism		Degradation rate	Yes	Yes
162-2		Anaerobic Soil Metabolism		Degradation rate	No	No
162-3		Anaerobic Aquatic Metabolism		Degradation rate	Yes	Yes
162-4		Aerobic Aquatic Metabolism		Degradation rate	No	Yes
163-1		Soil thin layer chromatography		None	No	No
163-1		Adsorption/desorption		Kd, Koc	Yes	Yes
163-1		Soil Column Aged Leaching		Indicator of problems	Yes	No
163-2		Lab Volatility		??	Yes	No
163-3		Field Volatility		Difficult to perform	No	No
164-1		Soil Field Dissipation		Indicator of problems	Yes	No
164-2		Aquatic Field dissipation		Indicator of problems	No	No
164-3		Forestry Field Dissipation		Indicator of	No	No

Old Guide-line No.	New Guide-line No.	Study Name	Potential value	Comments	Often Done	To be Changed ?
				problems		
164-4		Tank-mix Combination Field Dissipation		Indicator of problems	No	No
164-5		Long Term Dissipation		Few	No	No
166-1		Prospective GW (Draft)		Worst case leaching data	As needed	No
201-1		Droplet Size Spectrum	Drift models	Covered under SDTF	No	SDTF
201-2		Field Spray Drift Evaluation	Drift models	Covered under SDTF	No	SDTF
??		Lab Foliar Washoff	Critical for foliar applied runoff			Yes
??		Lab Foliar Volatilization	Critical for foliar applied runoff			Yes
??		Lab Foliar Degradation	Critical for foliar applied runoff			Yes
??		Aquatic Exposure Modeling Study	Guidance for model conduct	Under way via FEMVTF	Tier 2 & above	New
??		Field Foliar degradation	Critical for foliar applied runoff			New
??		UV-Visible Adsorption Spectrum	Interpreting Quantum yield			Yes
??		Metal complexation constants				New
??		Fate-o-cosm study			Tier 2	New

Old Guide-line No.	New Guide-line No.	Study Name	Potential value	Comments	Often Done	To be Changed ?
??		Large Scale Basin Monitoring study				New
??		Small Scale Simulated Runoff Study	Validation/ comparison			New
??		Plant Uptake study	Mass balance			New
??		Subsoil Degradation and Adsorption/Desorption Studies	Valuable for leaching to GW			New
??		Aquifer Degradation Studies	Valuable for leaching to GW			New

3.6.1.2. Recommended General Improvements to FIFRA Part 158 studies

The Workgroup decided that there were some relatively simple changes to existing studies that c**ould potentially benefit simulation modeling.** These suggested changes are enhancements of a list of changes produced in May 1993 by Henry Nelson (US EPA OPP) as an output from the FIFRA Exposure Modeling Workgroup. Nelson , 1993). The ECOFRAM Aquatic Exposure Workgroup believes that these changes can be made without hindering the original purpose of the regulations, which was to provide data for the qualitative fate and transport assessment of each pesticide, and in some cases will substantially improve it. The Workgroup is recommending the following actions related to the generation of FIFRA data useful for modeling:

1) The Subpart N process needs to be re-examined in detail by OPP EFED and subsequently modified so that they appropriately support the proposed ECOFRAM recommended risk assessment process. Guidance needs to be provided so that registrants can easily identify the most appropriate number and kinds of data of data appropriate for the complexity of the Aquatic, Human or Terrestrial Risk Assessments needed to support the registration of their pesticides.
2) When the studies in subpart N are revised, the group strongly recommends that each study be prefaced by a clear section describing the OBJECTIVE of the study, the PURPOSE for which the resulting data will be used and appropriate information on how the magnitude of the study might depend upon the use pattern being examined (e.g. For a minor use crop, only two soils may be required to define laboratory degradation rate while for widespread use on corn, studies on upwards of four soils may be required). These introductions should clearly explain the possible

implications to the uncertainties associated with a risk assessment if the registrants supply a greater or fewer number of studies.

3) A mechanism needs to be developed to standardize reporting the output of subpart N studies so that a simple table of recommended modeling values is submitted (with cross-references to relevant submitted studies or memoranda) with justifications and information on the variability/ranges associated with each measurement. This reporting mechanism (see section 3.6.4) should ideally provide an electronic file suitable for transferring data directly into model input shells, etc.

4) Registrants must understand that if they believe their compound is dissipated as a result of processes not normally accounted for by Subpart 158 studies, it is their responsibility to provide sufficient data to describe the occurrence and quantify the rate of the additional process. In the absence of this information , it is likely that EPA OPP EFED risk assessors will make a conservative assumption in the absence of data. In most cases, this assumption will be that the dissipation process is not occurring.

5) EPA OPP EFED should provide detailed guidance on a required method for calculating rate constants from subpart N studies in order to standardize comparative risk assessments and simplify Agency review of studies. A suggested program (Esterley, 1998) is provided with the files associated with this report.

6) Some aspects of subpart N studies generate potential research needs:

- There is a need for a clearer understanding of the spatial variability associated with field soil degradation and related properties at both the micro and macro spatial scales
- There is a need to better describe the effects of water content, aeration, and microbial activity on chemical degradation in a way which can be routinely parameterized for use in modeling.
- There is a need for a compilation of literature data on the extent to which oxygen and organic carbon are transported to subsoils in infiltrating water and an assessment of how this relates to subsoil degradation.
- Better understanding of the typical “shape” of the distribution of each of the key measured variables should be developed from literature or practical work
- Information is needed on the relative importance of volatilization from leaf surfaces. If this information shows that this can be a significant route of dissipation, a laboratory study will need to be developed that can describe how foliar volatilization occurs. Also, guidance on when to require the study will also need to be developed. Methods to quantify foliar volatilization will also be needed for use in conjunction with guideline field dissipation studies.[1]

3.6.1.2.1.Recommendations to make specific improvements to FIFRA part 158 studies

Appendix 3-6 provides considerable details on the improvements to several studies that the workgroup recommends as minor modifications first proposed by Henry Nelson on behalf of the FIFRA Exposure Modeling Work Group (Nelson, 1993). For information, the topics where we consider that improvements to the study design would improve the quality of aquatic exposure modeling are briefly described below.

1) Obtaining Rate Constants For Degradate Formation And Decline

Objective To provide soil degradate formation and decline data for calculating rate constants suitable for use as input parameters in environmental fate and transport models where it is necessary to model degradate behavior in the environment.

2) Obtaining Hydrolysis Rate Constants As A Function Of Temperature

Objective To enable more precise estimation of hydrolysis rates under a range of environmental conditions when it has been shown that abiotic hydrolysis plays a driving role in determining the fate and transport of a product. Determination of the effects of temperature on hydrolysis are currently not required.

3) Determining Quantum Yields

Objective To improve calculation of direct photochemical transformations so as to allow for changes in the spectral quality of light fields with depth and type of water body. Estimation of quantum yield is currently not required in the current study.

4) Selection Of Multiple Soils For Soil Aerobic Dissipation Studies

Objective To provide sufficient measurements of laboratory soil degradation rate to provide an appropriate estimation of the mean and distribution of the topsoil degradation rate to permit probabilistic modeling of chemical transport. To provide a suitable selection, in both number and range of soils, for characterizing the variability and uncertainty of degradation rates at the sites where the pesticide might be used. Currently, only one aerobic soil metabolism study is required.

5) Enhancing Batch Equilibrium Study Design and Analysis

Objective To ensure that, when needed, adequate data on the magnitude and rate of adsorption and desorption behavior across a range of relevant soils under relevant environmental conditions and to provide information on how to appropriately extrapolate from the measured soils to other soils where the sorption has not been measured with a known level of confidence. Current studies generally do not provide good measures of the rate of adsorption and do not attempt to determine mechanisms of sorption other than some preliminary measures of sorption to soil organic carbon.

6) Conducting Aquatic Metabolism Studies Where Runoff Is Likely To Be Significant

Objective To provide separate measures of the water column aerobic degradation rate and the degradation rate in the benthic layer under anaerobic conditions for inclusion into surface water modeling.. Current studies provide information on mixed sediment-water column systems with a range of redox environments that not optimal for developing model input parameters.

7) Conducting Foliar Dissipation And Washoff Studies For Foliar Pesticides

Objective To provide data to characterize the processes operating on chemical reaching leaves and crop residues on the soil. These processes include degradation and washoff. Foliar processes can in some cases be the dominant route of dissipation for a chemical and thus significantly impact the amount of chemical available for transport during rainstorm events.

Note that this experiment is probably even more important to enhance the understanding of dissipation of residues on the foodstuffs for non-target terrestrial organisms.

8) Focusing Anaerobic Soil Metabolism Studies on Degradation in Subsoil Horizons and Aquifers.

Objective To provide information on degradation processes and rates in subsoils to improve the simulation modeling of pesticides after they have moved below the root zone. The current anaerobic soil metabolism study is focused on degradation processes in flooded surface soils such as would occur during rice culture and does not provide data useful under the redox conditions and biological activities found in subsoils and aquifers. This data is of particular importance for understanding the potential for pesticide to contaminate and persist in ground water, which is not within the purview of ECOFRAM. However, it may impact the nature and extent of chemical residues available for "return flow" to surface waters during periods of low flow, a process that can be considered when basin scale modeling is implemented..

9) Potential Of Uptake from Soil into Plants

Objective To provide details of the "removal" of chemical from the pool of material available for transport processes.

It has more of an impact on the amount of chemical in the root zone available for leaching and on the residues in the plant likely to contribute to the dietary load of non-target terrestrial organisms. However, because it may be an important route of dissipation in some cases, and in order to get the necessary complete information for the validation of improved, unified, models, the ECOFRAM team believes that the Subdivision N guidance should be expanded to provide guidance on how best to conduct these studies..

3.6.2. Recommended Geographic and Environmental Data Sources for Exposure Modeling

During the workgroup's discussions, the group frequently identified needs for either data sets where none currently exists or comprehensive data where the material is either "spottily" distributed throughout the USA or where the data exists but is not accessible in a usable format. The latter is particularly true of Geographic Information System (GIS) data where multiple formats and poor preparation of "meta-data" (the data fully describing the data in the GIS coverage and it's source) frequently result in incompatibility, uncertainty and, sometimes, error. Accordingly, the group prepared a summary table listing relevant datasets with some best estimates of where they may be obtained.

3.6.2.1. Compilation of Useful Data And Sources

The work group prepared a list of current resources of value for exposure assessment along with their current Internet locations. These are provided in the table in Appendix 3-7. In addition, some basic references for frequently updated spatial data are provided.

The workgroup recommends that EPA OPP EFED or ORD (in concert with other interested groups (e.g. ACPA, USDA NRCS, USGS NAWQA, etc)) manages a web page with approved databases and GIS coverages and associated meta-data in order to simplify the review of increasingly complex risk assessments.

Some key data sets deserve particular mention since they are frequently referred to in later sections.

3.6.2.2. ARS Pesticide Properties Database (ARS PPDB).

The ARS Pesticide Properties database (ARS PPDB; www.ars.usda.gov/arsdb.html) is a resource open to all and potentially offers on eof the most efficient places to determine appropriate model input parameters for those outside the EPA or industry. One of the strengths of the system is that is contains a more comprehensive list of variables than traditional references such as Wauchope and (XXXX). However, the system only has value if companies and USDA maintain the database as an up-to-date and effective tool. ECOFRAM recommends that the pesticide industry and USDA jointly support ongoing maintenance of the USDA ARS PPDB. Alternatively an alternative reliable long term repository for data useful for pesticide exposure modeling should be developed and maintained.

ECOFRAM recommends that companies should submit data for the PPDB firstly as soon as a registration is achieved and thereafter as soon as studies are approved by EPA. In the past, there was little benefit to industry to make results of environmental fate studies available to the public; however, in today's world it makes more sense for the company to ensure that accurate and up to date information is available. The use of old or incorrect data for estimating exposure may lead to unacceptable exposure estimations.

3.6.2.3. The EPA "One-Liner" Database

The "EPA one-liner" database is also publicly available (source….XXXXX). It reflects the values selected by EPA reviewers as they inspect pesticide submissions. It is used internally in OPP EFED during the course of evaluating the data submitted on a new active ingredient; however, once a registration has been approved, the information on that product was traditionally added to the publicly accessible portion of the database. One of the strengths of this data is that it provides information on all active ingredients and is somewhat more comprehensive than the ARS PPDB. However, while EPA is reorganizing its database structures and preparatory to the roll out of an improved version of the on-liner, the current version is "frozen" and no new product data is being made available.

ECOFRAM recommends that the EPA issue an up to date version of the one-liner database as soon as possible.

3.6.2.4. Land Resource Regions

management of the soils as reflected in land use patterns. These regions and areas represent nearly homogeneous areas of soil, climate, land use, water resources, elevation, topography, and potential natural vegetation.

3.6.2.4.1.Land Resource Regions

Land resource regions (LRR) are geographically associated groups of major land resource areas and consist mainly of areas that have very broadly related patterns of soil, climate, water resources, and land use. Land resource regions are delineated only on small scale national maps (1:7,500,000; 1:10,000,000; or smaller) and are most useful for national and regional program planning. Land resource regions are unique, continuous delineations, which approximate physiographic regions on small scale national maps.

3.6.2.4.2.Major Land Resource Areas

Major land resource areas (MLRA) are based upon aggregations of geographically associated land resource units and identify nearly homogeneous areas of land use, elevation, topography, climate, water resources, potential natural vegetation, and soils. Major land resource area boundaries reflect an appropriate generalization of land resource unit boundaries (as derived from state soil geographic database map unit boundaries). The approximate minimum size of a major land resource area that may be delineated is 580,644 hectares, or 1,434,803 acres. This minimum delineation is represented at the official major land resource area map scale of 1:7,500,000 by an area approximately 1 cm by 1 cm (0.4 inch by 0.4 inch). Minimum linear delineations are at least 0.3 cm (0.1 inch) in width and 2.5 cm (1 inch) in length. The Pacific and Caribbean Islands, which have land areas less than 580,644 hectares (1,434,803 acres) in size are excluded from the minimum delineation rule. Large existing major land resource areas may be subdivided to create more homogeneous areas as needed, provided that cartographic criteria regarding minimum delineations are met. The descriptions of the map units on major land resource area maps emphasize land use and water resource management. Generally, a major land resource area occupies one continuous delineation; but it may occupy several separate ones. Major land resource areas are most useful for statewide agricultural planning and have value for interstate, regional, and national planning.

3.6.2.4.3.Land Resource Units

Land resource units (LRU) are derived from the aggregation of map units of the state soil geographic (STATSGO) database. This is possible because each state soil geographic database map unit has a major land resource area designation in the state soil geographic database attribute file. The STATSGO-GRASS Interface software is a useful geographic information system tool for generating the first draft of the land resource unit map from a state soil geographic database. Based on a shared 1:250,000 scale, map unit boundaries on land resource unit maps largely coincide with those in the state soil geographic database. Land resource unit maps often depict areas that are cartographically too small to be

delineated on the national major land resource area map at 1:7,500,000 scale. Therefore, land resource units are not shown on the national major land resource area map. Land resource units are shown only on state maps.

3.6.2.4.4.USDA Agriculture Handbook No. 296

USDA Agriculture Handbook No. 296, Land Resource Regions and Major Land Resource Areas of the United States (Soil Survey Staff, 1981), represents an assemblage of information currently available about the land for farming, ranching, forestry, engineering, recreational development, and other uses. This assemblage consists of the land resource region and major land resource area map and the supporting land resource region and major land resource area map unit descriptions. Such land resource information (both analog and digital) is used at National, regional, and State levels:

- as a basis for making decisions about agricultural issues;
- as a framework for organizing and operating resource conservation programs;
- for the geographic organization of research and conservation needs and the data derived from these activities;
- for coordinating technical guides within and between states;
- for organizing, displaying, and using data in physical resource inventories; and
- for aggregating natural resource data.

The boundaries of the major land resource area (MLRA) and land resource regions are included as part of the 1992 Natural Resources Inventory (NRI) Database.

3.6.2.5. Ecoregion and Subregional Frameworks

Ecoregions provide a framework based on the commonalties with the region on ecological systems and relationship between organisms and their environment. There are various detailed characterizations (e.g. Omernik, 1987) but most of them include climate, physiography, geology, soils and vegetation. They offer a regional classification system based on natural phenomena and geography where environmental, climatological and hydrological similarities have combined to produce conditions supportive of a recognizable ecology. This potentially provides a useful classification for risk assessments.

Not only does the national ecoregion mapping provide a system with valuable potential, but increasingly, it appears that US states are classifying their own ecosystems using “ecological sub-regions”. For example, the US EPA Environmental Research Laboratory in Corvallis, OR in cooperation with EPA Region IV and Florida Department of Environmental Protection (FDEP) conducted research on the commonalties with the region on ecological systems and relationship between organisms and their environment. Following Omernik’s (1987) definition with some improvements, the aquatic ecoregions in Florida were grouped in three ecoregions: southeastern plain, southern coastal plain and southern Florida coastal plain. Also, within each ecoregion, sub-regions were defined based on the significant characteristics on landform, potential natural vegetation, land use/land cover, and soils. For additional information, contact the USEPA, Environmental Research Laboratory at (541) 754-4458.

3.6.2.6. Hydrologic Cataloging Units (HUC's)

A Geographic Information Retrieval and Analysis System (GIRAS) was developed in the mid 70s to put into digital form a number of data layers which were of interest to the USGS. One of these data layers was the Hydrologic Units. The map is based on the Hydrologic Unit Maps published by the U.S. Geological Survey Office of Water Data Coordination, together with the list descriptions and name of region, subregion, accounting units, and cataloging unit. The hydrologic units are encoded with an eight- digit number that indicates the hydrologic region (first two digits), hydrologic subregion (second two digits), accounting unit (third two digits), and cataloging unit (fourth two digits). The data produced by GIRAS was originally collected at a scale of 1:250,000. Some areas, notably major cities in the west, were recompiled at a scale of 1:100,000. In order to join the data together and use the data in a geographic information system (GIS) the data were processed in the ARC/INFO GIS software package. Within the GIS, the data were edgematched and the neatline boundaries between maps were removed to create a single data set for the conterminous United States. Purpose: The objectives were to produce maps showing base information and vulnerability to flooding; document the methodology and analysis used to produce them, and identify the ongoing monitoring, research, modeling, data management and distribution requirements needed to support integrated river basin management.

The HUC classification system divides the United States and the Caribbean into 21 major regions, 222 subregions, 352 accounting units, and further subdivided into 2,150 cataloging units that delineate river basins having drainage areas usually greater than 700 square miles

The base-map for hydrologic cataloging units is the "8-digit" HUC described above. However, in many areas, these hydrologic units have been further sub-divided to the "watershed" level (known as the 11-digit HUC definitions) which are essentially uniformly mapped at the 1:100,000 scale. The purpose of this is to provide a uniquely identified and uniform method of subdividing large drainage areas. Typically, 11-digit HUC watersheds range between 40,000 and 250,000 acres and are useful in many programs supported by the NRCS and others. In a few regions, these 11-digit watersheds have been divided into sub-watersheds (the 14-digit HUC). Typically, where it exists, this higher resolution HUC data is available as GIS coverages.

3.6.2.7. Digital Soils Databases

Unlike other parts of the world, the USA is fortunate to have comprehensive soils databases available as a result of government investment through the Soil Conservation Service (SCS) and latterly the National Resources Conservation Service (NRCS). The Natural Resources Conservation Service (NRCS) has the federal responsibility for the National Cooperative Soil Survey (NCSS) and federal leadership for collecting, storing, maintaining, and distributing soils information of privately owned lands in the United States. There is a highly detailed "paper" soils map for most if not all US counties available from the local NRCS offices. In addition the Federal Geographic Data Committee and the Office of Management and Budget have formally assigned the responsibility for national coordination of digital soils data to the NRCS.

NRCS has established three digital soil geographic data bases representing different intensities of soil mapping. Common to each soil geographic (spatial) data base is the linkage to a soil interpretations (attribute) record data base, which gives the proportionate extent of the component soils and their properties for each map unit.

With these digital data bases, users can store, retrieve, analyze, and display soil data in a highly efficient manner, as well as integrate the data with other spatially referenced resource and demographic data in a Geographic Information System (GIS).

The three soil geographic data bases are the Soil Survey Geographic Data Base (SSURGO), the State Soil Geographic Data Base (STATSGO), and the National Soil Geographic Data Base (NATSGO). Components of map units in each geographic data base are generally phases of soil series. Phases of series enable the most precise interpretation. Interpretations are displayed differently for each geographic data base to be consistent with the level of detail mapped. The soil interpretations record data base encompasses more than 25 soil physical and chemical properties for approximately 18,000 soil series recognized in the United States.

Information such as particle size distribution, bulk density, available water capacity, soil reaction, salinity, and organic matter is included for each major layer of the soil profile. Also included are data on flooding, water table, bedrock, subsidence characteristics of the soil, and interpretations for erosion potential, septic tank limitations, engineering, building and recreation development, and cropland, woodland, wildlife habitat, and rangeland management.

SSURGO, the most detailed level of information, is used primarily for farm and ranch conservation planning; range and timber management; and county, township, and watershed resource planning and management. Utilizing the soil attributes, this data also serves as an excellent source to review site development proposals and land use potential, make land use assessments and to identify potential wetland areas.

3.6.2.7.1.SSURGO

Using national mapping standards, soil maps in the SSURGO data base are made by field methods, using observations along soil delineation boundaries and traverses, and determining map unit composition by field transects. Aerial photographs are interpreted and used as the field map base. Maps are made at scales ranging from 1:12,000 to 1:31,680 and incorporated with comprehensive descriptions to produce the NCSS publications.

Digitizing is by line segment (vector) in accordance with NRCS-established digitizing specifications and standards for duplicating the original soil survey map. The mapping bases are normally ortho-photoquads or 7.5 minute topo-quads. Digitizing is done by NRCS or by cooperating state and local governments.

The soil survey geographic database consists of:

- spatial data, such as the digital soil survey map, and
- attribute data, such as the soil survey area map unit record data from the national soil information system and associated source information (metadata).

SSURGO data are collected and archived in 7.5 minute topographic quadrangle units, and distributed as complete coverage for a soil survey area usually consisting of ten or more quadrangle units. The adjoining 7.5 minute units are matched within the survey areas.

3.6.2.7.2.STATSGO

STATSGO is used primarily for river basin, state, and multi-county resource planning, management, and monitoring. Soil maps for STATSGO were made by generalizing the detailed soil survey maps. Where more detailed maps are not available, data on geology, topography, vegetation, and climate were assembled, together with satellite images. Soils of analogous areas are studied, and a determination of the classification and extent of the soils is made.

Map unit composition for STATSGO is determined by transecting or sampling areas on the detailed maps and expanding the data statistically to characterize the whole map unit.

STATSGO was mapped on the U.S. Geological Survey's 1:250,000-scale topographic quadrangle series. Soil boundaries were digitized by line segment (vector) to comply with national guidelines and standards.

The state soil geographic database consists of:

- spatial data, such as the digital soil maps compiled on the 1:250,000 U.S. Geologic Survey base map for an entire state, and
- attribute data, such as the statewide map unit record data from the state subset of the national soil information system.

STATSGO data are archived and distributed as complete coverage for a state. STATSGO data are joined between states.

3.6.2.7.3.NATSGO

NATSGO is used primarily for national, regional, and multi-state resource appraisal, planning, and monitoring, and is under development. It is the most general geographic soils database containing digital data developed nationwide on a scale of 1:7,500,000. The national soil geographic database consists of:

- spatial data, such as the digital major land resource area map, and
- attribute data, including data on map unit components and composition that are derived from the STATSGO file.

3.6.2.8. National Resources Inventory (NRI)

The National Resources Inventory (NRI) is an statistically-based inventory of land cover and use, soil erosion, prime farmland, wetlands, and other natural resource characteristics on non-Federal rural land in the United States. Inventories are conducted at 5-year intervals by the U.S. Department of Agriculture's Natural Resources Conservation Service (NRCS, formerly the Soil Conservation Service (SCS)), to determine the conditions and trends in the use of soil, water, and related resources nationwide and statewide.

The 1992 NRI was the most extensive inventory yet conducted, covering 170 data elements at some 800,000 sample points on the 1.5 billion acres of non-Federal land in the USA – some 75 percent of the Nation's land area. At each sample point, information is available for three years-1982, 1987, and 1992. Data is currently being summarized for 1997. Originated as a means of getting accurate natural resource information to USDA policymakers, the NRI has become useful to a variety of users.

The NRI contains three codes identifying the geographic location of each point by its Major Land Resource Area (MLRA), Hydrologic Unit Code (HUC), and County (represented by five-digit codes). The MLRAs are geographically-associated land resource units, which in turn are geographic areas, usually several thousand acres in extent, characterized by a particular pattern of soils, climate, water resources, and land use. Hydrologic Unit Codes (HUC) consist of eight digits denoting major stream drainage basins as defined and digitized by the U.S. Geological Survey. County five-digit codes are standard FIPS (Federal Information Processing Standards) identifiers in which the first two digits identify the State and the remaining three the individual Counties. With these geographies combined in a GIS and with the Federal lands masked out, the individual regions represent the smallest spatial feature that can be used to locate NRI samples.

NRI data are statistically reliable for national, regional, state, and sub-state analysis. The NRI was scientifically designed and conducted and is based on recognized statistical sampling methods. The data are used in national, state, and local planning, university research, and private sector analysis. They help shape major environmental and land-use decisions, hold considerable potential for contributing to analysis of potential pesticide off-site migration, fate and effects.

National Resource Inventory Data Characteristics

Data collected in the 1982, 1987, and 1992 NRIs provide a basis for analysis of 5-year and 10- year trends in resource conditions. Many data items in the 1992 NRI are consistent with previous inventories. In addition, the NRI is linked to the Natural Resources Conservation Service's (NRCS) extensive Soil Interpretations Records to provide additional soils information. Data elements consistent within the NRI database among the last three (1982, 1987, and 1992) NRIs are:

- Farmstead, urban, and built-up areas;
- Farmstead and field windbreaks;
- Streams less than 1/8 mile wide and water bodies less than 40 acres;
- Type of land ownership;
- Soils information-soil classification, soil properties, and soil interpretations such as prime farmland;
- Land cover/use-cropland, pasture land, rangeland, forest land, barren land, rural land, urban and built-up areas;

  The *cropland* land cover/use category includes areas used for the production of adapted crops for harvest, including row crops, small grain crops, hay crops, nursery crops, orchard crops, and other specialty crops. *Cultivated cropland* includes land identified as being in row or close-grown crops,

summer fallow, aquaculture in crop rotation, hayland or pastureland in a rotation with row or close-grown crops, or horticulture that is double cropped. Also included is "cropland not planted" because of weather conditions, or because the land is in a USDA set-aside or similar short-term program, or because of other short-term circumstances. *Non-cultivated cropland* includes land that is in a permanent hayland or horticultural crop cover; hayland that is managed for the production of forage crops (grasses, legumes) that are machine harvested; horticultural cropland that is used for growing fruit, nut, berry, vineyard, and other bush fruit, and similar crops.

- Cropping history;
- Irrigation-type and source of water;
- Erosion data-wind and water;
- Wetlands-classification of wetlands and deepwater habitats in the U.S. (1982 and 1992 only);
- Conservation practices and treatment needed;
- Potential conversion to cropland;
- Rangeland condition, apparent trend of condition.

New data elements added for the 1992 NRI included:

- Streams greater than 1/8 mile wide and water bodies by kind and size greater than 40 acres;
- Conservation Reserve Program land under contract;
- Type of earth cover-crop, tree, shrub, grass-herbaceous, barren, artificial, water;
- Forest type group;
- Primary and secondary use of land and water;
- Wildlife habitat diversity;
- Irrigation water delivery system;
- Food Security Act (FSA) wetland classification;
- For rangeland areas-range site name and number; woody canopy; noxious weeds;
- concentrated flow, gully, and streambank erosion;
- conservation treatment needed;
- Type of conservation tillage.

3.6.3. Developing Input Parameter Values From Environmental Fate Data.

The findings of the FIFRA Exposure modeling Task Force (FEMVTF) have provided insight that one of the major constraints to the reproducible and effective use of exposure models is inconsistencies in the selection of input parameters or the approaches used to calculate derived data (such as half lives).

3.6.3.1. Selecting Input Parameters

A critical component of simulation modeling for ecological risk assessment is the selection of input parameters used to represent the compound in the model. Obviously, if the parameters selected do not well reflect that character of the pesticide, then the accuracy of the simulation results will be suffer accordingly (in other words, Garbage In, Garbage Out). It has also become apparent that given the same set of environmental fate data, two different modelers will likely select different values to represent the pesticide in the models. For example, given the (hypothetical) set of aerobic soil metabolism half-lives in Table 3-8, one modeler may use the mean value of 32.9 days. A second modeler may decide that the half-life from the Bert soil is an outlier and exclude it from the mean calculation resulting in an input parameter of 17.1 days. A third modeler may use a value of 25 days because that is the value for the Mary silty clay loam which is more similar in texture to the soils for the crop he is modeling. This points out the need for clear guidance how estimate the input parameters from the environmental fate data. In fact, the problem is even more complicated than shown here since it is typically the case that different research groups would report different half-life estimates from the same degradation data sets depending upon what calculation method is locally preferred to estimate the half-life.

Table 3-8. Example aerobic soil metabolism half-lives.

Soil	**pH**	**Organic Carbon Content (%)**	**Half-life (days)**
Bob silt loam	8.1	3.2	17
Mary silty clay loam	6.5	6.4	25
Ralph loamy sand	6.2	1.5	8.5
Diana sandy loam	5.9	0.5	96
Lorraine fine sand	6.8	0.8	18

3.6.3.2. Recommendations for selecting model input values

Providing detailed guidance on how to estimate different input parameters is beyond the scope of this document. The workgroup has provided guidance on the general principals that need to considered in developing the methods for estimating each input parameter.

- All guidance, is simply that - guidance. There are always situations where the guidance does not apply. The modeler should have the option to use other estimation techniques provided that a sound rationale for not following the is provided.
- The sources of data that are acceptable for use in developing the parameter should be identified. In addition, sources that are not acceptable should also be detailed. For example, batch equilibrium studies are the preferred method for estimating soil-water partition coefficients. However, batch equilibrium studies that employed a cosolvent or emulsifier result in substantially smaller estimates than would be seen in the environment.
- Sources of variability, uncertainty and bias that are inherent in the input parameter need to be explained. For example, anaerobic soil metabolism studies are currently the recommended source of data for estimating subsoil

metabolism. A significant source of bias is that these studies are done on flooded surface soils, not subsoils. These studies tend to show faster degradation that is seen in subsoils. Metabolism studies in general have a large background variability, even within replicates on the same soil. In some cases, the coefficient of variation may be as high as 100%. There is also a substantial amount of variation between soils. The variability is also affected by scale affects as the laboratory measurement is made on a few grams of soil while the model is considering a field of 10 ha. Uncertainty results from the sample size which is usually less than three estimates coupled with the large background variability.

- In some cases, the assumption models have made about the form of the data are not valid. For example, metabolism data usually does not follow a first order model and sorption isotherms are usually not strictly linear. These differences need to be described.
- For input parameters that use summary statistics rather than direct measurements, guidance needs to provided on the methods used to estimate the statistic from the raw data. Examples of these kinds of parameters are the soil degradation rate, which is a statistic describing the slope of the log the concentration measurements over time and K_d which describes the slope of the sorption isotherm.
- Guidance needs to be provided on how to handle the stochastic nature of each input parameter relative to the purpose type of modeling being done. For probabilistic assessments such as a Monte Carlo assessment , the whole distribution of each parameter needs to considered. For screening level modeling, such as currently is being done in the Office of Pesticide Programs, single values which reflect the uncertainty in the input parameter are appropriate. For example, the current OPP EFED guidance recommends the upper 90% confidence bound on the mean half-life be used as the input parameter. If additional data become available, then the estimate of the half-life will go down reflecting the increased confidence in the value used.

3.6.3.3. Incorporating Uncertainty via input parameter selection

The recommendation in the last example above is a departure from the usual practice for handling uncertainty in regulatory assessment in that the uncertainty is considered as a factor in selecting the input parameter rather than as a safety factor applied to the final result of the risk assessment.

This has several advantages. First, the uncertainty in any input parameter is reflected proportionately to the sensitivity of the risk assessment to that parameter. For example, when the degradation rate in the top soil is fast, the uncertainty in the rate can greatly affect the EEC's. However, the EEC is relatively insensitive to uncertainty in the degradation rate when half-life is 100 days or longer. Secondly, handling uncertainty at the input parameter step makes it easy to account for additional data. The change in EEC will directly reflect the added knowledge gained by adding the data. Furthermore, this approach can suggest what data are controlling the uncertainty and suggest which additional data will best address the overall uncertainty in the risk assessment. In contrast, the safety factor approach makes it difficult to objectively relate the uncertainty in any particular data to the uncertainty in the overall assessment. Consequently safety factors are often applied in the same manner regardless of the quantity and quality of the data. This reduces the incentive for the registrant community to supply appropriate high quality data in support of pesticide registrations.

3.6.3.4. Approaches for Estimating Half Lives

As mentioned above, one critical step in the development of input parameters that is common to many types of environmental studies that generate model input parameters is the development of half life information. While the current models are coded to accept and use first order data; in practice much of the data from environmental studies, especially that associated with soil degradation/dissipation laboratory or field data, is poorly described by first order kinetics (Leake, 1995; Gustafson, 1990). Several groups have designed tools within their own research teams to standardize the process of calculating half life and related data from FIFRA sub-part 158 studies (Dyson et al, 1998). In addition, practical issues such as the analytical level of determination (LOD) mean that data points at the end of a study may be difficult to interpret and many different approaches for including or excluding such data points are available.

This wide range of choices of approach for handling experimental data and fitting degradation curves apparently currently results in EPA OPP EFED reviewers having to recalculate most submitted datasets to confirm the estimated half lives. This would appear to be a situation where clear guidance on an approved stepwise set of procedures (for example starting with first order approaches and progressing through more progressively more sophisticated options) as well as guidance on accepting and rejecting data points from within a study might help reduce confusion about how registrants can address OPP EFED concerns and be reasonably certain that they have determined the SAME half life that an EFED reviewer is likely to use. Such guidance would also ensure that all reviewers would generate similar values.

Again, it is beyond the scope of ECOFRAM to include direct guidance on this issue; however, the ECOFRAM workgroup recommends strongly that OPP EFED, together with a group of academic and industry experts, develops and agrees a guidance document based on consensus. In the interim, a definitive statement from EFED specifying a SINGLE method that everyone can agree to use would rapidly avoid duplication of effort.

3.6.3.5. Developing a Tool for Handling Experimental Data and Developing Half Lives.

While a consensus guidance document describing a systematic approach for handling data and developing half lives is an urgent need, the ultimate goal would be to develop a readily available “tool” that would implement the agreed upon approaches and could handle a standard input file format.

As an example, one tool developed to help standardize local calculations of half lives is provided on the attached CD-ROM as created by the DuPont Agricultural Products modeling team (Esterley, 1998). This tool is a relatively straightforward MS Excel macro that permits the selection of either first order or a two step “hockey stick” degradation kinetics with graphical output that most scientists regard as essential for gaining a useful understanding of the quality of ”fit” between the curve(s) determined and the raw data.

3.6.4. Recommendations For Reporting Environmental Fate Study Findings and Exposure Modeling Input Data

During the discussions about improving the risk assessment process, some apparently minor issues were raised that the workgroup realized could make a substantial improvement to the productivity and efficiency of the EPA OPP EFED study review and exposure modeling processes. This was also echoed by the group's representative for State regulatory issues.

One unfortunate result of the massive body of studies performed to address FIFRA requirements is that the key data and issues defining the environmental behavior of an active ingredient are often obscured by the plethora of data available. In addition, from a reviewer's perspective, the reports of studies on Environmental Fate and Transport are written by so many scientists across so many companies that, despite the Standard Evaluation Protocols (SEP's) and guidance documents, the formats and writing styles can be sufficiently different that it is difficult to readily abstract the data needed for modeling. It is therefore recommended that registrants submit various types of summaries of their data along with the official reports. The action rests with EPA OPP EFED to formally propose a format and system for submission, however, the ECOFRAM Aquatic Exposure Workgroup recommends three potential data dissemination methods.

3.6.4.1. Inclusion Of Specific Summary Data Tables At The Front Of Each Report

The first work group recommendation is that each report should contain a clear summary table at the front expressing the key parameters useful to fully describe the results of that study. Ideally, a format should be developed whereby this could be submitted electronically and readily transferred to model input files but, in the interim, a print based system will still be very helpful.

The recommendation is for EPA OPP, perhaps working together with ACPA, to prepare a "minimum data set" one page summary table for inclusion at the beginning of each submitted report. These will be study specific and while the effort of preparation is considerable, the long term savings are believed to be substantive. Appendix 3-8, offers some examples of the type of format envisaged to be useful.

It has been pointed out that the proposed "one page summary tables" are closely analogous to the "Level 1 summary documents" required for European Union (EU) pesticide study reports. As a move towards international harmonization (perhaps under the auspices of OECD), it might be sensible to ensure that any EPA recommendations should not be rigid as to format and should also encompass the minimum requirements of the EU Level 1 summaries.

3.6.4.2. Reporting Of A Full Summary Of All Data Relevant To Modeling In Each Submitted Risk Assessment

One of the most frustrating problems for EPA OPP EFED is that often the scientist assigned to perform the exposure modeling to support a risk assessment is unfamiliar with the chemical in question and therefore does not know which study results are most appropriate to select as model input parameters. Accordingly, it is recommended that registrants include a full summary of data relevant to aquatic exposure modeling when they submit a risk assessment or are aware

that Agency scientists are conducting an assessment. This recommendation is also being endorsed by the Fifra Exposure Modeling Task Force (FEMVTF).

To implement this recommendation effectively, there is a need to provide clear Agency guidance on how to select appropriate values for any model input parameters and also how best to express the variation around the single value initially selected. It is possible that this submission would include the one page summary statements mentioned in 3.5.4.1 above along with a table of recommended model input values and the rationale for selecting any single or representative values from multiple data points.

Ideally, a "tool" should be developed to enter this data into a simple electronic file (e.g. a commonly used spreadsheet) such that the source of every value is clearly documented and also so that the input values can automatically be read into the user friendly "modeling shells" being recommended by ECOFRAM. While such an electronic file tailored for direct connection with modeling shells is the ideal, even a paper record would result in a significant improvement in information transfer and reduction of repeat work.

Note that while the determination of guidance on how to select recommended modeling values is a matter of EPA OPP EFED policy, the development of an easy to use tool could cost-effectively be shared between EPA and industry.

3.6.4.3. Inclusion And Updating As Soon As Possible Of The ARS PPD Database For A Compound Once EPA Have Approved Values.

Finally, as described in section 3.6.2.2, the ARS Pesticide Properties Database (ARS PPDB) is rapidly becoming the primary resource for obtaining essential information on pesticidal active ingredients. The workgroup recommends that registrants should enter product data into the ARS PPDB within two or three months of obtaining EPA approval of a study.

3.6.5. Expressing Aquatic Exposure Estimates

One of the most difficult issues the group has grappled with is trying to find effective ways of describing the output of exposure models. Generally, the modeling community have had a very clear idea of the nature of their model outputs for some time but, in general, the communication of this understanding has been lacking. Since this is often the key feature in a risk assessment, this became an area for much discussion and the development of one powerful new tool.

The key "missing link" in the communication between the modeling community and the effects scientists appears to relate to the data density of even the historic and current output. Essentially, from multi-year model runs (where *n* is the number of years), there are *365 * n* sequential daily values available; furthermore, these values can also potentially be categorized by their Julian day identity into seasonal data sub-sets. Once this had been established, the second major deficiency of expressing exposure model output became apparent; this is related to imprecision in describing exactly what

population of region/soil/crop/agronomy/weather had been investigated to develop the output files. Examples of improved expression of exposure and risk were discussed earlier in chapter 2 (section 2.3.6.5)

3.6.5.1. Deterministic Expressions of Exposure

Historically, exposure was expressed as a few single numbers from "old style" Tier 1 risk assessments. Early PRZM/EXAMS modeling provided exposure either as the maximum annual daily "instantaneous" value or as the highest 96 hour average value obtained by running a "4 day wide" averaging window across the successive daily values. The significance of the underlying scenario assumptions was often contentious but was rarely considered within the context.

After GENEEC was developed, risk assessors became even more familiar with the use of "single" values to define exposure and, again, the use of this meta-model often obscures the underlying assumptions that define the model parameters that drive the exposure estimation.

It is essential that as the science of risk assessment develops after ECOFRAM, that, in addition to the formal reporting of the modeling exercise, ALL exposure estimates (whether deterministic or probabilistic) passed to risk assessors or used in text summaries etc should precisely specify:

- Tiering level
- Models and version used
- Region simulated
- The weather record period used (and location)
- Type of water body modeled
- Adjacency to field (i.e. directly adjacent or separated by a buffer)
- Cropping, agronomic and tillage practices simulated
- Application information (i.e. use pattern details)
- Scenario name (if standard) or details
- The exposure endpoint(s) reported
- The probabilistic context of the value(s)/distributions reported

3.6.5.2. Probabilistic Expressions of Exposure

More recently (e.g. SETAC, 1994), EPA OPP EFED and registrants have been employing a probabilistic format to express the DISTRIBUTIONS of exposure values. The general format is very similar whether the distribution is for values in a single scenario across 36 years (PRZM-EXAMS) or whether it represents a distribution of Xth percentile values across a range of scenarios representing a region (MUSCRAT).

Figure 3-10 displays a typical ….

PLEASE CAN SOMEONE ADD SOME GRAPHICS AND TEXT FOR THIS SECTION!!!

This format for expression of exposure is fundamental to the approach recommended by the ECOFRAM Aquatic teams and, as described above, is dependent upon specific reporting of the underlying information.

3.6.5.3. Expressing Time-Varying Exposure - the RADAR tool

NOTE THAT ALL OF THE DIAGRAMS AND TABLES NEED UPGRADING.

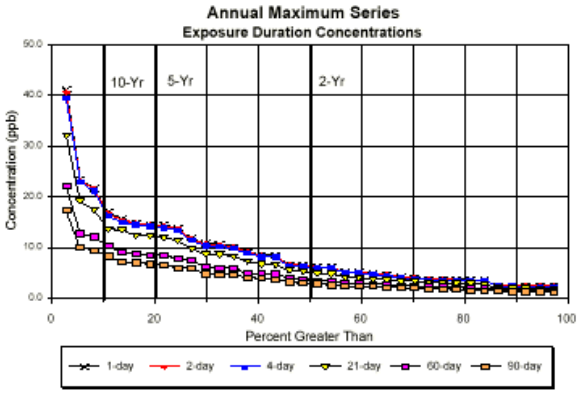
Pesticide concentrations in aquatic environments are variable and transient because of application frequency (residue availability), physicochemical properties that dictate mobility and persistence, and stochastic forces (e.g., rainfall) that drive the hydrodynamic response of the receiving water system.

Computer software has been developed to help analyze and characterize exposure (the contact between the bio-available fraction of the compound of interest and the organism of concern) and to help define the exposure profile (exposure exceedance relevant to a specific assessment endpoint). This software, designated RADAR (Risk Assessment tool to evaluate Duration and Recovery), was designed by and developed by ECOFRAM group members to evaluate time series concentration data for exposure event characterization.

3.6.5.4. Objectives of RADAR

RADAR is designed to evaluate any continuous record of time series data . The data may be model predictions or monitoring results. Several types of analyses are performed:

- Probability analysis on extreme value series. The extreme value series consists of the largest observation in a given time interval. Annual series and 30-day series are recommended by ECOFRAM for a Tier 2 analysis. Observations include peak concentration and 24-hour, 48-hour, 96-hour, 21-day, 60-day, and 90-day durations. A user-defined series may also be evaluated for extended Tier 2 analysis or Tier 3 applications. User-defined series may represent a sensitive life stage or the period of species and habitat co-occurrence based on migratory patterns. Example output is provided in Figure 3-11. Probabilities in Exhibit xx1 were calculated using the Weibull probability distribution.



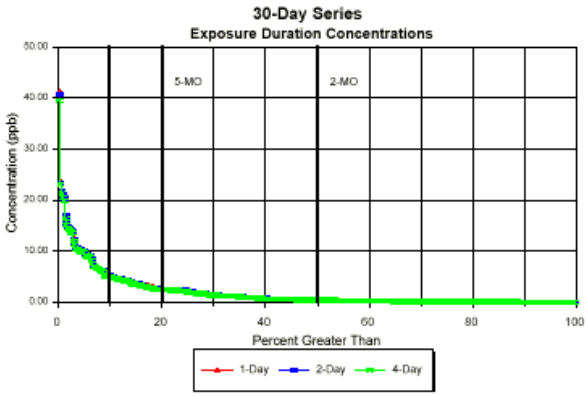


Figure 3-11
= exhibit 1

- Catalog and characterization of exposure events. Events are defined by concentration exceeding a threshold value. Calculations for each event include: the event duration, peak concentration, arithmetic mean concentration, geometric mean concentration, standard deviation of concentration within the event, peak concentration to average concentration ratio, number of inflections within the event, and dose commitment (the time integral of magnitude above threshold for event). The event duration is the elapsed time until the concentration drops below the threshold. Example output is provided in Table 3 -9.

EXHIBIT 2
RADAR Event Summary Table
(Pond Data Set)

Table 3-9 = Exhibit 2

Threshold Concentration = 2.0 ppb

Event No.	Date	Julian Day at Start	Peak Conc. (ppb)	Arithm. Avg. (ppb)	Geometric Mean (ppb)	Duration (days)	Recovery (days)	No. of Peaks in Event	Peak to Average Ratio	Dose Commitment (ppb-days)
1	4/30/48	121	10.20	5.13	4.60	82	283	6	1.99	257
2	4/30/49	120	3.77	2.79	2.74	25	340	1	1.35	19.8
3	4/30/50	120	13.90	6.23	5.30	87	278	3	2.23	368
4	4/30/51	120	8.60	4.26	3.97	84	282	4	2.02	190
5	4/30/52	121	4.17	2.89	2.83	44	321	3	1.44	39.2
6	4/30/53	120	5.17	3.30	3.18	50	315	3	1.57	64.9
7	4/30/54	120	41.20	12.10	8.35	143	222	3	3.40	1450
8	4/30/55	120	6.26	3.34	3.17	72	294	4	1.87	96.8
9	4/30/56	121	2.53	2.28	2.27	9	4	1	1.11	2.48
10	5/13/56	134	5.20	3.27	3.14	44	308	3	1.59	55.9
11	4/30/57	120	14.60	5.98	5.03	110	255	3	2.43	438
12	4/30/58	120	23.60	8.55	6.60	111	254	3	2.76	727
13	4/30/59	120	2.55	2.27	2.26	10	356	1	1.12	2.87
14	4/30/60	121	15.70	7.06	5.85	115	250	4	2.22	582
15	4/30/61	120	6.58	3.94	3.72	55	310	3	1.67	107
16	4/30/62	120	2.51	2.26	2.26	9	21	1	1.11	2.37
17	5/30/62	150	4.23	3.04	2.97	33	302	2	1.39	34.3
18	4/30/63	120	2.51	2.26	2.26	9	17	1	1.11	2.37
19	5/26/63	146	2.23	2.12	2.12	5	335	1	1.05	0.603
20	4/30/64	121	2.51	2.22	2.22	14	351	2	1.13	3.11
21	4/30/65	120	9.28	4.46	3.99	72	293	2	2.08	177
22	4/30/66	120	4.73	3.01	2.94	51	314	3	1.57	51.7
23	4/30/67	120	10.70	5.36	4.77	76	290	3	2.00	255
24	4/30/68	121	10.90	5.00	4.38	82	283	3	2.18	246
25	4/30/69	120	8.51	4.24	3.90	80	285	3	2.01	179
26	4/30/70	120	2.52	2.27	2.27	9	23	1	1.11	2.44
27	6/ 1/70	152	2.13	2.08	2.07	3	330	1	1.03	0.226
28	4/30/71	120	3.79	2.75	2.71	42	324	5	1.38	31.7
29	4/30/72	121	17.00	6.59	5.47	103	262	5	2.58	472
30	4/30/73	120	3.79	2.76	2.70	28	337	2	1.37	21.3
31	4/30/74	120	2.51	2.26	2.25	9	4	1	1.11	2.31
32	5/13/74	133	2.05	2.04	2.04	2	350	1	1.00	0.089
33	4/30/75	120	11.90	5.87	5.14	93	273	4	2.03	360
34	4/30/76	121	3.70	2.80	2.76	40	325	5	1.32	31.9
35	4/30/77	120	4.87	3.24	3.14	42	323	3	1.51	52
36	4/30/78	120	21.80	8.20	6.51	112	253	3	2.65	685
37	4/30/79	120	14.90	6.49	5.43	92	274	3	2.29	413
38	4/30/80	121	2.53	2.28	2.28	9	2	1	1.11	2.53
39	5/11/80	132	3.62	2.81	2.76	27	327	2	1.29	21.8
40	4/30/81	120	14.50	6.28	5.27	109	256	6	2.30	467
41	4/30/82	120	6.29	3.63	3.44	52	313	3	1.73	85
42	4/30/83	120	6.73	4.05	3.83	63	183	4	1.66	129

- Period of record summaries. Summary statistics are provided for both the complete data record and for a user-defined season throughout the period. Statistical information include the minimum, maximum, and average value of various event attributes. The program also summarizes the percent of time throughout the analysis period that concentrations exceed the threshold concentration. Example output is provided in Table 3-10

EXHIBIT 3
RADAR Period of Record Summary
(Pond Data Set)

Table 3-10
= Exhibit 3

```
 PERIOD OF RECORD SUMMARY STATISTICS

Event trigger is   0.200E+01
Analysis season is Julian Day:   90 through   150

                    COMPLETE PERIOD SUMMARY
          Peak Conc.  Avg. Conc.  Duration  Recovery

Minimum   0.205E+01   0.204E+01      2.      2.
Maximum   0.412E+02   0.121E+02    143.    356.
Average   0.825E+01   0.414E+01     55.    255.

No. of Events =   42
% Time above Threshold =  17.55

                    SEASONAL SUMMARY
          Peak Conc.  Avg. Conc.  Duration  Recovery

Minimum   0.205E+01   0.204E+01      2.      2.
Maximum   0.412E+02   0.121E+02    143.    356.
Average   0.840E+01   0.419E+01     56.    253.

No. of Events =   41
% Time above Threshold =  44.40
-----------------------------------------------

Event trigger is   0.100E+02
Analysis season is Julian Day:   90 through   150

                    COMPLETE PERIOD SUMMARY
          Peak Conc.  Avg. Conc.  Duration  Recovery

Minimum   0.102E+02   0.102E+02      1.      4.
Maximum   0.412E+02   0.220E+02     61.   2524.
Average   0.165E+02   0.129E+02     20.    910.

No. of Events =   14
% Time above Threshold =   2.16

                    SEASONAL SUMMARY
          Peak Conc.  Avg. Conc.  Duration  Recovery

Minimum   0.102E+02   0.102E+02      1.      4.
Maximum   0.412E+02   0.220E+02     61.   2524.
Average   0.165E+02   0.129E+02     20.    910.

No. of Events =   14
% Time above Threshold =   9.84
```

- Event tally based on user-defined sensors or triggers. This output provides the number of events that occurred within each year or seasonal period within each year. Events can be defined by threshold concentration alone and according to a minimum duration and a minimum inter-event "recovery" interval. Example output is provided in Table 3- 11.

EXHIBIT 4

Annual Tally of Events with and without Adequate Duration and Recovery
(River Data Set)

Year	No. of Events Exceeding C Alone	No. of Events Exceeding C + D	No. of Events Exceeding C + D + R
48	1	1	0
49	0	0	0
50	2	1	0
51	0	0	0
52	2	2	1
53	1	1	0
54	2	1	0
55	1	1	0
56	1	1	0
57	1	1	0
58	1	1	0
59	0	0	0
60	2	2	1
61	2	2	1
62	0	0	0
63	1	1	0
64	0	0	0
65	1	1	0
66	1	1	0
67	1	1	0
68	1	1	0
69	1	1	0
70	0	0	0
71	2	2	1
72	1	0	0
73	1	0	0
74	1	0	0
75	2	2	1
76	2	1	1
77	1	1	0
78	1	1	0
79	2	1	0
80	1	1	0
81	1	1	0
82	2	2	1
83	1	1	0

Concentration trigger (C) = 2.0 ppb
Duration sensor (S) = 4 days
Recovery sensor (R) = 7 days

Table 3-11

= exhibit 4

3.6.5.5. Sample Data Sets for RADAR:

Four data sets containing daily time series of pesticide concentrations were obtained for demonstration purposes. Each data set represents distinct lentic and lotic receiving water bodies within an otherwise consistent watershed. Because the data sets are used for demonstration purposes only, the exact characteristics and nature of their origin are not important and are not discussed in detail. The data sets may be loosely characterized as a headwater stream, a pond, a river, and a reservoir.

The data sets were created from model simulations. The simulations were patterned after US EPA's "standard pond" scenario for cotton in Yazoo County, Mississippi. The scenario represents cotton production on the Loring silt loam. Cotton received aerial applications of a hypothetical pesticide immediately post-emergent at an application rate of 1 kg

a.i./ha. Applications were assumed to occur with an efficiency of 75 percent. Simulations were conducted for 36 years of historical meteorology. Pesticide applications occurred for each year of simulation.

The pesticide was assumed to degrade on foliage, soil, water, and sediment with a 1st order decay rate of 0.0231 day^{-1} (corresponding to a 30-day half-life). Washoff was assumed to be relatively high (50 percent per cm of precipitation). An organic carbon-water adsorption coefficient (Koc) of 200 cc/gm was assumed

as shown in table 3-12, each data set varies according to the watershed and receiving water body size, fraction of the drainage area planted in cotton and treated with pesticide, and hydrodynamic characteristics of the water body.

Table 3-12: Characteristics of Sample Data Sets for RADAR examples

Environment	Drainage Area	Fraction of Drainage Area Treated	Simulation Model Used for Terrestrial Environment	Simulation Model used for Aquatic Environment
Stream	10 ha	100%	PRZM-3.12	n/a
Pond	10 ha	100%	PRZM-3.12	EXAMSII 2.975
River	20 mi2	35%	PRZM-3.12	RIVWQ 1.33
Reservoir	20 mi2	35%	PRZM-3.12	RESWQ 1.0

Stream System: Stream concentrations were predicted using the Pesticide Root Zone Model, PRZM, Version 3.12 (Carsel et al., 1998). Concentrations were calculated as total residue mass in runoff divided by runoff volume. This concentration profile is similar to that which might be experienced by an ephemeral or small headwater stream having 100 percent of the contributing drainage area treated with pesticide. Chemical dissipation occurred primarily through movement downstream (flushing).

Pond System. Pond concentrations were predicted using the Exposure Analysis Modeling System, EXAMSII, Version 2.975 (Burns, 1998). USEPA's standard pond scenario consists of a 10-ha field draining into a 1-ha x 2-m deep pond. Pesticide mass predicted by PRZM-3.12 for the edge-of-field simulation (both as dissolved residue in runoff water and adsorbed residue to eroded sediment) provided loadings into the pond. The pond also received drift loads of 0.05 kg a.i. (5 percent of the application rate) across the surface of the pond. Chemical dissipation from the water column occurred by degradation and partitioning to bed sediments.

River System. River concentrations were predicted using the Water Quality Model for Riverine Environments, RIVWQ, Version 1.35, (Williams et al., 1997). A 20-mi^2 watershed was represented for which 35 percent of drainage area was

assumed to be planted with cotton. Field runoff consisted of several PRZM simulations similar to those reported in the stream data set, except that pesticide applications across the watershed were staggered to occur over a 21-day application window. Drift loads of 5 percent of the application rate were assumed to occur to 10 percent of the stream/river surface area. An idealized watershed was represented by a single soil texture, uniform distribution of land use throughout the watershed, and the entire watershed receiving the same 36-year storm pattern history. Chemical dissipation occurred primarily through movement downstream although some in-system storage was represented in the simulation.

Reservoir System. Reservoir concentrations were predicted using the Water Quality Model for Reservoirs, RESWQ, Version 1.1, (Williams, 1998). Water discharges and pesticide mass predicted at the outlet of the river model provided the boundary conditions to the reservoir. The reservoir also experienced direct rainfall, evaporation, and outflow. Outflow varied according to operating conditions as a function of water storage.

Concentration time series for two example years of the 36-year simulations are shown in Figure 3-12. Results show the relative in concentration magnitude over time for all four data sets (stream, pond, river, and reservoir).

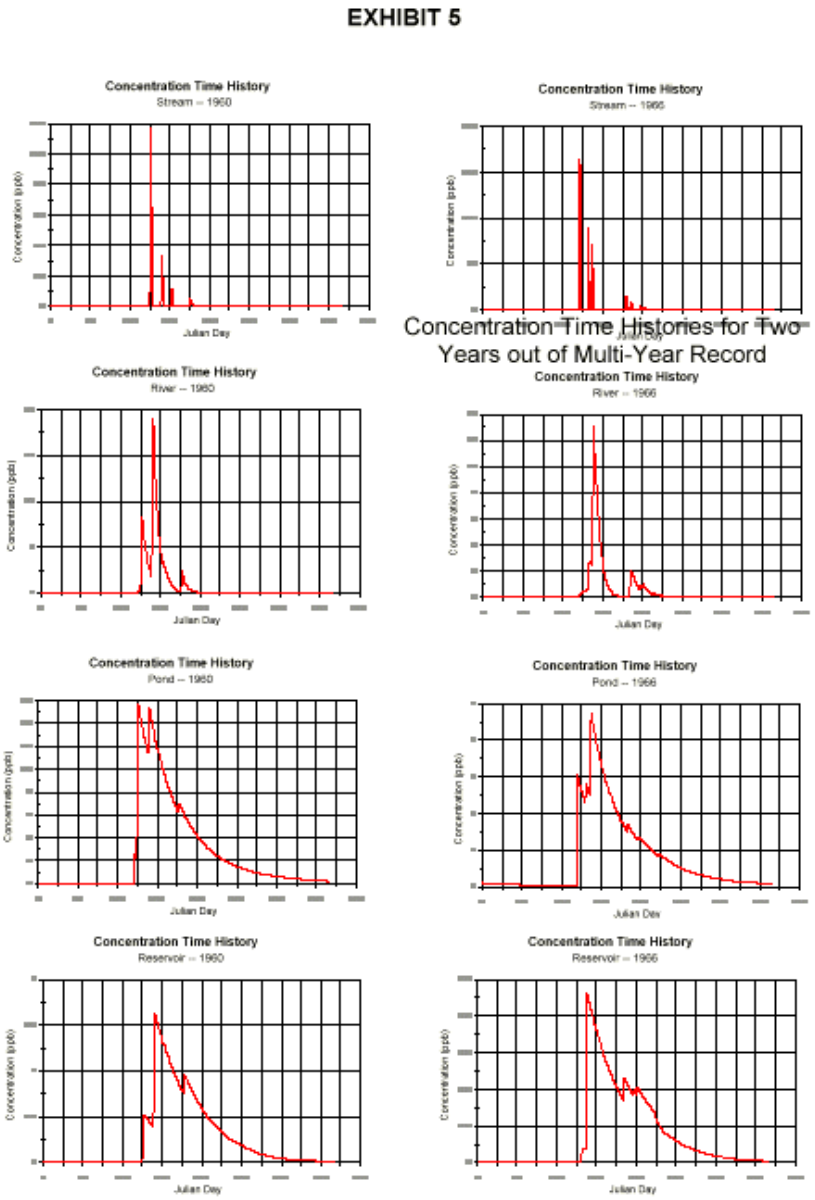


Figure 3- 12

= exhibit 5

3.6.5.6. Example RADAR Output

Frequency analyses for the four data sets are compared in Figure 3-13. . The figures illustrate the relative difference in hydraulic residence and dilution associated with a 24-hour exposure duration. Longer exposure durations have less relevance for comparison because of the relatively rapid flow rates associated with the stream and river data sets. For example, in a rapidly flushing system, the 21-day average concentration is generally the result of a higher exposure concentration persisting for significantly shorter duration.

EXHIBIT 6
Annual Exposure Profiles

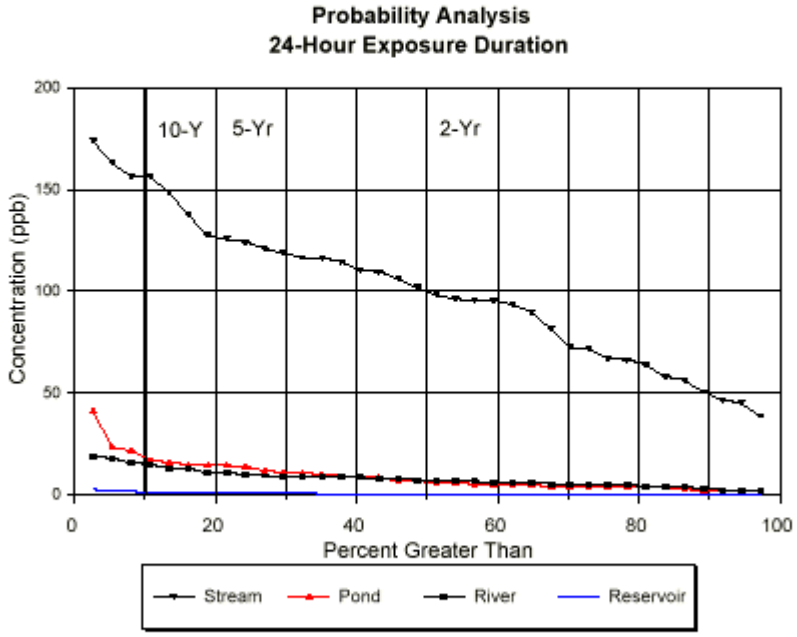


Figure 3-13
= Exhibit 6

Period of record summaries for all four data sets (stream, pond, river, and reservoir) are provided in Table 3- 13. . The table was created using default options for threshold concentrations (i.e., automatically determined by the software) and a hypothetical seasonal period of May 1 through July 15. This table may be used as supportive data during Tier 2 analysis to identify whether additional site-specific exposure profiles should be considered for evaluation.

EXHIBIT 7
Period of Record Summaries for Four Data Sets

(Automatically Scaled Threshold Concentrations)

STREAM DATA SET

Threshold Concentration	No. of Events	% Time Above Threshold	Peak Concentration			Average Concentration			Duration			Inter-Event Interval		
			Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
35	63	0.6	35.3	174	83.3	35.3	160	79.3	1	3	1	1	389	205
70	35	0.3	70.6	174	109	70.6	160	106	1	2	1	1	1099	371
104	17	0.15	106	17	136	106	160	131	1	2	1	243	2186	765
139	5	0.05	149	174	160	149	160	156	1	2	1	364	3285	2020
174	1	0.01	174	174	174	174	174	174	1	1	1	9740	9740	9740

POND DATA SET

Threshold Concentration	No. of Events	% Time Above Threshold	Peak Concentration			Average Concentration			Duration			Inter-Event Interval		
			Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
8	18	3.1	8.4	41.2	14.7	8.4	20.3	11.1	2	70	23	1	1791	701
17	4	0.54	17	41.2	25.9	16.8	26.8	20.8	2	40	18	1422	5097	2692
25	1	0.17	41.2	41.2	41.2	31.9	31.9	31.9	22	22	22	10816	10816	10816
33	1	0.07	41.2	41.2	41.2	37.1	37.1	37.1	9	9	9	10828	10828	10828
41	1	0.01	41.2	41.2	41.2	41.2	41.2	41.2	1	1	1	10836	10836	10836

RIVER DATA SET

Threshold Concentration	No. of Events	% Time Above Threshold	Peak Concentration			Average Concentration			Duration			Inter-Event Interval		
			Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
3.8	50	2.56	3.8	19	7.53	3.8	10.3	5.62	1	24	7	1	724	254
7.6	22	0.59	7.6	19	11.1	7.6	13.4	9.55	1	8	4	2	1450	588
11.4	7	0.16	13	19	15.3	12.5	15.2	13.7	1	5	3	6	4377	1542
15.2	3	0.04	16	19	17.7	16	17.5	17	1	2	2	1101	5340	3241
19.0	1	0.01	19	19	19	19	19	19	1	1	1	9625	9625	9625

RESERVOIR DATA SET

Threshold Concentration	No. of Events	% Time Above Threshold	Peak Concentration			Average Concentration			Duration			Inter-Event Interval		
			Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
0.54	14	3.67	0.55	2.68	1.13	0.55	1.31	0.8	2	81	35	2	2851	895
1.07	5	0.91	1.17	2.68	1.76	1.12	1.82	1.42	5	43	24	723	4743	2085
1.61	3	0.4	1.63	2.68	2.14	1.63	2.16	1.89	1	26	17	933	7696	3222
2.14	1	0.1	2.68	2.68	2.68	2.44	2.44	2.44	13	13	13	9706	9706	9706
2.68	1	0.01	2.68	2.68	2.68	2.68	2.68	2.68	1	1	1	9716	9716	9716

Table 3- 13
= Exhibit 7

Event summary information for both the river and reservoir data sets are presented in Table 3-14. . Analyses are based on a threshold concentration of 10 ppb. The output illustrates the relative dilution and attenuation of the respective systems with respect to pulse magnitude, frequency, and duration. The results from the pond analysis can also be compared to the event summary table in Exhibit 2 which was based on a lower threshold concentration (2 ppb). In general, the pond events in Exhibit 8 are of shorter duration, less frequent, and have longer inter-event recovery durations compared to the lower threshold concentration. This type of analysis can be used to characterize the concentration profile experienced at a particular location or multiple locations, and to assist in the design of laboratory pulsed exposure toxicology tests. The output can be extensive when multiple scenarios are being evaluated and as a result it is more appropriate for a focused Tier 3 analysis.

EXHIBIT 8
Event Summary for Pond and Reservoir Data Sets
(Threshold Concentration = 10 ppb)

Table 3- 14

= Exhibit 8

POND DATA SET
Threshold Concentration = 10.0 ppb

Event No.	Date	Julian Day at Start	Peak Conc. (ppb)	Arithm. Avg. (ppb)	Geometric Mean (ppb)	Duration (days)	Recovery (days)	No. of Peaks in Event	Peak to Average Ratio	Dose Commitment (ppb-days)
1	5/ 9/48	130	10.20	10.20	10.20	1	721	1	1.00	0.2
2	5/ 1/50	121	13.90	11.80	11.70	18	1442	2	1.18	32.0
3	4/30/54	120	41.20	22.00	20.30	61	1057	3	1.87	732.0
4	5/22/57	142	14.60	12.50	12.40	18	326	2	1.17	44.5
5	5/ 1/58	121	23.60	16.20	15.70	36	699	2	1.45	224.0
6	5/ 5/60	126	15.70	12.90	12.80	32	2524	2	1.22	92.7
7	5/ 5/67	125	10.70	10.50	10.50	3	370	1	1.03	1.4
8	5/12/68	133	10.90	10.50	10.50	4	1445	1	1.04	1.9
9	4/30/72	121	17.00	13.40	13.20	22	1075	2	1.27	74.0
10	5/ 2/75	122	11.90	11.00	11.00	7	4	1	1.08	6.9
11	5/13/75	133	10.30	10.30	10.30	1	1084	1	1.00	0.3
12	5/ 2/78	122	21.80	15.00	14.60	37	328	2	1.45	186.0
13	5/ 2/79	122	14.90	12.40	12.30	21	724	3	1.20	50.8
14	5/16/81	136	14.50	12.10	12.10	23	937	3	1.19	49.3

RIVER DATA SET
Threshold Concentration = 10.0 ppb

Event No.	Date	Julian Day at Start	Peak Conc. (ppb)	Arithm. Avg. (ppb)	Geometric Mean (ppb)	Duration (days)	Recovery (days)	No. of Peaks in Event	Peak to Average Ratio	Dose Commitment (ppb-days)
1	5/10/48	131	10.00	10.00	10.00	1	2206	1	1.00	0.0
2	5/26/54	146	13.00	12.00	12.00	3	716	1	1.08	6.0
3	5/14/56	135	11.00	10.50	10.50	2	362	1	1.05	1.0
4	5/13/57	133	16.00	12.80	12.70	5	5	2	1.25	14.0
5	5/23/57	143	13.00	11.50	11.40	2	1090	1	1.13	3.0
6	5/19/60	140	19.00	14.30	14.00	6	736	2	1.33	26.0
7	5/31/62	151	11.00	11.00	11.00	2	1446	1	1.00	2.0
8	5/18/66	138	13.00	12.00	12.00	3	1092	1	1.08	6.0
9	5/17/69	137	18.00	14.20	13.90	6	4376	2	1.27	25.0
10	5/16/81	136	15.00	13.30	13.10	4	5	1	1.13	13.0
11	5/25/81	145	11.00	11.00	11.00	1	950	1	1.00	1.0

Figures 3-14, 3-15 and 3-16 contain various graphical analyses of event properties. This type of analysis is difficult to perform and interpret across a wide spectrum of exposure environments, and therefore, more feasible to evaluate in a focused Tier 3 analysis.

EXHIBIT 9.
Analysis of Event Duration and Recovery

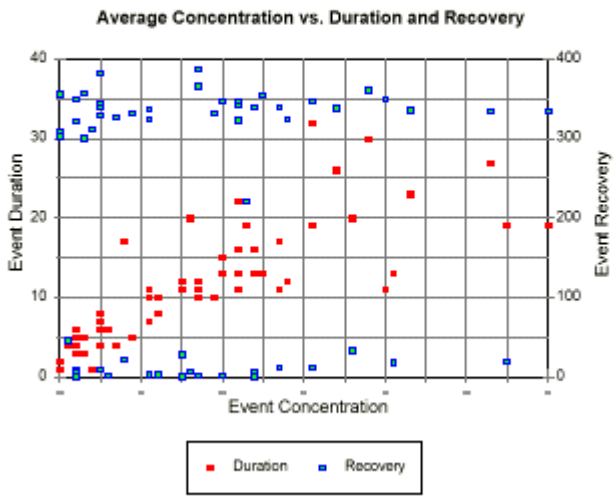


Figure 3- 14

= exhibit 9

EXHIBIT 10
Relationship between Event Peak and Average Concentration

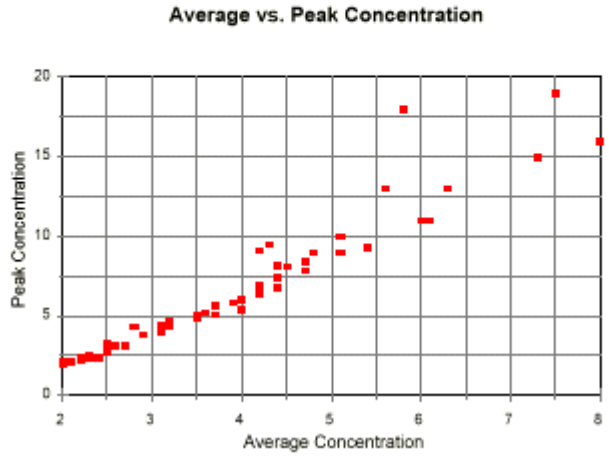


Figure 3-15

= Exhibit 10

2

EXHIBIT 11
Analysis of Multiple Threshold Concentrations

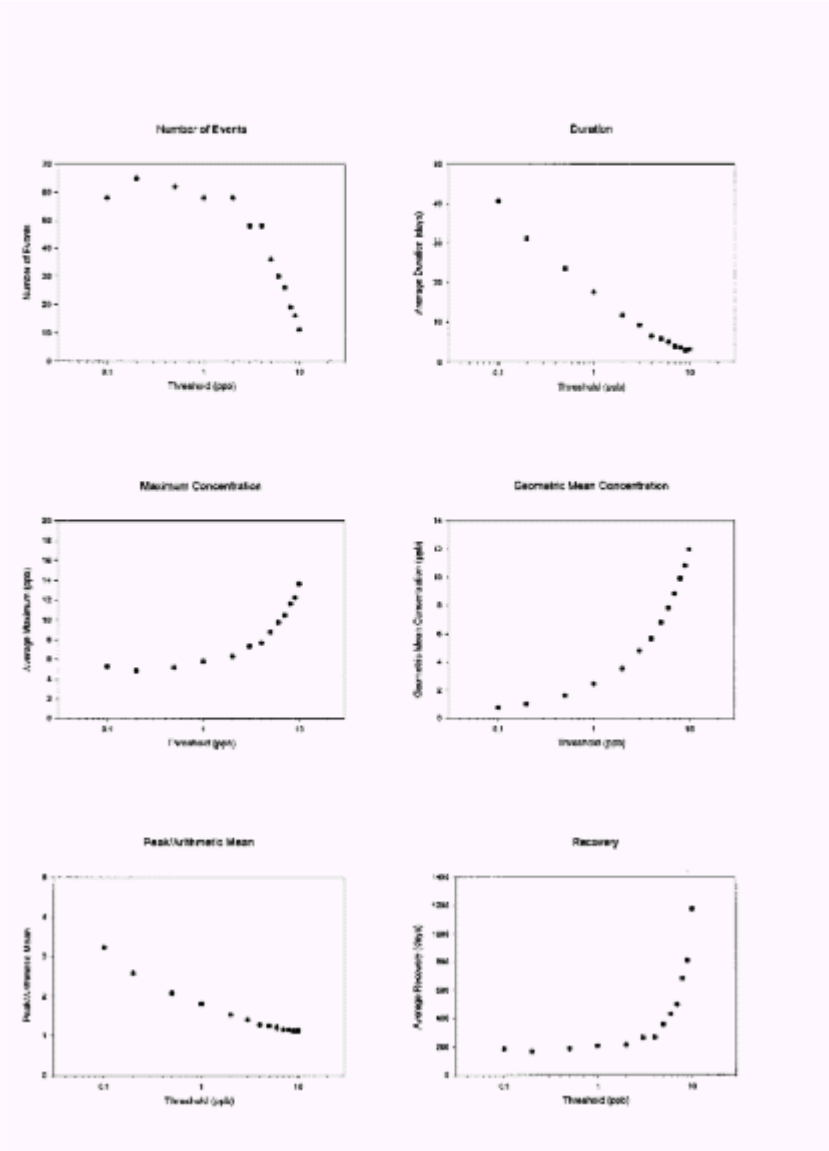


Figure 3- 16

= exhibit 11

3.6.5.7. Assumptions and Limitations of RADAR

The assumptions underlying RADAR are basically those inherent in the models and scenarios that generated the time series used for the run.

Generally, the limitations are also underlying-model-related

DO WE WANT TO ADD ANYTHING HERE?? OR OMIT THE WHOLE SECTION??

3.6.5.8. Recommendations for tool development/finalization

The ECOFRAM aquatic group strongly recommends that the RADAR tool is finalized and made publicly available via an EPA sponsored web site (and model support center) as soon as possible. A manual needs to be written and a user-feedback mechanism needs to be established in order that recommendations can be incorporated into future versions.

Suggestions already being incorporated into the model include:

- the ability to vary application days within a several day window (interesting "uncertainty factor")
- the capability to do on a six per year seasonal basis

HAVE WE ALREADY INCLUDED THIS?? WHAT ELSE HERE???

3.7. ECOFRAM Workgroup Recommended Process for Aquatic Exposure Estimation

The use of the exposure information obtained via the process described here is described fully in the chapter on the ECOFRAM Risk Assessment process (Chapter 2). This section provides supporting detail for each of the exposure tiers and options. In order to "future proof" the ECOFRAM report, each subsection sets out where possible to describe the idealized goal of the tier or process and then details are given of how the ECOFRAM Aquatic exposure group recommends the process should be implemented using tools available in 1998 and 1999 as well as recommending what additional research, data mining or tool development are needed to move towards the ultimate "ideal" goals.

Although not dwelt on specifically, it is very important that improvements in aquatic exposure estimation aimed at addressing Food Quality Protection Act (FQPA) concerns be developed in concert with ECOFRAM recommendations since many of the approaches and technologies are closely linked. The ECOFRAM team recommends that EPA OPP EFED makes special efforts to ensure that staff developing the FQPA and ECOFRAM processes communicate frequently.

3.7.1. Concepts behind a Tiered Process for Exposure Assessment and Refinement

As previously detailed, concentrations of agricultural chemicals to which aquatic organisms may be exposed are influenced by numerous physical, chemical, agricultural and meteorological factors and thus are spatially and temporally extremely variable. The extent to which this variability is defined in estimates of exposure reflects increasing effort, cost and difficulty.

Figure 3-17 exemplifies the exposure "surface" distribution of pesticide residues peaks in a farm pond across a 36 year period; the x axis is the water column residue each day within a year and the z axis represents the sequence of years (for clarity, just a short "season" from each of six years of data is shown).

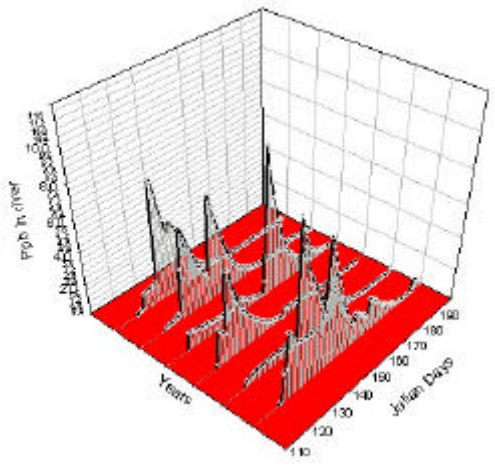
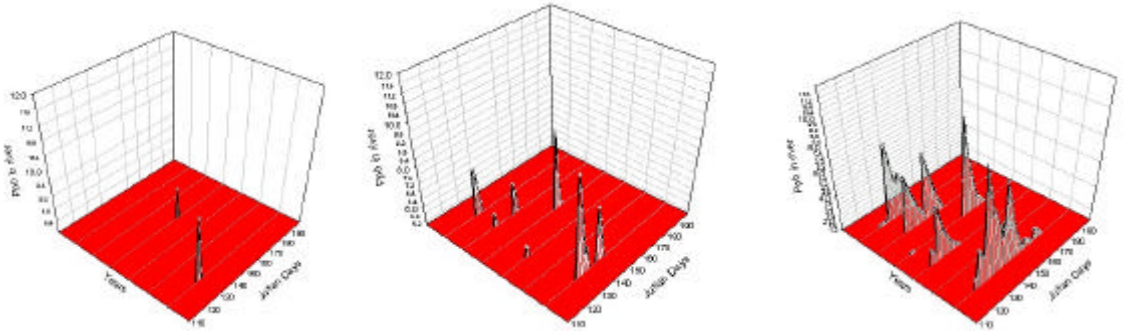


Figure 3-17. Example of monitoring data across a 6 year period

The concept behind the tiered process can be envisaged a drawing a rubber sheet over this surface increasingly closely. At a Tier 1 level (figure 3-18a) the sheet is designed to be highly protective and so only a very few residue peaks will exceed the single value estimated (a flat sheet). It is important to note that the extent to which the modeled surface is conservative could ONLY be expressed be expressed if the characteristics of the actual distribution were understood. Additionally, it can be seen that there is almost no information obtained about the characteristics of the exposure in terms of magnitudes of typical "events", duration of exposures, frequency of peaks etc. However, as the sophistication of the tier increases (figures 3-18 b and c), the rubber sheet becomes drawn more closely over the surface so that not only does the exposure estimate more closely approach the "true" distribution of exposures but that considerably more ancillary data is available to characterize details of the likely exposure patterns. It takes only a small mental shift to envisage how this might also apply to the spatial distribution of residues, regionally variable use patterns and the like.



Figures 3-18 a, b, and c. Demonstrating the concept of applying increasingly sophisticated Tiers to the data shown in Figure 3- 17.

Thus the goal as we progress through the tiers is to refine the understanding of exposures so that:

- the probability distribution of exposures of a given magnitude is better understood
- the distribution of spatial variation of potential exposures becomes clearer - e.g. in terms of variation
  - ◊ between water body types,
  - ◊ within a watershed and/or

- ◊ by region
- ◊ within a water body,

- the distribution of temporal variation of exposures in terms of
  - ◊ duration
  - ◊ frequency above a certain magnitude
  - ◊ intervals between "events"
  - ◊ seasonal differences
- the potential for exposure to be mitigated by various measures

Figure 3-19 depicts conceptual relationship between tiers in a different way. Tier 1 is a very tight distribution (in most cases as single value) that considerably exceeds the majority of values in the "true" distribution (the blue line with magenta highlights depicting the maximal areas of the distribution). The succeeding tiers serve to initially describe a distribution of exposures at a single worst case site and then refine that distribution until ultimately (especially with the incorporation of model validation via monitoring) the estimates approach the "true value" most closely.

Figures 3-20 and 3-21 (awaiting updates) show the same concept in terms of the individual distributions associated with each tier - one important issue with these graphs is that, for clarity, they cannot represent the relative sizes of the populations involved at each Tier. In reality, the population represented by Tier 1 is small relative to Tier 2. Moreover, because the Tier 2 scenarios represent that population of fields immediately adjacent to water bodies and 100% cropped and subsequently treated with the maximum number of treatments at the maximum label rate they in themselves represent only a very small fraction of the "true population" of sites receiving treatment with the chemical of interest (Tier 3). Tier 4 approaches reality even more closely because typically it will bring into play all the fields of the crop of interest that are UNEXPOSED as well as the other areas of the watershed which are not even the crop of interest. Tier 4 is thus a much greater population than any of the others.

The outline in the previous paragraph explains why the median of the distributions decrease steadily in moving from Tier 1 to Tier 2 to Tiers 3 and 4. The gray line in the diagram approximates the almost exclusively unexposed Tier 4 sites that, blended with the Tier 3 cases, combine to explain the real world (dark green) line.

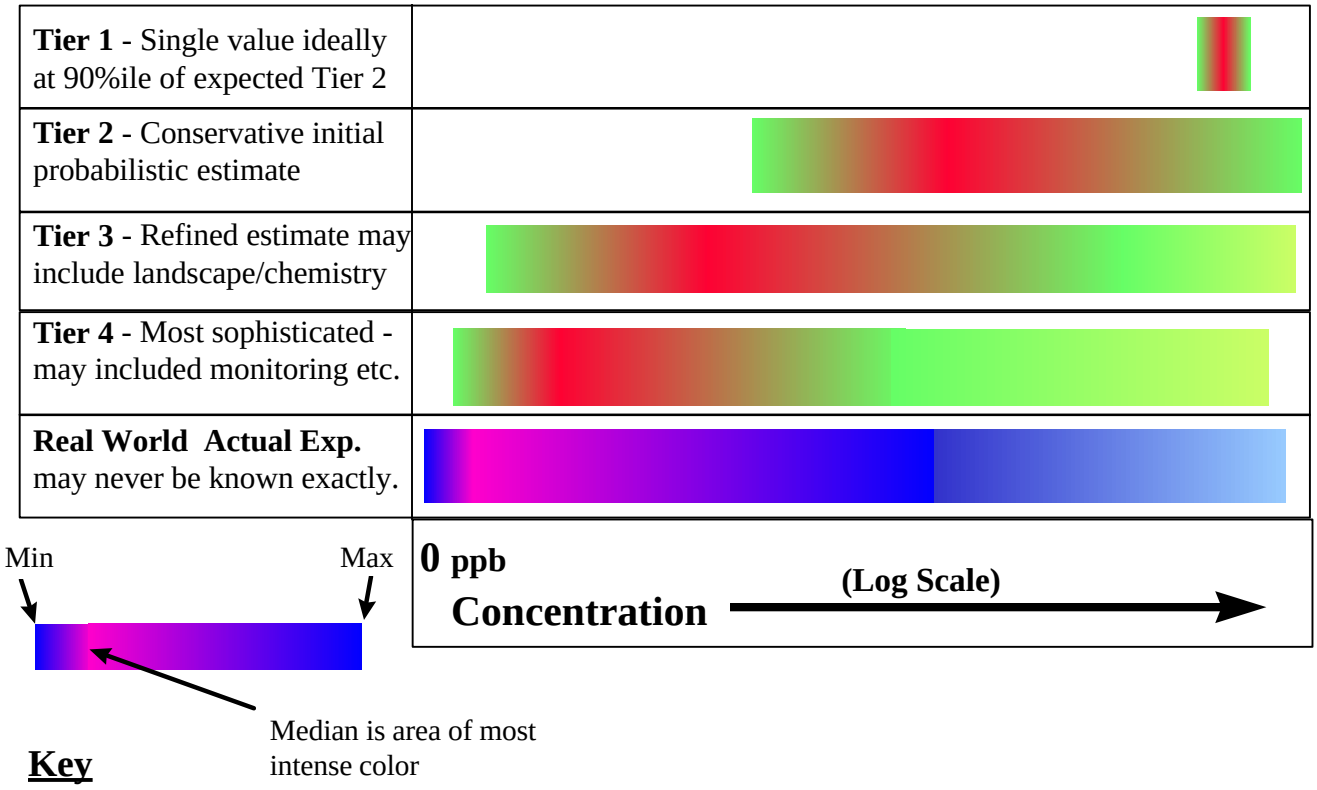
The most important conclusion arising from this is that Tiers 2 - 4 represent increasingly sophisticated approximations of reality based on exposure modeling and refined laboratory and field experimentation and normally can be related to one another. Additionally, they all drive the same risk assessment process. However, Tier 1 is an exception to this process because CURRENTLY it is an value generated from an arbitrary scenario that cannot be related to any subsequent Tier 2 modeling.

The ECOFRAM workgroup recommends that as soon as possible after an agreed "ideal" Tier 2 model is available, a series of Tier 1 "scenarios/mete-models" should be derived for major crop groups/agronomic situations to represent the 95th

percentile of the Tier 2 distribution expected across the national distribution of the crop. Clearly, actual distributions will be dependent on the combination of chemical properties, and thus it is recommended that for convenience the 95th percentile scenario should be based on some combination of estimated runoff volume and sediment movement predictions.

The fact that the progressive tiering process serves to "decrease" the mean estimate exposure is often misrepresented as a manipulation of the system to ease pressure on regulators and improve the position for Industry. In fact, the reason why the move towards progressively higher tiers only takes place on an as-needed basis is because the costs of progressively higher tier studies to both the registrant (in terms of conducting the studies) and to the EPA OPP (in terms of discussing, approving and reviewing the studies) increase somewhat exponentially. While, in an ideal world, the early tier models should be able to provide an accurate representation of reality, given the current state of aquatic exposure modeling science the progressive tiering system will be the only viable approach for some time.

Figure 3-19. The Conceptual Relationship between Tiers



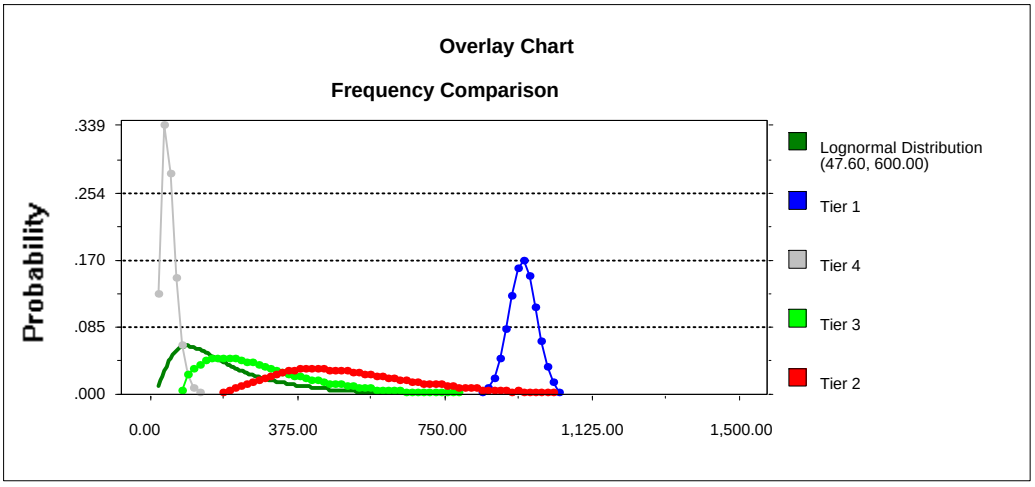


Figure 3- 20

Awaits update

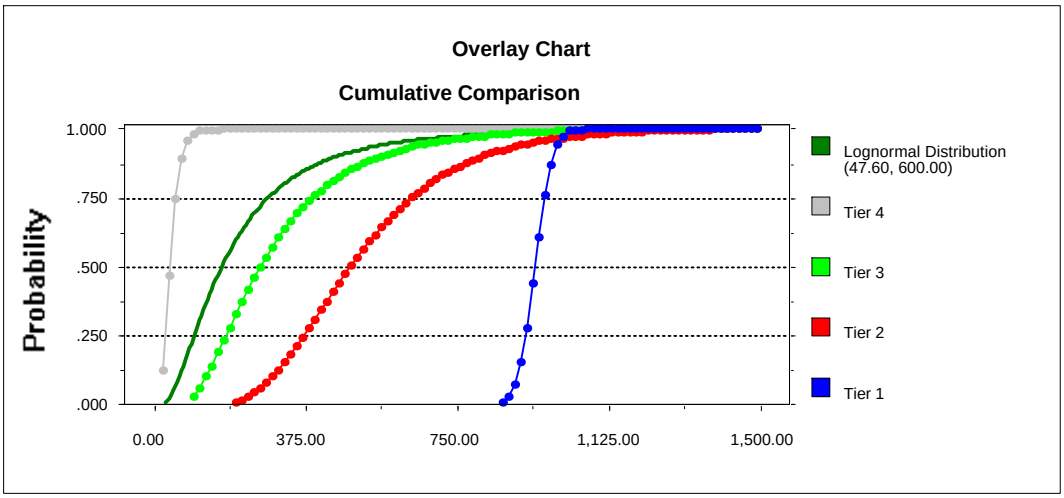


Figure 3-21

Awaits update

3.7.2. The Proposed ECOFRAM Tier Process:

Figure 3-22 - 3-24 and 3-28 in the sections below show the Aquatic exposure estimation process extracted from the overall ECOFRAM tier process covered more fully in the Risk Assessment chapter (Chapter 2). The guiding principle is that progression through increasingly refined estimates of exposure should be driven by indications of unacceptable risk, and the need to examine temporal/spatial distributions, consider mitigation options, or include chemical specific factors affecting exposure.

Methods of estimating exposure progress from simple screening estimates to refined, compound specific modeling and/or monitoring programs. For probabilistic risk assessments, it is anticipated that the focus of effort will lie with refined modeling which captures multiple regions, spatio-temporal variations, and event based information. While useful for conceptually organizing the process, it should be recognized that distinctions between tiers are not necessarily rigid. That is, appropriate combinations of toxicity values and estimates of aquatic exposure may exist across tier levels, depending

upon compound specific information. Additionally, it may sometimes be appropriate to "jump" tiers or perform additional studies on a compound specific basis.

Key advantages if the proposed tiered process is adopted include

- It will not change the existing FIFRA system - EPA OPP is still responsible for decision relating to ecological risk assessment and the ONLY group to make regulatory risk management decisions
- It will also increases efficiency since a registrant can, where appropriate, proceed to a "Tier 3" level risk assessment which can then be submitted to EPA OPP EFED for evaluation, acceptance and rejection as with any other submitted FIFRA study, and then, (if judged to have sufficiently characterized the uncertainty around the aquatic ecological risk) as a basis for regulatory decisions.
- It will provide a clearly defined "common language" for risk assessors and risk managers in both the registrant and regulator communities and thus, hopefully, enhance communication.
- In the same manner, it should simplify communication to the public about the current approaches to probabilistic risk assessment.

3.7.3. ECOFRAM Proposed Tier 1 - Screening Exposure Estimates

Figure 3-22 - The Aquatic Risk Assessment Process for Tier 1

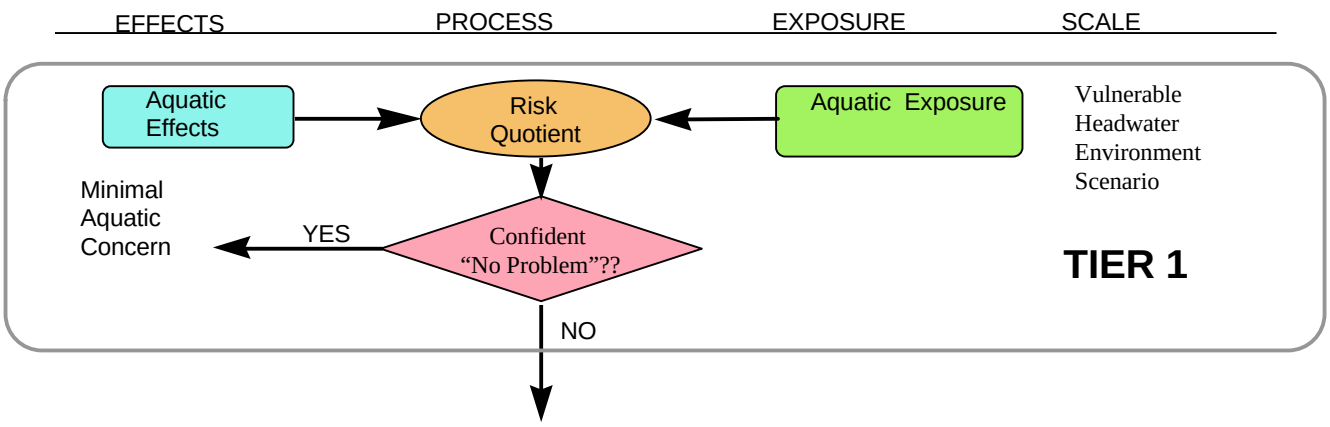


Figure 3-22 above depicts Tier 1; there is also a more general discussion about the application of Tier 1 and the amalgamation of exposure and effects data into a Tier 1 risk assessment in sections 2.3.1..1 and 2.3.5. The following section deals with the Tier 1 exposure characterization process; this tier is similar to the current Tier 1. All compounds require a Tier 1 exposure assessment.

3.7.3.1. Objective/Purpose

Tier 1 generically is designed to define the system at risk and help define scenarios for future modeling. It uses simple models to evaluate the possibility of risk to Avian, Terrestrial Mammals, Aquatics, Humans/FQPA or "the Environment", The objective is to use highly conservative assumptions such that the resulting exposure estimate will permit confidence

that a Tier 1 hazard assessment will not exposure the system of concern to harm. Tier 1 is designed to be **PROTECTIVE** rather than **PREDICTIVE**.

The resulting highly conservative exposure assessment is designed to

- Identify those pesticide products which a risk assessment indicates with high confidence to have minimal environmental/ecological concerns (e.g. minimal aquatic ecological risks);
- Focus any higher tier risk assessment work on combinations of use patterns and sensitive taxa (e.g. invertebrates, fish or aquatic plants) most likely to be of concern;
- Prioritize the use patterns for a product in terms of potential environmental exposures;
- Provide an assessment of whether acute or chronic concentrations may be of concern.
- Determine the potential need to consider sediment toxicity impacts. While it is currently not possible to evaluate sediment and pore water exposure using the standard Tier 1 exposure model, this functionality is recommended to be built into the next generation of exposure models.

3.7.3.2. Conceptual Ideal Tier 1 Process

Conceptually, an ideal Tier 1 will generate a conservative exposure assessment of likely aquatic system concentrations arising from pesticide runoff, erosion or spray drift entry in surface water immediately adjacent treated areas. The estimate will be generated using a single simulation model which will comprise a "user friendly" shell making use of approved surface water exposure models (either as a version with simplified inputs or via "meta-data" from pre-run model output). This is an important design feature because then as approved surface water and associated runoff models are improved, the Tier 1 meta-model can readily be revised.

The tool will use scenarios representing a wide range of crops and use patterns (either as relevant groups of crops or as individual scenarios). Ideally, there will be an opportunity to incorporate different types of water bodies but all will be directly adjacent to the treated area. Of particular importance is the need to be able to define the relative "severity" of the scenario in terms of a probability of aquatic exposure. The chosen Tier 1 "scenario severity" will be at a conservative return frequency set relative to the expected Tier 2 model predictions for transport processes (e.g. sediment and/or water movement). The scenario severity in regulatory use in 1998/99 are the 90^{th} and 95^{th} percentiles of erosion severity. Decisions about setting of "severity" of a Tier 1 scenario are a matter of EPA policy and were not the subject for discussion within ECOFRAM.

It is important to note that because the Tier 1 scenario severity value should be set RELATIVE to the Tier 2 output, (e.g. 95^{th} percentile for sediment transport) it is most often even more conservative when compared with the real world distribution of residues (see tiering concept section 3.7.1). It is likely that we will need to create a Tier 1 scenario for each major crop group; these should be linked to the Tier 2 results in terms of some combination of water runoff volume and sediment transport as in the current MUSCRAT system.

It is also likely to be useful that even at Tier 1, both national and regional scenario options should be available. For example, amongst the key variables driving the runoff process, the regional variation of storm frequency and intensity, are sufficient that to apply a national runoff storm assumption to a regionally applied pesticide would introduce avoidable uncertainties.

The output of the model runs would ideally provide water column instantaneous and various time interval concentrations for a static pond and a flowing water scenario and should include a simple error estimate. Ideally, sediment and sediment pore water concentrations will also be provided. Additionally, it would be useful for the model to provide an estimate of the typical "shape" of the time course of pesticide dissipation in the receiving bodies.

Only the most simple mitigation options (e.g. rate and application frequency reduction) should be investigated at this tier. It is not appropriate to perform model parameter modification or sensitivity evaluations with this tool.

The tier provides exposure estimates that allow a deterministic risk assessment of risk (quotient method). The decisions to be made at this Tier are

- Conservatively estimated concentrations for use pattern "X" indicate that in static and/or surface waters, no ecological hazard above the level of concern is likely to result from use of the product to taxa A, B or C.
- The predicted conservative exposure value when compared with a standard battery of toxicity test results suggests that the possibility of an adverse impact to taxa A, B or C exists. It is therefore necessary to progress to Tier 2 to refine the exposure estimate.

3.7.3.3. ECOFRAM Interim Recommendations for Implementing a Tier 1 Exposure Assessment Currently

The ECOFRAM Aquatic exposure work group has evaluated the generic needs of the proposed Tier 1 and developed the idealized process described above. However in the context of models and tools available in 1998/1999, ECOFRAM recommends that the following approaches be used.

Most needs can be accommodated by the use of GENEEC version 1.2 or 1.3 (see section 3.4.4.1). Tier 1 estimates are intended to provide reasonable worst case values (approximately 90th percentile) of potential concentrations of parent or key degradates in surface water immediately adjacent to treated fields via runoff, erosion and drift for initial deterministic assessments of risk (quotient method). It is recognized that the widespread use of GENEEC by EPA, state regulators and industry is linked to its accessibility to users with limited modeling experience and that this is desirable in an initial screening tool.

Tier 1 estimates using GENEEC, which is a "meta-model" of PRZM/EXAMS, are considered appropriate for generating protectively conservative assessments of the systems and taxa at risk, and whether the concern lies primarily with acute or chronic exposures. GENEEC is considered to provide reasonable worst case exposure estimates (90th percentile or worse)

for row crop scenarios in which static water bodies receive input from one or more applications of pesticides to adjacent acreage. Limitations however exist (specified in section 3.4.4.1.3) especially opposite scenarios for non-row crops and turf or for highly persistent compounds with moderate to high Kd and multiple seasonal applications. For scenarios, compounds or considerations for which GENEEC is not appropriate (see section 3.4.4.1.5), Tier 1 estimates should be obtained using PRZM/EXAMS. As with GENEEC, the intent is to provide conservative estimates for deterministic risk assessment. Appropriately severe, single site use scenarios are run over multiple years with approved weather data (e.g. standard 36 data set) providing temporal distributions of water concentrations in static ponds immediately adjacent to edge of fields. Appropriate toxicological endpoints are compared to the single 96th percentile exposure value (that for the 2nd highest of the 36 annual values) for assessment of risk. The use of PRZM/EXAMS within Tier 1 provides the opportunity to obtain a more refined estimate of reasonable worst case concentrations via incorporation of pertinent chemical input parameters and a better understanding of the temporal distribution of exposures.

3.7.3.3.1.Current Tier 1 Process - GENEEC

In almost all circumstances (see below) GENEEC should be selected as the model of choice. Section 3.4.4.1 fully describes the model, its underlying assumptions and limitations.

3.7.3.3.1.1.Selection of scenarios for Tier 1 GENEEC modeling

The row crop scenario for GENEEC (version 1.2) is fairly well understood and represents a meta-model of PRZM2/EXAMS output for a worst case scenario. In view of the fairly extensive validation of the PRZM/EXAMS systems, the ECOFRAM Aquatic exposure modeling work group recommends that this scenario is appropriate for most row crops and will tend to overestimate potential exposure.

Since late 1998, new GENEEC scenarios for rice, cranberries and rights-of -way have been available in a beta release of GENEEC ver 1.3 but these have not been approved for regulatory use. It should be borne in mind that these scenarios are NOT meta-models of existing models and are therefore not validated and should be used with caution presently.

3.7.3.3.1.2.Selection of GENEEC input values

Table 3-15 below provides some guidance for the selection of variables for the use of GENEEC version 1.2 or 1.3 as a Tier 1 model.

Table 3-15. GENEEC input guidance.

MODEL INPUT VARIABLE	COMMENTS
Application Rate (lbs ai/A)	Current label
Maximum No. of Applications	Current label
Koc	Mean value provided a correlation is demonstrated

	between OC and Kd
Kd	Lowest "non-sand" value
Aerobic Soil Metabolic Half-life (days) ADD A REFERENCE XXX	Maximum value. 2.3*half-life (n=1) 90% Upper Confidence Limit of Geometric Mean (n>1)
Is the pesticide wetted-in?	Yes or No
Depth of Incorporation (in.)	Current label
Spray Drift	Aerial = 5%; Ground = 1%; Granular = 0%
Solubility (mg/L)	Registrant submitted data
Aerobic Aquatic Metabolic Half-life (days)	Maximum. If stable, use 0.
pH 7 Hydrolysis Half-life (days)	Maximum. If stable, use 0.
Photolysis Half-life (days)	Maximum. If stable, use 0.

3.7.3.3.1.3.Tier 1 GENEEC Outputs

GENEEC currently provides water column concentrations which include instantaneous, 4, 21 and 56 day estimates. Currently, there is little opportunity to draw conclusions about the dissipation of the pesticide from the water column and no sediment information. However, limited guidance can be obtained by comparing the instantaneous and 4 day values.

3.7.3.3.2.Current Tier 1 Process - Simple PRZM3/EXAMS modeling

Where GENEEC is not applicable AND an estimate of chronic exposure is required OR if an estimate of sediment concentration is required, simple PRZM3/EXAMS modeling should be conducted. These circumstances are indicated by co-occurrence of all three of these three variables:

a) The compound of interest is relatively long lived in the environment (lab half life greater than 26 weeks).
b) The compound of interest has moderate to high K_D (e.g. > 2)
c) Multiple applications are made within a season and the application interval is less than 4 times the lab soil half life

For Tier 1, the assumptions underlying the use of PRZM/EXAMS are designed to be the same as for the use of GENEEC but if PRZM/EXAMS runs are needed, it is suggested that both GENEEC (Tier 1) and PRZM3/EXAMS output should be compared in a risk assessment report.

3.7.3.3.2.1.Selection of scenarios for Tier 1 PRZM/EXAMS modeling

This step in the tiered process is designed to mimic the PRZM/EXAMS runs used to generate the data on which GENEEC is based. Therefore, the scenario to be used is Yazoo, MS (see Appendix 3-5) using weather data for Jackson, MS (MLRA 131). {Note that in the initial generation of metadata for GENEEC, an incorrect weather file was used due to an error in PIRANHA coding}. The crop selected should be cotton but the impact of crop interception of rainfall should not be simulated.

3.7.3.3.2.2.Selection of Tier 1 PRZM/EXAMS input values

Table 3-16 below provides some guidance for the selection of variables for use in PRZM3/EXAMS Tier 1 modeling.

Table 3-16. Tier 1 PRZM-EXAMS modeling guidance.

MODEL INPUT VARIABLE	COMMENTS
Application Rate (lbs ai/A)	Current label
Maximum No. of Applications	Current label
Application Method	Foliar, Soil or Incorporated
Application Timing	At cotton planting
Application Efficiency	Aerial = 95%. Ground = 99%. Granular = 100%
Koc	Mean value provided a correlation between OC and Kd exists
Kd	Lowest “non-sand” Kd value
Aerobic Soil Metabolic Half-life (days) ADD REFERENCE XXXX	Maximum value. 2.3*half-life (n=1) 90% Upper Confidence Limit of Geometric Mean (n>1)
Foliar degradation	Stable
Depth of Incorporation (in.)	Current label
Spray Drift	Aerial = 5%; Ground = 1%; Granular = 0%
Solubility (mg/L)	Registrant submitted data
Aerobic Aquatic Metabolic Half-life (days)	Maximum. If stable, use 0.
pH 7 Hydrolysis Half-life (days)	Maximum. If stable, use 0.

Photolysis Half-life (days)	Maximum. If stable, use 0.

3.7.3.3.2.3.Tier 1 PRZM3/EXAMS Outputs

The output required is the upper 10th percentile concentration for instantaneous (peak), 4, 21, 60 and 90 day and annual and overall means. In addition, the upper 10th percentile concentration in sediment and sediment pore water for the same intervals. For Tier 1, it is suggested that both GENEEC (Tier 1) and PRZM3/EXAMS output should be compared in a risk assessment report.

3.7.3.3.3.Expressing Tier 1 Exposure Estimates and Progression to Tier 2

GENEEC produces a standard output of single values for each exposure duration period. For comparative purposes, output from Tier 1 PRZM3/EXAMS should be expressed in the same format. As highlighted in section 3.6.5, full details of the source of the output and any scenario details should accompany the report of Tier1 exposure output.

The exposure estimates from Tier 1 will be compared with deterministic point toxicity values as described in Chapter 2 (section 2.3.5.4). The decisions to be made at Tier 1 are

- Conservatively estimated concentrations for use pattern "X" indicate that in static and/or surface waters, no ecological hazard above the level of concern is likely to result from use of the product to taxa A, B or C.
  i.e. **NO FURTHER ACTION**, Report the Tier 1 results for these taxa
- The predicted conservative exposure value when compared with a standard battery of toxicity test results suggests that the possibility of an adverse impact to taxa A, B or C exists. It is therefore necessary to progress to Tier 2 to refine the exposure estimate.
  i.e. **PROGRESS TO TIER 2**. Include the Tier 1 results and interpretation in the Tier 2 (or higher) report.

3.7.3.4. Recommendations for improving Tier 1

These recommendations are divided into two sets; firstly, those appropriate for the longer term development of an improved Tier 1 exposure characterization process and secondly, those specifically related to enhancing the current GENEEC/ PRZM/EXAMS Tier 1 exposure assessment process.

Recommendations related to the CURRENT Tier 1 process

- GENEEC should continue to be used at present as a Tier 1 model (especially for row crops) provided its limitations are clearly specified.
- GENEEC must be considered to be a simple "trigger" in Tier 1, the exposure estimates stemming from GENEEC should only be used for simple "pass" or "Do more detailed exposure estimation" decisions.
- It is not appropriate to try to "tweak" GENEEC parameters on a compound specific basis.

- EPA should do some "validation" or "confidence building" for the risk managers in EPA and industry; particularly in regard to the relationship of its out put to Tier 2 predictions for a range of crops.
    - Comparisons should also be made to confirm that GENEEC does represent around the 95th percentile of a MUSCRAT simulation for a range of crops
- Comparison of Tier 1 GENEEC and PRZM/EXAMS simulations should be conducted for a range of products and crops to confirm the validity of the proposed Tier 1 PRZM/EXAMS input parameter selection guidance
- GENEEC should be made an official EPA model and must be made available from official EPA web sites along with full documentation
- The group recommends that a "EURO-GENEEC" be developed using a similar background to US GENEEC but using different assumptions appropriate to EU conditions
- GENEEC should be re-examined (and re-coded as needed) using latest PRZM and EXAMS code after the FIFRA Exposure Model Validation task Force (FEMVTF) has fed back initial results
- While it is recognized that the current additional scenarios (rice, cranberry and rights of way) will not be meta models of validated and approved regulatory tools; GENEEC (or its successor) is an appropriate vehicle to use for Tier 1 exposure estimates for these uses. Therefore further development and validations of these modules in the very short term is essential and worthwhile.
- Additionally, and following the same logic, specific turf and muck soil modules should be developed and validated

Recommendations for longer term improvements to a Tier 1 Exposure Assessment process

- A single Tier 1 model that addresses the needs of the idealized Tier 1 model (above) should be developed. Key parameters of a successful Tier 1 model include:
    - A range of national and regional scenarios that represent the 95th percentile of Tier 2 modeling in terms of water/sediment transport
    - Separate "scenarios" to represent the 95th percentile for major crop groups (in terms of some combination of water runoff volume and sediment transport)
    - Fast run time on a mid range PC
    - Small executable file
    - Does not require expert modeling knowledge to run
    - Limited weather data input file requirements
    - automatically produces reports in regulatory format
    - Sediment and water column concentration outputs
    - Indication of the typical "shape" of pesticide dissipation in a receiving body

3.7.4. ECOFRAM Proposed Tier 2 - Temporal-Spatial Exposure Characterization

Figure 3-23. The Aquatic Risk Assessment Process for Tier 2

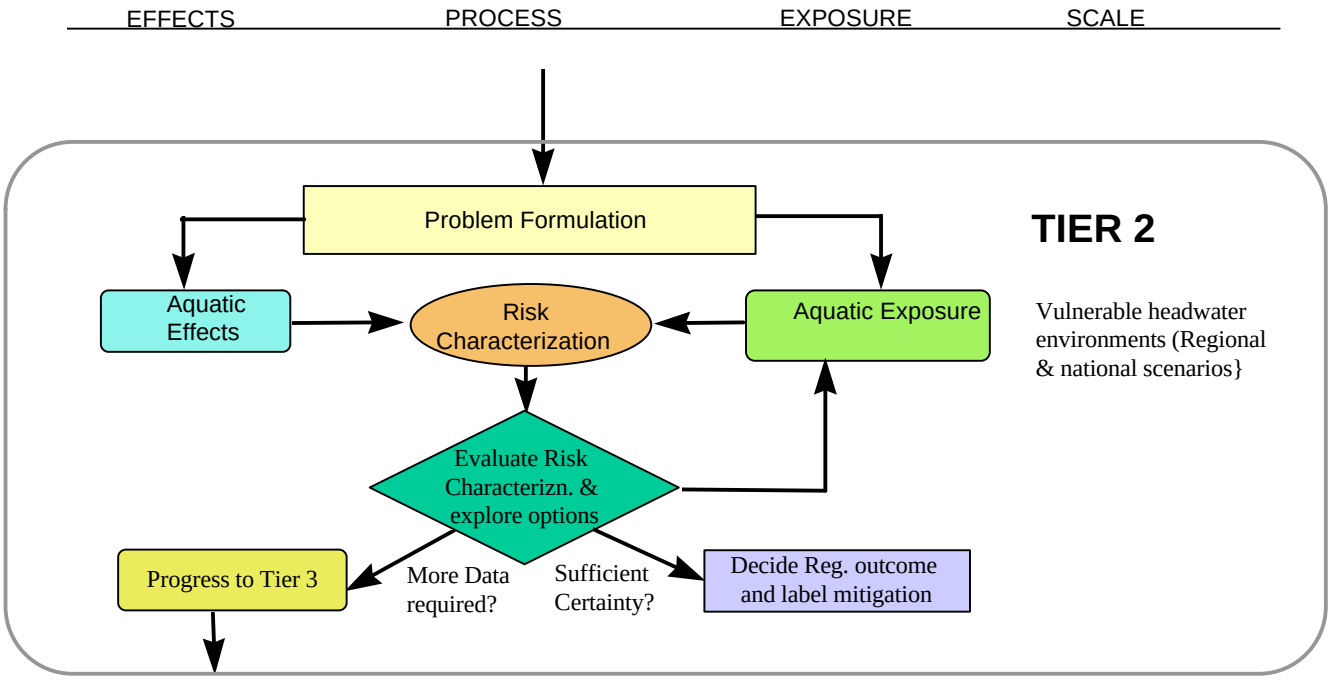


Figure 3-23 above depicts Tier 2, there is also a more general discussion of the application of Tier 2 and the amalgamation of exposure and effects characterizations to provide a Tier 2 risk assessment in sections 2.3.1.2 and 2.4.6. Most importantly, section 2.4.6.4 also describes the combination of Tier 2 exposure and effects outputs to produce Joint Probability Curves which are the fundamental feature of the proposed ECOFRAM Tier 2, 3 and 4 risk characterization steps.

From an exposure standpoint, work occurs in Tier 2 because the initial Tier 1 assessment did not provide a clear cut answer that there was “no problem” regarding potential aquatic ecological impacts. Since Tier 1 is designed to be protective rather than predictive, a substantial proportion of compound will require a Tier 2 exposure characterization.

The Tier 2 process is relatively specific and, one of the ECOFRAM workgroup’s objectives became the design of an idealized Tier 2 process which should be able to be conducted and interpreted by different risk assessors and risk managers reproducibly to provide broadly similar outputs.

3.7.4.1. Objective/Purpose

The intent of Tier 2 is to provide a distribution of exposure concentrations in surface water adjacent to treated fields for appropriate product use patterns,. Tier 2 differs from Tier 1 in that multiple scenarios are evaluated for a specific use pattern by incorporating spatial-temporal variability in use patterns (soils, weather, geomorphology) and additional

physicochemical processes are represented using a more mechanistic approach (deterministic models as opposed to meta-models). The tier remains conservative by focusing on headwater systems adjacent to treated fields and by using an upper bound confidence interval for chemical input parameter values.

The exposure assessment is designed to:

- Characterize spatial-temporal variations in exposure to headwater ecosystems;
- Produce monthly, seasonal, and annual frequency distributions;
- Provide a regional ranking of exposure;
- Prioritize environmental settings and/or use patterns in terms of potential exposure;
    - Identify use patterns that have minimal environmental/ecological concerns;
    - Focus future work on specific scenarios of concern.
- Address limited number of mitigation options;

3.7.4.2. Conceptual ideal Tier 2 process

Conceptually, Tier 2 would be an automated process with user input limited to product-specific properties that include the crop of interest; geographical restrictions that may exist because of pest/disease pressures or other market reasons; rates, frequencies, and methods of application; and chemical properties that dictate mobility and persistence. Two sets of chemical properties would be evaluated: a "conservative" estimate of chemical properties would form the basis of the risk assessment and a "best-estimate" set of parameters would be evaluated for risk characterization purposes.

Tier 2 would consist of standardized scenarios to allow chemicals to be evaluated under uniform and consistent procedures. Scenarios would represent realistic conditions under which the crop is grown and the pesticide is used. Scenarios would be grouped by region to reflect regional characteristics with respect to physiography, pedology, climatology, geomorphology, and environmental chemistry; scenarios to permit national scale risk assessments will also be required. Each region would contain two headwater systems characteristic of the region. Generally, these would include a lentic and lotic system capable of addressing different aquatic species and hydraulic residence. Systems would be defined such that they address both federal and state regulatory needs. Parameters that may vary between region include drainage area to water body size ratios, temperature, pH, and other water quality characteristics. For each water body, a range of soil and climate conditions would be represented appropriate for the use pattern.. For some regions, drain tile may an important pathway for source loadings to aquatic systems and appropriate for representation in the scenario.

Important processes that govern chemical fate and transport would be represented with state-of-the-art and/or accepted model technology. Models would appropriately allocate the applied pesticide to foliage, within the soil, or directly to the adjacent water body as a result of direct application or drift. The models would preserve water and chemical mass balance by simulating biological, chemical, and hydrological processes. Processes would account for various dissipation pathways

on foliage, soil, water column, benthic sediment media including foliar washoff and degradation, soil-water partitioning, leaching, runoff, plant uptake, hydrolysis, photolysis, and microbial degradation.

For most analyses, simulations would be conducted under variable weather conditions. Drift, washoff, runoff, leaching, degradation, advection, and dispersion could potentially vary as a function of weather. Weather records having at least 35 years of data are recommended to address end-point recurrence intervals of 10 years or less. Longer duration records are recommended to address longer-term return periods.

Output would reflect good modeling practices (Estes and Coody) and include the date that the simulation was conducted, the version of the software used to conduct the analysis, a point of contact for the individual who conducted the analysis, an echo of all input parameter values, and standardized output on simulation results. Output would be layered to address a hierarchy of analysis. One level of output would contain cumulative area-weighted probability curves (nationally and by region) for standard exposure duration concentrations in both tabular and graphical format. Probability curves include instantaneous peak concentrations, 24-hour, 48-hour, 96-hour, 21-day, 60-day, and 90-day durations for monthly, seasonal, and annual maximum series (per Section 3.6.5). Included in this level would be thematic maps indicating where soil/climate combinations are most likely to occur at different risk end-point levels. A second level of output would contain frequency distribution curves for each individual scenario. A third level of output would produce the summary information related to mass loadings (e.g., drift, runoff, erosion) for the scenarios closest to the assessment end-point criteria. This information can be useful in cause-and-effect analysis to address chemical migration pathways and to help outline potential mitigation alternatives. The output should also be combined with RADAR style output for statistical review of exposure events.

Ideally, Tier 2 would be constructed using modular (object-oriented) technology with respect to data bases and predictive algorithms so that the operational software could remain flexible in its ability to adapt as data sources, model technology, and risk assessment end points evolve.

3.7.4.3. ECOFRAM's Interim recommendations for current implementation of a Tier 2 Exposure Assessment

3.7.4.3.1.Integration with Existing Technology.

Tools that currently exist to accomplish this work include the Multiple Scenario Risk Assessment Tool (MUSCRAT). MUSCRAT is an automated processor linking the Pesticide Root Zone Model (PRZM) and the Exposure Analysis Modeling System (EXAMS) with crop, soil, and meteorological data bases. Limitations and/or suggested refinements to MUSCRAT would include better definition of regional-specific headwater systems (with maintenance of correlated values for important parameters by region/soil etc.); sediment and as well as water column concentrations; a national as well as regional area-weighted probability analysis; statistical analysis more directed toward actual risk by addressing crop production as opposed to crop suitability; an ability to address variability in drift loads based on meteorological data; and standardized output. PRZM and it's interface with EXAMS is limited in ability to address pesticide loadings at sub-daily

time resolution which may be important in smaller headwater systems. This would require that meteorological input changes in rainfall intensity either through sub-daily time steps or through some statistical definition of the storm event. PRZM would need to characterize the corresponding runoff hydrograph sediment yield, and chemograph, at a sub-daily time step. Lateral subsurface flow and tile drainage routines would also need to be developed for mass balance accounting. Algorithms in both PRZM and EXAMS and/or their successors need to be documented with respect to their ability to adequately simulate physicochemical processes important in the short-term and long-term dissipation of toxic residues, including foliar washoff, plant uptake, and the kinetics of soil-water partitioning. It could be advantageous if a subset of scenarios were similar in configuration to actual monitored systems (e.g., NAWQA or MESA programs) for model validation purposes.

Additionally, efforts are needed urgently to link EXAMS with AgDrift to produce an integrated probabilistic estimate of exposure with time that reflects the stochastic nature of both the drivers for runoff (already included in current models) AND the distributions of wind speed and direction that causes variation in the potential for drift entry to water bodies.

3.7.4.3.2.Inherent Assumptions.

While Tier 2 broadens the exposure characterization to some degree by representing a distribution in soil and weather combinations, the analysis is limited in its representation of landscape and water-body configuration. In reality, landforms contain an unlimited number of permutations in system heterogeneity. The intent in Tier 2 is to address regional tendencies in vulnerable headwater systems. A Monte Carlo analysis on other conditions can be addressed in a subsequent tier focused on specific scenarios or issues of concern.

Tier 2 is an important step in the risk characterization process and, because it may build-in additional environmental dissipation mechanisms and field data, it may sometimes result in exposure estimates that permit regulatory decisions to be made with sufficient confidence that the uncertainty has been adequately characterized. This is particularly true where additional Efate processes not included in Tier 1 (e.g. photolysis on leaf surfaces) are significant to compound dissipation. However, in many cases, Tier 2 will be unlikely to filter out products such that at least a minumum amount of Tier 3 activity will be needed.

3.7.4.3.3.Progression to Tier 3

Three decision points are possible from a Tier 2 risk assessment:

1) The risks are determined to be minimal and the registration process may continue;
2) Label modifications are required to ensure that the distributions of concentrations would not generate risks of concern; or
3) The exposure assessment needs to be refined to prove that the concentrations predicted to be of concern are unlikely to occur in practice.

Label modifications that can be addressed in Tier 2 include changes in application rate, timing, and frequency; changes in application method or formulation; and use restrictions. It is logical that Tier 3 would focus only on issues that remain of concern. Some of these issues could become formulated by a more intensive evaluation of model output for those scenarios showing highest concern. These include evaluating the predominate source of chemical loading (drift, runoff, drain tile, erosion); co-occurrence with sensitive non-target organisms; and key characteristics of the exposure event (e.g., magnitude, dose-commitment, duration, and inter-event recovery interval).

3.7.4.4. Recommendations for Improving Tier 2

In order to deliver the idealized Tier 2 process described in section 3.7.4.2 above several improvements are needed to the current exposure modeling procedure.

3.7.4.4.1.Scenario Selection

The first is to devise a better system for selecting relevant scenarios that that used for the current MUSCRAT process. It is important to recognize that some of the constraints originally considered when MUSCRAT was developed were the result of potentially slow processing times. Hardware improvements over the last two years have rendered some of these concerns as non-issues in 1999 and permit more sophisticated alternatives to be recommended.

One of the principle limitations of MUSCRAT is its reliance on STATSGO to link soil mapping polygons with the potential to produce crops. The data in STATSGO is old and, particularly for common crops, exaggerates the number of soils that might be used to produce crops. Many alternative approaches could be devised to address this and ECOFRAM recommends this activity be given a high priority. One example of such an approach is given below.

1) Create basic GIS coverages representing the maximum number of scenarios possible

- Prepare a GIS data set of "base polygons" formed by intersecting hydrologic unit boundaries (HUC8 - see section 3.6.2.6), Major land Resource area (MLRA - see section 3.6.2.4.) boundaries and county coverages. In some states where NRI (see section 3.6.2.8) data is also spatially linked to soil mapping units, this additional layer can be added to produce a more spatially explicit coverage.
- Link the "base" polygons derived above to the NRI
- Derive data for each of the base polygons for the following criteria:
    - Runoff potential (using the San Diego supercomputer data)
    - Cropping potential for each specific crop or common crop rotation pattern (using the NRI)
    - Cropping density (using the NRI)
    - Existence of a Community water system using surface water
    - Co-location with a NAWQA study unit and/or intensive sampling area

2) Use the basic coverages to develop a subset of polygons for specific crops

- For a specific crop, filter the "base" polygons for all known to have grown the crop over the last three seasons (NRI)
- From this subset, examine
    - the distributions of runoff sensitivity and cropping density
    - the distribution of base polygons between Ecoregions
    - the occurrence of polygons with features of special interest (e.g. NAWQA sites with monitoring data)
- Determine rankings of polygons against all these criteria

3) Select a suitable subset of crop specific polygons for a particular product

- Determine criteria for selection of scenarios for modeling purpose in hand e.g.
    - number of scenarios required
        - One for Tier 1
        - 20 - 50 for Tier 2
    - Balance of "real" polygons (polygons normally smaller than 50 sq.mi. where a detailed evaluation of local soils and cropping has been conducted - likely to be associated with polygons of special interest such as monitoring sites) versus "hypothetical " polygons (polygons where data from the included NRI points will be pooled)
    - Initially for "real" sites and perhaps later for all polygons, available remotely sensed data (e.g. MRLC program 152.1.67.36/us_maps.html) should be used to define the extent of agriculture (and perhaps of specific crops) within the unit.
- Select polygons as determined above by considering use pattern specific factors to generate the necessary "minimum" dataset necessary to generate a probabilistic exposure assessment that will adequately describe the uncertainty in exposure e.g.
    - Must include at least one scenario representing ~90th%ile of cropping density
    - Must include at least one scenario representing ~90th%ile of runoff potential
    - Should include at least one site for which there is monitoring data (e.g. NAWQA/MSEA)
    - Should include several sites for which there is a CWS drawing from Surface water with analytical data
    - Should represent the full range of ECOREGIONS and MLRA's representing this crop (or region)
    - Should represent the range of soil types for the crop
    - Should provide a balanced representation of the most significant cropping "regions" for this crop
    - Should include at least one coastal HUC8-MLRA if estuaries are of interest
    - Should include representation of the cropping "regions" with the highest application rate
    - Should include several "representative" (i.e. typical) sites as well as low exposure potential sites when they are important to reflect risk in certain regions (e.g. include a Southwest site for cotton even though runoff risk is low)
    - Should include sites representing conservative physical properties
- Express the significance (context) of the selected sites by displaying them within the distribution of all the polygons for this crop.

- Document the selected sites and make available to the regulated community via an EPA web page

4) Develop the necessary model parameters for the selected polygons and conduct the modeling.

- Using a "user friendly" shell similar to the current MUSCRAT, generate the model runs.
    - For real sites, specific input parameters will be available
    - For "hypothetical" sites, Monte Carlo approaches may be used to prepare combinations of input variables as needed.
- Exposure estimates made for various headwater environments.

3.7.4.4.2.Other needs for Tier 2 modeling

The ECOFRAM Aquatic Exposure Workgroup recognized other needs to improve Tier 2. To avoid duplication, they are given in sections 3.1.2.2.4 and 3.1.2.2.5.

3.7.5. Tier 3 - Refining Exposure

Figure 3-24. The Aquatic risk assessment process for Tier 3

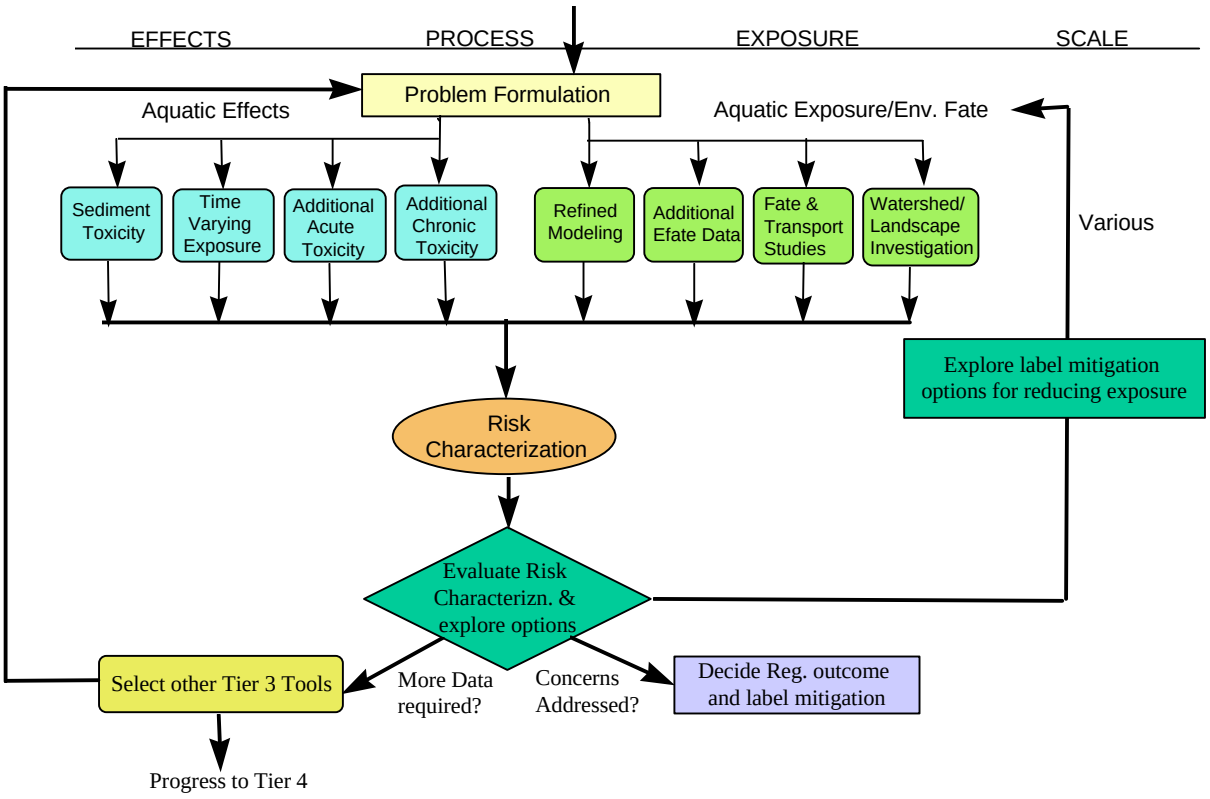


Figure 3-24 above depicts Tier 3; there is also a more general discussion of the application of Tier 3 and the amalgamation of exposure and effects characterizations to provide a Tier 3 risk assessment in sections 2.3.1.3 and 2.3.7. From an exposure perspective, work occurs in Tier 3 because either the Tier 2 output was too uncertain to justify any further regulatory debate and/or the Tier 2 predictions suggest that the chemical/use pattern is associated with unacceptable risk unrelieved by the simplest mitigation options. Although opportunities exist to refine the risk characterization from both the toxicity and exposure perspectives, the majority of effort traditionally centers around efforts tot refine the understanding of exposure. It is important to recall that the RISK CHARACTERIZATION process is identical to that in Tier 2 but the details produced by the exposure and/or toxicity analyses will be more refined. To achieve this refinement, the ECOFRAM aquatic groups recommend that a “Tool-box” approach be adopted so that rather than having mandated studies to conduct at a higher tier, the risk assessor should draw from a range of options.

Example tools or studies that could be incorporated in this Tier include:

- Refined Tier 2 modeling
- Refined input parameters based on additional laboratory fate data
- Better representation of actual landscape configuration in model scenarios (e.g., distance from application areas to water bodies, field size to water body size ratios, vegetative filter strips)

- Fate and transport studies to better understand and represent physicochemical processes (e.g. field dissipation studies using radio-labeled materials, small-scale runoff studies, fate-o-cosms)

3.7.5.1. Modeling the Impact of Mitigation Options on Exposure Estimates

Still to be amplified as marked below - I have had a go following the recent talk at ACS - Marty could you have a stab at improving this and addiing bits from your latest talk

The ECOFRAM group (and the FIFRA EMWG before it) had some philosophical debate about the value of trying to model the impact of various mitigation options given the likely relatively small impact of some technologies (e.g. perhaps 2 to 9 fold reduction of sediment transport by vegetative buffers against the relatively high uncertainties associated with the initial exposure estimations). After discussion, it was agreed that the exercise is a highly worthwhile one since it provides an evaluation of the likely scale of impact of the various techniques and, potentially, a ranking of the "mitigative value" of the approaches.

3.7.5.1.1. Current status

Clearly, although none of the existing FIFRA regulatory models have modules available to handle some of the most important aspects of the impacts of mitigation, several mitigation related processes MAY be incorporated into Tier 2 modeling already. For example, we can currently address:

Aerial application meteorological restrictions and buffers.

The Spray Drift Task Force AgDrift model already incorporates the potential impact of aerial buffering as well as the standard practice of allowing "swath offsets" upwind of a sensitive area. The underlying modeling is based on an extensive recent field database and may be considered relatively well validated. However, there is a problem because the current version of the AgDrift model is very deterministic in approach and prescribes buffers without considering the impact of additional alternative mitigation approaches. Moreover, the way the model assigns a buffer requirement is currently determined by an assumption of a wind speed of 10 mph; the system does not consider the regional probability of wind speeds in this assessment. There is a pressing need for developments to be made to AgDrift and its supporting regional wind speed and direction databases in order to incorporate the probability of drift into Tier 3 model refinements.

Reductions in application rate, frequency of application and modification of inter-spray intervals.

The standard Tier 2 models already permit ready manipulation of these parameters

Incorporation of chemical at application

Although poorly validated, routines exist within the current models to address making the chemical less available via incorporation AWAY from the active surface zone for runoff mixing

Improving rain-fastness and/or foliar degradation characteristics

Provided field data exist to support these two issues, they can already be incorporated into the existing model suite.

Tillage restrictions and limitation from use on highly erodible Lands (HEL)

This can be addressed to the extent represented by USLE factors (updated recently in the RUSLE manual ref xxxx). However, the capability with dealing with variable settings within a field is not yet present and the impact of crop residue and tillage status is currently based on sediment flow more than pesticide transport

3.7.5.1.2.Needs for future development of models

Marty to add aspects of his recent paper (certainly reference and general points here) We need to develop models that can examine the impact of buffers and mitigation measures

3.7.5.2. Generate Additional EFate data to improve the understanding of exposure estimates

Tools in this category might be adopted where it is thought useful to obtain information expected to reduce Tier 2 uncertainty by permitting replacement of default model assumptions with actual data (i.e. refining Tier 2 input data). One of the key points is that it can refine the understanding of chemical specific behavior not normally accounted for in the exposure estimation process.

Examples of what might be attempted here include:

- Additional laboratory aerobic/anaerobic soil, sediment or aquatic degradation studies to generate a more meaningful understanding of the relevant distribution of behavior. This could cover the increasingly common employment of studies covering a wider range of soils in order to plot a distribution and reduce the application of conservative assumptions by regulators. Alternatively, it might involve experiments to categorize the temperature and/or moisture degradative behavior of the compound of interest)if it was thought that the equations by Walker (xxxx, 1996??XXX) were not applicable
- Alternatively (if not conducted at an earlier tier), foliar washoff and/or degradation studies fall clearly into this category
- Adsorption/desorption studies are similar to laboratory degradation experiments. Work can either be conducted to expand the range of values across a relevant range of soils or “compound specific” issues such as the possibility of increasing adsorption upon “field aging” of residues can be investigated

There are many other approaches that can be considered in this category. The common link is that the work is conducted to refine and/or better characterize a Tier 2 input and then the Tier 2 work is repeated.

3.7.5.3. Conduct fate & transport studies to better represent and understand processes

Tools of this type might be investigated as options to increase the risk assessor’s confidence in the model’s predictions and particularly to help get a focus on the relative importance of “real world” processes or to determine if modeling using the regular approach is “missing” something. Essentially they are tools to verify or refine Tier 2 modeling inputs.

Some examples of useful additional Fate and Transport studies are given below. The work group provides several examples of studies that might prove useful. However, the key aspect here is that studies should be designed to meet a particular chemical/use pattern issue and, as such, the guiding principle should be to design a focussed and specific study on a case-by-case basis.

3.7.5.3.1.Fate-o-cosm Studies

Laboratory studies of the environmental fate of compounds may leave uncertainties concerning the behavior of chemicals in aquatic systems. Uncertainties, for example, may be related to concurrent and multiple degradation/metabolism pathways occurring in the environment which are not examined in the laboratory, questions concerning bioavailability of the compound, or the influence of different product formulations. Aquatic microcosm systems focused on providing additional information on the behavior of compounds in natural waters may provide an opportunity to address these and other questions.

Typically, aquatic fate microcosms conducted to date have used moderate to large (>5000 l), outdoor tanks established to mimic waters associated with agriculture (e.g. farm ponds) however systems could be established to represent various water quality parameters of interest. Smaller scale indoor systems might also provide useful information. Design considerations include compound formulation, dissolved vs. absorbed phase dosing, appropriate concentrations and biotic as well as abiotic characteristics of the system. Measurement endpoints should be focused on addressing specific uncertainties but typically concentrations of parent and relevant degradates over time, in water and sediment would be included. Residue concentrations in selected, targeted biota may provide refinement of exposure concentrations.

Results from fate microcosms may be used to refine the input parameters for exposure models, such as the aquatic dissipation rate, water/sediment partitioning, degradation within the sediments and estimated bioaccumulation rate. Since fate within microcosms represents combined factors (i.e. hydrolysis, photolysis etc) care should be taken not to account for mechanisms more than once.

3.7.5.3.2.Small-scale runoff studies

Small scale runoff studies (most often with simulated rainfall - SSRO studies) can provide opportunities to:

- Verify exposure model runoff predictions on one or more soils
- Investigate comparative runoff between the compound of interest and a benchmark compound for which monitoring data may already be available.

The strength of the SSRO study design is that it reduces many of the uncertainties that can render a classic large scale field runoff study useless (Hendley et al, 1995). The approach controls key variables such as

- timing of simulated rainfall relative to pesticide application date
- slope uniformity
- rainfall intensity and duration

The approach also controls key logistic issues such as

- Site selection
- sampling problems
- replicability
- timing and costs of resources to conduct the study

The approach is most useful for comparative studies (e.g. for investigating the impact of formulation changes as a potential mitigation tool but in addition studies have shown that the approach CAN provide sediment, runoff water and pesticide data that can usefully be "scaled" to help validate runoff model output.

3.7.5.3.3.Field soil dissipation studies using radiolabeled materials

A two-fold example here comes from the area of understanding soil dissipation. Currently, after most of the required subpart 158 studies are completed, a judgement is made that potentially all the major (>10%) metabolites identified in the earlier studies should be considered as potentially being available for transport to other environmental compartments and thus to potentially interact with non-target organisms. At this stage, this is a decision that makes sense from a regulatory perspective in the absence of further information. Additional studies (such as the field radio-labeled dissipation study mentioned below are prime candidates to focus transport concerns on the metabolite that ACTUALLY ARE of significance under "real world" conditions.

Similarly, Tier 2 exposure modeling and beyond use a default set of inputs based on the laboratory data to estimate degradation in topsoil. The only true scientific value that derives from conducting the subpart 158 field soil dissipation study (unlabeled material) is that the "real world" half-life data provides "checks and balances" on whether model processes mimic reality or whether they are "missing" an important factor. For example, some compounds can be degraded readily by anaerobic processes even in the uppermost soil layer; classical application of modeling would fail to represent this and would underestimate field dissipation rate and hence overestimate potential runoff transport across a season.

3.7.5.4. Refining Tier 2 Modeling

This option might be selected when the Tier 2 risk characterization indicated a need to better define the uncertainty associated with the modeled exposure concentrations. Alternatively, additional Efate data might be useful where knowledge of the chemical or use pattern suggested that incorporating additional variables might be necessary to properly define the environmental fate processes involved in the field. Refined Tier 2 modeling may also be critical to deciding which of several variables most strongly influences the ultimate exposure estimate (i.e. a sensitivity analysis).

Clearly, in order to conserve resource, sensitivity analyses should be run as early as possible in the process in order to ensure that only limited effort is expended on issues that are likely to have only minimal impact on the final estimates.

3.7.5.4.1.Examples of Refining Tier 2 models

Examples of what might be attempted include:

- Incorporate refined parameters and/or regionalize the earlier Tier 2 values
- Detailed evaluation using AgDrift of the probability of spray drift based on wind speed (and/or direction is a spatial analysis has been conducted.
- Examine the impact of mitigation alternatives in detail
    - placement, width, severity etc
- Run models using customized aquatic receiving water scenarios - perhaps selecting waterbodies other than ponds that are more suited to the region(s) in question.
- Run models using customized scenarios - perhaps building in temporal and/or spatial issues
- Probabilistic analysis techniques e.g. Monte-Carlo techniques to draw values from distributions describing key parameters to determine the most likely range of exposure estimates PLEASE CAN SOMEONE CONSIDER ADDING SOME FLESH HERE
    - There are several questions raised by these Tier 2 Monte Carlo based refinement options. In particular, tools must be developed to reproducibly describe the shape of a distribution and to agree and define the procedures by which we gather and report such data
- Compare Tier 2 modeling with benchmark monitoring data by running the "benchmark compound" under the same Tier 2 scenario as the compound of interest and then drawing comparisons. The comparative data, after due consideration of application rates, timing and likely market penetration of the new product, can then be linked to existing monitoring databases to make some conservative assessment of potential exposure under use conditions.
- Running secondary models that better represent system(s) (e.g. ResWQ, RICEWQ). As mentioned in original guidance from EPA, it is important that secondary models only be used "in extremis" and when the more usual Tier 2/3 approaches have been applied. The registrant must justify why selection of a secondary model was unavoidable and provide all results in comparison with classic Tier 2 output.

3.7.5.5. Improving the Representation of the actual Landscape Configuration in Model Scenarios

A relatively new approach that the ECOFRAM workgroup is recommending should be included in the "toolbox" of options available at Tier 3 is the investigation and refinement where necessary of the "reality" associated with various assumptions inherent in the model input parameters describing the model scenario. Use of this approach may be appropriate in order to refine the model scenario assumptions prior to rerunning Tier 2 modeling, characterizing model scenario assumptions in terms of the relative significance of the chosen scenario relative to the "universe" of such scenarios. Alternatively, the technique may be selected to improve the understanding of the regional or crop specific landscape or to refine the understanding of uncertainties association with spatial variability across the landscape.

Aspects of interest may include some or all of the following:

- Typical occurrence of the crop of interest in a watershed or region and the distribution of land cover types

- Information on the water bodies and their type/size/frequency within the area of interest. Additionally, regional spatial variation of water body type, depth, flow characteristics and volume may be significant
- Proximity of crop to water bodies. How often is the crop close enough to water bodies of various types for runoff or drift to be significant. How often is it directly adjacent.
- What percentage of water bodies of each type may be impacted
- Field size to water body size ratios and directional relationships between crop and nearby water bodies (e.g. how many wind directions will potentially lead to drift of residues to each water body
- Extent, position and characteristics (width and compositions) of vegetative filter strips or physical buffers between agriculture and water bodies
- Better understand weather parameter variability or the characteristics of water bodies
- Assess significance of spatial variability of land/soil with respect to areas planted with the crop of interest. For example, what proportion of crop is grown on runoff prone land.
- Assess significance of agronomic spatial variation

Since this is a relatively novel approach (Hendley et al, 1996;Mangels et al, 1997; Solomon et al, 1997), a detailed example is attached below.

3.7.5.5.1.An example of the Landscape Analysis Approach

Various landscape evaluation and modeling approaches were undertaken for the pyrethroid insecticides by the Pyrethroid Working Group (PWG - an association of the 6 US pyrethroid manufacturing companies). This information is in review for publication (Hendley et al, in press; Travis et al, in press)

3.7.5.5.1.1.Background:

The problem to be addressed was that the use of EPA's Tier 2 aquatic exposure assessment procedures for the use of pyrethroids on cotton resulted in anticipated pond concentrations exceeding the LOC for aquatic invertebrates. The application of MUSCRAT resulted in comparable exposure values; however, even then, the predicted exposures, decline curves and LOC exceedance produce predictions that were not congruent with the experience of several years sales or chemical fate results found in the extensive series of mesocosms run by the PWG companies in the late 1980's. As a result, the PWG decided to investigate the validity of some of the assumptions inherent in the existing Tier 2/3 models and developed a study design that can be considered as an example of a Tier 4 study.

The approach taken by the PWG at Tier 4 was to examine the probability of some of the key Tier 2/3 conservative assumptions co-occurring within a Mississippi cotton agricultural landscape. Although many more of the underlying assumptions merit more detailed consideration, this analysis focussed in particular on the first five of the following factors:

- Drift towards the pond occurs from all applications - i.e. the wind is always blowing to the pond

- No inclusion of the aerial label mitigation (buffer) statements when considering drift.
- No impact on runoff transport attributed to label mitigation (buffer) statements
- Slope/length was 0.4 (equivalent on MS soils to slopes ≥ 3%)
- No marginal vegetation present to reduce spray drift deposition
- 10 Ha watershed is 100% cropped with cotton
- Cropping and treatment occurs up to the edge of the pond
- Watershed (10 Ha) drains to 1 Ha pond (MS)
- Maximum number of applications are made at the maximum rate
- 100% of applications are made by air.
- Wind speed is 10 mph for all applications
- All soils are of high erodibility

3.7.5.5.1.2.Methodology

To investigate these factors, remotely sensed satellite imagery with 30 m pixel resolution (LANDSAT^{TM}) was classified to identify water bodies and land-use. This was then combined with USGS digital line graph data for roads and hydrology to produce a dataset that defined even small streams below the level of resolution of the basic imagery. The Landuse/Land cover (LULC) classification was designed to be conservative (i.e. if in doubt, classify a questionable pixel as cotton); the resulting classification proved to be in close agreement (within 7%) to the USDA county production statistics for that year. The accuracy of the classification was "ground-truthed" against nearly 12,000 acres across 4 regions within the county of interest and the overall accuracy found to be better than 90% for cotton.

The PWG selected a pool of potential counties for this analysis via the progressive process exemplified below

- Select all USA counties producing cotton (448)
- Select the top 50% of these based on cotton acres in 1987 (225)
- Select the top 50% of the above counties based on acres of water in the county (113)
- Select the top 50% of the above counties based on reported insecticide usage (57)
- Select the top 50% of the above counties based again on cotton acres (29)
- Eliminate counties isolated from typical cotton areas (26)
- Eliminate counties where water acres dominated by marine or Mississippi river (8)
- Eliminate counties where probable local cooperation was poor (6)

Of the final pool of counties, Yazoo, MS was selected because in addition to the fact that it represents both Delta and upland southern cotton, it has been the representative modeling scenario for both Tier 1 and Tier 2 exposure assessments for several years and moreover, an EPA approved region specific Tier 2 scenario was available.

Figure 3-25 shows the LU/LC coverage developed for the study at a low resolution showing the Delta (western) half of the county but also showing the escarpment that separates the Delta from the uplands. Interesting findings were that the

largest water bodies were "Oxbow" lakes (lakes arising from historical river meanders which became isolated from the main river channel as a result of natural sedimentation and flow changes) and that cotton appears to be frequently grown on the sandier materials deposited adjacent to old river courses.

3.7.5.5.1.3.Results of the Remote Sensing Landuse and Land cover data.

The classified imagery was used to assess the questions described above.

Composition of the region (i.e. the Land Use/Land Cover) - this provides the distribution of crops, roads, water bodies and woods etc. This permitted an assessment of the most susceptible water bodies (static ponds 46% of the water area) and an analysis of the distribution of sizes. Of the approximately 600 ponds, 427 were 5 acres or less but the majority of the pond acreages was contained in just 20 of the oxbow lakes.

Proximity of cotton to the water bodies - this analysis was performed by drawing imaginary margins (60, 120, 180 and 360 m) around each water body and examining the percentage of cotton present around each of the water bodies (see Figure 3-26). This analysis showed that:

- Over 92% of the ponds had no cotton within 60 m
- Over 68% of ponds had no cotton within 360 m of the pond.
- Relatively few of the ponds <10A had any cotton within 360 m.
- For ponds which DID have cotton within 360 m, only between 11 and 25% of the marginal area was composed of cotton.

Proximity of water to cotton fields - this involved a similar analysis to the cotton/water body example above- it showed that 65% of cotton fields had no water within 360 m.

Directional Interrelationship Between Cotton and Static Water Bodies: The third type of information derived from the Land use/Land Cover classification was an assessment of the extent to which cotton fields "surrounded" each water body (an assumption inherent in Tier 2/3 drift entry calculations is that the wind always blows towards the pond from the aerial applicator). This analysis was performed as shown in Figure 3-27 to assess whether cotton was present in each of the 8 cardinal quadrant directions from EACH pixel on the margin of the water body. These results were then combined to assess the overall susceptibility of the water body as a whole to drift from any direction. This analysis showed that:

- Only 4% of ponds have cotton with 360 meters and in all 8 possible wind quadrants
- Of the ponds with cotton within 360 meters, only 43% would receive drift from more than half of the possible wind directions
- This data may be combined with information on local hourly wind speed and direction to perform detailed assessments of the risk of drift entry to ponds.

Soil and Slope Information: Using some additional datasets on the soils and topography within the county, the co-occurrence of cotton cropping with soil and slope information was examined. From this, it was found that 92.5% of the cotton area has slopes less than 2% and only 3% has slopes >3%. Again, this is very different from the default assumptions used when following modeling Standard operating Procedures for Tiers 2/3

Composition of buffers to physical drift: An additional approach using a subset of the ponds in the county employed aerial photography with a resolution of 1 meter to obtain more detailed information about the vegetation physically separating water bodies from cropped areas. In this case, images were classified into agricultural and non-agricultural areas in the regions immediately adjacent to the ponds and then transects were drawn from a point at each meter along the edge of the agricultural field to the nearest point on the water body. The composition of the vegetation along each transect was analyzed by reference to the classified imagery. The results from this showed that:

- 54% of buffer areas (60 m or less) were comprised of dense trees
- Only 20% of buffer areas were bare ground or grass.
- The mean width of the dense tree areas of the buffers was 24 meters.

This indicates that there is a substantial level of occurrence of physical buffers between agricultural fields and water bodies that are likely to impede the drift of residues to the water body. Further research to determine the likely attenuation of drift that will be caused by different widths and compositions of buffers under different meteorological conditions.

3.7.5.5.1.4.Use of the Remote Sensing results to adjust modeling parameters.

The results from the remote sensing and land use classification were combined and the marginal composition values for each of the 597 ponds/lakes in Yazoo county were used to adjust drift and runoff simulation model input values as compared with the standard EPA Tier 2/3 assumptions. Only a limited subset of the data available from the Landscape assessments performed above was incorporated into the revised Tier 2 modeling:

- The area of cotton and other land uses present within the 0 - 60m, 60 -120 m, 120 - 180 m and the 180 - 360 m margins around each pond.

In addition to this spatial information, the reported distribution of aerial and ground pyrethroid applications to Mississippi cotton and the presence of the mandated no spray buffer areas from the pyrethroid labels was assumed in this modeling.

Simple conceptual models were created to allow the use of the measured percentages of cotton cropping in each margin around each water body to refine:

- the potential reduction in runoff relative to the Tier 2 assumption that 100 percent of the watershed is cropped with cotton. Untreated buffered areas or margins not cropped to cotton were assumed to attenuate sediment/adsorbed chemical transport by a factor agreed with EPA OPP EFED
- the potential reduction in drift entry relative to the Tier 2 assumptions was calculated using look up tables created using Agdrift that yielded a modified drift entry value based on the amount of cotton in each marginal area.

- Drift entry was also integrated over the width of the ponds using a series of assumptions for each of 5 static water body sizes.

The factors described above were computed for each pond and used to modify the 90th percentile Tier 2 output to produce a distribution of potential exposures representing the 597 ponds in the county. This produced a distribution of exposure estimates from which estimated exposure concentrations in the water column, sediment pore-water and sediment from a 90th percentile pond in a 90th percentile year could be derived These values were approximately 12 to 15 times lower than the original Tier 2 values indicating that this approach has the potential to result in significant reductions in exposure estimates.

3.7.5.5.1.5.Conclusions from the PWG Landscape analysis approach

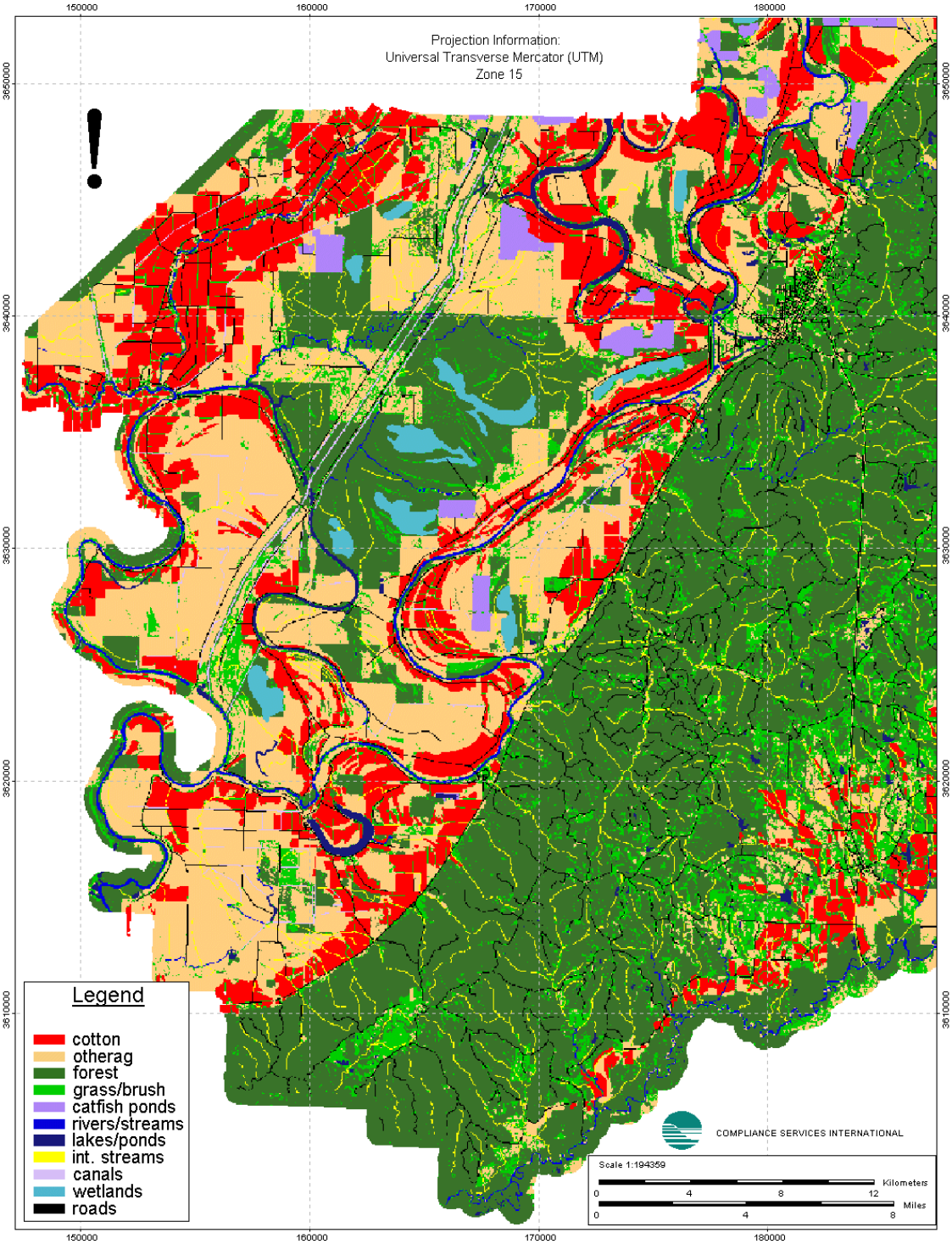
These results show that remote sensing/ landscape assessment approaches provide the potential to provide significant reductions to Tier 2 exposure estimates BASED on measured data acquired with a relatively high level of certainty and which can readily be placed in the context of a wider regional crop "universe"

It is also important to note that the PWG example only used a fraction of the landscape level information obtained. In reality the resulting Tier 3 exposure estimates are still highly conservative because the following assumptions were still not addressed.

- The Tier 2 model assumptions still assume that the maximum number of applications are made at the maximum rate. Data gathered by USDA shows that typically only 4 applications (instead of 6) are made at typically 60% of the labeled maximum rate
- The Tier 2 assumption that every cotton field is treated with pyrethroids
- The wind is always sufficiently strong to give Tier 1 drift levels (10 mph).
- All the chemical predicting as drifting reaches the pond (i.e. no allowance was made for the high incidence of wide physical buffers of dense trees.
- The Tier 2 assumption that implies the slope on cotton fields is 3 - 5 % sloped. The measured data shows this is a 97th percentile value for Yazoo county cotton
- The Tier 2 assumption that the soil erodibility is of a value shown by the GIS to be in the top quartile for Yazoo soils.
- The Tier 2 assumptions that mixing of runoff and drift entry will occur instantly whereas in reality (and particularly in the potentially more ecologically significant larger water bodies), the chemical concentrations will have dropped to undetectable levels before impacting organisms far away from the entry points.

The above points indicate that this approach offers great potential for reducing exposure estimation uncertainty by providing measured values in context in order to refine the model scenario assumptions.

Figure 3-25:: Land Use/Land Cover coverage for Yazoo County, MS generated from LANDSAT™ Satellite Imagery



Land use land cover classification for Yazoo County, MS. West side of study area

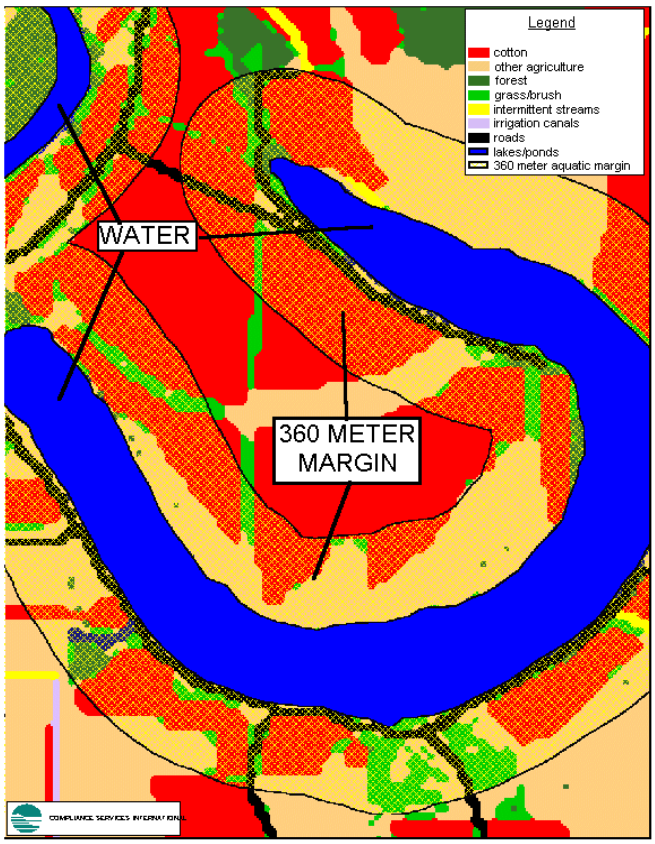


Figure 3-26: Example of how the composition of margins
around water bodies were determined

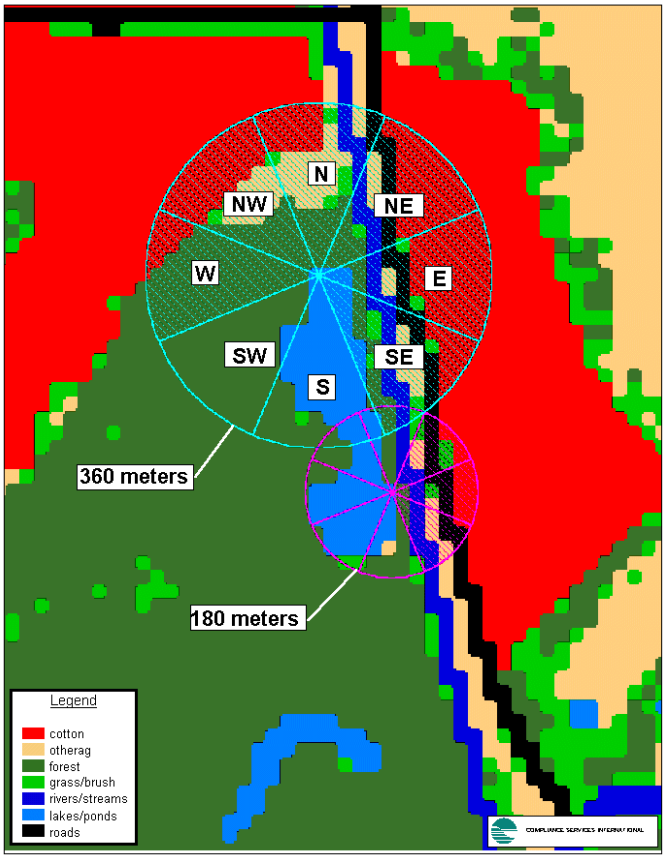


Figure 3-27: The determination of directionality of cotton relative to water bodies

3.7.5.5.2.Landscape Analysis Strengths:

Overall, the initial investigations of the utility of the landscape analysis approach were very encouraging and the PWG concluded that:

- Remote sensing and GIS can be used cost effectively to characterize the agricultural landscape and provide verifiable data to refine exposure assumptions.
- Measurements of the percentage of the crop of interest within various marginal areas around the water bodies judged most at risk can be obtained for exposure refinement and sophisticated modeling.
- Similarly, the approach can provide information on the probability of drift contamination from crops near water bodies. In fact, it should be possible to incorporate local data on wind speed and direction to provide even more sophisticated estimates of the probability of drift.
- Analyses of the soils and slopes characterizing the watershed can be performed.
- Additionally, higher resolution imagery can provide specific details about the identify of vegetation between water bodies and the crops of interest.

- Because this approach modifies many of the basic assumptions of Tier 2/3, the impact on predicted exposure can be very significant.

Some other general conclusions arising from the work included the demonstration that the water bodies of a region are highly diverse and there is a large proportion of ponds which will never receive contamination because no crops are nearby. These ponds can potentially serve as a source of recolonization and a "safety net" to protect bio-diversity.

3.7.5.5.3.Landscape Analysis Assumptions and Limitations

The concept of landscape level analysis is new and the assumptions inherent in the technology are only just being determined. However, there are clearly several basic lessons that have been learned already:

1) The rationale for selection of the target area(s) for the imagery needs to be understood in the context of the "universe:" of that crop on which the compound may be applied
2) The timing for obtaining the image should be managed to correspond to the time when the crop is most readily distinguished from other similar vegetation
3) The accuracy of the classification must be thoroughly understood.
4) With current technology, the resolution of the imagery is likely to be insufficient to pick out small waterbodies such as streams. These can be "added" to the classification using other datasets (e.g. USGS digital line graphs). However, if this is done, certain systematic errors can be introduced; for example, in the example above, each stream or road "became" 30 meters wide in the assessment.

Many other opportunities exist for other imaginative approaches to landscape level assessments. For example, the examination of changes in the landscape across time, integration of the data with flowing water models, links with precision farming etc.

The fundamental limitations of landscape analysis lie with the availability of up-to-date data, the quality of data, accurate geo-referencing of multiple coverages and obtaining suitable resolution for the base level imagery. The work group recognizes that improvements in the availability of suitable datasets supported by high quality "metadata" (the data describing the data and its sources) will be key to effective and uniform use of this type of analysis.

3.7.6. Tier 4 - Major Conditional Monitoring or Mitigation studies

Figure 3-28. The Aquatic risk assessment process for Tier 4

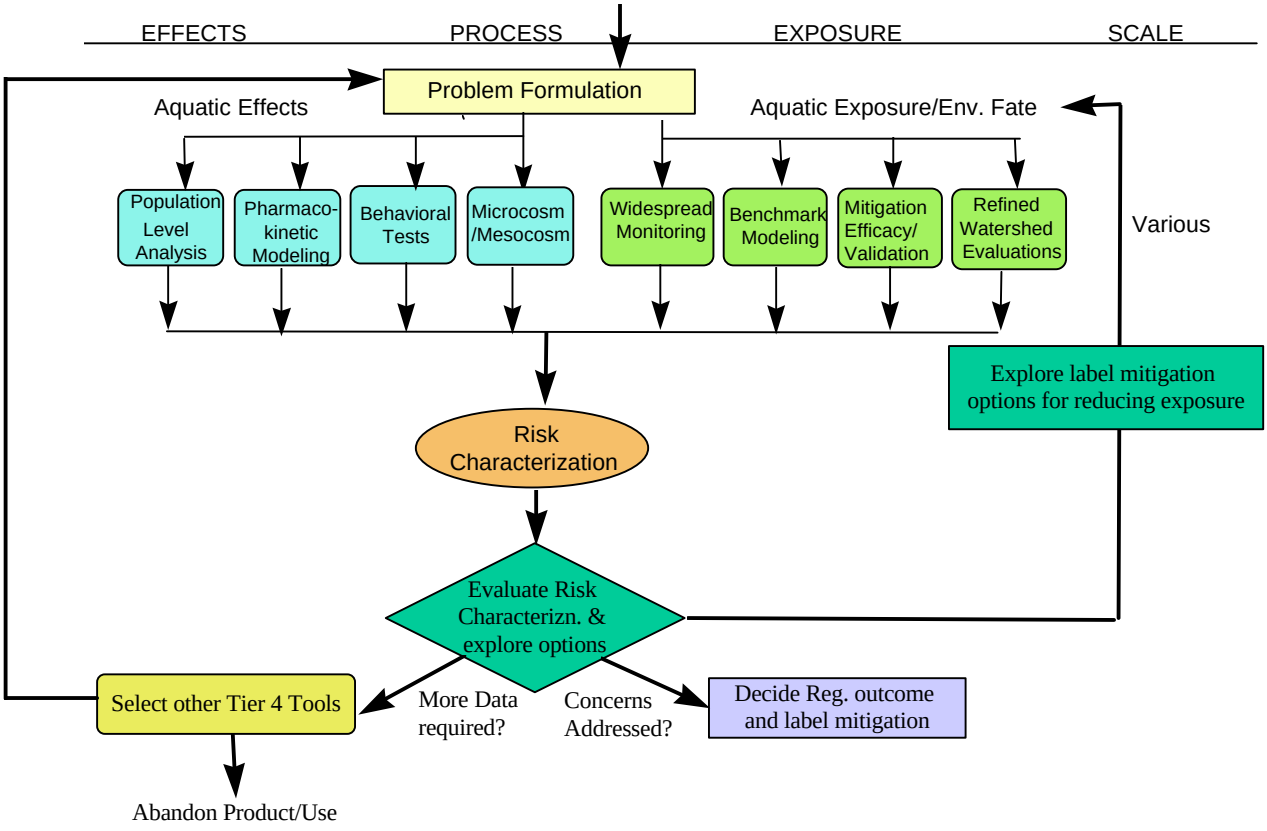


Figure 3-28 above depicts the Tier 4 process; there is also a more general discussion of the application of Tier 4 and the amalgamation of exposure and effects characterization to provide a Tier 4 risk assessment in sections 2.3.1.4 and 2.3.8. From an exposure perspective, work occurs at a Tier 4 level because a Tier 3 refinement of the Tier 2 risk assessment has still failed to adequately refine uncertainties in the Tier 2 risk assessment or the label mitigation steps necessary to achieve adequate ecological risk levels are not economically feasible. Tier 4 contains a variety of approaches, which would be selected on an as-needed basis to address specific issues related to reducing the uncertainty, incorporating additional variability, or otherwise better representing reality in the risk assessment process. Any work conducted under Tier 4 would likely focus around those conditions identified under Tier 3 as having unacceptable risk and be directed toward refining exposure estimates, understanding the factors that are causing unacceptable risk, and developing mitigation strategies to minimize unacceptable risk. As with Tier 3, the risk characterization process is identical to that in Tier 2 and the approach is again that of a “tool box” from which relevant options may be identified. The characteristic of Tier 4 studies is that they represent options with CONSIDERABLE COST IMPLICATIONS and would normally only be attempted as the outcome of discussion and agreement between the registrant and the EPA OPP EFED.

Example tools or studies that could be incorporated in this Tier include:

- Large scale monitoring studies to confirm model predictions
- Highly refined watershed models for Basins/larger receiving waters.
- "Benchmark" modeling/ monitoring to opposite similar chemicals
- Fullest evaluations of mitigation measure impacts

3.7.6.1. Large scale monitoring studies to confirm model predictions

The option of monitoring is becoming more frequently applied as a result of the Food Quality Protection Act (FQPA) legislation. It is an expensive option and clearly one where the programs have to be carefully designed with specific endpoints in mind. For example, studies designed to sample finished water destined for human consumption may not be of value for consideration in an ecological risk context. The workgroup discussed the topic and highlighted the need for great care in interpreting the output of the programs.

3.7.6.1.1.*Discussion of Pro's and Con's of Modeling and monitoring*

A series of strengths and weaknesses of monitoring in comparison with modeling were identified by the work group; these are summarized in table 3-17 below.

Table 3-17: ANALYSIS of PRO's and CON's of MONITORING vs. MODELING

MODELING	MONITORING
PRO	**CON**
Cost Effective (generally less expensive than monitoring)	Costly
Time involved is days to months	Time involved is weeks to years
Ability to evaluate "what-if" scenarios (e.g. climate, soil, application date)	Difficult to design cost effective AND technically viable sampling programs
Ability to evaluate effectiveness of some mitigation measures	May require many years of monitoring and/or paired studies to evaluate effectiveness
Ability to predict concentrations over a continuum in space and time	Handling non-detects is difficulty
Comparative exposure assessments are possible	Results are accepted as "true" values
Ability to simulate concentrations below analytical limits of quantification	Sampling represents discrete points in space and time that can only be put into context with modeling
	Study only represents one unique combination of conditions
	Can be constrained by analytical precision and LOD
	Results can be misleading if one year is a 1 in 100 event year!!
	Difficult to interpret results in a probabilistic fashion
	Cause and Effect may be difficult to assign (especially

	Biological)
CON	**PRO**
Uncertainty in model predictions due to mathematical representation of complex governing processes, programming and user errors and uncertainty in input parameter values.	Provides an actual measurement of chemical residue concentration, hydrologic response etc
Simplifications required in the representation of prototype systems	Avoids conservatism resulting from compounding conservative assumptions
There is general public reluctance to accept predicted data	When done well it is an excellent tool
Calibration is needed to assess how closely predicted values match reality	Accounts for the inherent heterogeneity of the system
Many of the input values have high uncertainties associated with them	There is a greater acceptance of measured data
The selected input parameters may not be environmentally feasible	There is public confidence in monitoring data

The conclusion of this analysis was that monitoring can usefully be thought of as another "model" with definable but relatively high uncertainties. This is particularly true for Surface Water where sampling timings can be critical to capturing an "event" of ecological significance.

The most powerful use of monitoring studies would be as a combination approach using thoroughly planned monitoring data across several years to calibrate models in which regulators have confidence. The modeling will provide probabilistic estimates of exposure across time and space to set the monitoring data into context by consideration of the actual rainfall experienced and the watershed(s) involved.

3.7.6.1.2.Aspects Of Different Monitoring Studies Used To Evaluate Pesticide Runoff

The workgroup also discussed some aspects of the various scales of monitoring operation that might be considered. The results are summarized in table 3-18 below. The conclusion reinforced the earlier statement that great care has to be taken to matching monitoring programs to exactly match the Tier 4 problem formulation.

Table 3-18: Summary of key aspects of the various scales of test watershed that might be used to generate monitoring data

Aspect	**Small-Scale Test Plots**	**Subbasins**	**Basins**
Drainage area size	<0.05 hectare	10 to 40 hectare	10 to >100 km^2
Flow regime	overland (partial)	overland, ephemeral streams, ponds	perennial streams, rivers, lakes, reservoirs
Point of interest	runoff potential	worst-case exposure	large-scale exposure, dilution
Site characterization	high	moderate/high	low
Control over system	high	moderate	low
Simulate precipitation	yes	difficult	no
Study duration	days	season-years	years
Field heterogeneity	neglected	represented	represented
Field-scale influences on pesticide transport	neglected	represented	represented
Artificial Drainage	low	label use	include as realist
Focus	research, idealized system	label use	reality
Calibration w/ transport model	event based	continuous simulation	multiple segments, continuous simulation
Extrapolating model to field scale	questionable	inherent	difficult to verify w/out observations
Extrapolating model to other fields	questionable	questionable	questionable

3.7.6.1.3.Use of existing monitoring data

Notwithstanding the earlier comments about the need to carefully tailor monitoring data to the specific Tier 4 issue, there is potential value to making use of results from ongoing government monitoring programs. The output of programs such as NAWQA, the Heidelberg monitoring work, MSEA studies, the mid-continent monitoring program or the Acetochlor Registration Partnership studies (see section 3.4.1 for more details of these programs) provides data on water samples of various types.

Although the water sample types may not be directly relevant to ecological endpoints, the data certainly can be used to try to calibrate the general level of transport of multiple pesticides from regions of interest. This data can be used to help refine watershed modeling etc. Under some circumstances, even though a formal validation may not be possible, the

generalized use of monitoring data may be used to provide an overall increased confidence about other pesticide transport assumptions and/or modeling approaches.

3.7.6.2. Highly refined watershed models for Basins/larger receiving waters.

TO BE COMPLETED - WHO CAN HAVE A STAB at this??

Basin style stream and river modeling incorporating NAWQA/MSEA sub-basins with existing monitoring data and using a ranking scheme for relative basin risk

Other modeling/spatial extrapolations with existing/historic monitoring, cropping & weather data

The questions underlying scenario selection are:

- What number of scenarios is needed to adequately address exposure?
- How are the scenarios to be ranked?
- How big an area should they represent?
- How do we characterize scenarios?
- How to put them into context (philosophy on sampling distributions)

3.7.6.3. "Benchmark" modeling/ monitoring to opposite similar chemicals

TO BE COMPLETED - WHO CAN HAVE A STAB at this??

3.7.6.4. Fullest evaluations of mitigation measure impacts

TO BE COMPLETED - WHO CAN HAVE A STAB at this??

4. Effects Analysis in Ecological Risk Assessment of Pesticides

This chapter describes the findings of the ECOFRAM Aquatic Effects Workgroup.

4.1. Introduction: Uncertainty in the Analysis of Ecological Effects in Aquatic Systems

The approach of the Aquatic Effects Workgroup to meeting ECOFRAM's charge was (1) to identify, through an initial brainstorming session, some of the chief contributors to uncertainty in the analysis of ecological effects, (2) to refine this list into a set of discrete, but interlocking, issues, and (3) to explore tools, processes, and strategies for reducing the uncertainties associated with each issue. The remaining subsections in section 4.1 are drawn from the Workgroup's initial discussions about the sources of uncertainty in effects analysis. These passages mainly pose questions, with a few hints at some possible answers. They are unrefined and incomplete, but they were a starting point.

For each of the major issues, subgroups evolved within the Workgroup and eventually produced a series of "white papers" outlining approaches to addressing particular sources of uncertainty. The white papers are presented in section 4.3 through 4.9. As these approaches took shape, the Workgroup as a whole—in cooperation with the Aquatic Exposure Workgroup—developed a framework for applying them in a sequential ("tiered") risk assessment process. The rationale for each stage of the process, and details about how the various tools come into play, are the subject of section 4.2.

Several years ago, Glenn Suter and Larry Barnthouse developed a scheme for categorizing uncertainties in ecological risk assessment. The scheme is still applicable, and has some important implications for ECOFRAM. The following is a brief definition of each of the three major types of uncertainty, along with examples from the list of uncertainties compiled by the Workgroup.

Natural stochasticity – temporal and spatial variations in environmental characteristics that affect responses of organisms, populations, and ecosystems to human interventions. This type of uncertainty cannot be eliminated or reduced through additional data collection. Knowledge of the magnitude of natural stochasticity is, however, useful because it sets the limits of precision of quantitative risk assessments. Moreover, characterization of the range of natural variations in exposure, sensitivity, etc. is essential to develop effective environmental protection and restoration strategies. Examples of this type of uncertainty include variability in responses of test organisms (due to variations in size, age, health, genotype, etc.), variability in susceptibilities of habitats and species, ecosystem-to-ecosystem variation, and geographic variability.

Parameter error – imprecise measurements of environmental degradation rates, uptake rates, LC50s, or other parameters used in assessment models. This type of uncertainty can be reduced (if not eliminated) by collecting additional information. The most important use of Monte Carlo uncertainty analysis in risk assessment is to assess the consequences of parameter errors in assessment models. Once a specific model has been developed and statistical distributions for its parameters have been specified, a Monte Carlo analysis is used to quantify (1) the uncertainty in prediction resulting from

the cumulative uncertainty in the parameters, and (2) the relative contributions of each of the individual parameter uncertainties to the overall uncertainty. Results of the analysis can then be used to design research programs to reduce the critical uncertainties. Examples of this source of uncertainty include species-to-species extrapolation using regression models, and confidence bounds on LC50s or NOECs.

Model error – incorrect specification of assessment models, including inappropriate selection or aggregation of variables, incorrect functional forms, and incorrect boundaries. This type of uncertainty is reducible by improving the validity of assessment models. However, there are no recipes for determining how much improvement is needed or when it is needed. Model errors are the most difficult kind to deal with in risk assessment, because there is no generally applicable method for determining their magnitude, their significance, or even their existence! Model errors typically are unrecognized until a critical experiment or observation shows that the model being used is providing unacceptably erroneous predictions. Examples of this source of uncertainty include extrapolation from lower to higher levels of ecological organization, extrapolation from laboratory to field, and extrapolation across major taxonomic boundaries (e.g., from fish to amphibians).

The above classification leads to the following two observations:

(1) Monte Carlo analysis, which is frequently (and erroneously) assumed to be synonymous with "probabilistic risk assessment," usually addresses only parameter error. Other probabilistic approaches (e.g., the exposure/effects distribution approach described by the Aquatic Risk Assessment and Mitigation Dialog Group (SETAC 1994), and further developed by ECOFRAM) can address both natural stochasticity and parameter error. None of these methods addresses model error.

(2) Most of the specific uncertainties identified by the ECOFRAM Aquatic Effects Workgroup at the outset of their discussions (described in Section 4.1.2) involve model error.

Several Workgroup members contributed additional comments regarding the classification of uncertainties in ecological risk assessment. These are summarized in the following paragraphs. Many of these comments overlap and reinforce each other, though certain differences in perspective are apparent.

* * *

Uncertainty sources (not discrete, and overlap occurs) include the following:

- conceptual model formation;
- incomplete information and data;
- natural variability and stochasticity; and
- procedural and design error (sampling plan; model choice; etc.) (Wentsel et al. 1996; U.S. EPA 1998).

Uncertainty analysis provides insight into the strengths and weaknesses of an assessment. It can also serve as the basis for making alternative risk management decisions or supporting the need for obtaining additional information to reduce the uncertainty. A weight-of-evidence approach provides confidence about the risk estimate and includes:

- sufficiency and quality of the data;
- corroborative information;
- evidence of causality; and
- identification of additional analyses, data or information.

There is no consensus on how to evaluate or apply weight-of-evidence in ecological risk assessment. Professional judgment is needed. Uncertainty can be discussed qualitatively, but formal quantitative approaches are difficult to complete and do not improve risk communication (RA/RM Commission). Some sources of uncertainty (e.g., exposure calculations) lend themselves to quantitative analysis, while other sources (e.g., species to species or high to low dose extrapolations) do not.

Most of the uncertainty in aquatic effects analysis is due to the need to extrapolate from single species studies (toxicity tests) to higher levels of biological organization (population, community, and ecosystem level effects). Additional uncertainty may come from extrapolation from biomarkers to effects on individuals, and from laboratory studies to field situations.

Uncertainty about ecological significance does not affect the precision and accuracy of risk characterization or the assessment process. The results have already been obtained before one puts the risks into perspective from a population level and higher. However, it does affect the risk manager. Misjudging ecological significance may result in a product reaching the market when it should not be registered (a function of use rates, application frequency, use patterns, etc.) or failure to register a product when it should or could be registered.

* * *

The individual organism has been the primary focus of ecological toxicology. This may be because ecological toxicology is derived from human-oriented mammalian toxicology which is concerned with the fate of individuals. All pesticide regulatory agencies including the U.S. Environmental Protection Agency (EPA) require standard laboratory studies on a limited number of species in order to determine toxicity to non-target organisms. The species tested act as surrogate species to predict effects on individuals, populations, communities, and ecosystems that will be exposed to the pesticide. The extrapolation from individuals tested in the laboratory to higher levels of ecological organization in the field introduces many sources of uncertainty into a risk assessment which can decrease the precision and accuracy of risk characterizations. The ultimate result is a less accurate description of the risks to risk managers which may result in bad risk management decisions.

* * *

Uncertainty can be from lack of data, natural variability of organisms or systems, or limits in fundamental knowledge. Extrapolation from individuals to the ecosystem, or from biomarkers to ecological impacts, are examples of uncertainty due to the limits of fundamental knowledge. Extrapolation from individuals to populations, or from laboratory to field, are

issues where there is some scientific information. Uncertainty analysis could identify parameters to study to resolve major uncertainties or to identify critical parameters in the estimation methods. Compounding protective assumptions can be more protective than the assessor intended.

* * *

From the many questions and issues raised in the initial brainstorming session, a consolidated list of topics emerged for discussion and further development. These included:

- Variability in individual response to pesticide exposure;
- Variation among species in sensitivity to pesticides;
- Time-varying and repeated exposures;
- Extrapolation from individual to population-level endpoints;
- Extrapolation to effects in and on ecosystems;
- Endpoint selection and characterization of toxicity; and
- Gaps in knowledge.

In the following subsections, each of these topics is discussed in turn.

4.1.1. Variability in Individual Response to Pesticide Exposure

Different ***life stages*** of an organism can exhibit different sensitivities to a toxicant e.g., larval fish are more sensitive than adults. Species tested in the laboratory are all a standard age, whereas all life stages of a particular species may be exposed to the pesticide in the field. Laboratory studies currently exist for different life stages of fish but not for aquatic invertebrates.

Surrogate species tested in the laboratory are free of ***parasites and disease*** and are well fed so they are generally "healthy." Organisms exposed to pesticides under field conditions may not be totally healthy due to disease or lack of food, which introduces another source of uncertainty.

The ***conditions*** under which species are tested in the laboratory (e.g., physical/chemical conditions including temperature, pH, hardness, and salinity) can have a great influence on the results of toxicity tests. Test results from different laboratories can vary by an order of magnitude for the same species due to different test conditions. Standard laboratory protocols and GLP reduce this source of uncertainty. The conditions under which test organisms are exposed to in the laboratory, however, are not necessarily the same as the conditions to which species would be exposed under field conditions, which vary both spatially and temporarily which could significantly influence sensitivities. Site-specific data, if collected and documented properly, should be given more weight in a risk assessment than default or other assumptions.

4.1.2. Variation in Sensitivity Among Species

If every aquatic ecosystem consisted entirely of *Selenastrum capricornutum*, *Daphnia magna*, and rainbow trout, ecological risk assessment would be much easier. Unfortunately, most aquatic ecosystems contain hundreds of species, and the most important species are usually unrelated to our standard toxicity test organisms. The test species have been selected in part because they are known to be sensitive to toxicants, so it is assumed that the test endpoints for these surrogate species will be protective of the biotic community. However, given the large number of aquatic species in North America, the expectation that the limited set of species that have been tested includes the most sensitive aquatic species (or a species approximately as sensitive as the most sensitive species) is doubtful.

One way to extrapolate from the standard test organisms to protect a wider range of species is to apply a safety factor to the lowest measured LC50. Another approach is to derive empirical extrapolation coefficients for taxonomically related species. These are common practices in the early stages of an ecological risk assessment.

Another approach could be to measure toxicity to a well-selected variety of species, assume that the sensitivity of species follows some probability distribution, and use statistical models to estimate the distribution of sensitivity within a community of species based on test data for a few species. Distribution analysis is a tool which could be used to determine a safe exposure level for a community based on data for a subset of tested species. This is the approach taken by EPA's procedure for derivation of Water Quality Criteria (EPA 1985), and recommended by the Aquatic Risk Assessment and Mitigation Dialog Group (ARAMDG, SETAC 1994) for pesticide risk assessment. Guild theory, which assumes that groups of organisms that use a common resource in a similar way will respond similarly to a toxicant, could also be used to predict effects on species untested in the laboratory.

Microcosm and mesocosm studies address variation among species sensitivities directly, by measuring effects on dozens of taxa in a single study.

4.1.3. Variation in Exposure Concentration Over Time

Pesticide exposure in aquatic ecosystems often occurs in pulses. Peak concentrations in the water column typically last only a day or two, then decline as various dissipative processes take effect. In some cases, such pulses may occur repeatedly during the course of a season. These exposure patterns are not incorporated into standard laboratory toxicity tests. The discrepancy between real pesticide exposure and laboratory exposure regimes introduces uncertainty into estimation of ecological effects.

For some pesticides and some species, a very brief exposure to a peak concentration may cause as much effect as if the same concentration were prolonged. For other pesticides and species, the time-averaged concentration may determine the

severity of the effect (though the appropriate time interval for averaging is not obvious). For most pesticides and species, we might expect the relationship between exposure pattern and effect to be somewhere between these two extremes.

Note that the problem is not the same as time-to-death at a constant concentration. Nor is it the same as describing the effects of different durations of a constant exposure. Furthermore, if the toxic impact is reversible (for example, recovery occurs after environmentally relevant durations of exposure) and this is not considered in the risk assessment, then the assessment may be too conservative in its outcome. A good understanding of the mechanism of action of the stressor is essential.

One approach that has been proposed for estimating effects of time-varying or repeated exposures is to link pharmacokinetic models (predict tissue concentrations over time) with internal dose-response models. Other researchers have taken an empirical approach, establishing time-varying exposure regimes in the laboratory and measuring effects on the usual bioassay endpoints. Microcosms and mesocosms incorporating realistic exposure regimes are another empirical approach.

4.1.4. Extrapolation from Individuals to Population-Level Endpoints

Many questions of interest in risk assessment relate to effects on the abundance, production, and persistence of populations. Responses at this level of organization cannot be predicted from laboratory toxicity tests alone. Sources of uncertainty for population analysis include (1) environmental variability in time and space, (2) variations in sensitivity among individuals and their various life stages, (3) stochastic birth and death processes, and (4) the lack of understanding of population dynamics. The first two sources of uncertainty have been discussed above. Stochastic birth and death result from the fact that each individual organism has an indeterminate life span, even if the average life span for the population can be precisely estimated. The true nature of how populations are maintained under natural conditions is not fully understood, therefore the impact of changes to birth rates, death rates, and recruitment caused by the introduction of toxicants is not fully understood.

Studies of effects of insecticides on zooplankton and miticides in terrestrial arthropods have shown that LC values were not a good predictor of effects at the population level (Day and Kaushik 1987; Daniels and Allan 1981; Walthall and Stark 1997). Day and Kaushik (1987) showed that *Daphnia galeata mendota* populations exposed to sublethal concentrations of the pyrethroid insecticide fenvalerate were able to sustain a rate of increase similar to that of unexposed controls. Daniels and Allan (1981) showed similar results in *Daphnia pulex* with the insecticide dieldrin. Working on *Acyrthosiphon pisum* and its response to the miticide imidacloprid, Walthall and Stark (1997) showed that the populations exposed to the 72-h LC60 were able to maintain rates of population increase similar to untreated controls. Walthall and Stark (1997) attributed this lack of population level response, even at exposure concentrations above the LC50, to compensatory mechanisms where the unaffected individuals were able to maintain heightened rates of reproduction due to decreased competition for limiting resources.

Population parameters such as the intrinsic rate of increase can be calculated for some species tested in the laboratory (e.g., *Daphnia magna*) because multiple generations are produced in the one- to four-week tests. Population models, when coupled to fate and transport models, could be used as a tool to predict the effects of pesticides on populations of aquatic organisms.

We also need to consider the implications of spatial patchiness in both exposure and population density for the impact of the pesticide on the population. We might imagine a grid, each compartment of which contains a particular population density and pesticide concentration. The organisms within each compartment will be affected depending on the pesticide concentration in that compartment. For example, consider the "refuges," the low exposure pockets of sediment within a farm pond. Benthic organisms in those pockets are more likely to survive, grow, and reproduce than organisms in a "hot spot" a few meters away. Now we have a spatial distribution of toxicological (and ecological) responses. From the point of view of population distribution and dynamics, how do the situations in each compartment of the grid add up to an overall impact on the population?

The same situation applies on a larger scale to water concentrations and more mobile organisms. We can think of pools and riffles, upstream-downstream, littoral-pelagic, surface-bottom, cove-mainstem, and other spatial configurations where these factors will come into play. Can we use the tools of population ecology (e.g., models of spatially varying population density, growth rate, and fecundity) to address this issue, at least on a generic basis, to get an idea of how the small-scale patchiness translates into an overall population response?

4.1.5. Extrapolation to Ecosystem-Level Endpoints

Four types of effects may occur at the ecosystem level that do not occur at the organism or population level: (1) effects on a population's ability to interact with populations of other species, such as the ability to avoid predators; (2) indirect effects on a population due to effects on the populations with which it interacts, such as reduction in the abundance of a predator due to toxic effects on prey; (3) changes in structural properties such as the number of species or trophic levels; and (4) changes in the functional properties of an ecosystem, such as primary production.

Organisms have a variety of physiological strategies to mitigate toxic effects. Analogous processes occur at the population level, mitigating the consequences for the population of effects on individuals. The same can be said at the level of communities (assemblages of populations) and ecosystems (assemblages of communities and their physical environment). Unfortunately, we don't have much direct evidence about limits of these mitigating processes, so we can't say how much damage a population, community, or ecosystem can sustain before the mitigating forces are exceeded.

In some cases, effects on a single population are clearly undesirable—for example if it is a population of an endangered species, or a species of high economic or societal value. From a purely ecological point of view, however, effects on an

individual population are not necessarily of concern as long as the function the population performs can be taken over by other species. Any aquatic ecosystem, especially in the temperate zone, exhibits "functional redundancy"; that is, multiple species are present to perform each critical function. This functional redundancy is critical to the persistence of the ecosystem as a whole.

The relevance of functional redundancy to the effects characterization is obvious. Reductions in a few sensitive populations are unlikely to impair the functions of the ecosystem. Although it is easy enough to invent a hypothetical chain of events whereby toxic effects on a population create ripples throughout the ecosystem, observations in mesocosms and in nature tell us the opposite is the normal situation—that is, an ecosystem is less sensitive than its most sensitive populations, just as a population is less sensitive than its most sensitive individuals. Thus, for example, the loss of amphipods and isopods from mesocosms exposed to a pyrethroid had no apparent impact on the ecosystem overall; several groups of organisms, including rotifers, chydorid copepods, chironomids, oligochaetes, and snails, expanded to fill the functional role of the missing populations (Giddings et al. 1999).

The conclusion that some population reductions are of no ecological significance is consistent with a risk management strategy that protects 90% or 95% of all aquatic species. Taking into account the fact that most population effects of non-persistent toxicants are temporary, due to the recovery mechanisms discussed above, it is clear that a risk characterization based on the 10th percentile of species sensitivity will be ecologically quite conservative.

Another aspect of ecological adversity is the duration of effect. Most aquatic invertebrates have short generation times and rapid rates of population growth, and are therefore able to recover quickly from population reductions. Several other factors contribute to the ability of aquatic invertebrates to recover from population reductions. Some individuals, especially of sedentary species, may escape exposure because of the non-uniform distribution of pesticide concentrations in water or sediment. Individuals inhabiting these internal refuges are a source for population regrowth when pesticide concentrations in other areas decline. Most zooplankton and aquatic insects produce resistant stages that can outlast periods of unfavorable conditions. Aquatic insect populations are renewed at least annually through deposition of eggs by adults from outside the ecosystem. In most natural open systems, such as a pond with areas receiving different amounts of exposure to runoff and drift, migration from less-exposed areas enables rapid population recovery in high exposure areas.

In light of the wide natural fluctuations in abundance that are typical of most aquatic invertebrates, what is the ecological significance of temporary effects of pesticides on aquatic populations?

Tools for addressing these questions include models of ecosystem structure and function (e.g., SWACOM), as well as microcosms and mesocosms. The models and experimental systems can be used to explore the ecological implications of pesticide effects that are temporary or are limited to a certain fraction of the populations in the ecosystem. Both tools have serious limitations: model validation, and extrapolation from microcosms and mesocosms to different kinds of ecosystems.

Also, to a large extent the question of ecological adversity goes beyond the realm of scientific inquiry and involves societal values and public perception.

4.1.6. Endpoint Selection and Characterization of Toxicity

Median effect levels (LC50 and EC50 values) are the most commonly available data for development of assessment measures. The level of uncertainty in parameter estimation is minimized at the midpoint of the regression curve. It has been suggested that lower effect levels such as the LC10 or the LC5 may be more appropriate for risk assessment (SETAC 1994). However, this recommendation was designed to consider some groups of compounds for which the slope of the concentration-response relationship is small. Typically, these relationships have been noted for toxicity studies where organisms not possessing the receptor system for the pesticide have been tested—for example, the effects of fungicides on crustacea. Most (95%) concentration-response slopes for insecticides tested in fish are greater than 1.4, and the median slope is 5 (SETAC 1994). Under these conditions, the difference between an LC50 and a smaller effect level, such as the LC5, is small. In these circumstances, the use of the LC50 for risk assessment is justified, particularly if the results can be evaluated using other test systems such as microcosms.

Results of chronic toxicity tests are typically expressed as No Observed Effect Concentrations (NOEC) determined using statistical hypothesis testing. However, NOEC determination is influenced by the range of test concentrations selected, the number of replicates used, and experimental variability. It is difficult to correct for this type of uncertainty within these data sets. Poor selection of concentrations for chronic tests may result in higher estimates of NOEC, and these systematic errors are thus likely to be non-conservative. Regression analysis offers some additional statistical power that uses data from the entire concentration range and is not restricted to the doses selected in the study. (The concept is reviewed in section 4.8.) However, a chronic toxicity test may be triggered because of the persistence of the compound ($t_{1/2}$ > 4 d) and not because of toxicological characteristics. In such cases the NOEC may be many fold higher than any predicted EEC, and generation of data (number of treatments) necessary to perform regression analysis would only drive up the cost of the study without changing the outcome of the risk assessment.

Much emphasis is placed on the use of molecular/biochemical biomarkers to predict toxic effects. In most cases, very little is understood about the relationship between a biomarker response and a resultant effect at the individual, population, or community level. One reason for this lack of understanding is the uncertainty associated with biomarker measurement. Another reason is the lack of understanding of the relationship between the biomarker and integrated ecological indicators, such as growth (e.g. relationship between P-450 induction and growth). Bias in assessing biomarker endpoints not related to survival or sustainability can cause systematic errors. This is an important area to consider as we move into the endocrine aspects of risk assessment. A sensitivity analysis needs to accompany any proposed biomarker (measurement endpoint) as it relates to an assessment endpoint. The analysis should address effects of experimental conditions on the biomarker, and the sensitivity of integrated endpoints (such as growth, survival, and reproduction) to changes in the biomarker (e.g. sensitivity of reproduction to plasma vitellogenin). Probabilistic risk assessment tools may

be able to quantify the probability that a given change in a biomarker would result in a specified change in an integrated endpoint.

4.1.7. Information Gaps

In itself the lack of information or relevant data on the toxicity of chemicals to groups of organisms (such as benthos, reptiles, or amphibians) or on the toxicity to specific processes or end-points within organisms (behavior, disease resistance, or carcinogenicity) will result in a decreased accuracy of risk characterization, and will subsequently result in increased uncertainty in risk management decisions. The following addresses some of the sources of uncertainty created by specific types of missing data.

Multiple stressors. Uncertainty resulting from ***confounding stressors*** may affect risk assessments. Thus, a natural event that accompanies a stressor (for example, runoff of sediments and soil particles will usually accompany runoff of a pesticide) may interact with the stressor being assessed and antagonize, synergize, or add to its effects.

Effects on benthic species. Current data requirements for aquatic toxicity focus on pelagic species (e.g. *Daphnia*, rainbow trout, bluegill, fathead minnow), thus to determine potential effects on benthic organisms often requires extrapolations to species with very different life history characteristics, biology and physiology. This species to species extrapolation is a major source of uncertainty, especially when made across taxonomic orders. Uncertainty of such extrapolations may also be compounded because it is necessary to assume that exposure in water is the same as in sediment. This introduces many more sources of uncertainty as, the fate of the chemical may be different in the sediment and water, and the uptake mechanism of the organism(s) may be very different.

Effects on reptiles and amphibians. Several investigators have reported on the decline of amphibian species on regional and local scales (SETAC Annual Meeting, 1993). As discussed by Birge (1993), the principal causes of amphibian population declines are likely to be: 1) progressive encroachment upon wetlands and other habitats; 2) primary and secondary effects of stress from point and non-point sources of pollution; and 3) natural phenomena that may affect survivorship of this unique group of vertebrates. Current toxicity assessment methodologies use surrogate species for determining ecological effects of pesticides. Amphibians are not typically included in these routine tests. Mayer and Ellersieck (1986) published a report on inter-taxon correlations of toxicity in aquatic organisms. The report included 66 species and 410 chemicals in a correlation matrix. Two species of amphibians were included: tadpoles of Fowler's toad and the western chorus frog. The chemicals tested were uniformly less toxic to amphibians than to the standard freshwater test organisms, indicating that these standard test organisms can serve as surrogates for amphibians. Similar conclusions have been reached by other amphibian researchers (Hudson *et al*. 1984; Schuytema *et al*. 1991).

Probability tools could be used to characterize the likelihood that amphibians will be more sensitive than standard test organisms. Such a model could be developed and tested based on amphibian toxicological literature currently available.

Another source of uncertainty is from estimating exposure, since amphibians and reptiles occupy both aquatic and terrestrial habitats. The lack of understanding of the ecology of many amphibians and reptiles (relative to mammals, birds and fish) also contributes as a source of uncertainty.

Behavioral effects. The effects of changes in behavior are likely underestimated by ecologists when considering pesticide effects. Current toxicity tests focus on mortality (acute tests) and reproductive success (chronic studies). For many animals, behavior associated with reproduction is critical to successful production of progeny, and feeding behavior may be critical for survival. Changes in behavior could also result in increased susceptibility to predation. Uncertainty in risk assessment could be caused by the failure to recognize altered behavior as an endpoint of toxicity. There are no protocols designed specifically to determine behavioral effects of chemicals. These types of effects introduce indirect changes to populations by causing changes to recruitment rates and/or birthrates. As indirect effects they may not be easy to quantify, nor are the resulting changes to population dynamics understood.

Generally, gross behavioral impacts on fish are noted in reports, but are difficult to interpret since their ecological relevance is unknown. In cases where a fish is severely impacted, and for all practical purposes would be ecologically dead (e.g., it is on the surface with tremors), interpretation is not too difficult. However, if the fish is described as quiescent but may still be responsive, ecological interpretation becomes much more difficult.

Effects on resistance to disease. Effects of chemicals on disease resistance in organisms could cause indirect mortality, not evident in standard toxicity tests. Changes in disease resistance could result in increased sensitivity to toxic chemicals, or cause other physiological changes which could alter reproduction and/or growth, thereby causing changes to the dynamics of populations.

Carcinogenic effects. While no carcinogenicity data are collected for aquatic species, they are generated for terrestrial. It is probably well beyond the realm of issues that can be addressed by our group at this time.

4.1.8. Approaches to Quantifying or Reducing Uncertainty

Effects analysis in most conventional pesticide risk asessments is based on a battery of acute and chronic toxicity tests. As expressed in the comments presented above, the ECOFRAM Aquatic Effects Workgroup determined that these standard data fail to address several critical sources of uncertainty, including:

- the responses of organisms under exposure conditions that more closely reflect actual pesticide use (which in turn requires an understanding of exposure patterns under different scenarios of interest);
- the toxicity of the pesticide to other species; and
- the ecological significance of expected effects.

Some uncertainties, particularly toxicity to untested species, can be addressed through analysis of statistical distributions. However, most of the uncertainties involve what we have called “model error.” Important examples include determining the effects of time-varying and repeated exposures, extrapolation to population-level and ecosystem-level endpoints, and most of the topics listed above under “Information Gaps.” As mentioned, such uncertainties are among the most difficult to quantify or reduce. They are not addressed by methods usually thought of as “probabilistic,” such as Monte Carlo analysis.

The ECOFRAM Aquatic Effects Workgroup interpreted its charge broadly, and explored a wide range of strategies for quantifying or reducing uncertainties in the ecological risk assessment. Most of the tools considered by ECOFRAM for higher-tier aquatic effects analysis are not, in fact, probabilistic, and do not address stochastic uncertainty as do many of the techniques for refined exposure analysis. However, they should be effective in reducing other kinds of uncertainty, especially uncertainty that results from incomplete knowledge of processes and relationships.

4.2. Effects Analysis in the Tiered Risk Assessment

This section reviews the stages of effects analysis in the tiered ecological risk assessment envisioned by the ECOFRAM Aquatic Workgroups (see section 2), and provides the rationale for use of specific tools and processes. Details about the tools are presented in sections 4.3 through 4.9.

4.2.1. Tier 1: Standard Toxicity Tests

Tier 1 is designed to be protective and not predictive. Tier 1 of the aquatic risk assessment is a deterministic analysis that involves the calculation of a risk quotient (generated by dividing the Estimated Environmental Concentration (EEC) by an appropriate effects measurement endpoint). The objectives of the Tier 1 assessment are to:

- Identify products that have minimal ecological concern even under conservative exposure scenarios;
- Focus higher tier risk assessment efforts, if needed, on combinations of use patterns and sensitive taxa (e.g., invertebrates, fish, or aquatic plants) most likely to be of concern;
- Indicate whether acute or chronic effects are of concern; and
- Determine the potential need to consider sediment toxicity impacts.

4.2.1.1. Selecting species and endpoints

The FIFRA statute and regulations require that no unreasonable adverse effects will result from the use of a pesticide. In ecological risk assessment, a standard battery of aquatic toxicity tests with surrogate species is used to represent the organisms potentially exposed to pesticides under field conditions. At Tier 1, these tests measure ecologically relevant endpoints on sensitive life stages, which are compared to conservative exposure scenarios to assess the potential risk to nontarget organisms.

Ecological endpoints are those which are directly related to observable changes in the abiotic and biotic components of an aquatic ecosystem (Suter 1993; U.S. EPA 1998c). Relevant assessment endpoints may include the sustainability and propagation of populations of organisms. The initial toxicity data are used to:

- Estimate acute and chronic toxicity of the active ingredient of each chemical to different aquatic organisms;
- Compare acute and chronic toxicity data with estimated environmental concentrations (EECs) to initially assess potential ecological risk;
- Provide data to determine the precautionary label statements to minimize potential acute hazard to the environment; and
- Indicate the need for higher tier effect studies (after Touart 1995).

Tier 1 effects characterization is based on a set of standard acute and chronic toxicity tests with fish, invertebrates, and algae. The set of tests recommended by ECOFRAM is generally consistent with those currently required under FIFRA (40

CFR 158.145). This suite of studies is also similar to the draft 40 CFR 158.145, expected to be adopted in 1999. These include acute toxicity tests with one invertebrate (*Daphnia magna*), two species of fish (warm water and cold water), and one or more species of algae or aquatic vascular plant. Species chosen were based on 1) convenience (e.g., stocks available, ease of cultivation, etc.); 2) applicability to environmental decisionmaking; and 3) relevance (i.e., ecological, economic (e.g., game species) or societal relevance). Mortalities and other observations should be reported at 24 hour intervals for acute studies, and the LC or EC_{50} (with 95% confidence limits) and slope of the concentration-response for each observation time should also be reported. Time-to-event analysis may provide better estimates of acute endpoint values than conventional probit analysis (see section 4.3) and could be used.

Currently if the pesticide is a herbicide, tests with additional aquatic plants (3 additional algal species and *Lemna*, a floating aquatic macrophyte) are required. In the future (according to draft 40 CFR 158.145), these studies may even be required for insecticides and fungicides, although initially as limit studies. However, ECOFRAM suggests that research address the relative sensitivity of algae to fungicides and insecticides as compared to herbicides. Particularly in the case of insecticides, some members of the Workgroup noted the logical inconsistency of allowing one species of the target group (arthropods) to represent all invertebrates, while requiring testing of five species of a non-target group (plants).

The 40 CFR 158.145 citation lists the full data requirements for registration or reregistration of pesticides. Part 158.145 specifies the types of data and information required by the USEPA to make regulatory judgments concerning the environmental safety of the pesticide (Touart 1995) as well as the type of substance (TGAI—technical grade of the active ingredient, or TEP—typical end-use product) to be tested. Subdivision E (Hazard Evaluation: Wildlife and Aquatic Organisms) of the pesticide assessment guidelines further describe the standards for conducting acceptable studies, guidance on evaluating and reporting of data, further guidance on when particular data are required and examples of protocols (Touart 1995).

If there is a potential for estuarine exposure, acute toxicity tests are also recommended for an estuarine fish, an arthropod, and a mollusk, although freshwater species can usually be considered as surrogates for marine species at Tier 1 (Hall and Anderson date?; others??). Chronic studies including an invertebrate (*Daphnia magna*) life cycle study and a fish early life-stage (ELS) study (usually with fathead minnow or rainbow trout depending upon acute sensitivity) are also recommended for Tier 1. Additionally, a life cycle study with a marine invertebrate (often mysid shrimp) and a fish early life-stage (ELS) study with a marine fish (typically sheepshead minnow) may also be submitted in Tier 1. While these chronic studies are currently only conditionally required under FIFRA (40 CFR 158.145), ECOFRAM considers that they should be included in Tier 1 for a more thorough assessment and to reduce the time required to reach a registration decision and most registrants typically provide these chronic studies with initial submissions, regardless of the current Tier 1 results. Additionally, the draft Part 158.145 includes these studies earlier in the tiered risk assessment process.

ELS studies determine the toxicity of the compound to embryo, larvae and juvenile fish stages, generating a NOEC, LOEC and MATC for survival, growth, and hatching. Invertebrate life cycle studies expose individuals through several

reproductive cycles, producing a NOEC, LOEC and MATC for survival, growth, and reproduction (numerous endpoints). Regression-based EC_x (where x represents a defined percent reduction of survival, growth or reproduction) estimates rather than the ANOVA-based NOEC approach were recommended by the Aquatic Effects Workgroup because the worldwide scientific community is moving toward the regression-based approaches (see section 4.8). Expert opinion within ECOFRAM favors the use of an EC_{10} for this endpoint, although a NOEC can be used if a study is scientifically acceptable but the data do not support a regression analysis.

The Tier 1 suite of studies is consistent with European Union Council Directive 91/414/EEC, European and Mediterranean Plant Protection Organization (EPPO) Decision-making scheme 6: aquatic organisms (1993; 1994), Environment Canada (1997), and the results from the Aquatic Dialog Group: Pesticide Risk Assessment and Mitigation (ARAMDG, SETAC 1994). Note that ARAMDG, like ECOFRAM, recommended that chronic studies be included in Tier 1 effects characterization.

Sediment toxicity tests are not suggested at this Tier. However, based on comparisons of the sediment pore water concentrations to *D. magna* acute and chronic results and knowledge of the persistence and partitioning behavior of the compound, the registrant may want to begin testing or even have completed the testing of a benthic organism such as *Chironomus* prior to moving ahead in the tiered risk assessment scheme.

4.2.1.2. Time-to-event analysis

The ECOFRAM Aquatic Effects Workgroup identified a number of advantages to the use of time-to-event (TTE) statistical techniques for analysis of standard toxicity test data. Time-to-event analysis uses models to estimate the effects of a treatment on events that occur through time (e.g., death, hatching). In TTE analysis, exposure duration—a crucial determinant of the consequences of exposure—is explicitly included. Including this information enhances the power of statistical tests for estimating endpoints such as the LC50, and for determining the influence of covariates (such as organism size or water temperature) on toxicity endpoints. These methods, though not familiar to most ecotoxicologists or regulators, are now easily implemented with PC-based statistical software.

4.2.1.3. Risk Quotients and Levels of Concern

Five methods for “environmental risk analysis” described by Barnthouse *et al*. (1982) were a quotient method, analysis of extrapolation error, fault tree analysis, analytic hierarchy method, and ecosystem uncertainty analysis. A quotient method was adopted by EPA for ecological risk assessment under FIFRA based on recommendations by the Aquatic Hazards of Pesticides Task Group of the American Institute of Biological Sciences (Cairns *et al*. 1978). In this approach, a risk quotient (RQ, more aptly a hazard quotient) is derived by dividing the Expected Exposure Concentration (EEC) by an appropriate measurement endpoint (*e.g.*, LC50, EC50, NOEC). By combining dose-response information with exposure estimates, a semi-quantitative estimate of the risk associated with the use of the chemical under the conditions of exposure

and the non-target population under consideration can be made. This approach is simple, straightforward, and requires relatively limited data.

Risk quotients are compared to a set of risk criteria to determine a potential regulatory concern. Three categories of regulatory concern above minimal risk have been established—high risk, restricted use, and endangered species. If the ratio of the derived risk quotient exceeds a given risk criterion, then a Level of Concern (LOC) is inferred. Where an LOC is indicated, risk management and/or further risk assessment refinement is warranted. Table 4-1 summarizes the criteria used for risk characterization with this ratio method.

Urban and Cook (1986) recognized several weaknesses of such a ratio method: (1) it does not adequately account for effects of incremental dosages; (2) it does not compensate for differences between laboratory tests and field populations; (3) it cannot be used for estimating indirect effects of toxicants (*e.g.*, food chain interactions); (4) it has an unknown reliability; (5) it does not quantify uncertainties; and (6) it does not adequately account for other ecosystem effects (*e.g.*, predator-prey relationships, community metabolism, structural shifts, etc.). However, the approach is useful for identifying products of minimal ecological concern and in focusing higher tier assessment efforts.

For acute effects, peak EEC's are compared to the EC_{50}s and LC_{50}s to calculate risk quotients for the species of invertebrate and fish tested. This approach is consistent with current U.S. EPA OPP risk characterization approaches (Urban and Cook 1986).

For chronic effects, the peak EEC is divided by the chronic endpoint (EC_x or NOEC) to calculate a chronic risk quotient. This risk quotient is conservative, because the chronic endpoint is measured after prolonged continuous exposure, whereas the peak EEC reflects an instantaneous maximum concentration. If chronic data are not available for the species that was most sensitive in the acute tests, then an acute-to-chronic ratio derived for another species may be used to estimate the chronic endpoint for the most sensitive species. The estimated endpoint would then be used as the measurement endpoint to calculate the chronic risk quotient.

The Aquatic Effects Workgroup discussed whether the acute EC or LC_5 (considered by ARAMDG) is more appropriate than the LC_{50} for calculating an RQ for comparison with a LOC of 0.1. Currently, 0.1 LC_{50}, equivalent to an LOC of 0.1, is used (Urban and Cook 1986) and is assumed to be a highly conservative estimate of the LC_5 (probably closer to an LC_1 due to the slope of the concentration-response curve; see section 4.5.1). Use of the LC_{50} value may be more appropriate because the studies are designed to determine this endpoint and there is less variability around this median value. However, an LC_5 is a point below which one would not expect to be able to discern any acute toxic effects in the organisms exposed under field conditions (SETAC 1994).

The ECOFRAM Aquatic Workgroups discussed whether the chronic risk quotient should be based on the peak EEC or a time-weighted average. Quantal endpoints such as mortality or hatching may reflect the effects of short-term exposure at

critical stages in the life cycle. Continuous variables such as growth generally reflect the effects of cumulative exposure, and a time-weighted average EEC may be more appropriate than the peak EEC for characterizing risk. However, because Tier 1 is intended to be protective, it may be advisable to avoid assumptions about cumulative vs. short-term effects; unless relevant information is available in a particular case, the chronic risk quotient should therefore be based on the peak EEC in Tier 1 (but not in Tier 2; see below).

The calculated acute and chronic risk quotients are compared with levels of concern (LOC; i.e. risk criteria) established by regulatory risk managers to reflect current policies and concerns. Table 4-1 shows the values current in Fall 1998. If the risk criteria are not exceeded, it is concluded that there will be minimal ecological concern from the proposed use of the product and the aquatic risk assessment process is judged complete. If the risk criteria are exceeded, the risk assessment process advances to Tier 2 analysis, but only for those taxa and application scenarios that continue to be of concern.

Thus the decision made at this tier may be either:

- Conservatively estimated concentrations for use pattern X indicate that in static waters, no ecological hazard above the level of concern is likely to result from use of the product to taxa A, B, or C.

OR

- The predicted conservative exposure value when compared with a standard battery of toxicity test results suggests the possibility of an adverse impact to taxa A, B or C. It is therefore necessary to progress to Tier 2 to refine the risk estimate.

Table 4-1. Criteria used for risk characterization in Tier 1 (modified from Urban and Cook 1986).

TAXA[a]	**EEC**	**MEASUREMENT ENDPOINT**	**LEVEL OF CONCERN (RISK CRITERIA)**
Invertebrate – acute	Peak[c]	48-h EC50 (*Daphnia*), 48 to 96-h EC50 (mollusk)[d] 96-h EC50 (mysid) [d]	0.05 / 0.1 / 0.5[e] 0.05 / 0.1 / 0.5[e] 0.05 / 0.1 / 0.5[e]
Invertebrate – chronic	Peak[c]	21-d EC10[b] 28-d EC10 (mysid)[bd]	1.0 1.0
Fish – acute	Peak	96-h LC50	0.05 / 0.1 / 0.5[e]
Fish- chronic	Peak[f]	35-d EC10[b] (warm water) 90-d EC10[b] (cold water)	1.0 1.0
Algae or Macrophyte	Peak[f]	96-h EC50 (algae) 14-d IC50 (duckweed)	1.0 1.0

[a] The measurement endpoint of the most sensitive species should be used to calculate the risk quotient.

[b] Use NOEC instead of EC10 if study is technically acceptable but data do not support regression analysis.

[c] EEC for pore water, if available, can be used for sediment risk assessment.

[d] Estuarine testing.

[e] 0.05 Level of Concern is applied for endangered species, 0.1 indicates a risk that may be mitigated by restricted use, and 0.5 or greater indicates a higher risk category.

[f] The comparison of peak exposure values with chronic toxicity data may be expected to be highly conservative for most endpoints and may be expected to "pass on" more products/use patterns to higher tier assessments.

4.2.1.4. Uncertainties remaining after Tier 1

The effects characterization of Tier 1 is based upon the following data: two to three acute fish species tests (2 freshwater, 1 estuarine, if required), one to two acute arthropod tests (one each of freshwater and estuarine, if required), one estuarine mollusk test (if required), one to five tests with algae or other aquatic plants, one or two (freshwater and/or estuarine) chronic fish early life stage tests, and one or two (freshwater and/or estuarine) invertebrate life cycle test. While many of the uncertainties in individual sensitivity, species sensitivity, species response to time varying exposures, and the extrapolation to populations and ecosystems have not been completely addressed, multiple taxa are being addressed with both acute and chronic data. The use of time-to-event analysis, and regression techniques for endpoint determination in chronic tests, will improve the certainty around the toxicity estimates used in the risk assessment. The use of sensitive life stages in the aquatic tests, the constant exposure throughout the duration of the test, the use of safety factors (LOC < 1) in the risk assessment, and the conservative nature of the exposure characterization, all result in a conservative Tier 1 risk assessment, which compensates for the uncertainties to be addressed in future tiers of the process.

4.2.2. Tier 2: Enhanced Data Interpretation

Effects characterization at Tier 2 is based on the results of the same acute and chronic toxicity tests used in Tier 1—that is, no additional laboratory tests are conducted. However, the data are used more comprehensively, and are coupled with interpretive tools (population level analysis) that address some of the sources of uncertainty inherent in the Tier 1 effects characterization, as explained below.

4.2.2.1. Extrapolation to population-level endpoints

Pesticides can potentially cause declines in non-target aquatic populations through acute mechanisms such as mortality, or through long term mechanisms such as prolonged exposures or protracted effects of acute exposures. A more complete discussion of population analyses for pesticides is developed in section 4.4. At Tier 2 it is possible to use information on typical population growth rates to interpret the effects of acute mortality events in localized populations. Populations of species that have relatively high intrinsic rates of increase, such as phytoplankton and zooplankton, may recover relatively rapidly after experiencing an acute mortality event. Species that have lower intrinsic rates of increase, such as amphibians and fish, will require longer periods of time for recovery of populations. Life table analysis methods described in section 4.4 can be used to estimate typical recovery times as functions of potential population growth rates.

Time-to-recovery analysis

The standard growth equation for populations in the absence of density dependence is as follows:

$$N_t = N_0 e^{rt}$$

Where:
N_t = Number of organisms present after a certain time period (t)
N_0 = Number of organisms present at beginning of time period
r = intrinsic rate of increase (per unit time)
t = duration of time period

This equation can be used to estimate the time required for the population to replace individuals lost in an acute mortality event. The greater the mortality, the longer is needed for the population to recover (see Figure 4-1). The time-to-recovery analysis is based on the following assumptions:

1. The intrinsic rate of increase used in the equation is a reasonable representation of the actual intrinsic rate of increase.

2. The organism has no "memory" (i..e., permanent physiological or behavioral impairment) of the event causing the mortality that might cause latent responses during the recovery period.

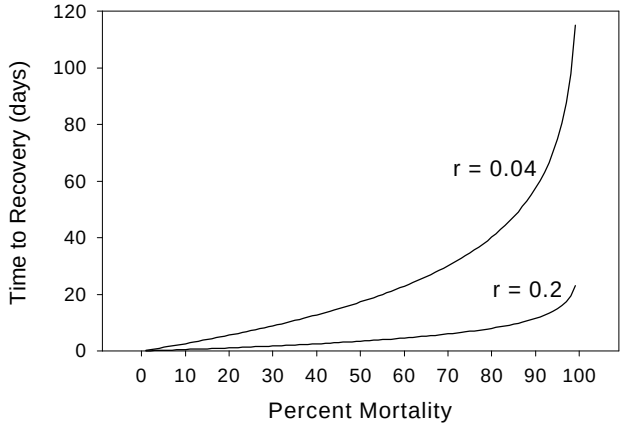


Figure 4-1. Predicted Time to-recovery to initial population numbers for two populations with different intrinsic rates of increase (*r*).

The relationships shown in Figure 4-1 can be used to convert concentration-effect curves for mortality (e.g., Figure 4-2) to concentration-effect curves for time to recovery (Figure 4-3).

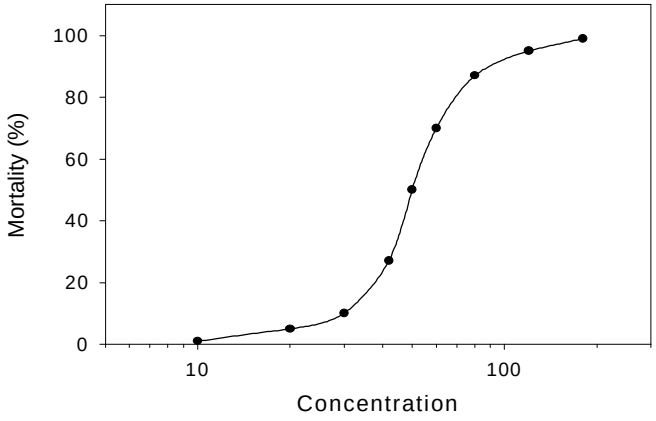


Figure 4-2. Concentration-effect curve for mortality, as derived from a standard acute toxicity test.

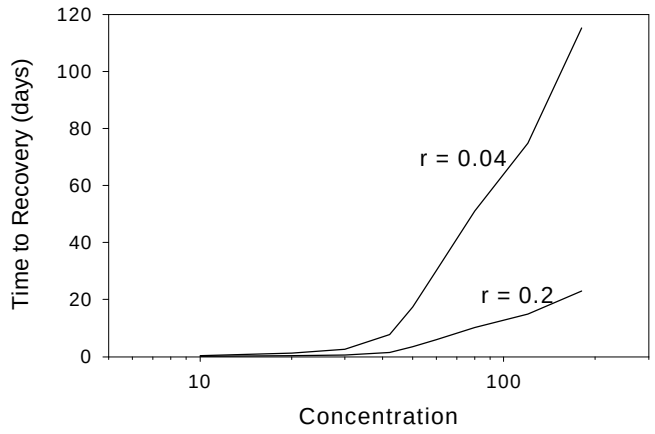


Figure 4-3. Concentration-effect curve for time to population recovery, derived by combining the relationships shown in Figures 4-1 and 4-2.

Since time to recovery can be expressed as a concentration-effect function, a Joint Probability Curve can be developed (see section 4.2.2.3) to examine potential recovery times for species at acute risk to pesticide exposure.

Although data in this example were hypothetical, similar generic graphs could be derived representing the standard test species used in ecological risk assessment. With proper consideration of the assumptions involved, these types of analyses can be instructive and aid in the interpretation of ecotoxicological data. To more fully understand the potential for population decline, a more thorough analysis of population effects should be considered (e.g. lifestage analysis, latency, etc.) as described in section 4.4. However, advanced population analysis is not conducted at Tier 2.

4.2.2.2. Joint Probability Curves

ECOFRAM's approach to characterizing risk at Tier 2 is to define the relationship between the magnitude of effect and the probability of occurrence for that effect. This approach integrates a probability distribution of exposure concentrations (see section 3.x.x) with concentration-effect curves for acute mortality, time to population recovery, or other effect endpoints. The result is a plot of probability of occurrence vs magnitude of effect, for which ECOFRAM has coined the term Joint Probability Curve (JPC).

The key to interpreting a Joint Probability Curve is an understanding of the derivation of the probability distribution of exposure upon which the JPC is based. The common current practice, using available tools such as PRZM/EXAMS with historical weather data, results in a distribution of annual maximum concentrations for a given site over a 36-year simulation period. Refinements in scenario selection and exposure characterization, described in section 3 of this report,

will lead to generation of a variety of exposure distributions. For example, the probabilistic exposure analysis might result in a distribution of exposure concentrations for 25 different sites representing a particular region and pesticide use pattern, with the concentration for each site being the 90th percentile of the annual maxima at that site over a 36-year simulation period. A family of such curves might be used to portray the distributions of 50th, 80th, 90th, and 95th percentiles for the same scenarios. The basis for each exposure distribution must be specified precisely (see section 3.x.x), and this specification is carried over into the interpretation of the corresponding JPC.

The following discussion uses a simple exposure distribution to illustrate how a JPC is constructed. In this example, the exposure distribution consists of 36 points, each of which is the annual maximum for one year of a 36-year PRZM/EXAMS simulation at a single site. The exceedance curve for this distribution is plotted in Figure 4-4. For any concentration along the horizontal axis, the curve indicates the frequency (on the vertical axis, as a probability) of years in which that concentration is exceeded at least once. For example, an annual maximum concentration of 10 is exceeded with a probability of approximately 0.2, or one year in five.

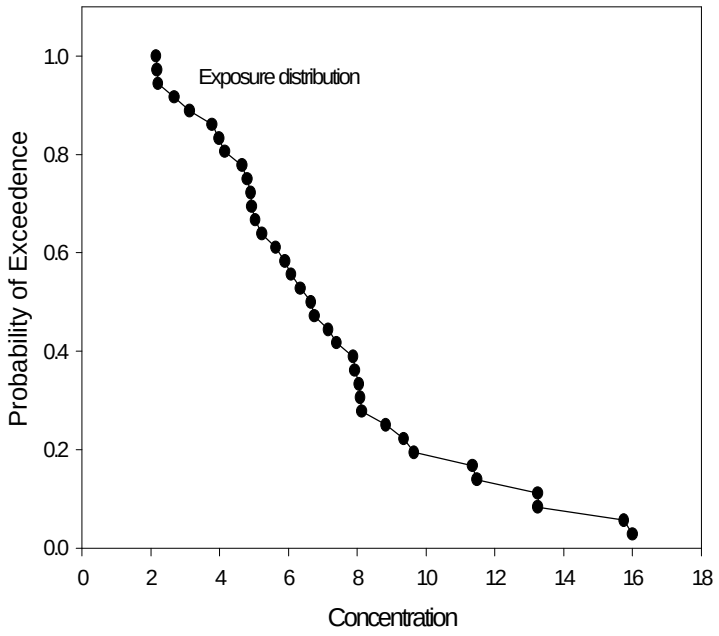


Figure 4-4. Exposure distribution (exceedance curve) of annual maximum concentrations over 36 years at a single site, based on PRZM/EXAMS output.

In this example of JPC construction, we will also use a simple effect endpoint: percent mortality of *Daphnia magna* after a 48-hour exposure, as measured in a standard acute toxicity test. The concentration-effect relationship measured in the toxicity test is shown in Figure 4-5. Note that only one point on this curve, the concentration corresponding to 50%

mortality (the LC_{50}), would be used in risk characterization at Tier 1 (not a JPC approach). Ignoring the rest of the curve at Tier 1 results in uncertainty about the variability of sensitivity among individuals in this species; use of the full curve at Tier 2 incorporates that variability into the risk characterization.

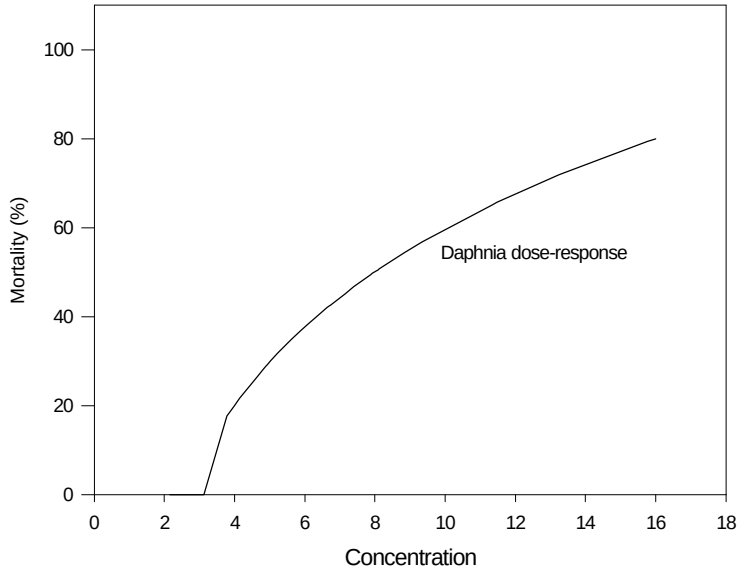


Figure 4-5. Dose-response relationship: 48-hour mortality of *Daphnia magna* as a function of exposure concentration, as measured in a toxicity test.

Because the exposure distribution (Figure 4-4) and the concentration-effect relationship (Figure 4-5) have the same horizontal axis (concentration), the two curves can be combined into one (the JPC). For any concentration, the exposure distribution indicates a probability of occurrence and the concentration-effect relationship indicates a corresponding magnitude of effect. For example, a concentration of 10 (as an annual maximum) is exceeded with a probability of about 0.2, and that concentration causes about 60% mortality. A concentration of 15 is exceeded with a probability of about 0.05, and that concentration causes about 75% mortality. The Joint Probability Curve is simply a plot of the pairs of values (exposure probability and % mortality) determined in this way (Figure 4-6).

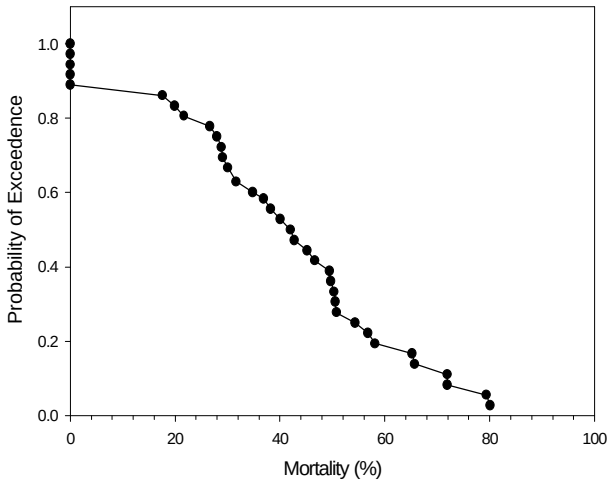


Figure 4-6. Joint Probability Curve derived from the exposure distribution shown in Figure 4-4 and the concentration-effect distribution shown in Figure 4-5.

The advantage of a JPC is that it allows a direct visual interpretation of the probability of exceeding any magnitude of effect. For example, Figure 4-6 shows that in about one year in five (probability 0.2), the annual maximum concentration will exceed that which causes 50% mortality of *Daphnia magna*.

The JPC paradigm can be used to integrate any exposure distribution (or family of distributions) with the concentration-effect relationship derived for any effect endpoint. For example, population-level analysis can produce a concentration-effect relationship with time to population recovery as the response (such as Figure 4-3), as discussed in sections 4.2.2.2 and 4.4. The population-level concentration-effect relationship can be integrated with the exposure distribution (Figure 4-4) to produce a JPC based on time to recovery (Figure 4-7). Likewise, in Tier 3, where the distribution of LC50 values among species can be used to define the relationship between concentration and percent of species affected (see sections 4.2.3.3 and 4.5), a JPC can be constructed using that concentration-effect relationship.

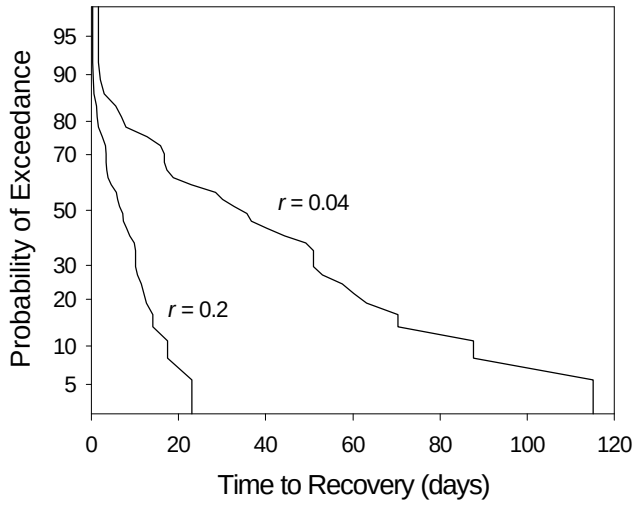


Figure 4-7. Joint Probability Curve showing the relationship between probability of exceedance and the time-to-recovery for hypothetical populations with intrinsic growth rates (*r*) of 0.2 and 0.04, based on concentration-effect curves shown in Figure 4-3.

4.2.2.3. Uncertainties remaining after Tier 2

No new aquatic testing has taken place for the Tier 2 analysis, beyond that conducted in Tier 1. However, the more detailed use of the data begins to address some of the uncertainties identified in the risk assessment process. The use of the full concentration-effect relationship in the development of Joint Probability Curves alleviates some of the uncertainty due to variation in individual sensitivity. Simple tools for population analysis are used to begin to extrapolate from effects on individuals to population-level responses. Variability among species has been partially addressed through evaluation of toxicity data for four or more species, but a more complete analysis of species sensitivity distributions may be conducted, if necessary, in Tier 3. The effect of variability in exposure concentration will also be addressed in Tier 3, if appropriate. Depending on the outcome of the Tier 2 risk characterization, further investigation of sediment toxicity and chronic toxicity may also be warranted in Tier 3.

4.2.3. Tier 3: The Toolbox

The assessment process through Tiers 1 and 2 follows essentially the same path for each product, and results in estimates of risk of acute and chronic effects on representative species under different scenarios of product use. Risk characterization at the end of Tier 2 is likely to establish that certain effect/scenario combinations have a relatively low risk, with sufficient certainty to support risk management decisions regarding those effects and scenarios. For other

effect/scenario combinations, remaining uncertainties (section 4.2.2.4) may warrant further resolution before a risk management decision can be reached. Since the nature of these uncertainties may be different for every pesticide, no single path can be defined for continuation of the risk assessment. Instead, Tier 3 involves application of one or more tools appropriate to the questions that need to be resolved.

4.2.3.1. Problem formulation and the rationale for tool selection

The previous tiers in the risk assessment process have identified the taxa and scenarios for which the risk criteria have been exceeded and which therefore require a more refined assessment. The problem formulation process in Tier 3 is dependent on the chemical (previous exposure and effects characterization and physicochemical data), the use pattern, and the taxonomic groups determined to be at risk in Tiers 1 and 2. There is no formal process or set of "required" studies at Tier 3, but instead a flexible, customized approach is used based on the expert judgment of the risk assessor. The risk assessor should closely consider the basic information developed at Tier 2 to determine the key factors that are influencing the predicted ecological risk and the uncertainties which remain. Once the key factors are identified, and the specific questions to be addressed are defined, the assessor must determine the most appropriate tools to refine the understanding of effects. The tools available in Tier 3 to accomplish this include analysis of time-varying or repeated exposure, additional acute toxicity studies, additional chronic toxicity studies, and sediment toxicity testing. Factors to be considered in selection of each of these tools are described in the following sections. Details about the tools are presented in Sections 4.5 through 4.8.

4.2.3.2. Analysis of time-varying or repeated exposure

The decision to focus on analysis of time-varying or repeated exposure (see section 4.6) would depend on the results of the exposure characterizations conducted in Tiers 2 and 3. If water bodies associated with a particular use pattern will be exposed to multiple inputs of a pesticide, or the pesticide concentration will vary significantly over time periods comparable to those used in standard laboratory toxicity tests, then an investigation of the effects of time-varying and/or repeated exposure should be undertaken.

Pesticide concentrations under field conditions typically vary over time. Organisms in the field often experience repeated exposures due to repeated pesticide applications or runoff and drift events. The results of the exposure event analysis can be used to help design laboratory toxicity studies simulating the exposures that sensitive taxa would experience under actual field conditions.

4.2.3.3. Additional acute toxicity studies to determine sensitivity distributions

The development of acute toxicity data for additional species to determine sensitivity distributions (see section 4.5) is recommended if acute toxicity concerns are not alleviated in the previous tiers, or substantial variability in sensitivity among taxa is demonstrated in previous tiers or is expected based on the pesticide's mode of action.

The additional species tested will 1) reduce the uncertainty associated with interspecies differences in sensitivity, 2) support a distributional analysis of species sensitivity, allowing estimation of the fraction of species affected at different exposure levels, and 3) generate more ecological information for site-specific analysis in Tier 4, if needed. Information generated in the exposure analysis will be used to determine the appropriate exposure duration for tests with additional species.

4.2.3.4. Additional chronic toxicity studies

The development of chronic toxicity data for additional species (see section 4.8) is recommended if chronic risk is demonstrated in lower tiers, exposure characterization in Tiers 2 and 3 has predicted that significant prolonged or repeated exposure is expected, the compound has a potential for bioconcentration (high K_{ow} or measured bioconcentration factor), or the mode of action or other data (e.g., reproductive effects in other organisms) suggests that chronic effects may occur.

The additional species tested will reduce the uncertainty associated with interspecies differences in sensitivity, and may allow a distributional analysis. The appropriate exposure regime would be determined based on information generated in the exposure analysis. Specific tests have not been identified as required because the risk assessment at this point should focus on compound of interest and its unique properties.

4.2.3.5. Sediment toxicity

A decision to focus the assessment on sediment toxicity (see section 4.7) would be based on the results of acute and chronic risk characterization using pore water concentrations (as determined by an exposure model such as PRZM/EXAMS) and the invertebrate toxicity tests from Tiers 1 and 2. Factors influencing partitioning of the pesticide between sediment particles and water, such as the octanol-water partition coefficient (K_{ow}) and the organic content of the sediment, are accounted for in this analysis. If the risk criteria established in Tier 1 are exceeded (see section 2.4.5.4), acute or chronic sediment toxicity tests with one or more sediment-dwelling aquatic invertebrates may be triggered. A sediment chronic test may also be triggered by results of a sediment acute test.

If sediment toxicity is found to differ substantially from that expected based on pore water concentrations, tests with additional sediment types may be required.

If the sensitivity of benthic species is found to be comparable to that of pelagic species already tested, data for pelagic species can be used to estimate the distribution of species sensitivity for benthic organisms. If this is not the case then it may be necessary to test additional benthic species to estimate the distribution of benthic species sensitivity.

4.2.3.6. Risk characterization using Tier 3 endpoints

As the complexity of the effects characterization increases through the use of the tool box available in Tier 3, so do the options for risk characterization in Tier 3. The focus of the Tier 2 risk characterization was the development of Joint Probability Curves that describe the potential magnitude of a response at any given exposure concentration (see Section 2.4.6.4). These same Joint Probability Curves can be generated for data developed in studies designed to address the effects of time-varying exposure, acute or chronic sediment testing, and additional acute or chronic testing. The species sensitivity distributions that may be generated in Tier 3 can be analyzed in a similar manner, with the effect variable being the number of impacted species at a particular toxicity threshold (see Section 4.5). If a concentration-effect relationship has been developed in chronic testing, then Joint Probability Curves can be established for these results as well.

4.2.4. Tier 4: Advanced Tools

The Tier 4 problem formulation step is highly individualized for each compound. Since many of the uncertainties in the effects characterization have begun to be addressed, the focus of Tier 4 is a refinement of these uncertainties. Effects characterization could follow a number of different paths depending on the questions to be answered. The types of problem to be addressed are often very specific but rarely easy to address. The typical case will be to design a specific experiment to address a particular issue.

The ECOFRAM Aquatic Effects Workgroup considered the following tools for Tier 4: population level analysis, pharmacokinetic or toxicokinetic modeling, microcosms/mesocosms, and behavioral tests. The first three of these are discussed in detail in sections 4.4, 4.6, and 4.9, respectively.

4.3. Time-to-Event Analysis

4.3.1. Introduction

Both exposure intensity (dose or concentration) and duration determine a toxicant's effect. The probability of an adverse effect rises if either is increased. However, the predominant approach to quantifying effects from toxicant exposure focuses on exposure intensity to the neglect of duration.

The conventional means of estimating consequences of exposure is to expose groups of individuals to various concentrations or doses of toxicant for a set duration. At intervals during the exposure and at test termination, the proportion of exposed animals that have died in each exposure group is determined (e.g., 3 dead of 20 exposed at 1 ppm = 0.15). Under the assumption of a log normal model, the probit of these proportions at each observation interval is plotted against the log of exposure concentration to produce a line (Figure 4-8). The LC50 and slope of this line allow estimation of effect at different concentrations for that exposure interval. Tanks with no or complete kills provide somewhat compromised information during maximum likelihood fitting of these types of data.

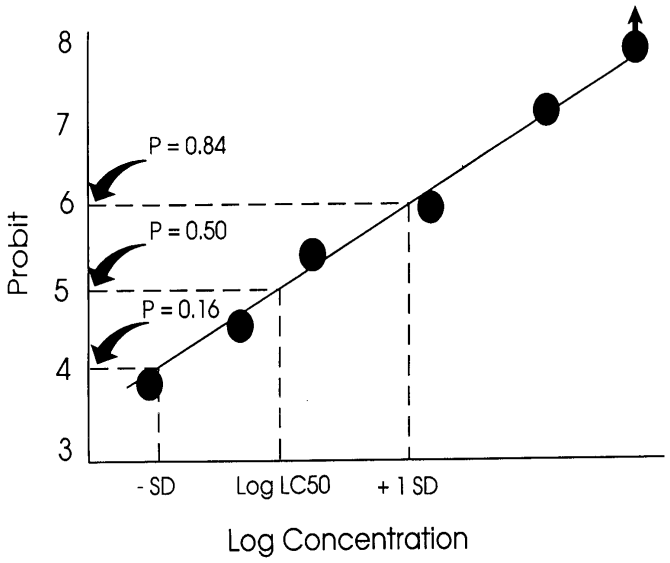


Figure 4-9. Conventional probit analysis of toxic effect measured after a single exposure interval, e.g., 96 hours.

This approach allows estimation of effect level in terms of the quality we attempt to control, concentration or dose. However, each LC50 determination does have imposed upon it a fixed duration of exposure that does not support prediction of effect at other times. Although analysis of data for each observation time (e.g., 24 hours, 48 hours, 72 hours, 96 hours) is possible, usually only the LC50 at termination (e.g., 96-h LC50) is reported or used in risk assessment.

Time-to-event (TTE) methods estimate effect in terms of duration of exposure with concentration (or dose) being held constant. Litchfield's method (Litchfield 1949) for estimating an LT50 is the approach most familiar to ecotoxicologists. It

is very similar to that just described for estimating LC50. In fact, Litchfield produced nearly identical methods for estimating LC50 (Litchfield 1949) and LT50 (Litchfield and Wilcoxon 1949). Instead of estimating effect as the concentration killing 50% of exposed individuals by a set time, effect is determined as the exposure duration required to kill 50% of individuals exposed to a set concentration (or dose) (Figure 4-9). This approach is seldom applied as environmental regulations tend to focus on controlling exposure intensity (concentration or dose) at or near a source, and duration is considered in a secondary context.

A less conventional, but equally appropriate, way of expressing toxicity is to hold concentration constant and estimate the duration of exposure required to kill 50% of exposed individuals (Figure 4-9). Like the probit methods detailed in Figure 4-8, a lognormal model is assumed for the data (proportion dying, duration of exposure). The top panel illustrates that a sigmoidal curve is expected through time with an increasing proportion of exposed animals dying as duration increases. An LT50 could be approximated from such a curve if a line were drawn to it from the proportion = 0.50 point on the y-axis and the corresponding x value read from the x-axis. This x value would approximate the LT50 for that exposure concentration (or dose). The bottom panel illustrates a slightly more formal means of doing this. The probit of the proportion dying at each time is plotted against the log of duration of exposure. If the assumption of a log normal model is valid, a straight line will be produced. Next, the LT50 and slope are estimated using one of several statistical methods that could include the maximum likelihood method described in Figure 4-8 for estimating the LC50. As can be done with the concentration-effect approach in Figure 4-8, levels of effect other than 50% mortality can be estimated with the slope of this line. This allows estimation of LTx or LCx effect levels where x is any level of effect from 0 to 100% mortality at a set time (LCx) or concentration (LTx).

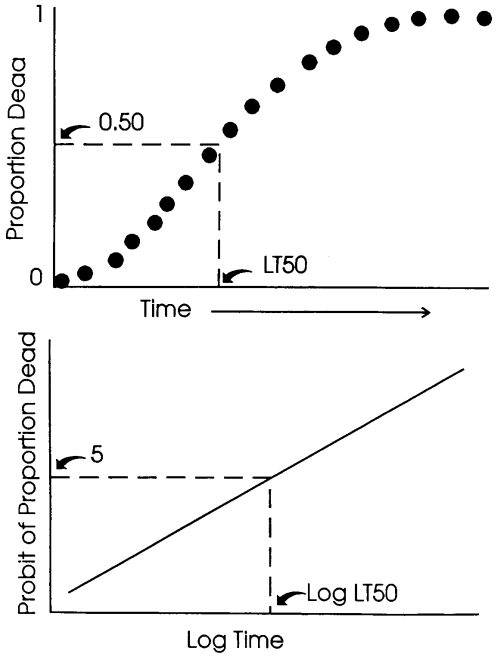


Figure 4-9. Time-to-event analysis of toxicity test data measured at a single concentration.

Both approaches have clear advantages and disadvantages. When one is selected over the other, a crucial component of exposure is ignored, either intensity (concentration) or duration. In conventional ecotoxicology and environmental regulation, exposure concentration is given primary consideration and exposure duration is considered in a more cursory fashion. As part of the convention, the standard duration of acute and chronic toxicity tests were established. This approach allowed for the development of testing regimes that were easily managed, had interpretable comparisons, and in the case of the acute tests, the 96-hour time period approached the incipient (time-independent) LC50.

The consequences of this compromise become more and more problematic as information derived from toxicity tests is applied to the increasingly complex demands of ecological risk assessment. Fortunately, well-established techniques exist in other fields that overcome these problems. Their application is convenient because of the widespread availability of desktop computers and inexpensive software. Now convention in ecotoxicology and environmental regulation remains as the major impediment to a more accurate prediction based on both exposure intensity (concentration or dose) and duration using time-to-event analysis.

4.3.2. Time-to-Event Methods: General

Time-to-event methods characterize the toxicity of a compound by modeling the exposure concentration and duration of exposure to a specified event. These methods draw on an experimental design in which groups of exposed individuals are monitored through time and times to some event are recorded for each individual. The event in question is often death but other types of events can also be handled. The only qualification is that the event can only occur in time (i.e., be a nonnegative value) for any individual. Some relevant examples of such time-to-event include times to loss of equilibrium, reach swim up stage, hatch, sexual maturity, spawning, flowering, first brood, achieving a certain instar, adult emergence from sediment, clinical appearance of cancer, or onset of disease. Exact times may be recorded if practical or time-to-event may be noted within an interval of time, e.g., death occurred between 12 and 16 hours of exposure. (Under current FIFRA guidelines, observations are made at least every 24 hours.) Also, some individuals may be censored in the data set. In the instance of a time-to-death experiment, survivors of the exposure at the termination of the experiment would be censored. The survivors' times-to-death are known only to be greater than the duration of the experiment. Because of this censoring, maximum likelihood methods are commonly used to fit time-to-event data.

Figure 4-10 is a flow diagram of the most widely applied TTE approaches. Kaplan-Meier methods are nonparametric and statistical differences between classes can be tested with several nonparametric tests. Conventional life tables are also applicable nonparametric methods. The semiparametric Cox proportional hazard model assumes no underlying distribution for the mortality curve but assumes that hazard (proneness to die at any time) remains proportional among groups such as males and females. They use maximum partial likelihood estimation to fit data. Fully parametric methods have specified underlying distributions for mortality and specific functions describing the influence of some covariate

(e.g., exposure concentration) on TTE. These methods use maximum likelihood estimation to fit data to the specified model.

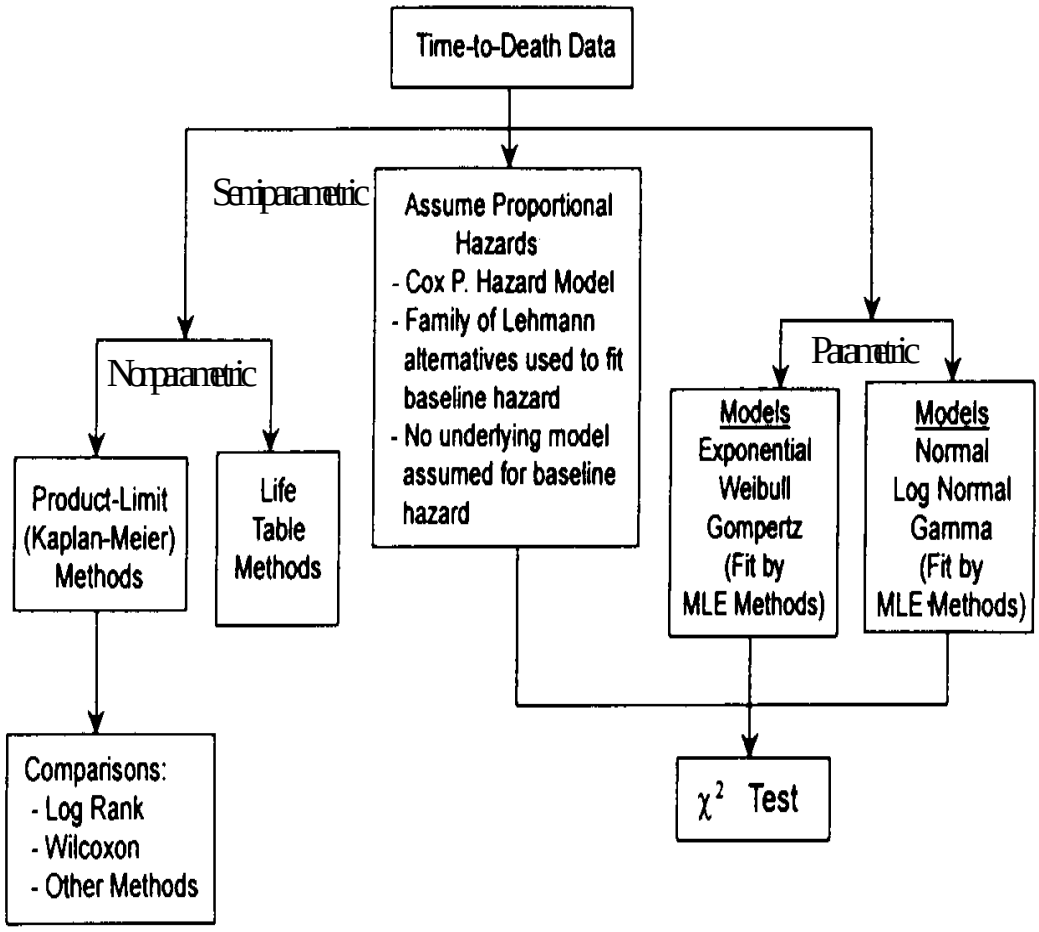


Figure 4-10. Time-to-death methods applicable to toxicity testing.

Each of these approaches can be used to fit time-to-event data, to predict time-to-events, and to test the significance of a covariate on time-to-event. An extremely powerful tool for fitting, predicting, and testing the significance of exposure intensity and duration is created by including exposure concentration (or dose) as a covariate in these methods.

4.3.3. Time-to-Event Methods: A Consideration for Use in Toxicity Evaluation

At first glance, these TTE methods appear only to be complicated versions of the Litchfield approach that offer no real advantage to the ecotoxicologist or environmental regulator. However, TTE does offer some advantages while maintaining the benefits of traditional toxicity evaluations. Listed below are several reasons why TTE methods should be considered for use in toxicity tests analyses. Published examples supporting each are referenced where possible.

Reason 1

Exposure duration, a crucial determinant of the consequences of exposure, is explicitly included in TTE methods. Explicit inclusion of duration is missing in the conventional approach.

As already discussed, consequences of exposure time are not incorporated into current methods, i.e., LCx and many NOEC/LOEC-associated methods. However, ecological risk assessments require accurate prediction of effect for different exposure durations. Figure 4-11 illustrates the loss of information occurring data are analyzed using concentration-effect methods instead of TTE methods. In a typical lethality test, several exposure concentrations (six here) are established and the proportion dying of all individuals exposed to each is estimated at one time. In Figure 4-11, open circles show such a data set for a 96-h exposure. One hundred percent mortality occurred before 96 h at the highest concentration, resulting in compromised data for that treatment in the analysis based on 96 h. (Under FIFRA testing guidelines, it is rare to have 5 concentrations with partial mortality.) If mortality (TTE) had been noted in each treatment at 6- to 12-h intervals, the temporal dynamics could have been captured and modeled.

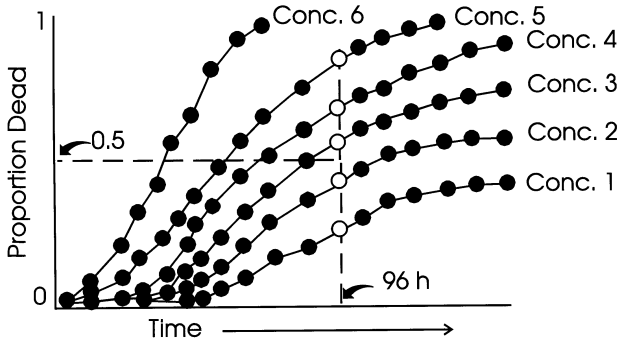


Figure 4-11. Comparison of information used in TTE methods (all circles) and information used in conventional concentration-effect methods (open circles).

By utilizing more of the data from the toxicity tests, some of the temporal variation is accounted for, power is increased, and a more accurate prediction is possible. ECOFRAM is also proposing the use of time-varying exposures for toxicity tests in Tier 3 (section 4.6), which will readily use TTE analysis for interpretation of results. Also, while neither the traditional statistical analyses nor TTE analysis completely consider the potential impact of latency effects (section 4.6.x.x), the time-to-event approach offers a means for eventual inclusion of the duration of exposure that is necessary to induce an effect.

Reason 2

Including TTE information enhances the power of statistical tests because more data are extracted per test treatment, e.g., ten TTE from each exposure tank versus one proportion dead from each exposure tank.

Figure 4-11 also demonstrates another important improvement associated with extracting TTE data during toxicity testing. Notice that only six data points would be available for analysis if the conventional concentration-effect methods were used. One of these data points (Conc. 6) would be censored and contribute less information than the other five points (open circles). We only know that some unknown concentration less than Conc. 6 would have produced exactly 100% mortality at 96 h. If TTE data were collected, many more data points (TTE for each individual) would be available for analysis. They would contain information about mortality through time as well as information for any specific time such as 96 h. Numerous authors (Gaddum 1953; Finney 1964; Sprague 1969; Newman 1995) point out the resulting increase in statistical power. All else being equal, TTE methods have higher statistical power than conventional concentration-effect methods because more data are used in the analysis.

Reason 3

Inclusion of TTE information does not preclude estimation of conventional endpoints such as the 96-h LC50.

As detailed in Newman and Aplin (1992), Newman (1995), and Newman and Dixon (1996), the conventional concentration-effect estimates (e.g., 96-h LC50) and associated confidence limits can be calculated easily from the results of TTE studies. Indeed, TTE estimates of LC values can be better than those from conventional analysis, because more information is generated to produce estimates and covariates can be incorporated that would otherwise contribute to unexplained variance (see *Gambusia* example below). Time-to-event will be particularly useful for compounds with short half-lives. Endpoint calculations can be made for relevant time intervals, which can then be compared to estimated environmental concentrations generated for that same time period.

Reason 4

Because of their enhanced statistical power, TTE methods allow important covariates (e.g., toxicant concentration or temperature) or important qualities of the individual that can be measured, to be included in predictive models.

As discussed in Reason 2 above, exposure concentration can be easily incorporated into TTE models, producing a time-concentration-effect model. This is primarily due to the efficient generation of data and consequent enhanced statistical power. While not generally considered in early tier toxicity testing, other important factors can also be included in TTE models, enhancing the accuracy of predictions. These include qualities of individuals that vary in natural populations or extrinsic factors (e.g., temperature, Table 4-2) that influence the outcome of exposure. Animal size (Newman and McCloskey 1996; Newman et al. 1994) and sex (Newman and Dixon 1996; Mulvey et al. 1994) are two important demographic qualities that can strongly influence effect (Figure 4-12, top panel) and can be included in TTE methods, but are normally controlled or ignored in conventional toxicity testing. The low statistical power of concentration-effect methods would make the inclusion of covariates difficult to interpret. Because of the complexity of adding covariates to the toxicity test design, these types of analyses would most likely be performed at Tier 4 in the risk assessment process, when specific questions need addressing for a particular compound.

Table 4-2. The effect of water temperature on time to reach sexual maturity for female mosquitofish (Mulvey et al. 1994).

Model Variable	Treatment Temperature	Variable Estimate (S.E.)	χ^2	Probability of obtaining a χ^2 of this magnitude by chance alone[b]
Intercept (μ)		4.07 (0.06)	4990	0.0001
Treatment (β)[a]	32° C	-0.70 (0.08)	77	0.0001
	25° C	0		
Scale (σ)		0.23 (0.03)		

[a] In these models, the effect of temperature on time-to-maturity is arbitrarily set to 0 ($\beta = 0$) for 25° C and that of 32° C adjusted relative to that level by the coefficient, β. The sign of the β for 32° C is negative and indicates that the time-to-maturity is shortened relative to that of the reference temperature of 25° C.

[b] Null hypothesis that the variable is 0 (df = 1), e.g., β for the 32° C treatment was not significantly different from that of the 25° C treatment.

In the performance of a TTE test, treatments are monitored through time and TTE are noted for individuals. Because each datum is associated with an individual, qualities of individuals can be noted for inclusion in models. For example, fish weight can be included in predictive models (Newman and McCloskey 1996) (Figure 4-12). Female mosquitofish were exposed to 0, 12.5, 15.0, 17.5 and 20 g/L of NaCl for 96 h. Times-to-death were recorded for fish with some fish surviving (time-to-death > 96 h) at lower concentrations. Fish differed in body weight, reflecting the variation in natural populations of these fish. The top panel of Figure 4-12 shows the predicted median time-to-death (LT50) for fish of different sizes exposed to different salt concentrations. The bottom panel expands predictions for an average weight fish; however, LT5, LT10, LT50, LT90 and LT95 values are predicted. This time-to-death model was able to predict the probability of death for fish as a function of exposure concentration, exposure duration, and fish size.

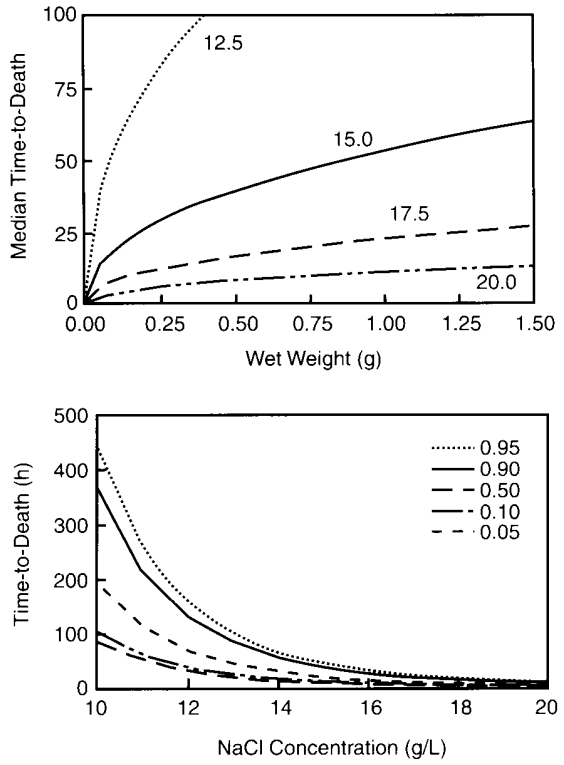


Figure 4-12**.** Results of a time-to-event analysis of fish mortality data (Newman and McCloskey 1996).

Many other examples are relevant to our use of time-to-event methods. Mulvey et al. (1994) modeled time-to-sexual maturity for normal and thermally-stressed fish (Table 4-2). In this study, genetic qualities of individuals were also included in models. Newman and McCloskey (1996) included zebrafish size in models of time-to-loss of equilibrium during benzocaine exposure. The effects of mosquitofish sex, body size, and genotype were also tested and modeled during mercury exposure (Newman and Dixon 1996).

Reason 5

Associated TTE models allow expression of risks as probabilities.

Depending on the method selected, TTE models allow easy expression of effects as risks (e.g., 5 of 100 are predicted to die after exposure to 2 µg/L for 48 h) or relative risks among different classes (e.g., exposure to 3 µg/L of toxicant increases the probability of death 15 times above that of control animals). This is consistent with the structure of the most comprehensive of human risk assessments and with the present movement in ecological risk assessment toward expression of risk as a probability. Calculations of risk relative to ecotoxicology scenarios are detailed in Dixon and Newman (1991), Newman (1995), Newman and McCloskey (1996), and Newman and Dixon (1996).

Reason 6

Results can be incorporated directly into well-established ecological, epidemiological, and toxicological models, e.g., population demographic models combining survival data with sublethal effects on reproduction and growth. This characteristic of the time-to-event results will be advantageous for the proposed use of population parameters in Tier 3 and 4 of the risk assessment process.

Most ecological models predict changes in ecological entities such as individuals or populations through time. Epidemiological models predict incidence of disease in populations through time. Ecotoxicological models should also be formulated to predict effects to individuals and populations over the duration of exposure. Exposure may include the entire lifetime of an individual, a critical part of an individual's life, or a short pulse as in the case of spray application of pesticides to crops. Except for the most fortuitous exposure scenarios (96-h pulse), conventional concentration-effect data are suboptimal information for inclusion in these types of models. In contrast, TTE models provide data that can be incorporated directly into ecological, toxicological, and epidemiological models.

Prediction of population consequences of exposure can be made with widely accepted demographic models if effects on survival and reproductive qualities were estimated through the life times of individuals. This is impossible with conventional time endpoint data. For example, if the time-to-first brood and production of young each day (m_x) were known for *Daphnia* held at a specific toxicant concentration, no demographic analysis (l_xm_x life table) could be done because survival information would be available only as an LC50 (or some other percentage) at a fixed time. Information about survival through time (l_x) is needed. If one could predict the proportion of individuals that will die each day (l_x), a complete l_xm_x life table could be constructed. Time-to-death methods generate such data (l_x). Important population qualities including the intrinsic rate of increase, age class-specific reproductive value, stable age structure, and sex ratio could then be estimated. A good illustration of this point is the work of Daniels and Allan (1981). In the *Daphnia* example used here, input of data from several *Daphnia* would allow the variation among individuals to be used to generate the likelihood of local population extinction (see the RAMAS PC-based program by Applied Biomathematics).

In sharp contrast to the LC50 and NOEC information usually derived from toxicity tests, intrinsic rates of increase and probabilities of local population extinction have clear ecological meaning. Newman (1995) discusses in more detail the linkage of TTE methods with life tables. Manly (1985) and Newman (1995) link TTE methods to population genetics models.

Predictive epidemiological models (Ahlbom 1993), including those used in human risk assessment, depend heavily on estimated probabilities of an effect under a specific exposure scenario. The compromised inclusion of time in ecotoxicological data inhibits the adaptation of methods from epidemiology to ecotoxicology. Time-to-death models resolve this problem, allowing calculation of effect probabilities. They are used widely in epidemiology, medicine, and toxicology now (see Ahlbom1993; Maribini and Valsecchi 1995).

Reason 7

Associated methods allow more candidate models to be explored, possibly resulting in more accurate prediction.

Many candidate models exist as described in textbooks (i.e., Marubini and Valsecchi 1995; Cox and Oakes 1984; Miller 1981) and ecotoxicological descriptions of TTE methods (Dixon and Newman 1991; Newman and Alpin 1992; Newman 1995; Newman and McCloskey 1996; Newman and Dixon 1996). This allows optimal data fitting and prediction accuracy. Several techniques can be used to select the best model (Newman 1995). In one case in which conventional methods were compared to TTE methods (Newman et al. 1994), the conventional model was among the worst for fitting lethality data.

4.3.4. Time-to-Event Methods: What are Their Shortcomings?

Time-to-event methods have several resolvable shortcomings. Many are shared with, but generally accepted in, conventional concentration-effect methods. Censoring is one example of a shortcoming shared by both approaches. Its effect is more pronounced with concentration-effect methods than with TTE methods because so little data are used per test by conventional concentration-effect methods. Because maximum likelihood and maximum partial likelihood methods used for concentration-effect and TTE methods become more biased as the number of data points being fit decreases, this censoring is more problematic for the conventional concentration-effect approach than for TTE methods. Latency (delay in responding after exposure; section 4.6.x) is another complication to applying both conventional and time-to-event methods. While neither method fully addresses latency, with sufficient information, a lag term may be added to time-to-event models that interpret the toxicity to account for latency. This cannot be done with conventional concentration-effect methods.

Other shortcomings are temporary and arise from longstanding convention in the field. There are large databases of LC50 information but very little TTE data exists. There is also the problem of unfamiliarity of most ecotoxicologists with these methods. This shortcoming can be countered by the enormous literature on TTE methods (e.g., books by Marubini and Valsecchi 1995; Cox and Oakes 1984; Miller 1981; Allison 1995) and the widespread acceptance of these methods in other disciplines.

Other shortcomings are unique to TTE methods and should be understood clearly. Chief among these is the increase in technician time needed in some cases to collect TTE data. The increase in technician time will depend on the frequency of time intervals for which observations must be made, and in the higher tiers the measurement of covariates that may be examined. However, the amount of information obtained per test is enhanced so much that the initial impression of increased time and cost associated with TTE methods is not accurate in many cases.

4.3.5. How Might Current Test Protocols Be Modified?

Current toxicity test data can be analyzed with time-to-event methods; however, some modification could improve results for some tests. The time intervals used could be optimized, perhaps using the results of a range-finding test. Similarly, the criteria for concentration selection need to be less rigid. Indeed, a range of concentrations with extensive mortality (minimal censoring) at each would be best for survival time modeling. The requirements can be relaxed relative to complete and partial kills. Linkage of the test results to reproduction (e.g., selecting similar durations of exposure for lethality and reproduction tests) would optimize the potential for linkage to demographic analyses.

Specifically, three important modifications could be made to current methods to improve their utility relative to predicting lethality through time and population consequences. First, death should be recorded at more time intervals. For a 96-h test, time intervals less than 24 hours would be important; however the frequency of those intervals can be determined by the characteristics of the compound and the availability of a technician. For a 21-d test, daily intervals would produce a sound data set. Second, linkage of survival to reproduction in tests would greatly enhance the potential for life table analysis and consequent predictions of population fate. While not requiring a change in test protocols, the use of reproductive data (e.g., *Daphnia magna* 21-d test) from all individuals, including those dying during the exposure, would allow direct use of life table methods to express effects in the population context. Third, it might be necessary to include more test levels and vary the 50% dilution factor that is required between levels to minimize the amount of censoring over time intervals. Conventionally ecotoxicologists have tried to minimize censoring at the final observation time (e.g., 96 hours).

4.3.6. Proposed Shareware to Conveniently Implement Time-to-Event Methods

Time-to-event analyses can be done with several commercial software packages; however, no shareware exists that is similar to the EPA shareware used extensively for conventional concentration-effect data. A straightforward program with an extensive manual would accelerate the implementation of time-to-event methods in environmental regulation. Such a program would accept data from a standard toxicity test. This would be efficiently performed using the data input capabilities of a package such as Excel.® Additionally, graphic presentation of data used in selecting the best model would be done optimally with such a program. Therefore, we suggest that the program be developed as an add-on to Excel® or some similar program.

Minimally, the nonparametric Kaplan-Meier and fully parametric method should be implemented. The nonparametric method could be used to generate simple survival estimates and associated confidence intervals (Greenwood's formula). The log-rank and Wilcoxon nonparametric tests should be included to test for differences, e.g., between replicate tanks. For fully parametric methods, the user should have the ability to select among the following models: exponential, Weibull, log logistic, and log normal. Model output should include measures of goodness-of-fit such as the log likelihood estimate and Akaike's information criterion. Parameter estimates and associated standard errors should be generated. A table or

graph of predictions (e.g., LCx or time-to-death estimates with standard errors) should be produced according to user-specifications. Again, the capabilities of a spreadsheet program such as Excel® would make the production of such output easy. Finally, the program should be capable of generating estimates of the probabilities of death under different exposure scenarios.

4.3.7. Existing Commercial Programs Implementing these Procedures

Application of time-to-event methods with the SAS statistical package has been illustrated relative to ecotoxicology in Newman (1995), Newman and McCloskey (1996), Newman and Dixon (1996), and Dixon and Newman (1991). An extraordinarily clear, practical guide has also been written by Allison (1995) for implementing these methods with the SAS statistical package. Particularly noteworthy in this practical guide is the treatment of time-dependent covariates, e.g., methods allowing inclusion of concentrations that vary with time. Despite the focus on the SAS statistical package in this treatment, a range of commercial PC-based software is currently available. They have been reviewed recently by Harrell and Goldstein (1997) and Goldstein et al. (1989). Harrell and Goldstein (1997) discuss favorably and provide information for purchasing thirteen such packages: BMDP, EGRET, EPICURE, EPILOG PLUS, LIMDEP, SAS, SPIDA, S-PLUS, SPSS, Stata, Statistica, Survival, and TRUE EPISTAT. They highlight advantages and disadvantages of each. Only one package (SURVCALC) is identified as having unresolved flaws. They give website addresses for obtaining relevant macros. (Allison (1995) also provides useful SAS macros.) They also refer to a user-generated macro for executing nonparametric time-to-event methods (Kaplan-Meier) with MINITAB. Although not reviewed, SYSTAT and GAUSS also perform time-to-event analyses.

4.3.8. Examples

4.3.8.1. Mosquitofish survival during acute NaCl exposure

The data of Newman and Aplin (1992) were reanalyzed to illustrate the application of survival time methods. Mosquitofish (*Gambusia holbrooki*) were placed in seven sets of duplicate tanks of a continuous-flow diluter. Thirty-eight to forty female fish ranging widely in size (wet weight) and averaging 0.136 g were randomly assigned to each tank. Times-to-death were noted every 8 h for 96 h. Fish weight was noted along with time-to-death.
Various models were assessed and a log logistic, accelerated failure time model with the covariates, ln wet weight and ln salt concentration, was selected for demonstration here.

$$\ln TTD = m + b_s \ln [NaCl] + b_w \ln Weight + e \qquad (1)$$

or

$$TTD = e^{m} e^{b_s \ln [NaCl] + b_w \ln Weight} e^{e} \quad (2)$$

where TTE = time-to-death, μ = intercept, β_s and β_w = coefficients for the effects of ln salt concentration and ln weight, respectively, and ε = an error term. Under the assumption of a log logistic model $e^{\varepsilon} = e^{\sigma W}$ where σ = a scale parameter and W = a metameter for the logistic curve associated with some proportion, e.g., 0.5 if the median TTE were to be calculated. Maximum likelihood methods were used to estimate μ, β_s, β_w, and σ. The W corresponding to a specific proportion can be found in a table or generated with a special function in many statistical or spreadsheet programs. Since W is 0 for the proportion of 0.5, the error term becomes $e^{\sigma 0} = e^{0} = 1$ for estimation of the median TTE. The fitted mosquitofish model was the following.

$$TTD_{50} = e^{15.211} e^{-4.1788 \ln [NaCl] + 0.2659 \ln Weight} e^{0.2017 W} \quad (3)$$

By changing W, predictions can be made for proportions dying other than 50%. Predictions can be made for any combination of salt concentration and fish weight within the range used to produce the model (Figure 4-12).

Conventional toxicity endpoints can still be estimated from survival models. For example, the 96 h LC50 can be estimated by rearranging Equation (1).

$$LC50 = e^{\frac{\ln 96 - m - b_w \ln Weight - s\ W}{b_s}} \quad (4)$$

Using the average fish weight in Equation (4), a 96-h LC50 of 11.26 is estimated. (Because survival time is estimated from these models, approximating the 95% C.I. for the 96 h-LC50 involves estimation of the concentrations corresponding to the 95% C.I. values for a predicted survival time of 96 h. The concentrations corresponding to the 95% C.I. of 96 h were approximately 11.09 to 11.44 g/L.) The 96-h LC50 is very close to that generated using the conventional trimmed Spearman-Karber method (11.58 g/L; 95% C.I. = 10.85 - 12.37 g/L). The associated confidence interval is narrower than that from the conventional trimmed Spearman-Karber method. By changing the weight, time (96 h here), or W in Equation (4), predictions can be made of LCx values for other proportions dying of various sized fish after different exposure durations.

4.3.8.2. Daphnia survival and reproduction

In a 21-day *Daphnia magna* test, survival and number of young produced were noted at days 0, 1, 5, 7, 9, 12, 14, 16, 19 and 21 days (Table 4-3). Exposure concentrations of the pesticide were 0, 3.7, 7.2, 17 and 32 µg/L. Because of the large number of surviving *Daphnia* at the end of the test, life tables were used to summarize these data instead of a parametric model as applied above. Also this allowed the inclusion of reproductive data in the analyses. Survival (l_x) and the average

number of young produced per female in the time period (m_x) are tabulated below for the control and highest concentrations only.

Table 4-3. Survival and production of young by *Daphnia* exposed to a pesticide.

Time (x, days)	Control (0 µg/L)		Highest (32 µg/L)	
	l_x (n=160)	m_x	l_x (n=81)	m_x
0-1	1.0000	0	1.0000	0
1-2	1.0000	0	1.0000	0
2-5	1.0000	0	1.0000	0
5-7	1.0000	0	1.0000	0
7-9	1.0000	0.275	1.0000	0.600
9-12	1.0000	1.888	0.9877	2.625
12-14	0.9875	9.525	0.9630	11.425
14-16	0.9563	14.600	0.9383	10.850
16-19	0.9375	14.100	0.7531	4.675
19-21	0.9250	14.612	0.0741	5.575
21	0.9250	14.063	0.0123	15.250

From this type of data and standard demographic calculations, population qualities can be generated such as the intrinisic rate of increase, mean generation time, and stable age structure of populations held at different toxicant concentrations. For example, a change from 0 to 32 µg/L resulted in a drop in the intrinisic rate of increase from 0.27 to 0.24 and a decrease in life expectancy of a neonate from 10.2 to 8.2 days. Stochastic modeling is also possible using the variation in mortality and natality among females in each treatment. Stochastic treatment of life table information would allow estimation of the probability of population extinction with different exposure concentrations.

Under conventional analysis of these data, a separate NOEC would be estimated by ANOVA/post-ANOVA methods for survival and reproduction. These NOEC values could not be used to predict consequences in the context of the population. They have statistical significance but minimal ecological meaning. Indeed, many question the statistical and biological validity of the NOEC (Stephan and Rogers 1985; Hoekstra and Van Ewijk 1992; Laskowski 1995; Newman 1995; Chapman et al. 1996).

4.3.9. Summary

The ECOFRAM Aquatic Effects Workgroup recommends that time-to-event statistical analyses be used for the interpretation of standard toxicity test data whenever possible. Time-to-event analysis utilizes models to estimate the effects of a treatment and tests the effects of covariates on events that occur through time (e.g., death, time to hatch). The useful information extracted from toxicity tests is greatly increased by including time-to-event data, while still offering many of the same functions (e.g., LC50 estimation) as traditional toxicity test evaluations. The reasons to consider time-to-event analysis as an enhancement to the risk assessment process are:

(1) Exposure duration, a crucial determinant of the consequences of exposure, is explicitly included. Including both duration and exposure on the characterization of toxicity is relevant to all toxicity tests, and therefore has the potential to impact all Tiers in the risk assessment process. In particular, however, the time-to-event analysis offers a useful tool for interpreting time-varying exposure scenarios (section 4.6).

(2) Including time-to-event information enhances the power of statistical tests because more data are extracted per test treatment, e.g., ten times-to-death per exposure tank versus one proportion dead per exposure tank. The increased power to detect biologically relevant differences in toxicity tests is important for valid toxicity tests to be used in a regulatory context.

(3) Inclusion of time-to-event information does not preclude estimation of conventional toxicological endpoints such as 96-h LC50. Indeed, estimation of conventional endpoints may be enhanced because of more complete use of information, which impacts the acute toxicity tests that may occur in Tiers 1 and 3. Also, the historical use of the LC50 readily allows for comparisons across compounds.

(4) Because of their enhanced statistical power and the fact that data are generated for individuals, time-to-event methods allow important covariates (e.g., temperature) or qualities of individuals (e.g., animal size, lipid content or sex) to be included in predictive models. Though the traditional toxicity tests generally used at Tiers 1 and 3 will not include covariates, specialized tests in Tier 4 may examine such functions.

(5) Associated models allow expression of risks as probabilities. As other methods of evaluating toxicity data have various models to which they are associated, time-to-event analysis has models that will express the results as a probability.

(6) Results can be used directly in well-established ecological, epidemiological, and toxicological models, e.g., demographic models combining survival data with effects on reproduction. The use of such models may be directly associated with Tier 3 of the risk characterization and assessment process which includes the option of examining population parameters.

(7) Associated methods with time-to-event analysis allow more candidate models to be explored and, consequently, result in more accurate prediction.

Together, these features of time-to-event techniques greatly improve our ability to predict consequences of exposures. Applicable are nonparametric (life tables, Kaplan-Meier methods), semiparametric (Cox proportional hazard models), and

fully parametric (accelerated failure time and proportional hazard models) methods. These methods are easily implemented with PC-based statistical software.

4.4. The Use of Population Models in Aquatic Effects Assessment

4.4.1. Introduction

The population is the smallest self-reproducing biological unit that is stable and persistent in time. For this reason, ecological risk assessors have long argued that the abundance and persistence of populations of organisms are more relevant as endpoints for assessment than are responses of individual organisms observed in controlled laboratory experiments (Suter 1993). The importance of population-level assessment has been reaffirmed by EPA in its Guidelines for Ecological Risk Assessment (EPA 1998). In the past, however, OPP and other program offices responsible for regulating chemicals released into the environment have emphasized risks to individuals. An assumption has been made that if the most sensitive or most exposed individuals within a population are protected, then the population will be protected. This approach has been justified on the grounds that too little is known about the responses of populations to chemical exposure to support regulatory application of population-level assessment methods.

However, some types of ecological issues, e.g., recovery of populations following short-term exposure events and evaluation of behavioral or sublethal physiological responses, are difficult to interpret using only laboratory-derived test data or small-scale field experiments. Moreover, the significance of particular hazard quotient values can be difficult to communicate to risk managers who must weigh costs and benefits of pesticide use. Most non-specialists have a better intuitive understanding of population-level endpoints (e.g., fish populations may be reduced or become extinct) than of individual-level endpoints (e.g., the *Pimephales promelas* NOEC for reproduction may be exceeded). This difficulty is not overcome by expressing the exposures in terms of probabilities. For all of the above reasons, integration of scientifically credible population-level risk assessment methodologies would enhance the value of pesticide ecological risk assessments.

This integration is now feasible, because both the theory and the practice of applied population biology have improved rapidly in recent years. Improvement has come in part because of the general availability of powerful computers and modeling software, and in part because of the needs of natural resource managers for quantitative tools to support recovery plans for endangered species and management plans for exploited fish populations. Approaches for integrating population biology with environmental toxicology have been developed and demonstrated, although none of these approaches have yet become part of routine regulatory practice.

The objective of this section is to show how this growing body of knowledge and methods can be applied to risk assessments for pesticides, using the same kind of tiered testing and assessment framework currently employed by OPP. This extension of the framework would provide a more meaningful interpretation of the test data that is more readily understood by risk managers and the general public.

4.4.2. Review of Applicable Approaches

FIFRA requires decision makers to incorporate analysis of risks and benefits of regulatory decisions. If the use of a pesticide is to be restricted, it must be shown that reductions in risks to ecosystems will outweigh economic benefits of unrestricted use. Ecological endpoints in the past have emphasized (1) predicted effects on individual exposed organisms, and (2) observed fish and bird kill incidents. However, neither predicted effects on individuals nor enumerations of kill incidents can provide scientifically rigorous or defensible estimates of the benefits of regulation. All organisms die. Except in the case of threatened or endangered species, the abundance and persistence of populations may be a more relevant endpoint. Ecological risk assessments for pesticides would be more useful and scientifically credible if it were possible to base decisions on risks to populations rather than risks to individuals, and to consider both *spatial scale* and *temporal scale* in the assessment. If only a small fraction of a population is exposed, or if the population recovers rapidly after exposure events, risks associated with pesticide use may be small even if lethal exposures occasionally occur. Some pesticides are acutely toxic but not persistent in the environment. Such substances are arguably preferable to persistent pesticides that have long-term chronic effects that might only be detected after substantial environmental damage has occurred. If it were possible to estimate the spatial variations in pesticide exposure and to evaluate the rate of recovery of exposed populations, this information could be used to design pesticide application regimes that would minimize ecological risks.

4.4.2.1. Model evaluation criteria

None of the above considerations are captured in the current FIFRA tiered assessment framework. However, they could be included in the alternative framework developed by ECOFRAM, if models could be found that extrapolate effects on individual organisms (mortality, reproduction, etc.) to effects on populations and ecosystems. The following criteria are relevant to evaluating the utility of the currently available approaches:

Endpoints: ability to characterize ecologically relevant effects, i.e., the abundance and/or persistence of populations.

Spatiotemporal resolution: ability to characterize the spatial distribution of exposures and effects; ability to account for variations in temporal exposure over a period of days, weeks, or months.

Generality: applicability to a variety of types of biota and exposure situations relevant to pesticide risk assessment.

Current degree of acceptance: degree of acceptance within the scientific community, as evidenced by the number of successful applications (e.g., in resource management or conservation biology), and the number of refereed publications that employ the approach.

"Data requirements" and "data availability" were not included as evaluation criteria, because within most of the major categories of modeling approaches one can find models possessing a wide a range of data requirements and availabilities. It is almost always possible to adjust a model to fit the available data.

The types of available approaches vary greatly in terms of level of detail and quantity of required supporting information. The five approaches described below are representative of the range of techniques that appear most applicable in pesticide risk assessment.

4.4.2.2. Life-table analysis and logistic models

Life-table methods quantify the influences of reproduction and mortality on the growth rates of populations. The fundamental relationship between reproduction, survival, and population growth rate can be simply expressed using the following equation:

$$\sum_{x=1}^{n} e^{-rx} l_x m_x = 1 \qquad (1)$$

where

l_x = the probability that an organism will survive from birth to age x,

m_x = the number of young produced by an organisms of age x, and

r = the rate of increase of the population per unit time, often referred to as the "intrinsic rate of natural increase."

Despite its simplicity, equation (1) illustrates some very important aspects of population dynamics that are relevant to assessing ecological effects of chemicals. First, note that the terms l_x and m_x are multiplicative. It is the *product* of these terms that determines the value of r. A given proportional decrease in survival at any given age is equivalent to the same proportional decrease in age-specific fecundity. In other words, from the population perspective, there is nothing qualitatively unique about reproductive effects as compared to effects on survival. Of particular importance for risk assessment, organisms with very long life spans and low reproductive rates have low intrinsic rates of increase compared with short-lived, highly fecund organisms. This suite of traits is also associated with vulnerability to increases in mortality caused by harvesting, habitat change, and (at least in theory) chemical exposure.

The growth rate (r) in equation (1) determines the rate at which a population grows or shrinks in time, starting from an initial population (N_0):

$$N_t = N_0 e^{rt} \qquad (2)$$

If *r* is greater than zero, the population will grow, and if *r* is less than zero it will decline. The lower the value of *r*, the more slowly a population grows, and the more vulnerable it is to stresses that decrease survival or reproduction. Very long-lived organisms with low reproductive rates and low rates of increase have always been disproportionately represented among endangered species. Regardless of taxonomic group, species with this life history pattern are uniformly at a high risk of decline as a result of sustained increases in mortality whether from natural sources or from anthropogenic sources.

Equations (1) and (2) are often expressed in the form:

$$\sum_{x=1}^{n} l^{-x} l_x m_x = 1 \qquad (3)$$

$$N = N_0 l^t \qquad (4)$$

where $\lambda \quad e^r$

A number of authors (Daniels and Allen 1981; Gentile et al. 1983) have used life-table methods to quantify impacts of chemical exposures on laboratory populations of cladocera. Munns et al. (1997) applied the method to mummichog populations naturally exposed to dioxins and PCBs.

The PondFX Worldwide Web site (www.ent.orst.edu/PondFS) maintained by Oregon State University supports a

contains a database on physicochemical characteristics of approximately 500 ponds in the United Kingdom, and a

simulation package employs the logistic population growth model:

$$N_t = l N_{t-1}\left[1 - \left(N_{t-1} \big/ K\right)\right] \qquad (5)$$

λ in equation (5) is the finite rate of population growth, and is estimated from life-table data. The term K in equation (5) is the "carrying capacity," i.e., maximum population size that can be sustained on a long-term basis. If the population size at time t is smaller than K, then the population will grow until it reaches K; if the population is larger than K it will decline until it reaches K. Carrying capacity is ecosystem-specific and cannot be estimated from life table data. In PondFX, default "large" and "small" values of K are provided for exploratory analyses. The default values can be changed by the user.

PondFX contains a "stochastic" option in which λ is interpreted in terms of the probability that an individual organism will reproduce during a given time interval. This type of stochasticity is termed "demographic stochasticity" by population biologists. If a population is reduced to a very small size and the probability of reproduction per organism is low, then the actual rate of population growth will be highly uncertain. By chance, demographic stochasticity can cause a small population to decline to extinction even if a deterministic model predicts positive population growth.

For any of the species included in the database, PondFX can simulate the decline and recovery of a population exposed to toxic levels of an agrochemical. Since the values of K are arbitrary, the time required for population recovery is determined by (1) the fraction of K to which the population is reduced, and (2) the population growth rate, λ.

The logistic model also has a continuous form, analogous to Equations (1) and (2):

$$dN/dt = rN(1-\frac{N}{K}) \qquad (6)$$

where

K = population carrying capacity.

Given an initial population size N_0, a population will grow (if $N_0 < K$) or shrink (if $N_0 > K$) until it stabilizes at size K. The population present at any given time is given by:

$$N_t = \frac{N_0 K}{N_0 + (K - N_0)e^{-rt}} \qquad (7)$$

Kooijman et al. (1983) described the use of Equation (7) and several variants for describing effects of chemicals on growth rates observed in algal cultures.

4.4.2.3. Age/stage-based models

The most flexible and widely-used approach to population-level assessment is the age/stage-structured projection model. In this approach, the number of individuals in each of an arbitrary number of age or size classes at time t is expressed in terms of the numbers present at time t-1:

$$\boldsymbol{N}_t = \boldsymbol{L}\boldsymbol{N}_{t-1} \qquad (8)$$

where $_t$ and $_{t-1}$ ***L*** is a matrix of age-specific

age/stage-based model is the Leslie matrix:

$$L = \begin{bmatrix} s_0 f_1 & s_1 f_2 & s_2 f_3 & \dots & s_{k-1} f_k & 0 \\ s_0 & 0 & 0 & \dots & 0 & 0 \\ 0 & s_1 & 0 & \dots & 0 & 0 \\ 0 & 0 & s_2 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & s_k & 0 \end{bmatrix} \qquad (9)$$

where

s_k = probability of survival from age k to age k+1

f_k = average fecundity of an organism at age k.

If all of the survival and reproduction parameters are viewed as constants, Equation (9) is equivalent to a life table. The advantage of the matrix form is that important phenomena such as environmental variability and population regulation can be introduced simply. The basic model can be made much more realistic simply by making the survival and reproduction parameters random variables, functions of environmental parameters, or population size. Rather than being represented as discrete age classes, organisms can be grouped by size, life-stage, or both. The matrix projection approach can simulate responses of populations to arbitrarily complex sequences of conditions, such as those produced by PRZM/EXAMS or other dynamic environmental fate models.

Caswell (1989) presents a detailed discussion of the mathematical properties of age-structured population models. Barnthouse (1993) and Emlen (1989) described the range of resource management and risk assessment applications to which age/stage-structured models have been applied. Some of these applications involve pesticides and toxic chemicals (e.g., Tipton et al. 1980, Samuels and Ladino 1983, Barnthouse et al. 1990). Barnthouse et al. (1990), for example, used matrix-projection models of well-characterized marine fish species (striped bass and gulf menhaden) to evaluate the influence of life history, environmental variability, and exploitation intensity on the responses of fish populations to toxic chemical exposure.

Recently, new methods have been developed for comparing the influence of different life-history characteristics on the rate of population growth (λ). These approaches are especially useful for analyzing models in which life-cycle processes are represented by stage rather than by age. In stage-based models, the probability that an organism in stage *i* during a given time interval will be in stage *j* during the next time interval is defined by a *transition probability* (a_{ij}). The numbers of organisms present in each class at time t is given by a matrix equation identical in form to Equation (3), except that the Leslie matrix (***L***) is replace by a more general *transition matrix*. In a transition, matrix, any element can potentially take a

nonzero value, denoting the probability of remaining in the same state or life-stage or probabilities of transitioning into two or more alternative states. The term *elasticity* (e_{ij}) (deKroon et al. 1986) has been applied to a measure of the proportional sensitivity of the population growth rate to each element of the population transition matrix (a_{ij}):

$$e_{ij} = (a_{ij} / l)(\partial l / \partial a_{ij}) \qquad (10)$$

Elasticities as defined by equation (10) measure the relative contribution of each life-cycle element to the population growth rate. Elasticities have been found useful in theoretical studies of the relative fitness of different life-history strategies, especially for organisms such as plants that have extremely complex life histories compared to most vertebrate animals. Refinements of the basic methodology have been described by van Groenendael et al. (1994) and van Tienderen (1995). Meyer and Boyce (1994) used elasticity to compare the influence of changes in fecundity and survival due to hypothetical pesticide exposures on bird populations with different age and size-structures.

The elasticity methodology itself does not provide any new approaches for modeling impacts of pesticides on populations. It may, however, be useful in the design of model-based assessment schemes. Models representative of a range of life-history types (small, fast-growing, short life-span vs. large, slow-growing, long life-span) would be developed. Elasticity analyses would be used to identify the life-cycle stages most strongly influencing the long-term population growth rate. These are the life stages at which pesticide exposure would be likely to have the greatest impacts.

4.4.2.4. Individual-based models

One potential limitation of the age/stage-based approach is that the aggregate mortality and reproduction parameters cannot explicitly represent mechanisms responsible for death or reproductive impairment. The sensitivity of an organism to a chemical may be related to its nutritional status, or may vary seasonally, or may be affected by the presence of parasites. Adverse effects of pesticide exposure may be expressed indirectly, through alterations in behavior. These kinds of phenomena can now be directly addressed using “individual-based” population models.

In an individual-based model, characteristics of populations are inferred from characteristics of the individual organisms. A model of the individual organism is constructed, including whatever physiological and behavioral processes are believed to be relevant. Properties of the population are inferred either by analytical solution of equations (for simple models) or by numerical simulation of the activities of hundreds or thousands of individual organisms (for more complex and realistic models).

Age- and stage-based models already account for the influence of age and (for some stage-based models) size on population dynamics, but individual-based models can expand the list of characteristics considered to *any* aspect of organismal biology believed to be relevant. For the purposes of pesticide risk assessment, the most relevant of these appear to be physiology and behavior. The general procedure is to develop a model of the individual organism to whatever level

of detail is required, and then to infer the properties of the population as a whole either by analytical solution of equations or by numerical simulation of the activities of hundreds or thousands of individual organisms.

Physiological characteristics included in individual-based models have emphasized metabolism, growth and contaminant pharmacodynamics. Work on metabolism was pioneered by Kooijman and Metz (1984), who examined the influence of contaminants on metabolism and population growth using *Daphnia* as a model organism. Hallam and Lassiter (Hallam et al. 1990; Lassiter and Hallam 1990) extended this approach to include (1) a thermodynamically-based model of the uptake of contaminants from aqueous media and (2) a definition of death in terms of the internal dissolved contaminant concentration within an organism. McCauley et al. (1990) and Gurney et al. (1990) developed an energetics-based model of *Daphnia* growth and reproduction and used the model to predict time-dependent changes in the age and size-structure of *Daphnia* populations in response to changes in food availability.

All of the above models were developed for aquatic organisms with relatively simple life-cycles. The emphasis in model analysis was on evaluation of general properties of the models through analytical investigation of the equations. DeAngelis et al. 1991 and Rose and Cowan (1993) developed models of fish populations that include metabolism, growth, foraging behavior, and prey selection as functions of the life stage and age of the fish. DeAngelis et al. (1991) even included the nesting and nest defense behavior of male smallmouth bass. The approach followed in developing both of these models was to use the existing extensive theoretical literature on bioenergetics, reproduction, and foraging of individual fish, coupled with exhaustive evaluation of the life history of specific fish species, to develop detailed models of each life-stage from egg through reproductive adult. Population-level consequences of changes in the physiology, behavior, or reproduction of individual fish are inferred by brute-force simulation of the birth, growth, and death of hundreds or thousands of individual fish. The models are calibrated to extensive data sets collected for specific fish populations.

The model of DeAngelis et al. (1991), for example, simulates the spawning, growth, and survival of a year-class of smallmouth bass (*Micropterus dolomeui*) in Lake Opeongo, Ontario. It is structured as a set of discrete submodels that simulate the daily activities and physiological condition of each individual fish in the model population. Reproductive behavior in smallmouth bass is quite complex. Adult males excavate nests, and after eggs are deposited in the nests the males defend the nests from predators for several weeks while the eggs hatch and develop through their early larval stages. Spawning behavior and spawning success have been shown to be both temperature and size-dependent. Larger males spawn earlier; larvae that are spawned early have a size advantage over larvae that are spawned late. Success in rearing a brood is related to the size and condition of the guarding males. The males do not feed during the brood period; smaller males and males in poorer condition at spawning abandon their nests much more frequently than do larger, healthier males. Environmental conditions also have an important influence on spawning success because storm events that cause water temperatures to fall below a critical threshold cause the males that have spawned to abandon their nests.

The model of DeAngelis et al. (1991) simulates all of these processes. Given an initial size/condition distribution of males and a specified daily temperature regime, the model simulates the nesting and brood-rearing success of each male over the course of the reproductive season. The probability of successfully rearing a brood and the number of young fish produced from each brood are defined as probabilistic functions of the size and condition of the male at the time of nesting.

The objective of the authors was to understand and explain the processes responsible for recruitment success in smallmouth bass: why more fish are produced in some years than in others and why large males spawn earlier than small males in spite of the increased risk of low-temperature events. Because of the physiological detail included in the model, however, it would be relatively easy to modify it to include lethal and sublethal effects of toxic chemicals. Jaworska et al. (1996) developed a model of largemouth bass that incorporated effects of PCBs on the growth of individual larvae and juveniles.

Individual-based models have also been applied to terrestrial biota. In many cases the emphasis has been on behavior rather than metabolism and physiology. Pulliam et al. (1992) developed a model of the Bachmann's sparrow population on the Savannah River Site, South Carolina, derived from the individual foraging behavior and habitat selection of the birds.

Lacy (1993) described a generalized computer program (VORTEX) that simulates the local population dynamics of terrestrial vertebrate populations. VORTEX was intended for use in the management of small populations threatened by habitat loss, environmental variability, and loss of genetic variation. The core of VORTEX is stochastic model of the birth, growth, reproduction, and death of each individual animal. At the start of simulation, an initial number of animals, age/sex structure, genetic composition, and carrying capacity are specified. At each subsequent time-step (normally one year, but modifiable by the user), mature animals mate and produce young. Both reproduction and survival are assumed to be density-dependent, with expected values changing depending on the relationship between the current population size and the carrying capacity. Reproduction and survival are subject to two sources of environmental variation: "normal" annual variation specified by a binomial probability distribution, and "catastrophic" variation that occurs randomly according to a uniform probability distribution.

Each simulation "run" produces a single stochastically-determined time-series of population sizes and age/sex/genetic compositions. The simulated population either persists throughout the simulation or goes extinct at some point during the simulation. Estimates of the probability of persistence and expected time-to-extinction of the simulated populations are obtained by performing multiple runs (hundreds or thousands).

VORTEX, in the version described by Lacy (1993), can simulate up to 20 populations, between which immigration and emigration can occur. In this form it can be viewed as a metapopulation model. VORTEX has been applied to a variety of endangered bird and mammal species (Lacy et al. 1989, Seal and Foose 1989, Seal and Lacy 1989, Lacy and Clark 1989, Maguire et al. 1990, Foose et al. 1992, Lindenmayer et al. 1993). VORTEX, unlike the model of DeAngelis et al. (1991) does not explicitly simulate ecological or physiological processes relevant to pesticide exposure and effects assessment.

However, information concerning (1) the distribution of doses within an exposed population and (2) dose-response relationships for reproduction and mortality could be used to modify the survival and reproduction functions used in VORTEX.

4.4.2.5. Metapopulation models

Most species do not exist as continuous interbreeding populations. They consist of subpopulations inhabiting patches of suitable habitat mixed in with patches or regions of unsuitable habitat. All are subject to environmental variability that may be either large or small. Small populations frequently go extinct, but habitat patches are then recolonized by colonists arriving from other patches. This view of species as "metapopulations" was first formalized by Andrewartha and Birch (1954), although they did not use the term. The first quantitative studies of metapopulation biology were published in the 1960s by MacArthur and Wilson (1967) and den Boer (1968). Levins (1969) is credited with developing the first formal model to specifically address the central question in metapopulation biology: how are (1) the fraction of occupied patches and (2) the expected time to extinction of the species as a whole affected by the probabilities of extinction and recolonization of individual patches?

Levins (1969) formulated a simple relationship between the fraction of habitat patches occupied by a species at any given time ($p(t)$), the rate of extinction of occupied patches (e), and the rate of production of propagules from each occupied patch (m). He reasoned that at any time t, mp propagules would be produced. Assuming equal probability of dispersal to occupied and unoccupied patches, a fraction equal to ($1-p$) of these would colonize unoccupied patches. At the same time, a total number of patches equal to ep would become extinct. The rate of change in p at any time would be determined by the equation:

$$dp/dt = mp(1-p) - ep \qquad (11)$$

It follows from this equation that the equilibrium frequency of occupied patches ($p^{*)}$ is determined by the ratio of the extinction (e) and colonization (m) rates:

$$p^* = 1 - e/m \qquad (12)$$

It is intuitively obvious even without Levins' model that if extinction is more likely than dispersal (i.e., e is larger than m) the species must become extinct. It is not, obvious, however, that the if these two parameters are similar in magnitude the fraction of occupied patches can be expected to be very small, even if the rate of dispersal of propagules from occupied patches is very high. Levins also investigated the influence of temporal variation in extinction and colonization rates on the size and probability of persistence of species subdivided into local populations.

The above model is clearly too simplistic to be of much value in the management of real populations. Many subsequent authors (see review by Hanski 1991) have replaced Levins' simple assumptions with more biologically realistic

representations of both the dispersal of organisms between habitat patches and the local dynamics of populations within patches. However, the fundamental processes and variables of interest, i.e., dispersal, extinction, percent occupancy of available habitat, and metapopulation persistence, have not changed.

Most early work involving metapopulation models was concerned with insect populations, either with understanding the reasons for persistence of insect species subject to wide fluctuations in local population abundance (den Boer 1968) or with designing control strategies to reduce the frequency of widespread pest outbreaks (Levins 1969). In the 1980s conservation biologists turned to metapopulation theory as a means of designing preservation strategies for vertebrate species that, although once widespread, were becoming restricted to isolated subpopulations because of increasing habitat fragmentation. The early models were extended to include influences of local population size (Hanski 1985), local population structure (Lande 1987) and spatial dispersal patterns (Ray and Gilpin 1991). The theory has also been extended to include predator-prey and host-parasitoid dynamics (Murdoch et al. 1985; Sabelis et al. 1991).

The relevance of this work to pesticide risk assessment comes from the observations that many wildlife species of management interest are, effectively, metapopulations. Their distribution patterns have been changed by decades of habitat conversion as the original forests and prairies of North America have been transformed into a mosaic of agricultural, urban/suburban, and successional landscapes. Pesticides of equal toxicity will have differential impacts on wildlife species depending on patterns of habitat utilization, degree of population isolation, dispersal ability, and other aspects of population biology included in metapopulation models. Lande (1987) formulated a model of extinction and persistence in territorial populations that is a direct descendent of Levins' (1969) original model.

Lamberson et al. (1992) described a metapopulation model of the Northern Spotted Owl (*Strix occidentalis caurina*). In their model habitat patches are defined as nesting territories and local populations are defined as nesting pairs. A nesting pair annually produces young according to either a fixed fecundity rate or a randomly varying fecundity rate. The juvenile birds disperse at the end of each breeding season, with juvenile males seeking an unoccupied nesting territory and juvenile females seeking a site occupied by a solitary male. The probability that a dispersing juvenile finds a suitable site before it dies is determined by the fraction the total landscape that consists of suitable sites, the fraction of those sites that is already occupied by nesting pairs, and the number of sites a juvenile can search before it dies. Adult birds are subjected to annual mortality, and nesting sites are subjected to disturbance through timber harvesting. Adults nesting on a harvested site must disperse and locate new, unoccupied sites.

Lamberson et al. (1992) used the model to evaluate the influence of initial population size, the proportion of the landscape suitable for occupancy by spotted owls, and the degree of interannual variability in fecundity (reflecting variability in food supply). In the absence of environmental variability, extinction always occurred if less than a fixed percentage of the landscape (determined by dispersal ability) was suitable; extinction never occurred if the percentage of suitable habitat was greater than the threshold. In the presence of environmental variability, there was a small probability of persistence for habitat suitabilities slightly below the deterministic threshold and a small probability of extinction for suitabilities

somewhat higher than the threshold. By examining a range of parameter values consistent with the current state of knowledge of spotted owl population biology, the authors found that the effective persistence threshold for the metapopulation lies somewhere between 10% and 25% suitability of available habitat.

Lamberson et al. (1994) used a different metapopulation model to evaluate the influence of patch size and spacing on the viability of the Northern Spotted Owl. The landscape was portrayed as a rectangular array of identical circular clusters containing potential owl habitat. Each cluster consisted of a collection of territories, some or all of which were assumed to be suitable as nesting sites. All of the space between clusters was assumed to be unsuitable habitat. This idealized landscape was intended to approximate the real landscape inhabited by spotted owls, which consists of patches of old-growth forest of with differing abilities to support spotted owls separated by areas of cut forest. Within each site, owl reproduction, survival, and dispersal were modeled in the same way as Lamberson et al. (1992), except that only females were considered. Dispersal was assumed to be successful if a juvenile female found an unoccupied but suitable territory within a specified number of searches.

Landscape parameters investigated by the authors included the percentage of the total landscape included within habitat clusters, the number of sites within each cluster, the percentage of sites within each cluster suitable for nesting, the fraction of sites within a cluster searched prior to exiting, and the rate of mortality during dispersal. The authors evaluated the influence of different reserve design patterns on the mean occupancy of nesting sites, defined as the fraction of suitable sites occupied by nesting females. They concluded that, in general, the sizes and spatial distributions of proposed Habitat Conservation Areas (HCAs) for Northern spotted owl is adequate, provided that the recovery of currently degraded habitat within the HCAs is rapid.

Lindenmayer and Lacy (1995a, b) used the multipopulation version of VORTEX (Section 4.4.2.4) to evaluate the metapopulation stability (expressed as probability of persistence in the metapopulation as a whole and the inter-annual variability in abundance of local populations) of Leadbeater's Possum (*Gymnobelidius leadbeateri*) in fragmented Australian old-growth forests. Effects of patch size and number on stability were simulated by varying the carrying capacities and numbers of local populations; no attempt was made to simulate the influence of inter-patch distance or spatial distribution. The authors found, like Lamberson et al., that increasing the size of patches enhanced the stability of the metapopulation as a whole. When all patch sizes were small, metapopulation extinction rates were invariably high and emigration actually *decreased* metapopulation stability.

Lande's (1987) and Lindenmayer and Lacy's (1995a, b) models are more obviously relevant to pesticide risk assessment problems than is the more species-specific model of Lamberson et al. Neither, however, may provide sufficient biological realism to support agrochemical regulation. In particular, neither provides for explicit consideration of local habitat requirements and distributions within agricultural landscapes. By following the example of Lamberson et al. (1992, 1994) population biologists could develop models specifically tailored to species and exposure regimes of interest in pesticide regulation. Such models could provide useful information for risk assessment if (1) the species of interest, because of its

intrinsic biological requirements or because of habitat fragmentation caused by habitat change, is restricted to relatively isolated subpopulations between which dispersal and recolonization occur, (2) pesticide applications have the potential to increase the risk of extinction of local populations, and (3) persistence of the species as a whole, not the persistence of individual local populations, is the regulatory endpoint of interest.

4.4.2.6. Spatially-explicit models

Spatially-explicit models may be thought of as extensions of individual-based or metapopulation models in which the organisms or subpopulations are distributed over a realistic rather than an idealized landscape (Dunning et al. 1995). "Suitable" and "unsuitable" habitat types can defined explicitly in terms of vegetation, topography, or soil type. Temporal changes in habitat suitability can readily be simulated. For management applications, spatially-explicit models can utilize landscape maps derived from aerial surveys and remote sensing.

The approach appears especially suited to the study of mobile animal populations that forage and disperse over large, heterogeneous areas. The spatially-explicit approach permits ecologists to integrate theory and observation on foraging behavior and reproduction in individual animals, relate these to specific measurable habitat characteristics, and infer influences of habitat change on populations. As noted by Pulliam (1994), information on environmental contaminant distributions and effects can easily be integrated into the same framework. Because spatially-explicit models often deal with individuals, the full array of individual physiological characteristics can also be incorporated. Such models can be thought of simply as individual-based models in which the location and directional movement of the organism are included as additional characteristics.

The most thoroughly explored and tested models of this type have been developed for populations of ungulates foraging in Yellowstone National Park (Turner et al. 1993, 1994) and for the population of Bachmann's Sparrow nesting on the U.S. Department of Energy Savannah River Site (Pulliam et al. 1992). Turner et al. (1993) simulated the influence of landscape heterogeneity on winter grazing in “generic” ungulates. A standard energetics model was used to simulate the daily foraging intake and energy balance of an animal as a function of body weight, forage availability, and activity level. The authors then investigated the influence of different ungulate movement “rules” and patterns of forage availability on the energy balance and survival of model populations. Landscapes in which resource patches (sagebrush-grassland communities) were randomly distributed across the landscape were compared with landscapes derived directly from vegetation maps for Yellowstone. During each time step of the simulation, an animal feeds on resources within the patch it occupies. It may move to another patch; the probability of movement increases as it feeds and depletes the forage at its current location. While an animal is moving between patches it cannot feed.

Results obtained from the model generally supported previous theoretical predictions that (1) when resources are abundant, landscape pattern and movement rules should have no influence on weight maintenance and survival, (2) when resources are scarce, aggregated resources (i.e., the real Yellowstone landscape) should support more animals than

randomly dispersed resources, and (3) when resources are scarce, behavioral rules that allow the animals to discern resource abundance at distant sites or to move over greater distances should improve survival.

Turner et al. (1994) extended their original model and used it to explore the effects of fire on free-ranging elk (*Cervus elaphus*) and bison (*Bison bison*) populations in northern Yellowstone Park. In the new analysis, the authors derived a six-category habitat map from GIS data maintained by the National Park Service and assigned to each category a winter forage abundance derived from actual field measurements (available separately for unburned sites and for sites burned during the 1988 fires). The foraging rule assumed that each animal visually searches within a circle around its current location and moves to the site with the highest quality; it may continue searching and moving until it either obtains its maximum daily intake or reaches its maximum daily movement distance. Because snow conditions are an important determinant of winter ungulate survival, snow was simulated in the model. A snow subroutine assigned monthly snow depth values to each grid cell based on observed data and on known influences of topography on snow depth. Foraging behavior and energetic costs were both assumed to be affected by snow depth.

The authors were able to calibrate and test their model using observed data collected both before and after the 1988 fire. For all three years, data were available on winter precipitation, fall elk/bison count, and overwintering elk/bison survival. After model parameters were calibrated so that overwintering survival during these three years matched the available data, simulation experiments were performed to evaluate the influence of winter severity, fire size, and fire pattern on ungulate survival. Observed snowfall during the most severe and most mild winters recorded in this century at Yellowstone were used to evaluate the influence of winter severity. Three levels of fire severity, expressed as the percentage of the study area burned, were examined. A range of alternative fire patterns was evaluated: a fragmented burn was simulated by distributing burned grid cells at random over the whole map; a clumped burn was simulated by generating a single patch of burned cells centered on an arbitrary location. Several intermediate patch distributions were also evaluated, including the actual observed burn distribution of the 1988 fire. In all, 24 different scenarios were evaluated.

The authors found that winter snow was the most important determinant of ungulate survival. Fire severity and pattern influenced survival only during average and severe winters. Provided winters were mild or average, large fires actually produced better long-term survival than small fires due to their stimulating effect on forage availability during post-fire winters. For small to moderate fires, ungulate survival was greater with clumped than fragmented fire patterns. The authors concluded that fires and spatial fire patterns have an important influence on ungulate population dynamics in Yellowstone only if severe winter conditions occur in the post-fire winter.

Pulliam et al. (1992) described BACHMAP, a generalized spatially-explicit population model for bird dispersal, applied to the Bachmann's sparrow (*Aimophila aestivalis*). The objective of the model was to describe influences of spatial variation in habitat suitability on the abundance and persistence of sparrow populations in a managed pine plantation. Only female birds are included, and the only life-history characteristic simulated is dispersal. Grid cells are identified with pine stands of different ages. Bachman's sparrows nest only in young (5 years old or less) or mature (>80 years old) pine stands. The

simulated plantation consists of a number of tracts of different ages. As the simulation proceeds, newly-seeded tracts become suitable nesting sites and previously suitable tracts age and become unsuitable. Trees are harvested on a 21-year rotation, except for a certain number of tracts of mature pine forest that provided a stable source of dispersing birds. The authors evaluated the influence of different model parameters on the abundance and persistence of populations simulated for 100 years (five rotations). They found that parameters relating to mortality and reproduction were more important than those relating to dispersal (site selectivity, dispersal mortality). Population size increased linearly with the number of tracts left in mature forest, but mature forest was not required to maintain viable sparrow populations.

Liu (1993) extended the BACHMAP model in two significant ways. First, he modified it to accept landscape classification information from a GIS. Second, he developed an economics subroutine that calculates growth, yield, income, cost, and net-present-value estimates for each tract. The extended model is coded in an object-oriented programming language, so that it is modular and can easily be adapted to different species or landscape types.

Other recently-published spatially-explicit models simulate physiology as well as behavior. Loza et al. (1992) described a model of cattle grazing on open rangeland that simulates the influence of physiological status (energy and water balance) on the grazing behavior and land use of grazing animals. Jager et al. (1993) described a spatially-explicit version of the smallmouth bass model of DeAngelis et al. (1991) that simulates reproduction, foraging, and growth in a riverine population of smallmouth bass.

The principal advantages of spatially-explicit models include flexibility and realism, especially realism with respect to spatial representation of the environment. Virtually any physical or biological process can be included in such models, provided a model of that process can be developed. Both short-term and long-term events can be simulated. Extremely detailed representations of the landscape, including direct interfacing with GIS systems, is possible. The object-oriented programming approach described by Liu (1993) appears to provide an important advance in modeling technique because it permits a generalized model structure to be specifically tailored to a variety of risk assessment scenarios.

4.4.3. State-of-Development of Modeling Approaches

Table 4-4 compares the five modeling approaches discussed in this report with respect to the evaluation criteria discussed above. All five approaches are highly flexible in form and can represent a wide range of populations of interest. Less data would in general be required to implement life tables and age/stage-structured models than to implement the other model types.

Table 4-4. Comparative evaluation of modeling approaches. H = high, M = medium, L = low.

	Models

Criteria	life table and logistic	age/stage-based	individual-based	Meta-population	Spatially explicit
Endpoints	**H**	**H**	**H**	**H**	**H**
Resolution	**L**	**L**	**H**	**M**	**H**
Generality		**H**	**M**	**H**	**L**
Acceptance	**H**	**H**	**M**	**M**	**L**

The five approaches differ significantly with respect to the other three evaluation criteria. Life tables, logistic models, and age/stage-structured models are, according to the definitions used in this report, spatially homogeneous. As normally applied, these models are used to characterize the long-term or steady-state behavior of populations. They can also provide estimates of rates of recovery of populations following transient pulses of chemical exposure, but cannot address effects of exposures on the spatial distribution of organisms. Individual-based models and spatially explicit models, in contrast, have arbitrarily high degrees of resolution. The activities of individual organisms can be simulated on any time-scale; the size of cells in spatially-distributed models can be made arbitrarily large or small. In both cases the resolution of the available data and the needs of the assessment are the limiting factors. Metapopulation models are intermediate in resolution: space can be at least implicitly represented in terms of immigration/emigration/extinction processes. Like age/stage-structured models, however, metapopulation models are generally best suited to addressing effects of long-term exposures.

As noted by Levins (1966), a tradeoff can usually be expected between generality and spatiotemporal resolution in models. Age/stage-structured models have been developed for virtually every type of living organism. The versatility of the metapopulation approach, at least when applied to vertebrates, is demonstrated by the number of species for which the multipopulation version of the VORTEX model has been implemented. In contrast, physiologically and behaviorally-oriented individual-based models such as those of DeAngelis et al. (1991) and Pulliam et al. (1992) are highly specific. The underlying theories of foraging, bioenergetics, and reproduction are quite general, but the number of species-specific parameters needed to implement an individual-based model can be quite large. Spatially-explicit models require, in addition, site-specific data on landcover, weather, and other environmental influences on the activities of the organisms being modeled.

With respect to degree of acceptance by the scientific community, life tables, logistic models, and age/stage-based models are by far the best-developed type discussed in this report. They are the type most people immediately think of when they hear the term “population model.” The Leslie matrix and its variants are the backbone of quantitative fisheries assessment, with literally hundreds of applications over 50 years. User-friendly modeling software is widely available. The more general stage-based models have been less widely used in management, although they are common in plant demography and applied entomology.

Metapopulation models have a much shorter history, but have become very widely used in conservation biology over the last decade. The more complex models, such as the multipopulation version of VORTEX, provide a useful extension of age/stage-based models for situations in which differential exposures to isolated subpopulations are important. This will often be the case for rare or endangered species, which are restricted to specific habitat types. Like age/stage-structured models, they can be relatively general and applicable to a variety of different life-history types, as has been shown by the ease with which the VORTEX model has been adapted to a variety of mammalian species.

Models that incorporate physiological or behavioral influences on individuals, or that involve explicit simulation of interactions between organisms and their surrounding landscape, are fundamentally distinct from any previous approach to population modeling. Such models represent the future rather than the present of population biology. The majority of published accounts of these kinds of models have appeared in the peer-reviewed literature only within the past three years. No standardized modeling software is available to support their development. Only a few scientists have had any significant experience in developing and applying these models. The object-oriented software described by Liu (1993) provides a general framework that would, if widely adopted, significantly simplify the programming aspect of model development. However, developing a sound biological content for the models will still be a major undertaking.

4.4.4. Integration into Tiered Testing Schemes

This section describes several ways in which population-level assessment approaches can be integrated into the tiered testing schemes discussed elsewhere in the ECOFRAM report. At least for early tiers, emphasis is placed on those approaches that are based on well-established relationships between life history and population dynamics that require little or no species-specific data.

4.4.4.1. Tier 1 approach

As currently envisioned, Tier 1 would not include any population-level assessment.

4.4.4.2. Tier 2 approach

Tier 1 and 2 effects testing would provide information on the acute toxicity of chemicals to a small number of fish and invertebrate species. Given estimates of maximum application rates, expected environmental concentrations, and frequencies of applications, life-table and logistic approaches can be used to assess whether repeated applications of substances that cause moderate levels of mortality could adversely affect exposed populations.

The intrinsic rate of natural increase, *r*, can be used to estimate the potential rate at which a population can recover from a disturbance that kills a fraction of the organisms (section 4.2.2.2). The necessary data are available for a wide variety of species.

Life-table data for both short-lived and long-lived species can be used to define a range of recovery rates that should bound the recovery rates of populations that could be exposed. The curves could be presented as a nomogram in a risk assessment guidance document.

At least for fish, Winemiller and Rose (1994) have shown that all North American species can be grouped into three basic patterns of survivorship and reproduction. These patterns can be used to define generic life history models that would be representative of the array of responses of most exposed species. This is consistent with the conclusion of Barnthouse et al. (1990), who showed that variations in life history between gulf menhaden (small and short-lived) and striped bass (large and long-lived) were small compared to uncertainties caused by lack of critical toxicity data.

4.4.4.3. Tier 3 and 4 approaches

Applications at higher tiers would differ depending the specific decision criteria that led to higher-level testing. Chronic effects applications would involve the use of age-structured population models to extrapolate results of full life-cycle tests or other chronic tests to effects on the long-term abundance of exposed populations. Data required for implementation are similar to those required for life-table analysis, except that (1) density-dependent regulatory processes must be considered, and (2) age or life-stage-specific mortality or reproduction parameters can be random variables instead of fixed values.

Specific approaches for using individual-based, metapopulation, or spatially-explicit models in Tier 3 and 4 assessments have not yet been developed. These would most likely be highly species-specific or environment-specific. The model(s) would have to be specifically designed to address the uncertainties (regional variability, effects on endangered species, indirect effects, unusual modes of action, etc.) that trigger a move to higher tiers.

4.5. Analysis of Species Sensitivity Distributions

Nearly every ecological risk assessment involves the difficult task of estimating the likelihood of effects on a large number of species based on toxicity data for a handful of representatives. Because species differ in their sensitivity to toxic chemicals, it can be assumed that some will be more sensitive and some less sensitive than *Daphnia magna*, rainbow trout, *Selenastrum capricornutum*, and other standard test species. When data are available for only a few species, a safety margin must be applied to account for the unknown sensitivity of untested species. Lack of information on variation in species sensitivity is thus a major source of uncertainty in ecological risk assessment.

The objective of analyzing species sensitivity distributions is to reduce this uncertainty as well as make sure that appropriate data have been selected for inclusion in the distributions. This section presents suggestions for criteria for selection as well as analysis of data. These suggestions apply to larger data sets such as may exist for substances that have been in use for some time, or as guidance for developing data sets in support of registrations of new substances.

A few chemicals have been tested for toxicity to dozens of aquatic species, and it has been found that species sensitivities (as indicated by standard measurement endpoints, such as LC50s) tend to be approximately log-normally distributed. (Selection of distribution models is discussed in section 4.5.3.) For example, Table 4-5 shows the distribution of LC50s for permethrin for 66 species. The species are ranked in order of decreasing sensitivity (increasing LC50); the rank of each species is converted to a percentile ($i/(n+1)$), where i is the species rank and n is the total number of species for which data are available), and transformed to a probability using the normal distribution. The LC50 is log-transformed, and the relationship between the normalized rank and the log LC50 is determined by least-squares linear regression. The distribution and the fitted line are shown in Figure 4-13. The percentage of species affected at a given concentration, or the concentration that would affect a given percentage of species, can be estimated from the regression. For example, in Figure 4-13, the 10th percentile is calculated to be 128 ng/L, meaning that 10% of the species have LC50s less than 128 ng/L.

Table 4-5. Species sensitivity distribution for permethrin (acute toxicity). GM = geometric mean for species.

Species	Group	LC50 (ng/L)	Rank	Percentile
Menippe mercenaria GM	Crustacea	18	1	1.49
Mysidopsis bahia GM	Crustacea	34	2	2.99
Chironomus salinarius	Insects	73	3	4.48
Asellus aquaticus	Crustacea	85	4	5.97
Hexagenia bilineata GM	Insects	100	5	7.46
Crangon septemspinosa	Crustacea	130	6	8.96
Nitocra spinipes	Crustacea	150	7	10.45
Procambarus blandingi	Crustacea	210	8	11.94
Gammarus pseudolimnaeus GM	Crustacea	251	9	13.43
Penaeus duorarum GM	Crustacea	305	10	14.93
Procambarus clarki GM	Crustacea	332	11	16.42
Penaeus aztecus GM	Crustacea	340	12	17.91

Species	Group	LC50 (ng/L)	Rank	Percentile
Aedes aegypti GM	Insects	345	13	19.40
Ceriodaphnia dubia	Crustacea	550	14	20.90
Chironomus plumosus	Insects	560	15	22.39
Daphnia magna GM	Crustacea	891	16	23.88
Culex pipiens quinquefasciatus	Insects	1,400	17	25.37
Homarus americanus GM	Crustacea	2,261	18	26.87
Odonata sp.	Insects	2,900	19	28.36
Uca pugilator GM	Crustacea	2,975	20	29.85
Menidia menidia GM	Fishes	3,108	21	31.34
Ictalurus punctatus GM	Fishes	3,136	22	32.84
Culex quinquefasciatus GM	Insects	3,153	23	34.33
Pycnopsyche sp.	Insects	3,200	24	35.82
Salvelinus fontinalis GM	Fishes	3,425	25	37.31
Alburnus alburnus	Fishes	4,000	26	38.81
Alonella sp.	Crustacea	4,000	27	40.30
Tilapia mossambica	Fishes	4,400	28	41.79
Hydropsyche augustipennis	Insects	4,400	29	43.28
Simulium venustum	Insects	4,500	30	44.78
Spicodiaptomus chilospinus	Crustacea	5,000	31	46.27
Cyprinodon macularius	Fishes	5,000	32	47.76
Cypria spp.	Crustacea	5,000	33	49.25
Eucyclops sp.	Crustacea	5,000	34	50.75
Salmo salar GM	Fishes	5,411	35	52.24
Mugil cephalus GM	Fishes	5,500	36	53.73
Oncorhynchus mykiss GM	Fishes	5,674	37	55.22
Eretes sticticus	Insects	5,800	38	56.72
Hydropsyche sp.	Insects	5,900	39	58.21
Tilapia aurea	Fishes	6,230	40	59.70
Diaptomus spp.	Crustacea	7,000	41	61.19
Ophiogomphus sp.	Insects	7,400	42	62.69
Hexagenia rigida	Insects	7,630	43	64.18
Lepomis macrochirus GM	Fishes	7,912	44	65.67
Micropterus salmoides	Fishes	8,500	45	67.16
Pimephales promelas GM	Fishes	13,141	46	68.66
Oncorhynchus kisutch	Fishes	17,000	47	70.15
Gambusia affinis GM	Fishes	17,582	48	71.64
Selenastrum capricornutum GM	Algae	19,108	49	73.13
Hydrachna sp.	Acarina	20,000	50	74.63
Anopheles stephensi	Insects	22,000	51	76.12
Atherinops affinis	Fishes	25,300	52	77.61
Oryzias latipes	Fishes	25,690	53	79.10
Menidia beryllina	Fishes	27,500	54	80.60
Cyprinus carpio GM	Fishes	30,186	55	82.09
Pollimyrus isidori GM	Fishes	32,249	56	83.58
Hydrophilus sp.	Insects	45,000	57	85.07
Cyprinodon variegatus GM	Fishes	62,350	58	86.57
Skeletonema costatum	Algae	92,000	59	88.06
Rana catesneiana	Amphibia	115,000	60	89.55
Crassostrea virginica GM	Mollusca	279,417	61	91.04
Limnaea acuminata	Mollusca	370,000	62	92.54
Poecilia reticulata	Fishes	440,000	63	94.03

Species	Group	LC50 (ng/L)	Rank	Percentile
Anguilla japonica	Fishes	750,000	64	95.52
Crassostrea gigas GM	Mollusca	2,612,470	65	97.01
Limnaea stagnalis	Mollusca	100,000,000	66	98.51

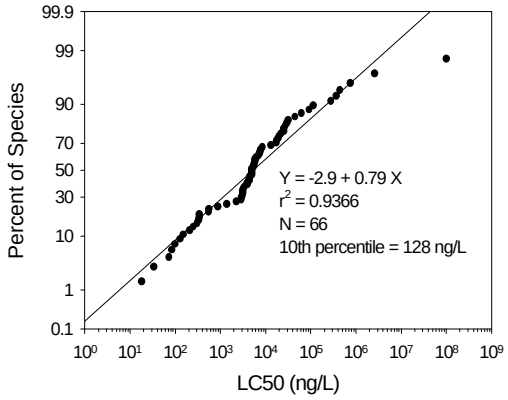


Figure 4-13. Distribution of LC50s for permethrin for all species tested.

4.5.1. Screening Data for Suitability

To ensure that the results of a distributional analysis are as representative as possible of the range of sensitivities that exist in environment being assessed, the data set should be as large as practical. As large data sets developed under specific Good Laboratory Practice (GLP) guidelines are not required for pesticide registration in most jurisdictions, reliable data from other sources should be included in the distributional analyses. Inclusion of these data requires that some selection criteria be used to ensure data quality. The following sections discuss criteria be used in selecting data from the open scientific literature.

4.5.1.1. Number of data points

Preliminary analysis of several data sets suggests that a minimum of 7 data points would be required to allow the distribution between the 5th and the 95th percentile to be described with acceptable certainty (Reference ?Mike N + David F). Aldenberg and Slob (1991) suggested that data for 5 species are required to estimate a community NOEC. Numerical Water Quality Criteria are derived from the toxicity data for 8 species (U.S. EPA 1985). Small data sets (4 to 6 data points) will probably require a different approach from large data sets, as it may not be possible to develop appropriate distributions. For small data sets, the use of variable uncertainty factors (i.e., higher LOC when data exist for more

species) may be more appropriate (Campbell et al. 1999), however, these should be derived from the known slopes of sensitivity distributions of substances for the same type of organisms and for the same class of pesticides.

4.5.1.2. Selection of effect measures

The Guidelines for Ecological Risk Assessment (USEPA 1998) define a number of suitability criteria for effect measures (measurement endpoints). One of the most important of these is a clear mechanistic and preferably quantitative linkage between the measure of effect and the endpoint that is being assessed. Because the assessment measures for characterizing the risk of pesticides in the ecosystem are normally at or above the level of the population, measures of effect that are relevant to sustainability of populations are more appropriate than those that may merely indicate exposure or adaptation. Measures of effect that reflect survival (mortality), growth, development, or reproduction should thus be chosen over bioindicator responses unless there is a clear linkage between the bioindicator and a population or community-level effect. Useful effect measures include acute and chronic LC and EC values (where the effect observed is clearly related to population sustainability).

With respect to the quality of the toxicity test, it is recommended that the US EPA (1985) criteria with respect to flow-through vs. static exposure and measured vs. nominal concentrations be used. Studies which do not conform to these criteria could be judged on supplemental knowledge of K_{OW} and stability in water. Where appropriate, time-varying toxicity data (see section 4.6) could also be used.

Where the only response concentration for a species is reported as a “greater than” value, this datum should not be used in the regression analysis. However, it should be included in the denominator (*n*) in the calculation of rank. These species are usually at low risk because they would only respond at high concentrations; however, because of differences between laboratories and in experimental designs, effects may be reported by some laboratories at concentrations greater than the maximum used in other laboratories. These situations would clearly require expert judgement.

Species toxicity data reported as a “less than” value should not be included in the calculation of the regression, but can be included in the calculation of risk.

Where multiple data are available for a single species and one or more of these are reported as greater than values, these values should be ignored.

Where responses are reported at concentrations above the solubility limit for the substance, they should be treated as greater than values, as discussed above. Formulants added to the end-use product may increase water dispersability. Although this does not increase solubility, emulsified active ingredients present at concentrations greater than their water solubility may be as biologically available as they are below their maximum water solubility. In these cases, the data could be used. In the case of permethrin (Table 4-5), more than one-third of the toxicity values are above the reported water solubility limit of 6,000 ng/L. These concentrations probably do not reflect actual exposure concentrations for dissolved

permethrin. It is appropriate to exclude these values from the regression, but to include them in the total number of data points (*n*) for the purpose of calculating ranks. When the permethrin LC50s in excess of the solubility limit are excluded from the log-normal regression, the fit of the line to the data improves (Figure 4-14). The position of the line changes slightly, resulting in a new 10^{th} percentile of 174 ng/L. For permethrin toxicity data in fish, only 10 of the 23 LC50s for the species tested were below the solubility limit. Including all values in the regression gave an $r^2 = 0.843$ and a 10^{th} percentile = 1,477 ng/L (Figure 4-15). Using only the points below the solubility limit, the regression gave an $r^2 = 0.936$ and a 10^{th} percentile = 3,475 ng/L (Figure 4-15). Note that excluding the values for the least sensitive species (those above the solubility limit) had the effect of increasing the slope of the regression and *increasing* the 10^{th} percentile of the distribution.

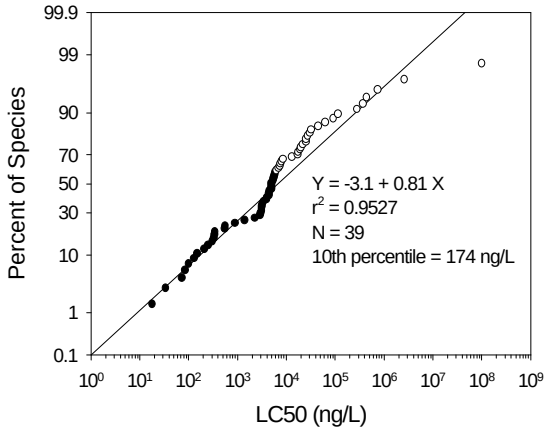


Figure 4-14. Distribution of LC50s for permethrin for all organisms with points above solubility limit (6,000 ng/L) excluded from regression. Filled circles: values below solubility. Open circles: values above solubility.

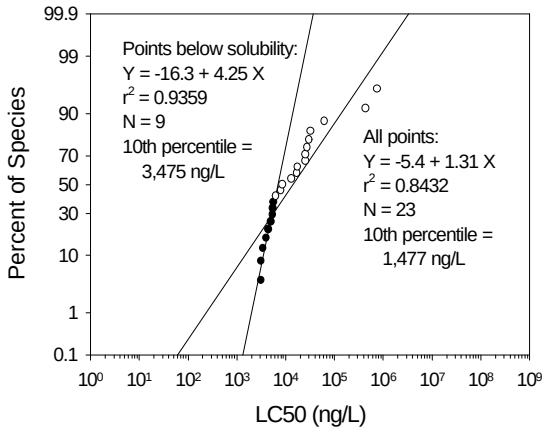


Figure 4-15. Distribution of LC50s for permethrin for fish. Filled circles: values below solubility. Open circles: values above solubility.

Where multiple data points for a single species include a stage (i.e., larvae) known to be inherently more sensitive, data for the most sensitive stage should be chosen over responses for less sensitive stages.

If, after the above criteria are applied, two or more data points are still available for analysis, the geometric mean of the remaining data points should be used as representing the sensitivity of that species. Although the geometric mean has been criticized for some uses (Parkhurst 1998), the procedure has traditionally been used to estimate means for toxicity data (US EPA 1985) and gives a more conservative (lower) estimate than the arithmetic mean would.

What about exposure duration (e.g. 48 h LC50 vs 96 h LC50)? Normalize (Giesy et al 1999)? Standardize (e.g., always use 96 h when available)? Always pick longest?

4.5.2. Grouping of Data

Analysis of species sensitivity distributions for a number of pesticides has shown that, when organisms of inherently differing sensitivity are grouped together, the resulting distribution did not display a good fit to the log-normal model. However, when data were segregated into groups such as fish, phytoplankton, etc., more data sets fit the log-normal model.

Many pesticides have some degree of specificity in their mechanism of action. For example, herbicides may be selectively toxic to some groups of plants (weeds versus corn) as well as being less toxic to animals and other organisms that do not possess the receptor system (say photosynthesis) for the pesticide. In such a case, it is appropriate to calculate the

sensitivity distributions separately for plants and animals (Figure 4-16). Similarly, an insecticide which acts on the nervous system of insects is unlikely to be highly toxic to plants, while organisms with well developed nervous systems (insects, other arthropods, and vertebrates) are likely to be more sensitive. However, as is illustrated in the case of permethrin (Table 4-5) even these organisms may show differences in sensitivity because of divergence in their physiology or biochemistry (Figure 4-17).

Specificity of action may not always be the case. For example some biocides, such as the chlorophenols, are similarly toxic to a wide range of organisms (hence their use as biocides) and the grouping of all organisms together for distributional analysis may be appropriate.

Thus, from a basic understanding of the mechanism of action of a pesticide, it may be possible to identify and group sensitive and less sensitive organisms. This allows the risk assessor to focus on the groups at higher risk and to devote less time and resources to groups that are exposed to very low or negligible risks. In addition, with a knowledge of the ecology of the potentially impacted system, it is possible to assess the likelihood that indirect effects will occur as a result of an effect on keystone groups of predator or prey/food organisms.

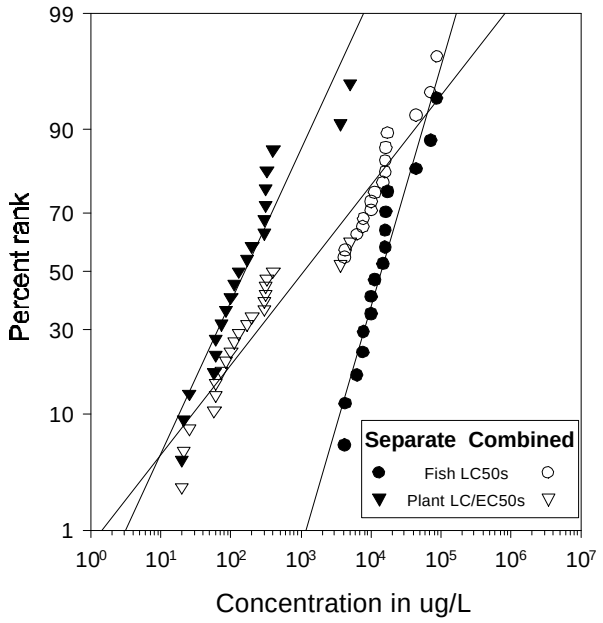


Figure 4-16. Distribution of toxicity values for an herbicide in fish and plants analyzed separately and combined into a single data set.

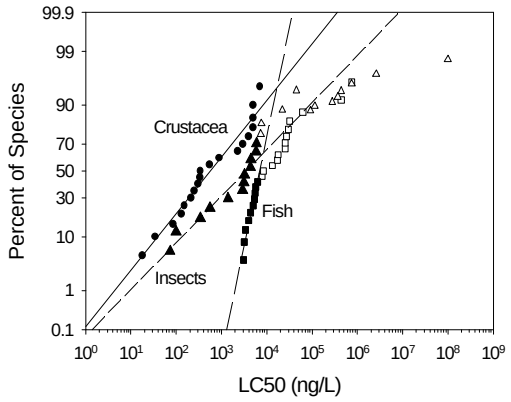


Figure 4-17. Distribution of permethrin LC50 values for fish (squares), crustacea (circles), and insects (triangles). Filled symbols: values below solubility; open symbols: values above solubility.

While the mechanism of action of the pesticide is an important criterion for grouping or organisms, habitat may also be important. For example, there may also be good mechanistic reasons to separate data for freshwater and saltwater organisms when it is known that one group has an inherently different sensitivity because of interactions between salinity and the pesticide of concern.

It is also possible to group organisms together on the basis of their reproductive strategy and life cycle. Thus, organisms which are able to recover rapidly from an adverse effect at the population level (reduction in population caused by mortality) may be considered differently from another group of organisms that may require a longer period of recover (section 4.4). For example, most algae have short reproductive cycles and would be expected to recover from a decrease in population more rapidly than a population of fish subjected to a similar reduction. Thus, the frequency of occurrence and the intensity of the effect that could be tolerated would be different.

Potential criteria for grouping of effects data are summarized in Figure 4-18.

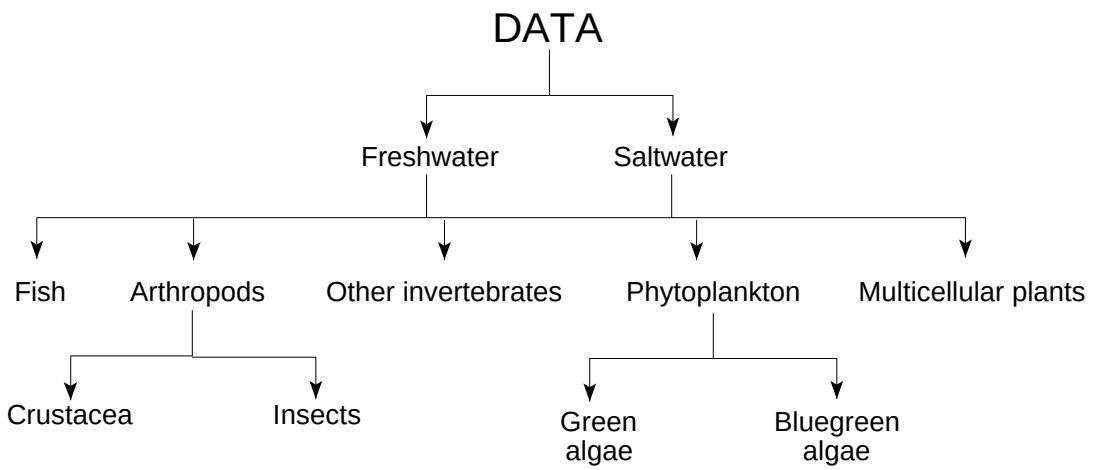


Figure 4-18. Possible groupings for toxicity/sensitivity data sets.

4.5.3. Choosing the Distribution Model

When determining the distribution of a set of toxicity data, it is necessary to assume an underlying model. Many years of experience in toxicology has shown that the underlying distribution for dose-mortality data within a single species is log-normal. While it is likely that different species will also respond to the log of the toxicant concentration, distributions of toxicity criteria for different species may not be log-normally distributed, particularly if there is inadvertent bias in the selection of test species. Although a number of distribution models for species sensitivities are possible, it is suggested that the log-normal model be used (Burmaster and Hull 1997) unless it is clear that another model gives a better fit.

As an alternative to the use of the log-normal distribution, the use of maximum likelihood, which is applied in various other situations that involve censored data, such as time-to-event modeling, is recommended. Many statisticians feel that maximum likelihood is more rigorous on statistical grounds than the log-normal regression approach. Maximum likelihood would require special computer programs to perform the iterative, numerical optimizations that such an approach requires. Used judiciously, the simple calculations required for log-normal regression will ordinarily prove to be practical. These calculations can be readily implemented in spreadsheets. However, with all of these approaches, biases in the selection of data or lack of availability of data can result in incorrect estimations.

Confidence intervals may be useful for assessing uncertainty in exposure distributions and for point estimates on these distributions. Similar approaches can be applied to distributions of species sensitivity. As with other uses of point estimates, the use of the distributional approach without confidence intervals assumes a sample large enough that sampling error contributes relatively little to the uncertainty in the overall risk assessment, relative to other sources of uncertainty. Methods for calculation of confidence intervals are available for log-normal (Wagner and Løkke 1991), logistic (Aldenberg and Slob 1991), and nonparametric bootstrap procedures (Jagoe and Newman 1997). A contrary

argument to use of confidence intervals for species sensitivity data is that this assumes that all species are equal in the sense of their role and function in the ecosystem and that they can be treated in a purely numerical fashion. Some species may be more important in the ecosystem than others (keystone) and, to use confidence intervals, these species would have to be weighted appropriately. The inherent difficulty in assigning weights suggests that the issue of confidence be handled in the risk characterization process by the use of expert judgement.

4.6. Effects of Time-Varying or Repeated Exposures

Contamination of surface waters from pesticides typically occurs in single or repeated pulses due to agricultural runoff, spray drift, or intermittent urban and domestic use. These input patterns typically result in a period of high concentration followed by a decline in concentration due to hydrological dilution, degradation, or partitioning from water to air or sediments. A second pulse may follow the first in a matter of days, or pulses may be separated by as much as a year of more. Standard laboratory toxicity tests using constant exposure concentrations typically do not investigate the toxicity of time-varying or repeated exposures (Hickie et al. 1995; Parsons and Surgeoner 1991a,b). The difficulty of estimating effects of realistic time-varying exposures from measurements made under constant exposure is often an important source of uncertainty in ecological risk assessment of pesticides. Evaluation of acute and chronic effects in aquatic environments due to pulsed exposures has been addressed by numerous authors (Buhl et al. 1993; Fischer et al. 1994; Barry et al. 1995; Holdway and Dixon 1985, 1986; Holdway et al. 1991) and has recently been reviewed by Handy (1994).

4.6.1. Descriptions of Time-Varying and Repeated Exposures

Figure 4-19 shows the most important features of time-varying exposure: duration (pulse width), maximum concentration (pulse height), time-weighted average concentration (area under the curve divided by pulse width), and time between pulses (sometimes referred to as “recovery time,” but not to be confused with the recovery time required for a biological entity to return to normal after a pesticide impact). A pulse, or exposure event, can be said to begin when the concentration exceeds a specified threshold, and to end when the concentration falls below the threshold

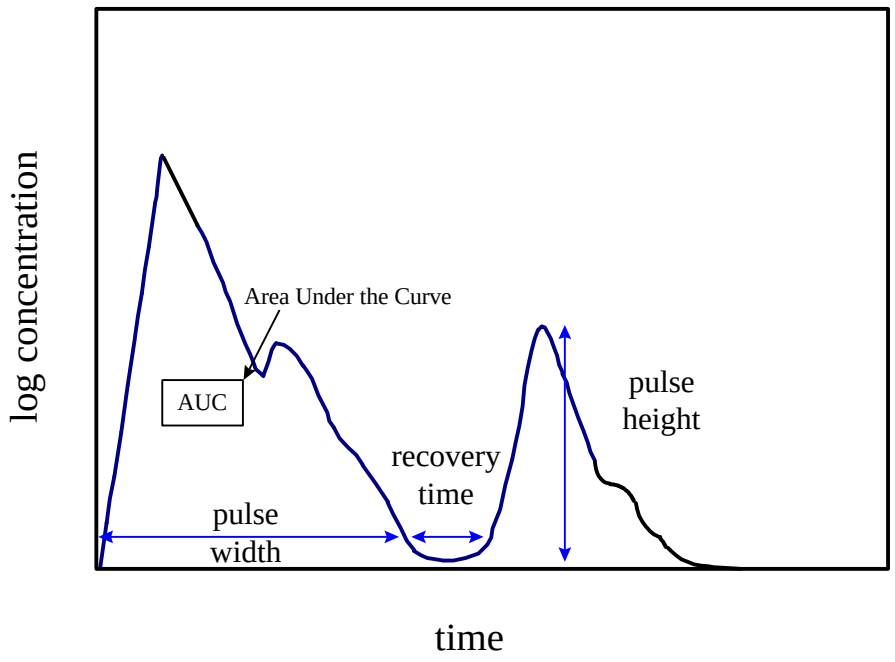


Figure 4-19. The principal features of time-varying and repeated exposure events.

RADAR (Risk Assessment tool to evaluate Duration and Recovery; Version 1.10; Williams 1998), a post-processor for PRZM/EXAMS, is a tool for characterizing time-varying exposures. The input to RADAR is the output from PRZM/EXAMS. The output from RADAR is a catalog of exposure events. An event begins when the concentration exceeds a selected threshold concentration, and ends when the concentration next falls below the threshold. The threshold concentration selected should usually be a function of the toxicity of the compound. For example, the threshold for evaluating acute exposure could be one-tenth the LC50, the LC10, or another acute endpoint. The threshold for evaluating chronic exposure could be the EC10, the NOEC, or another chronic endpoint.

For each event, RADAR reports the date, the maximum concentration, the average concentration (arithmetic mean), the geometric mean concentration, the duration, and the time to the next event ("recovery time"). RADAR also calculates the ratio of the peak height to the average concentration, the ratio of peak height to geometric mean concentration, and the area under the curve (which is equal to the average concentration times the event duration, in units of concentration-days). If the ratio of the peak height to the arithmetic or geometric mean is similar for all events, then one can assume that the peak shapes are similar.

Figure 4-20 shows a three-month portion of a PRZM/EXAMS simulation of pesticide concentrations in a low order headwater stream, along with a subset of the associated RADAR output. The threshold in this example is set at 2 µg/L. Concentrations exceed the threshold eleven times during the three-month period. Most events have a duration of one day, and no events have a duration longer than two days before returning below 2 µg/L. This is due to a rapid dissipation rate due to hydrologic dilution in the fast moving stream. Except for two events, the peak concentration equals the average, because the events last only a single day.

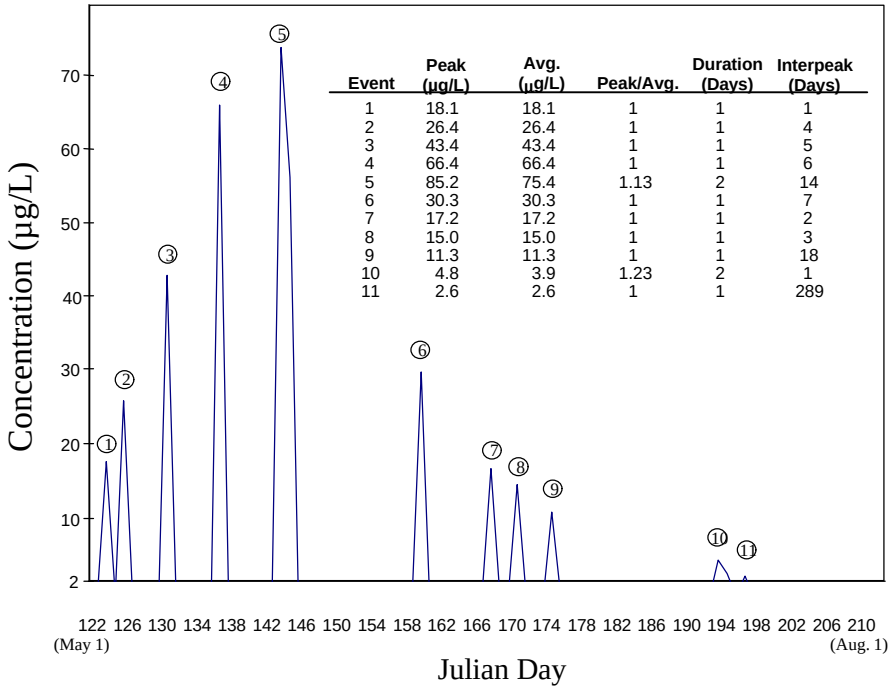
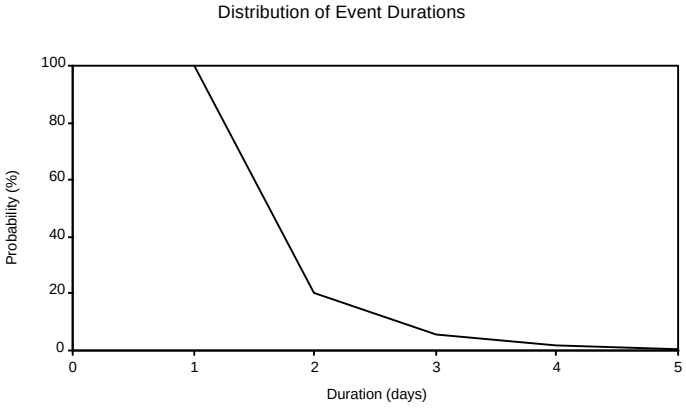


Figure 4-20. Example of PRZM/EXAMS output and RADAR analysis for a low order stream (e.g., edge of field for a headwater stream). Event threshold = 2 µg/L.

These parameters can be processed into cumulative distributions (Figure 4-21), subjected to trend analysis, sorted by duration or recovery times, etc. The distributions can be analyzed to determine, for example, the 90th percentile pulse length, 10th percentile of times between events, or the most likely combination of pulse length and interpulse interval.



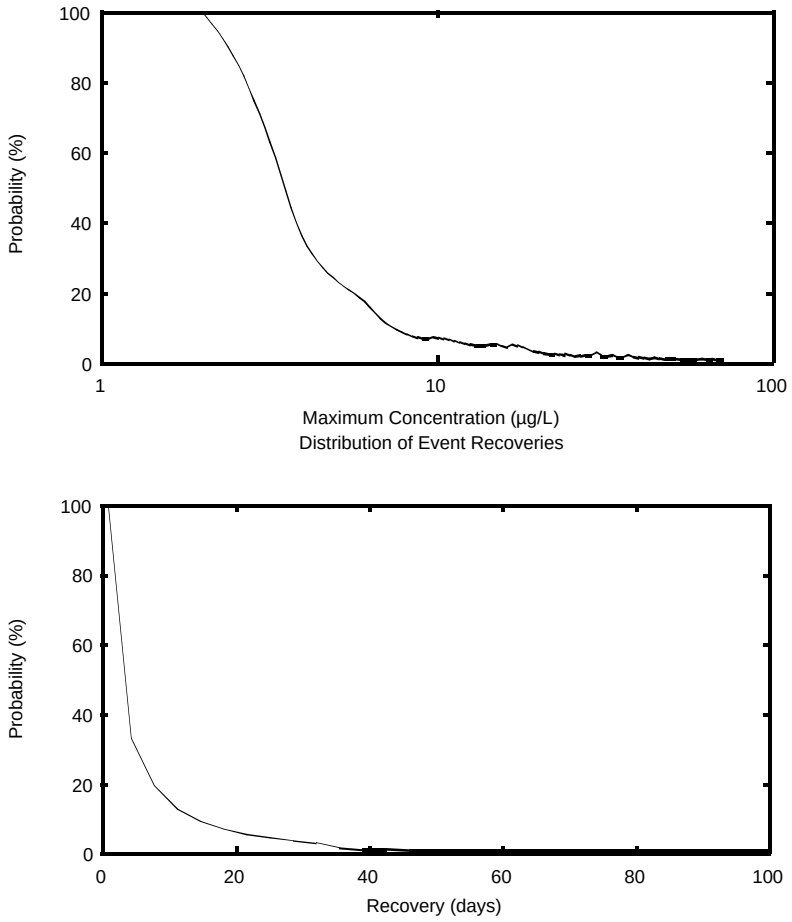


Figure 4-21. Distributions of event durations, event maxima, and intervals between events, based on 36-year PRZM/EXAMS simulation for a low order stream. Threshold = 2 µg/L.

All of the events in the distribution shown in Figure 4-21 (which represents a full 36-year simulation) are at least 1 day in length, with only 20% at 2 days and longer. Twenty percent of the events have peak concentrations of 7.5 µg/L or higher. Most events are followed by "recovery intervals" (time to next peak) of 1 to 7 days. From these data, a laboratory study representing these exposure parameters might be a pulse at 5 µg/L lasting one day, followed by a recovery interval of 4 days. Other scenarios are also possible if alternative percentiles are chosen from the probability distributions.

Similar information for a higher order (lower reach) stream is shown in Figures 4-22 and 4-23. The same input to PRZM/EXAMS is used for these scenarios as used to generate Figures 4-20 and 4-21, except the characteristics of the receiving water body are changed. Fewer, broader peaks are observed when compared to the headwater stream. Hydrologic dilution produces peaks of lower magnitude in the lower order stream as compared to the headwater stream. Recovery intervals are similar between the stream scenarios (subject to similar runoff regimes).

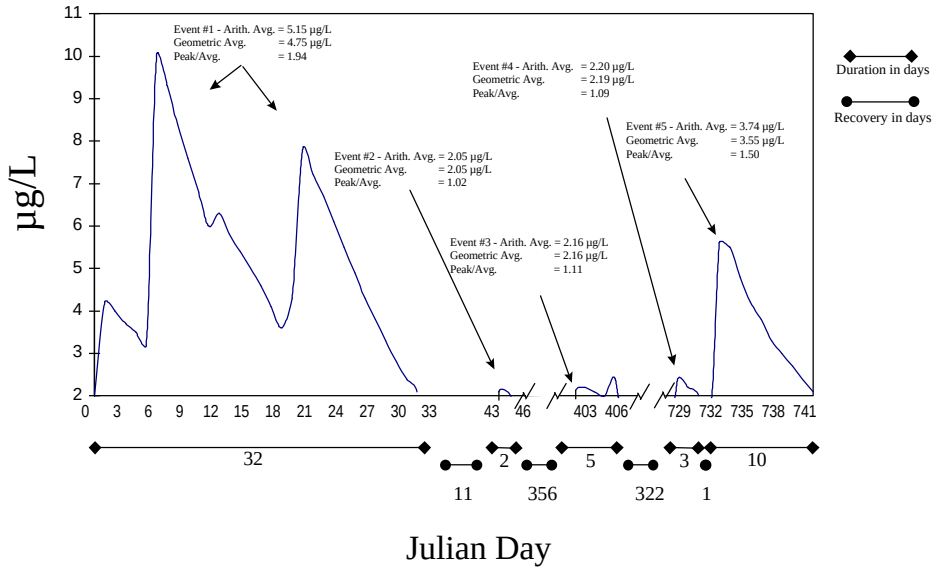
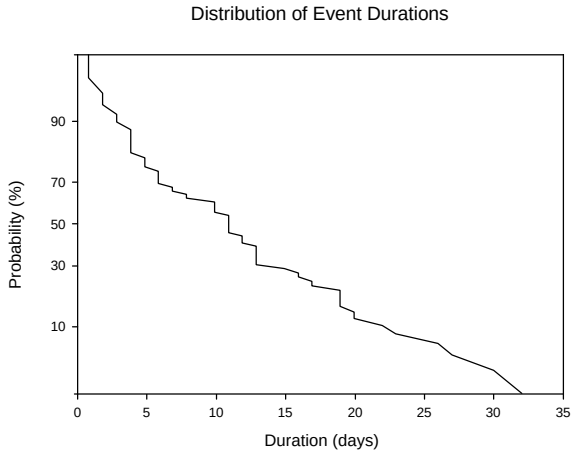
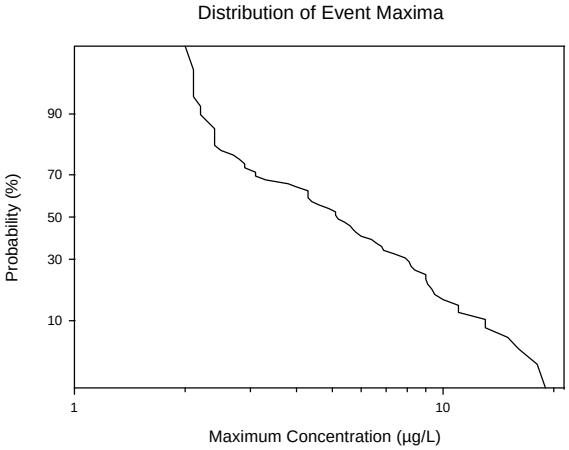


Figure 4-22. Example of PRZM/EXAMS output and RADAR analysis for a large stream. Event threshold = 2 µg/L.





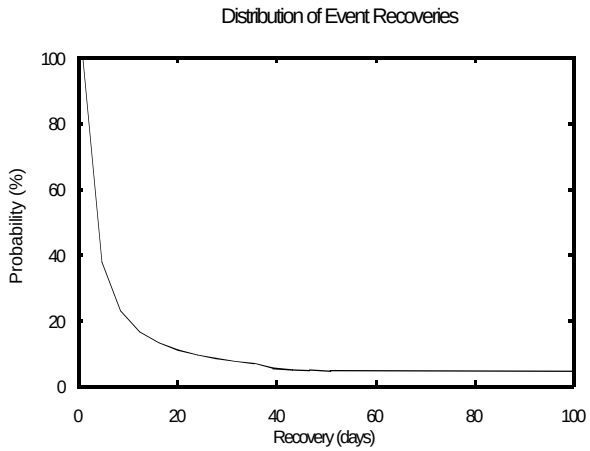
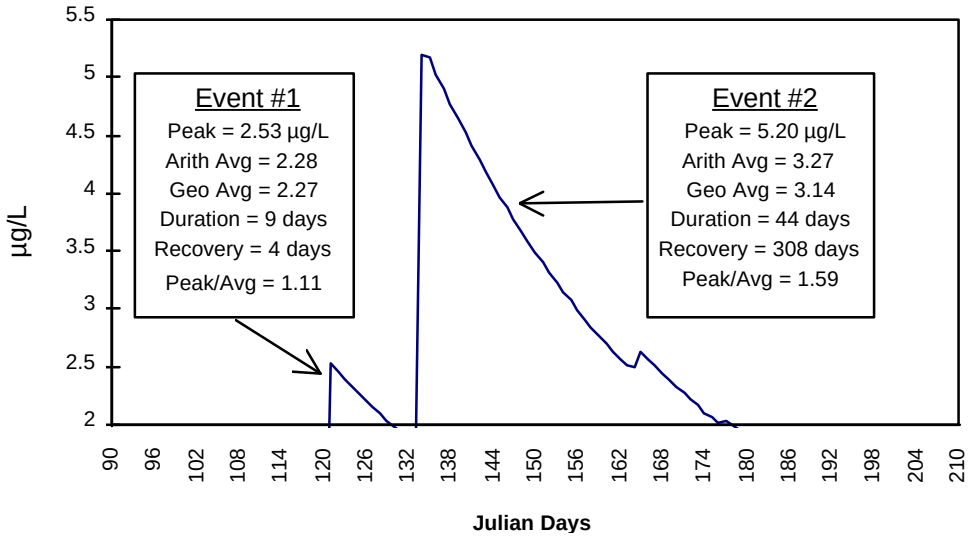


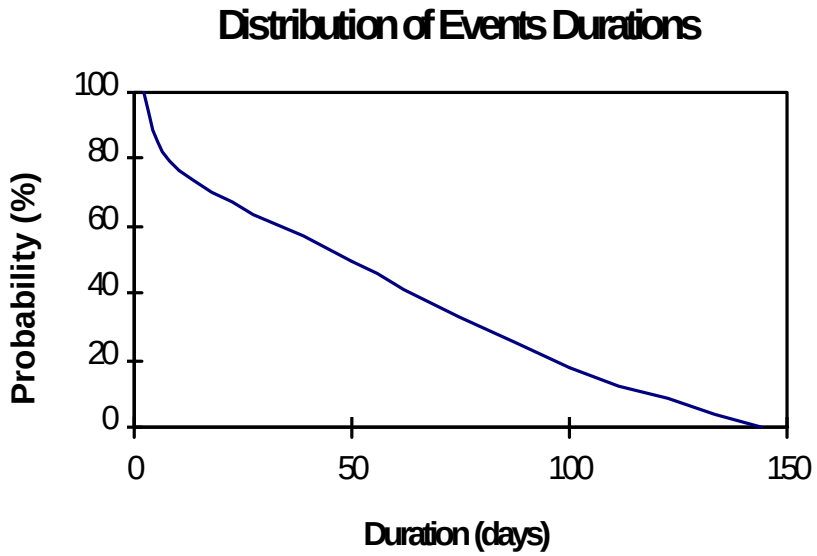
Figure 4-23. Distribution of event duration, maxima and recovery duration with event threshold at 2 µg/L (for a large stream).

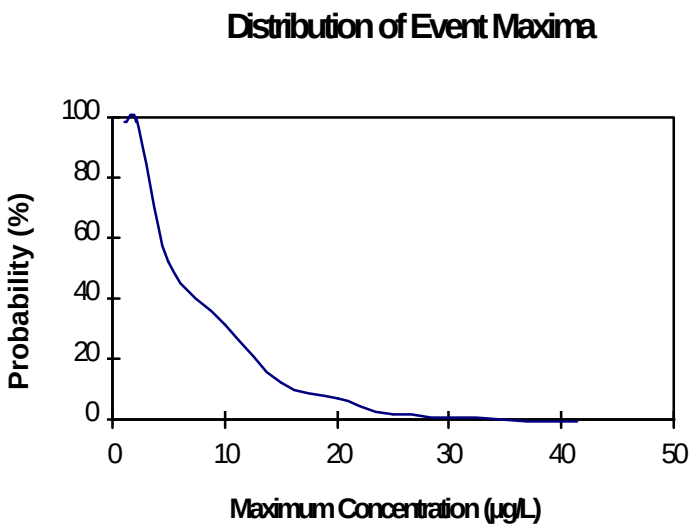
RADAR analysis for a pond is shown in Figures 4-24 and 4-25. Pulse durations in the pond are longer than both stream scenarios because of the lack of flow in the pond system. Recovery intervals in the pond can be quite long due to the lack of flow in and out of the pond.

Figure 4-24.



Example of PRZM/EXAMS output and RADAR analysis for a pond. Event threshold = 2 µg/L.





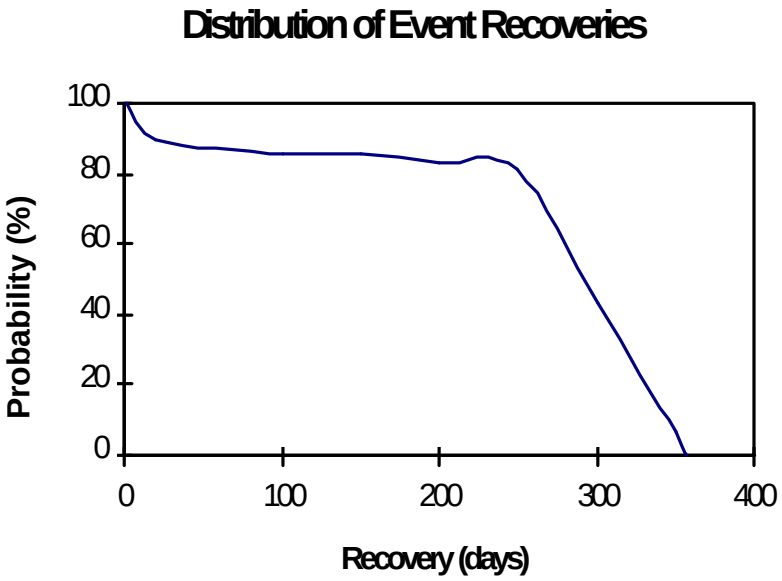


Figure 4-25. Distributions of event durations, event maxima, and intervals between events over a 36-year PRZM/EXAMS simulation for a pond. Threshold = 2 µg/L.

4.6.2. Potential Consequences of Time-Varying and Repeated Exposures

Time-varying or repeated exposures can have a variety of consequences:

- **Shorter exposure produces less effects.** Effects on individual organisms usually become more severe as exposure duration increases. In some cases, effects may be a function of the time-weighted average exposure. For example, a 2-day exposure at 2 µg/L may cause the same effects as a 1-day exposure at 4 µg/L or 4 days at 1 µg/L.

- **Post exposure, latent or delayed effects.** Effects may occur after exposure is terminated. Standard toxicity tests do not include a post-exposure observation period.

- **Cumulative individual effects:** the first pulse may weaken an organism by causing cumulative damage, such as irreversible interaction of the toxicant with the receptor (van der Hoeven and Gerritsen 1997;Verhaar et al. 1997) or by diverting energy from vital processes such as growth and reproduction, causing effects to become more severe with subsequent exposure.

- **Induced individual tolerance:** the first pulse may strengthen survivors through acclimation, or by induction of detoxification or biotransformation enzymes such as cytochrome P-450-dependent monooxygenases (Sipes and Gandolfi 1986) and mixed-function oxygenases (MFO) in fish (Burnison et al. 1996; Parrott et al. 1995), causing a lessening of response to subsequent exposure.

- **Individual selection:** the first pulse may remove weaker, more sensitive individuals and thereby select for hardier, more robust individuals, causing an apparent lessening in toxic response to subsequent exposure.

- **Ecological recovery**: after an exposure which affects a significant proportion of a population, the population may—or may not—recover before the next exposure.

4.6.2.1. Independence or dependence of effects of epeated exposures

The effects of a first exposure pulse may influence the biological response to a second pulse. The influence may be reflected in concentration-effect relationships (Figure 4-26a) or effect-vs-duration relationships (Figure 4-26b). In Figure 4-26a, the concentration-effect relationship after the first exposure is shown at left. Effects of the second exposure, shown at right in Figure 4-26a, may occur at lower concentrations than the first exposure (curve shifts to the left, effects enhanced), at greater concentrations (curve shifts to the right, effects reduced), or the same concentrations (independent).

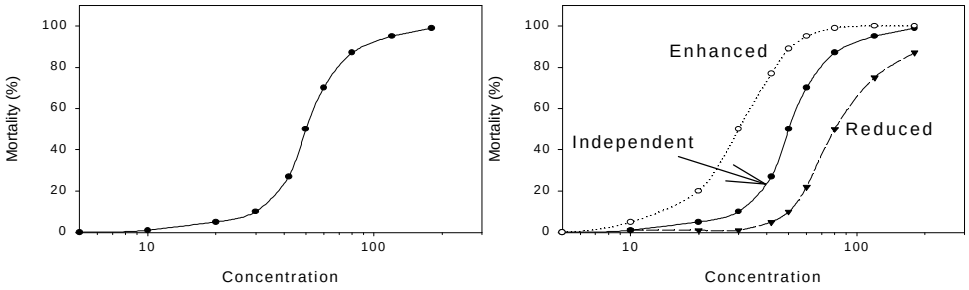


Figure 4-26a. Influence of previous exposure (left panel) on concentration-effect relationship of subsequent exposures (right panel).

In Figure 4-26b, the effect of the first exposure increases with increasing exposure duration as shown by the single line at the left. In the second exposure, the effect-vs-duration relationship may be steeper than after the first exposure (effects enhanced), less steep (effects reduced), or unchanged (independent).

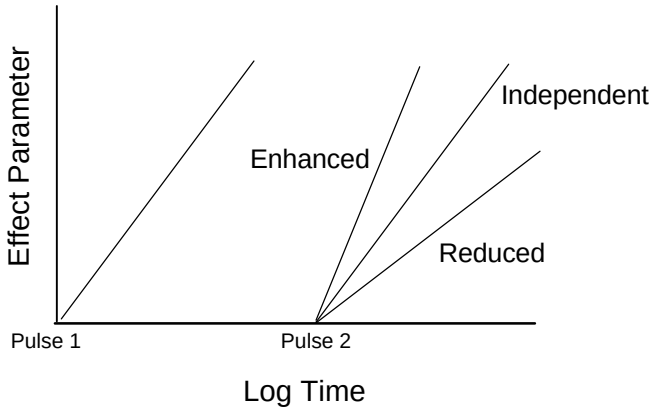


Figure 4-26b. Influence of previous exposure on the effect-vs-duration relationship of subsequent exposures to the same concentration.

4.6.2.2. Shorter exposure causes less effect

Jarvinen et al. (1988) studied the acute toxicity of chlorpyrifos, endrin and fenvalerate to fathead minnows in both single pulsed and continuous exposures. Varying combinations of exposure duration (1 to 96 hours) and recovery time (0 to 95 hours) were used, totaling 96 hours. Generally for these pesticides, the longer the exposure, the closer the effects were to the 96-h continuous exposure.

Heming et al. (1988) exposed early life stages of rainbow trout to pulsed and spiked doses of methoxychlor. The pulsed exposure scenario mimicked environmentally realistic exposures from the use of the pesticide to control biting fly larvae in western Canadian rivers. Survival, growth, and development of early life stages were assessed for 68 days after a pulsed exposure of 580 µg/L (biota returned to clean test water after 2 hours) and a spiked concentration of 30 µg/L (methoxychlor concentration decreased due to natural dissipation processes). No biologically significant effects were observed on any growth stage for either exposure scenario, although the pulsed concentration was nearly 20x the spiked level.

In a recent study (Hosmer et al. 1998), the effects of fenoxycarb, a non-neurotoxic, carbamate-based insect growth regulator, on growth and reproduction of *D. magna* were examined using a single pulsed dose. The exposure regime was based on laboratory fate data and field observations, and mimicked the reduction in fenoxycarb following application to natural waters. For both the pulsed and continuous exposure studies, reproduction was the most sensitive endpoint. A substantial reduction in toxicity was observed, with MATC values of 26 µg/L from the pulsed exposure and 0.0016 µg/L from the continuous exposure.

4.6.2.3. Effect related to peak concentration, not duration

Curtis et al. (in Parsons and Surgeoner 1991a) reported that intermittent exposure to fenvalerate was more toxic to fish than continuous exposure when daily mean concentrations were equal. Similar findings were also reported for copper and ammonia (Parsons and Surgeoner 1991a). However, to achieve equal daily mean concentrations the concentration administered intermittently was higher than that administered continuously. The observed effects were apparently related to the maximum exposure concentration rather than to the daily average.

4.6.2.4. Latency (delayed effects)

Van der Hoeven and Gerritsen (1997) studied the effect of chlorpyrifos on *Daphnia pulex*, reporting that the pesticide immobilized daphnids several days before death. Even when exposure was discontinued, immobilized *D. pulex* died, supporting the conclusion of irreversible effects.

In order to demonstrate latency (or lack thereof) in acute studies, observations must continue after the exposure is completed and the organism has been removed from the stressor (Figure 4-27). For example, effects of diflubenzuron (an insect growth regulator) on aquatic macroinvertebrates were not observed until molting began, some 2 to 4 weeks after a single exposure (Hurd et al. 1996). In chronic studies, lack of latency can be determined from observations during exposure. However, since endpoints such as growth are typically measured only at study termination, it is possible that observed effects are the result of events that occurred early in the exposure period.

Often, knowledge about the mode of action of a substance may be all that is needed to determine whether a substance has latent effects (e.g., diflubenzuron) or not. For example, most organic substances display a baseline or narcotic mode of

action (Lipnick 1993) that is believed to be a general disruption of membrane integrity (Abernethy et al. 1988). Narcosis occurs when the compound reaches a critical threshold or critical body residue (see section 4.5.6; McCarty et al. 1992). Such effects are not latent and are reversible unless death has occurred.

At an ecosystem level, complexity and nonlinear biological dynamics may create a latency period between the exposure event and effects (Landis et al. 1996; Matthews et al. 1996). Where it is possible to redesign bioassay protocols to determine whether latency exists or not, ECOFRAM recommends that the protocols be modified as long as the results are compatible with historical data from similar protocol.

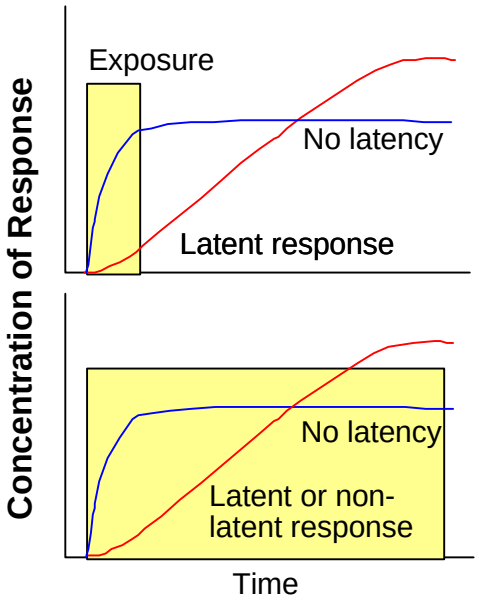


Figure 4-27. Illustration of latent (delayed) and non-latent toxicity responses (Solomon 1998).

4.6.2.5. Reversible effects with recovery between pulses

Toxicity tests with the midge (*Chironomus riparius*) showed that two 1-hour pulses caused significantly fewer symptoms of intoxication than two hours of continuous exposure to carbamate compounds, when at least 2 to 6 hours of clean water was provided between doses (Kallander et al. 1997). Mancini, Wang and Hanson (in Parsons and Surgeoner 1991b) and Clark et al. (1986) have also conducted tests which suggest that repeated exposures are less toxic to aquatic organisms than continuous exposures of equal total duration. This suggests that some level of detoxification or elimination of the toxicant during the toxicant-free period can reduce the toxic effects of the earlier exposures (Parsons and Surgeoner 1991a), and is dependent on the length of time between pulses (Wang and Hanson, in Parsons and Surgeoner 1991a).

Using algae (*Selenastrum capricornutum*) and field data on pulsed exposure to atrazine, Klaine et al. (1997) demonstrated that recovery from exposure up to 50 µg/L of atrazine was nearly instantaneous once the herbicide was removed from the overlying water.

4.6.2.6. Irreversible, additive, or cumulative effects

For some compounds, no difference in toxicity has been observed between time-varying or repeated and continuous exposures. This situation can occur when exposures are cumulative (compounds with slow depuration times) or when effects are irreversible or only slowly reversible (organism "memory;" van der Hoeven and Gerritsen 1997). A cumulative impact or hazard model may be useful in cases of organism memory or additivity to previous responses.

In a study by Kallander et al. (1997), no difference in the toxicity of organophosphorus (OP) compounds was observed between pulsed and continuous exposures. In fact, as suggested by Breck (in Parsons and Surgeoner 1991), pulse exposures may be additive for compounds with slow depuration times or with only slowly reversible or irreversible effects.

Repeated pulsed exposure to the herbicide bromoxynil over 28 days was reported to be more toxic to *Daphnia magna* than 28-day continuous exposure (Buhl et al. 1993). Reproductive parameters and growth (weight) were adversely affected at pulsed exposure levels of 20 µg/L as compared to continuous levels of 40 µg/L (sublethal effects) to 80 µg/L (survival).

In an investigation of five insecticides (technical permethrin, microencapsulated permethrin, fenitrothion, carbaryl, and carbofuran), mosquito larvae were exposed to the same insecticide concentrations in pulsed (two 1-hour exposures, separated by 6 to 24 hours) and continuous (2-hour exposure) tests (Parsons and Surgeoner 1991a). For insecticides other than microencapsulated permethrin tested in double pulse exposures, recovery from immobilization during clean water periods between exposures did not result in lower toxicity. Therefore, either the intervals between exposures were insufficient (6 hours for all except carbaryl, which was tested with a 24-hour period), or other irreversible toxic effects were occurring (Parsons and Surgeoner 1991a).

Microencapsulated permethrin was the only insecticide of the five tested which exhibited greater toxicity in the double pulse exposure test. The investigators speculated that some of the larvae immobilized after the first 1-hour exposure to microencapsulated permethrin recovered between exposures, which allowed them to ingest more capsules during the second exposure than those exposed continuously.

4.6.2.7. Population recovery

In a simulation of effects of single and multiple pulsed exposures on the population dynamics of the amphipod *Gammarus pulex*, Kedwards and Wood (1998) observed that population reductions and time to recovery were proportional to the magnitude of the exposure and inversely proportional to the rate of immigration. The magnitude of effects was inversely related to the age of the amphipods.

4.6.3. Selecting Tools for Investigating Time-Varying and Repeated Exposure

The decision to consider pulsed exposure assessment is best addressed on a case by case basis. However, there are several aspects that may drive one to consider pulsed testing. These are discussed in the following sections.

Figure 4-28 provides guidance on which direction to take when assessing the effects of time-varying exposures on ecological receptors.

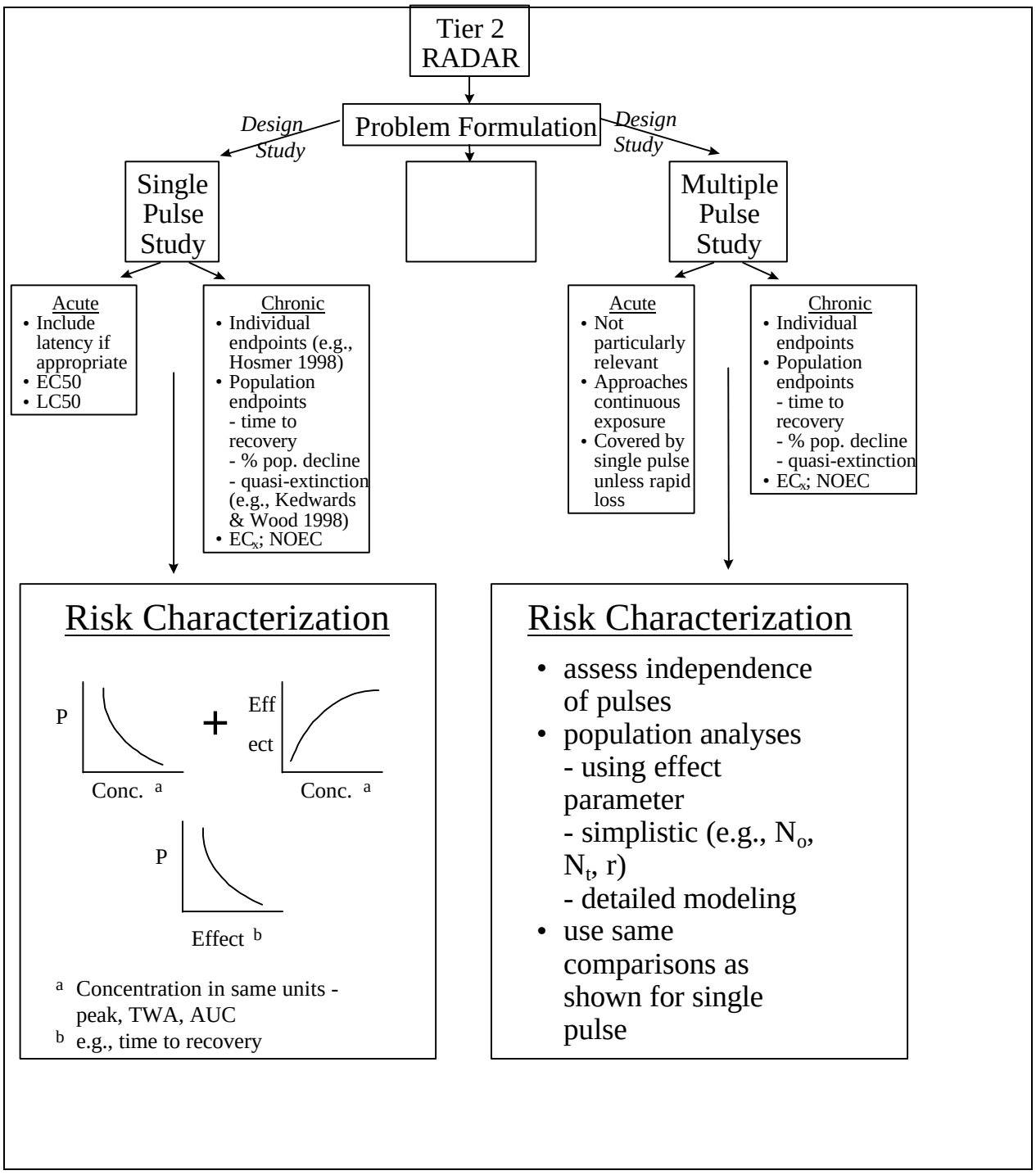


Figure 4-28. Decision matrix for analysis of time-varying exposures.

Depending on the time-varying exposure pattern, a single pulse or multiple pulse laboratory study could be run. If the pulses cannot be adequately or appropriately represented in the laboratory, pulse toxicity modeling could be completed. Acute and/or chronic studies can be designed, producing endpoints appropriate to the risk assessment endpoints. Toxicity studies should be extended to include delayed or latent effects, if expected. Chronic studies could address either individual (e.g., Hosmer 1998) or population endpoints (e.g., Kedwards and Wood 1998). Note that acute studies under a multiple

pulse regime are not particularly relevant because short multiple pulse exposure approaches continuous exposures unless a rapid loss of the substance occurs in the environment and test system.

For the single pulse case, a joint probability distribution (see section 4.2.2.3) can be used to characterize the risks (Figure 4-28). In the multiple exposure case, the pulses are assessed for their independence (Figure 26) to determine whether the responses are enhanced, reduced or independent for multiple pulses. An understanding of the independence (or lack of) of the exposures is helpful in characterizing the risks using population analysis or joint probability distribution analysis.

4.6.4. Laboratory Approaches

Pulsed exposure toxicity studies can be conducted using simple modifications of current study designs, provided the exposure profile is known and the endpoint is defined to provide toxicologically relevant estimates (Handy 1994). Such studies can be more expensive than standard studies, with the majority of the additional cost being due to additional samples that need to be analyzed for the test material to quantify the pulsed exposure. Interpretation of the exposure regime may be problematic, as one could base the interpretation on the peak concentration, area under the concentration curve, arithmetic or geometric average, etc. Consultation with the appropriate regulatory authority is recommended when developing pulsed toxicity test designs because these studies are not yet standardized.

Single-pulse exposures with defined maximum concentration or pulse duration (width of pulse) can readily be created in the laboratory. Exposures simulating degradation or hydrologic dissipation are more difficult to design in the laboratory. Flow rates could be altered in a flow-through study; semi-static or static renewal rates could be controlled to mimic these pulses; or static designs with periodic additions of pesticide could be used if the compound degraded rapidly. These approaches are discussed in the following paragraphs.

Static exposure. Some processes that can affect the concentration of a pesticide in the water column, especially volatilization, hydrolysis, photolysis, and biodegradation, may also take place in the exposure medium of a toxicity test. The exposure concentration of such a compound will decline during the course of a static toxicity test. Moreover, in a static test, the test organisms will be exposed to the pesticide's degradation products. If the rate of decline in the concentration approximates that expected in nature, the results of a static test may be more relevant to the risk assessment than results of a static-renewal or flow-through test. Of course, if degradation rates in the exposure solution are very different from those in nature, the results may be meaningless.

Static-renewal exposure. Virtually any temporal exposure pattern may be created in a static-renewal toxicity test, provided the renewals are frequent enough. In standard practice, test solutions are renewed daily, but renewal periods shorter than 24 hours are certainly feasible. Static-renewal exposures would be especially suitable for generating “square pulses” (i.e., exposure to a constant concentration for a set duration, followed by transfer to clean water) with relatively

stable test substances—a situation most relevant when real-world exposure is expected to be dominated by water flow, such as in small streams.

Flow-through exposure. Flow-through exposure systems are typically used to create constant exposure concentrations in toxicity tests, but they can be adapted to simulate pulsed exposures as well. Changes in exposure concentration can be brought about by changing the concentration of the stock solution or by changing the stock solution pumping rate, or both. The resulting changes in the exposure solution may be gradual (depending on the water replacement rate in the exposure container), not immediate as in a static-renewal test.

Microcosms. Microcosms simulating natural dissipation processes can be used to generate exposure solutions for static, static-renewal, or flow-through toxicity tests. For example, the pesticide can be applied to an outdoor tank containing natural sediment and natural water, where it will be subjected to the influences of volatilization, photolysis, hydrolysis, biodegradation, and sorption, all under conditions more realistic than laboratory single species studies. Water can be taken from the microcosm, periodically or continuously, for use in toxicity tests. Alternatively, organisms can be exposed in cages or other containers placed directly in the microcosm.

4.6.5. Time-varying toxicokinetic models

Pulsed exposure toxicity tests can be coupled with toxicokinetic modeling as a solution to the problems associated with predicting toxicant effects in non-steady-state field exposures. Such models may be useful for long recovery intervals, long pulses, or numerous repeated exposures (i.e., exposure scenarios not easily duplicated in the lab). Toxicokinetic models may be compartment-based, physiological-based, or energetics-based. These models can be useful tools for estimating changes in tissue concentrations resulting from absorption, distribution, metabolism, and elimination of a toxicant from an organism.

- Compartment-based models describe toxicant movement between compartments. For example, a simple two-compartment model may contain water (source) and organism (sink) compartments.
- Physiological-based models describe the accumulation and internal distribution of toxicants among multiple tissues. They can account for different rates of elimination from various tissues, but can require a great deal of detailed physiological data.
- Bioenergetic-based models describe toxicant accumulation and loss in terms of the organism's energy requirements, where the organism is treated as a single compartment and toxicant uptake is a function of the flux of water across the gills or food/sediment through the gut.

These models become particularly important in estimating the effect of a toxicant when evaluating non-steady-state, nonequilibrium exposures that may vary temporally or spatially. Understanding toxicant accumulation and distribution in an organism ultimately contributes to predicting its toxic effect.

To apply these models to evaluation of pesticide effects, the relationship between body residue levels and toxic effects must be known (see section 4.6.5). To define toxic effects based on body residue levels would also eliminate uncertainties associated with the bioavailability of the toxicant in question. While there are still a number of poorly defined species-specific and site-specific variables which affect the refinement of toxicokinetic models, they are gaining more wide-spread use in ecotoxicological evaluations and likely illustrate the future direction of ecological risk assessments (Landrum et al. 1992).

In this section three relatively simple toxicokinetic models are described: FGETS, PULSETOX and DEBtox. Their use in pulsed exposure testing and assessment is addressed. The decision as to which of these kinetic models is most appropriate will depend upon data availability; however, use of the simplest model that will adequately address the study question will minimize potential errors (Landrum et al. 1992).

Pulsed exposure toxicity tests can be coupled with toxicokinetic modeling as a solution to the problems associated with predicting toxicant effects in non-steady-state field exposures. Such models may be useful for long recovery intervals, long pulses or numerous repeated exposures, scenarios which are difficult to simulate in the laboratory. Although the results of these models should not be used directly in risk characterization, they will be useful in a weight of evidence approach to help understand the compound dynamics in time-varying exposures and the potential for effects.

Toxicokinetic models may be compartment-based, physiological-based or energetics-based. These models can be useful tools for estimating changes in tissue concentrations resulting from absorption, distribution, metabolism, and elimination of a toxicant from an organism. Their use in ecological risk assessment becomes particularly important for estimating the effect of a toxicant when evaluating non-steady-state, nonequilibrium exposures that may vary temporally or spatially. Understanding toxicant accumulation and distribution in an organism will ultimately contribute to predicting its toxic effect and allows determination of whether pulsed or repeated dosing will reach a critical body residue or concentration. In this section, three relatively simple toxicokinetic models are described: FGETS, PULSETOX, and DEBTOX. Their use in pulsed exposure testing and assessment is addressed.

4.6.5.1. FGETS

An example of a bioenergetic-based toxicokinetic model is Food and Gill Exchange of Toxic Substances (FGETS), which models the chemical uptake in fish from both food and environmental pathways (Barber, Suarez and Lassiter 1988). FGETS is based on thermodynamic potential and models the chemical exchange between fish and the aqueous environment that occurs across gill membranes and across gut walls from ingestion of toxicants (i.e., bioaccumulation from water and food) (Figure 4-29). An important aspect of FGETS is that it is a chemical-biological mechanistic model, where uptake is not considered an arbitrary action. The model can also calculate the time to reach lethality in fish assuming that the toxicant has a narcotic mode of action. FGETS can be run in 3 modes: laboratory, food chain (simulates 1 or 2 fish) and food web (simulates more realistic predator-prey interactions). Inputs for the 3 modes and various model assumptions are found in Table 4-6. FGETS incorporates data on the composition, structure and morphology of the

organism in calculating uptakes. An important aspect to this is tracking individual organism weight as a dynamic variable. Fundamental to the formulation of a dynamic energetic-based model is the relationship between the type of chemical, its mode of action or partitioning capability, and the physiological and genetic characteristics of the individual (Hallam and Lassiter 1994).

Figure 4-29. Output from FGETS – aqueous and fish concentrations

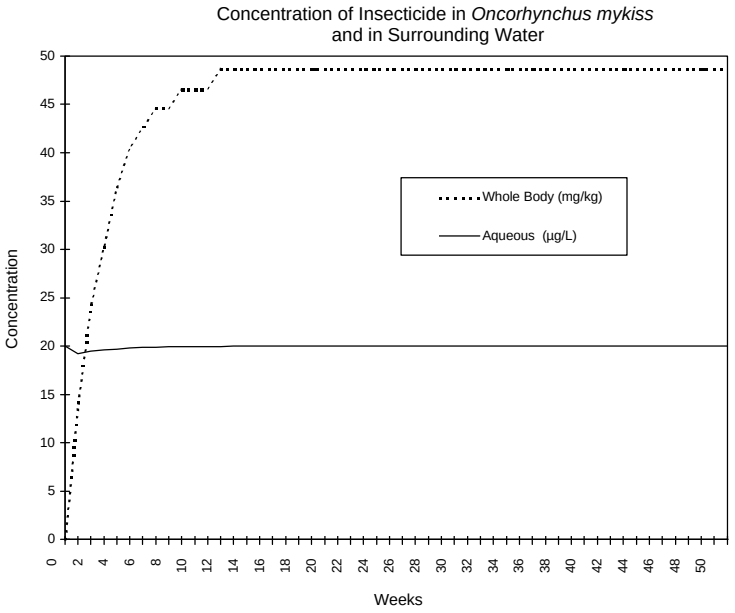


Table 4-6. Run modes, input parameters and assumptions for FGETS.

Common inputs to the Laboratory, Food Chain, and Food Web modes include:

- Molecular Weight, Volume
- Melting Point
- Log K_{ow}
- Fish Species
- Fish Weight
- Water Temperature
- Assume: food is in thermodynamic equilibrium with the water

Laboratory — defined as an aquarium with constant in- and outflows of water.

- Tank Flow Rate, Volume
- # Fish
- Concentration of Chemical in Food
- Length of Study
- Assume: aquarium with constant in- and outflows of water and volume of the tank and the number of fish from a single species remains constant

Food Chain — simulates one or two fish interaction. With one-fish, the fish is a predator that feeds on either plankton, benthic organisms, or generic fish. With two fish, one fish is the prey of the other. The prey species feeds on either plankton, benthic organisms, or generic fish and the predator feeds on the prey species according to a specific length-length relationship.

- Plankton or Benthic Chemical Concentration (constant)
- Prey Identification (only in two fish system)
- Predator Identification
- Assume: concentration of chemical in water, plankton, benthos and generic fish as well as water is constant during the length of simulation

Food Web — designed to describe more realistic predator-prey interactions. Fish may feed on each other, plankton, or benthos, according to a user-specified diet. The exposure conditions (water temperature and concentrations of chemicals in plankton, benthos and water) are arbitrary.

- Percent Diet Makeup of Prey (Time or Weight Dependent)
- Percent Diet Makeup of Predator (Time or Weight Dependent)
- Assume: unlimited prey resources and the physiologically active fraction of the gill is constant across all year classes for a particular species

Although FGETS has been available for several years, its current validation status is not known.

A similar model, modified from FGETS, was developed for *Daphnia* spp. (Hallam et al. 1990). Acute effects (mortality) of a lipophilic narcotic on a dynamic daphnid population are modeled, using uptake from both water and food. The model is based on the Lassiter and Hallam (1990) 'survival of the fattest' static theory in which the effect of a toxic exposure is analyzed by relating the Kow to the partition coefficient of the fat (lipid) and aqueous phases in the aquatic organism. For exposure of equal chemical activity, increasing lipid content and hydrophobicity increase the exposure duration tolerance without an effect (Lassiter and Hallam 1990). A dynamic approach was developed in order to couple the dynamic behavior of individuals with chronic or multiple acute toxicant (e.g., pulsed) exposures. The authors note that ecological risk assessment needs to be based not only on the attributes of the toxicant, but also on the biology of the exposed organism and it's population dynamics. This and other more complex toxicokinetic models are not considered for lower tiers within ECOFRAM Aquatic Effects framework. Additional population models are discussed in the Population Analysis chapter of this report.

4.6.5.2. PULSETOX

Another model, PULSETOX, is a residue-based, pulse-exposure toxicokinetic model for aquatic toxicology based on a simple one-compartment first-order kinetics (1CFOK) equation (Landrum et al. 1992; Hickie et al. 1995). PULSETOX

tracks the whole-body accumulation of a chemical in fish and predicts acute toxicity using previously established relationships between whole body residues and lethality (Figure 4-30).

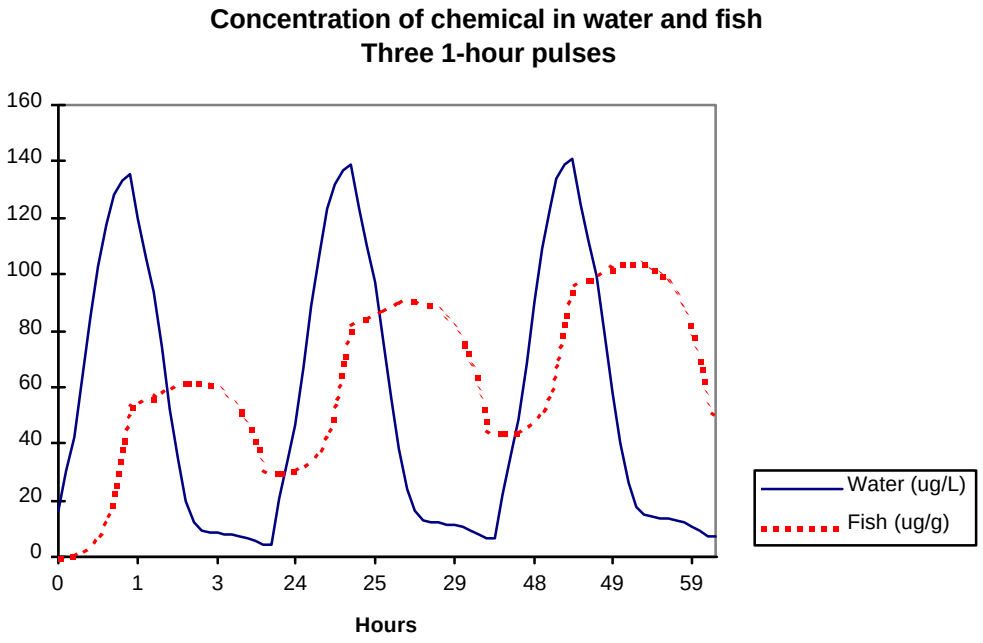


Figure 4-30. PULSETOX output — aqueous and fish concentrations.

This simple toxicokinetic model accounts for the effect of non-steady state, non-equilibrium accumulation from temporally varying exposures on toxicity using a fugacity approach. The model can be run in 2 modes: repeating exposure and cyclic or random exposure (Table 4-7). Required inputs are: K_{ow}, molecular weight, Henry's Law constant, organism volume, organism lipid fraction, bioconcentration factor (BCF), uptake and depuration rates, test chamber volume, toxicant concentration (from GENEEC or PRZM/EXAMS) and water and toxicant flow rate. The only loss mechanism from the system is via tank outflow; volatilization, degradation, etc. are not considered. PULSETOX assumes the following:

- the test chamber acts as a well mixed vessel
- the rate of change and absolute C_w at any point in time is a function of the test chamber volume, the flow rates of water, and the toxicant stream flow rate and concentration
- the only clearance of chemical from the system is via the tank outflow

Table 4-7. PULSETOX modes and input parameters.

For both **cyclic** and **random** exposures:
• Henry's Law Constant
• Volume of Organism
• Volume Fraction of Lipid

- K_{ow}
- Molecular Weight
- Bioconcentration Factor
- Uptake and Clearance Rate Constants
- Test Chamber Volume
- Water Flow Rate
- Toxicant Stream Flow Rate and Concentration
- Number, Duration, and Interval of Pulses

For the **random** exposure mode, the exposure conditions must be described for each exposure phase.

- the organism is a single compartment (works well for smaller organisms (Klee 1998)
- toxicokinetic rate constants k_1 and k_2 are independent of exposure concentration and do not change when the organism is intoxicated
- the toxicant concentration in the organism reaches steady-state if the external toxicant concentration is constant
- the population of organisms responds in classic dose-response manner
- individual response near instantaneous when the organism achieves its critical whole-body dose
- the whole-body toxicant concentration is an adequate surrogate for the dose at the site(s) of action

A pulse LC50 defines the duration and magnitude of the exposure required for an organism to accumulate a dose equivalent to the lethal or critical body residue (CBR). The CBR is the minimum tissue concentration associated with an adverse effect. The concentration can be based on the whole organism or on a particular target organ and can provide a more direct measure of a predicted adverse effect than can external exposure concentrations (Env. Canada 1997). Such an approach may be an inappropriate indicator if toxicity is due to adsorption to gills or if the whole body residue is not representative of accumulation in specific target tissues (Handy 1994). Hickie et al. (1995) demonstrated that the toxicity resulting from pulsed exposures is primarily controlled by the rate of toxicant accumulation and depuration rate in the exposed fish and that the level of biological response is associated more with the accumulated dose than exposure concentration. Because the model is mechanistically based, it is useful in illustrating the effects on toxicity resulting from interactions among the number, duration and frequency of pulses. Although there is inadequate information relating biological responses with CBRs, the model assumes that the CBR is an acceptable, but not ideal, surrogate to the lethal dose and that residues predicted by PULSETOX can be interpreted in relation to lethal effects. CBR-based techniques are useful to see if a particular exposure or series of exposures approach the residue level where effects may be realized without having to test an organism in difficult laboratory study designs or prior to beginning laboratory testing programs.

PULSETOX can be considered partially validated; Klee (1998) presented a successful validation trial of the basic modeling algorithm used in PULSETOX, the 1CFOK model (Landrum et al. 1992). Although a pulsed exposure was not

addressed, the uptake, depuration and BCF of chlorinated benzenes and phenols in rainbow trout were adequately described by the model when compared to laboratory measurements using predicted vs. measured concentrations.

PULSETOX provided a useful deterministic approach for predicting effects of pulsed exposures. It also showed that there is a clear link between pharmacokinetics of the chemical and the time course of toxicity both within standard continuous toxicity tests and in independent pulse-toxicity tests. Such models may not be useful for chemicals that are highly degradable, are reactive or do not readily bioconcentrate. Although the model is thought to be less effective for toxicants that cause cumulative damage where toxicity could increase through time even though peak fish residues do not change with successive pulses, Meyer et al. (in Hickie et al. 1995) have modified the toxicokinetic model by the addition of a power term that was effective in describing the intermittent exposure toxicity with this type of toxicant.

4.6.5.3. DEBtox

Another model which may be used for pulse toxicity results and body residue analysis is the Dynamic Energy Budget toxicology model (DEBtox), an energetics-based model (Kooijman and Bedaux 1996). DEBtox (Version 1.0) is a software package designed to analyze results from standard aquatic toxicity tests. Results from tests on acute and chronic survival studies, fish early life stage studies, *D. magna* 21 day reproduction studies and algal growth inhibition can be input. The program produces the following outputs:

- Estimates of study parameters with standard deviations and correlation coefficients using different models for differing modes of action;
- The goodness of fit for the selected model with graphical presentation;
- Graphic presentation of the likelihood function of the no-effect concentration (NEC) with confidence intervals;
- Calculation of time dependent, concentration dependent and/or response dependent EC values;
- Statistical analysis of any single or combination of parameters based on the likelihood ratio test; and
- Analyze residuals and plot them as functions of concentration, exposure time or response.

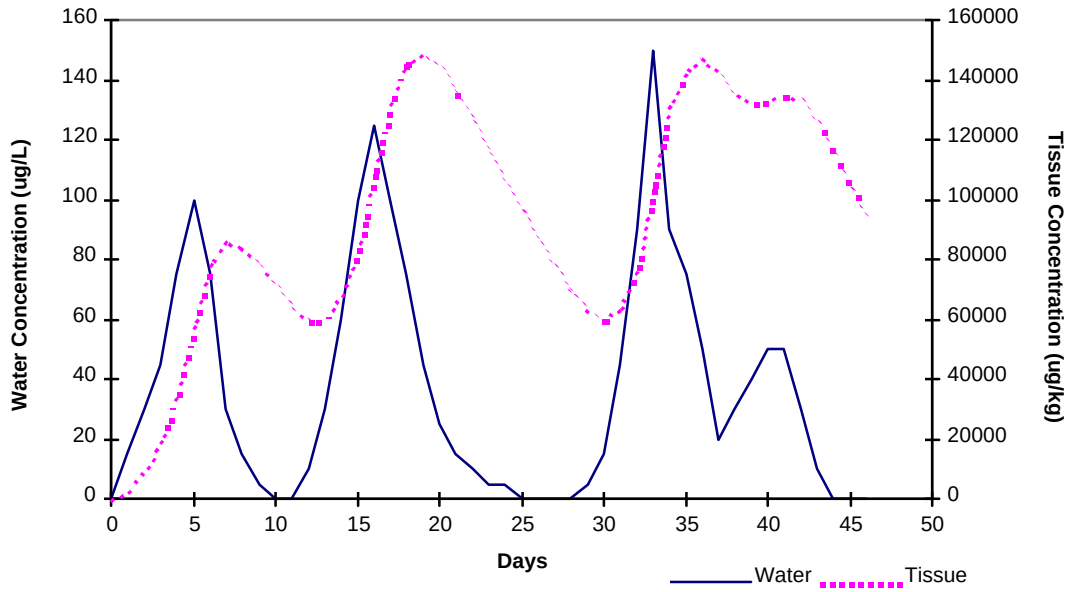
Although not specifically reviewed for this chapter, DEBtox may prove useful for analysis of data generated from time-varying or repeated exposure studies. The program primarily estimates parameter values by maximizing a nonlinear likelihood function for a survival experiment combined with a weighted least squares method. For growth and reproduction, a set of differential equations at initial conditions is solved using a 4^{th} order Runge Kutta numerical method. An elimination rate is essential to this analysis and dictates how fast a response builds up during exposure. In addition to various tabular outputs, graphs of time profiles, concentration profiles, the likelihood function for the NEC and various response surfaces (e.g., effect surface) are produced.

4.6.5.4. Other models

Several testing facilities have developed their own, simplistic spreadsheet models to calculate body residues from BCF studies in fish using concentration (in water, fish) vs. time curves, K_u and K_{dep}. Figure 4-31 describes an example of such

a spreadsheet that calculates tissue concentrations as a function of time-varying water concentrations, based on uptake and depuration constants. Any values for Ku, Kd, and the daily water concentrations can be entered and various tissue concentrations are generated. This approach has also proved useful for relating CBR, BCF and effect concentrations.

Figure 4-31. Spreadsheet-derived aqueous and fish concentrations



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4.6.5.5. Use of time-varying models

ECOFRAM proposes the use of the PULSETOX model to assist in the interpretation of time-varying or repeated exposure studies or to estimate effects from long pulses, long recovery intervals or numerous repeated exposures that would be difficult to test in the laboratory. The results from this modeling are not used directly in the Risk Characterization, but are useful in understanding the dynamics of the compound in environmental receptors. For pesticides with log K_{ow} at or above 3, a fish bioconcentration study is run at a concentration far below the LC50. A BCF, defined as the concentration in fish divided by the concentration in water (when equilibrium conditions are maintained), often at 1 or 2 concentrations, an uptake rate and depuration rate will be available from this study. Using these inputs, as well as others for PULSETOX, the time to reach a lethal body residue can be estimated using the default CBRs from Landrum et al.(1992) and others (see next section). Estimates of body residues and/or time to lethality can be estimated for other exposure concentrations or pulse durations. If a compound has a log K_{ow} less than 3, FGETS could be used to determine the depuration rate from the uptake rate (slope of the uptake curve) and the BCF (calculated from K_{ow} or water solubility). According to Spacie et al. (1995) and others, the BCF = K_u/K_{dep} where K_u (or K_1) is the uptake coefficient and K_{dep} (or K_2) is the elimination or depuration coefficient.

Besides measuring the BCF for compounds, numerous equations are available that can be used (ECETOC 1995; Bysshe 1990; Spacie et al. 1995) to calculate the BCF. Such QSAR equations can be based on many or specific classes of

chemicals and are based on one or more measured parameters (e.g., K_{ow}, water solubility, etc.). The following equations for calculating fish BCF values are listed in ECETOC (1995) based on general chemicals (see ECETOC document for specific references):

Equation	**log K_{ow} or WS range**	**Chemical class**	**r**
BCF = -1.32 + log K_{ow}	0.03-4.7	various	0.97
BCF = -0.4 + 0.79 log K_{ow}	1.0-6.9	various	0.93
BCF = -0.7 + 0.85 log K_{ow}	1.0-5.5	various	0.95
BCF = 2.79 - 0.564 log Ws[a]	0.001-50,000	various	0.7
BCF = 3.03 - 0.44 log WS	0.002-210,000	various	0.8
BCF = 2.02 - 0.47 log WS	0.0002-36,000	various	0.87

[a]WS = water solubility in mg/L

The correlation coefficients for the equations based on water solubility (0.7 to 0.87) are lower than those based on log K_{ow} (0.93 and 0.97, respectively). Additional equations, some specific for a particular class of compounds and others that use parameters such as molecular connectivity indices may also be found in the references cited above and others.

The time for reaching 95% of the body residue at steady state (t_{95}) may be estimated using the following equation (ECETOC 1995):

$t_{95} = 3/K_{dep}$ K_{dep} is depuration coefficient.

$K_{dep} = -0.414 \log K_{ow} + 1.47$

According to ECETOC (1995), uptake from food is only important if the log $K_{ow} > 4.5$ and the concentration in food is about 10^5 greater than water. Also, for compounds with log $K_{ow} < 4$, the typical time to equilibrium is less than 28 days. Therefore, studies where the uptake phase is conducted for 28 days (e.g., FIFRA, OECD 305) can produce meaningful steady state BCF values for compounds between log K_{ow} of 3 and 4. Above log K_{ow} of 4, BCF values may be underestimated because equilibrium may not have been achieved. Additionally, uptake of compounds with molecular weights greater than 700 may not be predicted by log K_{ow} due to steric hindrances (ECETOC 1995).

As an alternative to calculating the CBR, the whole body concentration may be measured during a typical toxicity study consistent with the time of death (or other effect). This is obviously a more costly method than using empirically derived ranges, calculating the value using TTE and FGETS, or other methods mentioned above. Although the true CBR for a particular effect would be measured, the cost and potential time lag between death and analysis of the body residue may be problematic.

There are additional considerations when working with CBRs. Is the CBR based on a threshold (instantaneous) or cumulative body residue (refer to Verhaar et al.1997). A threshold is probably the typical response since many compounds are considered nonpolar narcotics. In these cases, the arithmetic or geometric mean could be used to represent both the exposure concentration and the body residue. For cumulative CBRs, derived from reactive, irreversible or slowly reversible target interactions, the body residue should be determined using AUC or critical area under the curve (CAUC). Verhaar et al. (1995) have found this parameter to be constant and independent of exposure time for particular single species-compound interactions. For receptor-mediated or reactive toxicity, LC50 vs. time values decrease after achieving steady state bioconcentration and the incipient LC50 will be substantially lower than the 96h LC50 for many compounds.

4.6.5.6. Physiologically based pharmacokinetic or toxicokinetic models

Physiologically based pharmacokinetic (PBPK) or toxicokinetic (PBTK) models would only be employed at the 4th Tier and not unless the company's major product or an urgently needed pesticide was involved. Considering all the information presented, there are significant factors to consider that greatly affect the interpretation of toxicant residues in wildlife tissues which highlights the important role of physiologically-based toxicokinetic models to elucidate the intraspecies and interspecies differences affecting the development of CBRs. The coupling of these more complex kinetic models (more compartments, more linkages, "real" model of an organism) with CBRs allows for the estimation of when a chronic or acute toxic response is expected to occur under various exposure scenarios. This type of modeling also predicts of the time course for the toxic effect. Such methods should be able to elucidate the intraspecies and interspecies differences affecting the development of CBRs, making them useful for extrapolating responses to other species. Besides being an effective tool for predicting acute toxicity from pulse exposures, the concept of CBRs and toxicokinetics could be applied to other cases where exposure-response relationships are complex, for instance exposure via sediments, diet and for chemical mixtures (Landrum et al. 1992; Lien et al. 1994).

As with any model, the user needs to have a good understanding of the assumptions of the particular toxicokinetic model being used. For instance, many models will assume steady-state conditions whereby all organisms are assumed to internally act upon a toxicant in the same way when exposed to the same source of chemical activity. When these assumptions are clearly not appropriate, more complex toxicokinetic modeling should be attempted (Lassiter 1986). Pharmacokinetic models in general could be improved by a better understanding of CBRs, true dose-response distributions and the link between CBRs and modifying factors such as fat content, which may alter the toxicokinetics and toxicodynamics of a toxicant (Hickie et al. 1995). At some point in the future it is likely that from monitoring tissue residues in field-collected organisms, an assessment of an organism's or population's health can be made.

Pharmacokinetic modeling is the process of developing mathematical descriptions of absorption, distribution, metabolism and excretion of chemicals in biota (Krishnan and Andersen 1994). Such models can be used for interpolation, but should not be used for extrapolation outside the dose ranges, routes of exposure and species used to develop the model. Development of these models occurs in 4 steps: model representation, model parameterization, simulation and validation (Krishnan and Andersen 1994). Such models have been developed to describe the disposition of more than 100 chemicals

in mammalian species, and although more limited in scope than mammals, models for nonmammalian vertebrate species such as fish have also been developed (Nichols et al. 1994). There are many recent examples of pharmacokinetic modeling in fish (Bradbury et al. 1986; Erickson and McKim 1990; Hayton and Barron 1990; Clark et al. 1997; Lien et al. 1994; Nichols et al. 1996; and Tarr et al. 1990) and aquatic invertebrates (Hallam et al. 1990).

These higher level, more detailed models require more species-specific or habitat (environment)-specific information and assumptions; however, they are data intensive, the amount of parameterization needed may be prohibitively costly for most applications and the cumulative uncertainty in these models can be large if parameters are poorly specified or understood (Suter 1993). These models must be interpretable in terms of physicochemical, biochemical and physiological properties of the organism. They still represent significant simplifications of the true complexities of biological systems. Such detailed models are often simplified to one or two-compartment models as described above in order to reduce data and parameterization needs and possibly increase their utility (Nichols et al. 1994).

The principle application of PBPK models is the prediction of a dose to a target tissue, a body residue for a parent chemical or reactive metabolite or chemical concentration time course for specific tissues and organs (Krishnan and Andersen 1994; Nichols et al. 1994). PBPK models can help to reduce uncertainty associated with conventional dose extrapolation, dose-effect relationships and CBR estimation methods. However, in many cases, it might be more feasible and cost effective to conduct a microcosm or mesocosm experiment designed with specific effects endpoints or to monitor associated effects in the aquatic environment.

4.6.6. Interpreting Tissue Concentrations of Toxicants in Aquatic Organisms

There are a number of difficulties in the interpretation of toxicant residues in wildlife tissues. Toxicity elicited from the body residue of a contaminant will depend upon the age, sex, fat content and other variables of an individual within a species. Interspecies differences are also expected to be large. For example, when birds of six different species were administered the same chronic doses of lead which killed 50% of the tested birds, the maximum concentration in liver was 10 times greater than the minimum concentration for a particular species (Beyer et al. 1996). Variation in the wild would be expected to be even greater than that observed in these laboratory species. These results have implications in the use of the ecotoxicological modeling efforts described in the previous section. For instance, many toxicokinetic models assume steady-state conditions whereby all organisms are assumed to internally act upon a toxicant in the same way when exposed to the same source of chemical activity (Lassiter 1986).

A paper by Van Loon et al. (1997) addresses the problem associated with threshold levels for individual toxicants through the identification of CBRs for a chemical class of compounds. It is generally thought that narcosis-type toxicants are completely concentration additive and are intrinsically all equally toxic (Van Loon et al. 1997). Therefore, body residue levels that would cause a certain effect would be the same for all toxicants within this toxicological class (toxic

equivalence factor of 1.0). The differences in aqueous effect concentrations within this class is related to differences in bioconcentration factors. As reported in Van Loon et al. (1997), no-effect CBRs for baseline toxicity are:

Endpoint	***No-effect CBR (mmol/kg lipid)***
Mortality (fish)	25
Sublethal effects (fish)	5.0
Estimated ecosystem no effect level	0.25

* reproduced from Van Loon et al. 1997.

Total body residues may be quantified by measuring the total molar concentrations of chemical mixtures in one measurement. An advantage of working with CBRs is that for chemicals and chemical mixtures with only baseline toxicity, the CBR is constant for a certain endpoint (Van Loon et al. 1997).

Landrum et al. (1992) also investigated CBRs for the narcosis-type class of compounds (also cited in McCarty and Mackay 1993). Their findings indicated that residues which yield 50% mortality for acute exposures range from 2 to 6 mmol/kg for small fish and invertebrates to a wide range of neutral narcotics. If a tissue concentration required to produce 50% acute mortality is below 0.5 mmol/kg the toxicant acts by a specific mode of action which is indeterminate between 0.5 and 2 mmol/kg; however, recent data with halobenzenes and fish indicate that CBRs are not constant and decrease with greater exposure time (Chaisuksant et al. 1997). Residue concentrations needed to elicit chronic effects are much lower than those needed for acute mortality. For 50% mortality, the residue concentration for chronic exposure to non-polar narcotics is about 10% of that required to elicit an acute response (Landrum et al. 1992).

This approach also appears to be useful with sediment bound narcotic chemicals. Driscoll and Landrum (1997) exposed *Hyalella azteca* and *Diporeia* spp. to varying levels of fluoranthene in sediments. Rough estimates of the CBR for *H. azteca* after only 10 d exposures were 3.6 to 5.6 umol/g and 1 umol/g after 30 days. Because *H. azteca* is known to metabolize fluoranthene to more polar and possibly more toxic metabolites, fluoranthene was not acting solely as a narcotic compound in this study. For *Diporeia*, however, body residues of 2.7 to 6.5 umol/g after 30 day exposure resulted in very little toxicity. *Diporeia* is known not to be able to readily metabolize fluoranthene and has a higher lipid content (sequester nonpolar narcotics) than *H. azteca*, resulting in higher body residues and negligible toxicity in *Diporeia*.

One method for determining CBRs for toxicants in aquatic organisms assumes that the LC50 multiplied by the bioconcentration factor (BCF) represents the lethal or effect concentration in tissue (McCarty 1986 in Beyer et al. 1996; ECETOC 1995). Actual body residues are expected to be lower due to either non-steady-state conditions or incomplete transfer of the toxicant from the water column into the organism. Also, according to McKim and Schmeider (1991), BCF values are considered at steady state which may not be reached in toxicity tests of short duration with chemical have log K_{ow} >3. Using this methodology, numerous CBRs were estimated for dioxins in fish at various lifestages and for various effects. Lethal effects of TCDD in older fish were seen at CBRs of 0.2 ug/kg and higher, sublethal effects between <0.054

and 30 ug/kg. CBRs for lethal effects of TCDD in early lifestage fish ranged from 0.003 and 10 ug/kg, sublethal effects between <0.0003 and 8.3 ug/kg. This has serious implications when considering that these levels approximate actual measured concentrations in fish collected from unpolluted areas (Beyer et al. 1996). Note that a recent publication from Germany (Nendza et al. 1997) calculates the CBR for marine organisms using the NOEC from an acute study and not the LC50.

Determining CBRs for mercury in fish has been found to be problematic because the target organ for toxicity is the brain and not the muscle or whole-body tissue. In addition, it was noted that the rate of accumulation and exposure time affected the toxicity of methylmercury to fish. That is, larger amounts of methylmercury could be tolerated if accumulated over a longer period of time than a large single dose. It is thought that the reason for this is that, over time, the fish are able to redistribute methylmercury to proteins in skeletal muscle, thus reducing the quantity in the central nervous system. Although there is evidence that some species of fish are significantly more sensitive to mercury poisoning than others (e.g., the walleye). Nevertheless, brain, muscle and whole body CBRs have been developed for mercury in adult fish. In the brain, concentrations of 7 ug/g wet weight may cause severe lethal effects (the CBR in brain tissue for walleye is 3 ug/g wet weight). In axial muscle tissue, CBRs are 6 to 20 ug/g wet weight. Whole body CBRs for lethal or sublethal effects range from 5 to 10 ug/g. The estimated no-observed-effect CBRs in salmonids are 3 ug/g for the whole body and 5 ug/g for brain or axial muscle tissue (Beyer et al. 1996).

In other studies assessing the effects of toxic metal body residues to aquatic invertebrates, it was determined that toxic effects cannot be related to absolute body concentrations. The rate of physiological/biochemical detoxification and/or excretion was found to be the determinant factor for toxicity. Only if the different components of the total metal content of an invertebrate were identified and quantified could the significance of accumulated metal concentrations be understood (Beyer et al. 1996).

McCarty et al. (1993) investigated the estimation of CBR values in fathead minnows for the polar narcotic compounds, substituted phenols. The ability to estimate CBRs from the experimental data was affected by pH dependent ionization. When ionization-corrected toxicity data were assessed, several categories of CBRs were observed that were apparently related to different modes of action and generally fit the CBR classification schemes presented earlier in this chapter.

Although additional analytical measurement is required, estimated CBRs can be compared with tissue concentrations from laboratory studies to verify these data. CBRs may also be compared to tissue levels from field collected specimens in monitoring programs or incidents. CBRs can be useful components in ecological risk assessment (Env. Canada 1997) when used in a weight of evidence approach.

4.6.7. Population Analysis

Life history or age-stage models can be used to design pulsed toxicity tests a priori. In Tier 2, generic life history tables for several life history strategies in aquatic invertebrates and fish can be developed (see section 4.2.2.2). For each of type of life history strategy, a particular period of growth suppression or lethality and its corresponding impact on population dynamics can be described. A time-varying toxicity study can be conducted for a particular exposure period or frequency which might cause an ecologically significant effect on a population. Age-specific mortality or reproduction information can be used to determine the time required for recovery of a particular population, assuming that delayed effects do not occur and that effects are reversible and not cumulative. These analyses can address questions such as:

- Are single or multiple exposures relevant?
- Are intervals between exposure events sufficient to allow biological recovery?

For example, if the interval between exposures is shorter than the predicted recovery time for the population, a time-varying toxicity study may be warranted.

4.6.8. Use of Time-Varying Results in Risk Characterization

Figure 4-28 describes the Tier 3 risk characterization step for both single and multiple pulsed exposures. The probability of an exposure, derived from RADAR, for the time-varying exposure is then compared to the probability of an effect magnitude from a pulse exposure toxicity study or to the result from PULSETOX if additional effects testing was not conducted. In the former comparison, a probability of an effect curve is generated. Concentration units for both exposure and effects must be the same (e.g., peak, TWA, AUC). In the latter comparison, a weight of evidence approach is used to decide whether the probability of exposures will cause a critical body residue to be reached, producing a particular effect.

4.6.8.1. Laboratory-based approach

Results from laboratory-based pulsed exposure studies can be used in this risk assessment scheme in the same manner as typical toxicity studies. Effects based on peak concentration or AUC integration can be used and compared to exposure concentrations derived in the same manner. Exposure, characterized by a distribution of the probability of a particular concentration (e.g., peak concentration, AUC, pulse duration, geometric mean, or arithmetic mean), coupled with the effect (e.g., % mortality) vs. concentration (peak concentration, AUC, duration, geometric mean, or arithmetic mean) generates a Joint Probability Curve (section 4.x.x).

Time-to-event analysis (section 4.3) can be used to characterize the risks from time-varying exposures. TTE assists in determining whether the events are independent, antagonistic, additive or synergistic (see Figure 4-26).

Population analysis can be used a posteriori to address whether the results from a pulsed toxicity study could be ecologically significant, i.e., cause ecologically meaningful changes in population numbers. Age-structured models can be used to extrapolate acute or chronic measurement endpoints to population effects (see Population Analysis chapter). Risk characterization relates the exposure distribution to the population responses to determine a time to recovery, probability of a percent of population decline, probability that the population will decline below a quasi-extinction threshold, etc.

4.6.8.2. Toxicokinetic models

As mentioned earlier, time-varying models, such as PULSETOX, may be used to assist in the interpretation of effects from long pulses, long recovery intervals or numerous repeated exposures that would be difficult to test in the laboratory. The time to reach a lethal body residue can be estimated using default CBRs. Estimates of body residues and/or time to lethality can be estimated for other exposure concentrations or pulse durations. The results from this modeling are not used directly in the Risk Characterization, but are useful in understanding the dynamics of the compound in environmental receptors. The proximity of these concentrations to the CBR would be used in a weight of evidence approach in deciding whether effects are expected based on the particular exposure scenario.

4.6.8.3. Tier 4

Risk characterization in Tier 4 would be subject to professional judgment and not comparison of exposure and effects distributions as in Tier 3. Particular aspects of the pulsed exposure, either via monitoring (exposure and/or effects) or higher level modeling (e.g., PBPK) would be refined at this tier and used in a weight of evidence approach to assessing the ecological risks (see Chapter 2 for additional details concerning risk characterization in Tier 4).

4.6.9. Uncertainties

4.6.9.1. Laboratory studies

Potential problems and uncertainties associated with pulse-exposure toxicity testing are:

- The exposure regime used in the laboratory must be similar to that encountered in the field;
- Ability to test pulses of long duration and/or long recovery intervals;
- The relationship between exposure time and acute toxicity will differ among toxicants; and
- A post-exposure observation period may reveal that some test organisms recovered from their toxic effects (Parsons and Surgeoner 1991).

4.6.9.2. Toxicokinetic models

Uncertainties associated with and barriers to the use of toxicokinetic models in predicting toxic effects in aquatic organisms from whole-body residues are:

- The toxicodynamics of the compound must be considered, and are frequently poorly defined.
- The distribution of the compound between tissue compartments must be at a steady state.
- If equilibrium is not met, then the residue approach may not work for very short-term exposures.
- Defining toxic effects based on body residue levels reduces uncertainties associated with the bioavailability of the toxicant in question. While there are still a number of poorly defined species-specific and site-specific variables which affect the refinement of toxicokinetic models.
- FGETS and PULSETOX reduce uncertainty by allowing prediction of a CBR for laboratory studies which are difficult to conduct.
- Considerable research is needed to generate data in support of the establishment of CBRs for the most common environmental contaminants and for a wide range of receptors, including sensitive species (Landrum et al. 1992).
- When measuring CBRs, there is an operational lag time between when the effect occurs and the organism is retrieved and analysed (Landrum et al. 1992).
- High K_{ow} compounds will be more difficult to predict due to their bioavailability limitations.
- The development of CBRs for compounds with specific mechanisms of action will need to include exposures to a range of taxa to account for differences in sensitive species (Landrum et al. 1992).
- Bioaccumulation is a complex process involving biological and chemical factors including kinetics, equilibrium levels, tissue translocation, sequestration, excretion, and depuration. Body residues in an organism depends on age, health, sex, reproductive state, lipid content, trophic level, feeding habits, and ambient tissue concentrations.
- Analytical factors such as matrix interferences, extraction efficiency, methodological sensitivity, instrumentation, and variation in methodology will effect measured body residue levels (Maciorowski et al. 1985).
- A threshold level in tissue will generally refer to a single chemical. However, there are toxic potentials associated with residues resulting from mixtures of compounds that will not be adequately described by developing threshold levels for individual compounds. For instance, threshold effects of mercury may depend upon the concentration of selenium (because selenium will bind to mercury), DDT may stimulate the metabolism of dieldrin in animals, and different organochlorines may interact to effect the accumulation of residues in fish (Beyer et al. 1996).

4.6.10. Recommendations

The following recommendations are supported in this section:

- Time-varying exposure testing and modeling should be considered if exposure profiles and chemical behavior suggest pulsed scenarios (more realistic exposures).
- Time-varying exposures should be considered if the application interval, compound half-life and/or exposure modeling indicate that such exposures may occur.
- Pulse testing methods or guidelines (both acute and chronic) should be developed and validated for general use.
- Where it is possible to redesign bioassay protocols to determine whether latency exists or not, ECOFRAM recommends that the protocols be modified as long as the results are compatible with historical data from the same protocol.

- Validation trials should be conducted for both FGETS and PULSETOX.
- DEBtox should be investigated for its use in time-varying effects analysis.
- Time-to-event analysis of time-varying responses are useful tools for interpreting population effects.
- PULSETOX is considered useful when laboratory testing of time-varying exposure is not practical (e.g., long pulses, long recovery intervals or numerous repeated exposures).
- FGETS can be used to generate PULSETOX inputs.
- Higher level PBPK models may be useful at Tier 4, but monitoring is often more cost effective and less uncertain.
- PBPK models are useful for extrapolation to other species, especially larger species where contaminant dynamics are not considered instantaneous.

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4.7. Sediment Toxicity

4.7.1. Introduction

The US EPA is concerned with the potential for degradation of aquatic ecosystems through the contamination of bottom sediments by toxic compounds. Acting as a depository for pesticides and other pollutants discharged into surface waters from point and nonpoint sources, sediments are in contact with benthic and epibenthic organisms either directly or though the food chain. This section describes the Office of Pesticide Programs' current perspective on sediment toxicity evaluation of pesticides.

Until recently the impacts of pesticides to sediment dwelling organisms have not been generally considered in pesticide risk assessments. It has been established that pesticides in the water column are available and taken up by aquatic organisms and can result in adverse biological effects. It was assumed that once pesticides were bound to suspended or bottom sediments, their bioavailability was reduced and toxic effects would not occur. However, increasing evidence that this assumption is not universally correct led to the development of protocols and guidance documents to measure the bioavailability and the acute and chronic effects of chemicals in sediments on benthic and epibenthic organisms. In order to develop standardized methods for conducting sediment toxicity tests, protocol and guidance development is occurring in several venues such as harmonized OPPTS ecotoxicology guidelines, OECD guidelines, Environment Canada Biological Test Methods, and the ASTM Subcommittee E47.03 on Sediment Toxicology .

The database that is developed from the standardized test methods will be used in ecological risk assessments by environmental agencies to determine the degree to which ecological risks are likely to occur in the sediment layer and then regulate unacceptable impacts. However, at this time, OPP has not finalized the data requirement for sediment toxicity testing, and only a few pesticides with significant sediment-binding properties have data from these studies as part of their ecological effects database. Therefore, the use of sediment toxicity data in ecological risk assessments, even the deterministic (quotient) method, is relatively new. Once there is an adequate database, the best approaches for analyzing the data with probabilistic tools can be determined. Until that time, risk assessors need to be flexible in the risk assessment methodologies used to analyze these data.

4.7.2. Background

The U.S. EPA developed a "Contaminated Sediment Management Strategy" (US EPA 1997) to coordinate the several Agency programs that deal with sediment contamination in order to reduce duplication in effort and streamline the decision-making process in the various programs. The purpose, as described in the Strategy, is to "promote and ensure the use of consistent sediment assessment practices, consistent consideration of risks posed by contaminated sediment, the use of consistent approaches to management of contaminated sediment risks and the wise use of scarce resources for research and technology development." The Strategy is composed of six components: assessment, prevention, remediation, dredged

material management, research and outreach. The components that involve the Pesticide Program are assessment, prevention, research, and outreach. The Strategy proposed that the program offices use standard sediment toxicity study methods and chemical-specific quality criteria to ascertain if sediments are contaminated. The development of a National Sediment Inventory Database and a National Sediment Quality Survey will enable the several programs to share information and develop strategies of prevention and assessment. However, each of the program offices, which operate under different legislative mandates, can determine which tests best suit its needs and how to regulate the identified risks.

An Agency-wide Sediment Tiered Testing Committee determined that chemical and biological sediment test methods be standardized and used by all Agency programs, and that the test methods be set up as a tiered testing scheme that will provide more information and reduce uncertainty at higher tiers. As part of the Strategy and under its mandate established by FIFRA, OPP has been actively working toward including sediment toxicity issues in its current risk assessment process.

In 1990, as part of this initiative, OPP took part in discussions with the Conservation Foundation's Aquatic Effects Dialog Group (AEDG). Recommendations of the AEDG (1992) included establishing a tiered testing scheme for sediment toxicity testing. The scheme set up four tiers: Tier 1, equilibrium partitioning (EqP) calculations to estimate chemical concentrations in porewater and sediment; Tier 2, acute pore water and whole sediment toxicity tests with spiked sediment; Tier 3, chronic whole sediment toxicity tests with spiked sediment; and Tier 4, benthic community structure, colonization rate, laboratory toxicity tests with field collected sediment, and in-situ sediment toxicity testing with a mesocosm.

ASTM E 1706 - 95B lists several approaches that different programs of the U.S. EPA consider when assessing sediment quality. These are EqP calculations, tissue residues, interstitial water toxicity, benthic community structure, whole-sediment toxicity and sediment spiking, sediment quality triad, and apparent effects threshold. ASTM concluded that although each approach can be used independently to make a site-specific decision, the several methods should be integrated into a weight-of-evidence approach to provide the best means of assessing chemical effects in sediment-dwelling organisms.

ECOFRAM's charge is to develop a process and tools for predicting the magnitude and probabilities of adverse effects to nontarget species resulting from the introduction of pesticides into their environment. Either of these approaches, in whole or in part, may provide the best means of addressing this charge. The section will discuss some of these methods to determine if they can play a role in the probabilistic risk assessment process.

4.7.3. Equilibrium Partitioning Calculations

The U.S. EPA Office of Water uses the equilibrium partitioning method (EqP) as a first level screening method to set a chemical-specific Sediment Quality Criteria (SQC) for nonionic organic chemicals. It predicts the chemical-specific sediment toxicity from water column toxicity studies and the measured Koc value for that chemical. It uses the extensive

biological effects database that serves as the basis for the water quality criteria established by the Office of Water. This method establishes a sediment-specific criterion for each chemical, which can in turn be compared with field measurements to assess the likelihood of significant adverse effects. Finally, it provides regulators with information in a short period of time regarding the potential for the chemical to be bioavailable to benthic organisms.

The EqP method makes several assumptions, each of which has an unquantifiable amount of uncertainty associated with it. These assumptions are: 1) There is an equilibrium between the amount of nonionic organic chemical bound to the organic carbon of the sediment particles and the amount present in the pore water of the sediment. This is known as equilibrium partitioning. 2) This equilibrium provides the organism with the same level of exposure as occurs in a water-only system. 3) Different sediments can produce different biological effect concentrations for the same test species for some chemicals due to differences in the amount of organic carbon present in the sediments. These differences can be accounted for by normalizing for organic carbon content for all sediments being tested. 4) Chemicals bound to the dissolved organic carbon (DOC) in the water column are not bioavailable to exposed organisms. 5) Benthic organisms and organisms in the water column are similar in sensitivity to the chemical. Based on these assumptions, the concentration for the toxicity of a nonionic chemical to benthic organisms can be estimated from the toxicity data for water column organisms measured in water-only test systems and the partition coefficient value for the sediment organic carbon, the Koc value of the chemical.

To date OPP has not seen any value in using the EqP method as a first tier in assessing risks to benthic organisms. Surface water models such as PRZM/EXAMS II that are routinely used in the early stages of the risk assessment process calculate the concentration of the pesticide chemical in the pore water as well as adsorbed to the sediment. These models incorporate the assumptions listed above. The pore water concentration can be compared to the acute toxicity values from the freshwater invertebrate study to determine if benthic organisms are potentially at risk. The EqP method is not necessary in the deterministic risk assessment process, and it is unlikely that the EqP method will provide any value in a probabilistic risk methodology.

[JMG comment: But PRZM/EXAMS uses the EqP approach to estimate pore water concentrations. Maybe the specifics of the Office of Water calculations aren't needed, but the equilibrium partitioning approach is valid and in fact was recommended by ECOFRAM.]

4.7.4. Sediment Toxicity Testing

The USEPA■s Sediment Tiered Testing Committee selected four test methods for use within the tiered testing framework. These are: (1) ten day freshwater acute toxicity tests using *Hyalella azteca* (amphipod) and *Chironomus tentans* (midge) [USEPA, 1994, EPA/600/R-94/024]; (2) twenty-eight day freshwater bioaccumulation tests using *Lumbriculus variegatus* (freshwater oligochaete worm) [USEPA, EPA/600/R-94/024]; (3) ten day marine and estuarine acute toxicity tests using the amphipods *Ampelisca abdita, Rhepoxynius abronius, Hyallela azteca, Eohaustorius estuarius* and *Leptocheirus plumulosus* [USEPA, 1994, EPA/600/R-94/025]; and (4) twenty-eight day marine

bioaccumulation tests using *Macoma nasuta* (clam) and *Neries* spp. (polychaete worm). In addition, USEPA has drafted a revision of the methods for acute toxicity testing with freshwater invertebrates to include chronic test methods for a 42-day test with *Hyallela azteca* and a 50-day to 65-day test with *Chironomus tentans.*

In addition, OPPTS developed harmonized test guidelines for whole sediment acute toxicity testing with freshwater (OPPTS 850.1735) and marine invertebrates (OPPTS 850.1740). It is expected that the harmonized guidelines will be finalized soon. The requirements for this set of studies is given in draft 40CFR Part 158.145. OECD also has drafted guidelines for 28-day sediment toxicity testing. These proposed new guidelines are ✌Chironomid Toxicity Testing Using Spiked Sediment✍ and ✌Chironomid Toxicity Testing Using Spiked Water✍. ASTM has three published guides for conducting sediment toxicity tests. These are ✌Standard Guide for Conducting 10-day Static Sediment Toxicity Tests with Marine and Estuarine Amphipods (ASTM E 1367-92); Standard Guide for Designing Biological Tests with Sediments (ASTM E 1525-94a) and Standard Test Methods for Measuring the Toxicity of Sediment-Associated Contaminants with Fresh Water Invertebrates (ASTM E 1706-95b). Environment Canada developed a series of sediment toxicity tests for acute testing with marine/estuarine amphipods (EPS 1/RM/26), *Chironomus tentans* or *riparius* (EPS 1/RM/32) and *Hyallela azteca* (EPS 1/RM/33). This listing of toxicity testing is not meant to be all-inclusive but to show that there are a number of guidelines, protocols and guidance documents concerning rationales, methods and applicability regarding the various aspects of sediment toxicity testing.

The development of the testing schemes listed above was triggered by the concern that toxic chemicals that partition into the sediment layer in aquatic systems may potentially cause significant ecological effects in the organisms inhabiting that zone. However, not every chemical that enters aquatic ecosystems will accumulate in the sediments or be sufficiently toxic to affect the organisms there. Therefore, criteria need to be established to identify which chemicals will require sediment toxicity testing (Maund et al. 1997). OPPTS has drafted testing criteria that were presented to the OPP Scientific Advisory Panel (SAP) in 1996. These criteria take into account the environmental chemistry and toxicity properties of the pesticide in question. OPPTS will require sediment toxicity testing if any of these conditions are met. These criteria are: solubility $\leq$ 0.1 mg/l, Koc > 50,000, Kd $\geq$ 1,000, the pesticide persists in the sediments with a half-life $\geq$ 10 days, or the concentration in the interstitial (pore) water is equivalent to concentrations known to be toxic in the water column. Maund et al, also proposed several criteria which differ slightly from the OPPTS criteria. They proposed that sediment toxicity testing be required if all their proposed conditions are met. Their criteria are: Koc $\geq$ 1,000, DT_{50} $\geq$ 30 days for soil aerobic degradation and *Daphnia* 48-hr acute toxicity value < 1 mg/l or 21-day NOEC < 0.1 mg/l. At this time, the criteria proposed by OPPTS are expected to be finalized and accepted as the triggers for requiring sediment toxicity studies. OPPTS scientists believe that their criteria will provide the regulators with the best data set to assess risks from pesticides and other toxicants that partition to sediments.

In order to determine which test methods will provide data that will fit into the probabilistic risk assessment process, the measurement endpoints of the different test procedures are briefly mentioned. The risk assessment team needs to decide

during the problem formulation steps of each level of the risk assessment which test or combination of tests will best provide the data needed to answer the questions posed by the risk managers.

In the 28-day OECD guidelines, the measured endpoint is adult emergence. Larval survival and growth are optional measurements. The pesticide is measured in the overlying water, sediment and pore water. The major difference between the two guidelines is that the spiked water test simulates a pesticide spray drift event and covers the initial peak concentrations in the pore water. The spiked sediment test simulates accumulated levels of persistent pesticides in the sediment.

The short-term and long-term USEPA and ASTM studies are conducted in whole sediment spiked with the toxicant. The pesticide is measured in the overlying water, sediment and pore water. The endpoints measured in the ten-day studies are survival and, optionally, growth. The endpoints in the long-term chronic studies are survival, growth, reproduction and the number of adult male and females in the *Hyallela* test and survival, weight, female and male emergence, adult mortality, the number of egg cases oviposited, the number of eggs produced and the number of hatched eggs for the *Chironomus* test. The endpoints in the 28-day bioaccumulation studies are tissue concentrations of the toxicants and, possibly, lipid content.

4.7.5. Using the Data in a Risk Assessment

OPP currently uses the deterministic or quotient method for estimating ecological risk. In this process the LC_{50} value from the 10-day acute toxicity studies are compared to the estimated peak concentration (EEC) in the sediment/pore water complex. [EEC/LC_{50} is compared to a regulatory Level of Concern (LOC) (0.5 for acute risks to nonendangered species, 0.05 for endangered speciesand 0.1 for Restricted Use classification)]. PRZM/EXAMS II calculates the estimated concentration adsorbed to the sediments and in the pore water and converts these individual concentrations to the combined unit using a mass balance conversion. This is done because the toxicity value is based on exposure of the test organism to whole sediment, that is, the chemical bound to the sediment particles plus that dissolved in the pore water. These tests cannot determine which component of the sediment layer is primarily responsible for the toxic effects. Therefore, the EEC of the sediment/pore water complex more accurately provides information on the concentrations likely to be present in the modeled scenario. If the EEC/LC_{50} exceeds the regulatory LOC for acute risks, then the risk assessment proceeds to the next level.

The next logical step is to conduct the chronic studies to determine if risks occur from long-term exposures as well as short-term exposures. The toxicity values from the chronic studies are also compared to the EEC in the sediment/pore water complex, but the EEC is based upon a period of time analogous to the exposure period of the toxicity test. If the EEC/chronic toxicity value exceeds the regulatory LOC for chronic risks (1.0), then the risk assessment proceeds to the next level, the probabilistic method.

A probabilistic risk assessment requires that the exposure and effects data are presented as distributions of each set of data. Therefore, a series of acute toxicity tests using several sediments and more than one species, all following the same protocol, will be needed to provide an adequate database for each individual pesticide. This database will allow for a distribution analysis,such as joint probability curves, to determine magnitude and probability of impact on benthic and epibenthic organisms. Marine/estuarine species as well as freshwater species should be included in the testing phase if the chemical is expected to enter estuarine waters from spray drift and surface runoff. The types of sediments used to conduct this series of tests should be determined by the composition of the sediments found in the areas where the pesticide is used. Optimally, series of both acute and chronic studies should be provided, however, resources and willingness to expend significant amounts of time to conduct, analyze and evaluate several long-term studies may result in forgoing a more extensive database for chronic effects. If there are sufficient data on the life histories of the test organism(s), population models based on the results of the sediment toxicity studies can be used to predict the likelihood of a population decline and recovery in the selected species.

4.8. Considerations for Chronic Toxicity Testing

4.8.1. Chronic Toxicity Testing

The U.S. EPA's Standard Evaluation Procedures (e.g., U.S. EPA 1986) provide guidance on ecological testing requirements, and state the conditions upon which chronic toxicity testing may be required. The ECOFRAM aquatic risk assessment process will alter the current scheme by proposing the availability of some chronic toxicity testing in the earliest tiers of the risk assessment process. Rather than be a conditional requirement, the invertebrate life cycle test (*Daphnia magna*) and the fish early life stage test (ELS) would be conducted in Tier 1. The addition of this data in the early tiers will help to reduce some of the uncertainties associated with decision-making in that chronic endpoints are under consideration. Also, the data can be useful in the population level analysis that occurs in Tier 2 (Section 4.4), and in deciding the utility of performing time-varying exposures in Tier 3 (Section 4.6). The time-to-event analyses, proposed in Section 4.3, offer an improved statistical procedure for analyzing some of the data in chronic tests, such as time to hatch and time to swim-up.

Additional chronic toxicity testing may be necessary in Tier 3 or Tier 4 of the risk assessment process, depending on the outcome of the risk characterization in Tier 1 and 2. Chronic testing should be conducted if the results (NOEC or ECx) of the chronic tests exceed the risk quotient, as described in section 2.5.4.2. The data that may be generated at this level will address the uncertainties concerning potential effects on the population, with the focus on designated use patterns or previously identified environmental concerns. The fish life cycle test would be conditionally required for compounds with chronic risk quotients exceeding the fish LOC. Additional sediment testing may be necessary for a compound with high persistence and Koc, and guidance on these tests is rapidly becoming available (see section 4.7). Estuarine testing may be required if a compound has a use pattern in the vicinity of those environments, and may follow the available test guidance (e.g., mysid chronic test, the sheepshead early life stage test or life cycle test). These, or other additional tests (e.g., *Ceriodaphnia* life cycle test), may allow a distributional analysis of chronic data, similar to that proposed in Section 4.5 for acute data. However, the number of species needed to perform such analysis has not been determined, and the number of tests with U.S. EPA Guidance Documentation or Standard Evaluation Procedures is limited.

As mentioned, a fish life cycle test may be conducted in Tier 3, which has been designed to assess potential effects on the development and reproduction of fish species. However, it is often difficult to detect significant differences in reproduction because of the natural variance associated with fecundity of fish. The design of the fish life cycle test should be evaluated for potential ways to reduce the variance and increase the power of the test. ECOFRAM recommends the development of a dialogue group to assess the fish life cycle test and conditions upon which it would be required, which could coincide with the evaluation of the same test under the endocrine initiative in U.S. EPA's Endocrine Disruptor Screening Program (U.S. EPA, 1998).

4.8.2. Issues Related to Proposed Endocrine Toxicity Testing

The U.S. EPA has recently published their proposed policy for endocrine screening and testing (U.S. EPA 1998), termed the Endocrine Disruptor Screening Program (EDSP). While ECOFRAM acknowledges the tremendous effort and emphasis being placed on this program, the program is still currently in development. The screening and testing program may offer a process for the determination of a potential mechanism for toxicity. However, ecological risk assessments should be based on ecologically relevant endpoints, such as survivorship, growth, development, and reproduction. Any new test developed by the EDSP should be evaluated for their ecological relevance, and if appropriate can easily be incorporated Tier 1, 2, 3 or 4 of the ECOFRAM risk assessment process.

4.8.3. Issues Related to Endpoint Determination in Chronic Toxicity Tests

In the ecological affects assessment of the pesticide registration, the use of the No Observed Effect Concentration (NOEC) has become somewhat constitutional for determining the endpoints in chronic testing. The NOEC can be defined as "the highest concentration for which there is no statistically significant difference from the control (Cooney, 1995). Concurrently, the lowest observed effect concentration, or LOEC, is the lowest test concentration that is significantly different from the control. For chronic testing, the general experimental design is to expose organisms to one of five concentrations, which are separated by a factor of 2, or a control and/or solvent control (if necessary). The endpoints are measured (e.g., length, weight, reproduction, etc.) and hypothesis testing is used to determine the NOEC. As McClave et al. (1981) note, the experimental design will dictate the appropriate statistical procedure to use, and it may include a one-way, nested or other ANOVA model followed by a multiple comparison test to determine which treatment levels are different from the control (e.g., Dunnett's or Williams' test). Generally, a significance level (α) for detecting differences between means is set to equal 0.05, which controls the probability of making a Type 1 error (rejecting the null hypothesis when in fact it is true, i.e., saying there is a difference between the control and treatment groups when there is none). While the probability of making a Type 2 error (β = accepting the null hypothesis when in fact it is false, i.e., saying there is no difference between the control and treatment groups when they are different) should be considered, it is often neglected.

Endpoint determinations can be calculated through other techniques beyond hypothesis testing, such as various regression techniques to estimate the benchmark dose/concentration or inhibition concentrations, bounded-effect dose estimations, or bioequivalence calculations. In general, the regression techniques fit a linear or nonlinear model (e.g., probit, logistic, log-normal, etc.) to the data to predict an effective concentration (EC) producing a predetermined effect (x), or an ECx. This ECx is a benchmark concentration that theoretically will produce an effect at a given level (Crump, 1984). Bruce and Versteeg (1992) propose one such technique for continuous data using nonlinear regression. Bailer and Oris (1997) utilize the generalized linear model to predict the inhibition concentration (i.e., the concentration resulting in a predetermined level of inhibition in response relative to the control) for dichotomous, count and continuous data. Hoestra and van Ewijk (1993) build upon the premise of the benchmark dose, and propose a two step procedure that: 1) determines a

concentration that produces small effect with confidence intervals that bound the response and make it a reasonable concentration from which to perform an extrapolation, and 2) determines an effect level that acceptably small through linear extrapolation. Erickson and McDonald (1995) propose the use of bioequivalence tests to determine differences between controls and test levels with the level of similarity (bioequivalence factor) being set a priori and internalized into the statistics. The null hypothesis in bioequivalence test would state that the control and test are not bioequivalent, the alternative hypothesis would be that the effects of the control and test treatment are biologically the same, which is the opposite of the traditional null hypothesis approach.

4.8.3.1. Criticism of hypothesis testing and the NOEC

Over the years, there have been many criticisms raised on using hypothesis testing for determining the NOEC (Skalski, 1981; Stephan and Rogers, 1985; Bruce and Versteeg, 1992; Hoekstra and van Ewijk, 1993; Erickson and McDonald, 1995; Chapman et al., 1996, Bailer and Oris, 1997). These criticisms can be summarized as follows:

1. Hypothesis testing is based on the rejection of a null hypothesis, which typically states that there is no difference between the control and compound treatment level (Ho: $\mu_c = \mu_t$). The alternative hypothesis would state that the control and compound treatment levels do differ (Ha: $\mu_c \neq \mu_t$). Skalski (1981) and Erickson and McDonald (1995) note that scientific conclusions are based on the rejection of a null hypothesis, but the non-rejection of the null hypothesis is not necessarily accurate.
2. The derivation of the NOEC through hypothesis testing is dependent on experimental design (e.g., concentration selection and sample size) and variance. If the variance is high, the statistics may not be able to detect significant differences between the control and test levels, resulting in a Type 2 error (failure to reject the null when in fact it is false). Reducing variance through increasing sample size or changes in experimental design, may increase the ability to detect these differences. However, the amount to which sample size can be increased is limited by laboratory space and minimizing the number of organisms to be tested. Additionally, some responses are more inherently variable than others and are related to the biology of the organism, and therefore the ability to control these variables is also limited. A power analysis is one way to obtain information as to whether the test design was adequate to detect differences at a specified level. This specified level should be decided a priori, however power analyses are rarely performed, and the specified level of effect even more rarely defined.
3. For monotonic responses, the NOEC will decrease with increased sample size and a point may be reached where upon biologically insignificant differences are detected as statistically different (Erickson and McDonald, 1995). The NOEC would then represent an underestimate of the no effect level.
4. The most common multiple comparison test include the t-test, Bonferroni, Dunnett's and Williams', or perhaps a non-parametric test may be employed when the assumptions of normality or heterogeneity of variance cannot be met. While it is outside the scope of this document to provide a review of all of these various techniques, the choice of the multiple comparison test used will impact the NOEC (Chapman et al., 1996, Hoekstra and van Ewijk, 1993). Each test has its own strengths and weaknesses, which must be carefully considered prior to conduct of the experiment and statistics.

5. As defined, the regulatory endpoint, the NOEC, must equal one of the concentrations used in the conduct of the test. For threshold effects, the NOEC and LOEC determined through hypothesis testing brackets the threshold point, potentially the actual no effect level. If one assumes the ANOVA had enough power to detect significant differences, the NOEC will be an underestimate of the threshold level or no effect level. However, if the ANOVA did not have enough power to detect differences at a prescribed level of effect, and hence uncertainty in the NOEC, there may be uncertainty as to whether the NOEC is an underestimate or overestimate of the threshold level.
6. In a well conducted test with enough power to detect significant differences at the specified level, there is some comfort in that the NOEC may be a safe level in predicting no environmental impact. Inherently, however, the results of these tests may contain much more information than the NOEC provides. The relative slope of the curve provides valuable information to the risk assessment process, that may be lost by relying on the NOEC as the regulatory endpoint.

4.8.3.2. Regression techniques

The ECOFRAM Aquatic Effects group recommends the potential use of the regression techniques for the determination of an ECx value. McClave et al. (1981) note that a modeling approach, as opposed to hypothesis testing will provide more information to interpret the test results. Stephan and Rogers (1985), Bruce and Versteeg (1992) and Moore and Caux (1997) cite several advantages to regression techniques as follows:

1. Regression techniques offer a procedure for interpolation between untested concentrations, while hypothesis testing is limited to providing information on the levels tested. The only way to interpolate between the NOEC and LOEC is to use the arithmetic or geometric mean of these two numbers, which is dependent on the levels tested, but the point estimate obtained in the regression technique is independent of those levels.
2. Using regression analysis, the point estimate of the toxicity is not affected by to number of replicates, the variance and the preselected significance level used in hypothesis testing (usually $\alpha = 0.05$), however the confidence intervals around that point estimate will be sensitive to the number of replicates and the variability. These confidence intervals can be used to judge the adequacy of the model in predicting the toxicity.
3. It is not uncommon in chronic testing to have an inversion in the data or hormetic responses. These types of data are more difficult to handle in the ANOVA model, while the use of the correct regression model can describe the dose response relationship.
4. The quality of the data used in the regression model can be addressed through an examination of the confidence intervals.
5. The full dose-response relationship is considered in the derivation of the model, and hence valuable information is not lost.

The ECOFRAM recommends the use of the regression techniques, not only for the reasons outline above, but also because the full dose-response curve is necessary to predict the probability of exceeding a magnitude of effect, and is useful in predicting the time for recovery. Both of these parameters provide a risk manager valuable information to use in determining the potential effect of a compound and potential mitigation options.

Both the hypothesis testing (through the use of the power analysis) and regression techniques (through the choice of the ECx value) ultimately require a risk manager to decide on the level of acceptable impact in the environment. These decisions should be made a priori to the conduct of the test so that the correct experimental design is used. The decision on the level of impact for which to conduct a risk assessment will not be easy. However, a great deal of information may be available to assist in this matter, such as historical data from fisheries management and information on the life cycle of aquatic organisms.

The recommendation to use regression techniques for chronic endpoint calculations comes with some caution, because there is much similarity in the concerns for both regression and hypothesis testing approaches. While hypothesis testing is dependent on experimental design and other factors as specified earlier, the confidence intervals obtained when using regression are dependent on many of these same factors. While, the results of the hypothesis testing is dependent on the ANOVA model and multiple comparison test, the regression derived endpoint is dependent on the selection of the appropriate model as well. Also, the experimental design specified under current guidelines may not be able to provide adequate data for regression modeling. The use of regression models require a dose-response relationship, that include some concentrations producing partial effects (Moore and Caux (1997). To achieve this, greater flexibility in concentration selection criteria may be necessary, and the number of test levels may need to be increased with regression. Conversely, regression techniques could reduce the number of replicates than what is necessary in the hypothesis testing technique. The choice of the number of test levels will also be influenced by the criteria established for acceptable tests, and the desire to obtain minimal confidence intervals. Therefore, the need for a regression derived chronic endpoint should be balanced with the complexity of the experimental design such a test may require.

ECOFRAM recognizes that in many circumstances, a hypothesis testing approach to chronic testing may be adequate. In cases where no effects are observed at environmentally realistic concentrations, where a limit test becomes an option, or in a well designed experiment with low variance, the hypothesis testing approach is more than adequate to characterize the environmental risk of a compound. However, there are a great many circumstances where a regression technique may be invaluable in the risk assessment process. Therefore, guidance on conducting these tests should be developed, providing information on dose selection and statistical tools for data analysis.

4.9. Microcosms and Mesocosms

Microcosms and mesocosms are model ecosystems—physical models of ecosystem processes. The distinguishing feature of microcosms and mesocosms is the inclusion of multiple ecological components with the objective of simulating ecological processes as they occur in nature. Microcosms differ from mesocosms only in relative size: a microcosm is a small mesocosm, and a mesocosm is a large microcosm. There is not, and need not be, a definitive distinction between the two. In this section, for convenience, they will all be called microcosms, recognizing that the same principles apply to model ecosystems of almost any size, indoor or outdoor.

In the context of ecological risk assessment of pesticides, microcosms are used to integrate, corroborate, and extend the information derived from conventional laboratory toxicity tests and environmental fate studies. Microcosms of appropriate design can be used to measure the effects of pesticides on a large number of taxa under quasi-natural conditions, to identify sensitive species and environmental processes, to observe ecological recovery, and to determine the limits of pesticide exposure that do not produce ecologically significant effects. These applications of microcosms have long been recognized by environmental researchers (Giesy 1980; Giddings 1983; Franco et al. 1984) and in recent years the microcosm approach has gained general acceptance among regulators and decision makers involved in pesticide registration (SETAC-Europe 1992; Crossland et al. 1994; OECD 1996; Campbell et al. 1999).

4.9.1. Generic Microcosm Study Plan

The design of microcosm systems, and of microcosm studies, may vary widely depending on their objectives. However, studies intended to support pesticide risk assessments nearly always follow a similar study plan.

(1) Assemble (or enclose) water, sediment, and biota in a container. The container may range from a pond to an aquarium. Most studies that have been conducted for pesticide registration have used systems with little or no water flow.

(2) Allow the system to “stabilize.” This word is laden with theoretical ecological connotations, as are alternatives like “equilibrate” and “mature.” Such connotations should not be allowed to cloud the picture here; the point is simply that model ecosystems tend to undergo changes for a period of time after being assembled or enclosed, and it is usually best to let these changes run their course before applying the pesticide. It is also useful to determine the condition of the microcosms before pesticide treatment, both to establish their degree of uniformity and to provide baseline data for interpretation of subsequent pesticide-related effects.

(3) Apply the pesticide as a spray (to simulate spray drift), a soil-water slurry (to simulate runoff of soil containing pesticide residues), or an aqueous solution (to simulate runoff of water containing pesticide residues, or simply to establish a concentration of pesticide in the microcosm water).

(4) Monitor chemical and ecological endpoints before, during, and after pesticide application. Ecological endpoints typically include abundance of phytoplankton, periphyton, zooplankton, and macroinvertebrate taxa; macrophyte growth or biomass; fish survival, growth, and reproduction; and community production and respiration. Only

selected endpoints are likely to be monitored in any given study, depending on the concerns that led to the decision to conduct the study.

4.9.2. Advantages and Limitations of Microcosms

The microcosm approach has several advantages for higher-tier ecological risk assessment:

- Exposure is more realistic than in conventional toxicity tests, because natural processes that affect exposure (such as biodegradation, photolysis, and partitioning to sediments and suspended particles) are incorporated into the study.
- Responses of many taxa to pesticide exposure can be determined. A microcosm derived from natural sediment and water usually contains dozens of species of plants and animals representing a variety of ecological niches and taxonomic groups. Obtaining toxicity data for so many different taxa by conventional means (bioassays) would be expensive and time-consuming.
- Responses can be measured at the population, community, and ecosystem levels.
- Recovery of populations and ecosystem processes after pesticide impacts can be observed.

Microcosms also have certain serious limitations, which make them most appropriate for Tier 4 of an ecological risk assessment:

- Microcosm studies can be expensive. Even a simple microcosm study design is likely to cost as much as a life cycle study with *Daphnia*, and the most complex studies may cost well in excess of $1 million. Most microcosm studies are in the $0.2 to $0.5 million range.
- Results of microcosm studies are much more complex than results of single-species tests. A typical study generates thousands of measurements on several dozen endpoints, each varying with time, location, and exposure level. Statistical and ecological expertise are needed to analyze and interpret the data.
- Microcosm data tend to be highly variable, reflecting the variability of natural ecosystems. Coefficients of variation for taxonomic parameters typically range from 50% to 100%, making detection of subtle effects difficult. On the other hand, this property of microcosms permits pesticide effects to be evaluated in relation to the normal range of ecological variability.
- Though microcosms reflect natural situations much more completely than do lower-tier experimental systems, the simulation is still only approximate. Ecological communities in microcosms are isolated and confined, which can influence the severity of effects as well as the potential for recovery. Species with large individual size or home range are excluded. The range of hydrological conditions that can be simulated is also limited; lotic (flowing water) ecosystems are much more difficult to simulate than lentic (standing water) ecosystems.

4.9.3. The Evolution of Microcosm Standards

Microcosms have a long history of application to basic ecological research (Giesy 1980). The development of standardized laboratory-scale microcosms for ecotoxicological screening began in earnest in the 1970s (Metcalf 1977; Taub 1969,

1974; Giddings 1983, 1986; Franco et al. 1984). Larger outdoor systems were used for ecotoxicological research throughout the 1970s and 1980s (Hurlbert et al. 1972; Menzel and Case 1977; Solomon et al. 1980; deNoyelles et al. 1982; Giddings et al. 1984). Experience with these outdoor systems formed the foundation for development of simulated field study guidelines for FIFRA (Touart 1988).

The FIFRA guidelines emphasized fish as "integrators of the systems and to provide the requisite endpoints for risk management decisions" (Touart 1988). The requirement for measurement of fish reproduction implied the use of ponds of 300 m^3 or larger. Although fish were the ultimate focus of these studies, the minimal set of measurement parameters included water quality, gross production and community respiration (inferred from 24-hour continuous measurements of pH and dissolved oxygen), phytoplankton, periphyton, macrophytes, zooplankton (with cladocerans differentiated by size), emergent insects, and benthic macroinvertebrates. The recommended study design called for a minimum of 12 ponds, with three replicates at each of three exposure levels plus three controls.

As these guidelines were put into practice for pesticide registration, several technical and policy issues came to the fore. Technical issues included no-effect determination vs dose-response experimental designs, statistical approaches for detecting pesticide effects against the background of natural variability, design of systems appropriate to the questions being addressed, and interpretation of results. The Aquatic Effects Dialog Group (AEDG) discussed these issues at length and made many recommendations (AEDG 1992). In particular, the AEDG suggested that techniques be developed for the use of smaller systems and more focused study designs. Meanwhile, policy issues were raised concerning the objectives of the studies and their usefulness studies for registration and risk management decisions. The result of the policy concerns was a decision by EPA (Fisher 1992) to discontinue the use of ecological field studies in the registration process.

In response to an AEDG recommendation, a workshop on the use of smaller-scale microcosms for pesticide risk assessment was held in Wintergreen, Virginia, in 1991. The workshop report (SETAC/Resolve 1992) included proposed guidelines for outdoor microcosm studies. The same summer, a similar workshop took place at the Monks Wood Experimental Station, UK, which resulted in a similar set of proposed guidelines (SETAC-Europe 1992). At the European Workshop on Freshwater Field Tests (EWOFFT) in 1992, participants from Wintergreen and Monks Wood met with other experts and developed a unified set of recommendations (Crossland et al. 1994). Under the auspices of SETAC's Aquatic Model Ecosystem Advisory Committee, the EWOFFT recommendations were transformed into a proposed OECD guideline (OECD 1996) which, though still under review by OECD member countries, is now widely accepted as reflecting the basic principles of microcosm study design and conduct. Recent workshops including HARAP (Higher-Tier Aquatic Risk Assessment for Pesticides, Campbell et al. 1999) and CLASSIC (to be held in June 1999) continue to refine these principles.

The AEDG, Wintergreen, Monks Wood, EWOFFT, HARAP, and CLASSIC are highlights among a series of meetings dating from 1986, in which experts were called together for review and recommendations on microcosm and mesocosm studies. Besides leading to the de facto standards mentioned above, these meetings left behind a trail of commentary that

illuminates some of the key issues affecting the evolution of currently accepted principles. The following paragraphs summarize material found in the proceedings of an April 1986 meeting at George Mason University to review the proposed FIFRA guidelines, a workshop held by the National Agricultural Chemical Association (now ACPA) in October 1986 (NACA 1987), the June 1987 meeting of the FIFRA SAP (1987), a September 1987 workshop reviewing mesocosm research at the Duluth EPA laboratory (Siefert and Urban 1987), and a 1987 symposium sponsored by the Entomological Society of America (Voshell 1989).

Background information distributed by EPA before the George Mason workshop described the role of field studies at the highest tier of the ecological risk assessment process. Based on results of lower tiers, the Agency "may presume unreasonable adverse effects to aquatic organisms if expected residues of a pesticide exceed the no effect concentration.…Field testing is expected to improve assessment of potential ecological effects and fully consider impacts to populations and/or ecosystems." The document continued, "An aquatic mesocosm test allows intensive investigation into the biological effects of a pesticide at a range of likely exposures. The inherent control and replication in the mesocosm design should allow an assessment of subtle changes to ecosystem structure and/or function. Additionally, the results are extrapolatable to a wide range of pesticide uses and regions of influence when coupled with sound exposure estimates."

The passage cited contains several important concepts. Reference to "effects at a range of likely exposures" indicates an objective of determining an ecologically safe concentration, rather than simply a demonstration of safety at a single estimated exposure concentration (EEC). It also hints at a probabilistic exposure assessment. Both of these concepts are widely accepted today. The following sentence, however, has not been borne out by experience; even with "inherent control and replication," there is a large amount of uncontrolled variability in microcosm behavior, as well as a sensitive dependence on initial conditions, that interferes with detection of subtle effects. Finally, the statement about extrapolatability implies a promising strategy for use of microcosms: measure effects over a range of exposures, and use exposure estimation techniques to extrapolate to effects in a variety of situations.

The FIFRA guideline states two regulatory objectives: first, to provide registrants with "supportable means for negating presumptions of unacceptable risks," and second, to provide risk managers with "descriptive information on the extent of adverse impacts, both in duration and magnitude, likely to occur in aquatic systems which can then be evaluated in risk-benefit analysis" (Touart 1988). Many early reviewers commented that these objectives were not defined clearly enough to allow development of a sound study plan. The FIFRA SAP pointed to a "lack of clearly stated objectives of the test method and, consequently, considerable confusion about how the data will be used.…Rational discussion of alternatives is hampered by the lack of clearly formulated risk assessment questions.…The objective of a mesocosm study is better expressed as follows: 'to determine the maximum exposure level of the test pesticide that causes no ecologically significant changes in population or community structure or ecosystem function in the test system'" (FIFRA SAP 1987).

The difficulties that arose were summarized several years later at the EWOFFT workshop: "Subsequent experience indicated that the US EPA guidelines often resulted in the generation of data that were difficult to interpret and costs that were unreasonable in relation to the amount of new data generated" (Crossland et al. 1994). This statement is consistent with conclusions reached within the EPA itself, which led to the decision that "OPP will no longer require avian and aquatic field testing, except in unusual circumstances" (Fisher 1992). The FIFRA mesocosm experience left many people, both in industry and in regulatory agencies, skeptical about the entire model ecosystem approach. However, most experts (and ECOFRAM) now believe that microcosms and mesocosms can provide valuable information for higher-tier ecological risk assessment if each study is customized to address the specific concerns for a particular chemical. "It is of little value to define general objectives for field aquatic tests because of the many different problems that can arise in the hazard evaluation process.…It is necessary to define specific objectives for individual tests in the light of physicochemical properties, end use of chemicals, quantities manufactured and toxicological profiles.…Since the objectives will be different for each chemical it will be impossible to develop rigid protocols for field tests." (Crossland et al. 1994). This has become a guiding principle for the use of model ecosystems.

4.9.4. Study Objectives and Experimental Design

Microcosm studies usually follow one of two fundamentally different experimental designs, depending (as always) upon the objectives of the studies.

(1) If the objective is to establish the safety of a particular exposure regime—to "negate the presumption of unacceptable risk" (Touart 1988)—then the study should be designed to compare microcosms subjected to that exposure regime with untreated microcosms. Typically, the tested exposure regime corresponds to a benchmark scenario established in earlier tiers as being of concern, such as the 90th percentile of the annual maximum EEC values for a representative site over a 36-year modeling period. If successful, the microcosm study indicates that test systems subjected to this exposure scenario are, or are not, changed to an extent that is considered ecologically significant.

(2) If the objective is to establish the relationship between exposure and ecological response, then the study should include multiple exposure levels spanning the range from those that cause no ecologically significant effect to those that cause effects that are clearly detrimental and presumably unacceptable. If successful, the microcosm study reveals the full exposure-response relationship, from which the limits of ecologically acceptable effects can be inferred.

While either objective (and its corresponding experimental design) may be appropriate in a particular Tier 4 risk assessment, the second of the two alternatives is more consistent with the probabilistic approaches recommended by ECOFRAM, and with the recommendations of the FIFRA SAP (1987) and HARAP (Campbell et al. 1999). The first alternative provides information on only one exposure scenario, but not on whether other scenarios (reflecting other use

patterns, other regions, or other mitigation options, for example) are ecologically acceptable. For this reason, the HARAP workshop recommended that microcosm studies should incorporate five treatment levels (plus controls), including at least one that causes clear and interpretable effects (Campbell et al. 1999). The HARAP report listed three advantages of concentration-response studies:

- It is easier to judge the ecological significance of effects at one concentration by comparing them with effects at higher and lower concentrations;
- A clear concentration-response response relationship demonstrates the ability of the test system to detect effects when they occur; and
- Concentration-response results can be applied to a wide range of exposure scenarios.

Registrants are sometimes reluctant to conduct microcosm studies at exposure levels that exceed the reasonable worst-case EEC, on the grounds that (a) testing high concentrations might be misinterpreted as indicating the registrant's acceptance of these concentrations as realistic, or that (b) demonstrating effects at any exposure level, regardless of the improbability that such an exposure will occur, might jeopardize regulatory acceptance of the pesticide. Such reluctance leads to weak experimental designs and inconclusive experimental results. This situation can only be improved by assuring registrants that regulators will evaluate and interpret microcosm results in a scientifically sound risk assessment context, in which the relationship between exposure probabilities and ecological effects is clearly recognized and understood.

4.9.5. Treatment Regimes

Factors to be considered in designing the microcosm treatment regime include the route of application, the timing and frequency of applications, and the treatment levels. Like all other aspects of microcosm experimental design, the appropriate treatment regime will vary according to the properties and use of the pesticide, and the specific objectives of the study.

Application of the test substance to the microcosms may be intended to simulate as closely as possible the actual route of entry and exposure pattern expected in a particular use scenario. For example, if off-target spray drift is of concern, a formulated product may be sprayed directly on the microcosm surface using low pressure and very fine droplets to simulate drift deposition. Or, if runoff of soil containing pesticide residues is expected, field soil may be treated with technical grade active ingredient or with formulated product, weathered for a period of time under natural or controlled conditions, then mixed with water and added to the microcosms as a slurry.

However, if the objective of the study is to establish the relationship between exposure concentration and ecological response, then controlling exposure may be more important than simulating the physical route of entry of the pesticide. In such a case, direct addition of an aqueous solution into the microcosms water would be more appropriate than spray or slurry addition. This is the approach recommended by HARAP (Campbell et al. 1999).

4.9.6. Microcosm Monitoring Endpoints

Measurements made in a microcosm study typically include a subset of the following:

- Water quality (pH, dissolved oxygen, nutrients)
- Phytoplankton (pigments, taxonomic abundance)
- Attached algae (pigments, taxonomic abundance)
- Rooted plants (biomass)
- Zooplankton (taxonomic abundance)
- Benthic invertebrates (taxonomic abundance)
- Fish (survival, growth, reproduction).

Standard limnological and ecological methods are used for most measurements. Sampling techniques must be adapted to the scale of the microcosm. For example, benthic invertebrates are often monitored using artificial substrates—plastic structures with high surface area, Hester-Dendy plates, baskets of stones, or other devices providing uniform sampling units that can be deployed and retrieved without interfering with the rest of the system. Small-scale patchiness in the distribution of organisms, which can be overcome in larger systems by collecting larger, spatially-integrated samples, presents a special problem in smaller microcosms. Various solutions to these challenges are described in the technical literature (e.g., Hill et al. 1994; Graney et al. 1994).

As discussed above, the monitoring endpoints in any particular study are selected based on the study objectives, which are in turn determined by the specific concerns (uncertainties) remaining after Tier 3 of the ecological risk assessment. The results of the previous tiers are used to identify ecosystem components at risk and to select microcosm endpoints appropriately, with minimal monitoring of components not at risk. For example, there is little reason to monitor the effects of an insecticide on phytoplankton, if Tier 1 results indicate that phytoplankton are not sensitive. Similarly, if effects on fish are not of concern, then fish can be excluded from the microcosms—this, in fact, is generally recommended (Crossland et al. 1994; OECD 1996; Campbell et al. 1999) because (a) even large systems (like 0.1-ha ponds) cannot adequately represent the dynamics of most natural fish populations, (b) the presence of fish can distort other ecological interactions in the system, and (c) effects on fish can usually be measured more precisely in single-species studies. Although the potential for indirect effects may exist in either of the two examples just cited, such indirect effects on insensitive species are unlikely unless significant direct effects also occur on sensitive species (see section 4.9.7.4).

The timing and frequency of sampling are adjusted to correspond to the potential effects of concern. For example, if long-term effects and recovery of zooplankton populations are the uncertainties that have led the risk assessment beyond Tier 3, then it is not necessary to measure the immediate impacts and short-term population dynamics of zooplankton in the microcosm.

The level of resolution of taxonomic identifications may also be adjusted to meet the objectives of the study. It is often desirable to identify organisms to the species level for communities of greatest concern (for example, benthic macroinvertebrates in the case of an insecticide), and to use the results for multivariate and community-level analysis. For taxonomic groups of less concern, it may be sufficient to classify organisms into larger taxonomic groups (green algae, blue-green algae, diatoms, etc.), and spare the expense of full identification to species.

4.9.7. Interpreting Microcosm Results

Most people who have been involved with microcosm studies would probably agree that they are easier to perform than to interpret. There are several reasons for this, not the least of which is the sheer volume of data (often hundreds of thousands of individual observations) generated in a typical study. It is a challenge to abstract from this multidimensional database the overall relationships between pesticide exposure and ecologically significant effects, and investigators as well as reviewers have been known to miss the forest for the trees. The following subsections discuss certain aspects of microcosm results, recognition of which may help in interpreting and evaluating these studies.

4.9.7.1. Pesticide effects vs natural variability

Microcosms reflect many characteristics of natural ecosystems, including their variability. This variability (in space and time) can mask effects of pesticides. For example, Figure 4-32 shows the abundance of tanytarsid midge larvae over time in two microcosms treated with diazinon, and in two controls. Diazinon was applied three times, indicated by vertical dashed lines in Figure 4-32. Even before treatment, the abundance of these organisms in the four microcosms spanned a five-fold range. This can be interpreted as the normal range of tanytarsid density in these systems; changes smaller than five-fold would not be considered ecologically significant, even if they were indisputably caused by the pesticide.

Around the time of the third diazinon application, larval tanytarsids began to decline in all four microcosms, possibly due to predation by fish or to emergence into the adult form. If diazinon had caused severe mortality of tanytarsids, it would not have been possible to distinguish the effect from the natural decline in larval abundance.

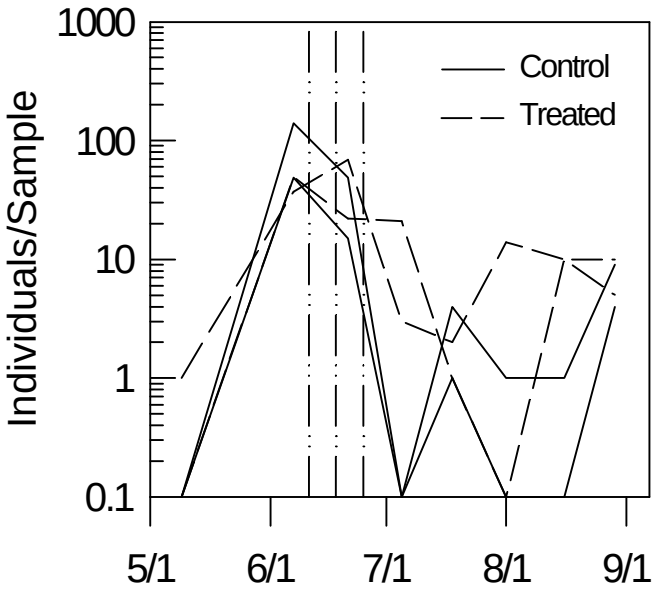

Figure 4-32. Tanytarsini abundance on artificial substrates in microcosms treated with diazinon. Each line represents abundance vs time for one replicate microcosm. Dashed vertical lines indicate times of diazinon treatment.

The tanytarsid example raises another consideration as well. Suppose the pesticide had caused tanytarsids to decline one week ***before*** the decline occurred in the controls. In that case, the cause-and-effect relationship would be apparent—that is, the decline in the treated microcosms could be clearly attributed to the pesticide—but could it be considered ecologically significant, if an identical decline occurred in the controls a week later due to natural causes?

Natural variability thus presents two problems for interpretation of microcosm results. First, it makes pesticide effects more difficult to distinguish. Second, natural variation over space (or between microcosm replicates) and over time makes it difficult to gauge the ecological significance of true pesticide effects, even when they occur.

4.9.7.2. Relative sensitivity of taxa

One of the benefits of the microcosm approach is the ability to measure the effects of chemicals on a wide variety of organisms, including many that are rarely, if ever, tested in single-species bioassays. In this way, microcosms address the uncertainty associated with extrapolation of toxicity results to untested species. Littoral (shoreline) communities are highly diverse, like other communities inhabiting ecological interfaces (hedgerows are another example). A typical microcosm derived from natural water and sediment is likely to contain forty or fifty species of zooplankton, two or three times as many species of algae, and several dozen species of macroinvertebrates. Not all of these species are present in numbers that can be analyzed statistically, but many of them are, and they can also be analyzed as taxonomic aggregates (blue-green algae, copepods, etc.). Microcosm results therefore represent a rich source of information on the sensitivity of large numbers of aquatic taxa.

For example, Table 4-8 summarizes the responses of zooplankton, macroinvertebrates, and fish to various levels of diazinon exposure in 10 m^3 microcosms and 300-m^3 ponds (mesocosms). The symbols in the table indicate statistically significant differences from controls on at least one sample event during the 6-month studies. Recovery is not considered in this data presentation. Exposure is expressed as the maximum 96-h time-weighted average (TWA) concentration in each treatment group. The results reveal a spectrum of sensitivity to diazinon, ranging from Cladocera, Pentaneurini, and Trichoptera (most sensitive) to Orthocladiinae and fish (least sensitive).

Table 4-8. Responses of aquatic taxa to diazinon in microcosms (Giddings et al. 1996) and mesocosms (Giddings 1992). Symbols indicate significant reduction (compared to controls) on at least one sample event in microcosms (circles) or mesocosms (squares).

		Maximum 96-hour Time-Weighted Average Concentration (µg/L)								
	Mesocosm	2.3	4.1	8.4	14	28				
Parameter	Microcosm		5.1	9.1	20	45	110	200	440	910
Total Zooplankton				●	●	●■	●	●	●	●
Copepods				●	●	●■	●	●	●	●
Cladocera		■	●■	●■	●■	●■	●	●	●	●
Rotifers					●■	●■	●	●	●	●
Total Insects				■	●■	●■	●	●	●	●
Diptera				■	●■	■	●		●	●
Chironomindae					●	■	●			●
Chironominae					■	■				
Chironomini				■	■	■	●	●	●	●
Tanytarsini				■	■	■				
Tanypodinae		■	■	●■	●■	●■	●	●	●	●
Pentaneurini		■	●■	●■	●■	●■	●	●	●	●
Procladiini				●	■	●■	●	●	●	●
Orthocladiinae						■	●	●	●	
Ceratopogonidae			●■	●■	●■	●■	●	●	●	●
Ephemeroptera				■	●■	●■	●	●	●	●
Odonata					■	■				
Trichoptera		■	●■	●■	●■	●■	●	●	●	●
Fish Survival							●	●	●	●
Fish Weight and Length										
Fish Biomass						●	●	●	●	●
Fish Reproduction										

4.9.7.3. Ecological recovery

The HARAP workshop concluded that one of the main criteria for determining the ecological significance of pesticide effects is the ability of populations to recover from impact (Campbell et al. 1999). HARAP defined recovery as “return of a measured parameter (e.g., the abundance of a population) to the normal range of the controls.” Population analysis tools

can be used to estimate the time to recovery from pesticide effects, especially at lower tiers (see Section 4.4), but microcosm studies allow direct observation of population recovery. An example is shown in Figure 4-33 (Giddings et al. 1996). The abundance of mayfly nymphs in microcosms declined in response to application of diazinon, with the magnitude of population reduction a direct function of the exposure level (expressed as the maximum 96-h TWA). Time to population recovery was also a function of exposure level. In microcosms exposed to 110 µg/L or less, mayfly populations were at or near control levels two months after treatment. In microcosms exposed to 200 or 440 µg/L, only one of the two replicates returned to the control range by the end of the study, and at 910 µg/L, mayflies failed to recover in either of the replicates. The no observed effect concentration for mayflies was 9.1 µg/L, but the highest concentration from which recovery occurred (which HARAP called the Ecologically Acceptable Concentration, EAC) was 110 µg/L.

In the outdoor microcosms used in this example, recovery probably occurred mainly through egg deposition by adults from outside the treated ecosystems. In other situations and for other taxa, other recovery mechanisms come into play. Most zooplankton species, as well as many benthic invertebrates, have short generation times and rapid intrinsic rates of population increase, and depressed populations return to normal levels rapidly when pesticide concentrations decline. Many aquatic species can produce stress-resistant resting stages that initiate population recovery. Some species, such as gyrinid beetles, can quickly recolonize affected habitats through dispersal from nearby unaffected populations.

For some taxa, such as amphipods, the isolation of microcosms from adjacent water bodies may severely restrict the potential for population recovery, a factor which must be taken into account in interpreting microcosm results. The HARAP report (Campbell et al. 1999) contains suggestions for overcoming, to an extent, the limitations on recovery potential caused by microcosm isolation. These include (1) periodic reintroduction of organisms to simulate immigration or reproduction, (2) placing organisms in cages within the microcosm to determine when conditions become suitable for recovery, and (3) periodically collecting water or sediment from the microcosm for use in laboratory bioassays.

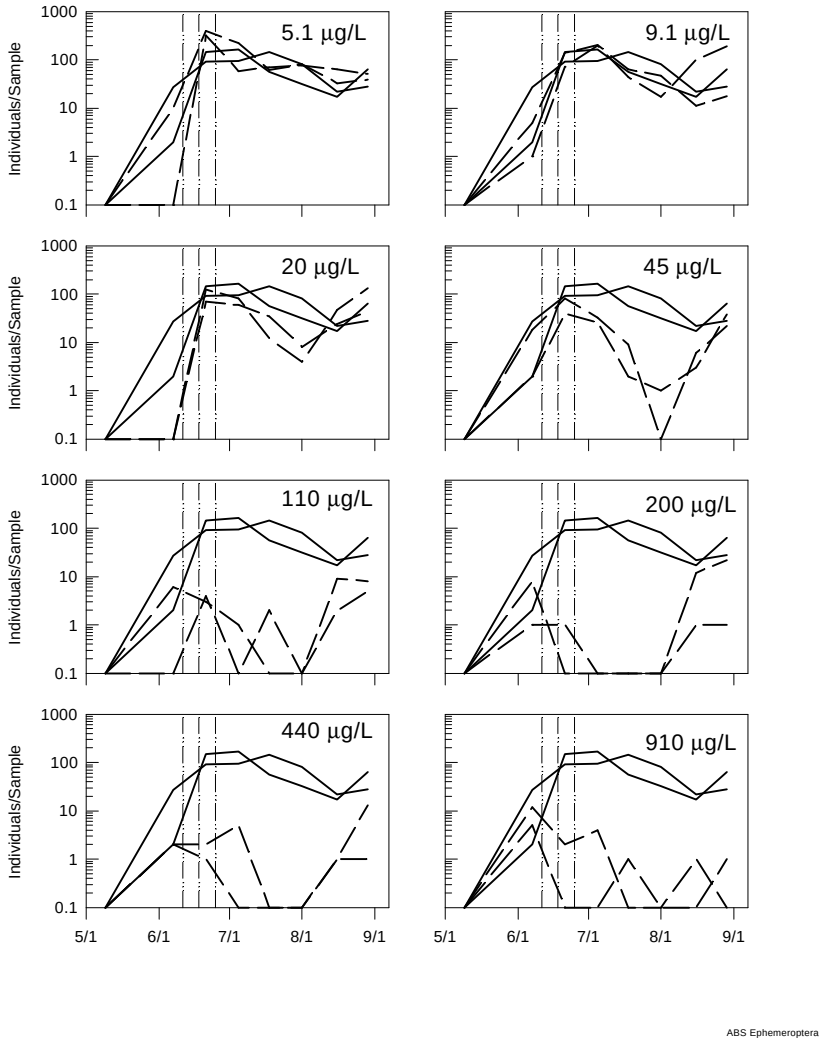

Figure 4-33. Abundance of mayflies on artificial substrates in microcosms treated with diazinon. Dashed lines represent individual microcosms, two replicates at each of the eight exposure levels (maximum 96-h time-weighted averages) indicated. Results for the two controls (untreated microcosms) are shown as solid lines in each panel for comparison. Vertical lines indicate diazinon treatment dates.

4.9.7.4. Indirect vs direct effects

Another benefit of microcosms is the ability to observe indirect pesticide effects caused by interactions among species. The potential indirect effects of greatest interest are:

- Reduction of a pesticide-tolerant species due to reductions in the abundance of a pesticide-sensitive food source; and
- Increase of a pesticide-tolerant species due to reductions in the abundance or activity of pesticide-sensitive competitors or predators.

Examples of the first type are rare, but some have been reported. For example, reduced growth of fathead minnows in enclosures treated with chlorpyrifos was interpreted as an indirect effect of reductions in zooplankton abundance (Brazner and Kline 1990). Observations of the second type of indirect effects are more common. Figure 4-34 presents an example from another microcosm study with chlorpyrifos (Giddings 1993). As cladocerans declined sharply after chlorpyrifos treatment, rotifers (which compete with cladocerans for food) increased in abundance.

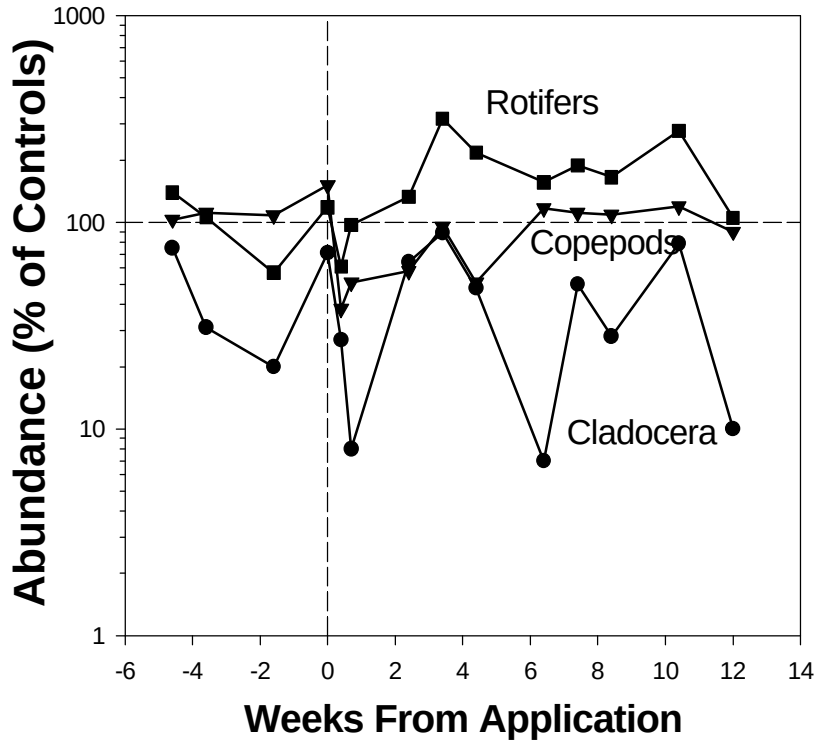

Figure 4-34. Abundance of cladocerans (circles), copepods (triangles), and rotifers (squares), as a percent of controls, in microcosms treated with chlorpyrifos. Dashed vertical line indicates time of chlorpyrifos treatment. Results shown are averages for three replicate microcosms. (Data from Giddings 1993.)

4.9.7.5. Determination of Ecologically Acceptable Concentration

The HARAP workshop defined an Ecologically Acceptable Concentration (EAC) as "the concentration at or below which no ecologically adverse effects would be expected" (Campbell et al. 1999). Though this definition does little to clarify the criteria for judging either ecological acceptability or ecological adversity, its significance lies in the implicit acknowledgement that ***some*** effects are not "ecologically adverse." This concept is consistent with risk assessment criteria that seek to protect a certain percentage of all species, whether it be 90% (SETAC 1994), 95% (EPA 1985; Health Council of the Netherlands 1993), or some other percentage. These approaches all recognize that ecosystems, like individual organisms and populations, can tolerate a certain level of damage. "For certain taxa or endpoints, effects

observed in a field study may be considered acceptable, if with appropriate expert ecological judgement, it is considered that they would not pose significant ecological risks to natural aquatic ecosystems" (Campbell et al. 1999).

There are no generally accepted quantitative criteria for evaluating ecological significance, and expert judgement is always required. However, the Aquatic Effects Dialog Group (AEDG 1992) proposed a set of qualitative factors that should be considered, including:

- Persistence of effects (consistent with HARAP's emphasis on ecological recovery);
- Strength of the exposure-response relationship (a strong relationship should be given more weight in the risk assessment than a weaker relationship); and
- Linkage among ecosystem components (effects on components that are strongly linked to other components are more ecologically significant than effects on components that are weakly linked).

One of the most important uses of microcosm data is to evaluate the ecological significance of effects and thereby to determine the EAC. As discussed in section 4.9.4, this requires a study design that incorporates a range of exposure regimes including at least one that produces no effects and at least one that produces clearly adverse effects. Results of a successful microcosm study allow the risk assessor and risk manager to observe the spectrum of ecological responses over a range of exposures, from which to reach an "expert ecological judgement" about the EAC.

Figure 4-35 depicts such a spectrum of responses for the pyrethroid insecticide cypermethrin, as compiled from four microcosm studies conducted in the UK (Crossland 1982; Getty et al. 1983; Farmer et al. 1995) and the US (Palmieri et al. 1992). This figure is similar to Table 4-8, except it indicates recovery as well as effects. The pooled results from the four cypermethrin studies reveal fairly consistent exposure-response relationships for major aquatic taxa (Giddings et al., in preparation). The lowest exposure level (30 ng/L) affected amphipods and isopods, and the constraints of the experimental system prevented these populations from recovering. Exposures of 100 and 300 ng/L caused effects throughout the invertebrate community, but (with the exception of amphipods and isopods) the effects were temporary. Only at 1,000 ng/L were other invertebrates (mayflies, mites, and oligochaetes) not observed to recover. There were no indirect effects on fish due to the reductions in invertebrate populations. These trends allow judgements to be made about the overall responses of the ecosystems. The effects of cypermethrin at 30 ng/L were taxonomically limited and can be considered non-significant from the standpoint of the ecosystem as a whole. The Ecologically Acceptable Concentration can be set conservatively at 30 ng/L. (Based on the observed recovery of all invertebrates except amphipods at 100 and 300 ng/L, it could be argued that the EAC is 300 ng/L.)

Figure 4-35. Summary of cypermethrin effects on microcosms.

Conc (ng/L)	Cladocera	Copepods	Rotifers	Chironomids	Mayflies	Caddisflies	Dragonflies	Amphipods	Mites	Oligochaetes	Snails	Fish
30	+	+	+	+	+	=	=	—		+	+	
100	(–)	(–)		(–)	(–)	(–)	=	—	=	+	?	=
300	(–)	(–)		+/(–)	(–)	(–)	+			+	+	=
1000	(–)	(–)		(–)	—		=	—	—	—	=	=

—	Reduction, no recovery
(–)	Reduction with recovery
=	No effect
+	Increase
?	Response uncertain

Solomon et al. (in preparation) analyzed the distribution of species sensitivity to cypermethrin and other pyrethroids using log-normal regressions, as described in section 4.5. The 10th percentile for acute toxicity of cypermethrin to arthropods was 6.4 ng/L. The EAC in microcosms, 30 ng/L, was above the 30th percentile for arthropods (Figure 4-36). These results indicate that the 10th percentile of the species sensitivity distribution is a conservative estimator of the EAC for cypermethrin. Similar conclusions can be drawn from comparison of microcosm results and sensitivity distributions for diazinon (Figure 4-37, Giddings et al. 1996), chlorpyrifos (Giesy et al. 1999), esfenvalerate (Giddings et al., in preparation), atrazine (Solomon et al. 1996), and a variety of non-agricultural chemicals (Versteeg et al. 1998).

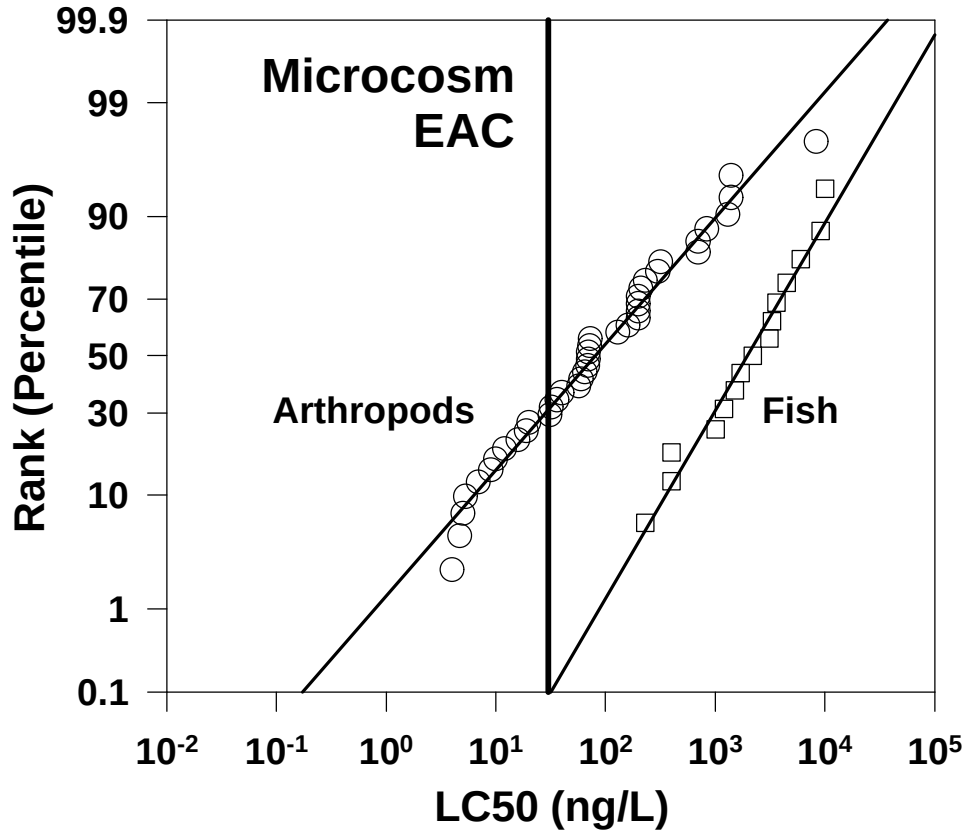

Figure 4-36. Comparison of Ecologically Acceptable Concentration (EAC) for cypermethrin (as determined in microcosms) with distribution of cypermethrin LC50 values for species of arthropods and fish (as determined in single-species laboratory tests).

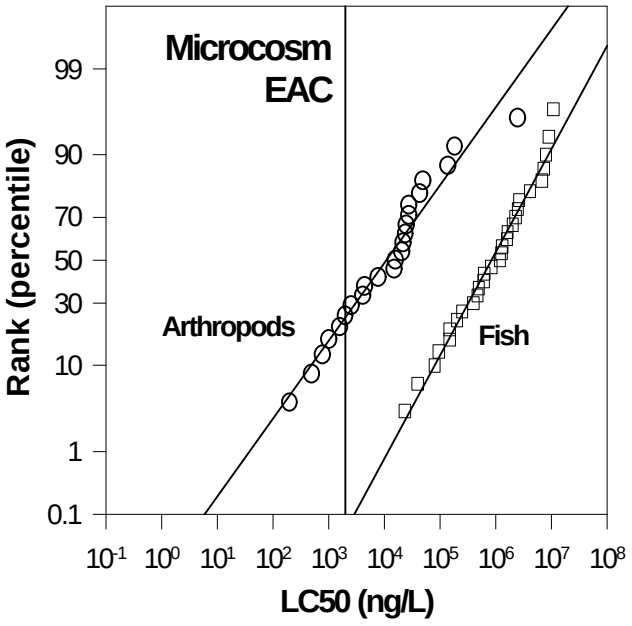

Figure 4-37. Comparison of Ecologically Acceptable Concentration (EAC) for diazinon (as determined in microcosms) with distribution of diazinon LC50 values for species of arthropods and fish (as determined in single-species laboratory tests).

4.9.8. Summary: Evaluation of Microcosms as Tools for Ecological Risk Assessment of Pesticides

The usefulness of microcosms as tools for higher-tier ecological risk assessment of pesticides has been affirmed by many expert groups (AEDG 1992; SETAC-Europe 1992; SETAC/Resolve 1992; Crossland et al. 1994; SETAC 1996; Campbell et al. 1999). Aspects of the microcosm approach relevant to the development of tools for reducing uncertainty in FIFRA risk assessments are summarized as follows:

- The microcosm approach has had an extensive historical development.
- Proposed OECD guidelines are adequate, though technical improvements will undoubtedly continue to come with experience. No single standard will be appropriate for all situations; each study must be designed to answer specific risk assessment questions for a particular chemical.
- Microcosm studies are relatively expensive and time consuming.
- Microcosm studies generates extensive data that requires expert ecological interpretation.
- Microcosms are appropriate for the highest tier of risk assessment.
- Microcosm techniques have been developed mainly for lentic littoral ecosystems, and less for lotic, pelagic, and marine or estuarine systems.
- The microcosm approach should be applicable for all chemical classes and pesticide uses.
- The question of microcosm “validation” has not been addressed above. Thought is needed on what validation means in this context, and how it can be achieved.
- The primary usefulness of microcosms in risk assessment is to address the question of ecological significance of potential effects—that is, to define the Ecologically Acceptable Concentration.

4.10. Conclusions and Recommendations

4.10.1. Effects Analysis in the Risk Assessment Process

- Ecological risk assessment should follow a tiered approach. Uncertainties are progressively reduced in each tier, until risk can be characterized with sufficient certainty to support a risk management decision.
- Tier 1 is intended to be protective, not predictive. Its objective is to identify chemicals whose ecological risk is clearly low enough to be acceptable. Therefore, conservative assumptions are used to prevent the possibility of mistakenly accepting a chemical that might in fact be hazardous.
- Effects characterization in Tier 1 is based on a set of standard acute and chronic toxicity tests with fish, invertebrates, and algae. The set of tests recommended by ECOFRAM is generally consistent with those currently required under FIFRA (40 CFR 158.145). They include acute toxicity tests with one freshwater invertebrate (usually *Daphnia magna*), two species of fish (one warm water and one cold water), and one or more species of algae or aquatic vascular plant. If there is a potential for estuarine exposure, acute toxicity tests are also recommended for an estuarine fish, an arthropod (usually *Mysidopsis bahia*), and a mollusk. Chronic studies at Tier 1 include an invertebrate (*D. magna* and/or *M. bahia*) life cycle study and a fish (warm water, cold water, and/or estuarine) early life-stage (ELS) study.
- In acute toxicity tests, mortality should be reported at 24-hour intervals, and the LC50 or EC50 (with 95% confidence limits and slope of the concentration-effect relationship) should be calculated for each observation time.
- Time-to-event analysis may provide better estimates of acute endpoint values than conventional probit analysis. Time-to-event analysis also provides a more complete characterization of effects, including effects after different exposure periods, and allows for better statistical analysis of covariates such as individual weight, water temperature, and other variables.
- Research is needed to address the relative sensitivity of algae to fungicides and insecticides, as compared with the sensitivity of the target organisms. Results of these investigations should be used to guide decisions about the number of algae and plant species to be tested in Tier 1.
- For evaluation of chronic toxicity test results, a regression-based estimate (ECx, where x represents a defined percent effect on a measured parameter) is preferable to an ANOVA-based (No Observed Effect Concentration) analysis. If the data are not appropriate for regression analysis but the study is otherwise reliable, the NOEC may be used instead of the ECx.
- Sediment toxicity tests are not recommended for Tier 1. However, if pore water concentrations can be estimated at this tier, they can be compared with acute and chronic toxicity data for water-column species to obtain a preliminary indication of the risk to sediment-dwelling species.
- Risk characterization for acute effects at Tier 1 is based on Risk Quotients, defined as the ratio of the peak Estimated Effect Concentration (EEC) to the acute EC50 or LC50 for the invertebrate and fish species tested. If the Risk Quotient exceeds a specified Level of Concern (LOC), the risk assessment proceeds to Tier 2.

- At Tier 1, the LC50 (or EC50) value is more appropriate for characterizing the results of acute toxicity tests than other values that have been proposed, such as the LC5 (or EC5). There is less variability around the estimated median value (i.e., LC50 or EC50) than the extremities of the distribution (e.g., LC5). Variation in individual sensitivity is accounted for using triggers (Levels of Concern) less than 1 with Risk Quotients based on the median value.
- Risk characterization for chronic effects at Tier 1 is also based on Risk Quotients, defined as the ratio of the peak Estimated Effect Concentration (EEC) to the chronic EC10 (or NOEC) for the invertebrate and fish species tested. If the Risk Quotient exceeds a specified Level of Concern (LOC), the risk assessment proceeds to Tier 2.
- Some chronic endpoints, such as growth, generally reflect the effects of cumulative exposure, and a time-weighted average EEC may be more appropriate than the peak EEC for characterizing risk. However, because Tier 1 is intended to be protection, it may be advisable to avoid assumptions about cumulative vs short-term effects, and to base the Tier 1 risk characterization on the peak EEC even for chronic endpoints.
- No further toxicity testing is conducted at Tier 2. However, data from the Tier 1 toxicity tests are used more completely in Tier 2 risk characterization, i.e., the full concentration-effect relationship, rather than a point estimate such as the LC50 or EC10, is used. The effects measured on test organisms are also put into a population-level context through the use of simple population analysis techniques, such as life table analysis.
- Risk characterization at Tier 2 defines the relationship between the magnitude of effect and the probability of that effect occurring. The probability distribution of exposure concentrations is integrated with concentration-effect curves for acute mortality, time to population recovery, or other effect endpoints. The result is a plot of probability of occurrence vs magnitude of effect, for which ECOFRAM has coined the term Joint Probability Curve (JPC).
- The JPC paradigm can be used to integrate any exposure distribution (or family of distributions) with the concentration-effect relationship derived for any effect endpoint. For example, the effect may be percent mortality among individuals in a test group, time to population recovery, or percent of species affected in a community.
- Tier 3 involves application of one or more tools appropriate to resolving the uncertainties remaining after Tier 2. Since the nature of these uncertainties may be different for every pesticide, no single procedure can be defined for Tier 3.
- If water bodies may be exposed to multiple inputs of a pesticide, or the pesticide concentration will vary significantly over time periods comparable to those used in standard toxicity tests, than an investigation of the effects of time-varying or repeated exposure should be undertaken. ECOFRAM explored a variety of laboratory-based and modeling approaches to this investigation.
- Development of acute toxicity data for additional species to determine sensitivity distributions is recommended if acute toxicity concerns are not alleviated in previous tiers, or if substantial variability in sensitivity among taxa is demonstrated in previous tiers or expected based on the pesticide's mode of action.
- Development of chronic toxicity data for additional species is recommended if chronic risk is demonstrated in lower tiers, if prolonged or repeated exposure is expected, if the compound has a potential for bioconcentration, or if the mode of action or other data (e.g., reproductive effects in other organisms) suggests that chronic effects may occur.

- Development of sediment toxicity data is recommended If expected pore water concentrations exceed the level of concern for invertebrate species tested in Tier 1, or if the pesticide is toxic and is predicted to accumulate and persist in sediments.
- The focus of Tier 4 is further refinement of uncertainties remaining after Tier 3, with particular emphasis on the efficacy of mitigation measures and/or extrapolation of the effects analysis to populations or ecosystems. Tier 4 tools may include advanced population models, advanced toxicokinetic models, microcosms and mesocosms, and behavioral tests.

4.10.2. Research Needs

- Guidelines are needed for laboratory toxicity tests with time-varying exposures. Objectives of such tests include (a) checking for latent responses; (b) checking for exposure-response reciprocity; (c) checking for cumulative effects of continuous or repeated exposure; (d) checking for reversibility of effects.
- General principles for evaluating time-varying exposure-response need to be developed. Appropriate exposure metrics (maximum concentration, time-weighted average, duration) need to be defined for pesticides with different mechanisms of action and for different taxonomic groups.
- Models of tissue residue concentration and effects (e.g., FGETS, PULSETOX, DEBTOX) need to be validated.
- Population models need to be developed, refined, and validated. Simple generic models (density independent) are needed for Tier 2; more complex models (incorporating density dependent factors) are needed for Tier 3; site-specific and species-specific models are needed for Tier 4.
- Acute and chronic toxicity testing guidelines need to be developed or refined for additional test species, including aquatic macrophytes, benthic insects, rotifers, copepods, and amphibians.
- Guidelines are needed for sediment toxicity tests with additional species. Guidelines need to be refined for selection of sediment types, spiking sediments with test chemicals, and maintaining appropriate test conditions.
- Guidelines for use of regression techniques for chronic test endpoint determination need to be developed, including instructions on the appropriate effects level for each endpoint.
- Guidelines for fish full-life cycle toxicity tests need to be modified to reduce the variability of measurement endpoints.
- A review of existing toxicity databases is needed to provide scientific support for setting the number and taxonomic distribution of species to be tested. In particular, the need for tests with multiple plant species at Tier 1 needs to be examined.
- Convenient software needs to be developed to allow routine and uniform application of time-to-event analysis.
- Convenient software needs to be developed to allow routine and uniform application of the joint probability approach to risk characterization software.
- Risk assessors and risk managers will need to be trained to use the tools and processes recommended by ECOFRAM.

5. Glossary of Aquatic Risk Assessment Terminology

ACPA	American Crop Protection Association
AGDISP	Agricultural Dispersion Model, a spray drift model developed by Continuum Dynamics in the USA
AgDrift	Software for evaluating off-site deposition of pesticides from aerial or ground applications based on data developed by the Spray Drift Task Force (SDTF)
ARAMDG	Aquatic Risk Assessment and Mitigation Dialog Group
ARP	Acetochlor Registration Partnership
ARS	Agricultural Research Service
ASAE	American Society of Agricultural Engineers
ASPF	XXX
BASINS	USEPA GIS Aquatic exposure estimation system that links information on source of pollutants with water quality
CHEMRANK	Software for ranking the potential for organic chemical to leach into ground water across a range of different soils and environmental conditions
CMLS	A transport model - Chemical Movement in Layered Soils
CN	Curve Number
CSRS	Cooperative State Research Service
CTIC	Conservation Tillage Information Center
DOM	Dissolved Organic Matter
ECOFRAM	Ecological Committee on FIFRA Risk Assessment Methods
EEC	Estimated Environmental Concentration (PEC in Europe)
EFED	US EPA Environmental Fate and Effects Division (sponsors of ECOFRAM)
EPICWQ	A transport model - Erosion Productivity Impact Calculator Water Quality
EPTC	Ethyl dipropylthiocarbamate
ESTF	Endangered Species Task Force
ET	Evapotranspiration
EXAMSII	Exposure Analysis Modeling System version II (currently at version 2.97)
FEMVTF	FIFRA Exposure Model Validation Task Force
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
FIFRA EMWG	FIFRA Exposure Model Working Group
FOCUS	Forum on the Coordination of Pesticide Fate Models and their Use
FQPA	Food Quality Protection Act
FSCBG	Forest Service, Cramer, Barry and Grim, a USDA spray drift model developed by the Forest Service in the USA

GENEEC	An exposure model GENeric Expected Environmental Concentration -
GIS	Geographic Information Systems
GLEAMS	A transport model -Ground Water Loading Effects of Agriculture Management System
HSPF	A water quality model - Hydrologic Simulation Procedure (Fortran)
HUC8	Hydrological Unit cataloging unit (specified to the 8 digit designator level)
INSREC	????
LANDSAT	????
LCCP	????
LEACHM	A research model that uses hydrology and a nitrogen balance to estimate nitrogen transport
LEACHP	A subroutine of LEACHM to provide pesticide transport
LEPA	Low Energy Precision Application
LOC	Level of Concern
LOD	Level of Detection
LS factors	Length Slope factors as used in the Universal Soil loss equation
LU/LC	Landuse/Land cover
MACRO	Leaching and preferential flow model developed by Nick Jarvis in Sweden, refers to Macropores in soil
MCL	Maximum Concentration Levels
Mitigation	Process of reducing estimate of pesticide associated risk by modifying use or land management practices.
MLRA	Major Land Resource Area (USDA land classification system)
MOC	Method of Characteristics
MPCA	Minnesota Pollution Control Agency
MRLC	Multi-Resolution Land Characteristics - a classified set of LANDSAT imagery
MSEA	Management System Evaluation Area
MUSLE	Modified Universal Soil Loss Equation
MUSCRAT	Multiple Scenario Risk Assessment
NACA	National Agricultural Chemical Association (now known as ACPA, American Crop Protection Association)
NATSGO	National Soil Geographic Database
NAWQA	National Water Quality Assessment
NAWWS	National Alachlor Well Water Survey
NCPS	Northen Cornbelt Sand Plain
NOAA	National Oceanographic and Atmospheric Agency
NRI	Natural Resources Inventory
OTTER	Other Tools to Evaluate Risk

PATRIOT	Pesticide Assessment Tool for Rating Investigations of Transport - an EPA Groundwater contamination prediction tool
PEC	Predicted Environmental concentration - European term for EEC
PECSW	Predicted Evaluation Concentrations in Surface Water
PECGW	Predicted Evaluation Concentrations in Ground Water
PEDON	A soil science technical term used to describe a characteristic soil profile
PELMO	Pesticide Leaching Model, a German regulatory leaching model developed from PRZM
PEM	????
PESTLA	Pesticide Leaching and Accumulation, a Dutch regulatory leaching model
PIRANHA	An integrated modeling shell that included PRZM, EXAMS and FGETS
POM	Particulate Organic Matter
PREAP	A probabilistic model shell that included GLEAMS
PRZM	Pesticide Root Zone Model
PWG	Pyrethroid Working Group
QA	Quality Assurance
RICEWQ	A transport model for water quality issues associated with rice culture
RIVWQ	A flowing water contamination model
RQ	Risk Quotient (in Europe, expressed inversely as a TER)
SciGrow	Screening concentration in groundwater, a USEPA regression equation to estimate peak concentrations of agrochemicals in groundwater
SDTF	Spray Drift Task Force
SEP	Standard Evaluation Procedure
SETAC	Society of Environmental Toxicology and Chemistry
SFWMD	South Florida Water Management District
SLOSS	?????
SSURGO	Soil Survey Geographic data base
STATSGO	STATe Soil GeOgraphic data base
STORET	Storage and Retrieval database, a USEPA database for compiling water quality data
STREAMpc	Stream Transport and Agricultural Runoff of Pesticides for Exposure Assessment Model, and EPA model simulate surface water quality
SWAT	A USDA Agricultural Research Service computer model to predict the effect of management decisions on water, sediment, nutrients, and pesticides yields in large ungaged river basins
SWRRBWQ	Simulator for Water Resources in Rural Basins, Water Quality model, a USDA model for simulation of surface water quality
TER	Toxicity to Exposure Ratio - European term - inverse of RQ
TF	Task Force
TOXSWA	Toxic Substances in Surface Water, a Dutch model for simulation of surface water quality

USDA/ARS	U.S. Department of Agriculture Agricultural Research Service
USEPA	U.S. Environmental Protection Agency
NRCS	National Resource Conservation Service, a division of the USDA (formerly the Soil Conservation Service (SCS)
USEPA OPP EFED	USEPA/OPP/Environmental Fate and Effects Division
USEPA/OPPT	USEPA/Office of Pollution, Prevention and Toxic Substances
USEPA ORD NERL	USEPA/Office of Research and Development /National Exposure Research Laboratory
USEPA-OPP	U.S. Environmental Protection Agency-Office of Pesticide Programs
USGS	U.S. Geological Survey
USLE	Universal Soil Loss Equation
VADOFT	Vadose Zone Fate and Transport
VARLEACH	Variable Leaching model, a model developed by Allan Walker in the UK
WASP5	Water Quality Analysis Program, a USEPA model for simulation of water quality
WEEDIR	??????
WEP	Water Erosion Prediction Project, a NRCS model to simulate soil erosion

6. References

Add Landscape risk assessment papers.

Add USDA Buffer reference and ref to the upcoming publication on buffering advice.

Abernethy, S., D. Mackay and L. McCarty. 1988. "Volume fraction" correlation for narcosis in aquatic organisms: the key role of partitioning. *Environ. Toxicol. Chem*. 7:469-481.

Ahlbom, A. 1993. *Biostatistics for Epidemiologists*. CRC/Lewis Publishers, Boca Raton, FL.

Aldenberg and Slob 1993 Ecotox Env Safety 25: 48

Aldenberg, T. and W. Slob. 1991. Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. *Ecotox. Environ. Safety* 18:221-251.

Allison, P.D. 1995. Survival Analysis Using the SAS System. A Practical Guide. SAS Institute, Inc., Cary, NC.

American Crop Protection Association (ACPA), 1995. Primary, Secondary, and Screening Models for Pesticide Registration: FIFRA Exposure Modeling Work Group, Washington, DC, April 1995.

Andrewartha, H.G., and L. C. Birch. 1954. *The Distribution and Abundance of Animals.* University of Chicago Press, Chicago, Illinois.

Ankley, G.T., W.J. Berry, D.M. DiToro, D.J. Hansen, R.A. Hoke, D.R. Mount, M.C. Reiley, R.C. Swartz and C.S. Zarba. 1996. Letter to the editor: Use of equilibrium partitioning to establish sediment quality criteria for nonionic chemicals: A reply to Iannuzzi et al. *Environ. Toxicol. Chem.* 15:1019-1024.

Aquatic Effects Dialog Group (AEDG). 1992. *Improving Aquatic Risk Assessment Under FIFRA: Report of the Aquatic Effects Dialogue Group.* World Wildlife Fund, Washington, DC.

ASTM. 1996a. Standard guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. E 1367-92. In Annual Book of ASTM Standards, Vol. 11.05. American Society for Testing and Materials, Philadelphia, PA.

ASTM. 1996b. Standard guide for designing biological tests with sediments. E 1525-94a. In Annual Book of ASTM Standards, Vol. 11.05. American Society for Testing and Materials, Philadelphia, PA.

ASTM. 1996c. Standard test methods for measuring the toxicity of sediment-associated contaminants with fresh water invertebrates. E 1706-95b. In Annual Book of ASTM Standards, Vol. 11.05. American Society for Testing and Materials, Philadelphia, PA.

Bailer, A.J. and J.T. Oris. 1997. Estimating inhibition concentration for different response scales using generalized linear models. *Environ. Toxicol. Chem.* 16:1554-1559.

Baker, D. B., 1993. The Lake Erie Agroecosystem Program: Water Quality Assessments. Agriculture, Ecosystems and Environment, Vol 46, pp 197-215.

Barber, M.C., L.A. Suarez and R.R. Lassiter. 1988. Bioconcentration of nonpolar organic pollutants by fish. *Environ. Toxicol. Chem*. 7:545-558.

Barnthouse, L.W. 1993. Population-level effects. Pp. 247-274 in G. W. Suter II (ed.), *Ecological Risk Assessment*. Lewis Publishers, Chelsea, Michigan.

Barnthouse, L.W., D.L. DeAngelis, R.H. Gardner, R.V. O'Neill, C.D. Powers, G. W. Suter, II, G.P. Thompson and D.S. Vaughan. 1982. *Methodology for Environmental Risk Analysis.* ORNL/TM 8167. Oak Ridge National Laboratory, Oak Ridge, TN.

Barnthouse, L.W., G.W. Suter, II and A.E. Rosen. 1990. Risks of toxic contaminants to exploited fish population: influence of life history, data uncertainty, and exploitation intensity. *Environ. Toxicol. Chem.* 9:297-311.

Barry, M.J., K. O'Halloran, D.C. Logan, J.T. Ahokas and D.A. Holdway. 1995. Sublethal effects of esfenvalerate pulse-exposure on spawning and non-spawning Australian crimson-spotted rainbow fish (*Melanotaenia fluviatilis*). *Arch. Environ. Contam. Toxicol*. 28:459-463.

Bartell et al. 1992

Bechmann, R.K. 1994. Use of life tables and LC_{50} tests to evaluate chronic and acute toxicity effects of copper on marine copepod *Tisbe furcata* (Baird). Environ. Toxicol. Chem. 13: 1509-1517.

Beyer, W.N., G.H. Heinz and A.W. Redmon-Norwood (eds.). 1996. *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations*. Society of Environmental Toxicology and Chemistry (SETAC). Lewis Publishers, Boca Raton, FL.

Bird, S.L., J. M. Cheplick, R. F. Carsel, M. J. Fendley. 1992. Piranha Version 3.0 PRZM Input Collatorpic (PIC) Version 2.0. Environmental Research Laboratory, U.S. Environmental Protection Agency. Athens, Georgia

Birge, W.E. 1993.

Bradbury, S.P., J.R. Coats and J.M. McKim. 1986. Toxicokinetics of fenvalerate in rainbow trout (*Salmo gairdneri*). *Environ. Toxicol. Chem*. 5:567-576.

Brazner, J.C. and E.R. Kline. 1990. Effects of chlorpyrifos on the diet and growth of larval fathead minnows, *Pimephales promelas*, in littoral enclosures. *Can. J. Fish. Aquat. Sci.* 47:1157-1165.

Brown and Reinert. 1992.

Bruce, R.D. and D.J. Versteeg. 1992. A statistical procedure for modeling continuous toxicity data. *Environ. Toxicol. Chem.* 11:1485-1494.

Buhl, K.J., S.J. Hamilton and J.C. Schmulbach. 1993. Chronic toxicity of the bromoxynil formulation Buctril ^{R} to *Daphnia magna* exposed continuously and intermittently. *Arch. Environ. Contam. Toxicol*. 25:152-159.

Burmaster, D.E. and D.A. Hull. 1997. Using lognormal distributions and lognormal probability plots in probabilistic risk assessments. *Human Ecol. Risk Assess.* 3:223-234.

Burnison, B.K., P.V. Hodson, D.J. Nuttley and S. Efler. 1996. A bleached-kraft mill effluent fraction causing induction of a fish mixed-function oxygenase enzyme. *Environ. Toxicol. Chem*. 15:1524-1531.

Burns, L.A. 1991. Exposure analysis modeling system: user's guide for EXAMS II, version 2.94. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Athens, GA.

Burns, L.A. 1997. Exposure analysis modeling system: user's guide for EXAMS II, version 2.97.5. . Ecosystems Research Division, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Athens, GA.

Bysshe, S.E. 1990. Bioconcentration factor in aquatic organisms. Chapter 5. In W.J. Lyman, W.F. Reehl and D.H. Rosenblat (eds.), *Handbook of Chemical Property Estimation Methods*. American Chemical Society. Washington DC.

Cairns, J., Jr., K.L. Dickson and A.W. Maki (eds.). 1978. *Estimating the Hazard of Chemical Substances to Aquatic Life.* ASTM Special Technical Publication 657. American Society for Testing and Materials, Philadelphia, PA. Pp. 239-279.

Campbell, P.J., D. Arnold, T. Brock, N. Grandy, W. Heger, F. Heimbach, S.J. Maund and M. Streloke. 1999. *Guidance Document (Draft): Higher-tier Aquatic Risk Assessment for Pesticides.* Report of a SETAC-Europe/OECD/EC Workshop, 19-22 April 1998, Lacanau Ocean, France.

Carsel, R. F., J. C. Imhoff, P.R. Hummel, J.M. Cheplick, and A. S. Donigian Jr. 1998. PRZM3, A Model for Predicting Pesticide and Nitrongen Fate in the Crop Rot and Unsaturated Soil Zones: Users Manual for Release 3.0. National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA (draft).

Carsel, R.F., C.N. Smith, L.A. Mulkey, J.D. Dean, and P. Jowse. 1984. User's manual for pesticide root zone model (PRZM): Release 1, Report EPA-600/3-84-109, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Athens, GA.

Caswell, H. 1989. *Matrix Population Models: Construction, Analysis, and Interpretation*. Sinauer, Inc., Sunderland, Massachussetts.

Caswell, H. 1996. Demography meets ecotoxicology: Untangling the population level effects of toxic substances, in *Ecotoxicology: A Hierarchical Treatment*, M.C. Newman and C.H. Jagoe, Eds., CRC/Lewis Publishers, Boca Raton, FL.

CERCLA document 1997

Chaisuksant, Y., Q. Yu and D. Connell. 1997. Internal lethal concentrations of halobenzenes with fish (*Gambusia affinis*). *Ecotoxicology and Environmental Safety* 37:66-75.

Chapman, P.M., R.S. Caldwell and P.F. Chapman. 1996. A warning: NOECs are inappropriate for regulatory use. *Environ. Toxicol. Chem.* 15: 169-186.

Chapman, P.M., R.S. Caldwell and P.F. Chapman. 1996. A Warning: NOECs are inappropriate for regulatory use. *Environ. Toxicol. Chem.* 15:77-79.

Clark, J.R., L.R. Goodman, P.W. Borthwick, J.M. Patrick, Jr., J.C. Moore and E.M. Lores. 1986. Field and laboratory toxicity tests with shrimp, mysids and sheepshead minnows exposed to fenthion. In T.M. Poston and R. Purdy (eds.), *Aquatic Toxicology and Environmental Fate: Ninth Volume*. STP 921. American Society for Testing and Materials, Philadelphia, PA, pp. 161-176.

Clark, K.J., W.L. Hayton, W.H. Gingerich and G.R. Stehly. 1997. Pharmacokinetics, metabolism and a physiologically based pharmacokinetic (PBPK) model of benzocaine in channel catfish. Abstracts, Society of Toxicology and Chemistry (SETAC) Annual Meeting, November 1997, San Francisco, CA.

CMA Ecological Risk Principles 1996

Cooney, J.D. 1995. Freshwater Tests. In G.M. Rand (ed.), *Fundamental of Aquatic Toxicology: Effects, Environmental Fate and Risk Assessment*. Taylor & Francis, Washington, D.C.

Cox, D.R. and D. Oakes. 1984. *Analysis of Survival Data*. Chapman & Hall, London.

Crossland, N.O. , F. Heimbach, I.R. Hill, A. Boudou, P. Leeuwangh, P. Matthiessen and G. Persoone. 1994. Summary and recommendations of the European Workshop on Freshwater Field Tests (EWOFFT). pp. xxv-xxxvii in I.R. Hill, F. Heimbach, P. Leeuwangh and P. Matthiessen (eds.), *Freshwater Field Tests for Hazard Assessment of Chemicals*. Lewis Publishers, Boca Raton, FL.

Crossland, N.O. 1982. Aquatic toxicology of cypermethrin. II. Fate and biological effects in pond experiments. *Aquat. Toxicol.* 2:205-222.

Crump, K.S. 1984. A new method for determining allowable daily intakes. *Fundam. Appl. Toxicol.* 4:854-871.

Daniels, R.E. and J.D. Allan. 1981. Life table evaluation of chronic exposure to a pesticide. *Can. J. Fish. Aquat. Sci.* 38: 485-495.

Day, K. and N.K. Kaushik. 1987. An assessment of the chronic toxicity of the synthetic pyrethroid, Fenvalerate, to *Daphnia galeata mendotae*, using life tables. Environ. Pollut. 44: 13-26.

Dean, J.D., P.S. Huyakorn, A.S. Donigian, K.A. Voss, R.W. Schanz, Y.J. Meeks, and R.F. Carsel. Risk of Unsaturated/Saturated Transport and Transformation of Chemical Concentrations (RUSTIC). Volume I. Theory and Code Verification. Environmental Research Laboratory. U.S. Environmental Protection Agency. Athens, GA.

DeAngelis, D.L. L. Godbout and B.J. Shuter. 1991. An individual-based approach to predicting density-dependent compensation in smallmouth bass populations. *Ecological Modelling* 57:91-115.

deKroon, H., A. Plaisier, J. Van Groenendael and H. Caswell. 1986. Elasticity: the relative contribution of demographic parameters to population growth rate. *Ecology* 67:1427-1431.

Den Boer, P.J. 1968. Spreading of risk and stabilization of animal numbers. *Acta Biotheoretica* 18:165-194.

DeNoyelles, F., Jr., W.D. Kettle and D.E. Sinn. 1982. The responses of plankton communities in experimental ponds to atrazine, the most heavily used pesticide in the USA. *Ecology* 63:1285-1293.

DiToro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* 10:1541-1583.

Dixon, P.M. and M.C. Newman. 1991. Analyzing toxicity data using statistical models for time-to-death: An introduction. In: Newman, M.C. and A.W. McIntosh (Eds.), *Metal Ecotoxicology: Concepts and Applications.* Lewis Publishers, Chelsea, MI.

Donigian, A.S., Jr., R.F. Carsel, J.C. Imhoff, P.R. Hummel, 1994. Addendum to the Users Manual for Release 2.0 of the PRZM-2 Model: Model Enhancements and Description of Bridge Programs for PRZM-2/HSPF and PRZM-2/WASP Applications. Environmental Research Laboratory, U.S. Environmental Protection Agency,

Driscoll, S.K. and P.F. Landrum. 1997. A comparison of equilibrium partitioning and critical body residue approaches for predicting toxicity of sediment-associated fluoranthene to freshwater amphipods. *Envrion. Toxicol. Chem*. 16:2179-2186.

Dunning, J.B., D.J. Stewart, B.J. Danielson, B.R. Noon, T.L. Root, R.H. Lamberson and E.E. Stevens. 1995. Spatially explicit population models: current forms and future uses. *Ecological Applications* 5:3-11.

ECETOC. 1995. The role of bioaccumulation in environmental risk assessment: the aquatic environment and related food webs. ECETOC Technical Report No. 67. October 1995. ECETOC, Brussels, Belgium.

Ecological Committee on FIFRA Risk Assessment Methods - www.epa.gov/oppefeed1/ecorisk/)

Edelmann and Burmaster 1997 HERA 3:223

Emlen, J.M. 1989. Terrestrial population models for ecological risk assessment: a state-of-the-art review. *Environ. Toxicol. Chem.* 8:831-842.

Environment Canada. 1992. Biological test method: Acute test for sediment toxicity using marine or estuarine amphipods. Environment Protection Series, EPS 1/RM/26.

Environment Canada. 1997a. Biological test method: Test for survival and growth in sediment using the freshwater amphipod (*Hyalella azteca*). Environment Protection Series, EPS 1/RM/33.

Environment Canada. 1997b. Biological test method: Test for survival and growth in sediment using the larvae of freshwater midges (*Chironomus tentans* or *Chironomus riparius*). Environment Protection Series, EPS 1/RM/32.

Environment Canada. 1997c. Environmental Assessments of Priority Substances Under the Canadian Environmental Protection Act. Guidance Manual Version 1.0. EPS/2/CC/3E. Chemicals Evaluation Division, Commercial Chemicals Evaluation Branch, Environment Canada. ISBN 0-662-25403-1.

EPA 1998. Guidelines for Ecological Risk Assessment. EPA/630/R-95/002F

EPIC, PRZM Input Collator. PIRANHA, 1992. Pesticide and Industrial Chemical Risk Analysis and Hazard Assessment, Version 3.0, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA.

Erickson, R.J. and J.M. McKim. 1990. A model for exchange of organic chemicals at fish gills: flow and diffusion limitations. *Aquat. Toxicol*. 18:175-198.

Erickson, W.P. and L.L. McDonald. 1995. Tests for bioequivalence of control media and test media in studies of toxicity. *Environ. Toxicol. Chem.* 14:1247-1256.

EU Council Directive. 1991. Concerning placing of plant protection products on the market. 91/414/EEC of 15 July 1991. Official Journal of the European Communities L 230, 19.08.91.

European and Mediterranean Plant Protection Organization (EPPO). 1993; 1994. Decision-making for the environmental risk assessment of plant protection products. Scheme 6: aquatic organisms. EPPO Bulletin. 23: 1-165; 24: 1-87.

European Union. 1991. Council Directive 91/414/EEC Concerning the Placing of Plant Protection Products on the Market. Official Journal of the European Communities. July 15, 1991.

Farmer, D., I.R. Hill and S.J. Maund. 1995. A comparison of the fate and effects of two pyrethroid insecticides (lambda-cyhalothrin and cypermethrin) in pond mesocosms. *Ecotoxicol.* 4:219-244.

FEMVTF, 1999. "Final report of the FIFRA Environmental Model Validation Task Force" in press

Fenelon, J.M., and Moore, R.C., in press, Transport of agrochemicals to ground and surface water in a small central Indiana watershed: Journal of Environmental Quality, v.27, no. 4.

FIFRA § 158 Statute - ADD REFERENCE

FIFRA SAP (Scientific Advisory Panel). 1987. *A Set of Scientific Issues Being Considered by the Agency on Aquatic Mesocosm Testing to Support Pesticide Registration.* Transmittal of the Final FIFRA Scientific Advisory Panel Reports on the June 25, 1987 Meeting. U.S. Environmental Protection Agency, Washington, DC.

FIFRA-EMWG; http//:www.acpa.org/public/science_reg /misc/em-model.html;

FIFRA-EMWG;; http//:www.acpa.org/public/ science_reg/misc/lysim.html

Finney, D.J. 1964. *Statistical Method in Biological Assay*. Hafner, New York.

Fischer, D.J., D.T. Burton, L.T. Yonkos, S.D. Turley, B.S. Turley, G.P. Ziegler and E.J. Zillioux. 1994. Acute and short-term chronic effects of continuous and intermittent chlorination on *Mysidopsis bahia* and *Menidia beryllina. Environ. Toxicol. Chem.* 13:1525-1534.

Fisher, L.J. 1992. Decisions on the Ecological, Fate, and Effects Task Force. Memorandum dated October 29, 1992. Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, DC.

Fontaine, D.D., Havens, P.L., Blau, G.E. and Tillotson, P.M., 1992. The Role of sensitivity analysis in Groundwater Risk Modeling for Pesticides. Weed Technology 6: 716-724

Foose, T.J., R.C. Lacy, R. Brett, and U.S. Seal. 1992. Kenya black rhinoceros population and habitat viability assessment. International Union for the Conservation of Nature and Natural Resources, Captive Breeding Specialist Group, Apple Valley, Minnesota.

Franco, P.J., J.M. Giddings, S.E. Herbes, L.A. Hook, J.D. Newbold, W.K. Roy, G.R. Southworth and A.J. Stewart. 1984. Effects of chronic exposure to coal-derived oil on freshwater ecosystems. I. Microcosms. *Environ. Toxicol. Chem.* 3:447-463.

Friege, H.L. 1986. Monitoring of the River Rhine-Experience Gathered from Accidental Events in 1986. Rome. p 132-143.

Gaddum, J.H. 1953. Bioassays and mathematics. *Pharmacol. Rev*. 5: 87-134.

Gentile, J.H., S.M. Gentile and G. Hoffman. 1983. The effect of a chronic mercury exposure on survival, reproduction and population dynamics of *Mysidopsis bahia*. *Environ. Toxicol. Chem.* 2:61-68

Getty, C., W. Wilkinson, H. Swaine, E.A. Drew and P.J. Davies. 1983. Cypermethrin: Effects of Multiple Low Application Rate Applications on Experimental Ponds. Report No. RJ0182B. ICI Plant Protection Division, Bracknell, Berkshire, UK.

Giddings, J.M. 1983. Microcosms for assessment of chemical effects on the properties of aquatic ecosystems. pp. 45-94 in J. Saxena (ed.), *Hazard Assessment of Chemicals—Current Developments. Vol. II.* Academic Press, New York.

Giddings, J.M. 1986. A microcosm procedure for determining safe levels of chemical exposure in shallow-water communities. pp. 121-132 in J. Cairns, Jr. (ed.), *Community Toxicity Testing*. ASTM STP 920, American Society for Testing and Materials, Philadelphia, PA.

Giddings, J.M. 1992. Aquatic Mesocosm Test for Environmental Fate and Ecological Effects of Diazinon. Report No. 92-3-4155. Springborn Laboratories, Inc., Wareham, Massachusetts.

Giddings, J.M. 1993. Chlorpyrifos (Lorsban 4E): Outdoor Aquatic Microcosm Test for Environmental Fate and Ecological Effects. Report No. 92-6-4288. Springborn Laboratories, Inc., Wareham, Massachusetts.

Giddings, J.M., K.R. Solomon and S.J. Maund. Probabilistic risk assessment of cotton pyrethroids in aquatic ecosystems: II. Mesocosm and field studies with cotton pyrethroids: observed effects and their ecological significance. In preparation.

Giddings, J.M., P.J. Franco, R.M. Cushman, L.A. Hook, G.R. Southworth and A.J. Stewart. 1984. Effects of chronic exposure to coal-derived oil on freshwater ecosystems: II. Experimental ponds. *Environm. Toxicol. Chem.* 3:465-488.

Giddings, J.M., R.C. Biever, M.F. Annunziato and A.J. Hosmer. 1996. Effects of diazinon on large outdoor pond microcosms. *Environ. Toxicol. Chem.* 15:618-629.

Giesy, J.P. Jr. (ed.). 1980. *Microcosms in Ecological Research*. CONF-781101. U.S. Department of Energy, Washington, DC.

Giesy, J.P. Jr., K.R. Solomon., J.R. Coates, K.R. Dixon, J.M. Giddings and E.E. Kenaga. 1999. Chlorpyrifos: ecological risk assessment in North American aquatic environments. *Rev. Environ. Contam. Toxicol.* 160:1-129.

Goldstein, R., J. Anderson, A. Ash, B. Craig, D. Harrington and M. Pagano. 1989. Survival analysis software on MS/PC-DOS computers. *J. Appl. Econometrics* 4: 393-414.

Graney, RL., J.H. Kennedy and J.H. Rodgers, Jr. (eds.). *Aquatic Mesocosm Studies in Ecological Risk Assessment.* Lewis Publishers, Boca Raton, FL.

Gurney, W.S.C., E. McCauley, R.M. Nisbet, and W.W. Murdoch. 1990. The physiological ecology of *Daphnia*: a dynamic model of growth and reproduction. *Ecology* 71:703-715

Gustafson, D.I. and Holden L.R. (1990). Non-linear pesticide dissipation in soil: a new model based on spatial variability. Environ. Sci. Technol. **24**: 1032 -1038

Hallam, T.G. and R.R. Lassiter. 1994. Individual-based mathematical modeling approaches in ecotoxicology: a promising direction for aquatic population and community ecological risk assessment. In R.J. Kendall and T.E.

Hallam, T.G., R.R. Lassiter, J. Li and W. McKinney. 1990. Toxicant-induced mortality in models of Daphnia populations. *Environ. Toxicol. Chem.* 9:597-621.

Handy, R.D. 1994. Intermittent exposure to aquatic pollutants: assessment, toxicity and sublethal responses in fish and invertebrates. *Comp. Biochem. Physiol. C* 107:171-184.

Hanski, I. 1985. Single-species spatial dynamics may contribute to long-term rarity and commonness. *Ecology* 66:335-343.

Hanski, I. 1991. Single-species metapopulation dynamics: concepts, models and observations. *Biological Journal of the Linnaean Society* 42:17-38.

Harrell, F.E. and R. Goldstein. 1997. A survey of microcomputer survival analysis software: The need for an integrated framework. *Amer. Statistician* 51: 360-373.

Harwell, M.A., W. Cooper and R. Flaak. 1992. Prioritizing ecological and human welfare risks from environmental stresses. *Environmental Management*, **16:**451-464.

Hatakeyama, S. and M. Yasuno. 1981. Effects of cadmium on the periodicity of parturition and brood size of *Miona macrocopa* (Cladocera). Environ. Pollut. 26: 111-120.

Hayton, W.L. and M.G. Barron. 1990. Rate-limiting barriers to xenobiotic uptake by the gill. *Environ. Toxicol. Chem.* 9:151-157.

Health Council of the Netherlands. 1993. Ecotoxicological risk assessment and policy-making in the Netherlands—dealing with uncertainties. *Network* 6(3)/7(1):8-11.

Heming, T.A., E.J. McGuinness, L.M. George and K.A. Blumhagen. 1988. Effects of pulsed- and spiked-exposure to methoxychlor on early life stages of rainbow trout. *Bull. Environ. Contam. Toxicol*. 40:764-770.

Hendley, P., D. Laskowski & H. Nelson, Poster, 8th International Congress of Pesticide Chemistry, Washington DC, July 1994;

Hendley, P.; Ekoniak, P. and Hill , I.R. 1995. Design of large Scale Field Runoff Studies for Pesticides. In "Agrochemical Environmental Fate - State of the Art" Eds. Leng, M.L.; Leovey, E.M.K. and Zubkoff, P.L. CRC Press Inc. Boca Raton, Florida. ISBN 1-56670-034-5

Hendley, P., C. Holmes, S. Kay, S.J. Maund, K.Z. Travis, and M. Zhang. Probabilistic risk assessment of cotton pyrethroids in aquatic ecosystems: III. Spatial analysis of the Mississippi cotton landscape. In preparation.

Hickie, B.E., L.S. McCarty and D.G. Dixon. 1995. A residue-based toxicokinetic model for pulse-exposure toxicity in aquatic systems. *Environ. Toxicol. Chem.* 14:2187-2197.

Hill, I.R., F. Heimbach, P. Leeuwangh and P. Matthiessen (eds.). 1994. *Freshwater Field Tests for Hazard Assessment of Chemicals.* Lewis Publishers, Boca Raton, FL.

Hoekstra, J.A. and P.H. Van Ewijk. 1993. Alternatives for the no-observed-effect level. *Environ. Toxicol. Chem.* 12:187-194.

Holdway, D.A. and D.G. Dixon. 1985. Acute toxicity of pulse-dosed methoxychlor to juvenile American flagfish (*Jordanella floridae* Goode and Bean) as modified by age and food availability. *Aquat. Toxicol*. 6:243-250.

Holdway, D.A. and D.G. Dixon. 1986. Impact of pulse exposure to methoxychlor on flagfish (*Jordanella floridae*) over one reproductive cycle. *Can. J. Fish. Aquat. Sci*. 43:1410-1415.

Holdway, D.A., D.G. Dixon and K.L.E. Kaiser. 1991. The acute toxicity of pulse-dosed, para-substituted phenols to larval American flagfish (*Jordanella floridae*): a comparison with toxicity to photoluminescent bacteria and predicted toxicity using log K_{ow}. *Sci Total Environ.* 104:229-237.

Hope. 1993.

Hosmer, A.J., L.W. Warren and T.J. Ward. 1998. Chronic toxicity of pulse-dosed fenoxycarb to *Daphnia magna* exposed to environmentally realistic concentrations. *Environ. Toxicol. Chem.* 17:1860-1866.

Hudson *et al*. 1984. Fish and Wildlife Service, Washington, DC,

Hurd, M.K., S.A. Perry and W.B. Perry. 1996. Nontarget effects of a test application of diflubenzuron to the forest canopy on stream macroinvertebrates. *Environ. Toxicol. Chem.* 15:1344-1351.

Hurlbert, S.H., M.S. Mulla and H.R. Willson. 1972. Effects of an organophosphorous insecticide on the phytoplankton, zooplankton, and insect populations of fresh-water ponds. *Ecol. Monogr.* 42:269-299.

Jager, H. I., D. L. DeAngelis, M. J. Sale, W. Van Winkle, D. D. Schmoyer, M. J. Sabo, D. J. Orth and J. A. Lukas. 1993. An individual-based model for smallmouth bass reproduction and young-of-year dynamics in streams. *Rivers* 4:91-113.

Jagoe, R.H. and M.C. Newman. 1997. Bootstrap estimation of community NOEC values. *Ecotoxicology* 6:293-306.

Jarvinen, A.W., D.K. Tanner and E.R. Kline. 1988. Toxicity of chlorpyrifos, endrin, or fenvalerate to fathead minnows following episodic or continuous exposure. *Ecotoxicol. Environ. Saf.* 15:78-95.

Jaworska, J.S., K.A. Rose and L.W. Barnthouse. 1997. General response patterns of fish populations to stress: an evaluation using an individual-based simulation model. *J. Aquat. Ecosys. Stress Recov.* 6:15-31.

Jessen, R.J. 1978. *Statistical Survey Techniques.* Wiley, New York.

Kallander, D.B., S.W. Fisher and M.J. Lydy. 1997. Recovery following pulsed exposure to organophosphorus and carbamate insecticides in the midge, *Chironomus riparius*. *Arch. Environ. Contam. Toxicol*. 33:29-33.

Kaplan, S. and B.J. Garrick. 1981. On the quantitative definition of risk. *Risk Anal.* 1: 11-27.

Kaushik, N.K., G.L. Stephenson, K.R. Solomon and K.E. Day. 1985. Impact of permethrin on zooplankton communities using limnocorrals. *Canadian J. Fish. Aquat. Sci.* 42:77-85.

Kedwards, T. and S. Wood. 1998. The influence of simulated perturbations on the population dynamics of *Gammarus pulex* (L.). Abstracts, SETAC-Europe Annual Meeting, Bordeaux, France, April 1998.

Klaine, S.J., P. Richards, D. Baker, R. Naddy, T. Brown, B. Joab, R. Casey, D. Fernandez, J. Overmeyer and R. Benjamin. 1997. Agrochemical fate and effects in terrestrial, aquatic and estuarine ecosystems. In *Environmental Behaviour of Crop Protection Chemicals*. Proceedings of an international symposium on the use of nuclear and related techniques for studying the behaviour of crop protection chemicals. International Atomic Energy Agency, IAEA-SM-343/13, pp. 247-263.

Klee, U. 1998. Development and testing of a body-residue based one-compartment first-order kinetic model for estimating the toxicity of mixtures of chlorinated organic contaminants to rainbow trout (*Oncorhynchus mykiss*). Ph.D. thesis, draft. University of Waterloo. Waterloo, Ontario, Canada.

Koivisto, S. and M. Ketola. 1995. Effects of copper on life-history traits of *Daphnia pulex* and *Bosmina longirostris*. Aquat. Toxicol. 32: 255-269.

Kooijman, S.A.L.M. and J.A.J. Metz. 1984. On the dynamics of chemically stressed populations: the deduction of population consequences from effects on individuals. *Ecotoxicology and Environmental Safety* 8:254-274.

Kooijman, S.A.L.M. and J.J.M. Bedaux. 1996. *The Analysis of Aquatic Toxicity Data* (includes DEBtox, vers. 1.0). VU University Press, Amsterdam.

Kooijman, S.A.L.M., A.O. Hanstveit and H. Oldersma. 1983. Paranmetric analyses of population growth in bio-assays. *Chemosphere* 17:527-538.

Krishnan, K. and M.E. Andersen. 1994. Physiologically based pharmacokinetic modeling in toxicology. In AW Hayes (ed.), *Principles and Methods of Toxicology*. Chapter 5. 3rd edition. Raven Press, New York. pp 149-188.

Lacher, Jr., eds., *Wildlife Toxicology and Population Modeling: Integrated Studies of Agroecosystems*. Lewis Publishers, Boca Raton, FL. pp. 531-542.

Lacy , R.C. 1993. VORTEX: a computer simulation model for use in population viability analysis. *Wildlife Research* 20:45-65.

Lacy, R.C. and T.W. Clark. 1990. Population viability assessment of the eastern barred bandicoot in Victoria. Pp. 131-146 in T.W. Clark and J.H. Seebeck (eds.), *The Management and Conservation of Small Populations.* Chicago Zoological Society, Brookfield, Illinois.

Lacy, R.C., N.R. Flesness and U.S. Seal. 1989. Puerto Rican parrot population viability analysis. International Union for the Conservation of Nature and Natural Resources, Species Survival Commission, Captive Breeding Specialist Group, Apple Valley, Minnesota.

Lamberson, R. H., R. McKelvey, B.R. Noon and C. Voss. 1994. Reserve design for territorial species: the effects of patch size and spacing on the viability of the northern spotted owl. *Conservation Biology* 8**:**185-195.

Lamberson, R.H., R. McKelvey, B.R. Noon and C. Voss. 1992. The effects of varying dispersal capabilities on the population dynamics of the northern spotted owl. *Conservation Biology*. 6:505-512.

Lande, R. 1987. Extinction thresholds in demographic models of terrestrial populations. *American Naturalist* 130:624-635.

Landis, W.G., R.A. Matthews and G.B. Matthews. 1996. The layered and historical nature of ecological systems and the risk assessment of pesticides. *Environ. Toxicol. Chem*. 15:432-440.

Landrum, P.F., H. Lee II, and M.J. Lydy. 1992. Toxicokinetics in aquatic systems: model comparisons and use in hazard assessment. *Environ. Toxicol. Chem*. 11:1709-1725.

Laskowski, R. 1995. Some good reasons to ban the use of NOEC, LOEC and related concepts in ecotoxicology. *OIKOS* 73: 140-144.

Lassiter, R.R. 1986. Design criteria for a predictive ecological effects modeling system. In T.M. Poston and R. Purdy, eds., *Aquatic Toxicology and Environmental Fate: Ninth Volume*. STP 921. American Society for Testing and Materials, Philadelphia, PA, pp. 42-54.

Lassiter, R.R. and T.G. Hallam. 1990. Survival of the fattest: implications for acute effects of lipophilic chemicals on aquatic populations. *Environ. Toxicol. Chem*. 9:585-596.

Leake C. R., Humphries, S.P. and Austin D.J. (1995). Factors influencing the modeling of pesticide degradation in soil and the estimation of half life (DT50) and DT90 values. 1995 BCPC Monograph No 62: Pesticide movement to water.

Levins, R. 1966. The strategy of model building in population biology. *American Scientist* 54:421-431.

Levins, R. 1969. Some demographic and genetic consequences of environmental heterogeneity for biological control. *Bull.Entomol. Soc.Amer.*15:237-240.

Lien, G.J., J.W. Nichols, J.M. McKim and C.A. Gallinat. 1994. Modeling the accumulation of three waterborne chlorinated ethanes in fathead minnows (*Pimephales promelas*): a physiologically based approach. *Environ. Toxicol. Chem*. 13:1195-1205.

Lindenmayer, D. B. and R. C. Lacy. 1995a. Metapopulation viability of Leadbeater's possum, *Gymnobelideus leadbeateri*, in fragmented old-growth forests. *Ecological Applications* 5:164-182.

Lindenmayer, D. B. and R. C. Lacy. 1995b. Metapopulation viability of arboreal marsupials in fragmented old-growth forests: comparison among species. *Ecological Applications* 5:183-199.

Lindenmayer, D.B., T.W. Clark, R.C. Lacy and V.C. Thomas. 1993. Population Viability Analysis as a tool in wildlife management: a review with reference to Australia. *Environmental Management* 17:745-758.

Lipnick, R.L. 1993. Baseline toxicity QSAR models: a means to assess mechanism of toxicity for aquatic organisms and mammals. In J. Gorsuch, F. Dwyer, C. Ingersoll and T.W. La Point (eds.), *Environmental Toxicology and Risk Assessment*. STP 1216. American Society for Testing and Materials, Philadelphia, PA, pp. 610-619.

Litchfield, J.T., Jr. 1949. A method for rapid graphic solution of time-per cent effects curves. *J. Pharmacol. Exp. Ther*. 97: 399-408.

Litchfield, J.T., Jr. and F. Wilcoxon. 1949. A simplified method of evaluating dose-effect experiments. *J. Pharmacol. Exp. Ther*. 96: 99-113.

Liu, J. 1993. An introduction to ECOLECON: a spatially-explicit model for ECOLogical ECONomics of species conservation in complex forest landscapes. *Ecological Modelling* 70:63-87.

Loza, H.J., W.E. Grant ,J.W. Stuth and T.D.A. Forbes. 1992. Physiologically based landscape use model for large herbivores. *Ecological Modeling* 61:227-252

Lumb, A.M., J.L. Kittle, and K.M. Flynn. 1990. Users Manual for ANNIE, A Computer Program for Interactive Hydrologic Analyses and Data Management. U.S. Geological Survey Water Resources Investigations Report 89-4080. Reston, VA.

MacArthur, R.H. and E.O. Wilson. 1967. *The Theory of Island Biogeography*. Princeton University Press, Princeton, New Jersey.

Maciorowski, A. 1998. Ecological Risk Assessment under FIFRA. Chapter 3 in Ecological Risk Assessment in the Federal Government. Draft report. Committee on Environment and Natural Resources. Washington, DC. 203 p.

Maciorowski, A.F., W.L. McCulloch and J.A. Fava. 1985. An approach to sewage sludge bioaccumulation potential tests. In R.D. Cardwell, R. Purdy and R.C. Bahner (eds.), *Aquatic Toxicology and Hazard Assessment: Seventh Symposium*. STP 854. American Society for Testing and Materials, Philadelphia, PA, pp. 253-268.

Maguire, L.A., R.C. Lacy, R.J. Begg and T.W. Clark. 1990. An analysis of alternative strategies for recovering the eastern barred bandicoot. Pp. 147-164 in T.W. Clark and J.H. Seebeck (eds.), *The Management and Conservation of Small Populations*. Chicago Zoological Society, Brookfield, Illinois.

Manly, B.F.J. 1985. *The Statistics of Natural Selection on Animal Populations*. Chapman & Hall, London.

Marshall, J.S. 1962. The effects of continuous gamma radiation on the intrinsic rate of natural increase of *Daphnia pulex*. Ecology 43: 598-607.

Martínez-Jerónimo, F., R. Villaseñor, F. Espinosa and G. Rios. 1993. Use of life-tables and application factors for evaluating chronic toxicity of Kraft mill wastes on *Daphnia magna.* Bull. Environ. Contam. Toxicol. 50: 377-384.

Marubini, E. and M.G. Valsecchi. 1995. *Analysing Survival Data from Clinical Trials and Observational Studies*. John Wiley & Sons, New York.

Matthews, R.A., W.G. Landis and G.B. Matthews. 1996. The community conditioning hypothesis and its application to environmental toxicology. *Environ. Toxicol. Chem*. 15:597-603.

Maund, S., I. Barber, J. Dulka, J. Gonzalez-Valero, M. Hamer, F. Heimbach, M. Marshall and P. McCahon. 1997. Development and evaluation of triggers for sediment toxicity testing of pesticides with benthic macroinvertebrates. *Environ. Toxicol. Chem.* 16:2590-2596.

Maund, S.J., K.Z. Travis, P. Hendley, J.M. Giddings and K.R. Solomon. Probabilistic risk assessment of cotton pyrethroids in aquatic ecosystems: V. Combining landscape-level exposure and ecotoxicological effects data to characterize risks. In preparation.

Mayer and Ellersieck. 1986. Fish and Wildlife Service, Resource Publication 160, Washington, DC.

MC report -- EPA

McCarty, L.S. and D. Mackay. 1993. Enhancing ecotoxicological modeling and assessment. *Environ. Sci. Technol.* 27:1719-1728.

McCarty, L.S., D. Mackay, A.D. Smith, G.W. Ozburn and D.G. Dixon. 1992. Residue-based interpretation of toxicity and bioconcentration QSARs from aquatic bioassays: neutral narcotic organics. *Environ. Toxicol. Chem*. 11:917-930.

McCarty, L.S., D. Mackay, A.D. Smith, G.W. Ozburn and D.G. Dixon. 1993. Residue-based interpretation of toxicity and bioconcentration QSARs from aquatic bioassays: polar narcotic organics. *Ecotoxicol. Environ. Safety*. 25:253-270.

McCauley, E., W.W. Murdoch, R.M. Nisbet and W.S.C. Gurney. 1990. The physiological ecology of *Daphnia*: a dynamic model of growth and reproduction. *Ecology* 71:716-732.

McKim, J.M. and P.K. Schmeider. 1991. Bioaccumulation: does it reflect toxicity? In R. Nagel and R. Loskill (eds.), *Bioaccumulation in Aquatic Systems*. VCH, Weinheim, Germany.

McLave, J.T., J.H. Sullivan and J.G. Pearson. 1981. Statistical analysis of fish chronic toxicity test data. In D.R. Branson and K.L. Dickson (eds.), *Aquatic Toxicology and Hazard Assessment: Fourth Conference*, ASTM STP 737, American Society for Testing and Materials, pp. 359-376.

Menzel, D.W. and J. Case. 1977. Concept and design: Controlled Ecosystem Pollution Experiment. *Bull. Mar. Sci.* 27:1-7.

Metcalf, R.L. 1977. Model ecosystem approach to insecticide degradation: a critique. *Ann. Rev. Entomol.* 22:241-261.

Meyer, J.S. and M.S. Boyce. 1994. Life historical consequences of pesticides and other insults to vital rates. pp. 349-363 in R.J. Kendall and T.E. Lacher, Jr. (eds.), *Wildlife Toxicology and Population Modeling*, Lewis Publishers, Boca Raton, Florida.

Miller, R.G., Jr. 1981. *Survival Analysis*. John Wiley & Sons, New York.

Moore, D.R.J. and P. Caux. 1997. Estimating low toxic effects. *Environ. Toxicol. Chem.* 16:794-801.

Mullins, J.A., R.F. Carsel, J.E. Scarbrough, and A.M. Ivery. 1993. PRZM2 User's manual, version 1.0. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Athens, GA.

Mulvey, M., G.P. Keller, and G.K. Meffe. 1994. Single- and multiple-locus genotypes and life-history responses of *Gambusia holbrooki* reared at two temperatures. *Evolution* 48: 1810-1819.

Munns, W.R. Jr., D.E. Black, T.R. Gleason, K. Salomon, D. Bengston, and R. Gutjahr-Gobell. 1997. Evaluation of the effects of dioxin and PCBs on *Fundulus heteroclitus* populations using a modeling approach. *Environ. Toxicol. Chem.* 16:1074-1081.

Murdoch, W.W., J. Chessson and P. Chesson. 1985. Biological control in theory and practice. *American Naturalist* 125:344-366.

MUSCRAT model -Development largely funded by American Cyanamid; model development performed by Waterborne Environmental Inc., Leesburg, VA, USA. ;

NACA (National Agricultural Chemicals Association). 1987. *Aquatic Risk Assessment Methodology Workshop.* October 8-9, 1986, Washington, DC.

National Research Council. (1983) Risk assessment in the Federal Government. Washington, DC: National Academy Press, 191 p.

National Research Council. (1993) Issues in risk assessment. Washington, DC: National Academy Press, 356 p.

Nelson, H., R. Parker, R.D. Jones, and S. Mostaghimi. 1997. Use of computer modeling, monitoring data, and cumulative exceedence curves in tiered pesticide aquatic risk assessment. MISSING ref

Nendza, M., T. Herbst, C. Kussatz and A. Gies. 1997. Potential for secondary poisoning and biomagnification in marine organisms. *Chemosphere* 35:1875-1885.

Newman, M.C. 1995. *Quantitative Methods in Aquatic Ecotoxicology.* Lewis Publishers. Boca Raton. 426 pp.

Newman, M.C. 1997. Noting time-to-event enhances prediction from toxicity test data. Prepared for Sept. 97 meeting of USEPA ECOFRAM.

Newman, M.C. and J.T. McCloskey. 1996. Time-to-event analyses of ecotoxicity data. *Ecotoxcology* 5: 187-196.

Newman, M.C. and M.S. Aplin. 1992. Enhancing toxicity data interpretation and prediction of ecological risk with survival time modeling: An illustration using sodium chloride toxicity to mosquitofish (*Gambusia holbrooki*). *Aquatic Toxicol.* 23: 85-96.

Newman, M.C. and P.M. Dixon. 1996. Ecologically meaningful estimates of lethal effect in individuals. In M.C. Newman and C.H. Jagoe (eds.), *Ecotoxicology. A Hierarchical Treatment.* Lewis Publishers, Boca Raton, pp. 225-253.

Newman, M.C., M.M. Keklak, and M.S. Doggett. 1994. Quantifying animal size effects on toxicity: a general approach. *Aquatic Toxicol*. 28: 1-12.

Nichols, J., P. Rheingans, D. Lothenbach, R. McGreachie, L. Skow and J. McKim. 1994. Three-dimensional visualization of physiologically based kinetic model outputs. *Environ. Health Perspectives* 102:952-956.

Nichols, J.W., J.M. McKim, G.J. Lien, A.D. Hoffman, S.L. Bertelsen and C.M. Elonen. 1996. A physiologically based toxicokinetic model for dermal absorption of organic chemicals by fish. *Fund. Appl. Toxicol*. 31:229-242.

OECD (Organization for Economic Cooperation and Development). 1996. Draft Proposal for a Guidance Document: Freshwater Lentic Field Tests.

OECD (Organization for Economic Cooperation and Development). 1998a. OECD Guidelines for the Testing of Chemicals. Draft proposal for a new guideline. Chironomid toxicity testing using spiked sediment. May 1998.

OECD (Organization for Economic Cooperation and Development). 1998b. OECD Guidelines for the Testing of Chemicals. Draft proposal for a new guideline. Chironomid toxicity testing using spiked water. May 1998.

[1]Omernik, J.M. 1987. Ecoregions of the Conterminous United States. Annals of the Association of America Geographers 77(1):118-125

OSWER EcoUpdate 1996; vol. 3(1)

Palmieri, M., J. Freda, H. Krueger, C. Reed, T. Springer, B. Sweeney, J. Jackson and D. Funk. 1992. An Evaluation of the Impact of Cypermethrin Exposure on Managed Aquatic Ecosystems. Study No. A89-2847. FMC Corporation, Princeton, New Jersey.

Parker, R.D., H. Nelson, and R.D. Jones. 1995. GENEEC: A screening model for pesticide environmental exposure assessment. pg. 485-490. In Water Quality Modeling Proceedings of the International Symposium, April 2-5, 1995. Orlando, FL.

Parker, R.D., H.P. Nelson, R.D. Jones, and S. Mostaghimi. 1997. Development of GENEEC for screening level estimation of pesticide exposure in the aquatic environment.

Parkhurst, D. 1998. Arithmetic versus geometric means for environmental concentration data. *Environ. Sci. Technol.* Feb 1 1998:92A-98A.

Parrott, J.L., P.V. Hodson, M.R. Servos, S.L. Huestis and D.G. Dixon. 1995. Relative potency of polychlorinated dibenzo-*p*-dioxins and dibenzofurans for inducing mixed-function oxygenase activity in rainbow trout. *Environ. Toxicol. Chem*. 14:1041-1050.

Parsons, J.T. and G.A. Surgeoner. 1991a. Acute toxicities of permethrin, fenitrothion, carbaryl and carbofuran to mosquito larvae during single- or multiple-pulse exposures. *Environ. Toxicol. Chem*. 10:1229-1233.

Parsons, J.T. and G.A. Surgeoner. 1991b. Effect of exposure time on the acute toxicities of permethrin, fenitrothion, carbaryl and carbofuran to mosquito larvae. *Environ. Toxicol. Chem*. 10:1219-1227.

Pratt, J.R. and N.J. Bowers. 1992. Variability of community metrics: Detecting chnages in structure and function. *Environ. Toxicol. Chem.* 11:451-457.

PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.0. National Exposure Research Laboratory U.S. Environmental Protection Agency, Athens, GA 30605-2720

Pulliam, H.R. 1994. Incorporating concepts from population and behavioral ecology into models of exposure to toxins and risk assessment. pp. 13-26 in RJ. Kendall and T.E. Lacher, Jr. (eds.), *Wildlife Toxicology and Population Modeling*. Lewis Publishers, Boca Raton, Florida.

Pulliam, H.R., J.B. Dunning, Jr. and J. Liu. 1992. Population dynamics in complex landscapes: a case study. *Ecological Applications* 2:165-167.

RA/RM Commission 1997

Ray, C. and M.E. Gilpin. 1991. The effect of conspecific attraction on metapopulation dynamics. *Biological Journal of the Linnaean Society* 42:123-134.

Reinert and Brown. 1993.

Richards, R. P. and D. B. Baker, 1993. Pesticide Concentration Patterns in Agricultural Drainage Networks in the Lake Erie Basin. Environmental Toxicology and Chemistry, Vol 12, pp 13-26.

Rose, K.P. and J.H. Cowan, Jr. 1993. Individual-based model of young-of-the-year striped bass population dynamics. I. Model description and baseline simulations. *Trans. Amer. Fish. Soc.* 122:415-438

Sabelis, M.W., O. Diekman and V.A.A. Jansen. 1991. Metapopulation persistence despite local extinction: predator-prey patch models of the Lotka-Volterra type. *Biological Journal of the Linnaean Society* 42:267-283.

Samuels, W.B. and A. Ladino. 1983. Calculations of seabird population recovery from potential oil spills in the mid-Atlantic region of the United States. *Ecological Modeling* 21:63-84.

Schober, U. and W. Lampert. 1977. Effects of sublethal concentrations of the herbicide Atrazine on growth and reproduction of *Daphnia pulex*. Bull. Environ. Contam. Toxicol. 17: 269-277.

Schuytema *et al*. 1991. *Arch. Environ. Contam. Toxicol.* 21:332-350.

Science Advisory Board, U.S. Environmental Protection Agency. (1990a) Reducing risk: setting priorities and strategies for environmental protection. Washington, DC. SAB-EC-90-021.

Science Advisory Board, U.S. Environmental Protection Agency. (1990b) The report of the Ecology and Welfare Subcommittee: Relative Risk Reduction Project, Reducing Risk. Appendix A. Washington, DC. SAB-EC-90-021A.

Science Advisory Board, U.S. Environmental Protection Agency. (1990c) The report of the Human Health Subcommittee: Relative Risk Reduction Project, Reducing Risk. Appendix B. Washington, DC. SAB-EC-90-021B.

Seal, U.S. and R.C. Lacy. 1989. Florida panther population viability analysis. International Union for the Conservation of Nature and Natural Resources, Captive Breeding Specialist Group, Apple Valley, Minnesota.

Seal, U.S. and T.J. Foose. 1989. Javan rhinoceros population viability analysis and recommendations. International Union for the Conservation of Nature and Natural Resources, Captive Breeding Specialist Group, Apple Valley, Minnesota.

SETAC.(in press) Multiple Stressors in Ecological Risk Management Workshop. SETAC Press. Pensacola, FL.

SETAC/Resolve. 1992. *Proceedings of a Workshop on Aquatic Microcosms for Ecological Assessment of Pesticides* (Wintergreen, Virginia, USA, October 1991). SETAC Foundation for Environmental Education and the RESOLVE program of the World Wildlife Fund.

SETAC-Europe. 1992. *Guidance Document on Test Procedures for Pesticides in Freshwater Microcosms.* From the workshop "A meeting of experts on guidelines for static field microcosm tests" (Monks Wood Experimental Station, Huntingdon, UK, July 1991). Society of Environmental Toxicology and Chemistry-Europe, Brussels, Belgium.

Siefert, R. and D. Urban. 1987. Aquatic Field Testing: Experimental Mesocosms and Field Techniques. Workshop held September 1987, Duluth, Minnesota.

Sipes, I.G. and A.J. Gandolfi. 1986. Biotransformation of toxicants. Chapter 4. In C.D. Klaasen, M.O. Amdur and J. Doull (eds.), *Casarett and Doull's Toxicology. The Basic Science of Poisons.* 3rd edition. Macmillan Publishing Co. pp. 64-98.

Skalski, J.R. 1981. Statistical inconsistencies in the use of the no-observed-effect levels in toxicity testing. In D.R. Branson and K.L. Dickson (eds.), *Aquatic Toxicology and Hazard Assessment: Fourth Conference*, ASTM STP 737, American Society for Testing and Materials, pp. 377-387.

Society of Environmental Toxicology and Chemistry (SETAC),. 1994. . Aquatic Dialogue Group: Pesticide Risk Assessment And Mitigation. Baker, J.L., A.C. Barefoot, L.E. Beasley, L.A. Burns, P.P. Caulkins, J.E. Clark, R.L.

Feulner, J.P. Giesy, R.L. Graney, R.H. Griggs, H.M. Jacoby, D.A. Laskowski, A.F. Maciorowski, E.M. Mihaich, H.P. Nelson Jr, P.R. Parrish, R.E. Siefert, K.R. Solomon, W.H. van der Schalie, editors.. Pensacola FL: SETAC Press.

Soenksen, P.J., Transport of agricultural chemicals in surface flow, tileflow, and streamflow of Walnut Creek watershed near Ames, Iowa, April 1991-September 1993: U.S. Geological Survey Water-Resources Investigations Report 96-4017.

Solomon, K.R. 1998. Latency of responses. Unpublished document prepared for ECOFRAM. 10 July 98. 6pp.

Solomon, K.R., D.B. Baker, P. Richards, K.R. Dixon, S.J. Klaine, T.W. La Point, R.J. Kendall, J.M. Giddings, J.P. Giesy, Jr., L.W. Hall, Jr., C.P. Weisskopf and M. Williams. 1996. Ecological risk assessment of atrazine in North American surface water. *Environ. Toxicol. Chem.* 15:31-76.

Solomon, K.R., J.M. Giddings and S.J. Maund. Probabilistic risk assessment of cotton pyrethroids in aquatic ecosystems: I. Distributional analysis of laboratory aquatic toxicity data. In preparation.

Solomon, K.R., K. Smith, G. Guest, J.Y. Yoo and N.K. Kaushik. 1980. Use of limnocorrals in studying the effects of pesticides in the aquatic ecosystem. *Can. Tech. Rep. Fish. Aquat. Sci.* 975:1-9.

Spacie, A., L.S. McCarty and G.M. Rand. 1995. Bioaccumulation and bioavailability in multiphase systems. Chapter 16. In G.M. Rand (ed.), *Fundamentals of Aquatic Toxicology*. Taylor and Francis. Washington DC. pp. 493-521.

Sprague, J.B. 1969. Measurement of pollutant toxicity to fish: I. Bioassay methods for acute Toxicity. *Water Res*. 3:793-821.

Spray Drift Task Force (1997a). "A summary of Aerial Application Studies". Ed. David Johnson. Stewart Agricultural Research Services Inc., PO Box 509, Macon, MO 63552.

Spray Drift Task Force (1997b). "A summary of Ground Application Studies". Ed. David Johnson. Stewart Agricultural Research Services Inc., PO Box 509, Macon, MO 63552.

Spray Drift Task Force (1997c). "A summary of Airblast Application Studies". Ed. David Johnson. Stewart Agricultural Research Services Inc., PO Box 509, Macon, MO 63552.

Spray Drift Task Force (1997d). "A summary of Chemigation Application Studies". Ed. David Johnson. Stewart Agricultural Research Services Inc., PO Box 509, Macon, MO 63552.

Stephan, C.E. and J.W. Rogers. 1985. Advantages of using regression analysis to calculate results of chronic toxicity tests. In R.C. Bahner and D.J. Hansen (eds.), *Aquatic Toxicology and Hazard Assessment: Eighth Symposium*, ASTM STP 891, American Society for Testing and Materials, pp. 328-338.

Stephenson, G.L., N.K. Kaushik, K.R. Solomon and P. Hamilton. 1986. Impact of methoxychlor on freshwater plankton communities in limnocorrals. *Environ. Toxicol. Chem.* 5:587-603.

Suter, G.W. II 1993. Ecological Risk Assessment. Lewis Publishers, Chelsea, Michigan. 538 pp.

Suter, G.W. II, L.W. Barnthouse, S.M. Bartell, T. Mill, D. Mackay and S. Patterson. 1993. *Ecological Risk Assessment.* Lewis Publishers, Boca Raton, FL.

Estes, T. & P.N. Coody,; http//:www.acpa.org/public/science_reg /misc/gmp-doc.html

Estes, T. Proc. Int. Symp. Water Quality Monitoring - ASAE - Orlando, Ed. C. Heatwole, 1995, 475-484.;

Tarr, B.D., M.G. Barron and W.L. Hayton. 1990. Effect of body size on the uptake and bioconcentration of di-2-ethylhexyl phthalate in rainbow trout. *Environ. Toxicol. Chem*. 9:989-995.

Taub, F.B. 1969. A biological model of a freshwater community: a gnotobiotic ecosystem. *Limnol. Oceanogr.* 14:136-142.

Taub, F.B. 1974. Closed ecological systems. *Ann. Rev. Ecol. Syst.* 5:139-160.

Thomas, LM. (1987) Environmental decision-making today. Environ Prot Agency J 13:2-5.

Tilman, D. 1996. Biodiversity: Population versus ecosystem stability. *Ecology* 77:350-363.

Tipton, A.R., R.J. Kendall, J.F. Coyle and P.F. Scanlon. 1980. A model of the impact of methyl parathion spraying on a quail population. *Bull. Environ. Contam. Toxicol.* 25:586-593.

Touart, L.W. 1988. *Aquatic Mesocosm Test to Support Pesticide Registrations.* Hazard Evaluation Division Technical Guidance Document. EPA/540/09-88-035. Office of Pesticide Programs, U.S. Environmental Protection Agency, Washington, DC.

Touart, LW. 1995. The Federal Insecticide, Fungicide, and Rodenticide Act. Chapter 21. In: Rand, GM. Fundamentals of Aquatic Toxicology. 2nd Edition. Taylor and Francis. Washington DC. Pp. 657-668.

Travis, K.Z. and P. Hendley. Probabilistic risk assessment of cotton pyrethroids in aquatic ecosystems: IV. Landscape-level exposure characterization. In preparation.

Turner, M.G., Y. Wu, W.H. Romme and L.L. Wallace. 1993. A landscape simulation model of winter foraging by large ungulates. *Ecological Modelling* 69:163-184.

Turner, M.G., Y. Wu, W.H. Romme, L.L. Wallace, and A. Brenkert. 1994. Simulating winter interactions among ungulates, vegetation, and fire in northern Yellowstone Park. *Ecological Applications* 4:472-496.

U.S. EPA (Environmental Protection Agency). (1992) Framework for Ecological risk assessment. Risk Assessment Forum, Office of Research and Development, Washington, DC. EPA/600/R-92/001.

U.S. EPA (Environmental Protection Agency). (1994) The new generation of environmental protection. Washington, DC. EPA/200/B-94-002.

U.S. EPA (Environmental Protection Agency). (1996) Proposed guidelines for ecological risk assessment. Federal Register 61(175):47552-47631.

U.S. EPA (Environmental Protection Agency). 1994a. Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates. EPA 600/R-94/024. Office of Research and Development, Washington, D.C.

U.S. EPA (Environmental Protection Agency). 1994b. Methods for Assessing the Toxicity of Sediment-Associated Contaminants with Estuarine and Marine Amphipods. EPA 600/R-94/025. Office of Research and Development, Washington, D.C.

U.S. EPA (Environmental Protection Agency). 1996a. Draft Ecological Effects Test Guidelines. OPPTS 850.1735. Whole Sediment Acute Toxicity Invertebrates, Freshwater. Office of Prevention, Pesticides and Toxic Substances, Washington, D.C.

U.S. EPA (Environmental Protection Agency). 1996b. Draft Ecological Effects Test Guidelines. OPPTS 850.1740. Whole Sediment Acute Toxicity Invertebrates, Marine. Office of Prevention, Pesticides and Toxic Substances, Washington, D.C.

U.S. EPA (Environmental Protection Agency). 1998. Contaminated sediment management strategy. EPA 823-R-98-001. Office of Water, Washington, D.C.

U.S. EPA (Environmental Protection Agency). 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. Report No. PB 85-227049. Office of Research and Development, U.S. Environmental Protection Agency, Duluth, MN.

U.S. EPA (Environmental Protection Agency). 1986. Hazard Evaluation Division, Standard Evaluation Procedure: Fish Early Life-Stage. EPA 540/9-86-138. Office of Pesticide Programs, U.S Environmental Protection Agency, Washington, DC.

U.S. EPA (Environmental Protection Agency). 1998. Guidelines for ecological risk assessment. EPA/630/OR-95/002F. Risk Assessment Forum, U.S. Environmental Protection Agency, Washington, DC.

U.S. EPA (Environmental Protection Agency). 1998. Endocrine Disruptor Screening Program: Statement of Policy. *Federal Register* 63(248):71541-71568.

Urban, D. J., and N. J. Cook. 1986. Hazard Evaluation Division Standard Evaluation Procedure: Ecological Risk Assessment. EPA-540/9-86-167. NTIS PB86-247657. National Technical Information Service, Springfield, VA.

Urban, Douglas J., and Norman J. Cook. 1986. *Hazard Evaluation Division Standard Evaluation Procedure: Ecological Risk Assessment*. EPA 540/9-85-001. United States Environmental Protection Agency, Washington, D.C. issued June 1986. (NTIS PB86-247657)

van den Brink et al. 1996 ETC 15: 1143

Van der Hoeven, N., and A.A.M. Gerritsen. 1997. Effects of chlorpyrifos on individuals and populations of *Daphnia pulex* in the laboratory and field. *Environ. Toxicol. Chem.* 16:2438-2447.

van Groenendael, J., H. DeKroon, S. Kalisz and S. Tuljapurkar. 1994. Loop analysis: Evaluating life history pathways in population projection matrices. *Ecology* 75:2410-2415.

van Leeuwen and Hermens 1995

Van Leeuwen, C.J., F. Moberts and G. Niebeek. 1985. Aquatic toxicological aspects of dithiocarbamates and related compounds. II. Effects on survival, reproduction and growth of *Daphnia magna*. Aquat. Toxicol. 7: 165-175.

Van Loon, W.M.G.M., M.E. Verwoerd, F.G. Wijnker, C.J. van Leeuwen, P. van Duyn, C. van deGuchte and J.L.M. Hermens. 1997. Estimating total body residues and baseline toxicity of complex organic mixtures in effluents and surface waters. *Environ. Toxicol. Chem.* 16:1358-1365.

van Tienderen. P.H. 1995. Life cycle trade-offs in matrix population models. *Ecology* 76:2482-2489.

Verhaar, H.J.M., W. de Wolf, S. Dyer, K. Legierse, W. Seinen and J.L.M. Hermens. 1997. An LC50 vs. time model for the aquatic toxicity of reactive and receptor-mediated compounds: consequences for bioconcentration kinetics and risk assessment. Abstracts, Society of Toxicology and Chemistry (SETAC) Annual Meeting, San Francisco, CA, November 1997.

Versteeg, D.J., S.E. Belanger and G.J. Carr. 1998. A data based comparison of single species and model ecosystem sensitivity. Abstracts, SETAC-Europe 8th Annual Meeting, Bordeaux, France. p. 281.

Voshell, J.R., Jr. (ed.). 1989. *Using Mesocosms to Assess the Aquatic Ecological Risk of Pesticides: Theory and Practice.* A symposium sponsored by Section E, Extension and Regulatory Entomology, at the 34th Annual Meeting of the Entomological Society of America, November 29-December 3, 1987, Boston, MA. Misc. Pub. 75, Entomological Society of America, Lanham, MD.

Wagner, C. and H. Løkke. 1991. Estimation of ecotoxicological protection levels from NOEC toxicity data. *Water Research* 25:1237-1242.

Walthall, W.K. and J.D. Stark. 1997. A comparison of acute mortality and population growth rate as endpoints of toxicological effect. *Ecotox. Environ. Safety* 37:45-57.

Wentsel, R.S., T.W. La Point, M. Simini, R.T. Checkai, D. Ludwig and L.W. Brewer. 1996. Tri-Service Procedural Guidelines for Ecological Risk Assessments. ADA 314323. Defense Technical Information Center, Washington, DC.

Williams, W. M. 1998. RADAR. Risk Assessment tool to evaluate Duration and Recovery. Version 1.10. Waterborne Environmental Inc.

Williams, W.M., 1998. RESWQ Users Manual: Version 1.10, Waterborne Environmental, Inc., Leesburg, Virginia.

Williams, W.M., J.M. Cheplick, A.M. Ritter, and C.E. O'Flaherty, 1997. RIVWQ Users Manual: Version 1.35, Waterborne Environmental, Inc., Leesburg, Virginia.

Winemiller, K.O. and K.A. Rose. 1992. Patterns of life-history diversification in North American fishes: Implications for population.

Wong, C.K. and P.K. Wong. 1990. Life table evaluation of the effects of cadmium exposure on the freshwater cladoceran *Miona macrocopa*. Bull. Environ. Contam. Toxicol. 44: 135-141.

7. ECOFRAM Aquatic Workgroup Report Appendices

The Appendices in this section are organized by chapter number and sequence within a chapter. For example, Appendix 1B refers to the second appendix from Chapter 1.

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7.2. Appendix 2-2: Details of Mitigation Factors and Approaches as suggested by ARAMDG (ARAMDG, 1994)

7.2.1.1. Selecting Mitigation Practices

Many factors interact to determine transport of pesticides from agricultural fields. These factors and their interactions need to be understood before appropriate decisions on potential mitigation options can be made. These factors can be categorized into:

1) Pesticide properties:
   - The major factors determining concentrations of pesticides in runoff from cropland are persistence and adsorption to soil.
2) Pesticide transport process:
   - Runoff Entry: The major factors are hydrologic; including the intensity and duration of precipitation and the rate of infiltration as affected by soil factors and conditions.
   - Drift Entry: The major factors are the wind speed / direction and the relative humidity in combination with the application method and the impact of the boom/nozzle/volume /pressure combination selected as it affects droplet size distribution.
3) Landscape
   - The major factors are the extent of occurrence of the crop of interest within the watershed, the area treated, the existence of natural or managed untreated buffers and presence of various soil/slope combinations
4) Application and management practices:
   - The major management factors to reduce field transport of pesticides are the rate, method, timing, and choice of applied pesticides; cropping sequence (in time and space); water management; and tillage or soil management systems. Field-to-stream transport of pesticides may be managed using mechanical structures, such as terraces, and use of landscape reconfiguration such as wetlands or buffer strips.

To determine the best combination of mitigation practices to reduce pesticide transport by runoff, mechanisms of loss and pesticide interactions with the soil and mitigation practices must be considered. Depending on soil adsorption in relation to other factors, pesticides can be mostly lost with surface runoff water, sediment, or water percolating out of the root zone (water which may return to the surface through base flow or artificial subsurface drainage). Erosion control is a good mitigation practice for strongly adsorbed pesticides. For moderately adsorbed pesticides, soil incorporation is a good mitigation practice that reduces the amount of pesticide in the thin surface soil "mixing zone" and thereby decreases surface runoff transport. Other practices that enhance infiltration can also reduce surface runoff but with a concomitant increase in leaching. The route of infiltration (e.g., through "macropores") can allow pesticides to percolate through the root zone more quickly than normally expected, resulting in "concentration spikes" that may be of ecological concern if a field has tile drains. However, for moderately to strongly adsorbed pesticides, leaching transport is usually much less significant than movement in surface runoff. For weakly or non-adsorbed pesticides, increased infiltration reduces runoff

but may enhance leaching. This appendix provides further details of runoff mitigation factors and practices recommended by the ARAMDG report (ARAMDG, 1994). USDA and others are starting various education programs to promote the importance of landscape management approaches for reducing pesticide and , more importantly, sediment transport in runoff (USDA, XXX) and EPA OPP EFED is collaborating with Industry to develop specific guidance documentation to standardize approaches of particular value for pesticide issues (EPA, in press). Unfortunately, the existing methodology for modeling pesticide runoff does not yet have proven tools for accurately predicting the impact of runoff mitigation practices.

Where drift entry of pesticide into aquatic systems appears to provide the most cause for ecological concern, different mitigation options apply. The Spray Drift Task Force (SDTF) has developed extensive documentation after conducting a wide ranging and comprehensive program of field studies. The field data has been analyzed to develop a suite of tiered models covering atomization as well as pesticide drift arising from aerial, air-blast and ground hydraulic applications. These validated models provide the necessary tools for calculating the potential impact of various options for mitigating drift including nozzle types, boom configurations, swath offsets, avoidance of stronger winds and volume/pressure combinations. The SDTF has also prepared various guidance materials and training programs to educate applicators in measures for drift reduction (e.g. SDTF, 1998a, 1998b, 1998c and 1998d).

The proposed ECOFRAM Aquatic tiered risk assessment approach permits the examination of the potential impact of very simple mitigation options (e.g. removing certain regions, reduction of rate, numbers and/or frequency of applications) at Tier 2. More sophisticated evaluation and modeling of mitigation options is one of the risk refinement 'tool box" options at Tier 3. At this point, the information developed can be presented to risk managers and interested parties to clearly present the strong and weak points of the various alternatives.

7.2.2. PESTICIDE FACTORS

The two primary chemical factors affecting the fate of field-applied pesticides, which must be understood to determine the most appropriate mitigation option, are persistence and adsorption to soil. Persistence of a pesticide is determined by the following properties;

- Resistance to microbiological and/or chemical breakdown;
- Solubility, which may affect its availability to be broken down or lost with water;
- Vapor pressure which affects potential volatilization losses to the atmosphere.

Breakdown or degradation of a pesticide to its degradation products or metabolites can be a concern if those metabolites also have toxic properties in the environment. Volatilization can be a particular concern when the pesticide is applied to crop residue rather than to the soil where it can be adsorbed. How quickly rainfall washes the pesticide from the crop residue to the soil will affect volatilization and persistence. Volatilized pesticides may be returned to earth with precipitation. As a first approximation, pesticide disappearance from the soil is assumed to be a first-order reaction,

which means the rate of disappearance is proportional to the amount present. The proportionality constant is inversely related to "half-life," which is the time it takes for half the pesticide to disappear.

The degree of soil adsorption is not only important in reducing possible pesticide volatilization, but also it largely determines how pesticides may be transported with excess water from treated fields. Based on their soil adsorption, pesticides can be grouped as (1) strongly adsorbed, lost mostly with sediment; (2) moderately adsorbed, lost mostly with surface runoff water; and (3) weakly or non-adsorbed, lost mostly with percolating water. As a first approximation, the concentration of soil-adsorbed pesticide is assumed to be directly proportional to its concentration in water under equilibrium conditions in a soil-water-chemical mixture. The proportionality constant (defined as K = the concentration in sediment or soil divided by the concentration in water) is often called the partition or adsorption coefficient. The properties of a pesticide primarily determine its potential to be adsorbed to soil. Soil properties (e.g., organic matter content, pH, and clay content) and environmental conditions (e.g., temperature and soil water content) exert a significant effect on both adsorption and pesticide persistence. With conservation tillage, surface crop residue can intercept sprayed pesticides, preventing them from reaching the soil, and altering their fate.

7.2.3. HYDROLOGIC FACTORS

The relative rates of precipitation/irrigation and infiltration into the soil during a rain storm are the primary hydrologic factors affecting agricultural pesticide concentrations and losses by the modes shown in the simple schematic of a portion of the hydrologic cycle (Figure App-1). A third factor would be the timing of the storm relative to pesticide application.

ADD FIGURES HERE

The infiltration rate relative to rainfall intensity or irrigation rate determines the time of initiation and the quantity of runoff (and by subtraction of runoff plus soil water storage from precipitation, determines the quantity of excess water leaching through the root zone; soil factors such as texture and soil condition such as degree of compaction affect infiltration rates; sandy, high-water-table soils may be a special case where all the rainfall infiltrates until their storage capacity is exceeded and runoff begins). Figure App-2 helps illustrate the importance of the time runoff begins as well as the route of infiltration. A fairly thin layer of surface soil, called the "mixing zone," often assumed to be about 1 cm thick, interacts with and releases pesticide to rainfall and overland flow. For moderately and particularly for weakly or non-adsorbed pesticides, the amount of pesticide remaining in the mixing zone decreases with time and the amount of water moving through this zone during a storm. Hence, the pesticide concentration in initial runoff water decreases with delay in runoff; furthermore, the decrease in concentration with time during runoff, once it begins, is primarily a result of leaching of the pesticide from the mixing zone. Reduction in the amount of pesticide in the mixing zone between the time of application and the first storm (and between storms) through degradation, volatilization, and/or movement by diffusion explains why pesticide concentrations and losses (depending on runoff volumes) are generally the greatest in the first runoff event after application and decrease with time during the season. As shown in Figure App-2, if the surface soil becomes saturated, some water may move through preferential flow paths or "macropores" and leach deeper or more

quickly than would be expected if the water had to flow through the whole soil column displacing the water below it. Conversely to increasing pesticide leaching, flow through macropores could reduce leaching if the pesticide is within the soil mass or aggregates, and water moving through macropores bypasses it.

7.2.4. MANAGEMENT FACTORS

Of all the management factors that affect pesticide concentration and losses from the field, the rate of pesticide application is the one factor that has the most direct and usually the greatest effect. The method of pesticide application can also have a major effect on surface runoff if it affects placement relative to the route(s) of infiltration. Timing of pesticide application relative to subsequent storms is another major factor that can affect concentrations and losses. Where possible, choice of pesticide and/or formulation (or additive) used, by affecting pesticide properties, can affect concentration and losses. Cropping sequence in both time and space (e.g., contour strip cropping), by affecting the needs for tillage, soil moisture, and weed and pest control, affects both hydrology and pesticide inputs and, thus, concentrations and losses. Tillage, by affecting erosion rates and hydrology, as well as needs for and method of pesticide application, can potentially affect concentrations and losses. Water management in terms of drainage and irrigation also affect hydrology and thus potential losses.

Structural practices, such as terraces, can reduce field-to-stream transport of pesticides by reducing sediment transport and runoff. Likewise, landscape reconfiguration, including the use of buffer strips and wetlands within watersheds or as riparian zones, can potentially attenuate the amount of pesticides carried with sediment and dissolved in water upon passage through these features.

In the following sections on mitigation practices to reduce pesticide runoff losses from treated fields and to reduce the field-to-stream transport of pesticides that are lost from treated fields, a rough estimate of the likely range of effect for each practice is given. It must be remembered this is just an estimate based on limited research (see Selected References) and/or professional judgement. A better estimate can be made for more specific sets of conditions. Computer simulation models do exist which can predict, with varying degrees of accuracy, pesticide fate and loss for any given set of conditions and practices.

7.2.5. FIELD LOSS REDUCTION

7.2.5.1. RATE/FORMULATION

Lower rate feasibility - Rate of pesticide application is one of the dominant factors affecting pesticide runoff losses. Pesticide runoff loss with sediment and water is roughly proportional to the amount of pesticide in the thin mixing zone at the soil surface and/or on crop residue or foliage. For example, if the amount applied is reduced by a factor of two, loss should be reduced by a factor of two. If this relationship deviates from linearity, losses should be reduced even more than the percentage the rate is reduced because the degree of soil adsorption usually increases as concentration (or the amount

applied) decreases. The feasibility of lower rates is dependent on both the amount needed to achieve the level of pest control desired and the accuracy of the application method. Realistically, rate reduction beyond 50% is not likely.

A reduced application rate can reduce other environmental losses (i.e. to groundwater and the atmosphere) and potential adverse biological effects as well as reduce energy and economic inputs. However, reduced application rate can increase the risk of pest escapes and economic losses.

The factors of weather, hydrology, soil, and chemical properties should not greatly influence the predicted effect of rate reduction.

Partial substitution - Partial substitution of the pesticide of concern by another pesticide or by other means of pest control can reduce the amount applied. The effect is the same as above where the predicted effect on pesticide runoff loss with sediment and water is roughly proportional to the amount of substitution and therefore the amount of pesticide in the thin mixing zone at the soil surface and/or on crop residue or foliage. With substitution, it is probably feasible to reduce the rate beyond that of rate reduction alone, possibly up to 80%.

Again, a reduced application rate can reduce other environmental losses (i.e. to groundwater and the atmosphere) and potential adverse biological effects as well as reduce energy and economic inputs, plus there is the potential for improved pest control with a mixture of pesticides or control methods. At the same time, there is the risk of reduced pest control with partial substitution; also, if one pesticide is substituted for another, the potential environmental impact of the substitute may be greater because of increased losses and/or greater toxicity.

If the combination of weather, hydrology, soil, and chemical factors favor greater loss of a substitute pesticide, the predicted benefit of this practice would be lessened.

Partial treatment - Partial treatment either on a field basis or within a row, e.g., band versus broadcast, or directed spray versus an over-the-top application, can effectively reduce the rate of pesticide application, and again pesticide runoff loss with sediment and water is roughly proportional to the amount of pesticide in the thin mixing zone at the soil surface and/or on crop residue or foliage. Where a pesticide is applied in a band over only a portion of the row-width, a 75% reduction is probably a realistic maximum compared to a broadcast application where the whole area is treated. "Spot treatment" or directed spray may allow greater reductions.

Again, a reduced application rate can reduce other environmental losses (i.e. to groundwater and the atmosphere) and potential adverse biological effects as well as reduce energy and economic inputs. However, a reduced application rate can increase the risk of pest escapes and economic losses, plus the untreated area generally requires alternative treatment; e.g., timely mechanical cultivation for weed control, which may increase the potential for runoff and soil erosion.

The potential for alternative treatment will be influenced by weather, hydrology, and soil factors that affect trafficability in the case of ground-applied treatments.

Choice of formulation - If different formulations are available, a formulation that alters soil adsorption and solubility can affect pesticide runoff losses. The degree of reduction will depend on the major transport mechanism for a certain pesticide in relation to the differences in its adsorption and solubility properties for the different formulations. Encapsulation represents a type of formulation which can directly influence the availability of a product for either leaching or runoff. Runoff loss reduction up to 50% is probably achieveable for some specific formulations, but measurements need to be made to verify their effect.

Other environmental losses may also be reduced. However, it is also possible that other environmental losses may be increased and pest control may be reduced.

Weather, hydrology, and soil factors are important. Where they combine for good erosion control, increased soil adsorption is a positive factor; where these factors combine for good infiltration, increased solubility should reduce surface runoff losses; however, leaching losses may be increased.

Soil erodibility special restrictions - Rate restrictions tied to highly erodible land unprotected by crop residue have the potential to reduce runoff losses. This targeting to areas where soil erosion is expected to be severe, where application rates may be restricted by some percentage, e.g., 25%, should reduce pesticide runoff losses. In this example the reduction would be at least 25% if maximum label rates were being used.

By targeting erodible areas that are likely more susceptible to both runoff and erosion, this restriction may be more beneficial than an area wide blanket restriction, especially where a negative effect in terms of greater risk from pests results from the reduced rate. Use of erosion control measures may also be promoted by this approach. However, a reduced application rate can increase the risk of pest escapes and economic losses. Frequently, the pesticide requirement for highly erodible soils may be greater than for other soils because pesticides are used for weed control in lieu of tillage. Selection of pesticide(s) becomes more critical for such soils.

The success of this targeting is related to weather, hydrology, and soil factors. A final factor (i.e. pesticide properties) which is important is that soil adsorption determines the potential for transport with eroded soil and the feasibility for this approach to be effective.

7.2.5.2. METHOD AND TIMING OF APPLICATION

Soil incorporation - Mechanical incorporation, e.g., PPI or pre-plant incorporated, or incorporation with irrigation, by reducing the amount of pesticide in the thin mixing zone at the soil surface and/or on crop residue or foliage, reduces the

interaction with and transfer of pesticide to runoff water and thereby reduces runoff loss. Reductions in the range of 25-70% are possible.

With incorporation, other environmental losses may also be reduced and pest control may be improved. However, mechanical incorporation with tillage may reduce soil protecting crop residue with conservation tillage and pest control may be reduced. Leaching losses may be increased; however, generally surface runoff losses are a bigger environmental concern than leaching losses.

The feasibility of using incorporation as a mitigation practice depends on the pesticide mode of action relative to position in the soil profile, and the potential for incorporation with irrigation depends on sufficient infiltration and solubility (in conjunction with limited soil adsorption) of the pesticide. The use or availability of adequate irrigation can also be crop specific.

Timing relative to expected/pending storms - For some situations and certain pesticides, a choice of timing of pesticide application(s) is possible, e.g., pre-emergence versus post-emergence. Given that the first storm after pesticide application will result in the highest pesticide concentrations in runoff, and that concentrations will decrease with time both during and between runoff events, increasing the expected time interval between application and intense storms causing significant runoff could reduce pesticide runoff losses in-part because intervening smaller, more gentle rains may move pesticide down out of the thin mixing zone at the soil surface. An additional positive effect is possible with post-emergence application of herbicides where the weeds that are allowed to grow before treatment provide some cover for the soil to reduce runoff and erosion similar to crop residue. Reductions up to 50% may be possible.

Other advantages include possibly extending the time for other operations and possible improved pest control. However, poor timing may also reduce pest control or increase other environmental losses.

The historical timing of runoff producing storms along with the mode of action and persistence of the pesticide will determine the feasibility of this practice (dependent on weather, hydrology, soil, and pesticide factors).

7.2.5.3. TILLAGE SYSTEMS

No-till - The increasingly common practice of no-till involves only minor soil disturbance at planting and leaves all the crop residue from the previous year on the soil surface. Erosion and sediment bound pesticides are usually reduced 50 to 90% with no-till. Runoff volume, at least on a growing season or annual basis, is generally less than that from conventional moldboard plow tillage, and while pesticide concentrations in no-till runoff may be higher, usually that total quantity of pesticide in runoff from no-till is less, sometimes much less, than from conventional tillage. The expected reduction in pesticide loss would be in the 0 to 90% range.

The other advantages, besides erosion control, include reduced time and energy inputs with tillage. However, use of no-till may

- require additional pesticide use (not an increase in rate of those used, but another product such as a "burn-down" herbicide);
- make it impossible to incorporate pesticides by conventional means, therefore, eliminating possible use of certan pesticides;
- increase runoff and volatilization of pesticides under conditions where they are intercepted by surface crop residue;
- increase runoff volume(s) from the first storm(s) after chemical application relative to soil loosened by tillage;
- and/or result in more macropores at the soil surface which may enhance deeper leaching of pesticides (i.e. pesticides are detected more quickly and at deeper depths than expected based on their adsorption to soil).

However, if no-till results in use of a different "mix" of pesticides, for example lower-rate, post-emergence herbicides, the total pesticide runoff loss may be decreased depending on individual pesticide properties. In addition, the strong soil adsorption properties of the burndown herbicides mostly used, paraquat and glyphosate, result in little environmental concern for runoff losses with the no-till system.

When soil (including slope) and weather conditions are conducive to erosion, and for strongly adsorbed pesticides, no-till has its greatest potential for reducing pesticide runoff.

Conservation tillage - Conservation tillage (i.e., reduced tillage or mulch tillage) involves some tillage but less than that of inversion moldboard plow tillage. To qualify as conservation tillage, at least 30% of the soil surface must be covered with crop residue after planting. The reduction in runoff and erosion expected with conservation tillage reduces the carriers and therefore runoff losses of pesticides. The likely range of reduction in runoff is 0 to 75%. Ridge tillage may be a special case where in addition to reduced pesticide losses from reduced runoff and erosion, reduced herbicide use through banding (feasible and generally done because of latter ridge rebuilding cultivation) further reduces losses.

Advantages, besides erosion control, include reduced time and energy inputs with tillage. However as with no-till, conservation tillage may require additional pesticide use (possibly, a "burn-down" herbicide); reduce the ability to incorporate pesticides by conventional means, therefore, may eliminate possible use of more "environmentally friendly" pesticides; under some conditions, increase runoff and volatilization of pesticides intercepted by surface residue; and/or result in more macropores at the soil surface possibly enhancing deeper leaching of pesticides, but to a much lesser degree than no-till.

This practice has the most potential for reducing runoff when soil (including slope) and weather conditions are conducive to erosion, and for strongly adsorbed pesticides.

7.2.5.4. WATER MANAGEMENT

Subsurface drainage - Artificial subsurface drainage, mainly by removing water from the soil profile between rainfall events, using drainage tubes and ditches, lowers the soil antecedent moisture content and somewhat increases infiltration during a rainfall event. Therefore, subsurface drainage delays and reduces the volume of surface runoff, which reduces both pesticide concentrations and the volume of runoff. Losses might be reduced from 0 to 50% with subsurface drainage, versus without, in areas that subsurface drainage is useful.

Other advantages are that subsurface drainage makes possible more timely field operations and provides for better soil moisture conditions for crop growth. However, increased infiltration may increase pesticide leaching (although subsurface drainage water intercepted by drainage tubes and returned to a surface water resource, with the exception of nitrate, will have a lower chemical concentration then surface runoff direct from a treated field).

Drainage is only needed and/or used in areas with potential for water-logged soils; the beneficial effect of subsurface drainage in reducing pesticide runoff losses is generally greater for less strongly adsorbed pesticides.

Avoid surface sealing/compaction - Surface sealing of unprotected soil and compaction due to traffic can reduce infiltration rates. Thus, surface sealing and/or compaction decreases the interval between initiation of rainfall and initiation of runoff, and also increases the rate, and therefore the volume, of runoff. Since pesticide concentrations decrease with time during a runoff event (as pesticide is leached down out of the thin mixing zone at the soil surface), more runoff, particularly early in the rainfall event when concentrations are higher, results in greater pesticide loss. Protecting the soil surface with living or dead crop residue absorbs rainfall energy and reduces sealing. Reduced or controlled traffic can reduce compaction.

Other advantages to controlling surface sealing/compaction include more infiltration and better soil aeration which generally means better growing conditions for crops and likely more microbiological activity. There are usually no disadvantages.

The problem of surface sealing/compaction is more important on soils with good internal drainage in areas with excess precipitation. Potential problems associated with sealing are worse for less strongly adsorbed pesticides.

Irrigation - Irrigation management practices can have a significant affect on the quantity and quality of water leaving the field associated with runoff. Specific practices which should be considered include:

> **Surge Flow,** as an application method of pulses used in furrow irrigation. The goal is to increase application uniformity along the furrow and reduce the amount of induced runoff, erosion, and percolation (and therefore, both runoff and leaching pesticide losses - this practice usually reduces total water input).

Low-Energy Precision Application (LEPA), as a type of center pivot or linear irrigation system which increases application efficiency and reduces the amount of excess water which is applied. This will minimize the potential for runoff.

Drip or Microjet, or other precision methods for irrigating which may be triggered by soil moisture monitoring can reduce the amount of excess water that is applied thus reducing runoff, erosion and percolation losses.

Furrow Diking, the practice of mechanically making small dikes within the furrows to pond water thus eliminating (in some areas it is illegal for irrigation tailwaters to leave the site) or reducing runoff and erosion.

High Volume Traveling or Overhead Guns, apply large volumes of water in short time. Where runoff is likely, more frequent applications of shorter duration will minimize the potential for runoff.

Reuse Pits, the practice of collecting irrigation tailwaters for reuse to eliminate runoff leaving the field.

Chemigation - On very permeable or very impermeable soils with high slope, the probability of leaching or runoff, respectively, is high. If this method of application is considered for registration, physical properties of the product and soil type will determine the mitigation options.

7.2.5.5. CROPPING

Strip cropping - In strip cropping, two different crops are planted in alternate strips, or three or more crops are planted sequentially in strips, usually on the contour or at least across the slope (or perpendicular to the direction of prevailing winds in areas where wind erosion is a concern). The width of strips range from a few meters up to 20 meters or more. The potential for strip cropping to reduce pesticide runoff losses results from possibly decreasing pesticide use, if one of the crops does not require the pesticide of concern, and decreased pesticide transport where the untreated crop could act as a buffer strip (discussed later) and/or reduce erosion, runoff and sediment transport, particularly if it is a close-grown crop acting like a vegetated filter strip (also discussed later). The potential advantage of reducing pesticide runoff losses is likely greater for more strongly adsorbed pesticides. With a 50% reduction in application, with equal alternating areas of treated and untreated crops, losses could be reduced up to about 75% over a monoculture treated crop. The feasibility of strip cropping is dependent on soils and slopes.

Other advantages include reductions in other environmental pesticide losses as well as reduced inputs and reduced erosion. Crop yields in some cases may be increased as well. Possible disadvantages include more management time spent keeping track of the locations of the strips and care in use of some pesticides on one crop if the adjacent crop is susceptible to pesticide damage. In addition, if narrow strip cropping is used, the beneficial rotation effect may be reduced

if pests move from one strip to another. For example, corn rootworm adults could move from soybean strips (rotated from corn the previous year in a corn soybean strip-cropped field) requiring an insecticide treatment.

Crop rotation - The use of crop rotation, e.g., corn following soybeans, has considerable potential to reduce pesticide runoff losses by reducing or eliminating the need for pesticides. For the example of corn following soybeans, the need for a root-worm insecticide is much reduced over that for continuously cropped corn. There may be a beneficial effect of reduction in soil and water losses as well where a rotation into a sod crop will reduce erosion and runoff while that crop is being grown, as well as have a carry-over effect to at least the first year out of sod. With total elimination of pesticide use, loss would be reduced 100%.

In addition to reduced pesticide losses, crop rotation often has the advantage of increased yields, with all other inputs being equal. One disadvantage is that economics due to needs, or lack of needs, for certain crops, or farm programs, do not allow the flexibility required to rotate crops (also true for strip cropping).

In addition to economics, including government incentives, the feasibility of crop rotations is determined by climate and soil factors.

7.2.6. FIELD-TO-STREAM TRANSPORT REDUCTION

7.2.6.1. STRUCTURES

Terraces/Detention Ponds - Terraces and detention ponds are used as a method of erosion control by constructing broad channels or dams across the slope of rolling land. The major type of terrace of economic importance used in the U.S. is the broad-base terrace. In constructing the channel, an embankment is usually constructed either to allow water to slowly drain down a more nearly level channel (graded terraces) or to dam the water and force infiltration (level terraces) or provide an outlet from the detention pond (tile-outlet terraces). Because of construction costs and the desire to avoid crop damage, most terraces built today are of the tile-outlet (or detention pond) type. As such, they are designed to release the runoff (e.g., about 5 cm in Iowa) from a 10-year 24-hour return interval storm over a 48-hour period through an underground tile system. In that period, infiltration might reduce runoff some, but the major effect is the reduction of sediment load in the outflow (usually by 80 to 95%) by deposition in the pond or terrace basin. Thus, the predicted effect of the terraces on pesticides transported with sediment and runoff would likely range from 5 to 90% reduction, depending on how much of the pesticide is adsorbed or transported with sediment.

Other advantages of terraces are obviously related to the effects of reduced erosion on the land and reduced sediment (and nutrient) transport to water resources. In addition, depending upon the water retention time of the ponds and the route of degradation, detention ponds may also result in greater degradation of the pesticide. This may be especially true if pesticides undergo rapid hydrolysis.

The concerns with terraces are their initial and maintenance costs, their effect on the "farmability" of the land, and the land they may take out of production (with steep slopes, push-up terraces are often constructed wherein the steep outer face is left in grass).

The effectiveness of terraces on the reduction of field-to-stream transport of pesticides is closely tied to the soil adsorption properties of the pesticide of concern. For strongly adsorbed pesticides the effectiveness will be much greater than for weakly or moderately adsorbed pesticides. For the particular case of tile-outlet terraces and a weakly or moderately adsorbed pesticide, like atrazine, there is concern that direct transport to a stream from the field through underground tile eliminates any possibility of attenuation in the transport process. The atrazine label was rewritten in 1993 to require a 66' buffer around either the inlet or the outlet to help alleviate this concern.

Constructed Wetlands - Constructed wetlands are designed to include saturated substrates, emergent and submergent vegetation, animal life, and water that simulate natural wetlands. Constructed wetlands have the potential for removal of pesticides dissolved in water and associated with sediment in surface runoff. In general, wetlands are expected to be effective in removal of suspended particles and pesticide attached to them, and not nearly so effective in removing pesticides dissolved in water. However, little quantitative information is currently available to better assess these potentials. Of particular importance will likely be the detention or travel time for flow through these impoundments or wetlands. The affect of wetlands on pesticide runoff losses might range between 0 and 90%.

Other advantages of constructed wetlands might be nutrient (particularly nitrate) removal from agricultural drainage and possibly the use of the wetlands as a source of surface water for some needs. Concerns include the cost of construction and maintenance and land taken out of production.

Pesticide properties, particularly soil adsorption and degradation modes, will likely be major factors in determining how effective wetlands can be in the reduction of field-to-stream transport of pesticides.

7.2.6.2. LANDSCAPE RECONFIGURATION

Buffer strips - A buffer strip is an area on a field border that is not treated with pesticide. It can be an area that is fallow, planted to the same crop as that within the field, or planted to some other crop (if planted to grass or some other close-grown forage crop, it will be considered a vegetated filter strip, as discussed later). The purpose of the buffer strip is generally three-fold; first, it can physically separate a resource of concern, e.g., a stream, from a treated area; second, it reduces the amount of pesticide used in the watershed (however, usually by only a few %); and third, if overland flow from the treated area passes over the untreated area, there is the potential for attenuation of the concentration of pesticide carried in the surface runoff by adsorption or deposition. Overall, the expected reduction in pesticide transport would likely range between 5 and 40%.

Other advantages would include reduced risk to the groundwater and the atmosphere with reduced pesticide application. Concerns for efficiency of the practice would involve relative areas of the contributing watershed and the buffer strip (the larger the ratio, the lower the efficiency) and the path of water flowing through the buffer strip (the more concentrated the flow, the less interaction with materials in the buffer strip and the less the attenuation). Economic disadvantages could come with decreased pest control (for the case where the buffer strip is in the same crop), decreased crop area (for the case where the buffer strip is kept fallow), and decreased crop production (for the case where the buffer strip is in another less productive crop, or one susceptible to the pesticide in runoff from the treated area).

Other major factors influencing the predicted effect include how strongly a pesticide is adsorbed. Transport of less soluble, more strongly adsorbed pesticides will be reduced the most by sediment deposition and/or runoff interaction with in-place soil. In a similar vein, a combination of climate, hydrologic, and soil factors resulting in more erosion could make this practice more effective.

Mixing/Loading/Handling Set-Backs - These set-backs are distances that must be maintained from a point of mixing/loading/handling to a water resource of concern such as a stream, lake, reservoir, or groundwater well. As such, they act in very much the same manner as a buffer strip, except they are protecting against a "point-source" type of contamination. With the exception of some inconvenience in certain instances, there is little cost to this method of potential prevention of catastrophic results from spills.

Vegetative Filter Strip - A vegetative filter strip is a buffer strip planted to grass or some other close-grown plants, normally of a forage type (but might include shrubs or even trees). As with the buffer strip, the purpose of the vegetated filter strip is to remove pesticides in solution or associated with sediment from runoff by filtration, deposition, infiltration, adsorption, decomposition, and/or volatilization. By both slowing runoff velocity and providing more biological surface area (living and dead) for interaction, the vegetative filter strip is expected to be somewhat more efficient than simple buffer areas for reducing the field-to-stream transport of pesticides, likely in the range of 10 to 60%.

Other advantages and concerns are similar to those discussed for buffer strips. Specifically, to be effective, runoff must not concentrate or channelize, but ideally passes through the vegetation in nearly uniform sheet flow. The vegetation must be erosion and pesticide resistant. The lower the ratio of contributing watershed to filter strip area, the longer the content time and the greater removal efficiency.

Removal efficiency depends on pesticide properties, with less soluble more strongly adsorbed pesticides likely to be more affected. In addition, as with buffer strips, climate, hydrologic, and soil factors resulting in more erosion could make this practice more effective.

Grassed-Waterways - Grassed waterways are in effect vegetative filter strips with a somewhat different orientation relative to inflow and outflow directions and somewhat different purpose. Grassed waterways are generally designed to collect overland flow perpendicular to their long dimension and then transport it, after a 90° turn, down gradient to a drainage outlet without erosion within the waterway. As such, the grassed waterway acts as a vegetated filter strip during the initial entry of runoff into it, with decreasing function as a filter as flow concentrates in the lower elevation of the channel or waterway. Because of generally much greater ratios of watershed to grassed areas, the likely range of field-to-stream transport reduction is 2 to 40%, being less than either buffer strips or vegetative filter strips.

Other advantages are the same as those for buffer or filter strips including erosion control. The concerns are also similar but with a particular concern for sediment deposition in the outer edges of the grassed waterway causing a rise in elevation resulting in a "dam". This dam prevents water from entering the waterway and causing concentrated flow and erosion in the unprotected soil bordering the waterway. Therefore, erosion control in the field above the waterway is necessary.

7.2.7. SUMMARY OF RUNOFF MITIGATION OPTIONS

Table App-1 provides a summary of all of the mitigation options discussed for runoff and provides the range of reductions expected and specific comments associated with each option. An important point to be remembered is that within these categories, the percent reductions are not necessarily additive. Implementing one option can possibly increase or decrease the percent reduction which may be obtained for implementing other options.

Table App-1. Mitigation Practices Summary Guide* for Pesticide Runoff Losses to Surface Waters

Practice	Potential Reduction of Surface RO Transport**		Comments
	strongly-adsorbd***	weak-/mod. adsorbed	
Field Loss Reduction: lower application rate	0-50%	0-50%	loss reduction should be > rate reduction; e.g., at 3/4 rate, loss should be reduced at least 25%.
partial substitution	0-80%	0-80%	environmental concerns may also exist for pesticide(s) used as substitute(s); upper range goes to 100% w. total elimination of use.
partial treatment	0-75%	0-75%	e.g., herbicide banding; loss or reduction in pest control and/or alternative treatments must be considered.
formulation	0-25%	0-50%	potential effects need to be documented in field, laboratory, and/or modeling studies.
soil erodibility/special restrictions	0-50%	0-25%	restrictions should be targeted to more strongly adsorbed pesticides used on highly erodible land.
soil incorporation	25-50%	35-70%	mechanical incorporation reduces the amount in surface mixing zone; more important for solution losses.
application timing	0-50%	0-50%	loss decreases with time between application and storm-runoff; probabilistic weather information could be used.
no-till	50-90%	0-40%	erosion control by 90% feasible; runoff volume reduction much less; herbicide wash off from residue may increase concns. in runoff.
conservation-tillage	40-75%	0-50%	erosion control less than for no-till; runoff reduction for first storm after application more reliable than for no-till.
subsurface drainage	0-20%	0-50%	subsurface drainage can reduce antecedent moisture and therefore runoff and erosion; infiltration can reduce surface concentrations for less strongly adsorbed pesticides.
avoid sealing/compaction	0-20%	0-50%	very similar to the effects of infiltration differences caused by subsurface drainage.
irrigation	0-25%	0-50%	improved management practices reduce RO./ erosion; greater infiltration could reduce concns for less strongly adsorbed pesticides.
strip cropping	0-75%	0-60%	possible combination of reduced use (untreated strips), plus buffer effect (sediment deposition on contour).
crop rotation	0-90%	0-90%	pesticide needed could be much reduced in some rotations.
Field/Stream Transp Redn: terrace/ detention ponds	20-90%	5-20%	sediment transport reduction; infiltration in basins could reduce runoff volumes and therefore losses.
constructed wetlands	20-90%	0-50%	this is a practice for which little quantitative information exists.
buffer strips	10-40%	10-25%	relative area untreated to total area important; assumed to be < 10%.
set-backs	0-50%	0-25%	protection from spills (point-source) during mixing/loading/handling.
vegetative filter strip	20-60%	10-40%	to work runoff must pass through at nearly uniform depth; removal more efficient for lower contributing area-filter strip ratio.
grassed waterways	10-40%	2-10%	similar to filter strip, but likely with higher contributing area-filter strip ratio; concentrated flow reduces effectiveness.

* The rough estimates of the likely range of effects for each practice are based on limited research and/or professional judgement.

** It should be possible to predict a more narrow range for potential reduction using mathematical modeling for a specific pesticide and a specific set of soil and environmental conditions.

*** Partition coefficient, or K, typically > 100.

7.3. Appendix 3-1. The National Water-Quality Assessment Program (NAWQA)

The National Water-Quality Assessment Program of the U.S. Geological Survey is designed to assess the status of and trends in the quality of the Nation's ground- and surface water resources and to link the status and trends with an understanding of the natural and human factors that affect the quality of water. The study design balances the unique assessment requirements of individual hydrologic systems with a nationally consistent design structure that incorporates a multi-scale, interdisciplinary approach. The building blocks of the program are Study-Unit Investigations in 60 major hydrologic basins (Study Units) of the Nation. The Occurrence and Distribution Assessment is the largest and most important component of the first intensive study phase in each Study Unit. A second important component of the study design is trends assessment.

The goal of the Occurrence and Distribution Assessment is to characterize, in a nationally consistent manner, the broad-scale geographic and seasonal distributions of water-quality conditions in relation to major contaminant sources and background conditions. The national study design for surface water focuses on water-quality conditions in streams, using the following interrelated components:

- Water-Column Studies assess physical and chemical characteristics, which include suspended sediment, major ions and metals, nutrients, organic carbon, and dissolved pesticides, and their relation to hydrologic conditions, sources, and transport.
- Bed-Sediment and Tissue Studies assess trace elements and hydrophobic organic contaminants.
- Ecological Studies evaluate the relations among physical, chemical, and biological characteristics of streams.

Sampling designs for all three components rely on coordinated sampling of varying intensity and scope at Integrator Sites and Indicator Sites. Integrator Sites are chosen to represent water-quality conditions of streams within large basins that are often affected by complex combinations of land-use settings. Indicator Sites are chosen to represent water-quality conditions of streams associated with specific individual Environmental Settings.

The national study design for groundwater focuses on water- quality conditions in major aquifers, with emphasis on recently recharged groundwater associated with present and recent human activities, by using the following components:

- Study-Unit Surveys assess the water quality of the major aquifer systems of each Study Unit by sampling primarily existing wells.
- Land-Use Studies use observation wells and selected existing wells to assess the quality of recently recharged shallow groundwater associated with regionally extensive combinations of land use and hydrogeologic conditions.
- Flowpath Studies use transects and groups of clustered, multilevel observation wells to examine specific relations among land-use practices, groundwater flow, and contaminant occurrence and transport and interactions between ground and surface water.

In selected locations, groundwater studies are co-designed with stream water-quality studies to investigate interactions between ground and surface waters. Overall, the broad range of coordinated spatial and temporal strategies employed for surface water and groundwater assessments is designed to describe the most important aspects of water quality in a consistent manner for the wide range of hydrologic environments of the Nation.

The primary objectives of the trends are to analyze past changes in water quality and to identify, describe, and explain (as possible) current and future changes and trends in water quality. The basis of the trend design of NAWQA is the characterization of the temporally-fine but spatially-coarse, less-intensive study phase as a subset of the temporally-coarse but spatially-fine intensive study phase in each Study Unit. One data attribute necessary for a reasonable trend monitoring network is that sampling intervals are fixed rather than event-based. The surface water and groundwater quality trends site network is a subset of the intensive study phase sites. The trends network is a subset and selectively represent unique national environmental settings.

7.4. Appendix 3-2: Progress and Plans of the Mid Continent Herbicide Project

For more details see
http://wwwrcolka.cr.usgs.gov/midconherb/index.html) or http://wwwrcolka.cr.usgs.gov/midconherb/midcon.pubs.html

The occurrence, transport, and fate of agricultural chemicals is being studied in a 12-State area in the upper Midwest as part of the U.S. Geological Survey Midcontinent Herbicide Project. Scientists are identifying factors that affect dispersal of these chemicals in surface and groundwaters from point of application and are evaluating the resulting effects in small streams and large rivers, at reservoir outfalls, in shallow groundwater, and in precipitation. The goal is to provide the general scientific basis needed to develop agricultural management practices that protect the quality of the region's water resources.

Status of Investigations

Surface Water

Regional reconnaissance to determine occurrence and temporal distribution of herbicides and nitrate in about 150 midwestern streams over a 10-state area (1989-90).

Temporal distribution of herbicides, metabolites, and nitrate in selected midwestern streams (1990-92).

Occurrence, distribution and transport of herbicides, insecticides, nitrogen, and phosphorus in the Mississippi River and several major tributaries (1991-93).

Occurrence and persistence of herbicides in the outflow from 76 selected midwestern lakes and reservoirs (1992-94).

Occurrence and transport of agricultural chemicals in the Mississippi River during the 1993 flood.

Effect of changes in herbicide usage on concentrations in midwestern streams (1994-95).

Longitudinal profiles of herbicides in the Mississippi River main stem, New Orleans, LA to St. Paul, MN (1990-95).

Groundwater Regional reconnaissance to determine the occurrence, seasonal distribution, and geographic distribution of herbicides and nitrate in near-surface unconsolidated and bedrock aquifers in parts of 12 midwestern states (1990-95).

Examine relation between herbicide, insecticide, and nitrate occurrence in groundwater and relative age of water using tritium. Determine occurrence of volatile organic compounds and surfactants in selected near-surface aquifers(1992-93).

Examine effects of the 1993 flood on water quality in unconsolidated rock aquifers (1993-94).

Relate land use, topography, and generalized flow system to agricultural chemicals in groundwater (1993-95).

Precipitation Regional assessment of the occurrence, long range transport, and deposition of herbicides in precipitation in 23 Midwestern and Northeastern states. Weekly samples of precipitation from 81 NADP/NTN sites for 19 months (1990-93).

Research on the transport of herbicides into a pristine watershed (Isle Royale National Park in Lake Superior) (1992-94).

Characterize pesticides in atmospheric vapors, particles, and rain water in the Mississippi River basin - 1995-96.

Significant Findings

Atrazine is, in general, the most frequently detected compound followed by ESA (an alachlor metabolite), deethylatrazine (an atrazine metabolite), metolachlor, cyanazine, cyanazine amide (a cyanazine metabolite), and alachlor.

Herbicide concentrations in surface water and rainfall are highly seasonal, with the highest concentrations occurring during storm runoff within a 1-3 month period following application to cropland. This phenomenon has been termed the "spring flush".

Herbicide concentrations in small to medium sized basins (100 to 5000 square miles) can exceed 50 ug/L for short periods (a few days) during storm runoff in May and June; concentrations in large rivers such as the Missouri, Ohio, and Mississippi can exceed 3 ug/L for periods of several weeks.

Peak herbicide concentrations, in general, are inversely related to basin size. Maximum concentrations decrease as basins size increases because as basins become larger a smaller fraction of the basin tends to be affected by runoff from individual storms. Also, as basin size increases, the percentage of cropland tends to decrease. Both of these factors result in dilution of the high concentrations in runoff from small predominantly agricultural basins.

Reservoirs can collect and store the spring flush of herbicides. This attenuates herbicide concentrations by lowering peak concentrations and increasing concentrations after the spring flush period. Reservoirs with long hydraulic residence times can maintain elevated herbicide concentrations in the reservoir and in reservoir releases year round. This can potentially affect use of the water for public supplies.

Concentrations of atrazine and cyanazine can exceed health-based limits for drinking water for several weeks in both small streams and large rivers. However, since drinking water regulations pertain to annual average concentrations health based limits are rarely, if ever, exceeded in large rivers. Annual average concentrations in small streams and in some reservoirs can exceed health based limits.

The adequacy of compliance monitoring requirements for herbicides in drinking water was tested using Monte Carlo techniques to simulate annual mean concentrations from daily concentration time series constructed for 10 midwestern rivers. The quarterly sampling required by the Safe Drinking Water Act generally underestimates annual mean herbicide concentrations. Bimonthly and monthly sampling more accurately estimated annual mean concentrations than did quarterly or annual sampling. The accuracy of estimates for all sampling schemes decreased as drainage basin size decreased. Measurable levels of herbicides (greater than 0.05 ug/L) occur year round in most midwestern streams and the lower reaches of the Mississippi River due to releases from reservoirs, aquifers, and leaching of more persistent herbicides, such as atrazine, from soils.

The mass transport of herbicides in streams varies from year to year and is highly dependent on climatic conditions during the spring and summer. A larger mass of herbicides is transported in wet years than in dry years. The total mass of atrazine discharged from the Mississippi River basin during four years (1991-94) ranged from about 1% of the total amount applied during 1992, a dry year, to about 3.5% during 1993, a record flood year.

Annual transport of herbicides is strongly correlated with herbicide use in medium to large sized basins (500 - 1,000,000 square miles).

Metabolites of atrazine, alachlor, and cyanazine constitute a significant fraction of the total herbicide mass in streams, reservoirs, rainfall, and groundwater. On the average, these metabolites constitute about 50% of the herbicide mass in reservoirs. Additional metabolites not presently measured because of the lack of suitable analytical methods could increase the percentage of metabolites to well above 50%.

Alluvial aquifers can become contaminated with herbicides during the spring flush period. Bank storage of water from streams containing high concentrations of herbicides can affect portions of the aquifer near the streams. Inundation of the flood plain and subsequent recharge by herbicide contaminated stream water can also cause contamination of these aquifers.

ESA, an ethane sulfonic acid metabolite of alachlor, is a major herbicide compound in streams, reservoirs and groundwater in the Midwest. Concentrations of ESA are often many times to an order of magnitude higher than the parent compound, alachlor. ESA, which probably exists as an organic anion, appears to be very stable and very mobile in the soil and water environment. Currently, ESA is believed to have low toxicity.

Deisopropylatrazine was shown to be a degradation product of cyanazine. It is also a degradation product of atrazine and simazine. Other cyanazine degradation products which were shown to occur in surface water in the Midwest include cyanazine amide, deethylcyanazine and deethylcyanazine amide.

Herbicides are detected in rainfall throughout the midwest and northeastern United States during April through July. Herbicides get into the atmosphere by volatilization (evaporation) from the land surface and subsequent transport by air currents and wind. Rainfall flushes these compounds from the atmosphere.

There is evidence for photodegradation of atrazine in the atmosphere to deethylatrazine.

The mass of atrazine and alachlor deposited annually in rainfall represents less than 1% of the mass of these compounds applied to cropland. This is believed to be considerably less than the amount of atrazine and alachlor that actually volatilize into the atmosphere each year.

Based on current drinking water regulations, nitrate is a greater drinking water problem in groundwater than herbicides. About 7% of the samples from this study exceeded the nitrate MCL of 10 mg/L, whereas only about 0.1% of the samples exceeded health limits for herbicides.

Herbicides are commonly detected in groundwater but detections are less frequent and concentrations are lower than in surface water.

Six of the seven most frequently detected pesticide compounds (herbicides and insecticides) in groundwater were metabolites. Metabolites were detected more frequently and generally in higher concentrations than the parent compounds.

Unlike surface water, herbicide concentrations in groundwater show little seasonal variation.

The total mass of herbicides transported annually in surface water and rainwater, and to groundwater represents only a small fraction, probably less than 5%, of the amounts applied annually.

Immunoassay can be a low cost screening tool for several herbicides in water, including atrazine, cyanazine, and metolachlor.

Concentrations of herbicides and nitrate in surface water can be modeled using statistical techniques like multiple linear regression and logistic regression. Geographic information systems are used to quantify values for potential predicting variables within the drainage basins associated with sampling locations. Important predicting variables in these models include: herbicide or nitrogen use, expenditures for herbicides or fertilizers, numbers of livestock, percentages of drainage basin in harvested cropland or particular crops, soil hydrologic group, and mean annual temperature and precipitation.

Selected References

Aga, D.S., Thurman, E.M., Yockel, M.E., and Williams, T.D., 1996, Identification of a new metabolite of metolachlor in soil: Environmental Science & Technology, v. 30, no. 1, p. 592-597.

Aga, D.S., and Thurman, E.M., 1995, Application of solid-phase extraction (SPE) for ultratrace analysis of herbicides in water and soil by enzyme- linked immunosorbent assay in New Frontiers in Agrochemical Immunoassay, Kurtz, D.A., Skerrett, J.H., and Stanker, L., eds., AOAC International, p. 123-136.

Aga, D.S., Thurman, E.M., and Pomes, M.L., 1994, Determination of alachlor and its sulfonic acid metabolite in water by solid-phase extraction and enzyme-linked immunosorbent assay: Analytical Chemistry, v. 66, p. 1495-99.

Aga, D.S., and Thurman, E.M., 1993, Coupling solid-phase extraction (SPE) and enzyme-linked immunosorbent assay (ELISA) for ultratrace analysis of herbicides in pristine water: Analytical Chemistry, v. 65, p. 2894- 2898.

Antweiler, R.C., Goolsby, D.A., and Taylor, H.E., 1996, Nutrients in the Mississippi River, in Contaminants in the Mississippi River, Meade, R.H., ed., U.S. Geological Survey Circular 1133, p. 73-85.

Battaglin, W.A., and Goolsby, D.A., 1997, Statistical modeling of agricultural chemical occurrence in midwestern rivers: Journal of Hydrology, v. 196, p. 1-25. Battaglin, W.A., Kendall, Carol, Goolsby, D.A., and Boyer, L.L., 1997, Plan of study to determine if the isotopic ratios d15N and d18O can reveal the sources of nitrate discharged by the Mississippi River into the Gulf of Mexico: U.S. Geological Survey Open-File Report 97-230, 18 p.

Battaglin, W.A., and Goolsby, D.A., 1996, Using GIS and regression to estimate annual herbicide concentrations in outflow from reservoirs in the midwestern USA, 1992-93 in Hallam C.A., Salisbury, J.M., Lanfear, K.J., and Battaglin, W.A., eds., GIS and Water Resources, American Water Resources Association, TPS-96-3, p. 89-98.

Battaglin, W.A., and Hay, L.E., 1996, Effects of sampling strategies on estimates of annual mean herbicide concentrations in midwestern rivers: Environmental Science & Technology, v. 30, no. 5, p. 889-896.

Battaglin, W.A., and Goolsby, D.A., 1995, Spatial data in Geographic Information System format on agricultural chemical use, land use, and cropping practices in the United States, U.S. Geological Survey Open-File Report 94-4176, 87 p.

Battaglin, W.A., Goolsby, D.A. and Coupe, R.H., 1993, Annual use and transport of agricultural chemicals in the Mississippi River, 1991-92: in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93-418, 12 p.

Battaglin, W.A., 1992, Estimation of agricultural chemical mass in groundwater by volume modeling techniques: thesis for Masters of Engineering, Colorado School of Mines, Golden, Colorado, ER-4284, 157 p.

Bratkovich, A., Dinnel, S.P., and Goolsby, D.A., 1995, Variability and prediction of freshwater an nitrate fluxes for the Louisiana-Texas shelf: Mississippi and Atchafalaya source functions, Estuaries, v. 17, no. 4, p. 766-778, December 1994.

Burkart, M.R., and Kolpin, D.W., 1993, Hydrogeologic and land-use factors associated with herbicides and nitrate in near-surface aquifers: Journal of Environmental Quality, v. 22, p. 646-656.

Burkart, M.R., Onstad, C.A., and Bubenzer, G.D., 1990, Research on agrochemicals in water resources, Trans., Am. Geophysical Union, v.71, no. 29, p. 980-988, 1990.

Burkart, M.R. and Ragone, S.A., 1989, Planned studies of herbicides in ground and surface water in the mid-continental United States, International Symposium on Integrated Approaches to Water Pollution Problems, paper, Volume III, International Water Resources Association, Lisboa, Portugal, June, 1989, p. III-475-477, 1989.

Coupe, R.H., Goolsby, D.A., Iverson, J.L., Zaugg, S.D., and Markovchick, D.J., 1995, Pesticide, nutrient, streamflow and physical property data for the Mississippi River and major tributaries, April 1991-September 1992: U.S. Geological Survey Open File Report 93-657, 116 p.

Coupe, R.H., Henebry, M.S., and Branham M.R. (with Illinois EPA), 1993, Assessing the effect of pesticides in agricultural runoff on aquatic life in the Sangamon River near Monticello, Illinois: Water, Science, and Technology, vol. 28, p. 569-573.

Goolsby, D.A., Thurman, E.M., Pomes, M.L., Meyer, M.T., and Battaglin, W.A., 1997, Herbicides and their metabolites in rainfall: Origin, transport, and deposition patterns across the midwestern and northeastern United States, 1990-1991: Environmental Science & Technology, v. 31, no. 5, p. 1325-1333.

Goolsby, D.A., Battaglin, W.A., Fallon, J.D., Aga, D.S., Kolpin, D.W. and Thurman, E.M., 1996, Persistence of herbicides in selected reservoirs in the midwestern United States: Some preliminary results: Iowa Groundwater Quarterly, vol. 7, no. 2, p. 11-16 (reprinted from U.S. Geological Survey Open-File Report 93-418).

Goolsby, D.A. and Pereira, W.E., 1996, Pesticides in the Mississippi River, in Contaminants in the Mississippi River, Meade, R.H., ed., U.S. Geological Survey Circular 1133, p. 86-101.

Goolsby, D.A., Scribner, E.A., Thurman, E.M., Meyer, M.T., and Pomes, M.L., 1995, Data on selected herbicides and two triazine metabolites in precipitation in the midwestern and northeastern Unites States, 1990-91, U.S. Geological Survey Open-File Report 95-469, 341 p.

Goolsby, D.A., and Battaglin, W.A., 1995, Occurrence and distribution of pesticides in streams of the Midwestern United States; in Leng, M.L., ed., Agrochemical Environmental Fate: State of the Art, Boca Raton, Fla., Lewis, CRC Press, p. 159-173.

Goolsby, D.A., 1995, Dissolved herbicides, in Moody, J.A., ed., Data report on Mississippi--Upriver Profiles, Chemical data for water quality samples collected during four upriver transects of the Mississippi River between New Orleans, Louisiana, and St. Paul, Minnesota, May 1990-April 1992, USGS Open-File Report 94-523, 297 p.

Goolsby, D.A., Boyer, L.L., and Battaglin, W.A., 1994, Plan of study to investigate the effect of changes in herbicide use on herbicide concentrations in midwestern streams, 1989-94: U.S. Geological Survey Open- File Report 94-347, 14 p.

Goolsby, D.A., 1994, Flux of herbicides and nitrate from the Mississippi River to the Gulf of Mexico during the 1993 flood: in Dowgiallo, M.J. ed., Coastal Oceanographic Effects of Summer 1993 Mississippi River Flooding: Special NOAA Report; U.S. Department of Commerce, National Oceanic and Atmospheric Administration, p. 32-35.

Goolsby, D.A., Battaglin, W.A., Fallon, J.D., Aga, D.S., Kolpin, D.W., and Thurman, E.M., 1993, Persistence of herbicides in selected reservoirs in the midwestern United States: Some preliminary results, in Goolsby, D.A., and others, eds.,Selected papers on agricultural chemicals in water resources of the midcontinental United States, Open-File Report 93-418, 12 p.

Goolsby, D.A., Battaglin, W.A., and Thurman, E.M., 1993, Occurrence and transport of agricultural chemicals in the Mississippi River basin, July through August 1993: U.S. Geological Survey Circular 1120-C, 22 p.

Goolsby, D.A., Boyer, L.L., and Mallard, G.E., 1993, Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93-418, 89 p.

Goolsby, D.A., and Battaglin, W.A., 1993, Occurrence, distribution and transport of agricultural chemicals in surface waters of the midwestern United States: in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93-418, p. 1-24.

Goolsby, D.A., Thurman, E.M., Pomes, M.L., Meyer, M., and Battaglin, W.A., 1993, Occurrence, distribution, and long range transport of herbicides in precipitation in the midwestern and northeastern United States: in Goolsby, D.A., and

others, eds., Selected papers on agricultural chemicals in water resources of the midcontinental United States: U.S. Geological Survey Open- File Report 93-418, p. 75-87.

Goolsby, D.A., Coupe, R.H., and Markovchick, D.J., 1991, Distribution of selected herbicides and nitrate in the Mississippi River and its major tributaries, April through June 1991: U.S. Geological Survey Water Resources Investigations Report 91-4163, 35 p.

Goolsby, D.A., 1991, Atrazine in the Midwestern United States: U.S. Geological Survey Director's Yearbook for Fiscal year 1990, p. 55-57.

Goolsby, D.A., Thurman, E.M., Clark, M.L., and Pomes, M.L., 1990, Immunoassay as a screening tool for triazine herbicides in streams, comparison with gas chromatographic-mass spectrometric methods, in Vanderlaan, Stanker, Watkins, and Roberts, eds., Immunoassays for Trace Chemical Analysis: ACS Symposium Series 451, chapter 8, p. 86-99.

Harvey, C.A., and Kolpin, D.W., and Battaglin, W.A., 1996, Use of geographic information systems and scanning technology to create high- resolution historical land-use data sets: U.S. Geological Survey Water- Resources Investigations Report 96-4100, 41 p.

Kolpin, D.W., Kalkhoff, S.J., Goolsby, D.A., Sneck-Fahrer, Debra, and Thurman, E.M., 1997, Occurrence of selected herbicides and herbicide degradation products in Iowa's groundwater, 1995: Groundwater, v. 35, no. 4, p. 679-688.

Kolpin, D.W., Sneck-Fahrer, D.A., Hallberg, G.R., and Libra, R.D., 1997, Temporal trends of selected agricultural chemicals in Iowa's groundwater, 1982-1995: Are things getting better?: Journal of Environmental Quality, v. 26, no. 4, p. 1007-1017.

Kolpin, D.W., 1997, Agricultural chemicals in groundwater of the midwestern United States: Relations to land use: Journal of Environmental Quality, v. 26, no. 4, p. 1025-1037.

Kolpin, D.W., Zichelle, K.E., and Thurman, E.M., 1996, Water-quality data for pesticides, nutrients, and volatile organic compounds in near- surface aquifers of the midcontinental United States, 1992-1994, U.S. Geological Survey Open-File Report 94-435, 47 p.

Kolpin, D.W., Nations, B.K., Goolsby, D.A., and Thurman, E.M., 1996, Acetachlor in the hydrologic system in the midwestern United States: 1994: Environmental Science & Technology, v. 30, no. 5, p. 1459-1464.

Kolpin, D.W., Thurman, E.M., and Goolsby, D.A., 1996, Occurrence of selected pesticides and their metabolites in near-surface aquifers of the midwestern United States: Environmental Science & Technology, v. 30, no. 1, p. 335-340.

Kolpin, D.W., Goolsby, D.A., and Thurman, E.M., 1995, Pesticides in near-surface aquifers: An assessment using highly sensitive analytical methods and tritium: Journal of Environmental Quality, v. 24, p. 1125-1132.

Kolpin, D.W., Thurman, E.M., 1995, Post-flood occurrence of selected agricultural chemicals and volatile organic compounds in near-surface unconsolidated aquifers in the Mississippi River Basin, 1993: USGS Circular 1120G, 20 p.

Kolpin, D.W., Burkart, M.R., and Thurman, E.M., 1994, Herbicides and nitrate in near-surface aquifers of the Mid-Continent United States: U.S.Geological Survey Water Supply Paper 2413, 34 p.

Kolpin, D.W., Goolsby, D.A., Aga, D.S., Iverson, J.L., and Thurman, E.M., 1993, Pesticides in near-surface aquifers: Results of the Midcontinental United States groundwater reconnaissance, 1991-92: in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93-418, p. 64-74.

Kolpin, D.W., Burkart, M.R., and Thurman, E.M., 1993, Hydrogeologic, water-quality and land-use data for the reconnaissance of herbicides and nitrate in near-surface aquifers of the midcontinental United States. U.S. Geological Survey Open-File Report 93-114, 61 p.

Kolpin, D.W., and Burkart, M.R., 1991, Work plan for regional reconnaissance for selected herbicides and nitrate in groundwater of the Mid-continental United States, 1991: U.S. Geological Survey Open-File Report 91-59, 18 p.

Larson, S.J., Capel, P.D., and Goolsby, D.A., Zaugg, S.D., and Sandstrom, M.W., 1995, Relations between pesticide use and riverine flux in the Mississippi River basin: Chemosphere, v. 31, no. 5, p. 3305-3321.

Liu, S., Yen, S., and Kolpin, D.W., 1996, Atrazine concentrations in near- surface aquifers: A censored regression approach: Journal of Environmental Quality, v. 25, no. 5, p. 992-999.

Liu, S., Yen, S., and Kolpin, D.W., 1996, Pesticides in groundwater: Do atrazine metabolites matter?: Water Resources Bulletin, v. 32, no. 4, p. 845-853.

Lucey, K.J. and Goolsby, D.A., 1993, Effects of short-term climatic variations on nitrate concentrations in the Raccoon River, Iowa: Journal of Environmental Quality, v. 22 p. 38-46.

Meyer, M.T, Thurman, E.M. and Goolsby, D.A., 1996, Cyanazine, atrazine, and their metabolites as geochemical indicators of contaminant transport in the Mississippi River: in Herbicide metabolites in surface and groundwater, Meyer, M.T. and Thurman, E.M., eds., ACS Symposium series 630, p. 288-303.

Meyer, M.T., 1994, Geochemistry of cyanazine and its metabolites: Indicators of contaminant transport in surface water of the midwestern United States, thesis for Ph.D. in Geochemistry, University of Kansas, Lawrence, KS, 362 p.

Meyer, M.T., Mills, M.S., and Thurman, E.M., 1993, Automated solid-phase extraction of herbicides from water for gas chromatographic-mass spectrometric analysis: Journal of Chromatography, v. 629, p. 55-59.

Mills, M.S., and Thurman, E.M., 1994, Preferential dealkylation reactions of s-triazine herbicides in the unsaturated zone: Environmental Science and Technology, v. 28, no. 4, p. 600-605.

Mills, M.S. and Thurman, E.M., 1992, Mixed-mode isolation of triazine metabolites in soil and aquifer sediments using solid phase extraction: Analytical Chemistry, v. 64, no. 17 p. 1985-90.

Moody, J.A., and Battaglin, W.A., 1996, Chemical character of the Mississippi River, in Contaminants in the Mississippi River, Meade, R.H., ed., U.S. Geological Survey Circular 1133, p. 31-39.

Moody, J.A., and Goolsby, D.A., 1993, Spatial variability of triazine herbicides in the lower Mississippi River: Environ. Science and Technology, v. 27., no. 10, p. 2120-2126.

Mueller, D.K., Ruddy, B.C., and Battaglin, W.A., 1997, Logistic model of nitrate in streams of the upper-midwestern United States: Journal of Environmental Quality, v. 26, p. 1223-1230.

Mueller, D.K., Ruddy, B.C., and Battaglin, W.A., 1993, Relation of nitrate concentrations to land use in the Upper Midwestern United States, 1989-90: in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93-418, p. 41-50.

Onstad, C.A., Burkart, M.R., and Bubenzer, G.D., 1991, Agricultural research to improve water quality: Journal Soil and Water Conservation, v. 46, no. 3, p. 184-188.

Pomes, M.L. Aga, D.S., Thurman, E.M., and Goolsby, D.A., 1996, An evaluation of a Microtiter plate ELISA method for the analysis of triazine and chloroacetanalide herbicides in storm runoff samples: Environmental Immunochemical Methods, Chapter 16, p. 170-182.

Scribner, E.A., Goolsby, D.A., Thurman, E.M., Meyer, M.T. and Battaglin, W.A., 1996, Concentrations of selected herbicides, herbicide metabolites, and nutrients in outflow from selected midwestern reservoirs, April 1992 through September 1993: U.S. Geological Survey Open-File report 96-393, 128 p.

Scribner E.A., Goolsby, D.A., Thurman, E.M., Meyer, M.T., and Pomes, M.L., 1994, Data on selected herbicides, two atrazine metabolites, and nutrients in storm runoff from nine streams in the midwestern United States, 1990-92, USGS Open-File Report 94-396, 144 p.

Scribner, E.,Thurman, E.M., Goolsby, D.A., Meyer, M.T., Pomes, M.L., 1993, Reconnaissance data for selected herbicides, two atrazine metabolites, and nitrate in surface water of the Midwestern United States, 1989-90: U.S. Geological Survey Open-File Report 93-457 77 p.

Tarte, S.R., Schmidt, A.R., and Sullivan, D.J., 1992, Floating sample- collection platform with stage-activated automatic water sampler for streams with large variation in stage: U.S. Geol. Survey Open File Report 92-149, 14 p.

Thurman, E.M., Goolsby, D.A., Aga, D.S., Pomes, M.L. and Meyer, M.T., 1996, Occurrence of alachlor and its sulfonated metabolite in rivers and reservoirs of the midwestern United States: The importance of sulfonation in the transport of chloroacetanilide herbicides: Environmental Science & Technology, v. 30, no. 2, p. 569-574.

Thurman, E.M., Mills, M.S., Meyer, M.T., Zimmerman, L.R., Perry, C.A., and Goolsby, D.A., 1994, Formation and transport of deethylatrazine and deisopropylatrazine in surface water: Environmental Science and Technology, v. 28, no. 13, December 1994, p. 2267-2277.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W., 1992, A reconnaissance study of herbicides and their metabolites in surface water of the midwestern United States using immunoassay and GC/MS: Environ. Science and Technology, v. 26, no. 12, p. 2440-2447.

Thurman, E.M. Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1991, Herbicides in surface waters of the Midwestern United States--Effects of the spring flush: Environmental Science and Technology, v. 25, no. 10, p. 1794-96.

Thurman, E.M., Meyer, M.T., Pomes, M.L., Perry, C.A., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with gas chromatography/ mass spectrometry for the determination of triazine herbicides in water: Analytical Chemistry, v. 62, p. 2043-2048.

Yen, S. Liu, S., and Kolpin, D.W., 1996, Analysis of nitrate in near-surface aquifers in the midcontinental United States: An application of the inverse hyperbolic sine Tobit model: Water Resources Research, v. 32, no. 10, p. 3003-3011.

7.5. Appendix 3-3: USDA Management Systems Evaluation Areas (MSEA)

7.5.1.1. USDA Management Systems Evaluation Areas (MSEA's)

The Management Systems Evaluation Area (MSEA) Program is part of an interagency initiative to evaluate the effects of farm management systems on water quality. The cooperating agencies of the MSEA Program are the U.S. Department of Agriculture's Agricultural Research Service (ARS) and Cooperative State Research Service (CSRS), the U.S. Environmental Protection Agency, the U.S. Geological Survey, and other Federal and State agencies.

The general goal of the MSEA Program is to reduce the effect of agriculture on the environment through the use of improved farm management practices. The cooperating agencies are collaborating on research ranging from laboratory experiments to 50 square kilometer watersheds. The research objectives are to (1) measure the effects of prevailing and modified farming systems on ground- and surface water quality, (2) understand the processes and factors affecting the fate of selected agricultural chemicals on ecosystems, (3) assess the effects of selected agricultural chemicals on ecosystems, (4) assess the projected benefits to water quality of implementing modified farming systems, (5) evaluate the socioeconomic impacts of using modified farming systems in the Midwest, and (6) transfer appropriate agricultural technology to farmers.

Five MSEA's were selected to represent the principal hydrogeologic settings and geographic diversity of prevailing farming systems in the Midwest. MSEA's in sand and gravel settings are located in Minnesota, Nebraska, and Ohio; those in loess and till settings are located in Iowa and Missouri. Research focuses on processes that affect groundwater quality at all MSEA's, but processes that affect surface water quality are also a major consideration at the Iowa and Missouri MSEA's. Several additional MSEA sites have also been created more recently (e.g. Mississippi Delta MSEA (An additional MSEA program is under development in the Mississippi Delta (The Mississippi Delta MSEA - http://www.sedlab.olemiss.edu/msea.html)

The Midwest MSEA is a series of five projects headquartered in Iowa, Minnesota, Missouri, Nebraska and Ohio:

(1) The Iowa MSEA evaluates the impact of agricultural management systems on groundwater quality within the loess and till settings of western Iowa

(2) The Northern Cornbelt Sand Plain (NCSP) MSEA is a multi-state project in Minnesota, North Dakota, South Dakota and Wisconsin. The NCSP MSEA evaluates the effects of irrigated agricultural management systems on groundwater quality in the surficial sand and gravel aquifers typical of the region. The NCSP MSEA sites are located on outwash sand plains in Minnesota, North Dakota, South Dakota and Wisconsin. The research sites are in east-central Minnesota at Princeton, in southeast North Dakota at Oakes, in east-central South Dakota at Aurora, and in south-central Wisconsin at Areana.

(3) The Missouri MSEA evaluates the impact of agricultural management systems on groundwater quality within the 10 million acre claypan soils region of the central Corn Belt. The Missouri project located in the 28-square mile Goodwater Creek watershed of northern Boone and western Audrain Counties of central Missouri to assess the influence of continuous corn and corn-soybean rotation on surface and groundwater quality of claypan soils for the 7750 ha watershed.

(4) The Nebraska MSEA evaluates the impact of agricultural management systems on groundwater quality. The impact of four nitrogen/irrigation management systems are evaluated on contamination of groundwater by agricultural chemicals. Three 33-acre "management blocks" on a farm near Shelton, overlay groundwater that contains an average of 32 ppm nitrite/nitrogen. A conventional irrigated field is used as a control to compare with "improved" practices under both surface and
sprinkler irrigation. A fourth management block is evaluated to determine the ability of alfalfa to scavenge nitrate-N from the irrigation water.

(5) The Ohio MSEA evaluates the impacts of agricultural management systems on groundwater quality in northern Ohio. Research is being conducted in the Darby Creek, Maumee River, Sandusky River, and Scioto River watersheds. Maumee River site is located on highly productive lakebed soils and evaluates how the agricultural runoff to wetland/reservoirs can be used for recharge, water table management, and sub-irrigation water supply. Scioto River sites in Union, Ross, and Pike counties are used to evaluate farming systems and water management under actual farming conditions. Hoytville research site evaluates water table management practices in a silty clay setting. Wooster research site evaluates a sub-irrigation/drainage system influence on ground- and surface water quality on a silt loam soil. Piketon research site is located in Pike County overlying sand and gravel Scioto River buried valley aquifer and evaluates nutrient cycling and nutrient placement, irrigation strategies, and water table management on coupled wetland – agricultural ecosystems.

Database development

Since 1991, the Management Systems Evaluation Areas (MSEA) Program has collected a variety of data directed toward the objective of evaluating the impact of current and new farming practices on water quality. These experiments were conducted at 10 sites throughout the Midwest in a combination of plot, field, and watershed scale studies. In all studies there was a common set of herbicides being evaluated: atrazine, alachlor, metribuzin, and metolachlor (as well as nitrate-nitrogen). Groundwater and soil column samples were collected for each treatment throughout the study. In Iowa and Missouri, additional measurements were made runoff from plots, fields, and watersheds. These measurements were event driven in both states. Iowa had additional measurements based on subsurface drainage from the soil that ultimately becomes surface water.

In all sites, records were maintained of the changes in herbicides (and nitrate-nitrogen) concentrations throughout the soil column over the course of the year. This permitted the evaluation of the disappearance of these compounds following application. Other variables included the deposition of herbicides and nitrate-nitrogen in precipitation through the year along with meteorological observations.

These databases are being developed for all sites. These will become available to other researchers who wish to evaluate models or compare other sites with the observations from the MSEA program. The overall description of the MSEA database is being prepared for release in late 1998. Following are details of specific research sites/methods and general observations by lead state (i.e. Iowa, Minnesota, Missouri, Nebraska and Ohio).

IOWA

The Iowa MSEA centers on three major sites—one in the western area (deep loess soil), one in the central area (Des Moines Lobe or thick glacial till soil), and one in the northeastern area (thin glacial soil at Nashua). The sites are characteristic of 35 percent of the state in that the land is used primarily for continuous corn or corn and soybeans.

Deep Loess Research Station

The Deep Loess Research Station in the western region has four watershed agricultural sites. Two of the four watersheds have a cropping practice of continuous corn, with disking as the tillage practice; another watershed uses continuous corn with ridge tillage; and the fourth watershed operates as a double-spaced parallel-terrace system with underground pipe outlets and ridge tillage. This variety allows comparison of runoff and water movement in three crop management systems.

Detailed studies are being conducted on the movement and persistence of atrazine and nitrate in the soil profile. The deep soils enable analysis of the rate of movement and of chemical transformations, and deep wells have been installed to examine movements within the root and vadose zones. Within each watershed the hydrologic balance is being measured to examine the patterns of water and solute movement in different farming systems.

Each watershed contains a weir system equipped to collect base flow and runoff samples for pesticide and nitrate analyses. Wells in each watershed are used to measure the height of the water table and to collect water quality samples each month.

In the ridge tillage watershed, deep wells were installed I 1991 to sample the movement of water and pesticides throughout the profile in different depths above the glacial till. These samples are related to microbial activity measured in the root zone and vadose zones.

Each pair of watersheds shares a complete meteorological station, which operates year round. A wet-dry precipitation sampler for every rain event above 2.5 mm.

Des Moines Lobe Area

Till-hydrology site. Research at the till-hydrology site focuses on measuring the movement of chemicals and the age of water at various depths to 150 m. Cropping systems include continuous corn and a corn soybean rotation with documented nitrogen and pesticides.

Deep wells are positioned to provide samples from each geological unit above the Mississippian Aquifer. Collected monthly, samples are analyzed for pesticide and nitrate concentrations. Additional samples collected for hydrogen-3 and oxygen-18 concentrations determine the age of the water from the various geological units.

A series of continuous corn conventional tillage plots and no-till plots receive nitrogen fertilizer at different rates and times to assess the affect of split applications on surface and groundwater quality. Piezometers in each plot quantify the movement and quality of water samples. A sump pump system measures the tile flow from each plot, and runoff collected from two of the plots is used to quantify the amount and quality of water lost from the surface.

Walnut Creek watershed. Walnut Creek represents a typical watershed in the Des Moines Lobe. Farming systems include a corn-soybean rotation, continuous corn, and corn-soybean-grain-legume rotation. The cropping systems selected for study depend upon the farmers' willingness to alter farming practices. Nitrogen fertilizers, chemicals, and tillage practices are varied within the corn-soybean rotation. Each variation in farming practices is documented to assess any related changes.

Study fields in the Walnut Creek watershed typify various portions of the landscape. These fields are monitored for surface runoff, tile flow, and groundwater quality. Atmospheric variables and soil samples area collected to determine the concentrations and degradation products of pesticides and nitrate in different portions of the landscape and the pesticide amounts in the root zone.

In order to track changes in water quality resulting from changes in farming systems, three stream sampling systems are used to continually measure stream height and temperature, rainfall, sediment, and water quality using a programmable data acquisition system. Nitrogen transformations are studied by analyzing anaerobic and aerobic conditions in the streambed and the flow of water down the stream and laterally from the surrounding fields.

A series of 24 tipping-bucket rain gauges are used to measure the intensity of rainfall throughout the watershed at 5-min intervals. After each rainfall, a wet-fry precipitation sampler is used to collect samples for pesticide and nitrate analyses.

A 320-ha subbasin is instrumented to measure the total surface runoff and tile flow from a collection of fields. Wells up to 10 m deep around the perimeter of the subbasin enable monthly measurements of the height of the water table

and the water quality. In additional, soil samples to a depth of 1.5 m are being taken eight times a year to measure pesticide concentrations.

Nashua Area

The three crop rotations at the Nashua site—continuous corn, soybean, and soybean-corn—are grown under four different tillage practices—ridge-till, no-till, moldboard plow, and chisel plow-disk. Alachlor and atrazine have been applied each year to the continuous corn crop, along with nitrogen, phosphorus, and potassium. Alachlor and metribuzin, along with nitrogen, phosphorus, and potassium have been applied to the corn-soybean rotations.

Experimental plots consists of 36 0.4-ha plots and a series of bedrock wells at various depths in a area adjacent to the plots. Monthly water levels in the wells are measured for hydraulic gradient and sampled for water quality.

Installed in the center of each plot is a tile line intercepted by a sump pump system. Each tile line is measured for flow rate, and water samples are periodically collected at specific flow volumes. Four plots have an H-flume to measure the surface runoff and automatic samplers to collect samples for surface water quality. Two piezometers installed at two depths in each plot measure the hydraulic gradient within the plot. Soil samples are collected eight times a year to a depth of 1.2 m for pesticide and nitrate concentrations.

Nashua has a complete meteorological station including a wet-dry precipitation sampler, which collects samples from rainfall events over 2.5 mm. These samples are analyzed for the pesticide and nitrate concentrations.

Observations from the Iowa MSEA (groundwater)

Deep Loess Research Station: Atrazine and metolachlor move rapidly through the loess soil profile. During the June and July period, concentrations, of atrazine in the unsaturated zone often exceed 3 µg/L. Both parent and degradates leach through the soil profile to depths of 30 m. Deisopropylatrazine is detected in groundwater samples from both lysimeters and shallow wells. Nitrate-N also moves through the soil profile, and in the loess soils there is a vertical movement to the saturated layer above the glacial till material and then a lateral movement that emerges as seepage flow along the stream bank. Concentrations of nitrate-N have increased in the seepage flow from less than 3 mg/L in 1972 to over
23 mg/L in 1994. This increase is related to the continual fertilization of the watershed at a N rate of 168 kg/ha/yr.

Walnut Creek and Till Hydrology Sites: Quantifiable amounts of atrazine and metolachlor were found in tile drains under fields. Concentrations increase in response to increased water movement into the drains because of preferential flow. Concentrations, however, are less than 0.5 µg/L. Increases in atrazine concentration in the tile drains are similar to the patterns in nitrate-N concentrations and indicate that direct water movement is the carrier of both materials. Alachlor and metribuzin and are rarely observed in the tile drains. Concentrations in the soil profile show a rapid decrease with

depth, and all herbicides are present at less than 1 µ/kg below 0.3 m. Nitrate-N concentrations are a function of the management practice and within the soil concentrations often exceed 15 mg/kg of soil at depths below 0.3 m.

There is a little movement of herbicides or nitrate-N into shallow wells. Atrazine exceeding 3 µg/L occurred once in 1650 observations. Only 2 percent of the samples exceeded 0.2 µg/L at depths greater than 3 m. Domestic wells in the watershed had no quantifiable amounts of atrazine or any other herbicide. Herbicide leaching through the soils in the Walnut Creek and the Till Hydrology sites is controlled by the timing of application relative to rainfall and infiltration, the high sorptive capacity of the soil, and degradation rates. Banding atrazine onto the crop reduces the concentration in the tile drainage water to less than 1 µg/L compared to over 2 µg/L in broadcast applications.

Nitrate-N concentrations decreased rapidly with depth. Concentrations averaged 11 mg/L at the 1.5-3 m depth interval and 2.0 mg/L at greater than 4.5 m. In the domestic wells sampled there was less than 1 mg/L nitrate-N. The water in the domestic wells is very old compared to recent times, approximately 10,000 to 40,000 years old. In the geologic units of the Des Moines Lobe landform there is the presence of high organic matter content that reduces the nitrate-N and limits the downward movement. Also, in this tile drained area only a small fraction, less than 10 percent, of the precipitation moves into groundwater. Changing the management practices to split application of nitrogen reduces the nitrate-N concentration in the tile drains.

Nashua: Atrazine, alachlor, and metribuzine have been detected at concentrations less than 3 µg/L in the tile drains. There is an increase in the concentrations and detections in the spring and after rain events because of preferential flow in glacial till soils. In wells around the site there were no quantifiable amounts of herbicides, and nitrate-N concentrations were less than 2 mg/L. Age studies of the groundwater reveal that this aquifer material has not been influenced by recent, within the past 50 years, agricultural activities. However, shallow wells exhibit concentrations of nitrate-N of 6 mg/L, indicating a coupling with the surface. There is considerable variation in the geological units, and potential for movement to deeper aquifers exists through outcrops, sinkholes, and agricultural drainage wells in this area.

Observations from the Iowa MSEA (surface water)

Deep Loess Research Station: Concentrations of atrazine and metolachlor in surface runoff have exceeded 80 µg/L during rain events. These concentrations are short-lived and the stream concentrations do not maintain the high levels after the event. Hydrographs of surface runoff, atrazine, metolachlor, and nitrate-N show that the peak concentrations occur just prior to peak flow. At peak flow, dilution occurs and the concentrations begin to decrease. There are relatively few runoff events in the ridge tillage in the ridge tillage watershed because of the runoff and erosion control aspects of this tillage treatment. The amount of atrazine and metolachlor lost due to surface runoff would be less than 1 percent of applied amounts. Deethylatrazine concentrations were less than atrazine concentrations in surface runoff. Hydroxy analogs were not detected in any of the water samples.

Walnut Creek Watershed: Loads calculated at several stream discharge sties show that annual herbicide loss varies due to the differences in weather patterns. However, the loads range from nearly 7 percent of that applied in 1993 with the occurrence of multiple runoff events to less than 0.2 percent in 1994. A portion of the stream discharge load is attributable to tile drainage and not surface runoff. Observations in the stream and from flumes at the edge of selected fields showed that atrazine concentrations reached 25 µg/L and metolachlor reached near 80 µg/L during runoff events in 1991. In 1992 there were no increases in the concentrations of atrazine or metolachlor in the runoff. Surface from fields within Walnut Creek is small and although there are fields with steeper slopes in the lower reaches of the watershed, the amount lost from these does not impact the load at conservation tillage practices because the field with ridge tillage has had no events with quantifiable atrazine or metolachlor loss since 1991.

Observations of large concentrations of atrazine, greater than 150 µg/L, and metolachlor, greater than 150 µg/L, have not been associated with practices in the field. Observations of these high concentrations have occurred in September during 1991 and 1994. These large concentrations were detected in a tile drain monitoring site at the end of a 350 ha subbasin. This subbasin has six tile inlets which couple tile drains directly to the surface. It was found that the cause of the large concentrations was due to the practice of cleaning the field sprayers in preparation for winter storage and the reinsert from the tanks was sprayed on the area downslope from the farm. During these two years there were rain events shortly after this operation that caused the surface water to run across the farmyard and into the tile inlet. The concentration peaks at this observation site were not repeated at any other location in the watershed and these loads were rapidly diluted so that the next station downstream recorded unquantifiable concentrations of both herbicides. This scenario does, however, show the need to separate field management from farmstead management practices in the evaluation of farming on water quality.

MINNESOTA

The Northern Corn Belt Sand Plain MSEA sites comprise the Anoka Sand Plain in Minnesota, the Wisconsin River Sand Plains in Wisconsin, the Oakes Irrigation Research Site in North Dakota, and the Big Sioux Aquifer area in South Dakota.

The research focuses on the effects of the following three cropping systems: (1) a field corn-soybean rotation utilizing ridge-till to reduce pesticide use; (2) a chemically intensive, ridge-till, sweet corn-potato rotation in wide use in the northern sand plains, and (3) continuous corn using conventional tillage and conventional pesticide and fertilizer application procedures.

All three systems are used at the Anoka Sand Plain site near Princeton and the field corn-soybean rotation with ridge till are used at the satellite locations in Wisconsin, North Dakota, and South Dakota. Data collected from the Princeton site are plotted to show the spatial distribution of agrichemicals in the saturated and unsaturated zones. These data are then compared with similar data collected at the satellite sites in North Dakota, South Dakota, and Wisconsin.

The Minnesota Pollution Control Agency (MPCA) conducts research at the Princeton site and other Anoka Sand Plain fields with a corn-soybean rotation to evaluate this system as a best management practice for reducing nonpoint-source pollution and achieving water quality goals within the surficial sand plain aquifer of east central Minnesota. Specific MPCA objectives are to (1) increase knowledge about the fate and transport of solutes within this hydrological setting and (2) assess methods to evaluate chemical transformations including nitrate reduction and movement of solutes.

Several techniques are being used to predict the existence and location of preferential flow paths for herbicides and nitrate. Soil variability is determined to a depth of 3 m at selected sites. Special attention is paid to within-pit variability of soils and features that may cause contaminant behavior, such as grain coatings, biopores, complex sediment layering, particle size, and surface charge characteristics. Infiltrometers are being used to measure the hydraulic properties of soil near saturation.

Evapotranspiration and photosynthesis are measured with portable chamber. Microclimate data are also being collected for use in predicting evapotranspiration and assessing the development of cropping and management systems that promote the efficiency of irrigation and that minimize agricultural chemical movement.

Farm Management Systems

Ridge-till field corn-soybean rotation. The field corn-soybean rotation uses a less-than-full-width ridge-till system in which crops are planted each year. The ridge-till system reduces the use of herbicides and fertilizer since applications are confined to the immediate vicinity of the corn; weeds between rows are controlled by the residue, which suppresses weed growth, and by subsequent cultivation.

The rate of fertilization depends on soil tests. The pesticides atrazine, alachlor, and metribuzin are applied according to recommendations contained in **WEEDIR** or a similar guide and insecticides are applied according to INSREC or a similar guide. Irrigation is done according to predictions of a state-of-the-science irrigation scheduling system.

A cover crop planted in early fall and winter-killed is being used following the soybean crop to control wind erosion and minimize nitrate movement during the winter. Usefulness of the corn crop residue for erosion control and nitrate immobilization is being determined.

Sweet corn-potato rotation. The sweet corn-potato rotation uses full-width tillage consisting of disk, chisel, and field cultivators. This tillage system will help retain crop residues.

Potato harvest is early and facilitated by a vine burndown to allow planting a cover crop that will scavenge nitrates, reduce soil erosion, and reduce weed competition. In the spring the area is disked before planting sweet corn. Two cultivations are used to control weeds during the season.

Fertilization consists of banded applications at a rate recommended by soil testing. A potato vine killer may be needed at early harvest to help establish the cover crop. Other pesticide use and vine killer may be needed at early harvest to help establish the cover crop. Other pesticides use and irrigation practices follow the guidelines mentioned previously for the field corn-soybean rotation.

Continuous corn. The continuous corn system is a conventional system with the exception that excessive irrigation is sometimes needed to ensure movement of the applied chemicals to groundwater. This system is established at the Princeton site in the groundwater recharge area of the Geological Survey.

Tillage is with full-width chisel plow. The rate of fertilization is that recommended by the University of Minnesota, and fertigation is used as needed. Atrazine and alachlor are used according to WEEDIR recommendations and insecticides, according to INSREC recommendations.

Data Collection

Soil samples taken from the Princeton site are used to determine the extent of herbicide and nitrate movement in the unsaturated zone in the ridge-till system. Two soil cores are collected per plot before pesticide application and at intervals of 2, 5, 11, and 18 weeks following pesticide application at depth increments varying from 0-15 cm to 213-244 cm. If neither herbicides nor nitrates are detected in samples taken postharvest, reapplication (spring) samples will not be taken for analyses. Because coring may alter the hydraulic properties of the soil around the opening, bentonite is used to backfill and seal each borehole.

The effect of the farming systems on the quality of the groundwater is being determined by analyzing water samples collected from multiport samples installed ungradient, within, and downgradient of each plot. Each of these contain six sampling ports installed 0.5 m deep in the saturated zone so the distribution of agricultural chemical concentrations can be plotted in three dimensions.

Water samples are also collected from groundwater observation wells, precipitation, and Battle Brook adjacent to the site. Samples collected from wells in off-site locations help determine the comparative concentrations of agricultural chemicals in these areas.

The three primary agricultural chemicals being analyzed in water are atrazine, alachlor, and nitrate. Concentrations of the pesticides metribuzin, metolachlor, turbufos, and phorate in water are also being determined, if they are applied to crops. In addition, analyses are done for several degradation products of atrazine (desethylatrazine and deisopropyl-atrazine) and alachlor (chloroalachlor and hydroxyalachlor).

Observations from the Northern Sand Plains MSEA

Minnesota: Atrazine concentrations never exceeded 0.09 µg/L at the top of the aquifer under the corn/soybean farming system, which is 3-4 m below the surface. These concentrations were indistinguishable from background levels. Under all cropping systems, atrazine concentrations averaged less than 0.05 µg/L to a 1.8 m depth in the aquifer and degradates were present in slightly greater concentrations than the parent compound. Alachlor and metribuzin were rarely detected in samples over the study period.

Observations of herbicides in the soil at 30 cm for all sampling times in 1992 and 1993 showed concentrations around 10 µg/kg. There was a greater concentration in the surface soil in the banded area under the row than in the interrow. Water movement patterns transport the material vertically below the row and not into the interrow area so it is expected that there is littler lateral movement of herbicide.

The corn/soybean cropping sequence resulted in low concentrations of nitrate-N in the soil profile. Concentrations during this cropping season were usually less than 5 mg/kg, but observations in shallow ground wells were often between 10 and 30 mg/L. However, background levels for this site ranged from 10 to 15 mg/L, suggesting that the aquifer received nitrate-N inputs from sources other than the corn/soybean farming under study. Although nitrate-N concentrations at the water table appear to be increasing, definitive conclusions about the performance of this farming system cannot be discerned at this time.

North Dakota: Under the sandy loam soil there were only four detections of atazine in the 93 samples collected in groundwater wells 4-6 m below the soil surface. There were no quantifiable amounts of alachlor or metribuzin under the ridge tillage systems. Observations of atrazine, alachlor, and metribuzin in the soil profile showed that these herbicides rarely moved beyond 15 cm in the soil.

South Dakota: Atarzine was detected in groundwater at the South Dakota site. The maximum concentration of 0.9 µg/L was observed 1 year after application, following early spring rains totaling 35 cm, that resulted in the aquifer water level rising 2 m. It is not known if atrazine leached from the surface soil, or was desorbed from the vadose zone by rising water.

Wisconsin: Significant detections were found in the groundwater at 0-0.9 and 0.9-1.8 m below the water table under the irrigated ridge-tillage system. Concentrations of atrazine exceeded 10 µg/L at 40 days after application in 1990. It was estimated that in this sandy soil, 1-2 percent of atrazine percolated into groundwater and it was also observed that deethylatrazine was found in greater concentrations than atrazine. In the soil, quantifiable amounts were not found below 0.6 m, although concentrations in suction cup lysimeters often exceeded 10 µg/L. Movement of atrazine in this medium textured sand is related to rapid water movement through the soil profile and the very low adsorption capacity of the soil.

MISSOURI

The Missouri MSEA is located in the Goodwater Creek watershed, an agricultural area in the north central part of the state near the town of Centralia. A unique feature of the site is that it lies within a claypan soil region. Claypan soils of the Midwest prairie are problem soils. A clay sublayer, beginning at a depth of 15-30 cm, restricts air and water movement and retards root development. The upper horizons are usually low in natural fertility and are often acidic unless corrective treatments are made. The total area of Midwestern claypan soils is about 4 million ha. The principal areas are in Missouri, Illinois, and Kansas. Secondary areas, where the soils are sufficiently like a claypan that claypan management practices apply, occur in Oklahoma, Indiana, and Ohio.

Research Design

Field farming systems. The following three farming systems are being evaluated on field-sized areas of 20-50 ha.

- High agrochemical system, consisting of a corn-soybean rotation with high fertilizer and herbicide applications for high-yield production (farming system 1).

- Medium agrichemical system, consisting of a sorghum-soybean rotation with fertilizer and herbicide applications based on long-term average yield (farming 2)./

- Low agrichemical system, consisting of a corn-soybean-wheat rotation with nitrogen fertilizer applications based on long-term average yields, soil testing, split fertilizer application, and a combination of herbicide banding and secondary tillage for weed control (farming system 3).

Nitrogen fertilizer inputs vary across the farming systems, whereas potassium and phosphorus are applied to all systems based on yield goals and soil testing. Applications of the herbicides atrazine and alachlor are graded from high to low in farming systems 1-3 by varying the application rates in systems 1 and 2 and by a combination of banding (to reduce herbicide applications) and secondary field cultivation in system 3. Primary tillage is similar among the farming systems. Crop scouting and recommendations for insect and disease control are made by the University of Missouri-Columbia Integrated Pest Management staff. Primary emphasis in the three fields is on assessing the impacts of the farming systems and groundwater quality and on evaluating their economic viability.

Plot farming systems. The high and low agrichemical farming systems are also evaluated on plots that have summit, sideslope, and footslope soils represented in each plot (0.3-ha plots). Three additional farming systems are also evaluated on plot sized areas: (1) high agrichemical, no-till corn-soybean rotation; (2) low agrichemical, ridge-till corn-soybean rotation; and (3) no agrichemical, continuous grass without harvest.

The emphasis of plot research is on evaluating farming system and landscape variability on crop yields and root-zone soil and water quality. Plot results are not intended to provide a comprehensive evaluation of groundwater quality.

Five well nests are installed within each field and groundwater is sampled for measurement of atrazine, alachlor, and dissolved nitrogen concentrations. Each nest is comprised of two to four wells based upon the depth to bedrock. Wells less than 7.5 m deep are sampled quarterly; deeper wells are sampled annually.

An automated weather station located in the farming system 1 field is used to measure precipitation, climate, and chemical concentrations in rain. Rainfall is measured on the two other fields using recording rain gauges.

Each field is instrumented with a weir, a water stage recorder, and a refrigerated pumping sampler to measure on an event basis erosion and concentrations and losses of dissolved nitrogen phosphorus, and pesticides.

The influence of macropores and soil cracks on the preferential flow of water and chemicals is being studied in the laboratory and field. Much of the research focuses on better understanding the processes affecting the formation of macropores and soil cracks. Techniques used include dyes, helium gas a flux, and computed area tomography. Grid lysimeters are also used to obtain detailed information on seasonal pathways and cycles of pesticides adsorption, movement, and persistence.

Pesticide degradation associated with row cropping and proximity to crop root is being studied in the laboratory and field using herbicide compounds labeled with carbon -14.

Observations from the Missouri MSEA (groundwater)

Soils at the Missouri site have a well developed claypan, and following warm, dry periods and subsequent soil cracking, have the potential for large preferential flow rates. Lysimeters positioned at 0.9 m below the soil surface showed that rapid leaching of atrazine and nitrate-N can occur within 24 hours of a rain event and the observed concentrations were above the drinking water standards. There was large spatial variation in the soils that gave rise to large variations in the observed concentrations in the lysimeter samples. The higher atrazine concentrations were associated more frequently with the high yield goal and high chemical input farming practice.

The claypan soil and structured loess material below the claypan limits groundwater recharge, and thus leaching to the glacial aquifer is minimal. However, there are detectable amounts of deethylatrazine in the glacial aquifer. Atrazine concentrations have not exceeded 0.12 µg/L and alachlor has not exceeded the quantitation limit in over 1000 well samples since 1991.

Observations of nitrate-N in shallow groundwater wells show a nitrate-N concentration below the corn-soybean rotation of 4.9 mg/L and 90 percent of the samples have less than 10 mg/L. Concentrations of nitrate-N in the grain sorghum-soybean rotation are 4.7 mg/L and 90 percent concentrations of less than 10 mg/L. Under the corn-soybean-wheat rotation with a reduced nitrogen input, the nitrate-N concentrations are 12.9 mg/L, and 80 percent exceed 10 mg/L and 40 percent exceed 20 mg/L. This rotation is being evaluated on a field found to have received both manure N fertilizer during

many years for the period of 1950 to 1980. These observations show the need to understand the past history of the site for evaluation. Past history of sites may make comparisons of current practices difficult in terms of water quality.

Observations from the Missouri MSEA (surface water)

Claypan soils limit groundwater recharge and promote surface and interflow. Surface runoff quality is the primary water quality problem within the Goodwater Creek watershed. Approximately 30 percent of the annual precipitation is lost due to surface runoff. Atrazine and alachlor along with atrazine metabolites are observed in surface runoff at concentrations that are 10 to 100 times higher than the drinking water standards. Hydroxyatrazine is always detected in surface runoff and base flow. Spatial sampling within the watershed has shown that atrazine concentrations vary but are prevalent enough to show that agriculture is a nonpoint source of pollution.

The 45 to 60 day period after application is the most vulnerable for surface runoff. Incorporation can lead to reductions in the concentrations in the surface runoff but might negatively impact sediment loss goals. In a corn-soybean rotation, the surface runoff weighted mean atrazine concentration exceeded 3 µg/L by 101 percent. The highest concentration was observed from fields without incorporation.

In the claypan soils there is the additional complication that occurs because the surface runoff infiltrates the alluvium aquifer surrounding the stream and then discharges this water into the stream as baseflow. Baseflow concentrations of atrazine are often greater than 3 µg/L because of this process. The alluvium aquifer is recharged during large surface runoff events and these events are when the herbicide concentrations are the highest. Concentrations of atrazine during the spring can reach to 320 µg/L and alachlor to 250 µg/L for the same periods. There is a difference among farming systems. The high input system maximums can reach 320 µg/L for atrazine and 250 µg/L and alachlor 130 µg/L. In the system without incorporation, atrazine peak concentrations were 1512 µg/L and alachlor of 583 µg/L. In Goodwater Creek the most significant impact of herbicides on groundwater quality is not from the leaching fields due to the infiltration of surface runoff water with its high load of herbicides into the alluvial aquifer bordering the streams. To date none of the changes in farming practices in the Goodwater Creek watershed have reduced surface runoff concentrations to near the drinking water standard. To reduce these concentrations will require adoption of farming practices that use less herbicides or completely eliminate the potential for surface runoff during this critical two-month period.

NEBRASKA

The principal site is in Nebraska's Central Platte Valley, a region where more than 90 percent of the land is under cultivation. Over 75 percent of the cropland is devoted to the continuous production of irrigated corn and about 10 percent is devoted to irrigated soybeans.

Research focuses on (1) farm management systems at the field level, (2) groundwater monitoring and assessment, (3) component research to extend knowledge of the rate and transport of agricultural chemicals under various management scenarios, and (4) assessment of socioeconomic factors affecting adoption of alternative management strategies.

Three 13.3-ha management blocks at the principal site are dedicated to the evaluation and demonstration of available technology packages for water, nitrate, and pesticide management on irrigated monoculture corn. Each technology packages for water, nitrate, and pesticide managment on irrigated monoculture corn. Each technology package is used as a single treatment on a block. Each block provides enough land for a full-scale demonstration and evaluation, as well as detection of treatment associated changes in groundwater quality.

Three technology packages being compared are (1) current farm practice, (2) best management practices with surface irrigation, and (3) best management practices with sprinkler irritation. The impact of these best management practices on groundwater quality is being evaluated directly through the use of multilevel sampling devices and indirectly through periodic sampling of the soil and water through the vadose zone. All three management blocks have the same pesticide program.

The current practice block receives a preplant application of ammonia without nitrification inhibitor, banded atrazine at planting for weed control, and conventional furrow irrigation with 12-hr continuous sets and end-of-field diking in lieu of tailwater recovery. The amount of fertilizer nitrogen is estimated according to guidelines that define a reasonable yield and account for residual nitrate in the soil and the nitrate content of the irrigation water.

The block dedicated to best management practices with surface irrigation receives laser-guided land grading, alternate-row surge irrigation, tailwater recovery, and irrigation scheduling according to crop water use. Any preplant ammonia is applied with a nitrification inhibitor. The herbicide applied at planting time is banded atrazine.

The block dedicated is to best management practices with sprinkler irrigation is served by a center pivot system with a corner unit. Irrigations are scheduled according to measured crop water use. A soil water deficit is maintained to provide for storage of rainfall. Nitrogen applications are split among a small preseason ammonia application if appropriate, with a nitrification inhibitor, and incremental applications via fertigation, with the latter based on results from frequent tissue testing. The herbicide treatment is the same as that used on the surface irritation block.

A fourth 16-ha treatment block is seeded to alfalfa. This block provides maximum removal of nitrate from the soil and irrigation water.

The impact of treatment is being directly evaluated through the groundwater monitoring and vadose zone sampling. Indirect estimates are made by evaluating the amount and distribution of irrigation water and the runoff volume of surface irrigation.

Because of lateral groundwater movement beneath the MSEA site, a uniformly managed “buffer zone” us established on the upgradient side of the 15-ha blocks to ensure an inflow of relatively good quality, shallow groundwater.

In 1990, several multilevel samplers-piezometers were installed. The resulting data is being used to define the localized water table and the areal and vertical flow at the site. Water is collected from multilevel samplers at various depths below the water table and analyzed.

Observations from the Nebraska MSEA

The site of Nebraska MSEA is on a silt loam soil with 4-5 m to the aquifer. It is expected that because of the rapid water movement in this setting from irrigation use, this area would have the highest frequency of detections of atrazine and nitrate N. Both atrazine and nitrate-N are found in the concentrations exceeding the drinking water standards. Observations of the age of the groundwater through tritium dating revealed that the age of the groundwater is very young in the upper part of the aquifer. Using this type of technique shows the impact of past and current management practices on groundwater quality. Through the age estimates of groundwater it was determined that the half-life of atrazine is between 10-20 years in this aquifer system. Current changes quickly reflect themselves in the upper aquifer. It was found that the atrazine metabolite, deethylatrazine, was present in the groundwater samples as a higher concentration than the parent.

Concentrations of nitrate-N in the upper aquifer responded quickly to changes in management. Atrazine concentrations in the upper aquifer responded quickly to changes in water management. Holding irrigation amounts close to plant requirements reduces root zone drainage. This serves to hold atrazine in the root zone longer and consequently allows time for atrazine to be biologically degraded. Parallel improvements in the managment of irrigation water and N fertilizer also increase the profit from the production system.

OHIO

The Ohio MSEA site located on a farm overlying the Scioto River Buried Valley Aquifer. Buried valley (or alluvial) aquifers are typically shallow, permeable, and unconfined and have high recharge rates. These aquifers exist along most streams and rivers in the Midwestern United States and have become a major source of water for public consumption. The aquifers are vulnerable to surface contamination because they embody short flow paths to the water table, which decrease the potential for adsorption, for chemical reactions between contaminants and minerals in the soil, and for boidegradation. In Ohio, groundwater pumped from buried aquifers serves the domestic water needs of about one-third of the population.

Three farming systems are being evaluated.

- Continuous corn tilled with a chisel plow. The herbicides used are atrazine and alachlor. Nitrogen is applied at a rate of 180 kg/ha.
- A corn-soybean rotation using no-till for the corn and chisel plow for the soybeans. Herbicides for corn are atrazine and alachlor, and for soybeans, alachlor and metribuzin plus chlorimuron-ethyl. Nitrogen at a rate of 180 kg/ha is applied to the corn phase of the rotation.
- This system is a ridge-till corn-soybean-hairy vetch rotation, with banded herbicide application. Nitrogen application for corn consists of residual nitrogen from the vetch cover crop and manure. The manure is applied at the rate of 56, 122 L/ha, and supplemental anhydrous ammonia is applied for a total nitrogen input of 130 kg/ha.

In all three systems, nicosulfuron and quizalofop is used to control johnsongrass.

In order to conduct saturated flow research, each farming system is established on a separate 10-ha field. Space and resource constraints prevent replicating these large fields, but small plot replicates are maintained nearby in order to obtain statistically valid measurements for research other than the saturated flow research.

The small treatment plots are arranged randomly in a complete-block statistical design; each plot is 0.4 ha. One of the following treatments is assigned to each plot: (1) continuous corn, (2) corn phase of a corn-soybean rotation, (3) soybean phase of a corn-soybean rotation, (4) corn phase of a corn-soybean-wheat cover rotation, (5) soybean phase of a corn-soybean-wheat cover rotation, and (6) wheat cover phase of a corn-soybean-wheat cover rotations.

Unsaturated flow. Water content distribution in the unsaturated zone is monitored on a biweekly basis. Water content data are collected by using a combination of soil cores and a neutron probe and frequency domain reflectory (FDR). Soil cores is collected monthly from each plot at depths of 0.0-0.15 m and 0.3-0.45 m. Access tubes installed in each large plot enable readings to be taken from the neutron probe and FDR. Using one of these methods, readings are taken biweekly at depths of 0.0-0.15 m, 0.3m, 0.9, and 1.5 m.

To monitor chemical movement in the unsaturated zone, soil cores and porous-cup suction samplers are used. Soil cores 25 mm in diameter are obtained, handled, and analyzed using regional quality protocols. The cores are taken at replicate locations in each plot at the following intervals: prior to spring tillage; 2 weeks past planting; in corn at silking and at physiological maturity; and in soybeans at R1 flowering, R6 full seed, and 2 weeks following each fertilizer application.

Pesticide and nitrate information are obtained from soil cores at depths of 0.0-0.15 m, 0.15-0.3 m, 0.45-0.6 m, and 0.85-1.0 m.

Saturated flow. The monitoring scheme for the saturated zone quantifies groundwater flow and quality on two scales and is designed to integrated with the monitoring scheme in the unsaturated zone. The local or regional scale monitoring network is designed to collect data at the research site and adjacent upgraident areas. The primary function of the network is to collect data that reflect land use practices beyond the boundaries of the research fields and to provide information on chemical migration from the research fields to the Scioto River. These data show changes in groundwater levels that are used in determining local variations in the directions of groundwater flow and in flow velocities and well as upgradient (back-ground) groundwater chemistry data.

The other scale, the block or site scale monitoring network, is designed to collect data from the individual 10-ha fields in the study site to identify differences in groundwater chemistry among the three management systems. This network also monitors changes in groundwater flow directions and flow velocities among the 10-ha fields.

Thirty-seven wells were installed; these include 11 water table wells, 4 bedrock wells, and 22 multiport wells. All wells were installed with the cable tool method, which allowed continuous sampling of the aquifer materials. During installation, every 1.5 m was cored using an oversized split-spoon sampler 0.1 in diameter. The cores were split into subsections for laboratory analysis by specific research activities.

The water table wells each have a 6.7-m PVC screen that straddles the water table. The wells are instrumented with incremental encoders that continuously monitor water levels to detect recharge events to the aquifer. Water table wells in the center of the three 10-ha fields and the wells conductance and temperature. Data from these probes augment the detection of recharge as it reaches the water table.

The bedrock wells have a 3.3-m PVC screen, the top of which is 1.5 m below the top of competent bedrock. Care was taken to ensure the wells were sealed from the overlying drift aquifer. Each well contains an encoder to monitor water levels in the bedrock aquifer located below the alluvial aquifer. Multiport wells are used to obtain water quality samples from various depths of the alluvial aquifer. These wells have stainless steel sampling ports and dedicated pumps at 3.7 m, 4.9 m, 6.1 m, and 7.3 m below land surface. Selected wells also have additional sampling ports at 12.2 m and 18.3 m below the surface. Backfill around the wells includes two grades of pure quartz sand. A coarse sand was placed around each sampling port and a fine sand was placed midway between sampling ports to deter vertical movement of groundwater. No bentonite seals were used in the well construction since organics tend to adhere to bentonite and could alter the groundwater chemistry.

Observations from the Ohio MSEA

In the silt loam soils in Ohio, measurements of nitrate-N and herbicides in water showed that within the upper 2 m there was fairly rapid movement within a year. Lysimeters placed at 1 and 1.5 m below the soil surface to intercept the water flowing from the bottom of the root zone showed that concentrations of nitrate-N were highest under continuous corn and the lowest, less than 5 mg/L, under a corn-soybean-wheat rotation. Nitrate-N levels in the groundwater at 13 m were near detection limits indicating nitrate-N is not moving deep into the aquifer. Herbicide movement was limited to the upper 0.3 m of the soil profile. There were only a few detections in the lysimeters of any of the herbicides and no detections in the groundwater samples. There is a history of atrazine use on this site; therefore, the lack of detection is not a result of too short of time period for movement to have occurred within the soil and saturated zones. The lack of movement of herbicides is thought to be related to the rapid degradation and adsorption in the upper portion of the soil profile.

7.6. Appendix 3-4 Four Mile Creek, Iowa.

Data on the field-to-stream transport of sediment and chemicals from an intensively farmed agricultural watershed were collected in a five-year study (1976-1980). Measurements were made for small (~ 6 ha) corn, soybean, and pasture fields; for two larger mixed cover watersheds, and at three stream sites (largest 5055 ha).

Annual inventories were made of land use and chemical inputs, and about 80% of the whole watershed was in row-crops, corn and soybeans, with 97 to 100% of those cropped areas treated with herbicide and about 58-80% of the corn treated with insecticides. Five herbicides, alachlor, atrazine, butylate, cyanazine, and 2,4-D represented at least 90% by weight of the herbicides used on corn. For soybeans, the five herbicides, alachlor, bentazon, chloramben, metribuzin, and trifluralin, represented at least 90% by weight of the herbicides used. Five insecticides, carbofuran, chlorpyrifos, fonofos, phorate, and terbufos, represented over 95% by weight of the insecticides used.

Chemical analyses for herbicides were run on samples of runoff from the small corn and soybean fields and the 5055-ha watershed for alachlor, propachlor, cyanazine, and metribuzin (some measurements were also made for paraquat and for atrazine in the stream; atrazine was not applied to the fields because of the corn-soybean rotation). The most severe runoff events occurred in 1979 when field runoff losses were as high as 7.2% of that applied (for metribuzin) most of which was associated with the water phase for all four of the herbicides studied. The maximum loss from the whole watershed was 2.0% (for metribuzin), and in general field losses (as a present-of-applied) were much higher than stream losses for the whole watershed, indicating some attenuation was taking place in the field-to-stream transport.

Because one of the primary purposes for collecting these data in this study was for mathematical model development/validation, additional data sets on climatic conditions and on herbicide content in field soils (by soil sampling) were collected. These data are available in electronic form from the Department of Agricultural and Biosystems Engineering, Iowa State University.

7.7. Appendix 3-5: Example of a current PRZM3-EXAMS scenario (Tier 2 September 1998)

Compound-specific PRZM Model Input Parameter - User Selection guidance:

MODEL INPUT PARAMETER (VARIABLE ID)	COMMENTS	MODEL
Aerobic soil metabolism half-life (DWRATE1,DSRATE1) Surface Horizon	2.3*half-life (n=1) 90% Upper Confidence Limit of Geometric Mean (n>1)	PRZM
Aerobic soil metabolism half-life (DWRATE2,3),DSRATE2,3) Subsurface Horizons	2.3*half-life (n=1) 90% Upper Confidence Limit of Geometric Mean (n>1) or 0.5 *DWRATE1	
Vapor Decay Rate (DGRATE1,2,3)	0	
Decay Rate on Foliage (PLDKRT)		PRZM
Foliar Extraction (FEXTRA)	0.5 - default value in absence of data	PRZM

- First-order pH independent rate constants (acid, neutral, alkaline) are used in the EXAMS pond.
- A dark control corrected first-order photodegradation rate is used in the EXAMS pond.
- Microbial-mediated degradation is considered as a separate first-order degradation process.

Representative PRZM/EXAMS Scenario

A representative scenario is presented in the following section. The scenario represents an high exposure conditions. The cotton field is in Yazoo County, Mississippi. It has a Loring silt loam soil, a fine-silty, mixed, mesic Thermic Typic Fragiudalf, in MLRA O-134. The Loring silt loam is a moderately well drained soil with a fragipan formed in loess on level to strongly sloping upland and stream terraces on slopes of 0-20 percent. The Loring silt loam is a Hydrologic Group C soil with SCS curve numbers that were measured on a real field in Yazoo County, Mississippi under cotton culture. There are approximately 101,000 acres of cotton grown in Yazoo County, which is the most of any county in Mississippi and among the top 10 percent in the U.S. (US Department of Commerce, 1994a). USLE C Factors were developed by George Foster at the University of Mississippi in consultation with Ronald Parker of the OPP EFED to represent a cotton field with one year tilled followed by two years under conservation tillage using RUSLE. The weather data is from weather station W03940 in Jackson, Mississippi. The weather data file is also part of the PIRANHA shell and is used to represent the weather for MLRA 131. This weather data was used rather than the MLRA 140 weather data as it was

expected to better represent the weather in Yazoo County. The PRZM 3.1 parameters describing this site are in the following tables.

The pond used is modified for generic use from the Richard Lee pond that is distributed with EXAMS and is the standard pond used for all EEC calculations. Modifications were made to convert the pond from 1 acre, 6 ft deep to 1 ha, 2 m deep. Additionally, adjustments were made to the standard pond by changing the water temperature to that which was more appropriate for the region being simulated. The temperature in the pond for each month was set to the average monthly air temperature over all 36 years calculated from the meteorological file that was used in the simulation. Additionally, the latitude and longitude were changed for each pond to values appropriate for the site. Finally, all transport into and out of the pond has been set to zero. The non-chemical specific parameters describing the ponds are listed in Appendix X

PRZM 3.1 Scenario Parameters

Table App-2. PRZM 3.1 climate and time parameters for a cotton field in Yazoo County, Mississippi.

Parameter	Value	Source	Quality
Starting Date	January 1, 1964	Met File	
Ending Date	December 31, 1983	Met File	
Pan Evaporation Factor (PFAC)	0.760	PIC	good
Snowmelt Factor (SFAC)	0.150 cm · K^{-1}	PIC	good
Minimum Depth of Evaporation (ANETD)	17.0 cm	PIC	good
Average Duration of Runoff Hydrograph (TR)	5.80 h	PIC	good

Table App-3. PRZM 3.1 model state flags for a cotton field in Yazoo County, Mississippi.

Parameter	Value
Pan Factor Flag (IPEIND)	0
Chemical Application Model Flag (CAM)	user defined
Bulk Density Flag (BDFLAG)	0
Water Content Flag (THFLAG)	0
Kd Flag (KDFLAG)	0
Drainage model flag (HSWZT)	0
Method of characteristics flag (MOC)	0
Irrigation Flag (IRFLAG)	0
Soil Temperature Flag (ITFLAG)	0
Thermal Conductivity Flag (IDFLAG)	0
Biodegradation Flag (BIOFLAG)	0
Partition Coefficient Model (PCMC)	NA
Initial Pesticide Concentration Flag (ILP)	0
Erosion Calculation Flag (ERFLAG)	4

Table App-4. Erosion and landscape parameters for a cotton field in Yazoo County, Mississippi.

Parameter	Value	Source	Quality
USLE K Factor (USLEK)	0.49 tons EI^{-1*}	PIC	good
USLE LS Factor (USLELS)	0.40	PIC	fair
USLE P Factor (USLEP)	0.75	**	fair
Field Area (AFIELD)	10 ha	standard	
NRCS Hyetograph (IREG)	4	PRZM Manual	Good
Slope (SLP)	6%	USDA-NRCS	Good
Hydraulic Length (HL)	354 m	PRZM-Manual	Good

* EI = 100 ft-tons * in/ acre*hr ** P Factor represent compromise for 1 year of conventional tillage and two years of no till.

Table App-5. PRZM 3.1 crop parameters for a cotton field in Yazoo County, Mississippi.					
Parameter	Value			Source	Quality
Initial Crop (INICRP)	1				
Initial Surface Condition (ISCOND)	1 (fallow)				
Number of Different Crops (NDC)	3				
Number of Cropping Periods (NCPDS)	20				
Parameters For First Crop (ICNCN = 1)					
Maximum rainfall interception storage of crop (CINTCP)	0.20 cm			PIC	fair
Maximum Active Root Depth (AMAXDR)	125 cm			PIC	fair
Maximum Canopy Coverage (COVMAX)	98%				
Soil Surface Condition After Harvest (ICNAH)	3 (residue)			PIC	
Date of Crop Emergence (EMD, EMM, IRYEM)	May 1			PIC	good
Date of Crop Maturity (MAD, MAM, IYRMAT)	September 7			PIC	good
Date of Crop Harvest (HAD, HAM,IYRHAR)	September 22			PIC	good
Maximum Dry Weight	0 kg m^{-2}				
Maximum canopy height (HTMAX)	120 cm				
	Fallow	Cropped	Residue		
SCS Curve Number (CN)	99	93	92	measurement	good
USLE C Factor (USLEC)	0.63	0.16	0.18	RUSLE*	good
Parameters For First Crop (ICNCN = 2)					
Maximum rainfall interception storage of crop (CINTCP)	0.20 cm			PIC	fair
Maximum Active Root Depth (AMAXDR)	125 cm			PIC	fair
Maximum Canopy Coverage (COVMAX)	98%				
Soil Surface Condition After Harvest (ICNAH)	3 (residue)			PIC	
Date of Crop Emergence (EMD, EMM, IRYEM)	May 1			PIC	good
Date of Crop Maturity (MAD, MAM, IYRMAT)	September 7			PIC	good
Date of Crop Harvest (HAD, HAM,IYRHAR)	September 22			PIC	good

Table App-5. PRZM 3.1 crop parameters for a cotton field in Yazoo County, Mississippi.					
Parameter	Value			Source	Quality
Maximum Dry Weight	0 kg m^{-2}				
Maximum canopy height (HTMAX)	120 cm				
	Fallow	Cropped	Residue		
SCS Curve Number (CN)	94	84	83	PIC	fair
USLE C Factor (USLEC)	0.16	0.13	0.13	PIC	good
Parameters For First Crop (ICNCN = 3)					
Maximum rainfall interception storage of crop (CINTCP)	0.20 cm			PIC	fair
Maximum Active Root Depth (AMAXDR)	125 cm			PIC	fair
Maximum Canopy Coverage (COVMAX)	98%				
Soil Surface Condition After Harvest (ICNAH)	3 (residue)			PIC	
Date of Crop Emergence (EMD, EMM, IRYEM)	May 1			PIC	good
Date of Crop Maturity (MAD, MAM, IYRMAT)	September 7			PIC	good
Date of Crop Harvest (HAD, HAM,IYRHAR)	September 22			PIC	good
Maximum Dry Weight	0 kg m^{-2}				
Maximum canopy height (HTMAX)	120 cm				
	Fallow	Cropped	Residue		
SCS Curve Number (CN)	99	83	83	Mesurement	good
USLE C Factor (USLEC)	0.16	0.12	0.09	RUSLE**	good
** developed by George Foster at the University of Mississippi, Oxford in consultation with Ronald Parker of OPP EFED using RUSLE.					

Table App-6. PRZM 3.1 soil parameters for a cotton field in Yazoo County, Mississippi.			
Parameter	Value	Source	Quality
Total Soil Depth (CORED)	155 cm	*	good
Number of Horizons (NHORIZ)	6	*	good
First, Second and Third Soil Horizons (HORIZN = 1, 2 , 3)			
Horizon Thickness (THKNS)	13.0 cm (HORIZN = 1) 23.0 cm (HORIZN = 2) 33.0 cm (HORIZN = 3)	PIC	good

Table App-6. PRZM 3.1 soil parameters for a cotton field in Yazoo County, Mississippi.

Parameter	Value	Source	Quality
Bulk Density (BD)	1.4 g $\cdot cm^{-3}$	*	good
Initial Water Content (THETO)	0.385 cm^3-H_2O $\cdot cm^3$-soil (HZ1) 0.370 cm^3-H_2O $\cdot cm^3$-soil (HZ2) 0.370 cm^3-H_2O $\cdot cm^3$-soil (HZ3)	*	good
Compartment Thickness (DPN)	0.1 cm (HORIZN = 1) 1.0 cm (HORIZN = 2, 3)	standard	
Field Capacity (THEFC)	0.385 cm^3-H_2O $\cdot cm^3$-soil (HZ1) 0.370 cm^3-H_2O $\cdot cm^3$-soil (HZ2) 0.370 cm^3-H_2O $\cdot cm^3$-soil (HZ3)	*	good
Wilting Point	0.151 cm^3-H_2O $\cdot cm^3$-soil (HZ1) 0.146 cm^3-H_2O $\cdot cm^3$-soil (HZ2) 0.146 cm^3-H_2O $\cdot cm^3$-soil (HZ3)	*	good
Organic Carbon Content	2.18% (HORIZN = 1) 0.49% (HORIZN = 2) 0.16% (HORIZN = 3)	*	good
Second Soil Horizon (HORIZN = 4, 5, 6)			
Horizon Thickness (THKNS)	30.0 cm (HORIZN = 4) 23.0 cm (HORIZN = 5) 33.0 cm (HORIZN = 6)	PIC	good
Bulk Density (BD)	1.45 g $\cdot cm^{-3}$ (HORIZ = 4) 1.49 g $\cdot cm^{-3}$ (HORIZ = 5) 1.51 g $\cdot cm^{-3}$ (HORIZ = 6)	*	good
Initial Water Content (THETO)	0.340 cm^3-H_2O $\cdot cm^3$-soil (HZ4) 0.335 cm^3-H_2O $\cdot cm^3$-soil (HZ5) 0.343 cm^3-H_2O $\cdot cm^3$-soil (HZ6)	*	good
Compartment Thickness (DPN)	1.0 cm	Standard	
Field Capacity (THEFC)	0.340 cm^3-H_2O $\cdot cm^3$-soil (HZ4) 0.335 cm^3-H_2O $\cdot cm^3$-soil (HZ5) 0.343 cm^3-H_2O	*	good

Table App-6. PRZM 3.1 soil parameters for a cotton field in Yazoo County, Mississippi.

Parameter	Value	Source	Quality
	·cm^3-soil (HZ6)		
Wilting Point	0.125 cm^3-H_2O ·cm^3-soil (HZ4) 0.137 cm^3-H_2O ·cm^3-soil (HZ5) 0.147 cm^3-H_2O ·cm^3-soil (HZ6)	*	good
Organic Carbon Content	0.12% (HORIZN = 1) 0.07% (HORIZN = 2) 0.06% (HORIZN = 3)	*	good

*USDA, Natural Resources Conservation Service, Soil Survey Laboratory, Pedon Database, Soil Series ID: 581MS-049-001, Hinds County, Mississippi. 1998. Location of data: http://vmhost.cdp.state.ne.us/~nslsoil/htbin/dbfnd4?series=loring.

EXAMS Scenario Input Parameters

2

Table App-7. EXAMS II pond geometry for standard pond.

	Littoral	Benthic
Area (AREA)	10000 m^2	10000 m^2
Depth (DEPTH)	2 m	0.05 m
Volume (VOL)	20000 m^3	500 m^3
Length (LENG)	100 m	100 m
Width (WIDTH)	100 m	100 m

Table App-8. EXAMS II dispersive transport parameters between benthic and littoral layers in each segment for standard pond.

Parameter	Pond*	Stream 1**	Stream 2***
Turbulent Cross-section (XSTUR)	10000 m^2	300 m^2	1200 m^2
Characteristic Length (CHARL)	1.01, 1.025 m	0.275 m	0.275 m
Dispersion Coefficient for Eddy Diffusivity (DSP)	3.0 x 10^{-5}	3.0x 10^{-5}	3.0x 10^{-5}

* JTURB = 1, ITURB = 2; ** JTURB = 3, ITURB = 4; *** JTURB = 5, ITURB = 6

4

Table App-9. EXAMS II sediment properties for standard pond.

	Littoral	Benthic
Suspended Sediment (SUSED)	30 mg L^{-1}	
Bulk Density (BULKD)		1.85 g cm^{-3}
Per cent Water in Benthic Sediments (PCTWA)		137%
Fraction of Organic Matter (FROC)	0.04	0.04

Table App-10. EXAMS II external environmental parameters for standard pond.

Precipitation (RAIN)	90 mm ·$month^{-1}$
Atmospheric Turbulence (ATURB)	2.00 km
Evaporation Rate (EVAP)	90 mm ·$month^{-1}$
Wind Speed (WIND)	1 m ·sec^{-1}
Air Mass Type (AMASS)	Rural (R)

Table App-11. EXAMS II biological characterization parameters for standard pond.		
Parameter	Limnic	Benthic
Bacterial Plankton Population Density (BACPL)	1 cfu $\cdot cm^{-3}$	
Benthic Bacteria Population Density (BNBAC)		37 cfu $\cdot (100\ g)^{-1}$
Bacterial Plankton Biomass (PLMAS)	0.40 mg $\cdot L^{-1}$	
Benthic Bacteria Biomass (BNMAS)		$6.0x10^{-3}$ g $\cdot m^{-2}$

Table App-12. EXAMS water quality parameters for standard pond.	
Parameter	Value
Optical path length distribution factor (DFAC)	1.19
Dissolved organic carbon (DOC)	5 mg $\cdot L^{-1}$
chlorophylls and pheophytins (CHL)	$5x10^{-3}$ mg $\cdot L^{-1}$
pH (PH)	7
pOH (POH)	7

2

Table App-13. EXAMS mean monthly water temperatures and location parameters for a cotton field pond in Yazoo County, Mississippi.	
Month	Temperature (Celsius)
January	6
February	9
March	12
April	16
May	20
June	24
July	26
August	28
September	25
October	18
November	13
December	10
Latitude	34^{o} N
Longitude	83^{o} W

4

7.8. Appendix 3-6: Detailed Recommendations for Improving FIFRA Part 158 studies

1) OBTAINING RATE CONSTANTS FOR DEGRADATE FORMATION AND DECLINE

Objective	To provide soil degradate formation and decline data for calculating rate constants suitable for use as input parameters in environmental fate and transport models where it is necessary to model degradate behavior in the environment.
Proposed Change:	The current guidelines require the identification of major degradates (occurring at greater than 10% of nominal), and degradates of toxicological concern. They do not require that rate of formation and decline of these degradates be estimated. We recommend that the existing subdivision N guidelines be altered so that additional measurements of significant degradate(s) be made so that there are an appropriate number of data so the rate of formation and degradation of each can be existing subdivision N . Guidance should also be provided on how to use these measurements to determine rate constants for significant degradate formation and degradation via non-linear regression or other appropriate statistical techniques. Note that the current guideline study often provides the data necessary for estimation of degradate formation and decline constants, though the estimates are of these values are usually not made.
Advantages to modeling:	The availability of degradate formation and decline rate constants for various processes allows simulation of environmental fate of the degradates when they are significant components of the toxicological profile of the chemical. This greatly improves the accuracy of the assessment of the of risk of the pesticide in the environment when there are significant toxic degradate produced.
Limitations:	May only be feasible for degradates generated via understood pathways. May not be possible across longer timelines for biochemically mediated processes (e.g. the microbial capability of soils in laboratory degradation studies tends to decrease across the course of the experiment). In studies measuring degradation, it may be advantageous to measure the inherent microbial activity of soil in the study.
When recommended:	Additional sampling point data may prove valuable when it is expected that the environmental fate of one or more degradates will require detailed investigation via simulation modeling. Registrants will accept that if specific degradate rate data is unavailable when necessary for environmental risk assessment, either regulatory delays or potentially highly conservative modeling assumptions may result.

Alternatives: As an alternative to incorporating additional sampling points into existing studies in case the results are needed later, registrants may elect to run degradate specific decline studies as the need arises As an alternative to incorporating additional sampling points into existing studies in case the results are needed later, registrants may elect to run degradate specific decline studies as the need arises. Note that this option does not address the formation rate constants.

2) OBTAINING HYDROLYSIS RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

Objective: To enable more precise estimation of hydrolysis rates under a range of environmental conditions **where it has been shown that abiotic hydrolysis plays a driving role in determining the fate and transport of a product**.

Purpose: Agricultural pesticides are used under a large range of environmental conditions; two key variables are temperature and pH. The current method only requires one temperature (25 ^{o}C) for the study and only determines (breakdown) rate constants as a function of pH. Thus the effect of temperature on the reaction rate is not considered. Temperature can be included in the form of Arrhenius equation. This would allow for the consideration of differences in water temperature due to geographic location and temporal differences when modeling.

Proposed Change: To measure laboratory abiotic hydrolysis at multiple temperatures and at pH's of 4, 7, 9 and minimum of three temperatures. The result is a second-order reaction rate and the Arrhenius constants. The pH values and temperatures selected should reflect the range of environmental conditions that represent the proposed use areas.

Advantages to modeling: For chemicals whose fate is particularly sensitive to hydrolysis AND where the degradation process is simple and understood; it may be of value to include the temperature sensitivity of abiotic degradation n exposure modeling where this is the most significant loss mechanism. This would allow for the consideration of differences in water temperature due to geographic location and temporal differences when modeling. There is also a side benefit of moving towards international guideline harmonization by adopting this suggested change.

Limitations: Not applicable in cases where the degradation route involves competing pathways. Potentially trebles the amount of work required under the hydrolysis guideline.

When recommended: This additional work should be required when hydrolysis is a key factor in the environmental behavior of a product. This can be achieved by a tiered approach as suggested earlier by NACA. A high temperature (e.g. 50EC), short duration screening study at more extreme pH values (e.g. pH 3, 7 and 11 - see OTS guidelines) would be conducted over 96 hours.

For ONLY those pH values where significant degradation occurs in this preliminary tier, the more sophisticated study may be conducted at three temperatures provided the initial study has demonstrated that the degradation process involves a simple pathway. [As far as permitted by the goal of International guideline harmonization, the lowest temperature should be around 1 0EC with the intermediate temperature in the range of 25 to 30EC][4]

If hydrolysis is a key factor for a product and if the rate constants are not provided for a range of temperatures and pH's, then potentially highly conservative modeling assumptions may be made by the Agency.

Alternatives: Even where hydrolysis is an important degradation mechanism for a product, the registrant may elect to omit this additional work where hydrolysis is not the primary loss process.

3) DETERMINING QUANTUM YIELDS

Objective To improve calculation of direct photochemical transformations so as to allow for changes in the spectral quality of light fields with depth and type of water body. The EXAMS model currently has much more sophisticated and powerful photolysis routines than are currently used in OPP EFED risk assessments as the parameters to run these routines cannot be estimated from the information generated with the current aqueous photolysis study. Modest changes in the data submitted with the study will allow for these routines in EXAMS.

Proposed Change: Include requests for the UV-visual absorption spectrum and reaction quantum yield determinations in subdivision N photolysis studies as already suggested during the Subdivision N Rejection Rate (199X) procedure. A tiered system (e.g. OTS guidelines) should be adopted to ensure that quantum yields are only measured where photolysis is a significant process for the chemical. Separate absorption spectra and reaction quantum yields to be computed for ionic species where appropriate. Spectral resolution should match that required for input to the EXAMS model.

Advantages to modeling: The values may be extrapolated to provide aquatic direct photolysis rate data that is appropriate for specific scenario that is being modeled.Limitations: Care needs to be taken in cases where the compound exhibits multiple adsorption bands within the 290 to 800 nm band, as in many cases (e.g., dyestuffs) some absorption bands are not associated with transformation reactions.

When recommended: Should be required as a standard in subdivision N aquatic photolysis studies.

Alternatives: None required.

4) SELECTION OF MULTIPLE SOILS FOR SOIL AEROBIC DISSIPATION STUDIES

Objectives: To provide sufficient measurements of laboratory soil degradation rate to provide an appropriate estimation of the mean and distribution of the topsoil degradation rate to permit probabilistic modeling of chemical transport To provide a suitable selection, in both number and range of soils, for characterizing the variability and uncertainty of degradation rates at the sites where the pesticide might be used.

Proposed Change: Currently, only one aerobic soil metabolism study is required. ECOFRAM proposed increasing the number of soils included in the laboratory soil program to provide a level of uncertainty appropriate to the significance of the use patterns for the pesticide All of the soils used should be relevant to the use pattern. Soils selected should be thoroughly characterized. It should be noted that there are substantial benefits in using soils that come from sites where field dissipation studies may be conducted and/or are used in other Subdivision N studies. Studies can be conducted with or without radio-labeling.

Advantages to modeling: The results may be used to estimate distributions of rate constant input parameters for the models and to correlate field and laboratory data. They may be critical in order to understand soil to soil quantitative variability for probabilistic approaches. The large background variability in metabolic degradation rates results in substantial uncertainty in the actual rate in the environment. Measurements on additional soils can substantially reduce that uncertainty.

Other advantages: It is perceived by EPA that this approach might offer registrants savings by ensuring that the field soil dissipation sampling intervals are appropriate

Limitations: Additional soils can substantially increase the required work load.

When recommended: Presently, the addition of extra soils remains at the registrants option.[5] It is likely that current efforts to revise metabolism in concert with the OECD will result in a minimum of 4 soils being required for aerobic soil metabolism. Current methods for estimating soil degradation input parameters account for the uncertainty due to limited numbers of

samples. Registrants will accept that they run the risk of conducting poorly designed soil field dissipation studies if they have not conducted aerobic studies in multiple soils.

5) ENHANCING BATCH EQUILIBRIUM STUDY DESIGN STUDY DESIGN

Objective

To ensure that, when needed, adequate data on the magnitude and rate of adsorption and desorption behavior across a range of relevant soils under relevant environmental conditions and to provide information on how to appropriately extrapolate from the measured soils to other soils where the sorption has not been measured with a known level of confidence

Proposed Change:

Current studies generally do not provide good measures of the rate of adsorption and do not attempt to determine mechanisms of sorption other than some preliminary measures of sorption to soil organic carbon. Key issues to be considered include:

Current guidance only requires that some attempt be made to show that equilibrium be approached. ECOFRAM recommends that the guidance should be modified so that useful estimates of the rate of adsorption and desorption can be estimated from the study. This will more accurate modeling of the adsorption-desorption process when the equilibrium assumption currently used in the models may not be accurate . It also makes it more likely that an accurate assessment of when equilibrium is reached will be made.

The continued use multiple soils with consideration given where appropriate to the addition of measurements on sediments and soil substrata. Multiple soils allow the accurate assessment of the nature of binding across soils. Currently, point estimates of Koc are made, but there is no requirement to determine Koc accurately describes the nature of the binding. Our experience has been the organic carbon content frequently cannot describe the magnitude of binding across soils. Additional guidance should be provided on methods for assessing the nature of binding across soils. Additional models for binding should also be considered such as Kss, binding to specific surface (Pionke and DeAngelis, 1985).

Advantages to modeling:

More sophisticated analysis of the modes of adsorption will greatly improve the estimation of pesticide fate and transport on soils with which no measurements were made. In cases where the sorption kinetics significantly impact the amount of pesticide in runoff, the accuracy of modeling will be improved commensurately. Note that both of these changes will require some recoding the fate and transport models for use.

When recommended: These changes should be made a routine part of the batch equilibrium study. As as they improve the general interpretability of the study and aid in their use as model input parameters.

6) MODIFYING AQUATIC METABOLISM STUDIES TO SEPARATE DEGRADATION IN THE WATER COLUMN AND THE SEDIMENT

Objective To provide separate measures of the water column aerobic degradation rate and the degradation rate in the benthic layer under anaerobic conditions for inclusion into surface water modeling...

Proposed Change: Current studies provide information on mixed sediment-water column systems with a range of redox environments. The aerobic aquatic metabolism study is well oxygenated while the anaerobic study is poorly oxygenated. Both studies use a mixed media with both a water column and benthic sediments present. In both cases there are likely to be a range of redox potentials with the most oxidized conditions a the top of the water columns and the most reduced conditions at the bottom the sediment layer. These systems do provide qualitative information on the degradation process but they are not optimal for developing model input parameters. We recommend that the aerobic soil metabolism study be replaced with a water column study containing suspended sediment, but no bed sediment. The anaerobic soil metabolism study should consist of a reduced bottom sediment with no water column kept under an inert atmosphere. pH and Eh should be monitored through the course of both studies.

Advantages to modeling: Studies conducted in this manner will provide data that is much more appropriate for use in surface water hydrology models such as EXAMS. .

Limitations: Careful consideration has to be given to using valid established aquatic systems for the experiment.

When recommended: Should be at the registrants option under the understanding that the assumption for the biotic aquatic degradation rate that will be made by EPA in the absence of aquatic metabolism data will be zero.

Alternatives: Estimates of aquatic metabolism can be made using the soil metabolism rate constants along with appropriate uncertainty factors to account for the extrapolation between media.

7) CONDUCTING FOLIAR DISSIPATION AND WASHOFF STUDIES FOR FOLIAR PESTICIDES

Objective: To provide data to characterize the processes operating on chemical reaching leaves and crop residues on the soil. These processes include degradation and washoff.

Proposed Change: There are currently to requirements or guidance for conducting foliar dissipation studies. However, foliar processes can in some cases be the dominant route of dissipation for a chemical and thus significantly impact the amount of chemical available for transport during rainstorm events. In addition, this data is probably even more important to enhance the understanding of dissipation of residues on the foodstuffs for non-target terrestrial organisms.. We recommend the addition of greenhouse foliar degradation and foliar washoff studies be added to the Subdivision Guidelines.

Advantages to modeling: This process may be an important factor in the fate of foliarly- applied pesticides. Consequently, this data is necessary to accurately estimate the exposure for foliarly applied pesticides.

Limitations: Additional work is required since these studies are not currently required. The current study design(s) may require re-examination during the process of guideline review; certain aspects might be cost effectively incorporated into existing field protocols.

When recommended: For aquatic risk assessment, it is acceptable to have the studies optional on theunderstanding that modeling assumptions made by EPA in the absence of data on the product are likely to be conservative (i.e. zero foliar dissipation rate and a very high washoff rate). However, these studies will likely be required for all foliarly applied pesticides for adequate terrestrial risk assessment.

8) FOCUS ANAEROBIC SOIL METABOLISM STUDY ON DEGRADATION IN SUBSOIL HORIZONS AND AQUIFERS.

Objective: To provide information on degradation processes and rates in subsoils to improve the simulation modeling of pesticides after they have moved below the root zone.

Proposed Change The current anaerobic soil metabolism study is focused on degradation processes in flooded surface soils such as would occur during rice culture. It does not provide data useful under the redox conditions and biological activities found in subsoils and aquifers. This data is of particular importance for understanding the potential for pesticide to contaminate and persist in ground water, which is not within the purview of ECOFRAM. However, it may impact the nature and extent of chemical residues available for “return

flow" to surface waters during periods of low flow, a process that can be considered when basin scale modeling is implemented.

Advantages to modeling — These changes will allow for the improved estimation of exposure during low flow conditions. This information is crucial for the accurate estimation of pesticide concentrations in ground water.

Limitations — Data generated is only of limited value with current environmental fate models for estimating surface water exposure. Basin scale models with the capability for handling ground water- surface water interaction will be needed to take advantage of this information in aquatic exposure assessment.

When recommended — These studies are recommended when there is substantial movement of the chemical into subsurface horizons and ground water.

Alternatives — In the absence of this data, the EPA may assume tha the rate of degradation in these media is zero.

9) POTENTIAL FOR UPTAKE FROM SOIL INTO PLANTS

Objective — To provide details of the "removal" of chemical from the pool of material available for transport processes. It has more of an impact on the amount of chemical in the root zone available for leaching and on the residues in the plant likely to contribute to the dietary load of non-target terrestrial organisms. However, because it may be an important route of dissipation in some cases, and in order to get the necessary complete information for the validation of improved, unified, models, the ECOFRAM team believes that the Subdivision N guidance should be expanded to provide guidance on how best to conduct these studies.

Proposed Change — There is currently no requirement for estimating plant uptake. The proposed study would estimate the amount of pesticide and/or degradate that is accumulated in the plant material and the rate at which it is accumulated.

]

Advantages to modeling — Provides for the more accurate characterization of a potentially important route of dissipation for aquatic exposure. For aquatic exposure, this mostly provides an additional sink, and appropriately accounting for this route of dissipation improves the accuracy of the estimation of exposure. However, this may be an important route of exposure in terrestrial systems.

Limitations	Similar data is already generated to support human health dietary exposure assessment and tolerance setting. It may be possible to combine those studies with this study in the same experiment.
When recommended	If there is evidence that substantial amounts of pesticide are translocated into the plant material or if there is concern that there might be significant dietary exposure in terrestrial environments.
Alternatives	In the absence of this data the EPA will assume that no pesticide is translocated into plants for aquatic exposure assessment. For terrestrial exposure assessment, an appropriate conservative assumption will be made, such as an amount equal to that in the transpired water will be accumulated in the plant. In some cases, data from crop residue studies an rotational crop studies used to support the human health risk assessments can be used.

7.9. Appendix 3-7 ECOFRAM Aquatic Exposure Workgroup lists of spatial and general data of potential value for Exposure estimation.

i) Relevant General Sources of data for Searching for New information

US Geological Survey:

water.usgs.gov/public/data.html

geology.usgs.gov/data.html

mapping.usgs.gov

www.nbii.gov/index.html

US Environmental Protection Agency

www.epa.gov/OW/soft.html

US Department of Agriculture, Natural Resouces Conservation Service

www.nrcs.usda.gov/TechRes.html

US Department of Agriculture, National Agricultural Statistics Service

www.usda.gov/nass

US Department of Agriculture, Agricultural Research Service

www.ars.usda.gov/arsdb.html

US Department of Commerce, National Oceanographic and Atmospheric Agency

ns.noaa.gov/NESDIS/NESDIS_Home.html

US Department of Commerce, US Census Bureau

www.census.gov

Office of Air and Radiation Model Support website

www.epa.gov/scram001

ii) Spatial Data Sets of potential value for Scenario generation in Risk Assessment (current Jan 1999):

Type	**Topic**	**Title**	**URL**	**Comments**
Raw	Regions	Ecoregions		
Raw	Regions	Federal EPA		
Raw	Regions	USDA Agricultural Units		
Raw	Regions	MLRA		
Raw	Regions	Land resource regions		
Raw	Hydrology	HUC8		
Raw	Hydrology	HUC11		
Raw	Hydrology	HUC14		
Raw	Hydrology	USGS Reservoir database		
Raw	Hydrology	REACH File 3		
Raw	Hydrology	USGS Hydrology DLG's		
Raw	Hydrology	Athens Pond data		
Raw	Hydrology	SURF your watershed site		
Raw	Soil	NATSGO		
Raw	Soil	STATSGO		
Raw	Soil	SSURGO		
Raw	Soil	SOILS5		
Raw	Soil	SOILS6		
Raw	Soil	MUIR		
Raw	Soil	PEDON		
Raw	Soil	State data		
Raw	Climate	30 yr average data (1953 - 1983)		
Raw	Climate	30 yr average data (1963 - 1993)		
Raw	Climate	8000 individual weather stations		
Raw	Climate	2000 first order stations		
Raw	Climate	15 minute precipitation		
Raw	Climate	STARS database of wind speeds and directions		
Raw	Climate	Athens PRZM "canned weather sets"		

Type	Topic	Title	URL	Comments
Raw	Climate	Climate Generator potential		
Raw	Slope	DEM - 1:250K		
Raw	Slope	DEM - 1:24K Spotty		
Raw	Slope	NRI		
Raw	Slope	LS factors NRI		
Raw	Slope	County soil map descriptions		
Raw	Slope	MUIR database		
Raw	Slope	USGS Topo DLG's		
Raw	Slope	Local county Topo maps		
Raw	Cropping	USDA County data - 1987		
Raw	Cropping	USDA County data - 1992		
Raw	Cropping	USDA County data - 1997 (due)		
Raw	Cropping	LULC coverage		
Raw	Cropping	MRLC (or LCCP) - in progress - Anderson Level I		
Raw	Cropping	MRLC (or LCCP) - in progress - Anderson Level II		
Raw	Cropping	LANDSAT tm - for fine detail		
Raw	Cropping	STATSGO - cropping capability		
Raw	Cropping	NRI		
Raw	Cropping	State information		
Raw	Cropping	USDA Reporting data		
Raw	Cropping	Planting and Harvesting Dates		
Raw	Cropping	Crop rotation from NRI		
Raw	Tillage	CTIC database		
Raw	Species	EPA Endangered Spp web page		
Raw	Species	ESTF / National Heritage data		
Raw	Species	NAWQA info		

Type	Topic	Title	URL	Comments
Raw	Species	State records		
Raw	Species	PIRANHA (fish)		
Raw	Species	Acquire		
Raw	Monitoring data	NAWQA		
Raw	Monitoring data	STORET		
Raw	Monitoring data	OTS canonical database of EXAMS environments		
Raw	Monitoring data	BASINS - 305b		
Raw	Monitoring data	Mid continent study		
Raw	Monitoring data	Pesticides in GW database		
Raw	Monitoring data	Heidelberg College data		
Raw	Monitoring data	State Monitoring programs		
Raw	Monitoring data	MSEA data		
Raw	Monitoring data	ARP Surface water data		
Raw	Monitoring data	Chemical company data		
Raw	Community Water	CWS locations in BASINS		
Raw	Community Water	DRINKS		
Raw	Community Water	EPA Office of water		
Derived	Runoff	MUSCRAT		
Derived	Runoff	San Diego GLEAMS runs		
Derived	Runoff	USGS coverage		

Type	Topic	Title	URL	Comments
Derived	Runoff	HSPF data		
Derived	Runoff	SWRRB and GLEAMS datasets		
Derived	Runoff	PIRANHA		
Derived	Water concentrations	BASINS		
Derived	Water concentrations	NAWQA		
Derived	Cropping	NAWQA Crop coverages		
Derived	Model scenarios	Existing EPA scenarios		
Derived	Model scenarios	FEMVTF datasets		
Derived	Model scenarios	MUSCRAT		
Tools	GIS access	USGS "Switchyard"		

7.10. Appendix 3-8: Example Summary Reporting Formats (Based On Florida DEP Template)

Highlight Summary Page for PRODUCT CHEMISTRY
[63-5,6,7,8,9,11,12,14, and 20]

Product/Brand Name: _____ EPA Reg.No._____
(Check one): _____ Technical _____ Formulation
Active Ingredient Chemical Name : _____
_____
_____
Active Ingredient Common Name:_____
STRUCTURE:

pH:_____ Vapor Pressure:_____
Melting Point:_____ Boiling Point:_____
Density, Bulk Density, or Specific gravity:_____
Octanol/Water partition coefficient:_____ Water Solubility:_____
Empirical Formula:_____ Molecular Wt.:_____
KOC:_____ KD:_____
Reference(s):_____
_____
_____
Oxidizing or reducing action:

Corrosion characteristics:

Flammability:

List of impurities associated with active ingredient (>0.1%):

Highlight Summary Page for LEACHING AND ADSORPTION/DESORPTION STUDIES [163-1]

Complete a separate form for each soil or aquatic sediment type tested.

Product/Brand Name:_____ EPA Reg. No._____
Active Ingredient Chemical Name:_____
Active Ingredient Common Name:_____
Description of soil(s) or sediment used
Soil Series Class Name:_____

%Sand:_____ Moisture Content:_____
%Silt:_____ Soil Bulk Density:_____
%Clay:_____ Cation Exchange Capacity:_____
%Organic Carbon"_____ pH of soil or sediment:_____
%Organic Matter: _____ (Factor applied to %OC = _____)
Concentration:_____ Temperature:_____
Soil/water:_____

Koc:_____Kd:_____Kf:_____1/n:_____units
Source of soil or sediment (attach summary if additional space is needed):_____
_____
Type of test used (check appropriate method), indicate method detection limit for parent compound and significant metabolites:
_____ Radiological Assay _____ Non-radiological
_____ Thin layer Chromatography _____ Soil Column _____ Batch Equilibrium Study

Details of aging of test pesticide in soil or sediment. Include temperature and moisture conditions, and how aged soil/sediment was used in test _____
_____
For Batch Equilibrium study:

Equilibrium Time; _____
Concentrations used: _____
Molarity or normality of calcium ion solution used:_____
Solvents used in test solution:_____
_____

Highlight Summary Page for HYDROLYSIS STUDIES
[161-1]

Complete a separate form for each water temperature or parent concentration tested.

Product/Brand Name:_____ EPA Reg. No._____
Active Ingredient Chemical Name:_____
Active Ingredient common name:_____
Water temperature:_____ pH's: _____ Solubility:_____
Analytical technique, indicate detection limit method for parent and significant compounds (check one):
_____ Radio-assay _____ other(specify):_____
Detection Limit_____ Units_____
Solubility of parent substance:_____ Water pH tested:_____
Method of adding chemical to test system (solvent, volume etc.) _____

Method of adjusting pH: pH = _____Method:_____
pH =_____Method:_____
pH =_____Method:_____

Products Formed: pH =_____Products:_____
pH =_____Products:_____
pH =_____Products:_____

Estimate of ai half life: pH =_____$T_{0.5}$:_____
pH =_____$T_{0.5}$:_____
pH =_____$T_{0.5}$:_____

Half life estimation by: pH = _____Method:_____
pH =_____Method:_____
pH =_____Method:_____

Highlight Summary Page for PHOTODEGRADATION STUDIES
[161-2, 161-3, 161-4]

Complete a separate form for each water type, soil light intensity, wavelength distribution and exposure duration tested.

Product/Brand Name:_____ EPA Reg. No._____
Active Ingredient chemical name:_____
Active ingredient common name:_____
Analytical technique, indicate detection limit method for parent and significant compounds (check one):
_____ Radio-assay _____ other(specify):_____
Detection Limit_____ Units_____
Extinction coefficient:_____
Media (check one): _____ water pH's": 1)_____ 2)_____ 3)_____
_____ soil Soil pH's: 1)_____ 2)_____ 3)_____
Soil description: 1)_____
2)_____
3)_____
Moisture content:_____ Light Conditions (check): _____ natural light _____ artificial light
If artificial light used, describe the source and relationship of spectrum to natural sunlight at a relevant latitude:
_____
If natural light was used, provide latitude, time of year, and atmospheric conditions_____
_____
Light intensity:_____ Wavelength distribution:_____
Duration of exposure:_____
Method of applying chemical to test system (solvent, volume etc.) _____

Method of adjusting pH: pH = _____Method:_____
pH =_____Method:_____
pH =_____Method:_____

Products Formed: system 1 =_____Products:_____
system 2 =_____Products:_____
system 3 =_____Products:_____

Estimate of ai half life: system 1 =_____$T_{0.5}$:_____
system 1 =_____$T_{0.5}$:_____
system 1 =_____$T_{0.5}$:_____

Half life estimation by system 1 = _____Method:_____
system 2 =_____Method:_____
system 3 =_____Method:_____

Quantum Yield : system 1 =_____Q. yield:_____
system 1 =_____Q. yield:_____
system 1 =_____Q. yield:_____

Highlight Summary Page for AEROBIC SOIL METABOLISM STUDIES
[162-1]

Use additional forms as needed:

Product/Brand Name:_____ EPA Reg. No._____
Active Ingredient chemical name:_____
Active ingredient common name:_____

	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Soil /sediment Identifier:					
Soil Series Class Name:					
Soil source:					
% Sand:					
% Silt:					
% Clay:					
% Organic Matter:					
Soil pH					
Soil Bulk Density:					
Cation Exchange capacity					
Moisture Content:					

Analytical technique, indicate detection limit method for parent and significant compounds (check one):
_____ Radio-assay _____ other(specify):_____
Detection Limit_____ Units_____

Degradate Name	**Soil 1 max %**	**Soil 2 max %**	**Soil 3 max %**	**Soil 4 max %**	**Soil 5 max %**

	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Parent $T_{0.5}$					
Method for $T_{0.5}$					
Parent DT_{50}					
Parent DT_{90}					
DT_{n0} Method					

Highlight Summary Page for ANAEROBIC SOIL METABOLISM STUDIES
[162-2]

Use additional forms as needed:

Product/Brand Name:_____ EPA Reg. No._____
Active Ingredient chemical name:_____
Active ingredient common name:_____

	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Soil /sediment Identifier:					
Soil Series Class Name:					
Soil source:					
% Sand:					
% Silt:					
% Clay:					
% Organic Matter:					
Soil pH					
Soil Bulk Density:					
Cation Exchange capacity					
Moisture Content:					

Analytical technique, indicate detection limit method for parent and significant compounds (check one):
_____ Radio-assay _____ other(specify):_____
Detection Limit_____ Units_____
Method for ensuring anaerobic status:_____
_____

Degradate Name	Soil 1 max %	Soil 2 max %	Soil 3 max %	Soil 4 max %	Soil 5 max %

	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Parent $T_{0.5}$					
Method for $T_{0.5}$					
Parent DT_{50}					
Parent DT_{90}					
DT_{n0} Method					

Highlight Summary Page for AEROBIC AQUATIC METABOLISM STUDIES
[162-3]

Use additional forms as needed:

Product/Brand Name:_____ EPA Reg. No._____
Active Ingredient chemical name:_____
Active ingredient common name:_____

	System 1	System 2	System 3
Soil/sediment Identifier:			
Soil Series Class Name:			
Water/sediment source:			
% Sand:			
% Silt:			
% Clay:			
% Organic Matter:			
Sediment pH			
water pH:			
Water temperature			
Water/sediment ratio:			

Analytical technique, indicate detection limit method for parent and significant compounds (check one):
_____ Radio-assay _____ other(specify):_____
Detection Limit_____ Units_____
Air flow conditions:_____
_____

Degradate Name	System 1 max %	System2 max %	System 3 max %

	System 1	System 2	System 3
Parent $T_{0.5}$			
Method for $T_{0.5}$			
Parent DT_{50}			
Parent DT_{90}			
DT_{n0} Method			

Highlight Summary Page for ANAEROBIC AQUATIC METABOLISM STUDIES [162-4]

Use additional forms as needed:

Product/Brand Name:_____ EPA Reg. No._____

Active Ingredient chemical name:_____

Active ingredient common name:_____

	System 1	System 2	System 3
Soil/sediment Identifier:			
Soil Series Class Name:			
Water/sediment source:			
% Sand:			
% Silt:			
% Clay:			
% Organic Matter:			
Sediment pH			
water pH:			
Water temperature			
Water/sediment ratio:			

Analytical technique, indicate detection limit method for parent and significant compounds (check one):

_____ Radio-assay _____ other(specify):_____

Detection Limit_____ Units_____

Air flow conditions:_____

_____

Degradate Name	System 1 max %	System2 max %	System 3 max %

	System 1	System 2	System 3
Parent $T_{0.5}$			
Method for $T_{0.5}$			
Parent DT_{50}			
Parent DT_{90}			
DT_{n0} Method			

Highlight Summary Page for FIELD DISSIPATION (SOIL) STUDIES
[164-1]

Product/Brand Name:_____ EPA Reg. No._____
Active Ingredient chemical name:_____
Active ingredient common name:_____

	Soil 1 Surf	Soil 2 Surf	Soil 3 Surf	Soil 4 Surf	Soil 5 Surf
Soil /sediment Identifier:					
Soil Series Class Name:					
Soil source:					
Soils5 MUID No.					
County/State/crop					
% Sand:					
% Silt:					
% Clay:					
% Organic Matter:					
Soil pH					
Soil Bulk Density:					
Cation Exchange capacity					
Moisture Content:					
Measured Parent K_{OC}					
Application rate (units)					
Number of applications					

Analytical technique, indicate detection limit method for parent and significant compounds _____
_____

Degradate Name	LOD (ppb)	Soil 1 max residue	Soil 2 max residue	Soil 3 max residue	Soil 4 max residue	Soil 5 max residue

	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Parent $T_{0.5}$					
Method for $T_{0.5}$					
Lab. Aerobic $T_{0.5}$					
Parent DT_{50}					
Parent DT_{90}					
DT_{n0} Method					

Was parent or any degradate found below surface layer - if so, provide details:_____
_____
_____
_____