FIFRA Scientific Advisory Panel Briefing Document for a Consultation on:

Monitoring Strategies for Pesticides in Surface Derived Drinking Water

EPA
United States
Environmental Protection
Agency

Table of Contents

List of Tables

List of Figures

Introduction

The Food Quality and Protection Act (FQPA) of 1996 mandates that the Office of Pesticide Programs (OPP) complete aggregate and cumulative human health risk assessments for pesticides with food tolerances. Aggregate risk assessments consider all routes of exposure, including drinking water. Cumulative risk assessments consider risks for multiple pesticides with common modes of action. The focus for this Scientific Advisory Panel (SAP) is to discuss issues associated with designing a survey to collect *pesticide monitoring data* for *drinking water derived from surface water* for use in chronic aggregate and cumulative human health risk assessments, and risk management decisions. Assessments of acute exposure will not be considered at this time.

The Agency uses a tiered approach for assessing pesticide concentrations in drinking water. This approach includes using screening models, pesticide occurrence data in ambient waters [*e.g.*, National Water Quality Assessment (NAWQA) Program], and when available, pesticide occurrence data in drinking water. Developing a systematic methodology for monitoring pesticide concentrations at drinking water intakes on surface water systems in pesticide use areas is an important and integral part of this approach, especially in the short term. For many reasons, ranging from cost considerations to practical limitations, OPP believes over the long term we must develop and validate models which can accurately predict pesticide concentrations at drinking water intakes on surface water systems in pesticide use areas. In March 2000, the Environmental Fate and Effects Division (EFED) and the United States Geological Survey (USGS) brought two regression based models to the SAP. The March SAP was very favorable in its review and comments and strongly encouraged EFED to continue down this path. Also, in August 1998, the Agency presented to the SAP, physically based basin scale models that could be used to estimate pesticide concentrations in drinking water. Work is continuing in EFED and the USGS to develop these models, but surface water monitoring data is needed to develop, test and effectively use them. Thus, it is EFED's view that given the high cost of collecting drinking water monitoring data, surface water monitoring data collected in the near term should both support the longer term goal of model development and should provide sound and meaningful data which can be used today in aggregate human health risk assessments.

Approximately two years ago, OPP initiated an effort to work with the Office of Water, other federal Agencies, and ACPA to develop a plan to collect data on drinking water derived from surface water sources nationally for use in human dietary pesticide risk assessments. Last year, ACPA presented OPP with a proposal for a one-year survey for pesticide occurrence in drinking water derived from surface water resources addressing acute and chronic endpoints for an approximate cost of $7 - $10 million. Although we were in agreement with elements of the chronic design, OPP had concerns about a number of the critical elements of the ACPA proposal. OPP is seeking to obtain input from SAP members on how to best approach the design of a multi-pesticide surface-water based drinking water monitoring study whose goal is to define for each targeted pesticide, the distribution of annual average concentrations in surface water which people drink across the pesticide's use areas for an approximate cost of $7 - $10 million. OPP would use the distribution of the annual average concentrations for *each targeted pesticide* in the aggregate human health risk assessment. Further, other information collected during the survey (*e.g.* information on pesticide use and watershed characteristics around the sampled systems) would be used by OPP to help target risk mitigation actions to those areas at highest risk.

For this SAP consultation, EFED is presenting six critical design elements, including the elements proposed by ACPA, for discussion. In addition, EFED is offering its current thoughts on what it views as a preferred approach for elements of this survey. Critical design issues are:

1. How to select pesticides?
2. How to approach community water system (CWS) site selection?

a. How to define CWS vulnerability (both urban and agricultural)?
b. Should the design be stratified based on CWS vulnerability?

3. What to sample – raw and/or finished drinking water?
4. How frequently should samples be taken at each system? Given cost constraints, how to select between the number of sites and the number of samples? What role should seasonality of pesticide use play in determining when samples are collected?
5. For how many years should sampling continue?
6. What type of ancillary data should be collected on watershed characteristics at the time of sampling?

These six design issues ultimately influence the information available to answer risk management questions. OPP recognizes there is a great deal of interplay between science, policy, and economics in the design of such a survey. Decisions on key survey design issues define the nature of the monitoring program. These issues are influenced by the needs of risk managers, which include answers to the following questions:

1. Is there a significant number of people and/or sub-populations (*e.g.*, the people served by a set of surface water-based CWS's) who will be exposed to annual average concentrations of a pesticide in drinking water at levels which would cause a significant chronic risk?
2. Can we identify and mitigate areas of high risk in a scientifically defensible manner.

Background

To characterize the occurrence of and exposure to pesticides in drinking water, the Agency uses all available reliable data; initially screening individual pesticides and gradually refining occurrence and exposure assessments. Refinements use more sophisticated models and incorporate available monitoring data. When the Agency has reason to believe significant exposure could occur, but uncertainties exist in the occurrence estimates, pesticide-specific monitoring has been required to better characterize pesticide occurrence. This section provides background on occurrence, exposure, and risk management issues specific to drinking water assessment as well as a description of several surface water monitoring programs which have been conducted or proposed to provide surface water monitoring data to the Agency.

Occurrence of Pesticides in Surface Water and Relevance to Survey Design

Pesticides in surface water tend to occur in pulses that can last from days to weeks to months, depending on the type of water body and the pesticide[1]. The occurrence of most pesticides in surface water from agricultural uses is seasonal, and is related to the timing of pesticide applications, rainfall or irrigation, and the size of the watershed. The predominant source of agricultural pesticide residues in surface water is related spatially to *where* the pesticide is used[1]. Thus, the occurrence of a pesticide in drinking water at a CWS above a level of concern is not a random event but is heavily influenced by whether that pesticide is used upstream of a CWS intake. Seasonal occurrence patterns of urban-use pesticides are less distinct in part because application occurs over longer periods of time than for agricultural use pesticides[1].

Since the water a person drinks typically comes from one or two sources, a monitoring survey must be capable of characterizing the pesticide concentrations to which an individual is exposed at local or substantial. It also needs to account for the fact that if a pesticide occurs, it will probably be there for several days in a row. In order for the Agency to sufficiently characterize pesticide occurrence in drinking

[1]Larson S.J., P.D. Capel, and M.S. Majewski. (1997?) *Pesticides in Surface Waters: Distribution Trends and Governing Factors.* Ann Arbor Press, Inc. Chelsea Michigan. 373 pp.

water derived from surface water, monitoring data must be able to estimate the following parameters for sampled CWS's throughout the pesticide use area: how frequently a pesticide occurs at an individual CWS; if it is likely to recur at the CWS at the same time each year; how long it persists at the CWS when it occurs, and the magnitude of the pesticide concentrations that occur. To fully assess the impact of a pesticide on drinking-water quality we also need to characterize: 1)how the parameters described above vary from one CWS sampled to another across the pesticide use area; 2)uncertainty in extrapolating from one sampled CWS to other CWS's in the pesticide use area; 3) and the error in extrapolating from the time period sampled to other times (for example, one year to another).

Most importantly, any survey design must well distinguish situations where a pesticide may be of concern from those where it is not. This is critical to reasoned risk management decisions. A good risk manager seeks always to reduce risk in the most cost-effective manner, by strategically tailoring use restrictions or limitations. The Agency must have sufficient confidence in the monitoring results that, given no detections for a specific pesticide, we can reasonably conclude that there will be at most negligible exposure, rather than the absence of detections were the consequence of a design flaw.

Use of Drinking Water (Surface) Monitoring Data in Risk Assessment

Estimating exposure to a pesticide in drinking water entails estimating both the occurrence of a pesticide as well as estimating the consumption of water by the relevant population. The Agency needs to be able to characterize pesticide exposure (occurrence and consumption) in drinking water at an appropriate regional scale for sensitive sub-populations and for the overall population in that region. EFED expects the results of this monitoring to be used by the Health Effects Division (HED) in combination with drinking water consumption estimates to develop either a point estimate of chronic human drinking water exposure or a distribution of chronic human drinking water exposure across the use area of the pesticide. Either of these would be combined with estimates of chronic exposure to the pesticide in food and/or chronic exposure to the pesticide from use in or around the home.

The monitoring should provide distributions of concentrations at individual sampled CWS's. From those data, one can also calculate an annual average concentration for each CWS and develop a distribution of annual average concentrations across sites. The full distribution, the distribution of the site means, or alternatively a selected point estimate (for example, the 95th percentile site in the distribution of annual means for CWS's in a region) can be used to estimate pesticide occurrence at CWS's within, for example, the pesticide's use area.

HED is currently developing tools to estimate exposure through food consumption based on the principle that exposure occurs to an individual over time. Accounting for the timing of pesticide occurrence in drinking water is important to consider in exposure assessment because higher concentrations may occur simultaneously with increased residential exposure as all these routes of exposure are associated with the application of the pesticide. The survey design needs to provide occurrence data at the appropriate level of spatial and temporal resolution so that risks from water could be appropriately added to other sources of dietary risks in a probabilistic manner (if desired) as well as to other sources of risk in an aggregate human health risk assessment.

Currently EFED provides HED with model-based annual mean concentrations which are equaled or exceeded every 10 yrs at a site. The site used in the model scenario is considered to be an upper 90^{th} percentile use site; that is, exposure at the use site is expected to be greater than exposure at 90% of sites used to grow a specific crop. There are no confidence bounds on the predicted concentrations. Model inputs are generally chosen to be representative of mean values for sites being modeled. Chemical specific inputs (*e.g.* aerobic soil half-life) are generally chosen to represent 90^{th} percentile values. The cumulative result of model site selection and chemical inputs is intended to predict concentrations at the higher range of the distribution concentrations likely to occur in surface water.

The standard for pesticide concentration data quality has four elements: (1) the summary statistic used to describe the exposure, (2) the fraction of the population protected, (3) the frequency at which an adverse concentration will occur, and (4) the confidence in the accuracy of the assessment.

1. For chronic human health risk, OPP is currently using an annual mean as the statistic to represent exposure in deterministic risk assessments. The mean over time at a site is better approximated using time-weighting for the estimate rather than a straight arithmetic mean. This is generally necessary because samples are not usually collected at equal intervals throughout the year, but concentrated when they are most likely to occur. Time-weighting accounts for the bias generated by these sampling methods.

2. HED uses the average dietary consumption (foods and water) of 10,000 individuals over a 3-day period along with pesticide occurrence on individual food items to estimate chronic exposure. Food residues are typically estimated using either monitoring data or residue field trials. The exposure through all dietary sources (all foods and water) will be summed to estimate aggregate dietary exposure. The dietary exposure is then compared to a toxic reference point (*e.g.* %RfD) and the Agencies determination wether the risk is acceptable or if mitigation is needed.

   To provide HED with data on pesticide exposure through drinking water, EFED is proposing to identify 95th percentile CWS's (the facilities at which the annual average concentration is at the 95th percentile), rather than the 90th percentile site used in modeling. Because of the uneven distribution of population among water supplies, and because small water supplies tend to be more vulnerable to pesticide contamination, this will protect a substantially greater portion of the population. Population weighting can be used to convert the design from a CWS basis to a population basis.

3. Since surface water concentrations vary over time it is necessary to identify a specific frequency at which a level will occur as a standard to characterize exposure at a given site. The standard for return frequency, or the frequency at which a level will occur, for modeled estimates of pesticide concentrations in surface water is once in ten years. In chronic dietary exposure assessments, average annual food residues may change due to use/usage changes resulting from climate, pest pressure, or market forces. Currently HED uses food residues averaged over five years. In the near future, HED intends to identify durations of exposure (six months to one year for chronic exposure), exceeding a toxic endpoint, that occur over a five year period. Food residue monitoring data collect within five years is used in exposure assessments.

4. There is no current Agency standard for data confidence. However, a standard is needed to design a statistically-based survey. EFED is proposing to use a 95% confidence value as a standard for the study.

Use of Drinking Water (Surface) Monitoring Data in Risk Management

EFED expects the results of this monitoring survey to be used by risk managers to target drinking water related risk mitigation actions in those areas posing unacceptably high risk. The local nature of drinking water exposure allows for geographically targeted risk management options. It is important to understand, once geographical areas have been identified, the relationship between the timing of pesticide application and occurrences of high concentrations. More information regarding the cause of the high concentrations will permit risk managers to impose the most tailored mitigation measures with the least impact to growers. Without this information, mitigation measures will be less discriminating. For example, if monitoring data shows that high concentrations in drinking water for a pesticide are associated with

applications during the non-growing season in northern California (a dormant application), risk mitigation could be focused on this specific practice in this location. Without these data, the use of the pesticide may be canceled on certain crops, not allowed in the western part of the US, or the dormant application of the pesticide may not be allowed nationwide.

Previous or On-Going Surface Water Monitoring

For previous studies, the Agency has looked at eight data objectives: four assessment and four developmental. The assessment objectives are:

1. Drinking water exposure assessment – estimate the frequency, magnitude and duration of exposure in drinking water across the national population and identifiable sub-populations. This objective is meant to support the human health risk assessments.

2. Aquatic exposure assessment – estimate the frequency, magnitude and duration of exposure to non-target life in aquatic ecosystems. This objective supports the ecological risk assessments.

3. Water quality assessment – determine the magnitude and frequency of the occurrence of a pesticide in water resources. This objective supports the Agencies pollution prevention goals and is not keyed to any particular identifiable risk.

4. Fate and transport assessment – determine the relative importance of the different routes and mechanisms of transport to and through a watershed or aquifer. This objective provides understanding of the pesticide's behavior in the environment and aids in making informed and appropriate risk management decisions for the pesticide.

The development objectives are:

1. The development of regression based, or empirical, models for describing the occurrence of pesticides in water resources. A sound tool of this nature would aid in differentiating pesticides requiring further refinement of drinking water concentrations from those that do not. The Agency is currently working with the USGS to develop models of this nature.

2. The evaluation and validation[2] of physically-based models. The Agency may also use physically based basin scale models for risk assessment. These models have different capabilities from empirical models and are particularly useful for evaluating potential risk mitigation options. Physical models must be validated against measured field data in order to verify that the model does in fact reflect reality. Successful validation exercises should build the confidence necessary to use these tools in a regulatory setting.

3. Development and testing of a vulnerability assessment tool or index for water resources. The ability to determine relative likelihood that a site will have frequent and/or high magnitude occurrence of a pesticide is a critical need for the OPP. A site vulnerability index would be valuable for many purposes including, designing future monitoring studies, putting data from older studies into context, identifying vulnerable sub-populations and using data from studies of that were not done at drinking water sites and using it to assess drinking water exposure. This subject is discussed in substantially more detail in the site selection process in the body of this document.

[2] We are defining validation in this case as "A comparison of measured values with values calculated by some model in order to determine the level agreement and circumstances or causes where there is substantial lack of agreement.

4. Development of improved and more powerful statistical methods for the interpretation of monitoring studies. An improved understanding of the structure and relationships that underlay pesticide concentration data will allow the development of improved tools for analyzing monitoring studies. These improved tools will allow regulatory decisions to made with increased confidence, or with less underlying data in the future.

OPP has in the past required surface water monitoring programs for specific pesticides as a condition of registration or re-registration. In addition, the Agency requires compliance monitoring for 16 currently registered pesticides under the Safe Drinking Water Act (SDWA) at community water systems (CWS). A key source of surface water monitoring data is provided to OPP by USGS National Water Quality Assessment Program (NAWQA). Overall, there has been limited drinking water monitoring of surface water, and the scope and nature of all monitoring program designs has been variable.

Design Elements of Submitted Monitoring Studies

Table 1 provides a summary of several surface water monitoring programs. A review of survey design elements reveals that there is a great deal of variety in approaches to survey design. The variety in design frameworks is influenced by the purpose, and the nature of the pesticides in the study. For example, the NAWQA study is designed to characterize water quality across the nation. Pesticides considered in the NAWQA survey were selected to represent those with greater use. Only ambient water from rivers and streams was sampled. In contrast, the purpose of the Unregulated Contaminant Monitoring Regulation (UCMR) is to provide data to further refine drinking water regulations as required under the SDWA. Pesticides in the UCMR appear on the Unregulated Contaminant List. Finished drinking water is only sampled in the UCMR. Other monitoring studies have been designed to focus on apparently highly vulnerable sites. These studies are generally conducted for a single pesticide and can be used for screening purposes to place other monitoring data into context. None of the study designs provide a complete design framework for a national-scale drinking water monitoring program.

Table 1. Examples of surface water monitoring studies used in drinking water assessments.

Study Identification	Crops	Type of Water	Study Duration	Sample Location	Watershed Vulnerability Considerations	Number of Sites	Sample Frequency
Acetochlor Registration Partnership	corn	Finished with raw samples on sites with activated carbon	7 years	CWS	Corn acreage in the watershed surface water body source	175	14 samples per year with biweekly sampling during use period
Atrazine	corn	Finished	6 years	CWS	None	5044	Quarterly Samples
Bromoxynil	corn, small grains, cotton	Finished Raw	1 year	CWS	Watershed size Pesticide Use Atrazine Detections	16	Pre- and Post treatment, two intervals during the growing season and monthly interval thereafter

Table 1. Examples of surface water monitoring studies used in drinking water assessments.

Study Identification	Crops	Type of Water	Study Duration	Sample Location	Watershed Vulnerability Considerations	Number of Sites	Sample Frequency
Fipronil	corn	Finished Raw	1 year	CWS	Watershed Six Pesticide Use Atrazine Detections	13	Pre- and Post treatment, two intervals during the growing season and monthly interval thereafter
Carbaryl	corn & non-ag uses	Finished Raw	1 year	CWS	Watershed Size Pesticide Use Atrazine Detections	20	Pre- and Post treatment, two intervals during the growing season and monthly interval thereafter
NAWQA	Agricultu ral land, Forrest, & urban areas	Ambient	1991-	Ambient	Targeted Land uses.	~60 intensive sites	Variable-depends on site designation
Pilot Reservoir Monitoring	Cotton Corn Peaches Non-Ag	Finished Raw	1 year	CWS	Pesticide Use Reservoir Size Reservoir Location	12 reservoirs	Variable
Unregulated Contaminant Monitoring Regulation	None	Finished	1 year every 3 years	CWS	None	~6400	Quarterly Samples

Submitted Proposal for a National Surface Water Drinking Water Survey for Pesticides.

The American Crop Protection Association (ACPA) has proposed a national-scale design framework for assessing daily peak and annual mean pesticide concentrations in surface water used for drinking water. Based on EFED's review of the ACPA submission the following are the essential features of the *chronic survey component* of the monitoring strategy proposed:

- ACPA's site selection process proposes a national drinking water survey based upon five geographically based analysis domains: four food regions and the coterminous United States. An additional five domains will represent "vulnerable" CWS's within these geographic areas.
- The counties in the contiguous 48 States comprising the top quartile of pesticide use intensity for any one of 25 target pesticides are identified as a "high pesticide use intensity area". When a CWS with a "small or medium" sized watershed occurs in the "high pesticide use intensity area" it is defined as a "vulnerable CWS". To identify CWS that are vulnerable to chronic exposure ACPA will select "CWS using reservoirs and having a higher use of products with chronic exposure issues".
- Monitor finished drinking water for one year, with triggers for extension if "regional pesticide use is too low to meet FQPA requirements".
- Use an optimized sampling strategy based on stratified, random sampling. For chronic exposure parameters, water samples will be collected systematically throughout the year at the required number of CWS in each domain. Strata will "be based on factors thought to be related to overall

CWS vulnerability: reservoirs vs flowing water, pesticide use intensity, population served, geographic diversity, *etc.*"

- Collect samples from each CWS an *average* of 10 times in a year depending on the type of water body. Sampling frequency will be adjusted based on the hydrologic nature of the water source, with less frequent sampling from reservoirs and lakes. Possibly composite samples seasonally to reduce to 4 "seasonal" samples per site.
- Analyze each sample for all 118 pesticides on the USGS multi-analyte schedules
- Develop a distribution of seasonal and annualized mean concentrations at each CWS for all 118 pesticides, including non-targeted compounds "with a maximum value to exceed the 95th percentile of CWS-years".
- Use seasonal and annual average concentrations to represent regional and national average concentrations for "vulnerable" CWS and for *all* CWS.

OPP believes the ACPA design framework for assessing *annual mean concentrations* could be an acceptable survey design with some modifications, including the site selection process, sampling frequency, vulnerability classification system, sampling raw and finished water, selection of priority group of pesticides, and study duration.

Critical Design Elements

Target Population

OPP is defining the target population for the survey as CWS's within the use areas of the selected pesticides. The population served by each CWS will be known and can be used to convert the data from a CWS basis to a population basis. By defining the target population in this manner, it is assumed runoff is the predominant route through which pesticides contaminate drinking water. Contamination resulting from routes other than runoff is expected to result in lower concentrations that are unlikely to exceed levels of concern.

Ultimately the Agency is interested in the human population consuming surface-derived drinking water and link these exposures to dietary assessments. Dietary (food-based) exposure assessments assume the food supply of the U.S. is evenly distributed. Drinking water, unlike food, is supplied from local sources – it is not nationally distributed. Surface source drinking water is generally processed at local public water facilities. Thus, pesticide exposure needs to be evaluated on sub-populations of humans in the U.S. deriving drinking water originating in a watershed where a pesticide is used (*i.e.* a CWS). Because each CWS serves multiple households, targeted monitoring of public water facilities is expected to be the most efficient approach in a monitoring study. Monitoring of in- house tap water would provide the most refined exposure concentrations of pesticides in drinking water. However, a study of tap water does not allow the Agency to meet its other regulatory objectives (*e.g.* model validation or information for risk management decisions). Further, tap water monitoring may be cost prohibitive given the variability in distribution systems and networks.

ACPA defines the target population of there study as CWS's obtaining some or all of there source water from surface water sources.

Pesticide Selection

Many strategies can be employed to select pesticides as analytes in a national survey of pesticides in drinking water and each strategy has advantages and disadvantages. It is critical to be aware that there is

an intimate link between site selection, chemical selection, sampling frequency, and the cost constraints of the survey. Although one can make an independent decision about which chemicals are most important to target and analyze in such a survey, the framework of the design and characteristics of pesticide use in the proximity of a water treatment facility during the survey will largely determine how well survey data represent the water quality impacts of each individual pesticide. It is reasonable to assume that national survey results will best represent the impact on surface-water quality from pesticides that are widely used throughout the country, rather than from pesticides used on speciality crops or pesticides with major non-agricultural uses, whose actual use areas are poorly defined. The methodology used to select target pesticides as analytes must be taken into account in determining the process to select appropriate monitoring locations.

The analysis of water samples for pesticide residues is the major factor in the cost of a monitoring survey. When costs are constrained, as they are in this survey, one way to maximize the information obtained and minimize analytical costs is to use multi-analyte methods, which provide concentrations for a large number of pesticides in one analysis. A downside of multi-analyte methods is that the data obtained may not be equally meaningful for all analytes. For example, if a pesticide is not used near any sampling locations, a multi-analyte method will still provide data. However, one cannot conclude that these survey results for that pesticide represent the impact on water quality in areas where that particular pesticide is actually used.

Possible chemical selection strategies based on risk, use site (crops), usage, environmental fate properties, anticipated regulatory decisions, analytical methodologies, or a combination of these criteria are described below. In the end risk managers play a major role in selecting chemicals for this survey.

Risk Based Selection

Pesticides with relatively higher risks can be targeted as analytes based on toxicity to humans and occurrence in drinking water. Toxicity and risk determinations can be based on studies reviewed by the Agency, and are typically summarized in Re-registration Eligibility Decision (RED) documents and in emergency exemptions (Section 18) and Section 3 science chapters.

The advantage of selecting pesticides based upon risk is that one can ensure that pesticides with potentially high risks (and which need refined estimates) will be included in the national drinking water survey and that data will be available to the Agency for use in risk assessment and risk management. One possible drawback of using this factor alone in selecting target analytes is that new data can change the Agency's conclusions about toxicity, or provide information about new areas of risk (*e.g.* endocrine disruption effects) about which the Agency is unaware at the time the survey is designed.

Pesticide Use and Crop Based Selection

Pesticides can be targeted as analytes for the survey based upon the crops that they are used on. For example, the herbicides, insecticides, fungicides, and fumigants used on cotton, corn and soybeans, and apples could be selected a s survey analytes. Good data on land use and pesticide use will be needed for this approach, as crop use areas will determine the geographic scope of the monitoring. An advantage of this approach is that, like the Pesticide Data Program (PDP) which supplies pesticide residue data on a crop specific basis for dietary assessments, these data clearly identify impacts of a specific pesticide use on drinking water quality. Also, the "national" scope of the program would be geographically defined as the pesticide use areas of these crops. Additionally, risk managers will have high quality comparative data about the relative impacts of alternative pesticides for a certain use on drinking water quality. One disadvantage of this approach is that, like PDP data, targeted data will not be gathered for all uses of a pesticide, and additional monitoring may be needed on an on-going basis focusing on other pesticide uses.

Pesticide Usage Based Analyte Selection

Pesticides can be targeted as analytes for the survey based on their overall national usage, high application rates, or on use intensity. EPA's National Survey of Pesticides in Drinking Water Wells selected analytes based in part on this criterion (at least one million pounds or more of use nationally in a specific year). An advantage of this approach, since pesticide usage or use intensity is strongly correlated with occurrence in surface water. Also, model predictions are directly correlated with pesticide application rate. Thus, there would be a greater likelihood that analytes identified based on these criteria would be found in such a survey. A disadvantage is that some compounds would not be included if they are not heavily used, yet these compounds could have an impact on water quality in local areas.

Environmental Fate and Transport Properties Based Analyte Selection

Environmental fate and transport properties of a pesticide determine in part if there is the potential for that pesticide to be transported via surface runoff to surface water which may be a source of drinking water. Pesticide environmental fate properties affecting runoff potential include: water solubility, acid-base dissociation constants, ionic properties, soil/sediment sorption coefficients, and environmental stability or persistence. Some examples of screening procedures to determine if a pesticide is not likely to occur in runoff are the methods of Goss[3], Hornsby[4] and the FIRST and PRZM models. In general, highly water soluble pesticides tend to stay in the aqueous phase, and can have a greater potential for runoff. Ionic chemicals and pesticides that exhibit acid-base characteristics may be more prone to offsite transport in the dissolve phase, which is typical when the solution pH enhances the formation of anionic species. For example, DCPA dimethyl ester is immobile; however, when hydrolyzed to mono- and di-acid species it is quite mobile and easily transported in runoff. Pesticides with lower sorption coefficients are generally more prone to runoff in the dissolved phase than those with higher sorption values. Another factor affecting runoff potential is persistence, which can be predicted from aerobic and aquatic metabolism half-lives. Pesticides which are more persistent are generally more available to be transported in runoff.

One important advantage of using this criterion is that chemicals that are persistent and mobile and therefore have a greater likelihood of being detected in surface water will be selected, if they are not removed or transformed during water treatment processes. Another advantage is that if one can identify a sub-group of pesticides which have common or comparable fate and transport properties and select one compound to represent each sub-group, survey results could be applied to pesticides which were not analytes but which are members of that sub-group. A disadvantage of this approach is that there may not be adequate fate data available to draw conclusions about all pesticides, degradation products, or transformation products.

Regulatory Based Analyte Selection

The Office of Pesticide Programs is operating under congressionally mandated deadlines to reassess tolerances for all pesticides. The Food Quality Protection Act (FQPA) sets a timetable for tolerance reassessment. Based on this criterion, one could select the next group of pesticides for which monitoring data is needed for tolerance reassessment decision making. Another option is to use the pesticides on the Office of Water's Unregulated Contaminant Candidate list (UCCL) (established by the SDWA) as analytes in the survey. The Agency will consider developing drinking water standards (maximum contaminant levels) for these pesticides based in part on monitoring data. An advantage of using this selection strategy is that when regulatory decisions are made the best scientific data will be available. A disadvantage is that risk management decisions could be made in the near-term that change target pesticide uses, use areas and

[3]Goss, D.W. 1992. Screening Procedure for Soils and Pesticides for Potential Water Quality Impacts. Weed Technol. 6(3): 701-708.

[4]Hornsby, A.G. 1992. Site-Specific Pesticide Recommendations: The Final Step in Environmental Impact Prevention. Weed Technol. 6(3); 736-742.

application rates that would make the survey results inapplicable.

Analytical Methodology Based Selection

Using this criterion, pesticides and degradation products with validated analytical methodologies of acceptable precision and accuracy would be included analytes. The USGS NAWQA program has established multi-analyte analytical methods with very low limits of detection for a large number of pesticides (118)[5]; however some of these methods have low analytical recoveries. The major advantage of this selection strategy is that several analytical methods already exist, and if these methods are determined to be acceptable, analytical method development will not affect the time required to implement the survey. A disadvantage is that certain pesticides, pesticide degradates, or pesticide transformation products which are toxic may not be included because analytical methods are not available. Also, multi-analytes methods may not provide data of equivalent quality for all compounds or if compounds are not used, because the method is not optimized for all compounds. Detections of analytes for which methods are not optimized may in some instances be of some use in defining lower bounds of exposure in FQPA drinking water assessments on a case by case basis.

The ACPA proposal for a national survey adopted this approach for analyte selection. Analytes were identified for which there is a validated NAWQA analytical method (identified as NAWQA schedules: 2001, 2002, or 2060). About 118 analytes would be analyzed using this approach. Data would only be reported for those compounds whose registrants agree to participate in the Survey[6].

Combination of Several Criteria in Analyte Selection

A combination of the criteria listed above can be used to rank potential analytes from which a target list can be selected. This combination would take into account risk or toxicity concerns, use intensity and rate, surface water runoff potential, and the availability of acceptable analytical methodologies. For each pesticide one would consider and weight these factors separately (e.g, large, medium, and small use). The cumulative or total score is used in the relative ranking and final selection of the target analytes.

Using this weighting, ranking, and selection method has the advantage that a number of different key factors can be considered simultaneously in selection of analytes. For example, including the criteria described in the example above, selected analytes would be toxic to humans, be more likely to occur in surface waters, and have available validated analytical methods of acceptable sensitivities. If different criteria are included, analytes would be selected that reflect those criteria. For example if analytical methodology, use site, and environmental fate and transport criteria are chosen, selected analytes would have existing analytical methods, be used on specified crops, and be more likely to occur in surface waters. One possible disadvantage of using multiple factors in analyte selection is the relatively longer time needed to collect all the required information before the ranking and final selection of the target analytes can be completed. Other disadvantages are described above under individual factors.

Design Framework

The sampling strategy framework is the foundation of a monitoring program. There are two sampling approaches, probabilistic and non-probabilistic. Probabilistic methods use random sampling, but may divide the sample space into predefined subsets. Non-probabilistic methods such as haphazard sampling and judgement sampling do not sample randomly and thus require a homogeneous population over time and

[5]Larson, S.J., R.J. Gilliom, and P.D. Capel. 1999. Pesticides in Streams of the United states–Initial Results from the National Water-Quality Assessment Program. U.S. Geological Survey. Water-Resources Investigations Report 98-4222. Sacramento, California.

[6]American Crop Protection Association (ACPA). 1999. A National Survey of Pesticides in Drinking Water Obtained from Surface Sources. Paper submitted to OPP EFED.

space for an unbiased estimate.

Probabilistic sampling strategies include simple random sampling, stratified random sampling, two-stage sampling, cluster sampling, systematic sampling, and double sampling[7]. Each of these sampling strategies are useful to optimize the design efficiency for addressing spatial and temporal distributions of contaminants. The simplest probabilistic sampling strategy is random sampling. This sampling approach is useful when there is no prior knowledge of the population of interest. The stratified random sampling strategy is useful when the population of interest can be divided into homogeneous subgroups. The stratified random sampling approach should allow for equivalent or more precise estimation of the mean than the simple random sampling strategy. Cluster sampling strategies are useful when the units of the population cannot be sampled individually, such as a school of fish. Systematic sampling strategies are useful for sampling a dispersed population of interest using systematic or random sampling along a predefined grid pattern. Systematic sampling can lead biased estimates of the mean because of unknown patterns in the population of interest. Also, the distinct patterns or non-randomness in the population of interest may prevent an accurate estimate of the sampling error.

Non–probabilistic sampling methods such as haphazard sampling are not appropriate for a national drinking water survey because of the non-random nature of pesticide use. Judgement sampling is a more appropriate approach because sampling can be focused within pesticide use areas. The heterogeneous highly structured nature of judgement sampling is expected to bias estimates of the mean pesticide concentrations. This type of sampling can be associated with current targeted surface monitoring studies for assessing pesticide concentrations at vulnerable CWS's within pesticide use areas.

ACPA has proposed a stratified random design based on five domains.

Domains of Interest

The study is designed around domains, which are distinct portions of the population for which data collected will meet minimal standards of accuracy. In this survey, the domains are collections of CWS's grouped according to common factors such as pesticide usage, crop areas, regions, and watershed vulnerability. For example, to draw conclusions about CWS's in a pesticide use area, CWS's would be the target population and the pesticide use area would be the logical domain. Domains need to be constructed in a manner allowing for calculation of a statistical inference. For instance, the minimum desired statistical inference may be the mean annual concentration at the 95th percentile site with 95% confidence with a two year return frequency. Domains should be chosen to reflect the target population. Domains may overlap (*e.g.* pesticide use area for multiple compounds) or CWS's may be assigned to separate domains (*e.g.* national food region domains).

Pesticide Use Domains

Pesticide use domains are CWS's with target pesticide use in their watersheds. The advantage of using pesticide use as a domain is that survey results will provide information about drinking water quality at CWS's in watersheds where the pesticide is used. Additionally, the use of pesticide use as a domain should make the design more efficient because CWS's with multiple target pesticides will be included in several pesticide domains. Importantly, data will be collected for assessing pesticide co-occurrence for cumulative exposure assessments. A disadvantage is that site selection is somewhat more

difficult because the same CWS may fall into multiple domains. ACPA's proposal dealt with the issue of overlapping pesticide use areas by making one joint domain consisting of multiple pesticides defined by "higher use intensity." A drawback to this approach is that domains are not optimized for any pesticide in

[7](Gilbert, 1987)

particular. This means (1) the data for each specific pesticide will be of poorer quality, and (2) it becomes more difficult to make risk management decisions for individual pesticides.

Regional Domains

Regional domains are spatially chosen to provide a regional estimate of pesticide concentrations in drinking water. Regional domains may be based on geopolitical boundaries, physiographic regions (*e.g.*, coastal plain region, *etc.*), hydrologic boundaries (*e.g.* USGS Hydrologic Unit Code), or a grid system. Regional domains do not overlap (*i.e.* individual CWS's fall in unique domains), which simplifies site selection. Monitoring in regional domains should capture a broader array of environmental conditions because of the geographic dispersion of sampling sites. This type of information is useful in model development, identification of regional mitigation factors, and regional assessment of pesticide exposure for sub-populations of people. A disadvantage of using large regional domains (Western US v. North Eastern US) is that there will likely be a substantial number of sites selected in which there is little or no target pesticide use. This makes risk management decisions abut individual pesticides more difficult.

ACPA has proposed five regional domains (one national and 4 USDA food regions). They have also recommended using "vulnerable" strata as a sub-domain in each region.

Crop Use Area Domains

Crop use area domain can defined as a specific area where a particular crop is grown (*e.g.*, cotton, corn, *etc.*). An advantage of using crop use area domains is the ability to capture a broad array of compounds used on common crops. Overlap is likely for CWS's in domains of crops used in common crop rotations (*e.g.*, corn and soybean), and this should increase the efficiency of the design. A disadvantage is major pesticides are used on multiple crops.

Vulnerability Domains

Vulnerability domains can be defined as the set of CWS's likely to have high concentrations of a pesticide or a set of pesticides in water (a fuller discussion of vulnerability is provided below). An advantage of this approach is that risk managers will have available better data for these more vulnerable CWS's. If vulnerability is used as the stratification criteria, the most vulnerable strata could be used as a sub-domain. A drawback to this approach is that it can substantially increase the number of samples needed in the survey.

Stratification

Stratification is the process of separating homogeneous groupings within a domain for more efficient characterization of the distribution[8]. Stratification enables one to reduce the number of samples needed or to increase the level of confidence using the same number of samples. Because we do not have good information about concentration distributions, the degree of improved confidence by stratification is uncertain. Vulnerability may be described using watershed characteristics, hydrologic characteristics of the surface water body, and proximity of pesticide application area to water source supply. Geographic criteria can be used as regional strata.

Vulnerability Strata

For the purpose of this drinking water survey design, it would be advantageous to have a simple system for defining vulnerability categories for comparing the relative risks of surface water contamination between watersheds for each chemical. A vulnerable CWS is one likely to have frequent pesticide detections and/or high levels of pesticides in raw water. Vulnerability should be related to pesticide usage and watershed characteristics. Using a vulnerability index offers several potential advantages in designing a drinking water monitoring study. A vulnerability index would allow a more focused design aimed at

[8] (Gilbert, 1987)

watersheds expected to produce greater than average pesticide concentrations in surface water. It might also be used to identify specific types of water bodies associated with CWS intakes expected to have higher pesticide concentrations. By developing a stratified sampling strategy based on vulnerability, the study design can have more statistical power to address its goals. In a study attempting to characterize upper percentile occurrence, sampling would be focused on those watersheds and water bodies with higher vulnerability.

The International Life Sciences Institute (ILSI), recommends that the vulnerability of the CWS's be used as strata in survey design for assessing pesticides in drinking water[9]. The ILSI guidance for drinking water survey design suggests: "The sampling population should be stratified by classifying the use regions and assessment areas into higher- and lower-risk isopleth's and ranking individual supplies by vulnerability" and further suggests using GIS as a tool for quantifying vulnerability. Specific characteristics associated with increased risk were identified as "intensity of pesticide use, climatic factors (*e.g.* rainfall history), contributing-area characteristics (*e.g.* geology, slope), source of supply, type of water delivery function, and proximity to the application area."

The type and size of the water body from which drinking water is derived can have an effect on the magnitude and duration of pesticide loadings. Persistent chemicals may accumulate in water bodies with long hydrologic residence times, such as reservoirs and lakes, while water bodies with shorter residence times are less likely to accumulate pesticides. The size of the water body is also expected to affect vulnerability. For instance, small rivers, reservoirs, and lakes are likely to have higher pesticide concentrations than large ones because pesticide loads into larger water bodies would be diluted. In order to design a study for characterizing pesticide exposures through surface derived drinking water it is necessary to monitor a range of water body types. Sampling of drinking water intakes associated with different types of water bodies (*e.g.* rivers and reservoirs) in watersheds with a range of predicted vulnerabilities should be included in the study design.

It is likely the effectiveness of certain criteria in predicting vulnerability will vary from chemical to chemical. For a pesticide, historic levels of runoff may be a good predictor of vulnerability, while for another pesticide, usage in the watershed may be the most effective indicator. Since it is not known which factors are likely to be the best indicators of vulnerability, it may be advantageous to use more than one vulnerability indicator. Stratifying using two independent potential indicators of vulnerability would double the chances of producing results consistent with the stratification and provide twice as much information on means to mitigate surface water contamination. The simplest way to use multiple criteria of vulnerability would be to use two vulnerability criteria, each with two categories. For instance, the two criteria might be historic runoff levels and pesticide usage within the CWS's watershed. Each of these two criteria may have two categories: high and low. This would create a two dimensional matrix with four categories of risk: low-low, low-high, high-low, and high-high. This type of vulnerability index does not attempt quantify the magnitude of difference between different categories but could be used to stratify CWS's allowing for higher risk CWS's to be over-sampled.

ACPA has proposed to stratify by vulnerability, dividing CWS's selected for monitoring in the chronic survey into high and low vulnerability groups, and selecting "CWS's using reservoirs and having a higher use of products with chronic exposure issues". ACPA will identify a "higher pesticide use intensity region" based on the total use intensity of target pesticides.

Regional Strata

[9]A Framework for Estimating Pesticide Concentrations in Drinking Water for Aggregate Exposure Assessments. International Life Sciences Institute. Washington, D.C., 1999.

Regional strata can be developed to group CWS's with similar geographical properties, such as climatic conditions, soil types, land management practices, *etc.* This stratification system assumes CWS's within a defined region will be more similar than CWS's in different regions. An advantage is the relative ease of stratification. A disadvantage is that CWS's may be in different portions of the distribution even if they are geographically close.

A number of approaches to site selection have been used in past monitoring programs. An overview for some of these approaches is presented.

Site Selection

ACPA Site Selection Strategy

The site selection process proposed by ACPA for chronic exposure is based upon five geographically based analysis domains – the conterminous United States and the 4 food regions defined by USDA. Monitoring sites are CWS's which derive their water from surface water. Sites located within each domain are classified as vulnerable or non-vulnerable. ACPA uses a three step process to identify and select the sites:

1.
   a. Identify the counties in the lower 48 states which represent the top quartile of use intensity (based on USGS estimates) for each of 25 target pesticides. This area is referred to as the "higher pesticide use intensity area". Note that if as few as one of the 25 pesticides is used in a county, that county is included in the "higher pesticide use intensity area", even if no other pesticide is used
   b. Identify all CWS's which obtain some or all of their source water from surface water. Classify each CWS based on the size of its watershed (small/medium/large).
2.
   a. Identify all vulnerable CWS's that occur in medium and small watersheds in the "higher pesticide use intensity area". To identify CWS's that are vulnerable to chronic exposure ACPA will select "CWS's using reservoirs and having a higher use of products with chronic exposure issues". This would exclude CWS's using major continental rivers or Great Lakes, which would be left in the "non-vulnerable" category."
   b. Identify all CWS's that are *not* vulnerable to "chronic exposure."

      (It is not clear how product use factors into identifying CWS's that are vulnerable to "chronic exposure". Sites initially meeting the criteria for vulnerable and non-vulnerable would be verified via phone contact to assess the accuracy of the intake surface water source, pesticide use data and other ancillary information such as population served.)

3. In each of 4 food regions, identify 59 vulnerable and 24 non-vulnerable CWS's. (It is not clear how CWS's will be selected from the list of candidates)

This results in a total of 236 vulnerable and 96 non-vulnerable surface water based CWS's being selected for monitoring nationally, or a total of 332 out of the 10,728 CWS's where monitoring is occurring. For urban sites ACPA proposes to work with the Agency to obtain non-crop pesticide use data for compounds of interest and include any counties in the higher pesticide use intensity area that would reflect such use.

ARP-Acetochlor Site Selection Strategy

The Acetochlor Registration Partnership (ARP) is conducting an ongoing surface water monitoring study to support the registration of acetochlor. In addition to acetochlor, the ARP has analyzed for atrazine, and alachlor. This study includes 175 sites in 12 states. Sites were selected from among surface water source supplies in these states that did not blend with ground water and that had more than 5% corn acreage in the watershed above the drinking water facility. The original intent was to select 25 sites in each of seven states, Iowa, Illinois, Indiana, Kansas, Nebraska, Minnesota, and Wisconsin, representing 80% of the anticipated acetochlor use area, but it was determined that several states such as Minnesota and Wisconsin did not have 25 facilities that met the criteria. The number of sites in other states were expanded, and two other corn belt states, Ohio, and Missouri were added. In addition three east coast states Delaware, Maryland, and Pennsylvania were added in deference to the needs of the state agencies rather than to meet the needs of OPP for risk assessment.

The sites were selected using a stratified, rather than a statistical random approach. Sites were placed in one of five bins. Two bins were based on hydrology of the source water, a Great Lakes bin, and a Continental Rivers bin. The remaining sites were placed in bins based on corn acreage in the watershed, 5 to 10%, 10 to 20%, and greater than 20%. More sites were selected from the bins with higher corn intensity.

Watershed-based Site Selection Strategy

The Agency is currently developing a watershed-based approach to site selection. This approach has some similarities to the ARP design but supports a statistical selection rather than one based on judgement. ILSI,1999 also recommends using pesticide use area as a domain. To facilitate the site selection process the Agency believes geographic information systems (GIS) should be used to evaluate the potential vulnerability of a CWS to pesticides in surface water.

Site Selection Tools

The process of identifying vulnerable sites is dependent upon various data sources describing the location of the CWS's, the hydrography of the watershed in which they are located, land use within the watershed, pesticide use within the watershed, and other ancillary data (*e.g.* soil runoff potential or annual precipitation).

The first step in creating a site selection tool is identification of the CWS intake locations. According to EPA's Office of Water there were approximately 170,000 public water systems (PWS) in the United States as of 1999. A public water system: "provides water for human consumption through pipes or other constructed conveyances to at least 15 service connections or serves at least 25 people for at least 60 days a year." EPA has defined three subcategories of PWS's:

- Community Water System (CWS): A PWS that supplies water to the same population year around
- Non-Transient Non-Community Water System (NTNCWS): A PWS that regularly supplies water to at least 25 of the same people at least six months per year, but not year around. (*e.g.* schools, factories, office buildings or hospitals)
- Transient Non-Community Water Systems (TNCWS): A PWS that provides water in a place such as a gas station or campground where people do not remain for long periods of time.

Currently OPP and USGS have a quality assured (QA) database containing the location of intakes for CWS's drawing from surface water serving a population of 10,000 or greater. This database was constructed in a joint effort with EPA's Office of Water and USGS. This data set represents approximately 20 percent of all surface water CWS's and 167 million people. The USGS National Water Quality

Assessment (NAWQA) program expects to complete quality assurance of a database containing location information for all surface water intakes for CWS's serving 25 people or more by the end of summer 2000. Initially EPA will use the data set of CWS's serving 10,000 and greater to delineate watershed boundaries and then augment this data set with the CWS's serving 25-10,000 once it is available. The Office of Water is currently updating the Safe Drinking Water Information System (SDWIS) database which includes locations for all PWS's. However, until this updated database undergoes complete QA/QC its utility may be limited. Therefore, NTNCWS's and TNCWS's are not included in the site selection tool under development.

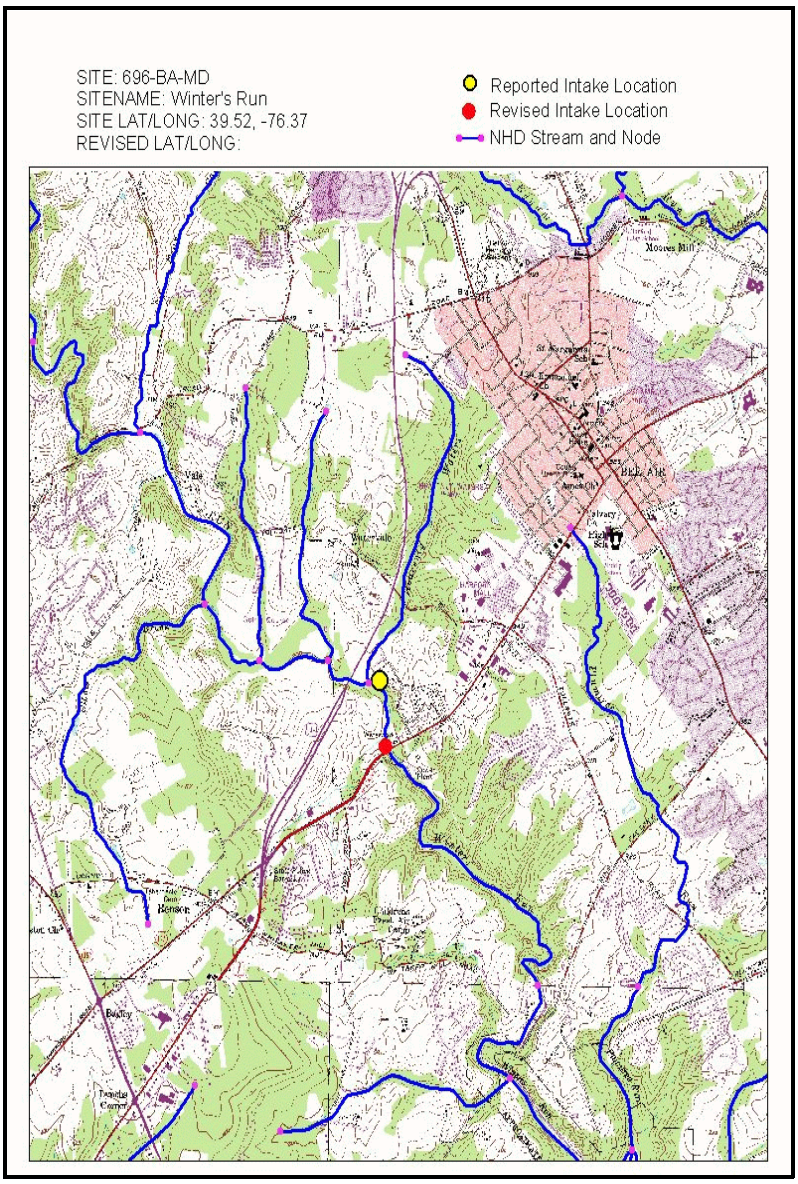

Figure 1. Sample QA map for verifying CWS location.

The next step in the process is to associate the CWS intake location with a specific river reach or water body and then delineate a watershed boundary. EPA is using the National Hydrography Data set (NHD) for this purpose. The NHD combines USGS digital line graph hydrography data with the EPA river reach file version 3 (RF3) creating an enhanced data set which describes surface water features such as lakes, streams, rivers, springs and wells at 1:100,000 scale. Currently the NHD is available for most of the conterminous United States. It is expected missing regions will be completed soon.

Preliminary analyses indicate that a manual interactive step is essential to determine that the proper reach is selected. In many cases, the nearest reach is not the actual reach where the intake is located. This is important because identifying the wrong reach can have an impact on the delineated watershed. To verify the intake is assigned to the correct reach USGS Digital Raster Graphs (DRG) or Digital Ortho Quads 1:24k or similar product are needed to verify site location (*e.g.*, use location name and information from DRG to verify site is located correctly). As a quality assurance step a standardized map of site location with DRG streams can be plotted and sent to the CWS for verification (Figure 1).

Once the CWS has been assigned to the proper reach a watershed boundary is delineated within a cataloging unit (CU). The CU's of the NHD are based on 8-digit hydrologic unit code (HUC). Initial work has shown the CU-to-CU connectivity in NHD is poor. Therefore our method will delineate a watershed

within a CU and superimpose boundaries for upstream CU's during a subsequent step. This processes is illustrated in Figures 2 and 3.

Once a watershed boundary has been defined for a specific CWS various data sets can be intersected with it and watershed statistics calculated. The first data layer to be added will describe land use and land cover (LU/LC). There are two data sets the agency proposes using for this purpose: the National Land Cover Data (NLCD); and the Geographic Information Retrieval and Analysis System (GIRAS) LU/LC.

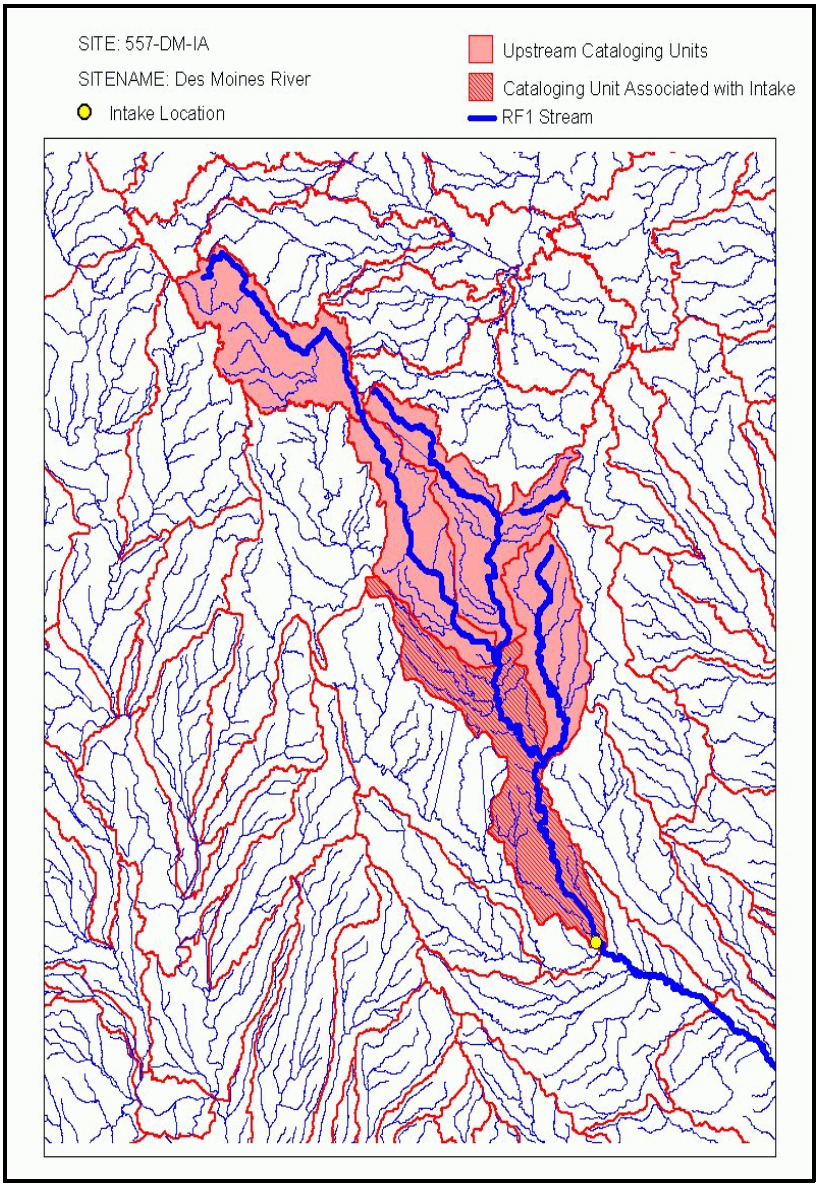

Figure 2. Upstream and surrounding cataloging units for delineated basin.

The NLCD is based on 30-meter Landsat thematic mapper data collected in the early 90's. As with all LU/LC data there are certain limitations. For example the NLCD data for Washington state contains the caveat "Crop types in the irrigated areas were difficult to reliably distinguish; row crops are likely to be under represented where no field observations or other ancillary information was incorporated[10]." Further the NLCD is not complete at this time. Fifteen states remain to be completed including Texas and the Dakotas. Since the NLCD is incomplete a separate data source is needed to fill in the blanks.

Where as the NLCD is based upon a single data source, GIRAS is a compilation of aerial photographs and previous LU/LC maps with some of the data dating to the early 70's. Also, the spatial resolution is 200-400-meters as opposed to 30-meters for NLCD. Although GIRAS is composed of older data it does provide a complete coverage for the contiguous United States. For the GIS tool being created GIRAS will serve two purposes: Fill in the gaps of the NLCD; and compared with the NLCD to determine the variation in LU/LC statistics (*e.g.* percent agriculture in a watershed).

Once the LU/LC data is intersected with the watershed boundary the amount of agricultural or urban land within the watershed can be calculated. Then the amount of agricultural land within a basin can have

[10]National Land Cover Data read me file for Washington State version 06-01-99.

pesticide use data apportioned to it and an estimate of pounds active ingredient applied in the watershed calculated. Since there are no known sources of pesticide use data in urban or non-agricultural areas urban sites can be selected based upon the amount of urban land in the CWS watershed. The greater amount of urban land use in the watershed the more likely a CWS would be selected for sampling.

The pesticide use data is the same used for the USGS National Water Quality Assessment Pesticide National Synthesis Project annual use maps. This data set was chosen because it is accessible, non-proprietary, and is from data corresponding temporally with the NLCD. The disadvantage is that the data represents an average use of a particular pesticide for the entire state and does not necessarily represent local practices. Also, Census of Agriculture data for county level crop acreage is sometimes censored due to non-disclosure rules. Therefore, the utility of basing a site selection strategy on use alone is of questionable value. This data allows for determining potential areas where the pesticide of concern is used and may allow for categorizing use areas into a high, low and no use category. Further, the smaller the watershed delineated, the less likely use data and to a certain extent LU/LC data will be accurate. This illustrates the need to follow up the selection process with telephone interviews or reconnaissance trips to the potential monitoring sites.

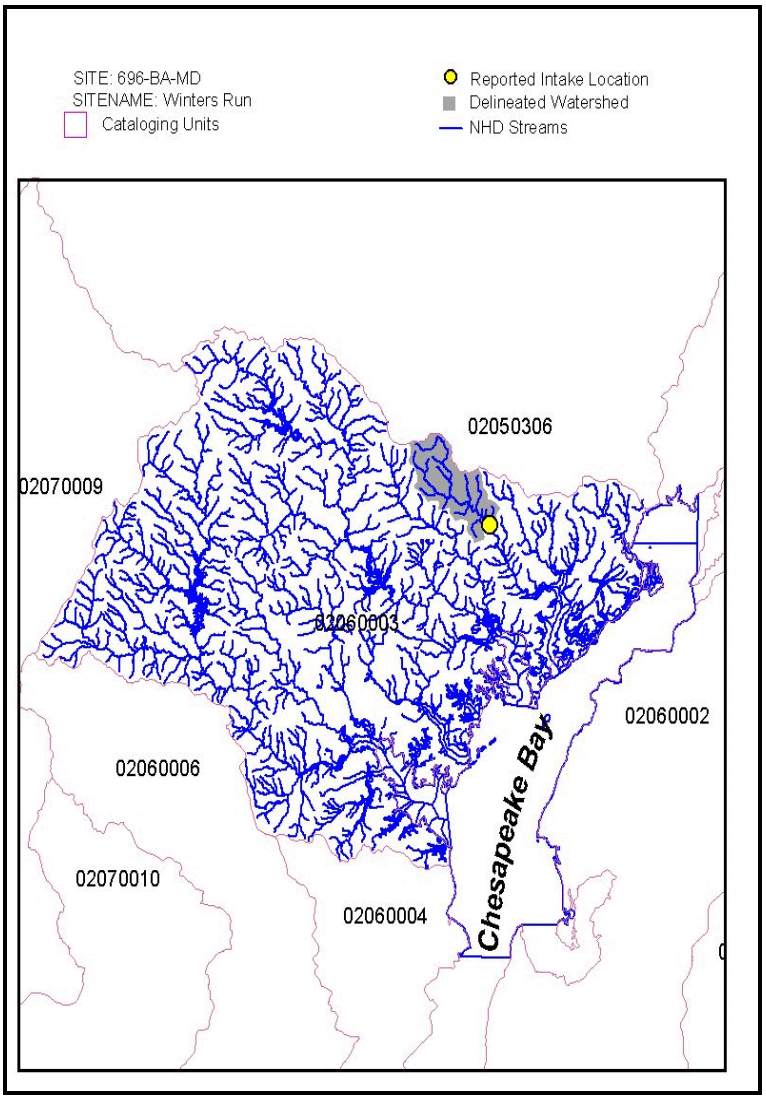

Figure 3. Delineated basin boundary within an individual cataloging unit.

Number of Sites

The number of CWS's sampled needs to be balanced against the number of samples collected from each CWS in order to reduce the total uncertainty in the study. Uncertainty in the results from pesticide sampling can come from four main areas: year to year variations, variations due to sampling location, variations due to the method in which the mean annual concentration is measured, and uncertainty due to chemical analysis. In a one year study we have no control over year to year variations and the uncertainty due to chemical analysis is fixed by the analysis method, so the most important compromise is between the number of sites measured and the number of samples taken from each site for calculating the annual mean concentration.

The best compromise depends on the goals of the study, more locations will batter describe the spatial variation in pesticide concentrations in the use areas, while more samples per location will be able to provide more accurate data on the temporal variability of pesticide concentrations. The pesticides of interest and the fate properties of those pesticides are thus required in order to properly determine how to distribute samples.

The number of sampling locations required to determine a given percentile of a distribution with a given level of confidence can be determined by using order statistics with minimal assumptions about the distribution. Knowledge of a percentile alone may not be sufficient to determine if a chemical poses no risk to a definable sub-population. Distributions of pesticides may be highly skewed, meaning that the water systems above the known percentile could have pesticide levels significantly higher than any sampled sites.

Calculation of the sample size required to estimate a given percentile with a given confidence is outlined as follows. If we sample n sites and measure a quantity x in each of them, we can write the probability that the largest measurement, $x_{(n)}$, is less than some quantity u, as the probability that all measurements x_i are less than u

$$P(x_{(n)} < u) = P(x_1 < u, x_2 < u, ..., x_n < u)$$

Assuming that all the x_i are independent, we can multiply the individual probabilities together

$$P(x_{(n)} < u) = P_1(x_1 < u)\, P_2(x_2 < u) \ldots P_n(x_n < u)$$

and assuming the cumulative distribution functions (cdf's) are identical, $P(x<u) = F(u)$, this can be shortened to

$$P(x_{(n)} < u) = F^n(u) = G(u)$$

Where F is the cdf for the x_i and G is the cdf for $x_{(n)}$. We can then differentiate this to get a probability density function (pdf) for the largest element,

$$g(u) = nF^{n-1}(u)\, f(u).$$

The assumption of independent identically distributed random variables, is critical because without it we can't make the step of multiplying the individual cdf's together and the function above does not describe the pdf of the largest element of our sample. The pdf above can then be used to show[11] that

$$P[F(x_{(n)}) > \beta] = 1 - \beta^n$$

which says that at least a fraction β of the population has values of x less than $x_{(n)}$ with probability $1 - \beta^n$. If we let $\gamma = P[F(x_{(n)}) > \beta]$ then $1 - \beta^n = \gamma$, *where* β is the quantile, γ the confidence limit, and n is the number of samples taken. Solving for n gives

$$n = \ln(1-\gamma)/\ln\beta.$$

For example, to ensure 95% confidence that the largest sample is at or above the 95th percentile of the distribution would require $n = \ln(1\text{-}0.95)/\ln(0.95) = 58.4$ samples and we would round up to59 to be sure we were within the set bounds. Similarly, 90% confidence in the 99.9th percentile would require 2302 sampling sites. This example is the same as what ACPA has proposed.

[11]Guttman, I, S. S. Wilks, and J. S. Hunter. 1982. Introductory Engineering Statistics, 3rd edition. John Wiley, New York.

Number of Samples

Choosing the number of samples required to define the average value at a site is not as straightforward. Samples taken from a water body are clearly not independent, identically distributed random variables, as required by the approach outlined above. Instead, the concentrations follow a pattern over the year, and how the sampling times coincide with this pattern can have an important effect on the average value of the samples. To calculate an annual mean value with perfect accuracy would require sampling at twice the rate of the fastest fluctuation, but would never fit within budget constraints.

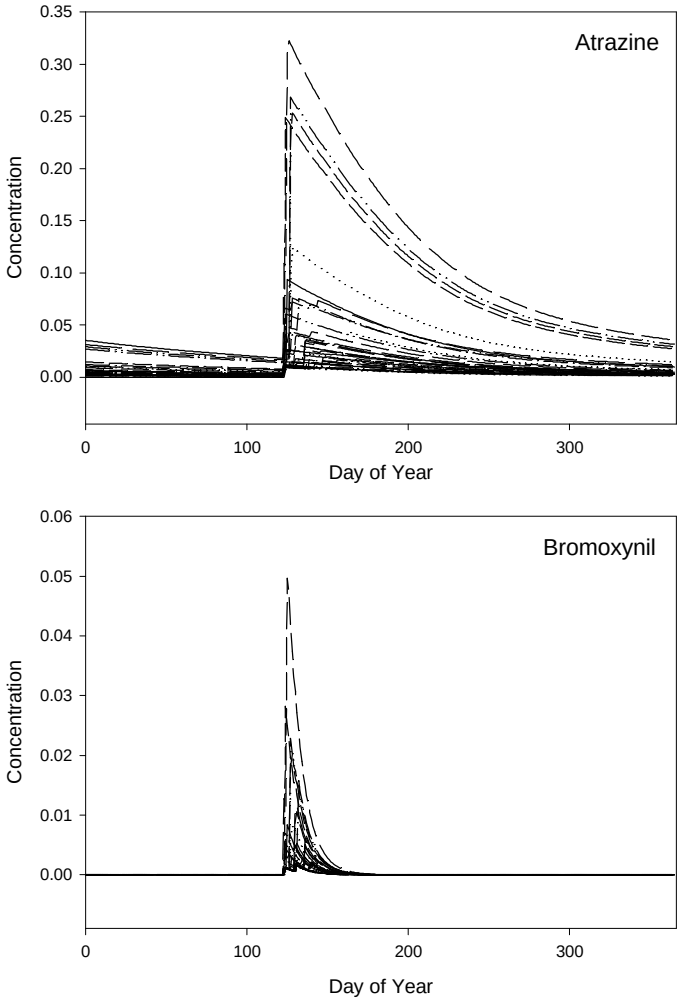

Figure 4. Yearly concentration profiles for atrazine and bromoxynil simulated by PRZM-EXAMS.

Because we can't sample enough to capture every nuance of the signal, we would like to know how much error is associated with sampling at longer time intervals. Without knowing the shape of the yearly concentration curve it is impossible to quantitatively determine the error associated with less frequent sampling or to define an ideal schedule of less frequent samples. Instead to illustrate the possible errors we look at some examples.

The shape of a yearly concentration curve (or chemograph) is dependent on many variables including the fate characteristics of the chemical, the use of the chemicals, the weather in the area and the hydrologic characteristics of the watershed. Of these, the weather and hydrologic properties cannot be defined well enough to aid in determining the deeded sampling frequency. However, the fate characteristics of the chemicals to be sampled can be used with modeling, to help determine the number of samples needed to define a yearly average concentration. Models would be run (as in Figure 4) to get an estimate of the shape of the chemograph, and this curve would then be used to determine the number of samples needed.

Measuring an average yearly concentration requires measuring the area under the concentration curve for the entire year. Persistent compounds, in which concentrations vary slowly throughout the year will thus

exhibit smaller errors with long sampling intervals than short-lived compounds because a simple interpolation between sampling points will more closely approximate the true concentration profile over the year. For example, Figure 4 shows PRZM/EXAMS simulations of two pesticides under identical environmental and cropping conditions for 36 years. (The PRZM/EXAMS model was used because we did not have access to daily field data for two such pesticides under similar conditions.) Atrazine, the more persistent of the two, is present (at least at low concentrations) throughout the entire year but bromoxynil degrades rapidly and disappears approximately one month after application. Even with no simulation of sampling, it is clear that monthly sampling is inadequate to characterize the mean concentration of bromoxynil. With a peak lasting only a month, it would be quite possible to miss the presence of bromoxynil entirely.

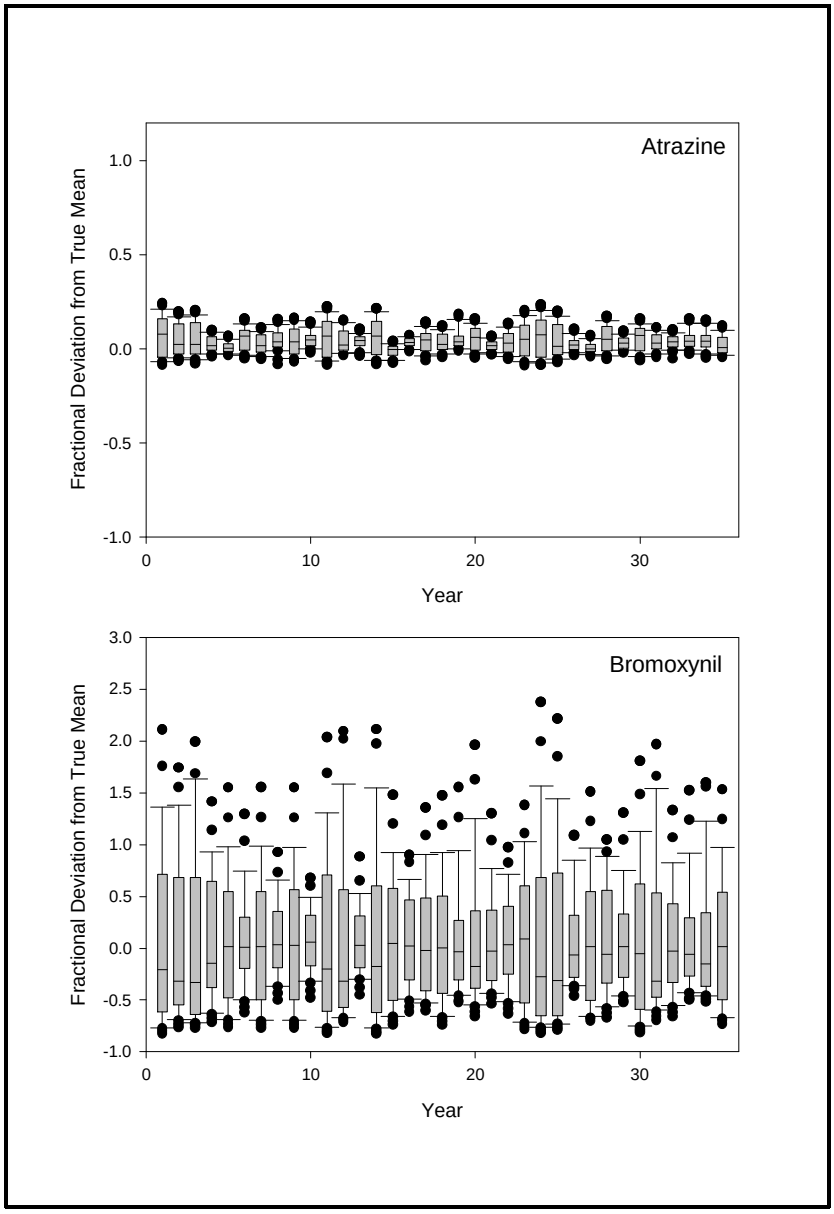

Figure 5. Variations due to 28-day sampling.

Figures 5 and 6 show the variability associated with sampling the model output shown in Figure 4 at 7 and 28 day intervals. These figures show the difference between the sampling at a 7 or 28-day interval and sampling daily, and are reported as a fraction of the annual mean. The simulated sampling was carried out for each possible starting date, *i.e.* for 7-day sampling, sampling simulations were run with the first samples taken on the 1st, 2nd, 3rd, 4th, 5th, 6th and 7th day of the year and repeated every 7 days. Naturally for the 28-day interval (Figure 6) there were 28 sampling simulations. ACPA has proposed collecting an average of 10 samples or four seasonally composited samples at each CWS.

Sample Timing

Modeling, as described above, is one way to estimate the sampling frequency required for an acceptable measurement of yearly average concentration. Different sampling intervals for atrazine and bromoxynil show much higher variability with less frequent sampling and higher variability with the more quickly degrading bromoxynil. Sampling atrazine at a 28-day interval gives measurements between +20% to −10% of the true mean (in this case the "true mean" is the mean calculated from daily model output values). Sampling bromoxynil at the same interval can yield results as much as 2 times the true mean or as little as 25% of the true mean. The deviations from the true modeled mean, as shown in Figures 5 and 6, should be less than the inaccuracy in the analytical method in order to keep overall measurement errors to a minimum.

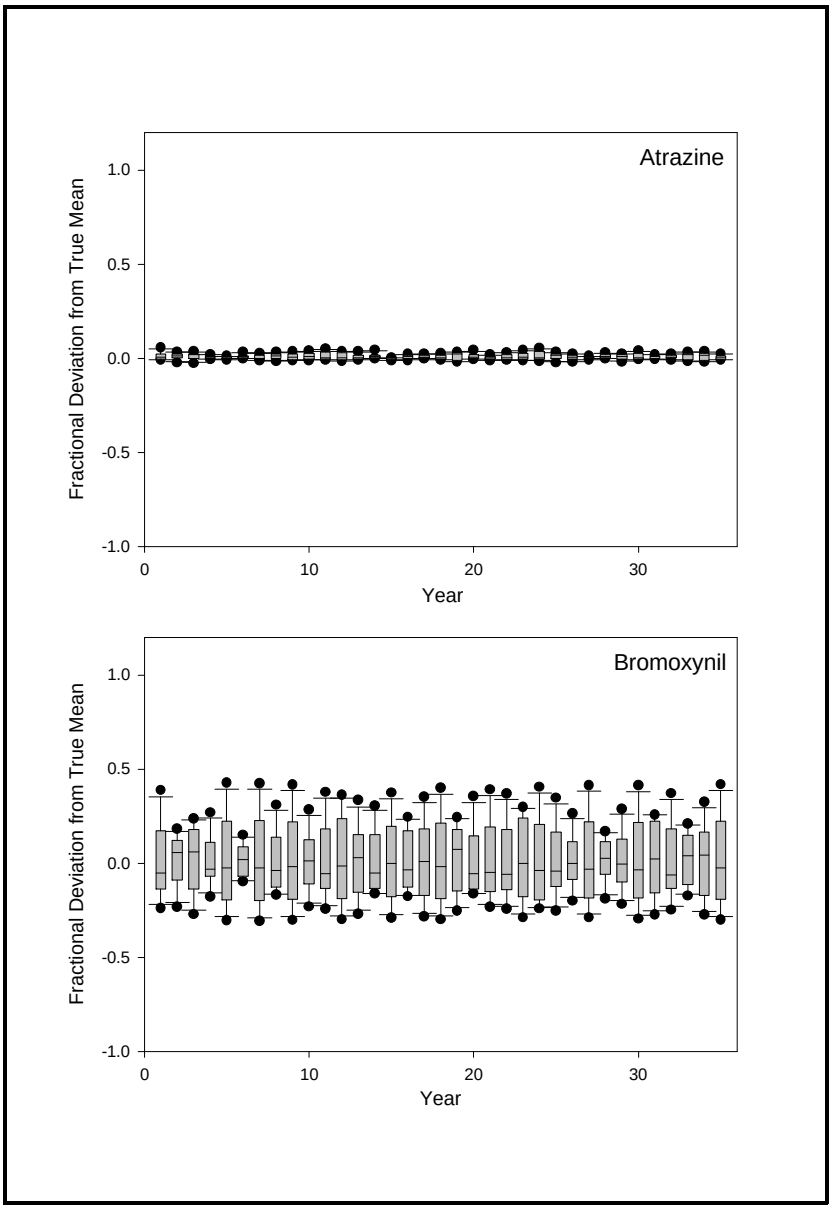

Figure 6. The range of yearly averages possible with a 7-day sampling interval

Disadvantages to using this approach are that concentrations in nature can fluctuate more rapidly than model predictions. More rapid fluctuations in concentration require more frequent sampling and thus this approach give an underestimate of the error associated with each sampling interval.

To reduce the number of samples, sampling could be concentrated around the time of application, when chemograph fluctuations are most pronounced. This method should yield results similar to sampling all year at the higher rate, because fluctuations in concentration are smaller and less rapid outside of the time of application. For example, if half of all samples were taken between days 100 and 200 (inspection of Figure 4 shows this is the period of greatest change) and the remaining half take at longer intervals during the rest of the year. The period of more frequent sampling would depend on local use patterns for each pesticide in the survey and should vary both between pesticides and between geographical regions. The ARP study collected 14 samples per year with biweekly samples during the spring and summer. If the concentrations at any particular site remained elevated past August, the ARP continued biweekly sampling until levels declined to background levels.

This approach assumes there are no rapid fluctuations in concentration during the periods of infrequent sampling, an assumption that holds up well with modeled output but may be less valid with real data. If there are important concentration spikes during the infrequent sampling period, these may show up in some of the CWS chemograph's and can be used (after completion of sampling) to assess the assumption of little fluctuation during that period.

Another way to get around the problems associated with too few samples would be to use composite samples. If samples were taken in small amounts at rapid intervals and mixed together, then the result would be the mean value of all the small samples over the time of sampling. The problem with composite samples is that it is more difficult to keep samples fresh. In a 30-day composite, by definition, the first sample is 30 days older than the last, and if the chemical of interest changes in those times the final result will not be an accurate mean value of concentration over the 30 day time.

ACPA has proposed to sample each CWS systematically through out the year with "less frequent sampling of water from reservoir's and lakes."

Number of Samples v. Number of Sites

The tradeoff between how many sites to sample and how many samples taken from each site is difficult to quantify because of the unknown nature of the shape of the chemograph at each site. We can use statistical methods to help define the number of samples needed to achieve a defined confidence in a given percentile, but that number is valid only when taking a simple measurement with no error. Any practical sampling method will introduce errors and sampling at infrequent intervals will introduce large errors. These errors must be balanced against the desired accuracy when making the tradeoff between sampling many sites and sampling more often.

Because sampling must be carried out frequently for an accurate measurement of the annual average concentration, it will also yield a reasonable estimate of the peak concentration. For a limited study, as proposed here, the sampling is limited to long-lived compounds in which the peaks decay slowly and thus can by found by infrequent sampling. If peak decay can be shown to follow a recognizable decay curve, it may also be possible to extrapolate a peak value from that curve.

Raw and Finished Water

Water is typically treated before distribution to consumers. Most treatment plants use conventional treatment such as coagulation/flocculation, sedimentation, filtration, and disinfection with a chlorine compound or ozone. Some plants also use advanced filtration processes (*e.g.* activated carbon and reverse osmosis). Some water treatment facilities located in agricultural areas adjust treatment during times of pesticide use to reduce concentrations and subsequent exposure, at added cost. Because some pesticides are not stable in the presence of strong oxidizing agents such as chlorine, or at elevated pH, pesticides concentrations may be reduced or removed through treatment. In addition to degradation, during chemical

disinfection with chlorine and ozone certain pesticides are transformed to other compounds which may have toxicological significance.[12,13,14]

Ideally, tap water should be sampled and analyzed for levels of pesticide residues in drinking water. However, tap water represents a composite of source waters from supply intakes subjected to varying treatment effects, distribution allocation, and mixing in distribution systems[15]. The sampling options for a national survey design are described for: finished water only; raw water only; and a combination of raw and finished water.

Finished Water

Finished water samples are collected at the outflow from a water treatment plant. Sampling finished water more closely represents the water people drink, so survey results can be used directly to assess human exposure. In addition, the magnitude of residues (parent and transformation product) measured represent the combined effects of treatment.

Sampling only finished water means no information will be collected on the concentration of pesticides entering water treatment facilities, so the Agency cannot assess the burden placed upon CWS's to remove pesticides. Also, pesticide concentrations in finished water cannot be linked to watershed characteristics or other factors that could be used by risk mangers to mitigate exposure. Since treatment is variable between water treatment plants and within the same plant over time, an additional source of variability is introduced. To assess CWS vulnerability during the site selection process one would have to know the treatment processes used at the CWS and the effects of treatment on all pesticides. If this is not done, a system with advanced treatment methodologies which remove pesticides could erroneously be characterized as "vulnerable." Further, finished drinking water data is not adequate for model development or validation, because simulation and regression models simulate natural hydrologic processes and agronomic practices, not treatment effects. Finally, data cannot be used to evaluate the effectiveness of treatment for reducing pesticide concentrations without collection and analysis of temporally paired raw and finished water samples. ACPA has proposed sampling only finished water in their survey.

Raw Water

Raw water is sampled at a CWS intake prior to treatment. Since raw water does not reflect the effects of treatment, data interpretation (including identification of causative factors) is simplified. Based on raw water analyses and ancillary data collected in the watershed, pesticide concentrations can be correlated to hydrologic factors and sources of contamination when identifying possible measures to mitigate high concentrations. Analyses of raw water samples will enable predictive computer models to be developed and validated. In addition, since raw water samples represent the impact that pesticides have on the aquatic environment as a result of their application, this occurrence data is directly relevant for ecological assessment.

Few people drink water directly from a surface water body. Pesticide concentrations in raw water can serve as a conservative estimate of pesticide residues in drinking water or, if the effectiveness of treatment

[12]Adams, C.D. and S.J. Randtke. 1992. Removal of Atrazine from Drinking Water by Ozonation. Jour. Amer. Water Works Assoc. 84(9): 91-102;

[13]Magara, Y., T. Aizawa, N. Matumoto, and F. Souna. 1994. Degradation of Pesticides by Chlorination during Water Purification. Wat. Sci. Tech. 30(7): 119-128;

[14]Acero, J.L., K. Stemmler, and U.V. Gunten. 2000. Degradation Kinetics of Atrazine and Its Degradation Products with Ozone and OH Radicals: A predictive Tool for Drinking Water Treatment. Environ. Sci. Technol. 34(4): 591-597.

[15]A Framework for Estimating Pesticide Concentrations in Drinking Water for Aggregate Exposure Assessments. International Life Sciences Institute. Washington, D.C., 1999.

technologies at removal of a specific pesticide can be reliably predicted, they can be used to estimate finished drinking water concentrations. Also, data on transformation products cannot be obtained if solely raw water samples are collected. Finally, data cannot be used to evaluate the effectiveness of treatment at reducing pesticide concentrations from raw to finished water without collection and analysis of temporally paired raw and finished water samples.

Raw and Finished Water

Collecting raw and finished water samples could significantly affect the overall cost of the survey. Therefore, a number of alternatives were considered: fully paired samples (one raw and one finished); fully paired samples (one raw and one finished) with reactive analysis (the finished sample is analyzed only if residues are detected in the raw sample); and paired samples for the samples collected during the pesticide use season, with reactive analysis.

There are many advantages in sampling *both* raw and finished water, as described above. Finished water analyses provide a better representation of the water people drink, including the opportunity to characterize transformation product concentrations, if desired. Raw water analyses provide a measure of pesticide loading to a water treatment facility, results can be linked to possible mitigation options, and data can be used to develop and validate predictive models. Raw water data can be used directly for ecological risk assessment. Importantly, data for paired samples can be used to evaluate the combined effects of treatment and processing on pesticide concentrations.

Although this option resolves many of the disadvantages identified above in sampling just raw or finished water, a disadvantage is increased cost of analysis. If fully paired samples are collected and analyzed at each sampling interval, the analytical costs would essentially double. Reactive sampling would reduce added costs of paired samples. Further, it is difficult to collect temporally paired raw and finished water samples.

Duration of the Study

The mean annual concentration for a given pesticide at particular CWS within the pesticide's use area varies from year to year. Factors affecting variability at a particular CWS may be related to climactic conditions (*e.g.* timing and intensity of rain events), long-term usage trends (*e.g.* increasing market share of the pesticide or changing cropping patterns), and/or short-term trends (*e.g.* a change in pest pressure).

Rainfall can vary greatly from year to year. In years with low rainfall, pesticide runoff is lower. Seasonal variation in rainfall can also greatly affect pesticide runoff. Rain events occurring shortly after pesticide applications produce higher runoff concentrations. This is confirmed by monitoring and modeling results for many pesticides. In monitoring studies atrazine, alachlor, cyanazine, and metolachlor concentrations are strongly correlated with application timing and intensity and year-to-year variability in peak measured concentration is large[16]. In PRZM[17] modeling used to estimate runoff from a variety of soil types under different management practices, pesticide runoff loads are strongly correlated to simulated rainfall intensity and timing.

Pesticide use varies greatly from year to year. Climactic conditions and other factors influence pest intensity and thus pesticide use. Additionally label restrictions may limit the availability of a given chemical

[16]Larson S.J., P.D. Capel, and M.S. Majewski. (1997?) *Pesticides in Surface Waters: Distribution Trends and Governing Factors*. Ann Arbor Press, Inc. Chelsea Michigan. 373 pp.

[17]Carsel, R.F., J.C. Imhoff, P.R. Hummel, J.M. Cheplick, and A.S. Donigian, Jr. PRZM-3, 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. Office of Research and Development. US EPA 30605-2720.

in certain regions from year to year which may in turn lead to higher use of other chemicals. Alachlor and metam sodium exemplify long term trends of changing pesticide usage on a national scale. In 1995, approximately 19-24 million pounds of alachlor and 49-54 million pounds of metam sodium were used in agricultural crop production[18]. In 1983, 55-60 million pounds of alachlor and 5-8 million pounds of metam sodium were used. On a regional scale, the changing pest pressures can have an even greater effect on short term trends on pesticide usage and application frequency. After completion of the USDA Boll Weevil Eradication Program (BWEP) insecticide applications to cotton in the Southeast decreased 88%[19]. Growers prior to the BWEP made 10 to 12 applications per year. After the BWEP growers averaged two applications per year.

One Year Study

A one year study will meet the resource and cost constraints and while the data collected from one year of sampling will be useful, it will also have limitations. A one year study is unable to capture year to year variability, and a study conducted over this period may not be representative of typical conditions and is unlikely to reflect upper percentile values. Because pesticide concentrations in surface water are highly variable, results of any study conducted over a single year must be viewed within the time frame of the study. The magnitude of pesticide concentrations in drinking water sources must be considered in relation to usage and to weather during that year. Any statistical analysis (*e.g.* percentile or tolerance bound) of a 1-year study would be limited to the year in which the data was collected. For instance, the 95th percentile value would represent the 95th percentile concentration during that year.

One Year Study With Limited Monitoring Beyond One Year

A one year study with continued monitoring of a fraction of the original sites in subsequent years will conserve resources and focus monitoring on sites previously found to have high pesticide concentrations. However, the full monitoring program would last only one year, so year to year variability across sites would not be measured. In addition, limited CWS monitoring and the method of site selection after the first year, would make it difficult to draw any statistical inference regarding the results.

A survey design using one year of full monitoring and supplemental monitoring for subsequent years would be more costly than a one year study and the results from subsequent years would not improve the statistical power of the study. However, data collected from subsequent years could be used to estimate year to year variation in the annual mean concentration at certain sites. With the proper ancillary data at multiple year monitoring sites, it may be possible to correlate annual mean concentrations with particular factors. ACPA has proposed sampling for one year with unspecified triggers for extended monitoring at some sites.

Multiple Years of Monitoring

A multiple year monitoring study will better account for climatic variability, temporal variability, variation in pesticide usage and other factors. ILSI recommends a multi-year study for adequately estimating pesticide concentrations in surface water. The major limitation in existing monitoring data is the absence of systematic, long-term studies that collect frequent samples over time to identify long-term trends of concentrations in surface waters: "From the studies reviewed, little can be concluded about the long-term trends in pesticide occurrence in surface waters of the United States for several reasons. The major reason

[18]Aspelin, A.L. and A.H. Grube. (1999) Pesticide Industry Sales and Usage 1996 and 1997 Market Estimates. Biological and Economic Analysis Division, Office of Pesticide Programs, US EPA 20460. Available at http://www.epa.gov/oppbead1/pestsales/97pestsales/97pestsales.pdf

[19]US Department of Agriculture. (1991) National Boll Weevil Cooperative Control Program: Final Environmental Impact Statement - 1991 volume 1. Animal and Plant Health Inspection Service. Hyattsville Maryland, 20782.

is the general lack of consistent long-term studies in which the same sites are sampled over a number of years..... The normal seasonal variations in concentration, combined with year-to-year variations caused by differences in weather and agricultural practices, make comparison of recent and past concentration data tenuous."[16]

A survey design conducted over three or more years will be more expensive than the options mentioned above, however, the data could be more easily used to statistically analyze year to year variability from site to site and improve upon many existing studies.

Ancillary Data

Ancillary data are needed for watershed characterization, classification of watershed vulnerability, population weighting, assessment of water treatment processes, and development of watershed scale modeling approaches for source water protection and dietary exposure. Additionally, ancillary data are needed to confirm or "ground-truth" the data used in the watershed characterization tool.

Watershed characterization requires data on pesticide use including application rate, timing , total pesticide applied, types of crops, types of soils, agronomic practices, hydrologic characterization (flow rate), precipitation; physical watershed properties including watershed size, topography, and proximity of the pesticide application area to the CWS. Several of these properties including pesticide use intensity and areal extent of B soils have been identified by ILSI[9] and USGS[20] as critical factors in predicting pesticide run-off.

Ancillary data for water treatment processes are needed to assess the impact of water treatment on pesticide removal and transformation. Additionally, information on the population served is required for population weighting. Each CWS in the survey requires identification of the source water, geographic coordinates of the CWS, type and timing water treatment processes, source water quality information, flow rate through the CWS, and population served. To date ACPA has not committed to collect ancillary data for their study.

EFED's Proposed Monitoring Design Framework

EFED is assessing design criteria for conducting a statistically-based survey to assess annual average pesticide concentrations in surface source drinking water for FQPA exposure assessments. This section presents the general thinking of EFED regarding the design criteria discussed above.

Assumptions, Constraints, and Biases

It is assumed that pesticide exposure through drinking water occurs at CWS's with pesticide application in their upstream watersheds. This assumption is based on the premise that pesticide transport into surface waters is controlled through runoff and short-range spray drift. Such an approach does not consider pesticide deposition from long-range atmospheric transport including fog banks, wind erosion of sediment, or rainfall. Further, it is assumed:

- $10 million is available to support a one year monitoring study.
- The minimum analytical cost is $500.00 per sample for a single analyte or a single group of analytes (*e.g.*, USGS analytical schedule).

[20]SPARROW SAP, March 2000

- Based on a $10 million budget and a $500 sample analysis cost, the survey will be able to process no more than 20,000 samples.
- There are a limited number of facilities capable of handling 20,000 samples per year.
- Urban land use/land cover density in the basin can serve as a surrogate for non-agricultural pesticide use.
- If there is a substantial lack of cooperation from CWS's, survey design requirements will not be met.
- There is error in county-level pesticide use, and further error may be introduced when interpolating any county-level data to new geographic boundaries (*i.e.* watershed boundaries).

The survey needs to address both the spatial and temporal variability of pesticide concentrations in drinking water. Climatic conditions (magnitude and timing of precipitation), surface water body type, watershed size, and pesticide use area, intensity and environmental fate properties, are factors controlling pesticide concentrations in surface water. The survey needs to consider these variables in assessing the vulnerability of each CWS to pesticide contamination. Within financial constraints, the design framework must be capable of assessing sub-populations of CWS's serving small, identifiable human populations. Effects of water treatment on pesticide removal and transformation need to be evaluated in order to assess pesticide levels in finished drinking water. Also, pesticide use and watershed characteristics must be verified to facilitate data interpretation. The survey results should provide data for model development and evaluation, and for identification of mitigation strategies. The recommended data quality standard for the survey is a distribution of annual mean values across CWS's so that an upper 95% confidence bound can be placed on the upper 95th percentile of the distribution for the year of the study. The prediction accuracy was selected to guard against the cumulative error of assessing distributions for multiple pesticides (ILSI, 1999). A total of 59 sites per domain are required to achieve this accuracy, but this number does not guard against the cumulative error of assessing multiple compounds. When assessing multiple compounds, the number of sites in any domain could increase depending on the designation of an "acceptable" minimum prediction accuracy for describing a population or sub-population in the design framework.

Design Structure

OPP believes a random stratified design is an efficient sampling strategy for a national scale drinking water survey for assessing annual mean pesticide concentrations. Chemicals selected in the survey should be selected according to their relative risk, extent of use, and environmental fate properties. Compounds with high risk for chronic non-cancer or cancer effects, high extent of use, and which exhibit high mobility and persistence in terrestrial and aquatic environments will be considered as high priority pesticides. The list of priority pesticides will define the target population for the survey. The target population is the CWS's within each of the pesticide use areas. This assumes that pesticide occurrence in drinking water is dependent on runoff.

The use area of each selected pesticide will be survey domains. CWS's should be selected randomly from within each pesticide use domain using watershed vulnerability strata. A vulnerability classification system needs to be developed to establish the stratification system. The addition of regional and vulnerability sub-domains may be considered in optimizing the study design framework . EFED proposes using a GIS site selection tool to evaluate which domains and strata are used.

Balancing the number of sites and samples per site requires consideration of the number of domains in the study, the minimum prediction accuracy required in the survey, development of an acceptable sampling frequency for measuring annual mean pesticide concentrations, and the water sampling strategy for raw and finished drinking water. The maximum number of domains, in light of assumptions, uncertainties, and limitations in the study design, is approximately 16. This implies that16 pesticides may be evaluated in the survey. The number of selected pesticides considered in the survey is expected to decrease with the addition of sub-domains in the survey, increased sampling frequency, and the addition of paired raw and finished water samples. However, it is possible to expand the number of selected pesticides in the survey through relaxation of the minimum prediction accuracy and accounting for common CWS's within the pesticide use areas.

Design Efficiency

Accounting for overlap of pesticide use in the survey could increase the design efficiency through inclusion of CWS's with multiple selected pesticide use in the watershed. However, EFED is concerned if CWS selection is solely based on location in multiple pesticide use domains the CWS's will not be selected randomly. The selection of pesticides with similar national use areas is expected to increase the likelihood of selecting CWS's with multiple pesticides used in the their watersheds. The areal extent of pesticide use is one factor considered in the recommended chemical selection process.

Sampling Frequency and Timing

The sampling frequency at each CWS is an important factor in measuring the annual mean pesticide concentration in drinking water. OPP is recommending that 14 samples/year with focused sampling across the pesticide use period is the minimum sampling frequency for assessing the annual mean pesticide concentration in drinking water. This sampling frequency was selected as a minimum design element because empirical evaluation of monitoring data indicate 14 samples/year appears to be reliable for assessing annual means for corn herbicides in static and flowing surface water bodies. However, a universal sampling frequency in a multi-pesticide design may not be appropriate because the sampling frequency should be designed to capture concentration peaks for a reliable measure of annual mean pesticide concentrations. OPP's assessment suggests sampling frequency appears to be linked to environmental persistence; less persistent pesticides will require a higher sampling frequency. Other factors expected to impact sampling frequency are the flow rate of the surface water body and proximity of the pesticide application sites to the location of the water intake. Flowing surface water bodies (such as rivers and streams) are expected to have higher variability in pesticide concentrations and thus may need higher sampling frequencies.

Study Duration

The recommendation of a one year study is based on financial constraints, rather than on scientific merit. While a one year study can provide useful information, it is not capable of providing information on the year to year variability. The study could be lengthened by reducing the number of pesticides. However, this approach was not chosen because it would limit the number of selected pesticides in the survey design.

Based only on the scientific merits, the Agency recommends that monitoring studies be conducted for multiple years. A multiple year study will allow the assessment of climactic variability and variations in pesticide management practices on the annual mean concentrations.

Chemical Selection

OPP recommends a combination approach that considers the pesticide use pattern, environmental fate properties of the pesticide, risk, and availability of analytical method. We believe this type of approach will identify the pesticides that can be appropriately assessed with a national survey and provide the Agency with the necessary data for risk assessment and management decisions.

Raw and Finished Water

In light of funding constraints, OPP believes a minimum sampling approach is to collect paired raw and finished water samples with analysis of all raw water samples and fewer finished water samples. Reactive analysis of finished water samples is recommended based on the detection of target pesticide concentrations in raw source water. The feasibility of this approach is dependent on the stability of each pesticide in finished water.

A preliminary literature review suggests that most pesticides are unlikely to be removed but may be transformed through conventional water treatment processes. However, granular activated carbon has been shown to remove most pesticides. Also, water softening, pH-adjustment for corrosion control, disinfection with chlorine and ozonation have been shown to remove or transform some pesticides. The ability to assess the impact of water treatment processes in the survey design is another important variable.

Ancillary Data

Ancillary data are required for watershed characterization are pesticide use information including the total amount and application rate, types of crops, type of soils, agronomic practices, hydrologic characteristics, precipitation, and physical watershed characteristics. These data are needed to assess mitigation options for source water protection. Information on the water treatment processes including type of water treatment processes, source water quality information, and flow rate through the CWS's are needed to evaluate the impact of water treatment on pesticide removal and transformation. The population served by each CWS in the survey is also needed to allow for population weighting pesticide concentrations for the dietary exposure assessment.

Census for Major Facilities

OPP is considering as part of a design framework that CWS’s serving large populations of people (*e.g.*, New York, Chicago, and Los Angeles) be automatically included in the design.