UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

January 29, 2009

MEMORANDUM

SUBJECT: Transmittal of Meeting Minutes of the FIFRA Scientific Advisory Panel Meeting Held October 28 - 31, 2008 on Selected Issues Associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative and Toxic Characteristics

TO:
Debbie Edwards, Ph.D.
Director
Office of Pesticide Programs

FROM:
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Designated Federal Official
FIFRA Scientific Advisory Panel
Office of Science Coordination and Policy

THRU:
Steven Knott
Executive Secretary
FIFRA Scientific Advisory Panel Steven M. Knott
Office of Science Coordination and Policy

Frank Sanders
Director
Office of Science Coordination and Policy

Attached, please find the meeting minutes of the FIFRA Scientific Advisory Panel open meeting held in Arlington, Virginia on October 28 - 31, 2008. This report addresses a set of scientific issues being considered by the Environmental Protection Agency pertaining to Selected Issues Associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative and Toxic Characteristics.

Attachment

cc:

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OPP Docket

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SAP Minutes No. 2009-01

A Set of Scientific Issues Being Considered by the Environmental Protection Agency Regarding:

Selected Issues Associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative and Toxic Characteristics

OCTOBER 28 - 31, 2008
FIFRA Scientific Advisory Panel Meeting,
Held at the
Environmental Protection Agency Conference Center
Arlington, Virginia

NOTICE

These meeting minutes have been written as part of the activities of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), Scientific Advisory Panel (SAP). The meeting minutes represent the views and recommendations of the FIFRA SAP, not the United States Environmental Protection Agency (Agency). The content of the meeting minutes does not represent information approved or disseminated by the Agency. The meeting minutes have not been reviewed for approval by the Agency and, hence, the contents of these meeting minutes do not necessarily represent the views and policies of the Agency, nor of other agencies in the Executive Branch of the Federal government, nor does mention of trade names or commercial products constitute a recommendation for use.

The FIFRA SAP is a Federal advisory committee operating in accordance with the Federal Advisory Committee Act and established under the provisions of FIFRA as amended by the Food Quality Protection Act (FQPA) of 1996. The FIFRA SAP provides advice, information, and recommendations to the Agency Administrator on pesticides and pesticide-related issues regarding the impact of regulatory actions on health and the environment. The Panel serves as the primary scientific peer review mechanism of the EPA, Office of Pesticide Programs (OPP), and is structured to provide balanced expert assessment of pesticide and pesticide-related matters facing the Agency. Food Quality Protection Act Science Review Board members serve the FIFRA SAP on an *ad hoc* basis to assist in reviews conducted by the FIFRA SAP. Further information about FIFRA SAP reports and activities can be obtained from its website at http://www.epa.gov/scipoly/sap/ or the OPP Docket at (703) 305-5805. Interested persons are invited to contact Myrta R. Christian, SAP Designated Federal Official, via e-mail at christian.myrta@epa.gov.

In preparing the meeting minutes, the Panel carefully considered all information provided and presented by EPA, as well as information presented by public commenters. This document addresses the information provided and presented by these groups within the structure of the charge.

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Selected Issues Associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative and Toxic Characteristics

OCTOBER 28 - 31, 2008
FIFRA Scientific Advisory Panel Meeting,
Held at the
Environmental Protection Agency Conference Center
Arlington, Virginia

Steven C. Heeringa

Steven G. Heeringa, Ph.D.
FIFRA SAP Chair
FIFRA Scientific Advisory Panel
Date: January 29, 2009

Myrta R. Christian

Myrta R. Christian, M.S
Designated Federal Official
FIFRA Scientific Advisory Panel
Date: January 29, 2009

Federal Insecticide, Fungicide, and Rodenticide Act
Scientific Advisory Panel Meeting
October 28 – 31, 2008

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INTRODUCTION

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), Scientific Advisory Panel (SAP) has completed its review of Selected Issues Associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative, and Toxic Characteristics. Advance notice of the meeting was published in the *Federal Register* on July 23, 2008. The review was conducted in an open Panel meeting held in Arlington, Virginia, from October 28 – 31, 2008. Dr. Steven G. Heeringa chaired the meeting. Myrta R. Christian served as the Designated Federal Official.

This Scientific Advisory Panel meeting addressed selected scientific issues associated with assessing the potential ecological risks resulting from use of a pesticide active ingredient which has persistent, bioaccumulative, and toxic (PBT) characteristics. EPA posed specific charge questions to the SAP on issues involving:

- The range and combination of characteristics of persistence, bioaccumulation, and toxicity that should employ a modified approach to ecological risk assessment;

- The need for changes to the conceptual model used to evaluate the potential ecological effects of pesticides with varying P and B characteristics;

- Toxicity endpoints and methods OPP should consider when assessing pesticides with varying P and B characteristics;

- Pathways of potential exposure that should be considered in assessing the ecological risks of a pesticide with varying P and B characteristics;

- Data and model(s) appropriate for estimating and characterizing bioaccumulation and estimating steady and non-steady-state pesticide residue concentrations in biota;

- Data and model(s) appropriate for estimating and characterizing environmental fate in soil, water and sediment; and

- Data and model(s) most appropriate for assessing exposure to biota through multiple pathways.

The Office of Pesticides Programs (OPP) had recently completed ecological risk assessments on several pesticides with varying P and B characteristics. OPP drew on information and analyses from these assessments to illustrate the evolving approach OPP is using to address selected issues and how differences across chemicals – for example, in terms of data, characteristics, and available models – influence OPP's approaches. This meeting with the SAP was the first of what OPP anticipates will be several meetings over the next few years to improve OPP's evolving approach to evaluating pesticides with varying P and B characteristics.

Drs. Steven Bradbury (Director, Special Review and Reregistration Division, OPP) and Donald Brady (Director, EFED, OPP) offered opening remarks at the meeting.

The agenda for this SAP meeting included presentations from the Environmental Fate and Effects Division (EFED) in the OPP and the Office of Research and Development (ORD) as well as public comments.

PUBLIC COMMENTERS

Oral statements were presented as follows:

Jay P. Overmyer, Ph.D., from Syngenta, on behalf of CropLife America
Lynn S. McCarty, Ph.D., on behalf of Valent USA Corporation
Stuart Z. Cohen, Ph.D., on behalf of AMVAC Chemical

Written statements were provided by:

Lynn S. McCarty, Ph.D. and J.A. Arnot, Ph.D. through Robin Charlton, on behalf of Valent USA Corporation
Stuart Z. Cohen, Ph.D., on behalf of AMVAC Chemical

SUMMARY OF PANEL DISCUSSION AND RECOMMENDATIONS

The EPA is charged with assessing the risks of pesticides in the environment. The methods for conducting these assessments were developed for materials with relatively short half lives and transport potential. Thus, in determining potential risks from persistent, bioaccumulative, and toxic (PBT) chemicals that have significant long-range transport (LRT) properties, there is a need to consider longer time periods, chronic impacts, far-field impacts, and additional receptors. The Panel was provided with data from four PBT chemicals and was asked to consider ten charge questions relevant to the issues presented in the conduct of risk assessments of PBT pesticides.

Overall, the Panel was impressed with the documentation and oral presentations provided. The extent of information and details presented in the case studies were on target for Panel use. The Panel commended EPA for its hard work in developing the White Paper provided for the Panel's consideration. Because of the extensive information presented in the White Paper and the clarity of the charge questions, the Panel was able to conduct in depth discussions and provide the EPA with specific recommendations.

1. Assessing Exposure to Parent and Degradation Products. When assessing the potential ecological risks of proposed pesticide uses, the Agency is charged with considering both the parent compound and any degradation products of concern. The Panel was asked to comment on the strengths and limitations of the methods presented in the White Paper, whether these methods reflect the current state of the science, and to identify additional methods that could be recommended for pesticide risk assessments.

The Panel felt that these were well defined by the EPA and agreed that the Formation/Degradation kinetics was more realistic than the Residue Summation or Total Residue approaches. The approach used for modeling the fate and transport of parent and degradation products reflects the state of the science since low concentrations of compounds generally behave independently as long as the production of the compound is modeled correctly. However, more information on the approach used by the Agency to assess the toxicity/biological impacts of mixtures of parent and degradates should be provided, including mode of action considerations and structural similarity analysis. Where experimental data are unavailable, consider using estimation tools such as CATABOL that predicts metabolic pathways, potential stable intermediates, and general information related to relative biological persistence. The Panel also felts that any assessment associated with the toxicity and biological impacts of both parent and degradates consider the impacts of the chemicals as a mixture rather than individually.

2. Interpretation of Aquatic Degradation Rates for Persistent Pesticides with High Sediment Sorption Coefficients. The Panel was asked to comment on the strengths and limitations of the Agency's approach of using total system half-life for assessing pesticide persistence in aquatic metabolism studies, especially considering the environmental fate data typically available to support pesticide registration decisions.

The approach described in the White Paper includes four pathways for degradation. Each of these processes has a separate time scale. In general, each of these processes can be significant, and they interact. The approach has both strengths and limitations. Its main strength is in mimicking the combined and short-term transient processes reflecting pesticide behavior in the aquatic system. Its limitation is that the test involves too many fate processes simultaneously. The whole-system half-life does not allow quantification of any specific kinetic parameters useful for fate modeling. Therefore, ideally, the experimental design should be revised.

However, under the assumption that the proposed experimental protocol must be followed, or data derived using these guidelines need to be interpreted, the majority of the Panel believes that the Agency's proposed whole-system half-life approach does overcome the effects of sorption and other transport processes, and the derived half-life is a better description of the persistence of the chemical in the whole system.

In summary most Panel members agreed that the use of whole-system half-life is an improved approach over the use of water concentration for interpreting pesticide persistence in the whole system. It is critical that processes such as sorption be excluded in the half-life calculation under non-equilibrium or non-steady-state conditions. The Agency should also consider the possibility of revising the experimental design so that ambiguity is eliminated in data interpretation and parameters generated may be useful for fate and transport modeling.

3. Sediment Dynamics. As part of its baseline ecological risk assessment process, OPP uses environmental fate and transport computer models to generate estimated environmental concentrations of a pesticide in surface water, pore water and sediment. The Panel was asked to comment on the strengths and limitations of OPP's current approach for modeling pesticide transport between the water column and benthic region, to comment on the strengths and limitations of simulating pesticide burial as a process that renders pesticides permanently unavailable for biological interaction, and to comment on the strengths and limitations of models described in the White Paper with respect to modeling pesticide transport via sediment dynamics.

To support their responses, the Panel provided a review of the most significant processes affecting sediment-water fluxes and transport prior to addressing each of the charge questions. This review is provided in detail in the response section of this document.

The sediment-water flux of chemicals is primarily due to sediment erosion/deposition, molecular diffusion, and bioturbation. Each of these processes acts in a different way, and hence each must be described and modeled in a different way. The use of a lumped parameter and the associated concept of a well-mixed surficial layer in the bottom sediments should be discouraged. For a better model, a one-dimensional, time-dependent model was suggested.

Burial is a major removal mechanism and must be included, either explicitly or implicitly. In addition, as sediments are deposited on the bottom, the sediment-water flux processes immediately begin to act. For highly hydrophobic chemicals, these fluxes will continue to act for many years and the bottom sediments can serve as a major and long-lasting source of chemical to the overlying water. This process must be included for these chemicals.

The Panel agreed that treatment of sediment dynamics in the models described in the White Paper is not satisfactory. Parameters are undetermined and undeterminable, and some processes are not described realistically. The particle processes in ECOMSED are better than the other models, but it has been superseded by SEDZLJ.

With regard to differences between static ponds and flowing waters, the Panel agreed that in static ponds, sediment erosion, scour, and bank erosion would not be significant, almost by definition. Bioturbation is likely ubiquitous and significant depending on the numbers and types of organisms. Molecular diffusion is always present, but typically less significant than particle and bioturbation processes. Deposition of incoming sediments needs to be considered. In streams, however, all of the above processes can be significant depending on local conditions including topography and flow conditions.

The Panel suggested several short and long term pathways for improvements to the current approaches. These include improvements in determining parameters for PBREN, pesticide burial, sediment-water flux, and erosion rates.

4. Aquatic Bioaccumulation Methods. Traditionally, OPP's assessment of pesticide bioaccumulation potential in aquatic organisms has relied extensively on the use of bioconcentration factors (BCFs). The Panel was asked to comment on the need to consider alternatives to the BCF method for assessing the bioaccumulation potential of organic pesticides with PBT characteristics and to comment on the applicability of the Agency's approach of using multiple methods for assessing bioaccumulation potential of organic pesticides.

The Panel generally agreed that alternatives to BCF are required to assess bioaccumulation of PBT organic pesticides. These alternatives need to take into account accumulation from the diet, trophic transfer, and when and where it occurs in aquatic food webs. Bioaccumulation modeling may be a good first approximation for some compounds and under certain conditions. However, serious problems arise when the focal compound is metabolized or non-equilibrium conditions prevail. The White Paper goes a long way in recognizing many of these issues but the Panel felt it is deficient in addressing the issue of birds and mammals to the same degree as the lower aquatic food web. Consideration of birds and mammals was recognized by the Panel as a challenge to the process, and a tiered approach to this problem was suggested to address PBT issues. In addition the Panel provided comments on PBT issues related specifically to the use of Kow, BCF, biotransformation, implications of long-range transport, and contaminant concentrations that may be above solubility limits. The Panel provided suggestions for additional data needs, specifically dealing with laboratory-based trophic transfer experiments, revisions to current food web models, links between aquatic and terrestrial ecosystems, and the need to model or monitor individual tissue compartments in some organisms.

5. Terrestrial Bioaccumulation in Terrestrial Food Webs. The Agency currently assesses risks to terrestrial vertebrates that result from direct deposition of pesticides on food items that inhabit the treatment area. In general, this assessment is considered to provide relatively "high end" estimates of acute exposure through the ingestion pathway. At this time, however, the Agency does not routinely assess pesticide bioaccumulation in terrestrial food webs in non-target sites, in part, because the methods and tools for assessing bioaccumulation in terrestrial food webs are not as developed compared to those for aquatic food webs. The Panel was asked to comment on factors to identify when bioaccumulation potential in terrestrial food webs may be important and to comment on the current state of the science underlying existing terrestrial food web bioaccumulation models and their relative strengths and limitations.

The Panel agreed that the factors to identify depend on spatial scales, the characteristics of the ecosystem under consideration, and the route of delivery of the pesticide. Nevertheless there was general agreement that Kow and Koa are the most important parameters in attempts to assess bioaccumulation potential in terrestrial food webs. There was no discussion about the relevance of Koc, possibly because Kow may be able to substitute for it in most cases. In long-range transport scenarios, Henry's Law constant, water solubility, vapor pressure, and measures of persistence (e.g., hydroxyl radical scavenging rate) also assume importance.

Methods and tools for assessing bioaccumulation are not as developed in terrestrial as those in aquatic ecosystems, but the Panel felt this is principally because of lack of effort to date, not the fundamental difficulty of doing it. The Panel recommended that local terrestrial models be developed to the same level of detail as local aquatic models are at present. It is not clear whether bioaccumulation potential in terrestrial animals with aquatic based food webs is being appropriately considered, especially if there is another trophic link in the terrestrial part of the food web. The main challenge of developing models to assess PBT pesticides in terrestrial animals has to do with how the models are assembled and calibrated rather than defining appropriate sets of equations. The Panel discussed multiple approaches and suggested ways to improve the modelling process.

6. Toxicity: Incorporating Multiple Exposure Routes. The Agency is considering using a tissue residue approach (TRA) for quantifying chemical toxicity to address the concern that PBT chemicals in aquatic ecosystems may have important routes of uptake other than water. The Panel was asked to comment on the strengths and limitations of the TRA for addressing pesticide toxicity from multiple exposure routes and to comment on the strengths and limitations of using measured and predicted tissue residue-effect relationships that are derived from water-only exposures in laboratory toxicity tests.

The tissue-residue approach for toxicity assessment (TRA) is basically the use of tissue concentrations as the dose metric for characterizing toxicant potency. There are several advantages to using tissue residues over exposure concentrations (e.g., water, sediment, or diet) to calculate toxicity metrics. These include a large reduction in toxic response variability among all species for a given compound, an improved ability to address mixture toxicity, an increased use of information on modes and mechanisms of toxic action, a likely reduction in the number of species needed to characterize toxicant potency, the potential to improve ecological risk assessments, and the generation of more scientifically defensible tissue, water, and sediment toxicity guidelines or criteria. A keystone concept for the TRA is that the body/tissue residue reflects the target "dose" better than the traditional dose because the closer the dose surrogate is to the actual site of toxic action the less it is influenced by myriad modifying factors. The TRA is not intended to replace ambient dose metrics but to enhance information about toxic responses. The Panel noted that applicability of the TRA may be limited by highly metabolized compounds and the potential for additional data requirements.

Water-only exposures are acceptable in a TRA approach, as are dietary-only exposures when determining dose-response based on tissue concentrations. The strength here is that the route of uptake is less important when using TRA; however, sufficient time must be provided for internal redistribution of the toxicant due to circulatory differences in distribution to tissue. The Panel noted that toxicity or bioaccumulation predictions may not be accurate because not all compounds are amenable to QSAR modeling. This limitation supports the need for measured values over those determined with models. Additionally, several doses and longer time periods of exposure should be explored because many toxicants exhibit multiple modes of action that are dose and time dependent. To capture these differences, a wide range in doses is needed and long-term exposures are essential.

7. Screening for Long-Range Transport Potential. Currently, OPP's ecological risk assessment process relies heavily on monitoring data for assessing long-range transport concerns. However, this process does not *a priori* screen for long-range transport potential prior to pesticide release in the environment. The Panel was asked to comment on the strengths and limitations of available tools for screening the long-range transport potential of pesticides.

The Panel provided a discussion of issues related to long-range transport (LRT) and addressed strengths and weaknesses of the Organization for Economic Co-operation and Development (OECD) screening tool. Issues related to defining long-range transport are presented. Beyond the 100km OECD definition of LRT, there are numerous considerations to account for in models (e.g., regional or continental transport, cross-boundary transport, transport into remote ecosystems, etc.). A discussion of empirical evidence for LRT provided a background for some of the issues presented to OPP regarding PBT pesticides. Models, including the OECD screening model, were discussed relative to their strengths and weaknesses and how they compare to empirical data. The Panel recommended a tiered approach to LRT screening and provided suggestions on how to build that approach. One issue that was raised concerned how to link local pesticide use to far-field exposures (and potential effects). Panel recommendations were provided to improve model parameters, to combine modelling and data collection schemes, and to utilize validated local-scale models in concert with a GIS-based approach to scale to regional or larger areas of concern.

8. PBT Risk Assessment Issues: The Panel was asked to comment on the extent to which the Agency has identified and characterized the unique or problematic issues associated with assessing ecological risks of pesticides with PBT characteristics, and to comment on the need for the Agency to incorporate refinements in the tools and methods it uses to assess ecological risks of these compounds.

The Panel agreed that the Agency has identified and illustrated many of the unique issues related to the ecological risk assessment of PBT&LRT chemicals. The White Paper illustrates that the Agency is not only willing to address these issues but has made substantial progress towards identifying assessment methods that are more appropriate for this class of chemicals. However, the review Panel found that some of the issues that are unique to these chemicals could be highlighted for more detailed consideration, along with some issues that were not discussed that should be considered. These issues are described by the Panel in reference to chemical loss pathways, toxicity issues, source considerations, life cycle issues, fate and transport of parent chemical and degradation products and issues of scale.

A number of refinements to the OPP/EFED's existing assessment methodology, and new hazard metrics or assessment methodologies were also discussed both in the White Paper and by the Panel. The Panel agrees that there is a need for the Agency to incorporate refinements in the tools and methods for PBT&LRT chemicals. The extent of refinement may depend on policy related factors that are beyond the scope of this review, but also on factors that are unique to this class of chemicals. The refinements that are proposed and illustrated in the White Paper are a leap forward for the Agency and the Panel agrees that these refinements are rooted in the science.

However, it is likely that the issues associated with PBT&LRT chemicals will require a very different assessment approach than has historically been used within the Agency and this possibility should be explored further. For example, the current approach continues to focus on the field and pond scenario despite the recognition that the time scale and spatial range of impacts for these chemicals might not be captured in the current methods. The Panel suggested that a number of methods and assessment tools are available that are designed specifically for PBT&LRT chemicals. Many of these methods and tools are already in use by other groups in EPA or in other jurisdictions and the OPP/EFED should take advantage of this expertise and experience. Regardless of the path chosen by the Agency to assess these chemicals, the Panel strongly encourages the Agency to base their advances, refinements and changes on the best available science and to make all practical efforts to verify any new/revised approach to the fullest extent possible.

9. Example Pesticide Assessments. Given the data available, as illustrated in the pesticide examples provided in the White Paper, the Panel was asked to comment on whether the Agency has used these data appropriately to the fullest extent possible in assessing ecological risks of pesticides with PBT characteristics, and on the methods it has used to characterize environmental persistence, bioaccumulation, toxicity and long-range transport potential of the example pesticides.

Some of the Panel members recognized and acknowledged that the proposed approaches and methods used for the example pesticides represent a significant change to the current approach to ecological risk assessment. There was general consensus that the Agency appears to be on the right path towards being able to better assess pesticides with PBT characteristics, although there remain many details still to be addressed or worked out.

Further, the Agency should be commended for offering real chemicals as case studies to illustrate the challenges related to PBT&LRT chemicals and to explore the tools and methods that are currently available for both screening and assessing these chemicals. The examples were informative and useful. In general, the examples demonstrate a willingness in the OPP/EFED to adapt their standard modeling approach in response to the unique challenges presented by this class of chemicals. For example, the Agency is clearly interested in improving the way their current models include sediment dynamics to improve the models' applicability to persistent organic pollutants (POPs). However, the Agency's interest in improving or adapting the existing field scale assessment models assumes that these types of models are the appropriate next step in assessing chemicals that are flagged as PBT&LRT by screening tools.

Finally, the Panel stated the need for dialogue between risk assessors and risk managers to ensure that the results are a) fulfilling the needs of the risk managers and b) interpretable and understandable by the risk managers, including the degree of variability and uncertainty.

Regarding methods utilized, the Panel generally agreed that given what EPA had to work with, the Agency provided a good outline of the process and results of analyses. The Panel provided a discussion concerning the two aspects that need to be considered in responding to this question; first the registrants' submitted data; and second the other data/information which is used to help characterize the risk (e.g., non-chemical specific model inputs, assumptions). A series of considerations in each of these areas was presented by the Panel.

10. Problem Formulation. The Agency is considering refinements to its problem formulation process to improve the ecological risk assessment of pesticides with PBT characteristics. The Panel was asked to comment on the Agency's proposed process for identifying (screening) pesticides for potential PBT risk assessment issues that need to be addressed and on the priority for developing new models, methods, and information for addressing PBT issues.

The Panel agreed that, as a first step, the criteria listed for identifying persistence, bioaccumulation potential and toxicity (in Table 8.2, National and International Screening Criteria for Classifying Chemicals According to PBT and LRT Characteristics) appear to be reasonable. Meeting the criteria for a particular attribute will help the Agency identify where it should focus its efforts. The Panel presented a revised version of Table 8.1 from the White Paper with specific comments and priorities for action. The Panel also discussed the role of modeling in directing risk assessments for all pesticides and in particular its use for PBT chemicals. Figure 1 from the White Paper was discussed and the Panel provided several suggestions for modifying the figure and the processes outlined within the figure.

Finally, two Panelists noted that there are lessons to be learned from the early-mid 20th century regarding the importance of long term ecological consequences of using PBT pesticides. Thus, some of the problems associated with evaluating the risks from PBT pesticides may have been considered previously. One Panelist also emphasized the global transport characteristics of PBT pesticides and suggested that the traditional methods for risk assessment may be inadequate. This panelist noted that to evaluate the risk associated with a PBT pesticide, a higher level of scientific scrutiny and data generation may be needed.

PANEL DISCUSSION AND RECOMMENDATIONS

Agency Charge

1) Assessing Exposure to Parent and Degradation Products.

When assessing the potential ecological risks of proposed pesticide uses, the Agency is charged with considering both the parent compound and any degradation products of concern. In several of the case studies presented in this White Paper, the Agency has illustrated three approaches for assessing the PBT characteristics and exposure to parent and degradation products. When parent and degradates are considered sufficiently similar in their environmental fate and toxicological properties or when these properties were unknown for the degradates, the Agency has used the Total Residue (TR) method (i.e., the Agency modeled the combined parent and degradate using a common set of environmental fate and toxicological data). In situations where the environmental fate and toxicological properties of the parent and degradate are available and considered sufficiently dissimilar, the Agency has modeled the environmental fate separately using the Residue Summation (RS) or Formation/Degradation kinetics (FD) methods (i.e., modeling individual residues from the parent and degradation products).

- Please comment on the Agency's characterization of the strengths and limitations of these methods and the conditions under which each method should be applied. (1.A)

- To what extent does the Agency's use of the total residue (TR) and individual residue methods (RS, FD) reflect the current state of the science for assessing exposure to combined parent and degradate compounds? (1.B)

Please identify any methods the SAP would recommend for addressing combined exposure to parent and degradate compounds based on the data typically available for pesticide ecological risk assessments as described in this White Paper. (1.C)

Panel Response

Response 1.A

The Panel felt that the strengths and limitations of the different approaches were well defined by the Agency in the White Paper and agrees that the Formation/Degradation kinetics (FD) method is more realistic than the Residue Summation (RS) or Total Residue (TR) approaches.

Whereas the TR approach is most conservative based on the examples provided in the White Paper, it is less realistic and should be avoided unless the lack of data dictates the selection. One Panel member suggested that the general appropriateness of the TR method may be limited because there are relatively few degradates that have similar environmental fate properties or toxicity to the parent pesticide. Most degradations transform chemicals to more polar compounds that can be eliminated or even mineralized. Given that toxicity and mode of action are likely to change with the functional group alteration that occurs during metabolism, the assumption of additivity should be made with caution. That being said, if the properties, including toxic actions are the same and it is reasonably supposed to be additive, then a toxic-equivalency approach might be taken. If the degradates are not toxic or have very low bioaccumulation potential, it may be possible to ignore them altogether. If data constraints dictate the use of the RS approach, a temporal offset for the "application" of transformation products should be considered, based on data from transformation studies. This would better mimic the actual process taking place. In situations where different transformation processes result in the formation of different degradates in the soil and the water phases, caution should be used in applying the TR or RS methods and in the subsequent PRZM/EXAMS modeling.

Another panel member went further and suggested that sufficient metabolism data should always be required so that the FD approach can be used. However, the Panel acknowledged that this would present a challenge for re-evaluation situations where existing data may not allow use of FD unless reliable estimation methods become available. The overall approach discussed is not only applicable to PBTs but to all pesticides.

Ultimately the importance or impact of the selected approach will need to be viewed in the context of the overall variance (or uncertainty) in the assessment. As indicated in the presentation by Dr. Mackay, the best precision that can be expected with a multimedia fate model of the type required for assessing chemicals with PB&LRT characteristics is about a factor of 2 or 3 (often much higher) (see also Cowan et. al. 1994). Because many of the models that we use in fate and exposure assessments are deterministic we get a single number and often neglect the fact that the number represents the central tendency of a range of possible outcomes. Any changes in the estimated environmental concentration from the different approaches should also consider changes in contribution to the overall uncertainty in the modeling assessment.

In general, the more input data that is available, the better the assessment in terms of representing reality. However, making decisions with less input data does not necessarily mean that the decisions are wrong. Finally, comparing results for a range of chemicals to get a better idea of variability/uncertainty is recommended.

Response to charge question 1.B

The approach using both the parent compound and degradates for modeling fate and transport reflects the current state of the science since low concentrations of compounds generally behave independently as long as the production of this compound is modeled correctly (temporally and spatially). One member of the Panel considered the fate and transport modeling at field scale to be too narrowly focused for persistent and bioaccumulative chemical with long-range transport potential but consideration of both the parent and degradates is important regardless of the scale of the assessment.

More information on the approach used by the Agency to assess the toxicity/biological impacts of mixtures of parent and degradates, should be provided, including mode of action considerations and structural similarity analysis.

Response to charge question 1.C

Where experimental data are unavailable, consider using estimation tools such as CATABOL that predicts metabolic pathways, potential stable intermediates, and general information related to relative biological persistence. It is anticipated that CATABOL will soon be incorporated into EPISuite property estimation program improving usability, access and outside review. Another possibility that was suggested was to use information from in vitro biotransformation assays as conducted for the identification of persistent drug metabolites in human studies.

The Panel also felt that any assessment associated with the toxicity and biological impacts of both parent and degradates consider the impacts of the chemicals as a mixture rather than individually. The Panel also understood that current approaches used to estimate mixture impacts are relatively limited and will likely change and hopefully improve within the near future.

The Agency's consideration of parent and degradates in the fate and exposure part of their assessment is important when the degradates have similar or greater persistence and/or toxicity compared to the parent chemical. The approach can be used with modeling to estimate persistence overall (Pov) (Fenner et al., 2005; Klasmeier et al., 2006) as an important hazard metric for these chemicals. Pov is mentioned in the White Paper but only in reference to long-range transport. This information could be brought forward to the assessment of fate and exposure.

Another existing approach to assessing the combined fate of parent and degradates would be the EPA's recently developed Total Risk Integrated Methodology (http://epa.gov/ttn/fera/index.html), which provides a fate and ecological risk assessment modeling tool (TRIM.FaTE) to track multiple chemicals simultaneously from source to sink. The advantage of a modeling system like TRIM.FaTE is that it provides the opportunity to model at the near-field scales of the field and static pond but also include more representative temporal (years) and spatial (continental, global) scales in the assessment for PB and LRT chemicals. At the same time, the TRIM.FaTE approach provides feedback mechanisms (mass balance) between compartments to account for differences in the physiochemical properties of parent and degradates that can result in accumulation or persistence in different parts of the environment.

Additional Discussion points

The Panel developed the following list of discussion points that did not necessarily fit within any of the various sub-questions, but were thought to be relevant within the context of the general topic area.

- Use data for representative "historical or benchmark" pesticides to evaluate and refine assessment methods, especially models.
- Consider impacts of chirality/stereoselective processes through initial structural evaluations of the parent compound.
- Better define the approach used to evaluate the potential impacts of pesticide formulation on environmental fate assessment. It was difficult to determine how this was done from

the examples in the White Paper. For example, how might the use of a nanoparticle-based delivery formulation impact the assessment?

- Transparency. The Panel felt that it was very important to document all assumptions made in the modeling efforts, including the selection of appropriate input properties.
- Uncertainty. Model uncertainty and uncertainty associated with the various model input parameters should be considered and documented.
- Sensitivity analysis. What properties/processes or inputs really drive the results of the overall assessment? If a sensitivity analysis determines that an input property is particularly important then extra care must be taken to use the most appropriate value, or range of values.
- It wasn't clear how ionizable chemicals were evaluated relative to their pKa's, environmental pH, and chemical form (neutral and charged form.)
- The choice between the three methods described in this charge question represents a microcosm of the bigger issue of assessing chemicals with PBT characteristics. Whether the Agency decides to use existing tools or develop new approaches, it is important to recognize that this process will be heavily influenced by models, and these models, whether they are used individually or in concert, need to be assembled in a systematic, transparent and defensible manner. This process is described very clearly in a recent report by the USEPA Council for Regulatory Environmental Models (http://www.epa.gov/crem/index.html) and it is recommended that the Agency consult this document before and during the preparation of their approach for assessing these chemicals.

Agency Charge

2) Interpretation of Aquatic Degradation Rates for Persistent Pesticides with High Sediment Sorption Coefficients.

The environmental fate of persistent pesticides with high sediment sorption coefficients is often influenced by dissipation processes (*e.g.,* sorption on sediment) rather than degradation processes (*e.g.,* hydrolysis, metabolism, photolysis). In aquatic metabolism studies, the sorption process can be a most important process in removing pesticide from the water column. This removal process, however, is not considered as a degradation pathway because the pesticide is simply transferred from the water column to the sediment. Therefore, the total system half-life of the pesticide in aquatic metabolism studies is used to represent the most accurate degradation rate in aquatic environments.

Considering the environmental fate data typically available to support pesticide registration decisions, please comment on the strengths and limitations of the Agency's approach of using total system half-life for assessing pesticide persistence in aquatic metabolism studies.

Panel Response

During discussion, the Panel consulted the OECD guidelines on aquatic sediment metabolism studies, for which the charge question was intended to address. The experimental system consists of a sediment layer and an overlying water layer, with the water to sediment ratio as 3:1 or 4:1. The pesticide is added into the water, after which pesticide concentrations in both sediment and water phases are measured over time. The question is how to assess pesticide persistence, especially pesticide dissipation from the overlying water.

The panel believes that multiple processes simultaneously take place in the sediment-water system when the pesticide is spiked into the overlying water, and the potential impact of these processes on data interpretation is especially pronounced for PBT pesticides. When the chemical is introduced, the chemical is probably thoroughly mixed in the overlying water. It then starts to degrade but it also diffuses into the bottom sediment where it adsorbs to the sediment and exists in dissolved and sorbed form. For a highly hydrophobic chemical, the chemical concentration in the sediment is much higher near the sediment-water interface than in the interior. The chemical may only diffuse a few millimeters into the interior and certainly will not be uniform throughout the sediment layer. Because of this degradation/diffusion/sorption process, the chemical concentration in the water decreases. The concentration in sediment (C_s) is expected to decrease very slowly, as expected for PBT chemicals. Eventually, because of degradation, C_w decreases to a low enough level that there is diffusion and desorption of the chemical from the sediment back into the overlying water. Meanwhile, there is still diffusion and sorption continuing within the bottom sediment. In the long term, the decrease of the concentration in the overlying water (C_w) with time is due to the combined processes of (1) degradation in the overlying water, (2) diffusion of the chemical into the bottom sediments and, at a later time, diffusion of the chemical back into the overlying water, and (3) degradation, adsorption, desorption, and diffusion of the chemical in the sediment.

The experiment as designed therefore includes (1) degradation of the chemical in the overlying water, (2) diffusion of the chemical from the water into the sediments and subsequent adsorption, (3) at a later time, diffusion and desorption of the chemical into the overlying water, and (4) degradation of the chemical in the bottom sediment. Each of these processes has a separate time scale. In general, each of these processes can be significant, and they interact. The measured half-life will also depend on the water/sediment volume ratio, a parameter which is somewhat variable in the experimental design.

The strength of such a setup is that it mimics short-term transient pesticide behavior in the aquatic system. Clearly, the experiment displays two or more fates, as outlined above. An implication from quantifying the fractions associated with sediment and water gives some insight into the amount involved with short-term water column fate and the long-term bed-sediment fate. It mimics rather than simulates. Its limitation is that the test involves too many fate processes simultaneously. None of the individual water or sediment or degradation kinetic parameters can be clearly isolated using this test. Models require these specific kinetic inputs. The whole-system half-life, although characteristic of the pesticide and sediment-water system, does not allow quantification of any specific kinetic parameters useful for fate modeling. Therefore, ideally, the experimental design should be revised. In the future the Agency should consider seeking additional information on all the important degradation processes likely to occur within the pond scenario. One Panelist suggested that the pesticide be spiked into the sediment, instead of the overlying water.

However, under the assumption that the proposed experimental protocol must be followed, or data derived using these guidelines need to be interpreted, the majority of the Panel believes that the Agency's proposed whole-system half-life approach does overcome the effects of adsorption and other transport processes, and the derived half-life is a better description of the persistence of the chemical in the *whole system.* The derived half-life may approximate the half-life for PBT pesticides in sediment due to their predominant association with the sediment phase, but does not reflect the behavior of the pesticide in the water phase.

Alternatively, especially in the case when interpretation of existing data from previous assessments is necessary, the half-life can be calculated by using data points after initial phase distribution is completed, or when apparent equilibrium is reached. In the case of the included example (Figure 3.12, p. 62 in the White Paper), data after day 15 should be used for calculating the half-life. Again, this half-life reflects the persistence of the pesticide in the whole-system or sediment, but not in water.

In summary most Panel members agreed that the use of whole-system half-life is an improved approach over the use of water concentration for interpreting pesticide persistence in the whole system. It is critical that processes such as adsorption be excluded in the half life calculation under non-equilibrium or non-steady conditions. The Agency should also consider the possibility of revising the experimental design so that ambiguity is eliminated in data interpretation and parameters generated may be useful for fate and transport modeling.

One Panel member agrees with the first three paragraphs, but has a different viewpoint for the remaining portion of the response to this question. This Panel member's recommendations are as follows.

Because of these multiple processes, the half-lives of the chemical degradation (in the water, in the sediment, or whole system) cannot be determined unambiguously from the proposed experiment. As an example, consider the long-time behavior of the pesticide in the experiment. The pesticide degrades in the overlying water with a certain degradation rate. The pesticide degrades in the bottom sediment with a certain degradation rate (different from that in the overlying water). The pesticide diffuses from the bottom sediment to the overlying water at a certain rate due to molecular diffusion. The long-term behavior of the pesticide is governed by the interaction of these three processes (not including sorption rates, which are most significant initially).

Over long periods of time, there are three rates which must be determined so as to interpret the experiment properly. At most, EPA only measures two quantities, $C_w(t)$ and $C_s(t)$, which is insufficient to unambiguously determine three parameters. This can be demonstrated analytically. Non-unique (i.e., multiple) choices of parameters will result; endless arguments will then result as to which choice of parameters is correct. The experiment is flawed, especially for chemicals with high partition coefficients.

Separate experiments using water and sediment to independently derive half-lives due solely to degradation are proposed. These experiments are relatively straightforward and easy to interpret. This will give unique and defensible results.

The suggested experiment, where the pesticide is spiked into the sediment, is invalid. The interpretation of the experiment has the same difficulties as described above, i.e., non-unique and indefensible results. The results will be even more difficult to interpret than the present experiment for high K_p chemicals because of the enormous amount of chemical in the sediment.

The Panel member does not believe that the proposed EPA experimental protocol must be followed, or should be followed. The Panel member does not believe that the whole system half-life approach overcomes the effects of adsorption and other transport processes. Results of these experiments can only be properly interpreted by considering all four significant processes and using a modeling approach similar to that proposed in the response to question 3.

Agency Charge

3) Sediment Dynamics.

As part of its baseline ecological risk assessment process, OPP uses environmental fate and transport computer models to generate estimated environmental concentrations (EECs) of a pesticide in surface water, pore water and sediment. The EECs are generated using the EXAMS model parameterized to represent a static farm pond receiving pesticide mass in runoff from a treated agricultural field simulated by PRZM. It is assumed by OPP that EECs generated from this scenario are conservative representations of expected pesticide concentrations not only in this farm pond but also in small first and second order streams that receive runoff-containing pesticide residues from many fields. Currently, the OPP modeling approach accounts for movement of pesticide mass between the water column and benthic region using a set of "lumped" parameters (PRBEN) and a mass transfer coefficient. These parameters are intended to implicitly account for pesticide mass transfer due to processes such as diffusion, settling, resuspension and other processes that tend to mix the sediment layer with the water column. The current OPP modeling approach does not include inflow of sediment to the water body which could lead to burial of sediment containing pesticide through deposition.

- Please comment on the strengths and limitations of OPP's current approach for modeling pesticide transport between the water column and benthic region which relies on the use of lumped parameters to represent multiple transport mechanisms (e.g., diffusion, settling, resuspension) in static ponds.

- In the context of screening-level and refined assessments, please comment on the strengths and limitations of simulating pesticide burial by sediment in static ponds as a process that renders pesticide permanently unavailable for biological interaction (i.e., not bioavailable).

Please comment on the strengths and limitations of models described in the White Paper with respect to modeling pesticide transport via sediment dynamics. Which processes associated with sediment-based pesticide transport (e.g., sediment enrichment, settling, re-suspension, burial, bioperturbation, pore water diffusion, scour, and bank erosion) would be most important to consider in static ponds? Which processes would be most important in flowing water systems?

Panel Response

GENERAL COMMENTS FOR QUESTION 3

Figure 4.1 (p.72 of the White Paper) depicts the conceptual model used by EXAMS while Figure 4.5 (p. 79) depicts the conceptual model as used by OPP. Significant improvements to the description of pesticide transport as described in these figures would be (1) a more detailed description of the sediment-water fluxes of pesticides and (2), as part of this, the inclusion in these processes as well as transport in the overlying water of finite rates of pesticide sorption between sedimentary particles, including aggregates, and surrounding water, in the overlying water and in pore waters. An accurate description of sediment-water fluxes is intimately related to an accurate description of finite sorption rates, especially for hydrophobic chemicals with large partition coefficients, K_p.

In order to respond most efficiently to the EPA's questions, a brief review of the most significant processes affecting sediment-water fluxes and transport [chemical sorption, sediment erosion/deposition and transport, molecular diffusion, bioturbation (referred as bioperturbation in the Agency's charge)] is given first; this is followed by a more direct response to the questions and suggestions for improvements.

Sorption and partitioning of hydrophobic organic chemicals (HOCs)

Adsorption and desorption experiments have been done with several different HOCs. Typical results for desorption experiments for a monochlorobiphenyl (MCB, $K_p = 10^3$ L/kg), hexachlorobenzene (HCB, $K_p = 10^4$ L/kg), and a hexachlorobiphenyl (HCBP, $K_p = 3 \times 10^4$ L/kg) are given in Figure 3.1. Shown is percent of sorbed HOC which is desorbed as a function of time. Desorption times are long (tens of days), much longer than typical particle transport times in ponds, rivers, and lakes (minutes to hours). Desorption times are proportional to K_p and increase as K_p increases. All the MCB and HCB desorbed completely during the experiments; HCBP was at 80% desorption at 200 days and was still desorbing when the experiment concluded at 230 days.

Long-term experiments have also been done to investigate the nonlinear behavior of isotherms (C_s as a function of C_w, where $K_p = C_s/C_w$) of some HOCs. It was demonstrated that the isotherms for all eight HOCs tested were linear as long as the mass of the sorbed HOC was small by comparison with the mass of organic carbon on the sediments; for larger sorbed HOC concentrations, the isotherms were nonlinear (the hockey-stick curve). This is shown in Figure 3.2 where C_{oc} (the mass of HOC sorbed to the sediments divided by the mass of organic carbon in the sediments) is plotted as a function of $K^o_{oc}\, C_w$ ($K_{oc} = C_{oc}/C_w$).

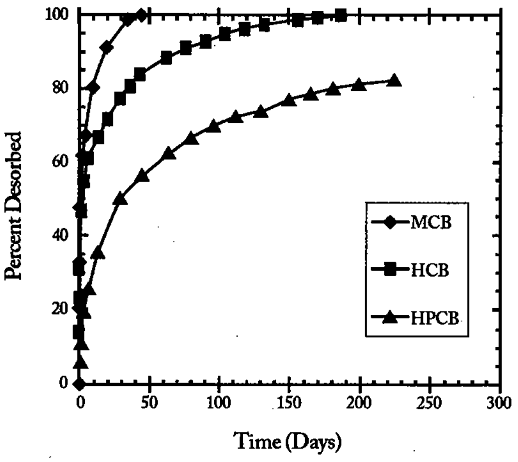


Figure 3.1. Desorption experiments with HCB, MCB, and HCBP. Percent desorbed as a function of time. From Lick, 2008.

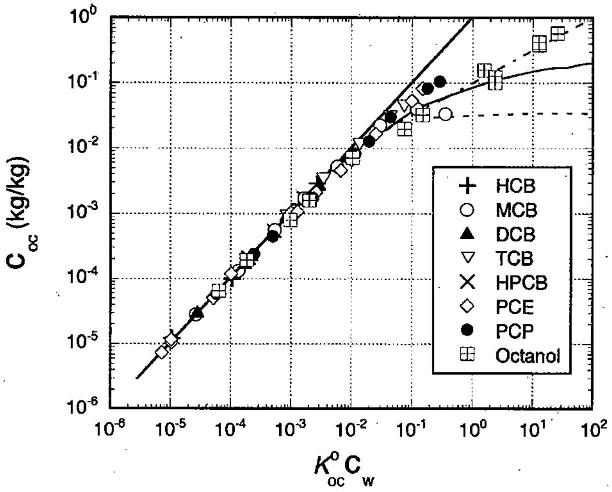


Figure 3.2. Partitioning for organic chemicals. C_{OC} as a function of $K^0_{OC}C_W$. From Lick, 2008.

The extent of the nonlinearity was limited by the solubility of the HOC. Solubility is the maximum amount of chemical that can be dissolved in water. Above solubility, the chemical precipitates and should be treated as a precipitate. Solubility and sorption are independent parameters; in particular, solubility is not related to the nonlinearity of the isotherms. For HOCs with low solubility in sediments with moderate to large amounts of organic matter, the isotherms were always linear. For low organic soils and chemicals with polar or ionizable functional groups, isotherms may be non-linear.

Sediment erosion/deposition and transport

As sediments are transported in the water column, the contaminants associated with these sediments are also transported in the water column where they may adsorb or desorb depending on conditions in the overlying water relative to chemical equilibrium conditions. Because erosion rates are highly variable in space and time (by orders of magnitude), contaminant fluxes due to erosion/deposition are also highly variable in space and time. During calm periods and average wind and flow conditions, these fluxes are relatively small and are probably comparable with the fluxes due to molecular diffusion, bioturbation, and groundwater flow. However, major storms and floods can cause movement and mixing of bottom sediment by erosion/deposition more rapidly and to depths much greater than that possible by these other processes. The contaminant flux during and immediately after the storm/flood events are due to the erosion of particles with their sorbed contaminants and the subsequent desorption of these contaminants into the surrounding water would also then be much greater than the contaminant fluxes due to these other processes. However, once the water flow rate subsides, re-suspension becomes low as the bottom shear stresss of flowing water falls below a critical level, the stream water becomes clear and displays very low suspended solids concentrations. At this point in time other processes control the contaminant flux from the bed to the water column. Among these, bioturbation is dominant if macrofauna exist in or on the sediment bed. Due to the short but intense fluxes involved, re-suspension appears to contribute a significant chemical mass to the water column; however, the majority of HOC mass released to the water column occurs over those long time-periods between storm/flood events. In general re-suspension accounts for 25% and other processes account for 75% of this total flux (Thibodeaux, 2005). As bottom water flow decreases in an aquatic system such as ponds, lakes, and reservoirs, particle re-suspension as a contaminant flux process is even less important than in flowing streams.

In the modeling of sediment transport, processes and quantities that may be significant include (1) erosion rates as a function of shear stress and depth in the bottom sediments, (2) particle/floc size and density distributions, (3) settling speeds as a function of particle/floc size and density, (4) deposition rates, (5) flocculation of particles, (6) erosion into suspended load and bedload, (7) bed armoring, and (8) bed consolidation.

Erosion rates depend on at least the following sediment properties: bulk density, particle size, (mean and distribution), mineralogy, organic content, salinity of pore waters, gas volume fraction, and oxidation and other chemical reactions. This dependence is not well known; because of this, erosion rates cannot be accurately determined from only a knowledge of sediment properties, all of which are not generally measured. However, erosion rates of relatively undisturbed sediments from bottom cores can be measured by Sedflume as a function of shear stress and depth in the bottom sediment.

Figures 3.3, 3.4, and 3.5 are examples of how erosion rates vary as a function of shear stress and depth in the sediment. The measurements were made by the use of Sedflume on relatively undisturbed cores. The sediment in Figure 3.3 is relatively fine-grained, is cohesive, and is fairly uniform with depth. The sediment in Figure 3.4 is layered with a mix of fine-grained and coarser-grained sediments. Erosion rates change by orders of magnitude as a function of shear stress and depth in the sediments. The results shown in Figure 3.5 show a layer of constant properties at the sediment-water interface. This was due to deposition after a large flood and was not due to mixing by organisms. This type of layer is quite common in aquatic systems.

In order to investigate the effects of finite sorption rates on the transport of an HOC, calculations were made of the transport and fate of polychlorinated biphenyls (PCBs) during storms of different magnitudes on Green Bay. An example calculation is shown in Figure 3.6 and illustrates the large differences, typically four to five, between a calculation with an equilibrium assumption and that including finite rate sorption.

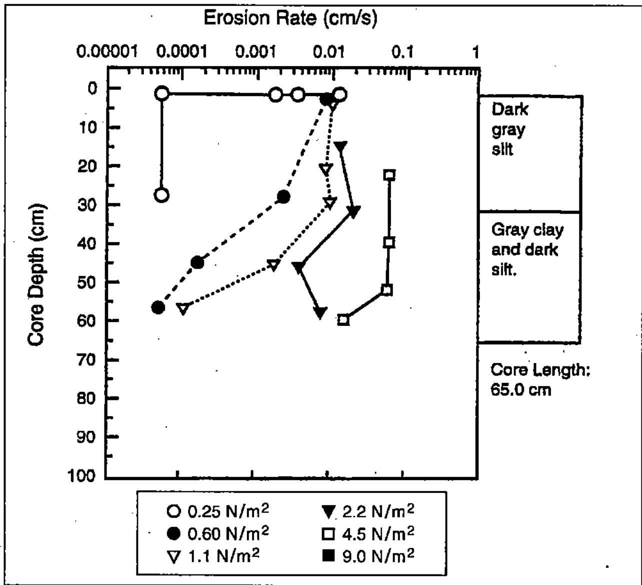


Figure 3.3. Trenton Channel, site 3. Erosion rate as a function of depth with shear stress as a parameter. From Lick 2008.

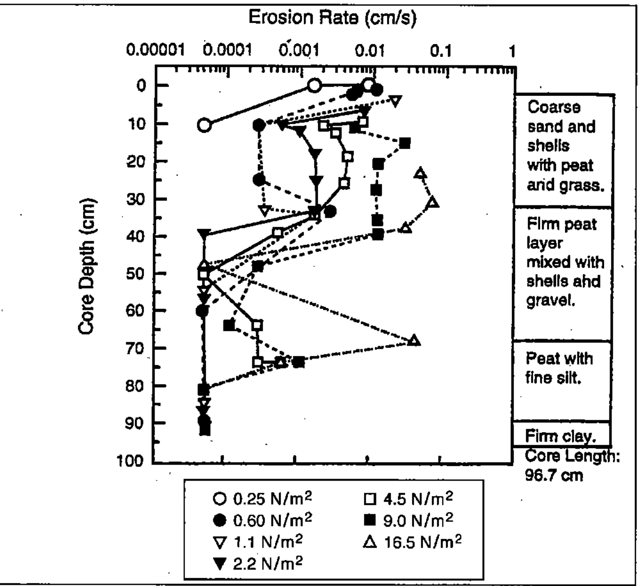


Figure 3.4. Trenton Channel, site 4. Erosion rate as a function of depth with shear stress as a parameter. From Lick 2008.

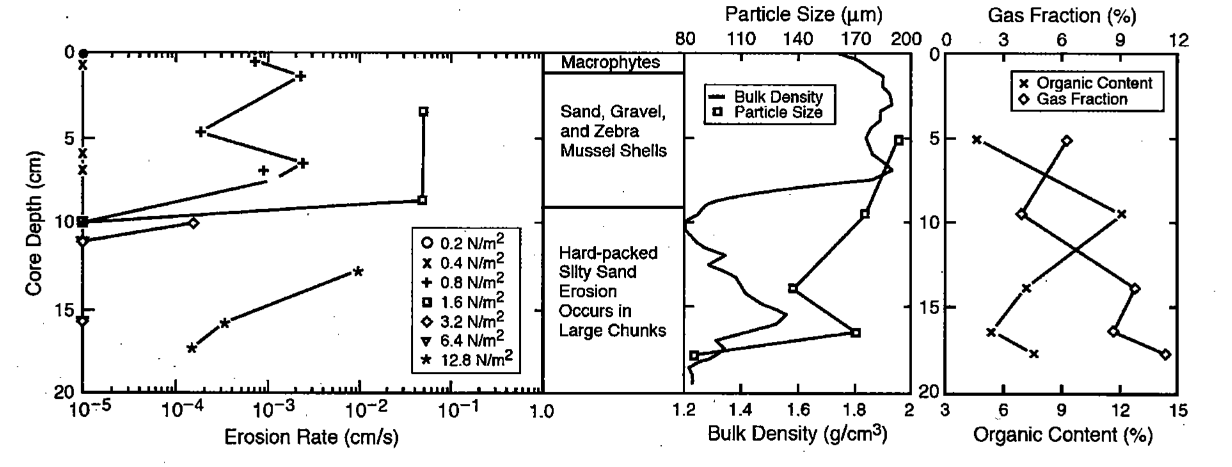


Figure 3.5. Kalamazoo River, core 61-1. Erosion rates and bulk properties as a function of depth. From Lick 2008.

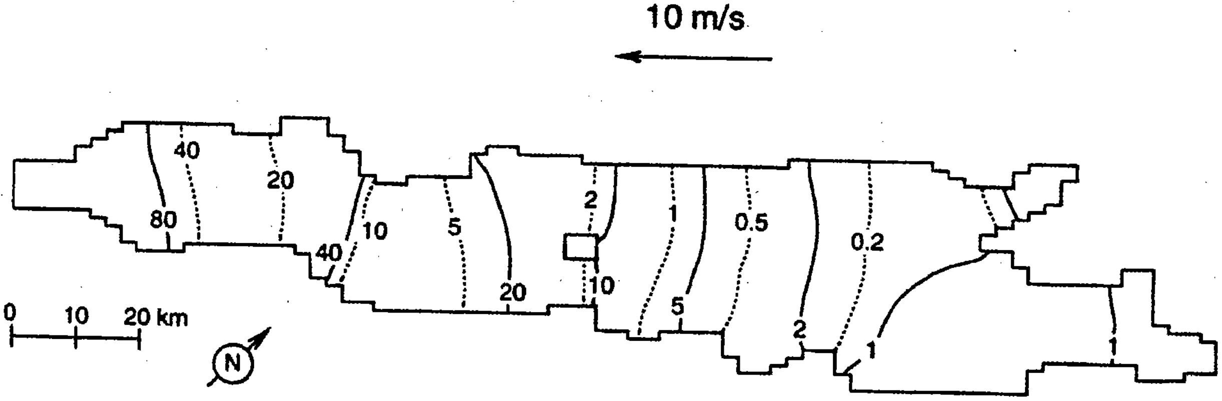


Figure 3.6. Concentration of PCBs in Green Bay at the end of the 14-day event. Solid lines are for the equilibrium calculation whereas the dashed lines are for the non-equilibrium case. C_w in ng/L. From Lick 2008.

Molecular diffusion

In order to investigate molecular diffusion of HOCs and the effects of finite sorption rates on this diffusion, experiments and modeling were done for HOCs with a range of K_ps from 10 L/kg to 5 x 10^4 L/kg and with two different sediments. For HCB diffusing from the overlying water (with a dissolved concentration of C_{wo}) into clean sediments, the measured HCB concentrations on the solids, C_s, as a function of depth with time as a parameter are shown in Figure 3.7. Due to sorption, the diffusion of HCB into the interior is much slower than that of a non-sorbing chemical (e.g., tritiated water, THO). Despite the length of the experiments (512 days), (1) significant changes in C_s are limited to a few millimeters near the sediment-water interface, and (2) measured values of C_s/C_{wo} near the surface are generally less than 0.1 of their equilibrium value at the surface (where C_s/C_{wo} in equilibrium should equal K_p, i.e., 1.2 x 10^4 L/kg). Results of a numerical simulation, which necessarily included non-equilibrium sorption, are shown as the solid lines.

Calculated values of C_s and K_pC_w, both normalized with respect to C_{wo}, are shown in Figure 3.8 as a function of depth at different times from 4 to 512 days. It can be seen that C_s and K_pC_w are quite different and are therefore not in local chemical equilibrium with each other, or even close to equilibrium, even after 512 days.

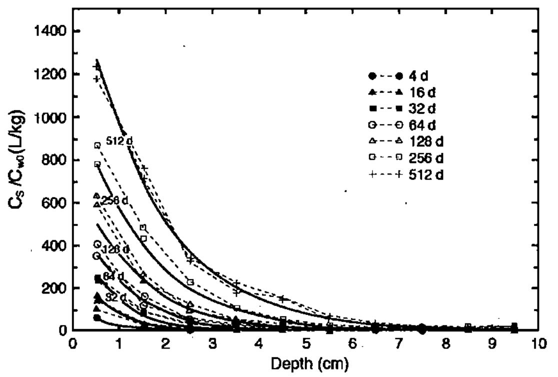


Figure 3.7. Experimental and theoretical results for the molecular diffusion of HCB into consolidated Detroit River sediment. C_s/C_{w0} is shown as a function of depth at times from 4 to 512 days. From Lick 2008.

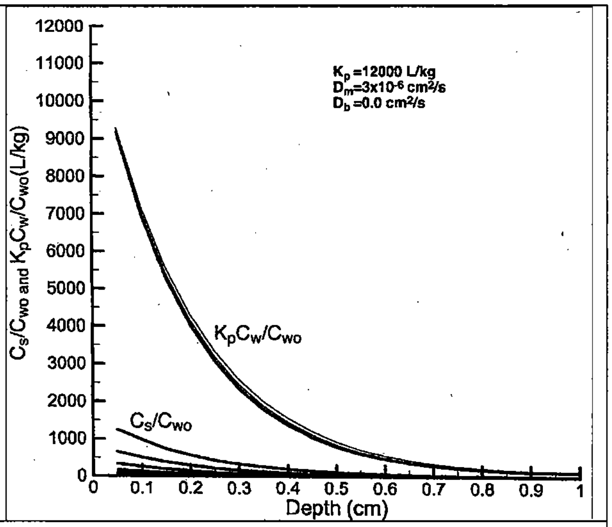


Figure 3.8. Calculated results for the molecular diffusion of HCB into consolidated Detroit River sediment. C_s/C_{w0} and K_pC_w/C_{w0} are shown as functions of depth at times of 4, 16, 32, 64, 128, 256, and 512 days. From Lick 2008.

Results for other HOCs are similar except that, as K_p decreases, (1) the chemical diffuses more rapidly into the interior, and (2) values of C_s/C_{wo} tend to approach their equilibrium value of K_p at the sediment-water interface more rapidly.

In order to illustrate the dependence of the sediment-water flux on K_p and time, numerical calculations were made for $K_p = 10^6$, 10^5, 10^4, and 10^3 L/kg and for times up to 100 years; results are shown in Figure 3.9. For $t > 0$, each flux decreases with time; as K_p increases, the flux decreases less rapidly with time. Mass transfer coefficients are generally from 1×10^{-6} to 10×10^{-6} cm/s, or about 0.1 to 1 cm/day.

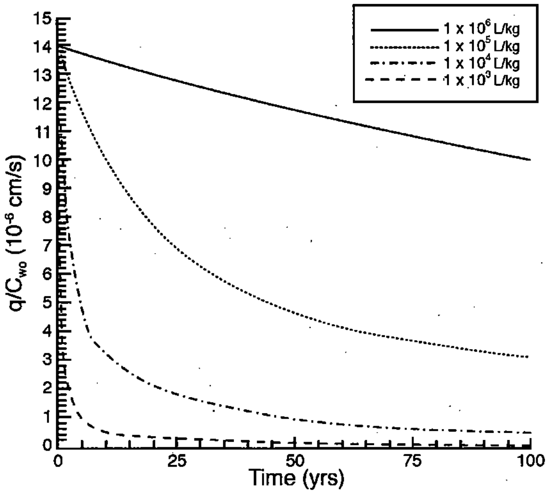


Figure 3.9. HOC flux in Detroit River sediments due to molecular diffusion as a function of time with K_p as a parameter. From Lick 2008.

Bioturbation

Of the processes that mostly govern the sediment-water flux of chemicals (sediment erosion/deposition, molecular diffusion, and bioturbation), bioturbation is probably the least well understood and quantified. The reasons are the large variety of benthic organisms which may be present in surficial sediments and the different ways in which they affect the sediments.

In order to investigate the effects of organisms, experiments and modeling were done with three benthic organisms (*Lumbriculus variegatus*, an oligochaete and vertical burrower; *Chironomus tentans*, a more horizontal burrower; and *Hyalella azteca*, a shallow-layer mixer). These three organisms are representative of benthic organisms in fresh water. Representative results for *Lumbriculus variegatus* are shown for the concentration of HCB, C_s/C_{wo}, as a function of depth at different time intervals up to 96 days in Figure 3.10. A well-mixed layer is not evident at any time.

Calculations of the HCB concentrations were then made for all three organisms for longer times; results for *Lumbriculus variegatus* are shown in Figure 3.11 as a function of depth at the end of the experiment and at times of 1, 3, 5, and 10 years. As time increases, C_s/C_{wo} near the surface increases but also becomes more uniform with depth; this is due primarily to the feeding of the oligochaetes at depth, the deposition of the fecal pellets at the surface, and the resulting downward convection of a sediment layer with the velocity w(x). In addition to the convection, some physical mixing of the sediments by the organisms does occur, but this also decreases with depth. The result is that C_s/C_{wo} decreases rapidly at depths of 2 to 4 cm. A well-mixed layer slowly appears and becomes more distinct as time increases; the thickness of this layer increases with time. In the field, densities and types of organisms are not constant over periods of years but fluctuate locally in space and time, depending on the season, big events such as floods and storms, and ecological succession after big events. Because of this, the formation and maintenance of extensive and distinct well-mixed layers due to organisms probably do not occur very often.

On the basis of these and related experimental and modeling results, the following conclusions were made. For HOCs with large partition coefficients, a well-mixed layer due to non-erosion/non-deposition processes is slow to form and generally does not exist; an effective thickness of this layer is time-dependent, depends on K_p, is difficult to define, and is even more difficult to quantify. Because of this, the use of a general mass transfer coefficient along with the assumption of a well-mixed layer is not recommended.

In Figure 3.12, the sediment-water flux of HCB as a function of time is shown for all three organisms at densities of $10^4/m^2$, for *Lumbriculus variegatus* at a density of $10^3/m^2$, and for molecular diffusion alone. Mass transfer coefficients for the benthic organisms generally range from 1 to 10 cm/day, but depend on the organism, its density, and the K_p of the chemical. Such numerical values have been reported for various field studies during time periods when particle re-suspension is virtually absent (Thibodeaux & Bierman, 2003, Erickson et al., 2005, Thibodeaux, 2005).

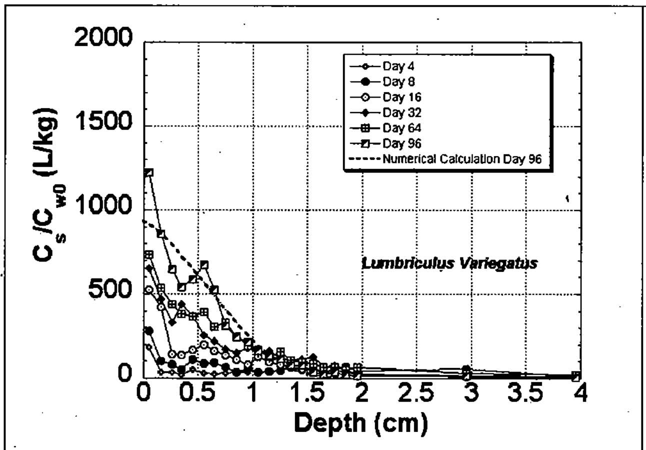


Figure 3.10. Flux of HCB in Lake Michigan sediment due to bioturbation by *Lumbriculus variegatus*, density is $10^4/m^2$. Experimental results are for times of 4, 8, 16, 32, 64, and 96 days whereas the calculated results are for 96 days. From Lick 2008.

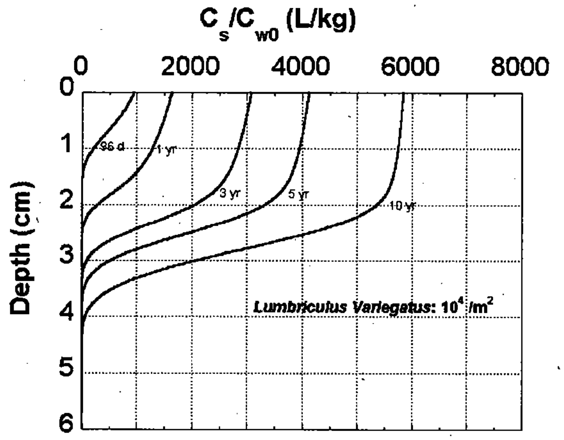


Figure 3.11. Calculated results for Cs/Cw0 as a function of depth due to bioturbation by *Lumbriculus variegatus*, density is $10^4/m^2$. From Lick 2008.

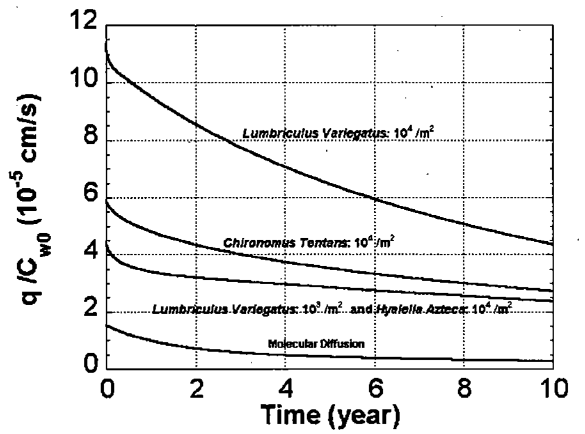


Figure 3.12. The sediment-water flux of HCB due to bioturbation as a function of time. Results are shown for three organisms at a density of $10^4/m^2$, for *Lumbriculus variegatus* at $10^3/m^2$, and for molecular diffusion. From Lick 2008.

RESPONSES TO REQUESTS FOR SPECIFIC COMMENTS

(1) Please comment on the strengths and limitations of OPP's current approach for modeling pesticide transport between the water column and benthic region which relies on the use of lumped parameters to represent multiple transport mechanisms in static ponds.

PRBEN

The parameter PRBEN is defined as the mass of chemical transported into the bottom sediment divided by the total mass of sediment introduced into the pond (chemical in bottom sediment and in overlying water). In the OPP standard pond, PRBEN is set to 0.5.

As a sorbed chemical is introduced into a pond or river, the chemical is transported with the sediment particle and desorbs at a finite rate to the surrounding water. How much chemical is transferred from the particle to the water during settling before the particle deposits on the bottom depends on the ratio of the desorption time, τ, to the settling time, $t_s =$ D(depth)/w_s(settling speed of the particle), i.e., $\tau w_s/D$. If $\tau > D/w_s$, then almost all of the chemical is transported to the bottom. For a typical settling speed of 10^{-1} cm/s and a depth of 10 m, D/w_s is 10^4 s. In other words it takes approximately 3 hours for a particle to go from water surface to the bottom of the pond at 10 m depth. For HOCs with large K_p, τ is much greater than this. In this case, PRBEN is approximately 1.0.

When K_p is relatively small and w_s is small, $\tau w_s/D$ would also be small. In this case, the chemical would equilibrate in the water column with almost all of the chemical dissolved in the water, i.e., PRBEN is approximately zero.

A simple procedure to determine intermediate values of PRBEN is as follows. Assume that the chemical desorbs in an exponential manner, i.e., $C_s = C_{so} \exp(-t/\tau)$. This would be approximately true for a relatively clean pond with little dissolved pesticide in the water. For a settling time of $t = D/w_s$, then PRBEN would equal $\exp(-D/w_s\tau)$. Other simple approximations can also be made for limiting conditions and should be investigated to see which is most useful. A more accurate determination of this quantity is given below.

Sediment-water fluxes of pesticides

The sediment-water flux of chemicals is primarily due to sediment erosion/deposition, molecular diffusion, and bioturbation. Each of these processes acts in a different way, and hence each must be described and modeled in a different way. In general, they occur more-or-less simultaneously and there are interactions among them. The use of a lumped parameter and the associated concept of a well-mixed surficial layer in the bottom sediments should be discouraged. For a better model, a one-dimensional, time-dependent model (a set of vertical boxes mainly to describe sediment-water fluxes adequately, see below) is suggested. This would be used to describe the flux processes individually, to determine PRBEN and to quantify the overall flux process, and to demonstrate the differences between different aquatic systems (ponds, rivers, large lakes, etc.) in a quantitative manner. The components of this model exist and have been verified by comparison with experiments.

(2) In the context of screening-level and refined assessments, please comment on the strengths and limitations of simulating pesticide burial by sediment in static ponds as a process that renders pesticide permanently unavailable for biological interaction (i.e., not bioavailable).

Burial is a major removal mechanism. It must be included, either explicitly or implicitly (see below). In addition, as sediments are deposited on the bottom, the sediment-water flux processes described above immediately begin to act. For highly hydrophobic chemicals, these fluxes will continue to act for many years and the bottom sediments can serve as a major and long-lasting source of chemical to the overlying water. This process must be included for these chemicals.

(3) Please comment on the strengths and limitations of models described in the White Paper with respect to modeling pesticide transport via sediment dynamics. Which processes associated with sediment-based pesticide transport (e.g., sediment enrichment, settling, re-suspension, burial, bioturbation, pore-water diffusion, scour, bank erosion) would be most important to consider in static ponds? Which processes would be most important in flowing water systems?

SEDZLJ

The treatments of sediment dynamics in the models described in the White Paper are not satisfactory. Parameters are undetermined and undeterminable. Processes are not described realistically. ECOMSED is better than the rest, but it has been superseded by SEDZLJ.

SEDZLJ is a general sediment transport model. It includes the use of erosion rate data from Sedflume as a function of depth and time, multiple sediment size classes, settling speeds as a function of particle (aggregate) size and density, a unified treatment of suspended load and bedload, and bed armoring. In recent applications, it has included bed consolidation. It is valid for all types of sediments, including the limits of cohesive and non-cohesive sediments. It has been applied to the Fox River, the Lower Duwamish Waterway, the Passaic River (sponsored by EPA and Army Corps of Engineers), and other rivers and aquatic systems. In these applications, it has generally been coupled with chemical transport models which include sediment bed dynamics, sediment-water fluxes, and the sorption and partitioning of the chemical to the sediments.

SEDZLJ is a sediment dynamics model. For transport calculations, it is coupled with a hydrodynamics model. In the above applications, it was coupled with EFDC (Environmental Fluid Dynamics Code, supported by the EPA), a model which has been used quite widely.

Processes in static ponds as compared with streams

In static ponds, sediment erosion, scour, and bank erosion would not be significant, almost by definition. Bioturbation is more-or-less significant depending on the numbers and types of organisms. Molecular diffusion is always present. Deposition of incoming sediments needs to be considered.

In streams, all of the above processes can be significant depending on local conditions including topography and flow conditions. Flow conditions can change by orders of magnitude.

SUGGESTIONS FOR IMPROVEMENTS

For hydrophobic chemicals with large partition coefficients, the present procedures and models are flawed and need improvement. During the meeting, EPA requested improvements to their present procedures that (a) could be implemented relatively easily and quickly and (b) more thorough but more complex and time-consuming procedures that could be implemented in the near future. In that spirit, our suggestions are as follows.

Short-term improvements

1. Improve the value for PRBEN as briefly described above.

2. Allow a simple description of burial. Incoming pesticide is associated with incoming sediment mass; this latter process must be retained. When this is done, allow sediment to be transported (down) out of the benthic layer (burial). In this approximation, the benthic layer is assumed to be mixed with some pre-determined thickness.

3. Better values for the sediment-water fluxes should be used. The values given in the White Paper are low by one to two orders of magnitude.

4. A relatively simple description of sediment erosion (i.e., a resuspension velocity) should be used. The values of resuspension velocity and deposition should be chosen such that the suspended sediment concentrations are reasonable (e.g., 30 mg/L).

Longer-term improvements

The problem with the present procedure, even with the above improvements, is that the model still incorporates a mixed layer at the sediment-water interface (benthic layer) with an unknown and undeterminable thickness. The choice of the thickness of this layer is somewhat arbitrary (usually somewhere between 3 and 15 cm for fresh water but possibly much deeper for estuarine and salt waters. The thickness of this layer is crucial to the long-term behavior of the solution.

1. To make the above (short-term improvement) model reasonably accurate, realistic, and defensible, the sediment-water fluxes (resuspension/deposition, molecular diffusion, and bioturbation) must be described more accurately. Each process is different and must be described differently. If this is done, a more accurate determination of the fluxes will be obtained. In addition, a very important result is that the problem of the arbitrary thickness of the benthic layer disappears; there is no benthic layer in this type of calculation.

2. A better determination of PRBEN is as follows. Simple adsorption/desorption between a sediment particle and the surrounding water with a dissolved pesticide concentration of $C_w(t)$ can be described by

$$dC_s/dt = -(C_s - K_pC_w)/\tau$$

The concentration of the total amount of chemical in the water, $C_T(t)$, at any time would be

$$C_T = C_w + \rho C_s$$

where ρ is the suspended sediment concentration. $C_T(t)$ would change due to soil and pesticide runoff and due to deposition of the suspended sediment with its sorbed pesticide. With these inputs and the above two equations, the amount of chemical in the overlying water and that deposited could be calculated. This would give an effective value for PRBEN although this parameter is no longer needed.

3. To include the above improvements (and possibly more), a one-dimensional, time-dependent model is suggested (possibly based on EXAMS or AGRO but including the above suggestions). This model should consist of boxes in the vertical with a box for the water column, with a flux to the atmosphere) and several boxes in the bottom sediment near the sediment-water interface to describe the sediment-water flux processes. A logarithmically increasing thickness of these layers with depth is proposed. This will allow a more accurate description of these processes. The mass of the run-off soil with its associated pesticide needs to be included as does a better determination of PRBEN and the associated desorption of the pesticide on the particles as they settle and deposit on the bottom.

4. The model and the parameters associated with the model need to be extended to include a variety of systems, e.g., small and large ponds, small streams, and possibly estuaries.

5. Validation. In order to make these improved models believable and defensible, the predictions of these models need to be validated by comparison of the model results with field measurements for a variety of surface waters.

The Solubility Issue.

This issue was raised by several OPP presenters but it was not a specific question directed to the Panel. One Panelist felt this issue should be a part of Question 3 because it arises related to the EXAMS and PRZM model sediment dynamics subject. This Panel member's comments are as follows.

OPP has developed a conceptual approach to handle the problem and it appears on page 57-60 of the White Paper. The conceptual model offers a solid phase consisting of a precipitate of pure pesticide in addition to a sorbed sediment phase and a water phase. Presently EXAMS and PRZM are not designed to accommodate the fate and transport of a solid precipitate. The general practice adopted by OPP is to "constrain" the predicted model EECs in water to the limit of solubility measured for the pesticide active ingredient. The solubility constraint does not appear to be a mathematical modeling procedure but a post-modeling or off-line constraint adjustment.

The AGRO Model mechanism described on page 60 of the White Paper contains a modeling approach. As described in a presentation by Dr. Mackay (Canadian Environmental Modeling Centre, Trent University) and in the White Paper it involves modeling the formation of a chemical precipitate followed by its dissolution back to the water phase over time. This description suggests a kinetic process involving the mass transport of chemical from a mass of solid material to the water. It appears conceptually correct. However, a simpler thermodynamic approach is a short-term fix that may be easily adapted to EXAMS or PRZM.

It is the opinion of one reviewer that the solubility exceedence occurs because the linear equilibrium assumption (LEA) theory, which forms the basis of sediment-to-water hydrophobic chemical partitioning, alone does not constitute a robust adsorption isotherm. For a model situation involving high chemical mass loading, m (kg), into an aquatic system containing a known water volume, V(m^3), and sediment mass, M_s(kg), it is possible for a model that uses only the sediment-to-water partition coefficients as surrogate isotherms for the estimated equilibrium freely dissolved concentration in water, C_w(mg/L), to exceed the measured chemical solubility, S_w (mg/L), in water. A brief review of the literature on the subject of contaminant sorption to soils and natural solids for evidence and data on chemical partitioning near or at the solubility limit was conducted. A well known authority on the subject presented numerous published data-sets that included PBTs and hydrophobic chemicals (Chiou, 2002). None contained data on sediment-to-water partitioning at or beyond the solubility limit. The highest concentrations used in water were 60 to 80% of solubility. There are good reasons for this low cut-off limit. First, it is a difficult laboratory procedure to prepare saturated solutions of low solubility chemicals. Second, as the limit is closely approached there is the possibility for un-dissolved crystals to be present in the aqueous phase that will yield a flawed experiment or test. So, the solubility limit is avoided, experimentally.

The data presented by Chiou (2002) and that reviewed by numerous other investigators display excellent linearity of partitioning over the ranges studied. Even at the conceptual stage Chiou (2002) presents graphic illustrations of sorption with linear shapes truncated short of the solubility. However, he does acknowledge the thermodynamic limit of solubility. He uses the measured chemical solubility to numerically investigate solute partitioning into the soil organic matter (SOM) (see Chiou (2002) page 119-120). He uses the solute solubility in water to estimate chemical solubility in SOM and presents numerical values for several PBT-like substances; see his Table 7.2 on p. 120. His point is that the thermodynamics of PBTs in soil/sediments reflects the solvent nature of the SOM; he fails to address the SOM loadings beyond the solubility limit. The thermodynamic "solvent theory" vs. "adsorption theory" for soil-to-water partitioning was a debated issue in the past. However, in the case of chemical vapors in a gas mixture adsorbing onto solid surfaces the literature contains extensive evidence that the pure component vapor pressure fixes the upper limit of the chemical concentration in the gas phase at high chemical loading on the solid phase. Apparently the gas-solid equilibrium system is easier to handle, experimentally.

In the final analysis it is proposed here that a sediment-water isotherm be constructed by invoking basic thermodynamic principles that utilizes both approaches. A disjoint isotherm with "hockey stick" (HS) shape results by combining the LEA with the measured solubility limit. The essence mathematical of the HS is as follows, for $C_W < S_W$, $C_s = K_dC_W$ and for $C_s > K_dS_W$, $C_W = S_W$. However, an additional constraint is that the PBT mass balance must be maintained. Figure S-1 illustrates the concept for p,p′ - DDT in a sediment-water system. It will be used in an example calculation to present the approach.

The DDT example uses a static pond of dimensions $A = 10,000\ m^2$, water 3m, and a sediment depth 5 cm for illustrating the use of the HS isotherm for equilibrium calculations. The water volume, V_w, is 3E7 liters. Using sediment solid density of 1.25 kg/L and volume 5E5 L M_s is 6.25E5 Kg. DDT is assumed to have a solubility, $S_w = .015$ mg/L and sediment-to-water partition, $K_D = 600$ L/Kg.

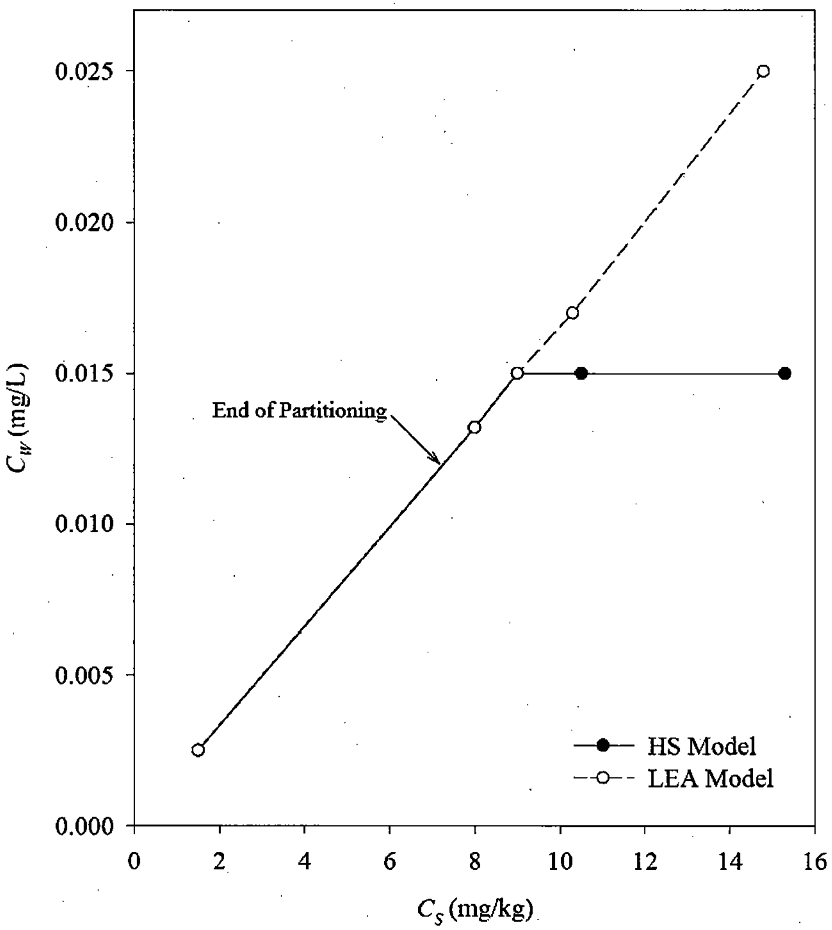
The Lavoisier conservation of mass (i.e. mass balance) is used in EXAMS to model the PBT in all compartments as well as the total system. In this simple 2-phase equilibrium system m (kg) denotes the mass of DDT placed into the static pond system. For the LEA portion of the model the Lavoisier mass balance result is $C_w = m/(V_w + M_sK_D)$ and $C_s = K_DC_W$. Calculated values of C_w and C_s appear in Table S-1 for various m loadings onto the system; these are denoted 1 through 5 and appear on Figure S-1 as well. The solubility is exceeded for the mass loadings of 7 and 10 Kg; the LEA produces C_W values of .017 and 0.025 mg/L, respectively. Both exceed the solubility. The HS-model includes the LEA provided $C_w \leq S_W$. When S_w is approached or exceeded the Lavoisier mass balance algorithm for equilibrium is: $C_s = (m - V_wS_w)/M_s$ This mass balance result is used instead of $C_s = K_dC_w$. The C_w is equal S_w and the calculated values of C_s for the 7 and 10 Kg loadings appear in Table S-1 and denoted 4′ and 5′. See the graphical result in Figure S-1 as well. The two C_s values for the HS model are larger that those of the LEA model. The additional mass of DDT forced onto the sediment solid phase may be a solid precipitate, it may also be adsorbed onto the solid inorganic surfaces of the sediment or it may become associated with the SOM "solvent". Nevertheless, it is a mute point from a modeling perspective; thermodynamic principles cannot be violated. The HS isotherm approach maintains these basic principles. It is provisional because it is unlikely such an abrupt change in the slope of the isotherm actually occurs in the vicinity of the LEA-solubility intersection; see Figure S-1. Some experimental data would be nice.

By implication the LEA model does not constitute an isotherm. It is just a partition coefficient and its use as an isotherm in equilibrium models can result in the violation of a basic thermodynamic principle. Whether used explicitly or implicitly in fate and transport modeling the assumption that a partition coefficient is an equilibrium isotherm is a slippery slope. The same applies for the vapor phase when Henry's constant for water equilibrium and for soils when the K_{oa}, octanol-air partition coefficient, is used for obtaining the soil-to-air partition coefficient.

S-1: Calculated Results – DDT Equilibrium in Sediment-Water System

Model	M(Kg)	C_s(mg/Kg)	C_w(mg/Kg)	Solubility?
LEA-1	1.0	1.5	.0025	below limit
LEA-2	6	8.9	.0148	below limit
LEA-3	6.08	9.0	.015	at solubility
LEA-4	7.0	10.3	.017	above limit
LEA-5	10	14.8	.025	above limit
HS-4′	7.0	10.5	.015	at solubility
HS-5′	10	15.3	.015	at solubility

Figure S-1. *p,p'*-DDT in sediment-water system



The following is a different perspective in response to question 3 from one of the Panel members.

Sediment Dynamics

As part of its baseline ecological risk assessment process, OPP uses environmental fate and transport computer models to generate estimated environmental concentrations (EECs) of a pesticide in surface water, pore water and sediment. The EECs are generated using the EXAMS model parameterized to represent a static farm pond receiving pesticide mass in runoff from a treated agricultural field simulated by PRZM. It is assumed by OPP that EECs generated from this scenario are conservative representations of expected pesticide concentrations not only in this farm pond but also in small first and second order streams that receive runoff-containing pesticide residues from many fields. Currently, the OPP modeling approach accounts for movement of pesticide mass between the water column and benthic region using a set of "lumped" parameters (PRBEN) and a mass transfer coefficient. These parameters are intended to implicitly account for pesticide mass transfer due to processes such as diffusion, settling, resuspension and other processes that tend to mix the sediment layer with the water column. The current OPP modeling approach does not include inflow of sediment to the water body which could lead to burial of sediment containing pesticide through deposition.

This reviewer has serious conflicts with the above response to Q-3. The basic disagreement is about the conventional view that particle re-suspension is the dominant mass release process in aquatic systems and all other processes including bioturbation are secondary. Recent studies of field data indicate otherwise.

The basic principles of disagreement are:

a. The level of scientific understanding and maturity of the bioturbation process. Bioturbation as a transport processes in sediment layers has a long history of observation and quantification of rate parameters. The field was spear-headed in the 1970s by benthic marine scientists (McCave, 1974; Berner, 1980; Boudreau, 1997; Boudreau, 2001) and has been applied to freshwater systems (Thibodeaux and Bosworth, 1990).

b. Ability to parameterize the bioturbation process. It is just as difficult a task specifying site-specific bioturbation related chemical transport parameters based on laboratory studies using a limited number of sediment samples as it is quantifying the ones for re-suspension. Both are very complex processes and possess a high degree of uncertainty. However, for generic screening or LEVEL-1 simulations for pesticides applied to a hypothetical receiving pond and other aquatic sites average rate parameters are readily available for both bioturbation and re-suspension.

c. Mixing in top sediment layers. Particle mixing in the top layers of bed-sediment has been demonstrated over the last 40 years by numerous investigators in both the lab and field context. The radionuclide data supporting particle mixing are immense in number (Thoms et al., 1995).

Since these principles underlie the entire question of sediment dynamics all three sub parts are impacted. Comments on the three parts are addressed next; they are denoted as 1), 2), and 3).

1) OPPs current approach using the lumped parameters to represent multiple transport mechanisms in static ponds.

A brief OPP review of mass transfer coefficients (MTCs) that have appeared in the literature appears on page 91 of the White Paper. A value of 8.17 E-9m/s was selected for use in EXAMS; it is the kinetic parameter in the flux equation that quantifies the movement of pesticide mass between the water column and the benthic compartment. This single value is intended to represent all means of pesticide exchange that includes exchange through the aqueous phase as well as mixing of sediments between the two compartments. It is noted on p. 84 of the White Paper that the MTC of the standard pond relies upon variables specific to the environment rather than the pesticide being modeled.

In the White Paper review it was noted that there was wide variability in the range of estimates and that the value chosen for the OPP standard pond is within this range. It was further noted that the effect of change on the estimated EECs is uncertain. On this latter point for the chemodynamics modeling of 2,3,7,8-TCDD in a lake the estimated EECs were highly dependent on the numerical values of the MTCs sediment (Valsaraj, et. al. 1997). Concentration in the water column varied from 0.0023 to 0.51 mg/L assuming molecular diffusion and bioturbation respectively as the operative transport mechanism in the bed. This is a factor of 200. The effect of the magnitude of the MTCs on model predictions of EECs is also documented in a SETAC study (Cowen, et. al., 1995). It presents the results of a fate and transport modeling study comparing various computer models. A key finding was that the most important differences in model predictions of concentrations arose because the modelers did not use the same values of the MTCs; large discrepancies resulted for chemicals with extreme physical-chemical properties.

The strength of the lumped parameter approach is the form of the flux equation; see Eqn. 4.3, p. 85 of the White Paper. It is most convenient and appropriate to use the pesticide concentration difference between the freely dissolved aqueous phase pore-water in the bed and the overhead water column. The MTC, $K_{TRANSFER}$(m/s), as defined is appropriate for accommodating all the diffusive-type transport mechanisms that include the in-bed solute molecular diffusion, Brownian diffusion of aquasols, bio-diffusion of particles by macrofauna, and the water-side boundary layer "film-diffusion". It is inappropriate for the particle setting and re-suspension driven chemical transport processes. However, it is appropriate for the particle mixing processes of bioturbation within the bed which results in the turnover and circulation of bed particles and pore water. These bio-diffusion coefficients have been used for decades in modeling marine system chemodynamics (Boudreau, 1997.). As defined the bioturbation bio-diffusion coefficient does not account for the biotic ejection and subsequent setting of fine particles with the water column.

It is recommended that appropriate particle re-suspension and deposition driven chemical flux expressions be adopted and used in conjunction with Eqn. 4.2, p. 85 of the White Paper. OPP is correct in assuming that the MTC is dependent upon variables specific to the environment. By this it is meant that $K_{TRANSFER}$ is a function of type of water body, flow hydraulics, temperature, biota abundance, bed material composition, etc. However, the mass transfer coefficient of pesticide between the water compartment and the benthic compartment of the standard pond is a function of physiochemical properties of the pesticide being modeled. See the comments in the next section that address the important pesticide transport processes in the static pond.

The PRBEN is also characterized as a lumped sediment process. It is defined as a fraction between 0 and 1 that routes the sediment-borne chemical mass input for the EXAMS model. When PRBEN is zero, all sediment-borne material enters the water column. When it equals 1 all is routed to the benthic zone. The approach taken by OPP appears on p. 90 of the White Paper. A default value of PRBEN equal 0.5 is presented. It does not reflect the thermodynamic partitioning preference PBTs have for adsorbing to solid surfaces in the aquatic system. In the short term an alternative approach is offered below.

The sediment-borne mass of the PBT that departs the watershed is presumably a known mass quantity. The mass of sediment in the pond is M_s(kg) and its water volume is V_w(L). The chemical mass ratio is M_sC_s/V_wC_w which is equal to $(M_g/V_w)K_d$ where K_d(Liter/kg) is the sed-to-water partition coefficient. Using the definition of PRBEN fraction the estimating equation is: PRBEN = $(M_sK_d/V_w)/(1 + M_sK_d/V_w)$. This estimating algorithm anticipates the general routing patterns expected based on the hydrophobic properties of the individual PBTs. This approach may need to be revisited depending upon how the runoff slurry from PRZM is handled as an input for pesticide burial in a future screening-level model.

2) Comments on simulating pesticide burial by sediments in static ponds as a process that renders pesticide permanently unavailable for biological interaction.

As presently structured the volume of water and the mass of soil leaving the PRZM model of the treated field are not accounted for in the standard pond scenario. See p. 77 in the White Paper. However, the PBT mass mobilized from the treated field does enter the EXAM modeled pond. This appears to be a very conservative approach that will yield large EECs. Coupled with spray drift entering the pond, the total mass of PBT may exceed the chemical sorbtive "buffering" capacity of the standard pond water plus solids system. This approach may be a factor responsible for the EXAM model producing concentrations in water that exceed its solubility in water. Such exceedances are depicted in Fig. 3.10 p. 59 of the White Paper. The solubility exceedance issue is addressed separately. It was not specified as an Agency question *per se* and is therefore included as a separate topic in the Panel response to question 3. It is presented here in the context of a limitation. Omitting burial is an unrealistic assumption. By allowing burial in the standard pond model the issue of EXAMS producing EECs that exceed the solubility may dissolve itself.

Simulating pesticide burial in the context of screening-level and refined assessments in static ponds or alternative aquatic systems does not render pesticides permanently unavailable in the absolute sense of the meaning of permanent. However, clean layers of soil, as used in the in situ capping process remediation for historically contaminated sediments, do provide significant chemodynamics transport resistances and may in some cases provide excellent protection of aquatic and sediment dwellings organisms. Very thin layers, 1 to 8mm, were found to reduce the flux of benzoic acid 81 to 96% (Talbert et.al, 2001). Chemical flux reductions of 99.99% have been predicted for capping layers 30 cm thickness (Thibodeaux, 2002). Long-time buried deposits of PCB, metals, pesticides etc in the net depositional zones of water bodies including streams is evidence of the 50 to 100 year persistence of these chemicals. Clean sediments now cover many of these deposits and health ecosystems have returned to the surface waters and bed surface layers. The point is that chemical burial at depth has resulted in their persistence but has also provided on-going low levels of contaminant flux to aquatic species and effectively disconnected the pathway for ecological risk. The releases are low so as to render the buried hazardous material effectively not bio-available. In situ capping is an engineered and managed remediation technology (NRC 1997) and pesticide burial in static ponds under the right circumstances of deposition may be similarly managed. The management of caps involves periodic surveys to efficiently assess and re-capping if necessary. In situ capping is viewed as enhanced natural recovery. The so-called natural recovery remediation technology (NRC, 1997) is an alternative. It depends on nature providing fresh particles from the watershed to do the capping. The EPA and state agencies have been approving both technologies in recent years.

The short answer is that burial may never be permanent at some sites. But, it is a manageable technology for ponds, lakes and low flow streams. Properly designed, it can render the pesticides mass effectively "not bio-available". For selected pesticides with low rates of anaerobic degradation and destruction, in-bed sediment burial assessment at both the screening-level and refined levels should always be simulated.

3) Comments on modeling pesticides transport via sediment dynamics and ranking processes associated with sediment-based pesticides transport.

This subject has received much study in the last two decades as federal and state agencies addressed the bed sediment contamination problem across the Nation. The EPA funded South and Southwest Hazardous Substance Research Center at LSU focused most of its efforts on this subject during its 25-year existence. Over the time-period three studies were published which summarize numerous research results and rank the chemodynamics processes associated with sediment-based transport (Reible et.al., 1991; Thibodeaux, 2005; Thibodeaux and Mackay, 2007). A listing of estimated MTCs for PCB and benzene taken from the 2007 document appears in Table 3.1. It contains numerical values representing six basic processes and relevant subsets for a total of eleven. This table will be used as a basis for ranking and discussing the most important MTCs for PBTs in static ponds and flowing streams.

Static ponds. OPP standard pond scenario is a set of defined parameters intended to represent rural agricultural ponds; see p. 78-79 of White Paper. The MTC used in EXAMS for the static pond scenario is 8.17 x 10^{-10} m/s or 0.071 cm/d; see Table 4.7, p. 85 of White Paper. This value represents molecular diffusion in a 5 cm layer; see line four in Table 3.1 for the numerical values for PCBs and benzene. It is the opinion of this reviewer that the static pond value used in EXAMS is much too conservative of an assumption; the process is typically much faster. Agricultural farm ponds usually develop a rich abundance of macrofauna that dwell directly on and within the upper layers of the sediment. These organisms are not unlike those observed in marine, estuarine, riverine and lacustrine systems. This process has long been recognized as a facilitator of contaminant transport in bed sediment (Bosworth and Thibodeaux, 1990). Experimental data on bioturbation driven mass transport in laboratory microcosms are likely best to represent the environmental conditions present in static ponds. Laboratory measured MTCs representing PBTs ranged from 1.0 to 10 cm/d (Thibodeaux et.al, 2001).

Based on the above, the OPP constant value of 0.071 cm/d is not conservative for static ponds. A value 100 times larger is likely more appropriate. Particle re-suspension from bed to water column driven by wind generated water currents in the static pond is likely an important transport process as well. Table 3.1 contains particle re-suspension “equivalent’ MTCs, they range from 400 to 8600 cm/d for PCBs. These are typical values for flowing streams and likely overestimate the magnitudes of wind-driven static pond MTCs. Re-suspension subsides when the water currents subside so that the large MTCs represent a short-term pulse event superimposed on the normal long-term diffusive processes.

Flowing streams and other water bodies. This section considers some of the broad aspects of the sediment bed MTCs representative of various types of waterbodies receiving pesticide runoff from treated fields. Evidence has been accumulating to show that an overall MTC must be used to account for the simultaneous diffusive processes. The well known two-resistance theory is the operative principle that yields the overall MTC. It accounts for chemical partitioning between sediment solid phase and water (Thibodeaux and Bierman, 2003). See Ch. 5, Environmental Chemodynamics (Thibodeaux, 1996) for related reading on the subject.

When using the two-resistance theory the water-side MTC also enters as a significant transport parameter in the case of bioturbation driven chemical transport. See the range of values in line two of Table 3-1. It is denoted as B in cm/day and is strongly flow dependent. Limited field and lab data indicate 5.5-8.5 cm/day for lakes & stratified non-flowing rivers, 12-25 impoundments on rivers, 19-36 for streams and 28-52 cm/day for high-end streams (Thibodeaux, 2005, Erickson et al., 2005).

A conservative value of B for static ponds is 8.5 cm/day. However, this is for very strongly hydrophobic chemicals. For chemicals with known Kds the appropriate form of the two-resistance theory for estimations is: Kw= 8.5 (Kd x density)/[Kd x density + 8.5 x h/ Db], where Kw (cm/day) is the overall MTC accounting for the bed and the "film" on the water side, Kd = Koc x foc in L/kg, density = bed solid density or approx. 2.5 kg/L x (1-bed porosity), h is the average bioturbated bed depth, 10 cm. for marine but 5 cm for freshwater ponds is likely very reasonable, Db is bio-diffusion coefficient and 0.03 cm^2/day is a field-derived conservative value. Typically values have been found to range from 0.01 to 0.04 cm^2/day (Erickson et.al, 2003). If a healthy benthic community macrofauna drive the bioturbation of particles in the bed and this bio-diffusion sediment dynamic process dominates all other "diffusive" transport processes. During storm events particle re-suspension/re-deposition, a non-diffusive process, dominates but when this process subsides bio-diffusion resumes. For a "theoretical" pond with no hydraulic thru-flow to re-suspend/re-deposit sediment the bioturbation process likely accounts for nearly 100% of transport.

Closure. Particle re-suspension and settling combined with bioturbation are the most important chemodynamic transport processes at the sediment-water interface in all cases. Both need to be factored into both the screening-level and refined assessment models. The former is storm event driven and of short duration. However, the equivalent MTC is very large. The latter is active between the storm events. A study of three river models comparing PCBs re-suspension and solubilization processes from bed sediment to the water column was performed (Thibodeaux, 2005). Eight simulations were evaluated and the results suggest that both processes contribute significantly to the sediment-bed to water exchange process. The contribution of the particle fraction re-suspension process ranged 0 to 99% with a median value of 25%, the soluble fraction (bio-turbation driven) ranged from 1 to 100% with a median value of 75%. It appears that molecular and Brownian diffusion are less important. The process of sediment enrichment, scour, and bank erosion are less well studied and therefore difficult to quantify.

Table 3-1: Estimate MTCs (cm/d) at Sediment-Water Interface

Process	Total PCBs	Benzene
1) Particle re-suspension	400-8600	0.26-5.6
2) Benthic boundary layer	13.0-320	18.0-450
3) Molecular diffusion (solutes)		
Thin layer (1 mm)[2]	3.5-4.1	5.7-6.7
Bio-available layer (5 cm)	0.038-0.071	0.062-0.12
In-situ cap (20 cm)	0.0059-0.0094	0.015-0.0097
4) Brownian (colloid) diffusion (5 cm)	0.0049-0.0092	$3.2E^{-6}$-$6.0E^{-6}$
5) Pore-water advection		
solutes	0.023-0.26	0.023-0.26
colloids	0.0088-0.010	$5.8E^{-6}$-$6.5E^{-5}$
6) Bio-diffusion (5 cm)		
particles	4.1-127	0.0027-0.083
pore water solutes	0.0054-0.17	$3.5E^{-6}$-$1.1E^{-4}$
pore water colloids	0.0021-0.064	$1.4E^{-6}$-$4.2E^{-5}$

(Thibodeaux and Mackay, 2007)

Agency Charge

4) Aquatic Bioaccumulation Methods.

Traditionally, OPP's assessment of pesticide bioaccumulation potential in aquatic organisms has relied extensively on the use of bioconcentration factors (BCFs). BCFs consider direct chemical uptake through aqueous exposure routes only. For organic chemicals with PBT characteristics, bioaccumulation from non-aqueous exposure routes (e.g., diet and sediment) can be substantial. For these chemicals, risk assessments in other Agency programs (e.g., Office of Water ambient water quality criteria, Superfund site risk assessments, Office of Research and Development ecological risk assessments) have used a combination of laboratory-, field- and model-based methods for incorporating bioaccumulation via multiple exposure routes. In the pesticides program, a similar integrative approach is being considered for assessing the bioaccumulation potential of organic pesticides with PBT characteristics. This approach considers the type and quantity of data typically available for pesticide ecological risk assessments, relative strengths and limitations of each bioaccumulation assessment method, and uncertainty associated with bioaccumulation predictions using each method.

- Please comment on the need to consider alternatives to the BCF method for assessing the bioaccumulation potential of organic pesticides with PBT characteristics.

Please comment on the applicability of the Agency's approach of using multiple methods (including laboratory-, field- and model-based methods) for assessing bioaccumulation potential of organic pesticides as illustrated in the White Paper.

Panel Response

Alternatives to BCF are required to assess bioaccumulation of PBT organic pesticides. These alternatives need to take into account accumulation from the diet, trophic transfer (or biomagnification), and when and where it occurs in aquatic food webs. Bioaccumulation modeling may be a good first approximation for some compounds and under certain conditions. However, serious problems arise when the focal compound is metabolized or non equilibrium conditions prevail.

The ability to predict uptake and elimination rates for some taxa may not be possible. This is especially true for rates of metabolism, which can be quite variable among taxonomically similar species. There is no QSAR for this variability.

Under equilibrium conditions, the bioaccumulation of non-metabolized compounds may be somewhat predictable. Unfortunately, equilibrium between various environmental compartments (water, sediment, tissue) rarely occurs in dynamic environments such as streams and estuaries. Equilibrium may be relatively common in agricultural ponds; however, we are interested in protecting against adverse effects from PBT compounds in a variety of ecosystems.

Further, there is a need to develop approaches that provide a more comprehensive view of the entire aquatic food web (especially species with particular concerns like amphibians and ones likely to have the highest BAFs like birds and mammals that consume fish or other aquatic organisms). The White Paper goes a long way in recognizing many of these issues but the Panel felt it is deficient in addressing the issue of birds and mammals to the same degree as the lower aquatic food web. Enhancing consideration of birds and mammals is a challenging issue but perhaps can be addressed using a tiered or "as required" approach that will be described below.

The approaches are:

1. Lab studies to measure BCFs in various species
2. Lab studies that try to address bioaccumulation (uptake from water and diet, microcosms)
3. Controlled field studies that use mesocosms –high cost, don't address the full extent of foodwebs
4. Open field studies –which aren't a great option for new chemicals
5. Bioaccumulation models for food webs of select parts of foodwebs.

A modeling approach is desirable for PBT pesticides because of the low demand on time and resources involved in their use and their potential to deal with issues in a fairly holistic manner. The examples in the White Paper and some of the presentations shown to the Panel demonstrated that there are some good models currently available that could either be used "as is" or following some further revisions.

Taking a model-based approach requires that they be used wisely. This includes:
- having a sound knowledge of their limitations,
- understanding the uncertainties in model structure associated with both inputs and outputs
- not using them for chemicals or situations that they were not designed for.

The Panel suggests using an approach that has modeling at its core where lab or field data is collected with a mind to either:

- verify that the assumptions made in the model (or models) are reasonable, OR
- provide sound information to adjust model parameters appropriately for that chemical. (The evaluation of Pesticide #4 in the White Paper provides an example of this).

Specific Issues:

Log Kow

The Arnot/Gobas model suggests that significant accumulation from the diet by fish and other organisms with gills starts at about log Kow 4.5. There is evidence from field studies and modeling work (e.g., Kelly and Gobas 2001) that bioaccumulation from the diet can occur at lower log Kow's in air-breathing organisms (β-HCH being one such example). These values or ones close to them can be used to direct the need to assess dietary bioaccumulation.

- Studies of dietary assimilation efficiency in fish, birds and mammals show that this parameter is largely independent of log Kow up to about log Kow 7.5-7.8, after which alpha starts to decline.
- There are considerable data limitations (uncertainties) in setting some model parameter values for very hydrophobic chemicals in bioaccumulation models. One such example is gill uptake efficiency parameter.
- Getting reliable Kow values remains a problem, especially for very hydrophobic chemicals. When faced with a range of values (of an order of magnitude or more) from the literature, simply choosing the middle value probably is not the best path forward. The value derived using the best lab methods should be the preferred one. If no values are deemed reliable, then the value should be measured using the slow-stir method.
- The statement that Kow can be used to determine which route of uptake is predominant (water versus dietary) is based on an equilibrium between environmental compartments (water and sediment). Equilibrium is likely rare in the environment, therefore dietary uptake could be very important for low Kow compounds where water concentrations are below predicted equilibrium values.
- Uptake and elimination kinetics that are determined with Kow can be inaccurate. Hydrophobicity is not related to the rate of uptake. The use of Kow for estimating the rate of elimination is important only for non-metabolized compounds.

Bioconcentration Factors (BCFs)

BCFs don't work for hydrophobic organics on their own, but they can still provide useful information. Water to organism partitioning is an important process in the bioaccumulation of hydrophobic chemicals, especially for smaller gill breathing organisms with a high surface to volume ratio. Dietary uptake becomes a progressively more important process for organisms at higher trophic levels that also tend to be larger. Thus, dietary uptake needs to be part of any bioaccumulation assessment. For non steady-state and equilibrium conditions, the uptake of compounds via all sources is generally additive.

Benefits of BCF type studies include:

- a measure of BCF or chemical partitioning (still important at base of aquatic foodwebs)
- water to plankton partitioning is the largest single-step change in concentration in aquatic food web
- can provide information on bioavailability, uptake/elimination kinetics, and estimate time to steady-state (SS)
- can be used to estimate kinetics for other sizes using allometry
- can be used to compare against model estimates
- utility increased if growth rate and lipid content measured,
- provide some indication of whether chemical may be prone to biotransformation,
- opportunity to measure metabolites.

Caveats/limitations

- Was water solubility exceeded?
- Were co-solvents used? What effect do they have? A co-solvent applied with the pesticide will likely be very important for assessing bioavailability and bioaccumulation after application
- Was there sufficient time to reach steady-state? (If no then BCFs can be derived from k1/k2 ratio),
- One Panelist suggested that bioturbation be considered and quantified. This process will certainly affect the bioavailability of sediment associated PBTs and also increase bioaccumulation. This issue is cross-cutting for a number of charges.

Lab-based dietary uptake or trophic transfer studies (fish and inverts)

The BCF test is acceptable for bioaccumulation assessment; however, for PBTs the EPA should require a dietary based bioaccumulation test and a biomagnification test. The biomagnification test would cover two or more trophic levels. The existing dietary test (Aquatic Food Chain Transfer, OPPTS 850.1850) is not a biomagnification test because it's only one trophic level. One option is to expand that dietary test by feeding the small test fish that have consumed dosed pellets to a piscivore, such as rainbow trout.

Food web model revisions (algae-fish)

The Arnot/Gobas model is a good start.

- A generic foodweb definition approach may need to be revised for dynamic models, especially for species that live more than one year. It may be necessary to add age classes for larger/longer lived species.

- In defining diet of organisms, the % benthos is a sensitive parameter when dealing with hydrophobic contaminants and the Panel sensed there is considerable uncertainty of what the right value should be.

- Several recent studies show dramatic effects of water temperature on POPs kinetics in fish (e.g., Buckman et al., 2007). Temperature is also a significant driver of growth rates of fish and other poikilotherms (virtually zero or negative in winter). These would suggest that realistic water temperature profiles be incorporated into dynamic models.

- In very productive systems like agricultural ponds, "Biodilution" of contaminants may be a factor where algal production of lipid or organic carbon may be sufficient to reduce water concentrations or alter overall organic carbon pool size.

- Algae produce large quantities of dissolved organic carbon (DOC) which will have a large impact on bioavailability and bioaccumulation. Work with copper toxicity in microcosms showed that massive doses of copper in these systems were rendered non-toxic due to tolerant algae species releasing DOC and reducing the bioavailability (Meador et al., 1993). This is also important for seasonal variability in primary production. In the winter, algal production declines, DOC is reduced, and complexed compounds can be released to a more bioavailable form (Meador et al., 1998).

- Additional species of concern. Several Panelists suggested that organisms other than fish should be considered, including amphibians.

Birds and Mammals

The present approach outlined in the White Paper involves simple point estimates of daily intake of chemical by a list of birds and mammals based on concentrations derived from the foodweb model output. These dietary exposure levels are then compared to available toxicity endpoints like NOAECs and LOAECs by calculating RQs. This approach is built on an underlying assumption that steady-state is achieved and there is currently no evaluation to verify this assumption for either acute or chronic endpoints. Generally time to steady state (TSS) increases with the body size of organisms.

The elegant examples of dynamic models for "lower food web" in the White Paper and presentations show that for PBT pesticides the organisms (such as a 1 kg fish) are often chasing a steady-state condition. This causes potential problems for using the current approach for deriving RQs for birds and mammals.

The current RQ approach for birds and wildlife is OK as a Tier I assessment and may be sufficient if RQ values for birds or wildlife are either far below the LOC of 1.0 or far higher. The gray zone where RQs are hovering around the LOC is where further effort is needed.

This effort has to involve dynamic modeling for specific species or receptors of concern. Developing these models and integrating them with exposure data is a significant challenge but there are a number of existing models that can at least be used as a starting point. Examples include:

- Birds and eggs (Norstrom et al., 2007)
- Tree swallow nestlings (Nichols et al., 1995)
- Terrestrial mammals (Armitage and Gobas 2007)

- Marine mammals (Hickie et al., 1999)

These models are all similar in having components that describe the biology, bioenergetics, and then kinetics of the chemical. Once developed, they are relatively easy to adapt to other "similar" species. A great advantage of dynamic models is that they provide estimates of tissue concentrations that dovetail nicely with Critical Body Residue approach to toxicity for both acute and chronic toxicity.

Aquatic/Terrestrial foodweb overlap needs to be considered. Quite a few species obtain prey from both, great example being mink which has been used in toxicology studies for many POPs including PCBs. Mink are opportunistic predators and will eat a tremendous range of prey including fish, crayfish, earthworms, frogs, small birds.

Biotransformation Issues.

There is currently no reliable way to estimate *in vivo* biotransformation rates for chemicals. Structure-Activity Relationships (SARs) analyses can provide some general guidance as to whether structures are likely to be metabolized, but not rates. This is a challenging issue that can dramatically affect risk quotients (RQs).

Examination of the POPs such as PCBs show that lower organisms have limited capacity to metabolize most congeners, while higher vertebrates species have quite variable capabilities (e.g., arctic cod vs. ringed seals vs. beluga vs. polar bears; Muir et al., 1988; Muir et al., 1990). The Panel makes this point to illustrate that without tools to predict Km values for species of interest, the EPA is advised to assume there is no metabolism unless there is contrary experimental data. However, it was pointed out by one Panelist that this approach is extremely conservative and has in some cases led to possible misinterpretation when applied to mammals.

John Arnot's PhD thesis (2008) includes a chapter exploring a SAR approach to estimating Km values for small fish using data for several hundreds organic chemicals. It is a step forward but there is still a considerable amount of unexplained variability.

A final point here is that existing bioaccumulation models for hydrophobic organics were developed for neutral organics. As such they should not be used for polar or ionic compounds, including metabolites.

LRTAP and Bioaccumulation

Concentrations of PBT chemicals in ecosystems far removed from areas of use will probably display either a dampened pulse time course or may not be detectable. The pulse-effect could well diminish with distance. This would suggest that a steady-state bioaccumulation modeling approach might be acceptable for a far-field assessment.

Solubility, Bioavailability, Bioaccumulation

The White Paper addresses the issue of water concentrations that exceed solubility in a positive way and recognizes there may be a difference between laboratory and field in what is defined as "dissolved." The working definition of "dissolved" in the field is method-based and may or may not be synonymous with "bioavailable". This problem applies to hydrophobic organics in general.

Agency Charge

5) Terrestrial Bioaccumulation in Terrestrial Food Webs.

The Agency currently assesses risks to terrestrial vertebrates that result from direct deposition of pesticides on food items that inhabit the treatment area. In general, this assessment is considered to provide relatively "high end" estimates of acute exposure through the ingestion pathway. At this time, however, the Agency does not routinely assess pesticide bioaccumulation in terrestrial food webs in non-target sites, in part, because the methods and tools for assessing bioaccumulation in terrestrial food webs are not as developed compared to those for aquatic food webs.

- Please comment on factors (e.g., physico-chemical properties) the Agency can consider to identify when bioaccumulation potential in terrestrial food webs may be important to consider in its pesticide ecological risk assessments?

Please comment on the current state of the science underlying existing terrestrial food web bioaccumulation models and their relative strengths and limitations.

Panel Response

While methods and tools for assessing bioaccumulation are not as developed in terrestrial as those in aquatic ecosystems, this is principally because of lack of effort to date, not the fundamental difficulty of doing it. The variety of potential exposure routes and the heterogeneous nature of terrestrial ecosystems make bioaccumulation potential difficult to assess in ecosystems as a whole. However, it is not any more difficult in practice in a defined scenario than in aquatic systems. The challenge is to choose representative real world exposures via air, water, soil, and vegetation and link these to appropriate food webs. Terrestrial risk assessment is not done in as much detail as in aquatic ecosystems. The Panel recommended that local terrestrial models be developed to the same level of detail as local aquatic models are at present. The emphasis in this Question is on PBT, but terrestrial risk assessment is not currently adequate for any chemical when compared to the state of the art for aquatic ecosystems.

It is not clear whether bioaccumulation potential in terrestrial animals with aquatic based food webs is being appropriately considered, especially if there is another trophic link in the terrestrial part of the food web, e.g., a raptor eating a swallow which is feeding on emergent insects. Too often the air-water interface is an impassable barrier in conceptualization of risk assessment.

- ***Please comment on factors (e.g., physico-chemical properties) the Agency can consider to identify when bioaccumulation potential in terrestrial food webs may be important to consider in its pesticide ecological risk assessments?***

The answer to this question depends to a considerable extent on spatial scales (i.e., field, local, regional, global), the characteristics of the ecosystem under consideration, especially whether the food web is soil or vegetation based, and the route of delivery of the pesticide (directly to soil vs. air-to-vegetation partitioning). For example, Koa is very important for describing air to plant and air to soil partitioning but is not as important if the pesticide was applied directly to the soil. Nevertheless there was general agreement that Kow and Koa are the most important parameters in attempts to assess bioaccumulation potential in terrestrial food webs. There was no discussion about the relevance of Koc, possibly because Kow may be able to substitute for it in most cases. In long-range transport scenarios, Henry's Law constant (air-water partitioning), water solubility, vapor pressure and measures of persistence (e.g., hydroxyl radical scavenging rate) also assume importance.

Kow has been related to plant root uptake and Koa to air leaf transfer in plant uptake models. Both parameters are indirect measures of the actual process so direct measurements would be preferable but are rarely available. For root uptake, measured BCF and transpiration stream concentration factors (TSCF) are available for some compounds (McKone et al., 2007; Dettenmaier et al., 2008).

In general, organic chemicals can directly contact above ground plant tissues through vapor and particle deposition or below ground tissues by way of the roots. Atmospheric deposition pathways to above ground plant components are likely to be more important for hydrophobic compounds ($\log Kow > 3.5$) while the root sorption and uptake pathway is generally more important for less hydrophobic compounds ($\log Kow < 3.5$). If the edible portion of the plant is below ground (e.g. carrots, potatoes, sugar beets) then diffusion of the contaminant from the soil vapor or solution is likely the dominant mechanism for uptake of these compounds. However, in this case, very hydrophobic compounds ($\log Kow > 5$) may be of less concern due to their strong sorption to soil organic matter, low soil pore water concentrations, and slow diffusion into the plant in comparison to the plant growth rate

In addition to food chain exposures, it may also be important to consider atmospheric fate for chemicals with PB and LRT characteristics. Although inhalation exposures may be exceedingly low, the chemical mass in the air is likely to be an important transport/mixing process leading to the accumulation in non-target areas over long time horizons. It is important that the transport processes in the individual media not be de-coupled because the feedback processes linking the major environmental compartments (i.e., sediment-water-air-soil-biota-indoor-outdoor) over very long timeframes appear to be important for PB compounds. Likewise, the kinetic constraints of mass transport for these chemicals are also important because for some of the biotic compartments, the time to steady-state may exceed the lifetime of the organism or plant. Moreover, the kinetics of removal from individual compartments in combination with environmental partitioning control the overall persistence of the chemical in the system.

In short, although Koa, Kow and degradation/metabolism rates are good indicators of terrestrial accumulation, it is important to consider these physical-chemical properties in the context of a fully coupled multimedia mass balance model early in the process.

As part of a tier 1 assessment, basic physical-chemical properties can be used in screening fate (and exposure) tools such as the level III mass balance models of Mackay (www.trentu.ca/academic/aminss/envmodel/), McKone (http://eetd.lbl.gov/ie/ERA/caltox/index.html) and Van deMeent (http://www.rivm.nl/bibliotheek/rapporten/719101029.html). These models are relatively easy to parameterize and use and can inform on the applicability of more sophisticated models (and the interpretation of PB and LRT data). At a minimum, these unit world type models can provide insight into the approximate distribution of the chemicals in the environment and a first approximation of how much of the mass that is applied in a given application scenario will move away from the site of application (i.e., the contribution to the global cycle) and where it likely to accumulate.

These relatively simple models also provide the opportunity to assess important factors or modelling parameters. Understanding the "why" of the predictions is as important at this stage of the assessment as understanding the "what". Sensitivity analysis is an important tool that should be used at the early stages of the assessment and these models are amenable to a range of different sensitivity analysis approaches.

Guessing on persistence in organisms has proven to be difficult for some current use chemicals. Non lipid-partitioning mechanisms of biomagnification may be more the rule than the exception. One Panellist suggested that perhaps the definition of persistent and bioaccumulative should be redefined to account for non lipid-partitioning mechanisms. Tissue distribution, rates of metabolism and excretion, and formation of persistent metabolites with different properties from the parent compound are not adequately described by current conceptual and mathematical models which are based on neutral, hydrophobic organohalogen compounds. In addition to sequestering in lipid pools, PB compounds have shown specific binding to liver proteins (highly halogenated, high log Kow –octachlorodibenzo-p-dioxin (OCDD), binding to transport proteins in blood (pentachlorophenol, hydroxyl - polychlorinated byphenyl (PCB), caught in enterohepatic circulation (mimicking bile acids? - Perfluorooctanesulfonic acid (PFOS), and formation of persistent metabolites not detected in standard analytical protocols (such as methysulfone-PCBs). Most of these mechanisms were not suspected and discovered accidentally. It pays to think outside the box as much as possible when dealing with new chemical classes.

Chirality (optical activity) is an important property in the biological activity (and therefore toxicity) of chemicals as well as their susceptibility to biotransformation. Chiral compounds have two enantiomeric structures, which form with equal probability in ‘bucket’ chemical synthesis. This property was not discussed by the Panel, but there are many examples in the scientific literature showing it to be extremely important in the bioaccumulation of a number of organohalogen compounds, particularly α-HCH and various chlordane components and metabolites.

Even for chemicals which fit the hydrophobic/lipophilic model of distribution and bioaccumulation, assumptions and relationships derived for aquatic organisms and food webs cannot be directly applied to birds, mammals, reptiles and amphibians. As an example consider the bell-shaped dependence of uptake and clearance of PB chemicals in fish on log Kow, derived from Fisk et al. (ET&C 1998, 17:951-961; shown in part by Dr. Cohen in his presentation on behalf of AMVAC Chemical). Assimilation efficiency from the diet and clearance half-life rise and then decrease above log Kow 7, leading to significantly lower bioaccumulation potential of high log Kow compounds. By contrast, Drouillard and Norstrom (2000) showed that assimilation efficiency of PCB congeners in birds (ring doves) was barely log Kow dependent (0.86-0.97, log Kow 5-7.8). Clearance rate of PCB congeners in another bird, the American kestrel, fell off exponentially ca. a factor 10 between log Kow 5.7-7.8 (Drouillard et al., 2001). The 120-day uptake BMFs in kestrels increased linearly with log Kow 5.7-7.6, and appeared to begin levelling out thereafter. This dependency was true for both the non-metabolized and metabolized congeners, which fit on separate regression lines.

Field BMFs of non- or slowly-metabolized PCBs and other organohalogen compounds in herring gulls, probably close to steady-state with their fish diet, confirmed that BMFs increased with increasing log Kow 5.5-7.6, although it was more like a factor 2 than 10 (Braune and Norstrom 1989). Gobas et al. (2003) also found that biomagnification factors of very hydrophobic substances (log Kow > 7) in terrestrial biota did not drop off with increasing Kow. The dissimilarity in the log Kow dependence of clearance rate, BMF and assimilation efficiency in birds and fish is probably due to two factors: less efficient loss of lower log Kow compounds in air-breathers than in water-breathers, and higher temperatures and metabolic rate in homeotherms than poikilotherms increasing the rate of transport of high log Kow compounds among compartments within the animal. It can be concluded that hydrophobicity as represented by log Kow has some effect on clearance rates in birds and mammals, especially for poorly metabolized chemicals, but the effect is not as strong as in fish.

Gobas et al. (2003) concluded that chemicals with a log Koa > 5 can biomagnify in terrestrial food chains if log Kow > 2 and the rate of chemical transformation is low. However, further proof is needed before accepting these limits without reservations. The relationship was validated in a plant-mammal-mammal food chain. The higher log Kow (mostly in the 5-7 range) PB chemicals used to define the upper end of the BMF/log Kow regression were highly halogenated, which tends to protect them from biotransformation. Chemicals with log Kow < 4 have fewer halogens, or are not halogenated and therefore tend to metabolize faster in birds and mammals. Three of the chemicals (tetra-, penta- and hexachlorobenzene) defining the low end of the regression are known to be metabolized in mammals, birds and even fish. It is therefore most likely that metabolism in addition to respiratory losses contributed to the BMF/log Kow relationship.

Similar cautions apply to the Armitage and Gobas (2007) model for bioaccumulation of PB compounds in the soil-earthworm-shrew food chain. In this case, the maximum modeled BMFs are concluded to be 6-7, which is very low for non-metabolized compounds in a mammal, suggesting that metabolism is occurring in addition to possible loss through respiration. It is risky to infer clearance mechanisms from models because overestimates of one route can compensate for underestimates in another. Direct experimental verification of the importance of respiratory loss of low log Koa chemicals in air-breathing animals is needed.

A log Kow limit of 4 for BMF > 1 is well-supported for water-dwelling and -breathing animals where the mechanism of excretion via gills is available. But this limit may be too high for terrestrial animals that lack this mechanism. Biomagnification of compounds with log Kow 3-4 is usually not high in birds and mammals, but BMFs > 1 do occur. A good example is β-HCH, which has a BMF of 9.3 in herring gulls (Braune and Norstrom 1989), and is found at relatively high concentrations in some Arctic seabirds.

Biodegradation in soils and biotransformation rates in animals and plants must be considered as important parameters in any assessment of bioaccumulation in terrestrial ecosystems. Emphasis on modeling POPs in aquatic ecosystems has historically tended to ignore the role of biotransformation in bioaccumulation because most legacy PBT compounds for which the models were developed are halogenated and not metabolized well or at all in aquatic biota, including high trophic level fish. Thus, existing models have assumed compartmental transfer is driven by partitioning, both in the environment and within organisms. Recent food web models incorporate metabolism, but often there are no experimental clearance data to include, and this becomes a fitted parameter, lowering the reality of the model. To date we know of no studies where such fitted metabolic rate constants have been verified by applying them to alternate bioaccumulation data sets. The Pesticide 4 example in the White Paper showing significant metabolism in fish and invertebrates despite a high log Kow illustrates the importance of including rate of biotransformation as part of the risk analysis.

In terrestrial ecosystems metabolism may have a bigger role in persistence, at least in birds and mammals, than in aquatic ecosystems. Terrestrial homeotherms possess significantly higher capability than most fish to metabolize a wide variety of compounds (Norstrom and Letcher, 1997). Although data are more limited, reptiles and amphibians also seem better at biotransformation than fish. It is worth pointing out that conclusions concerning bioaccumulation potential in terrestrial mammal and bird and bird food chains, e.g., the statement by Gobas et al. (2003) that biomagnification factors in terrestrial food-chains are much greater than those in aquatic food-chains, are only applicable to poorly metabolized chemicals. Newer classes of pesticides are more likely to undergo significant biotransformation.

The types of biotransformation and metabolites formed, and to some extent the enzymes responsible, are similar among mammals and birds, but rates of biotransformation may be species specific. A fruitful area to consider would be to evaluate data on rates of metabolism of existing PB chemicals, e.g., PCBs, organochlorine (OC) pesticides, to see if some generic empirical relationships on size (usually allometric body weight) and broad taxonomic categories can be generated. This would lend some credence to the idea that data on surrogate species could be used, e.g., for all mammals, all rodents, all birds, all passerines, etc. For example, Glaser and Connolly (2002) showed that whole-body clearance rate of p,p'-DDE (log Kow 6.5) was a function of $W^{-0.3}$ among bird species. When this relationship was used with annual average values for parameters in an avian bioaccumulation model (Norstrom et al., 2007), steady-state fish-bird egg BMFs were predicted to be relatively constant (47-55) and independent of weight among herring gulls, osprey and bald eagles (Hinck et al., 2009).

- ***Please comment on the current state of the science underlying existing terrestrial food web bioaccumulation models and their relative strengths and limitations.***

It is generally regarded that models for soil/plant systems are not as advanced as animal models. The problem should thus be considered as two separate but linked sub-models. The first model should simulate chemical distribution in soil, plant and within-soil organisms, while the second sub-model describes bioaccumulation by animals either singly or organized into one or more representative (generic?) food chains. The soil-based model would have inputs from direct pesticide application, spray drift and atmospheric loading (mainly an LRT consideration). This sub-model would thus describe the addition of the chemical to the terrestrial ecosystem and its entry into the organisms at the base of the food web. Since it is well known that different plants have different capacities for uptake of pollutants any such model should be capable of including uptake by a variety of representative plant species. In addition, herbivores tend to select specific parts of plants to eat so the plant models should include multiple compartments including foliage, fruits and seeds. It is likely that models of organic chemical uptake in plants will improve as more empirical data become available. A recent review by Collins et al. (2006) established that although current plant uptake models may be suitably calibrated they are inadequately validated against a broad range of datasets. The model by Trapp et al. (2007) is an example of one of the more recent models available for predicting plant uptake.

One notable item here is that current EPA models do not generate concentrations of pesticides in air (other than spray drift) so inclusion of the air to plant uptake pathway will require additional fate modelling.

As discussed in the aquatic bioaccumulation modelling response, there are many good bioaccumulation models available for animals such as birds and mammals. These include models for birds (Norstrom et al., 2007, Nichols et al., 1995) and mammals (Armitage and Gobas 2007, Kelly and Gobas 2001). All of these models have similar basic structures (but differ in level of biological detail), thus they provide a general modelling framework that is fairly readily adaptable to other species. The common elements being descriptions of: biology/life history, bioenergetics, diet description and chemical kinetics. These models are fundamentally sound in structure (i.e. equations used), but evaluating how well they are calibrated requires further detailed examination. It is noteworthy that the terrestrial bioaccumulation models developed by Kelly and Gobas (2001) and Armitage and Gobas (2007) represent very simple food chains. For example caribou are assumed to eat lichen exclusively and wolves only eat caribou. Furthermore, lichen is assumed to accumulate chemical just from air and snowmelt with no interaction with soil. The earthworm-shrew model is also a very simple one step food chain with no involvement of plant uptake.

The main challenge of developing models to assess PBT pesticides in terrestrial animals has to do with how the models are assembled and calibrated rather than defining appropriate sets of equations. Some of the specific challenges include:

- selecting appropriate or representative species to include in the model(s).
- trying to define one or more generic food chains that provide reasonable spatial coverage for

the USA.

- dealing with issues of diet heterogeneity for many terrestrial species; while food chains are typically shorter than in aquatic ecosystems, terrestrial species may use a broader range of items.
- issues of mobility of organisms (large or variable home range, migration).
- dealing with species that have a mixed aquatic/terrestrial diet such as mink. Mink are a good candidate species to include in modelling scenarios since they have been widely used as a model species in terrestrial toxicity studies.
- defining biology of individual species and the level of detail needed to adequately model bioaccumulation tendencies (e.g., seasonal changes in lipid stores, diet composition and feeding rate; contaminant transfers associated with reproduction).

Although no specific conclusions were reached, the notion that there are kinetic limitations in environmental partitioning and bioaccumulation of high log Kow compounds was frequently mentioned for both aquatic and terrestrial food chains. There is ample evidence that non-equilibrium kinetics dominates for legacy PB compounds (mostly neutral organohalogen compounds) with log Kow >7.5. Neither equilibrium partitioning nor steady-state bioaccumulation models can therefore adequately model these processes. Dynamic models also have the advantage that they can take into account reproduction, seasonal changes in diet, fasting and the like, which are important in bioaccumulation.

If we put this question into the context of the overall uncertainty in the assessment, which is quite high, it can be concluded that existing terrestrial assessment tools are fairly well developed. Certainly this depends on how much resolution (temporal and spatial) one wants to put into the assessment. For the chemicals with PBT characteristics it may be okay to accept less spatial and temporal resolution in exchange for much broader coverage.

The Panel believes that the tools (models/equations) that are available to assess terrestrial fate are adequate and appropriate for POPs, so the question shifts to whether or not we have identified the best use of these tools to address this particular issue. Based on what has been provided in the White Paper and presentations, the Panel is not convinced that an appropriate conceptual model has been fully developed. A few examples are given below of things that need to be considered when developing the conceptual model for chemicals with PBT&LRT characteristics along with some suggestions on how to transform the conceptual model to a "regulatory environmental model" for these chemicals.

Spatial scale - The current OPP approach to terrestrial fate seems to be primarily focused on near-field accumulation of the pesticide (the exception being the LRT assessment). The driving assumption appears to be that focusing on near field will represent the highest ecological exposures. This may be true if the vulnerable organisms or habitats happen to be near the treatment areas but for chemicals with PB and LRT characteristics we should not be surprised to find them in places where we didn't use them. Therefore, it is important to provide adequate spatial scale in the conceptual model and the assessment to capture the unique "hazards" presented by these chemicals.

Temporal scale - Given the comment on spatial scale, another aspect of the conceptual model is the time-frame of the assessment and for this particular class of compounds this scale needs to be quite large. Although resolution is also important and should be built into the assessment, one member of the Panel suggested that for this particular class of compounds the assessment should first focus on an overall duration that is adequate to capture the potential long term behaviour of the chemicals both during and after use (i.e., over the full lifecycle of the product). This "lifecycle" view of the assessment requires an understanding of the possible use patterns for a given chemical. In other words, for this particular class of chemicals it is going to be very important to understand not only the recommended application practice (i.e., pounds per acre) but also the possible aerial coverage and primary region and season of use for the product.

Transport processes - Given the high overall persistence and mobility of these chemicals, it will be important that the conceptual model include characterization of feedback pathways that control the long-term mass balance. There are many opportunities for improving the transport and transformation modelling but it is easy to become overwhelmed by the complexity and need for large amounts of modelling input data. For example, focusing on uptake in individual plants may not be as important in the overall assessment as understanding the interaction between things like a moving air mass and a forest canopy. Tools are also required to evaluate the initial transfer of the pesticide into the atmosphere at the site of application, whether by volatilization or in association with wind-driven particles. In short, understanding the primary compartments of the system (air, aerosol or dust particles, water, soil sediment and vegetation) should be a high priority because they tend to control the mass balance and fate. Once these compartments are reasonably worked out then plugging select food webs into the system that highlight the important endpoints of the assessment can be done. With this it is recommend that modelling scenarios evaluate both near-field and long-range transport scenarios with food webs located at various distances from source regions. Importance of direct volatilization and sorption of pesticides to particles that are wind driven from application site should also be evaluated

Endpoints or "receptors" - Regarding the assessment endpoints in the current conceptual model, the Panel recognizes that OPP is somewhat constrained to the classic definition of ecosystems (i.e., plants and animals) but for this particular class of chemicals it is essential that human exposures be included in the assessment. In fact, human exposures may dominate the final outcome in the assessment. The OPP/EFED should consider human health risk assessment when developing fate and exposure models, particularly at the conceptual model development stage, keeping the human "receptor" in mind may help focus (and simplify) the assessment. For example, considering uptake and accumulation in vegetation, it may be more important to look at the uptake as a process for introducing POPs into the food chain than looking at individual components of the food chain as endpoints. Certainly there are important effects that should be considered for vulnerable parts of the terrestrial food web but ultimately the most important terrestrial receptor for this particular type of chemical, for PBTs, will likely be accumulation in humans. In addition, knowledge gained from human health risk assessments may aid in modeling/assessing bioaccumulation in wildlife. Certainly there are data/studies (e.g., toxicity studies, metabolism, residue trials, etc.) which could be relevant. EPA may want to explore if any of human exposure models (e.g., aggregating routes of exposure) may be useful.

Suggested approach - Once the overall conceptual model is established it may not be necessary to develop modelling tools from scratch. Models are available that are sufficient for at least some of the lower tier assessments if not some of the higher tiers. For example, the BETR model (MacLeod et al., 2001) provides a continental scale dynamic mass balance model that is composed of eco-regions where each region is a "unit world" type model. The current version of the BETR model also includes a relatively simplistic description of food distribution so eco and human exposures can be considered (MacLeod et al., 2004). This type of tool can provide a means to explore the relationships between applications in one region and exposures or fate in other distant regions. More detailed mass balance models are also already available within the Agency, including the TRIM modelling tool (http://www.epa.gov/ttn/fera/trim_fate.html), which provides a mechanism to develop specific scenarios. These existing models begin to capture combined aquatic and terrestrial fate and accumulation process in a way that is relevant to PB and LRT chemicals and the use of these existing tools should be considered as a relatively near-term opportunity for assessing these chemicals.

Ultimately one of the biggest concerns in the longer term is how quickly these chemicals might turn up in human tissues and at what levels. These models can begin to reveal this. More importantly, these models are amenable to detailed sensitivity analysis so that not only can the modelling provide estimates of exposures but also insight into important transport/transformation pathways.

Agency Charge

6) Incorporating Multiple Exposure Routes.

For a number of organic chemicals with PBT profiles, aquatic organism exposure via non-aqueous routes (diet, sediment) can be important relative to direct exposure from water. Most standard aquatic toxicity test studies submitted to the Agency for pesticide registration do not incorporate realistic chemical exposure through the diet (e.g., water only exposures). Therefore, toxicity reference values (TRVs) from these studies may underestimate actual environmental effects. To address this concern, other Programs within the Agency have proposed using a tissue residue approach (TRA) for quantifying chemical toxicity (e.g., Office of Water, Office of Research and Development). For quantifying toxicity of organic pesticides with PBT characteristics, the Agency is also considering the use of the TRA.

- Please comment on the strengths and limitations of the tissue residue approach for addressing pesticide toxicity from multiple exposure routes and other methods the SAP deems appropriate.

In the context of the tissue residue approach, please comment on the strengths and limitations of using measured and predicted tissue residue-effect relationships that are derived from water-only exposures in laboratory toxicity tests.

Panel Response

1. Strengths and weaknesses of TRA.

General

The tissue-residue approach (TRA) for toxicity assessment is basically the use of tissue concentrations as the dose metric for characterizing toxicant potency. There are several advantages to using tissue residues over exposure concentrations (e.g., water, sediment, and diet) to calculate toxicity metrics. These include: (1) a large reduction in toxic response variability among all species for a given compound; (2) an improved ability to address mixture toxicity; (3) an increased use of information on modes and mechanisms of toxic action; (4) a likely reduction in the number of species needed to characterize toxicant potency; (5) the potential to improve ecological risk assessments; and, (6) the generation of more scientifically defensible tissue, water and sediment toxicity guidelines or criteria. A keystone concept for the TRA is that the body/tissue residue reflects the target "dose" better than the traditional dose (e.g., water, air, soil/sediment, or diet) because the closer the dose surrogate is to the actual site of toxic action the less it is influenced by myriad modifying factors. Our intention for the TRA is not to replace ambient dose metrics but to enhance information about toxic responses. There are several publications that explain the concepts and application of the TRA in more detail (McCarty and Mackay 1993, Di Toro and McGrath 2000, Di Toro et al., 2000, Barron et al., 2002, Hendriks et al., 2005, Traas et al., 2004, Beckvar et al., 2005, Steevens et al., 2005, and Meador 2006).

Strengths

1. Often large reduction in variability (orders of magnitude) between effective concentration (ECp) and effect tissue residue (ERp) (p=% or proportion responding).
2. Integrates over exposure routes. All exposure routes incorporated.
3. Advantageous for assessing toxicity in the field. Collect and measure pesticide and quickly know how well organisms are doing.
4. Integrates over time and space in field.
5. Good for mixture toxicity, but need information on modes and mechanisms of toxic action (MoOA and MeOA). Useful mainly for non interactive toxicity; response addition and dose addition of toxicants.
6. Highly defensible for translating back to water or sediment concentrations and water or sediment quality criteria (WQC or SQC). One approach is to use 95% LCI of the species sensitivity distribution (SSD) and calculate water or sediment concentration via rearrangement of bioaccumulation factor. BCF can be modeled or calculated, e.g., 95th percentile of the cumulative distribution function (CDF) for all species BCFs.
7. Tissue-based toxicity metrics are relatively time independent.
8. Fewer species may be needed to assess toxicity. The low variance results in a smaller confidence interval around the mean (for normally distributed data); hence fewer data points are needed to obtain a more precise estimate of this value. This also applies to the 95% LCI of the HC_{05} from a species sensitivity distribution because this is a variance dependent statistic.

Limitations

1. Highly metabolized compounds; however, metabolism does not preclude use of TRA for toxicity assessment. For example, PAHs in vertebrates are highly metabolized (99+%). For many PBT compounds, this will not be an important issue.
2. High information requirements - toxic action (MoOA and MeOA), metabolites.
3. Few studies are available that provide TRA data. Also most studies assess only Lowest Observed Effects Residue (LOER) and few endpoints (mortality, growth, and reproduction). Three databases are available, ERED [(US Army Corps of Engineers (ACOE)] (1999), Javinen and Ankley (1999), and PCBres (2008).
4. Need to develop toxicity testing framework to acquire high quality data.
5. Some confounding factors (lipid, organism health, temperature, etc.); however many of these are the same for toxicity metrics based on ambient exposure.
6. Need to consider toxicity of metabolites.

Charge 6 part B.

Comment on strengths and weaknesses using measured and predicted tissue residue-effects relationships from water only exposures in laboratory toxicity tests.

Strengths

1. Water-only exposures are acceptable, as are dietary-only exposures when determining dose-response based on tissue concentrations. Sufficient time must be provided for internal redistribution of the toxicant due to circulatory differences in distribution to tissue.

2. Route of uptake is less important.

Weaknesses

1. Toxicity or bioaccumulation based on model predictions may not be accurate. Not all compounds are amenable to QSAR modeling. Measured values are preferred.

2. Several doses should be tested because many toxicants exhibit multiple modes of action that are dose dependent. To capture these differences a wide range in doses is needed and long-term exposures are essential.

3. Sufficient time for exposure needed for those toxicants that exhibit time dependent critical body residue (CBRs), which usually mitigates after 4 days.

Points to consider

- There is limited information in the White Paper for TRA. Most information is in the 60 page document "Tissue-based Criteria for Bioaccumulative Chemicals" (2005) that was provided on the CD. In this document, the TRA for toxicity assessment was presented in good detail.

- Using measured tissue-residue effect relationships is preferred, especially if EC_p values are calculated. The LOERs are of low utility for providing insights into dose-response relationships or underlying principles and they are dependent on the quantal nature of allocating exposure concentrations (often few and far between), a function of sample size (often low), highly prone to Type II error (finding no effect when in fact an effect exists), low power of the test, and a bright-line significance value ($\alpha = 0.05$) that ignores biologically important results. Additionally, the No Observed Effects Residue (NOER) is often used, which also exhibits the potential flaws listed above. The NOER is not based on a toxicity response and therefore represents negative evidence.

- Data mining can be useful to determine CBR values (when time matched or time corrected). For example, $ER_{10} = BCF*EC_{10}$

- Metabolite toxicity. Metabolites may be more, less, or equitoxic compared to the parent compound. Phase I metabolism reactions (oxidation) increase both the solubility and reactivity of the parent molecule and can be more toxic than the parent compound. Reactive metabolites are generally not considered by the tissue residue approach for toxicity assessment. Phase II reactions (conjugation) nearly always result in less toxic metabolites. In general, however, metabolites tend to be less toxic than parent compounds because of changes in hydrophobicity, conjugation, sequestration, etc. that occurs as a result of biotransformation. One exception may be for metabolites of narcotic mode of action compounds because they may be able to contribute to non-specific membrane disruption.

- The Agency should use caution with assumptions of acute toxicity and additivity of response based upon QSARs. Examples of compounds with similar structure with significantly different modes of action include DDT isomers and chiral insecticides (pyrethroids). The assumption of baseline toxicity (narcosis) is a simplistic approach and should be avoided because specific mechanisms of toxic action are common for most organic compounds. Consequently, knowledge regarding the mode or mechanism of action is very important to the assumptions utilized in the TRA.

- A given toxicant can act by multiple modes & mechanism of action and can be dose and time dependent. For example, PAHs and PCBs can act by baseline toxicity at high doses causing lethality and by a variety of specific mechanisms of action at lower doses (e.g., immunosuppressant, endocrine disruptor, growth inhibitor, teratogen, mutagen, and others).

- When using this approach for toxicity assessment, there is a need to consider tissue residues in individual animals, and in some cases, within individual tissue compartments seasonally and over their lifetime. Many factors can control toxic tissue concentrations, such as seasonal or migratory changes in fat stores, maternal transfer of contaminants by females, and biotransformation. Without these considerations, it will be difficult to apply predictions of effect at the population level.

- The Panel discussed the general lack of data and protocols on how to predict chronic effects from acute data and how EPA may approach the problem. The Panel debated specific measurements of residue levels in critical tissues (based on mode of action or site of storage). One Panelist suggested that for small organisms, whole body residues should be sufficient.

Recommendations

- Tissues. Whole body measurements are likely sufficient for small species. Consider specific target tissue and physiologically-based pharmacokinetic (PBPK) models. The Panel generally felt that liver, lipids, and gonadal tissues were good selections. If the pesticide is neuroactive, brain may be another possibility.

- Consider long-term (chronic) exposures, e.g., >10 days, which are more likely to result in sublethal responses. Determine low ER_p (p = fraction responding), e.g., ER_{10}. These are important for protecting against adverse, population-level effects in field-exposed species.

- Consider additional responses. Inhibition of behavior, olfaction, and immunocompromise can result in mortality. Also, enhanced responses (hormesis) may lead to adverse effects.

- The Panel highly recommends lipid normalization for most organic toxicants because of the control this factor can have on toxicity (Lassiter and Hallum 1990).

- Data mining. Can determine tissue residue metrics (e.g., ERp) using BCF and ECp. Could use modeled bioaccumulation values and measured ECp values.

- Define and clearly state assumptions and limitations for the tissue residue approach.

- The Panel recommends determining tissue-based toxicity metrics using TRA for all bioaccumulative compounds. This approach is not limited to PBT compounds.

- Need to develop toxicity testing framework to acquire high quality data.

Agency Charge

7) Screening for Long-Range Transport Potential.

For some pesticides with PBT characteristics, long-range transport (i.e., transcontinental and intercontinental transport) has been well documented. Currently, OPP's ecological risk assessment process relies heavily on monitoring data for assessing long-range transport concerns. However, this process does not *a priori* screen for long-range transport potential prior to pesticide release in the environment. Difficulties in linking local use patterns of pesticides to far-field (*e.g.,* intercontinental) deposition and exposure in a modeling framework is considered a major challenge in screening and assessing long-range transport potential.

1. Please comment on the strengths and limitations of available tools for screening the long-range transport potential of pesticides (e.g., the OECD screening tool for long-range transport).

Panel Response

The report of the Panel on Assessing Long-Range Transport Potential begins with a consideration of transport scales and briefly reviews the evidence for transport of pesticides to remote ecosystems. This is followed by an overview of modeling techniques that are available to screen chemicals for long-range transport potential (LRTP), including the OECD Screening Tool. Some estimates of LRTP have been derived from monitoring data and these are compared to model outputs. Discussion of the Charge ends with the Panel recommendations in the area of evaluating chemicals for LRTP.

The Panel also considered a related issue from the White Paper (pp. 28-29):

> "Difficulties in linking local use patterns of pesticides to far-field (*e.g.*, intercontinental) deposition and exposure in a modeling framework is (sic) considered a major challenge in screening and assessing long-range transport potential."

This implies a need to go beyond simply ranking chemicals for LRTP to a more quantitative understanding of pesticide emissions and migration away from source regions. This response concludes with deliberations and recommendations of the Panel in this area.

Scales of transport

Although the term "long-range transport" is frequently used, the meaning is not always clear. The text of the Stockholm Convention (UNEP, 2001) mentions "potential for long-range environmental transport through air, water or migratory species", but the scale of transport is not specified. The OECD (2001) defines long-range transport of air pollutants as "the atmospheric transport of air pollutants within a moving air mass for a distance greater than 100 kilometres." Within North America, scales of transport that might be considered "long range" are:

The U.S. as a source:

- Southern and Midwestern U.S. to the Great Lakes
- U.S. to Canada and the Arctic
- U.S. to Europe
- U.S. urban and agricultural areas to remote high elevation ecosystems.

The U.S. as a recipient:

- Trans-Pacific – Asia to U.S.
- Canada to U.S.

- Mexico to U.S.
- Africa to southeastern U.S.

Empirical evidence for long-range transport of pesticides

Atmospheric transport of organochlorine and current-use pesticides (OCPs, CUPs)

From the perspective of rapidly mobilizing from the field and long range transport, the air appears to have the advantage. Once in atmosphere, pesticide advective transport is more rapid and its interphase transport from the soil is immediate and constant in comparison to the water media.

Studies in the 1960s and early 1970s identified pesticides in ambient air across the U.S. (reviewed by Majewski and Capel, 1995). The earliest indication of long-range atmospheric transport of OCPs was obtained by measurements in Sahara dust carried from Africa across the subtropical Atlantic Ocean to the Caribbean (Risebrough et al., 1968, Seba and Prospero, 1971). More recent efforts have focused on air transport of pesticides and other semivolatile chemicals across the Pacific from Asia (Bailey et al., 2000; Harner et al., 2005; Killin et al., 2004; Primbs et al., 2008a, b). Some OCPs were elevated at Mount Bachelor Observatory in Oregon's Cascade Range during Asian transport events, while most CUPs were related to spring application periods in the western U.S. (Primbs et al., 2008a). Models predict episodic intercontinental transport of lindane across the Atlantic and Pacific oceans (Zhang et al., 2008).

Long-range transport of OCPs to arctic and antarctic regions was first recognized over four decades ago by the occurrence of these chemicals in snow and biota. Since then, many investigations have documented atmospheric transport of OCPs on a global scale, and routine atmospheric monitoring programs have been established in the Arctic (AMAP, 2004; Su et al., 2008) and the Great Lakes.(Sun et al., 2006a,b). Investigation of OCPs in air across continental regions and worldwide has been facilitated through deployment of passive air samplers in Canada, the U.S. and Mexico (Gouin et al., 2005; Shen et al., 2004, 2005; Wong et al., 2008), Europe (Jaward et al., 2004), Asia (Jaward et al., 2005) and globally (Pozo et al., 2006, 2008).

Current-use pesticides (CUPs: modern herbicides, insecticides and fungicides) have been measured in air and deposition in the U.S. (Foreman et al., 2000; Goolsby et al., 1997; James and Hites, 1999; Majewski et al., 1998) and Canada (Yao et al., 2007, 2008; and reviewed by Tuduri et al., 2006a,b). OCPs and CUPs have been found in air, precipitation and biota of remote high elevation regions of the U.S., Canada and Europe (reviewed by Daly and Wania, 2005). Recent studies in North America have been conducted in the Sierra Mountains (Ackerman et al., 2008; Hageman et al., 2006) and the Rocky Mountains (Ackerman et al., 2008; Daly et al., 2007a; Hageman et al., 2006; Usenko et al., 2007; Wilkenson et al., 2005) and mountains of Costa Rica (Daly et al., 2007b). Transport of CUPs to the Arctic has been documented through measurements in air, snow, ice, seawater and lakes (Ackerman et al., 2008; Hageman et al., 2006; Hermanson et al., 2005; Jantunen et al., 2008; Muir et al., 2004).

Oceanic transport

Far less attention has been paid to ocean transport of pesticides. Historical loadings of hexachlorocyclohexanes (HCHs) to the western Arctic Ocean are thought to have resulted from major releases in Asia followed by transport through the atmospheric and ocean currents. A mass balance box model for HCHs in the Arctic Ocean suggests that both transport pathways were important in the 1970s and 1980s. Following declines in atmospheric concentrations due to large-scale bans and restrictions in Asian countries, ocean transport overtook the atmospheric pathway in the 1990s (Li et al., 2004). CUPs have been found in surface seawater on a transect extending from the Gulf of St. Lawrence, through the Labrador Sea to the eastern Canadian Archipelago and Hudson Bay, but it is not clear if the source is ocean transport, atmospheric deposition or both (Jantunen et al., 2008). A review of endosulfan in Arctic Ocean surface water identified higher concentrations at the periphery than in the high Arctic (Weber et al., 2006). This might indicate ocean transport through inlets to the Arctic Ocean, or greater atmospheric deposition in the low Arctic.

Long-range transport assessment

To protect against long-range atmospheric transport, a two-day degradation half life in air is used internationally in regulations that identify persistent chemicals. The SETAC Working Group on Multimedia Partitioning, Overall Persistence and Long-Range Transport Potential (Scheringer et al., 2009) noted that at the average long-term wind speed of 4.5 m s^{-1} in the middle atmosphere of Europe, two days corresponds to a travel distance of 777 km.

Multimedia models are available for assessing LRTP which consider air and ocean transport, air-soil and air-water exchange, particle and gas phase wet and dry deposition, degradation rates in air, soil and water.

Meteorologically driven Eulerian or Lagrangian air transport models can be used to quantify the advection, dispersion and reaction behavior as the pesticide moves away from the source region. However, these models require much more sophistication in usage and computer time and were not considered further by the Panel.

Outputs of models

Multimedia models can be classified as "transport-oriented" and "target-oriented". Transport-oriented models describe the potential for transport in the mobile media air and/or water with simultaneous exchange with the surface media, while target-oriented models describe the percentage of emitted substance that migrates to surface media in selected target regions as a consequence of transport in air and/or water and subsequent deposition (Fenner et al., 2005). Some outputs of these models are (Scheringer et al., 2009):

- Characteristic Travel Distance (CTD) = distance over which air concentration drops by 1/e = 0.63.
- Spatial Range = percent of the earth's circumference over which 95% of a chemical can be distributed.

- Overall Persistence (P_{OV}) = steady-state residence time with respect to degradation.
- Transfer efficiency: Ratio of the deposition flux from air to surface media in a target region, F_{dep}, and the continuous emission flux in the source region, E: TE = F_{dep}/E.
- Arctic Contamination Potential (ACP) from Globo-POP (Brown and Wania, 2008; Czub et al., ES&T 2008; Wania et al., ES&T 2003, 2006). ACP = mass of chemical in the Arctic divided by the mass or emission in the global environment.

Outputs of Globo-POP include "chemical space" diagrams which illustrate the primary compartments of partitioning (air, water, soil) and mode of transport ("flyers", "swimmers" and "hoppers") as related to the K_{AW} and K_{OA} of the substance. Similar chemical space diagrams map the ACP for the physical environment alone and with bioaccumulation considered (e.g., Figure 1 in Wania, 2006; Figure 1 in Brown and Wania, 2008). Similar modeling has been done to derive a Mountain Contamination Potential (Daly et al., 2007b).

Model comparisons

Several comparisons of models have been conducted recently. Fenner et al. (2005) evaluated seven transport-oriented (ChemRange, ELPOS, CalTOX, SimpleBox, Impact 2002, CEMC LII and LIII) and two target-oriented models (Globo-POP and BETR North America) with 3175 hypothetical chemicals having a wide range of partitioning properties and degradation half-lives and spatial scales ranging from regional to global. All models but one was steady-state, open system (Level III), run under scenarios of fixed environmental parameters (e.g., temperature, OH radical concentrations, first-order loss rates). Globo-POP is a non-equilibrium, dynamic, open system (Level IV) model, run with temperature-dependent partitioning properties and degradation rates. The various models were run under different assumptions of environmental compartment sizes (volumes of air, water, soil, sediment). Table 1 in Fenner et al. (2005) summarizes the features of the nine models. Rankings of the chemicals according to P_{OV} were highly correlated among all models, although absolute values of these output metrics varied according to the model. Differences were found in the LRTP comparisons between the two target-oriented models and the other transport-oriented models. Differences for Globo-POP were also attributed to the latter models' use of temperature-dependent properties and degradation rates. Fenner et al. (2005) concluded that:

- "All nine models, when used in the correct context, provide credible and useful descriptions of the complex interactions between the environment and chemical pollutants."

The SETAC Working Group (Scheringer et al., 2009) provides references to several other model intercomparison studies and concludes that:

- Multi-media box models are appropriate tools to rank chemicals on their persistence and LRTP.
- On time scales of days to weeks, the dynamic air flow used in atmospheric models leads to transport of chemicals along certain trajectories that is faster than the long-term average of atmospheric mixing implemented in box models.

OECD Screening Tool

The OECD Screening Tool (Wegmann et al., in press) is a Level III (steady-state) model for screening chemicals for CTD, P_{OV} and TE. It operates under the following parameters:

- Compartments are ocean surface water, soil, and tropospheric air; there is no freshwater, no groundwater and no sediment.
- Dimensions of the compartments are 30% land and 70% water, a depth of 10 cm and 100 m for soil and water, respectively, and a height of 6000 m for air.
- Input parameters are K_{OW} and K_{AW}, and the three first-order degradation half-lives for soil, water and air.
- Constant temperature (25°C), rainfall is continuous.

The Tool authors discuss the following limitations and recommendations for users:

- The Tool does not calculate realistic concentrations because the emission is generic (100 mol h^{-1}).
- Phase partitioning is calculated on the basis of K_{OW} and K_{AW}. Sorption to suspended solids in ocean water is described by an estimate of K_{OC} that is derived from K_{OW}; sorption to aerosol particles is described by a gas-particle partition coefficient, K_p, derived from K_{OA}. The relationships used to estimate K_{OC} and K_p are automatically used for all chemicals. This may lead to incorrect results for chemicals whose sorption behavior is not directly determined by K_{OW} and K_{OA}.
- The Tool provides the option to perform a Monte-Carlo analysis of the model results which show in a quantitative and transparent way the influence of uncertain chemical property data on the results for Pov, CTD and TE. It is recommended that users apply this function in order to understand how the uncertainty ranges of chemical properties translate into the uncertainty of the model results and to identify the most influential chemical properties.
- It is useful to interpret results from the Tool not on an absolute scale but relative to results for other chemicals.

Comparisons of model outputs to empirical data

Several studies in which air, water or sediment concentrations of persistent chemicals have been measured across latitudinal gradients have been used to estimate empirical CTDs. Some examples are given below:

- Shen et al. (2004, 2005) deployed passive air samplers from Central America to the Canadian Arctic. These were designed to integrate air concentrations of OCPs over a 12-month period, and estimates of CTDs were derived from air concentration gradients from low to high latitudes. Ranking of OCPs for CTDs agreed well with output metrics of three models, absolute values agreed in some cases, differed in others.

- CUPs were measured in water samples in lakes from New York, southern Canada and the Arctic (Muir et al., 2004). Agreement between empirical and modeled CTDs improved when variable OH radical concentrations and intermittent precipitation were introduced into the models.
- Measurements of PBDEs and PCBs were made in lake sediment cores from northern New York to the Canadian Arctic, and empirical half-distances were compared with outputs from two steady-state and one non-steady-state models (Breivik et al., 2006). Large differences were noted among model predictions of LRTP. Key processes which were identified as in need of improvements in modeling were, intermittent rain, particle deposition, the "forest filter effect" and photolysis in sorbed state. Breivik et al. (2006) make the following statements about the regulatory significance of their study:

  > "… current steady-state models are at risk of underestimating the potential for LRT, not only for water-soluble chemicals that tend to be deposition-controlled as previously recognized but also for chemicals that are strongly sorbed to particles in the atmosphere."
  >
  > "A higher tiered approach involving non-steady-state models may thus be desirable in order to capture substances with an episodic transport potential to remote areas."

Many more data sets are available as a result of continental- and global-scale passive air sampling campaigns (Jaward et al., 2004, 2005, Pozo et al., ES&T 2006, 2008, and studies reviewed by Scheringer et al., 2008). These could provide opportunities for comparing measured and modeled CTDs, as noted by the SETAC Working Group (Scheringer et al., 2009). The WG also discussed other issues of special relevance to CUPs and other emerging chemicals of interest:

- It is necessary to consider transformation products of less persistent chemicals. Examples given by the WG include oxons of organophosphate pesticides, transformation of fluoroteleomer alcohols to their carboxylic acids, and debromination of higher PBDE congeners.
- Particle-gas partitioning of OCPs, PCBs is well described by K_{OA} or vapor pressure. This is not true for polar CUPs, which are also sorbed to mineral matter and are more affected by aerosol water content. (Arp et al., 2008a, b; Götz et al., 2007, 2008; Sadiki and Poissant, 2008; Sauret et al., 2008).
- Improved transport modeling for polar compounds has been achieved using polyparameter linear free energy relationships (ppLFERs) to describe particle-gas interactions (Götz et al., 2008). Such relationships account for hydrogen bonding and electron donor-acceptor interactions as well as simple hydrophobic partitioning.

Panel recommendations on persistence and long-range transport

- Employ a tiered approach for assessing the atmospheric LRTP of pesticides and their persistent transformation products:

Tier 1: Is estimated (EPISUITE: AOPWIN) or measured atmospheric degradation half-life >2 day?

Tier 2: Use OECD Screening Tool and compare outputs to those of known PBTs.

Tier 3: Use more sophisticated models (steady- and non-steady-state) to assess LRTP and P_{OV}.

- The potential for LRTP should be proactively assessed and evaluated based on measurement of the pesticide in remote areas.
- The potential for LRTP should be included in the overall risk characterization.
- Atmospheric deposition to large bodies of water, such as oceans and the Great Lakes, should be considered in the generic conceptual model.
- Improvements in LRTP model parameters are needed to accommodate the special requirements of CUPs:

    a) Particle-gas partitioning not simply described by K_{OA} or vapor pressure, consider using ppLFERs.

    b) Investigations are needed of CUPs transformations in the gas phase and on particles, and LRTP of transformation products.

    c) AOPWIN may not be accurate for complex molecules like CUPs. Experimental measurements of OH radical reaction rates are needed (Atkinson et al., 1999).

- Measurements and modeling need to be improved to assess the LRTP of pesticides via ocean currents.
- Continue to evaluate modeled LRTP characteristics against empirical data.

Linking local use and far-field deposition and exposure for CUPs

Panel discussions in this area were directed at moving toward quantitative description of transport and deposition vs. simple ranking of chemicals. Long-range transport begins at the source, and emission factors for LRTP models are usually generic; e.g., an assumed X tons of pesticide emitted to water, air or soil and within a specified geographical area. Pesticide emission factors are not necessary for ranking of chemicals for LRTP, but essential for estimating mass of chemical mobilized and transported. Emissions depend on quantities of pesticides applied, seasonality of usage and factors affecting volatilization (see below). In some models, pesticide usage is apportioned according to geographical region and crop application rates and emissions are estimated based on assumptions about the proportion of primary emissions that enter soil, air and water (MacLeod et al., 2002) or by using regionally gridded soil concentrations and applying an air-surface exchange model (Li, 2001; Li et al., 2001; Ma et al., 2003, 2005).

Processes that move pesticides off-site include:

- Spray drift during application.

- Precipitation arriving onto the soil surface or emerging plants, which solubilizes pesticides and erodes soil particles containing sorbed pesticides. This combined runoff slurry is quickly delivered to a pond, stream or estuary.
- Pesticide volatilization into the atmospheric boundary layer (ABL), continuously: during and after application, and during and after rainstorms.
- Pesticides entering the ABL on soil dust due to mobilization by wind action during dry periods.

Volatilization of pesticides from soil depends on many factors:

- Physicochemical properties of the pesticide: K_{OW}, K_{OA}, K_{AW}
- Formulation
- Application (foliar spray, soil surface, soil incorporated)
- Soil characteristics (texture, moisture, organic matter content)
- Soil mixing (bioturbation, plowing)
- Micrometeorology

Other important factors are competing losses of applied pesticides by plant penetration, photodegradation and washoff from plant surfaces (Leistra et al., 2007; Preuger et al., 2005). Many experimental measurements of pesticide fluxes have been made in situations where pesticides were freshly applied or present as historical residues using micrometeorological techniques (e.g., Kurt-Karakus et al., 2006; Majewski et al., 1993; Leistra et al., 2007; Preuger et al., 2005 and papers cited therein). Other techniques involve the use of flux chambers (Waite et al., 2007), edge-of-field air sampling to measure off-site transport (Waite et al., 2001) and measurements of air concentrations over agricultural fields without concurrent micrometeorology (Bidleman and Leone, 2004; Bidleman et al., 2006; Spencer et al., 1996; Waite et al., 2001). Models for predicting pesticide emissions from soils have been published (e.g., Leistra et al., 2007; Reichman et al., 2000 a, b; Scholtz et al., 2002a, b).

Fewer situations have been described in which both measurements and models have been applied to assess local pesticide fluxes and/or air concentrations, but in these the agreement is generally good (Leistra et al., 2007; Scholtz and Bidleman, 2006; Scholtz et al., 2002b).

Panel recommendations on linking local pesticide use to far-field exposure

- Improve models for predicting pesticide emissions from soils (volatilization and dust transport):

  a) Develop further understanding and modeling of soil-side transport processes, including plowing and bioturbation.

  b) Revisit underlying theories of mass-transport correlations for pesticides from the surface to the ABL.

c) Develop appropriate soil-to-air and plant-to-air partition coefficients for dry, damp and wet surfaces.

- There is a synergy in combining modeling with data collection, whereby models point out areas where experimentation is needed, and experimental results calibrate and improve models. Such synergy has been evident in the few studies where both measurements and models have been applied to estimating pesticide fluxes. There is a wealth of experimental data on pesticide emissions from local fields which has not been subjected to modeling evaluation, and this presents an opportunity to "mine" these data retrospectively for modeling.

- Validation of soil-air models on local scales may allow extension to regional scales, using GIS land use and pesticide application data to predict seasonally varying emissions. Such information could provide more quantitative input of pesticide source emissions to LRT models, thereby improving the link between regional usage and far-field exposure.

Comments, questions discussed

Comment: A comment was submitted in writing concerning the LRTP and P_{OV} estimates made by the OECD Screening Tool for Pesticide 2, (which was identified as pentachloronitrobenzene, PCNB).

Comment: It was pointed out by one Panel member that some statements in the White Paper (p. 161) concerning Pesticide 2 (PCNB) were incorrect. Specifically: "Pesticide 2 was detected in air over Saskatchewan despite no evidence of Pesticide 2 use in the monitoring area. In a study of long range transport of organochlorines based on detection in the snow of the Canadian Arctic, one of pesticide's degradate D1 was one of the most prominent pollutants found."

Comment: One Panelist emphasized the global transport characteristics of PBT pesticides and suggested that the traditional methods for risk assessment may be inadequate. This panelist noted that to evaluate the risk associated with a PBT pesticide, a higher level of scientific scrutiny and data generation may be needed.

Question: What is the relevance of detecting a chemical in a remote region? Is the single detection of a nanogram signal an important finding?

Response: There is likely no definitive answer. A key point is to note whether concentrations are increasing or decreasing with time; increases might require us to think about why. Again, no definitive answer here but the topic needs more discussion.

Question: Are emissions to air from PRZM used in any way for eco-risk in near field?

Response: Spray drift is included in PRZM. There is an atmospheric emissions module in PRZM, but it is not presently used.

Comment: There is a need to follow intermediate transport of pesticides, field to urban and surburban transport, from farm field to living room floor.

Question: With regard to LRT, pesticides have areal sources, not point sources. How can emissions over wide areas be evaluated for inclusion in LRT models? What role can trajectory analysis play in assessment of LRT?

Response: There is a way to evaluate pesticide air concentrations over wide areas through use of passive samplers, air shed maps, source region impact factors (which use trajectories).

Question: Have ppLFERs been applied to assess water-particle partitioning in aquatic ecosystems?

Response: The research groups in Switzerland are using ppLFERs to model partitioning to particles in both air and water. See Arp et al., 2008a, b; Götz et al., 2007, 2008, and references therein.

Comment: The Wania et al. "Arctic Contamination Potential" modeling approach could be adapted to receptor regions other than the Arctic to evaluate the transport potential between source regions and areas of interest such as The Great Lakes.

Response: A paper has been published in which "Mountain Contamination Potential" is introduced (Daly et al., 2007b). A "unit transfer matrix" has been developed to predict loadings of toxaphene to the Great Lakes Basin (MacLeod et al., 2002).

Question: What about application of the AGRO model to estuaries and oceans?

Response: There is no mention of estuaries specifically in AGRO. One participant thought that AGRO would not be appropriate for estuaries. Ocean transport models are not that sophisticated, because they do not take into account regional segmentation of water bodies within an ocean (e.g., the Arctic Ocean) or the multitude of currents. Ocean models are being evaluated more now and improvements are being made.

Question: How does riverine input compare to atmospheric transport/deposition?

Response: Older studies of large water bodies (e.g., Great Lakes, oceans) estimated that riverine inputs of PCBs and OCPs were small compared to atmospheric deposition. However, this has not been evaluated for CUPs.

Comment: As an overarching issue, U.S. EPA should include a greater consideration of the effects of temperature on the risk assessment of PBT pesticides. Discussion over the week highlighted this where temperature affects physical chemical properties (water solubility, vapor pressure, K_{AW}, K_{OA}), LRT processes and potential, chemical persistence, the biology of organisms and bioenergetics (lipid content, respiration rates, feeding rates) and chemical kinetics such as uptake and elimination rate constants.

Agency Charge

8) PBT Risk Assessment Issues

In this White Paper, the Agency describes a number of issues it has encountered when assessing persistence, bioaccumulation, toxicity and long-range transport in its aquatic and terrestrial ecological risk assessments involving pesticides with PBT profiles. In addition, the Agency has identified various methods and approaches that it is considering for refining its ecological risk assessment process specifically to address these PBT and LRT-related issues. Please comment on:

- The extent to which the Agency has identified and characterized the unique or problematic issues associated with assessing ecological risks of pesticides with PBT characteristics,
- The need for the Agency to incorporate refinements in the tools and methods it uses to assess ecological risks of these compounds

Panel Response

The Agency has identified and illustrated many of the unique issues related to the ecological risk assessment of PBT&LRT chemicals. A number of refinements to the OPP/EFED's existing assessment methodology and new hazard metrics or assessment methodologies have also been discussed. However, the Agency's approach continues to be focused on the field and pond scenario despite the recognition that a number of methods and assessment tools are available that are designed specifically for PBT&LRT chemicals. It is likely that this class of chemicals will require a very different modeling approach than has historically been used within the Agency and this possibility should be explored further. Significant modifications to current practice may be needed. However, the White Paper illustrates that the Agency is not only willing to address these issues but has made substantial progress towards identifying assessment methods that are more appropriate for this class of chemicals.

Please comment on the extent to which the Agency has identified and characterized the unique or problematic issues associated with assessing ecological risks of pesticides with PBT characteristics.

The Agency is to be commended for recognizing a number of unique issues associated with assessing ecological risks of PBT&LRT pesticides. The EPA did a good job with most of the scientific issues presented in the White Paper. Important aspects of PBT pesticides discussed in the White Paper include long-term accumulation of these pesticides on and near the site of application; identification of the appropriate forms (parent or degradates) of pesticide to include in fate and toxicological assessment; loss pathways for these pesticides through environmental and biological processes; long range transport potential and bioaccumulation of PBT pesticides in aquatic and terrestrial food webs. However, the review Panel found that some of these aspects could be highlighted for more detailed consideration along with some issues that were not discussed that should be considered.

The Panel's comments are consolidated into sections focused on chemical loss pathways, toxicity issues, source considerations, life cycle issues, fate and transport and issues of scale. The comments are focused on the challenges associated with these chemicals and do not assume that the Agency will adopt and/or develop any particular modeling framework. Discussion of modeling needs and opportunities are provided in other sections.

Chemical loss pathways

Understanding potential degradation pathways for persistent chemicals will be critical for understanding their long-term fate in the environment. In addition to the degradation processes included in the existing assessment methodologies, several specific degradation pathways were discussed by the Panel, including microbial degradation, transformation or movement with decomposers and metabolism.

The role of microbial degradation in reducing the concentrations of PBT pesticides in aerobic and anaerobic environments should be considered. Errors in estimating microbial degradation correctly may result in over- or under-estimation of exposure concentrations in both the aquatic and terrestrial environment. Microbial degradation may be difficult to estimate - results from laboratory experiments may be dependent on "site-specific" factors and may be difficult to generalize.

Decomposers should be included as a compartment in the food web models. The figure on page 32 of the White Paper should incorporate a trophic transfer to the decomposer trophic level. PBT pesticides will eventually enter the decomposer level when living material dies. Although some of these chemicals can persist and be redistributed in the environment, ignoring this important trophic level may result in errors in estimating the amount of PBT pesticides that are mobile and/or bioavailable. The decomposer pathway may also represent a unique transport mechanism by which chemicals are moved into pristine environments via migratory pathways of fish and oth

The Panel also agrees with the need to consider metabolism and metabolites very carefully because the metabolite may also be persistent and for reasons other than lipophilicity. There may be a need for an exhaustive review of measurements of these breakdown processes and models because, as recognized by the Agency, these breakdown products may ultimately be more important than the parent (example given for pesticide 4) that go beyond simple partitioning.

Toxicity issues

Chronic toxicity assessments are a critical issue. Biota will likely not be subjected to acute effects beyond the field/pond scenario but the long-term low dose from widely distributed chemicals may have important impacts that do not show up in current laboratory effects studies. Subtle, non-lethal chronic effects due to persistence of low doses of PBT pesticides should therefore be considered. Low-dose effects might include feminization or loss of reproductive capacity, behavioral changes that reduce the likelihood of reproduction or increase the likelihood of predation, and combined effects from multiple stressors (chemical, biological and physical).

Discussion of the likelihood of these types of effects should be included in the problem formulation. The long persistence of the PBT pesticides also suggests that mixtures between these pesticides and other persistent substances may present additional hazards that need to be addressed.

The distributed low-dose nature of these PBT&LRT chemicals makes it important to identify all likely target organisms for effects testing. For example, benthos and epibenthic organisms are not currently included in the effects assessment and may be particularly important for PBT chemicals. In addition, aquatic and/or marine mammals may represent a unique niche that is susceptible to the accumulation of PBT chemicals and subsequent effects.

Source considerations

Because PB&LRT chemicals persist and migrate over large spatial areas, there is a need to characterize the pattern and spatial scale of application beyond the single field scenario. The potential long term source of these chemicals in the environments, such as off-site transfers during applications and long-term re-emission from application sites will likely dictate how much of the chemical is added to the regional and/or global distribution so knowing the extent of application is an important part of the assessment. Just understanding the target pest and/or crop can provide bounding estimates for long-term area-release scenarios from multiple applications.

Current United States Department of Agriculture (USDA) projects may provide opportunities to look in greater detail at watershed scale behavior of chemicals. In 2003, the USDA initiated a multi-agency effort, the Conservation Effects Assessment Project (CEAP), to quantify the environmental benefits associated with conservation practices. The Agency may be able to use the modeling and monitoring data collected by CEAP to refine the fate and transport modeling of PBT pesticides. One goal of the CEAP is to develop a set of regionalized models to assess environmental benefits resulting from the adoption of conservation practices. Pesticides are an environmental stressor in several of the CEAP watersheds. The models used to simulate pesticide movement in the CEAP watersheds include many of the models discussed in chapter 4 of the White Paper including PRZM-EXAMS, APEX-EPIC, SWAT, BASINS, AnnAGNPS, and REMM. An object oriented modeling system to facilitate simulation model development, evaluation and deployment is another component of the CEAP modeling effort. Model performance of edge-of-field and watershed scale models is evaluated across a range of spatial and temporal scales in some of the CEAP watersheds. Watershed models that simulate the movement of PBT pesticides from the application site to regional water bodies will be necessary as the Agency evaluates their concentration and accumulation in environmental media over the period that these substances are likely to persist in the environment. The modeling effort underway in the CEAP watersheds may aid in the Agency's refinement of the models discussed during this Panel. The CEAP watersheds may also provide data to the Agency to evaluate sources and concentrations of pesticides measured in surface waters, sediments, soil and the atmosphere. For more information see the CEAP web site at: http://www.nrcs.usda.gov/technical/nri/ceap/index.html.

Ultimately, for these chemicals there is a need to know the overall contribution of pollutant loading to the environment beyond the area where it is applied over the lifetime of the product.

Lifecycle issues

The Agency must recognize that there is a shift in risk in space and time for chemicals that have PB&LRT characteristics. It will be important to consider the risk after 10, 20 30 years of use and the rate of clearance from the global system at the end of the chemicals useful life to limit the likelihood of surprises.

This issue relates to the aerial scale of use, which the Panel thinks is important for this particular class of chemical. This use pattern will ultimately impact the risk. There is also a temporal separation between the benefit and risk which may impact the way these compounds are assessed.

In addition, there is a social aspect that the Agency needs to be aware of for these chemicals because the risk and benefit may be separated in both time and space. There is particularly important for this class of chemicals that the Agency be very careful in considering the social dimension where risk may be distributed not only to other regions of the U.S but across international borders by long-range transport.

Fate and transport issues

The key aspect related to fate and transport for this class of chemicals is the need to understand transport well beyond the edge of the field. This will require not only longer range (time and space) models such as water sheds and atmospheric and long-range transport but also an understanding of the feedback linkages among environmental compartments. For example, the Agency must include clear bidirectional links between aquatic and terrestrial systems and across interfaces between individual compartments such as atmosphere and the forest canopy.

There is also a need to consider additional receptors as possible transport or exposure pathways for these pollutants. For example, spiders eat emergent insects and birds eat spiders, emergent insects (e.g., mayflies) and anadromous fish (e.g. salmon) can transport large amounts of carbon and, hence contaminants from aquatic to terrestrial systems. Another example is that at least 99% of PCBs are carried back into some of our most pristine watersheds by fish.

The ability of PBT pesticides to persist longer in the environment creates an opportunity for them to occur in unexpected locations. New exposure scenarios may need to be developed to minimize the opportunity that an important exposure pathway is missed. Identifying the perhaps unexpected environments where pesticide accumulation could occur will be crucial in characterizing the risks associated with these pesticides. Models can help in this area but also examining current agricultural practices may suggest the need for additional terrestrial or aquatic exposure scenarios.

Currently, the Agency estimates the expected concentration of pesticides in aquatic environments using a scenario that maximizes the transport of pesticides into a hypothetical agricultural pond by selecting soils with high erosive and runoff potential along with the regional meteorological data that maximizes precipitation in the growing area of the crop. The 10 ha cropped watershed drains directly into the agricultural pond in the scenario described in Table 2.2 of the White Paper. One Panel member noted that in the agricultural landscape of United States, a non-cropped area often separates the cropped field from a pond or stream. This non-cropped area contains a different cover type than the crop and often will contain a different type of soil. If the cover type over the non-cropped area reduces the surface water flow and traps more sediment than the cropped area, the PBT pesticides could accumulate in this area as runoff from the treated area passes through the non-cropped area. If the soil in the non-cropped area contains more organic material than the treated field or has other characteristics that maximize the retention of PBT pesticides, the concentration of the pesticides in the soil of non-cropped area may be greater than the concentration of the pesticides in the field. The types of organisms found in this non-cropped area may differ substantially from those found in at the application site. Terrestrial exposure scenarios should examine accumulation of PBT pesticides in soils of non-cropped areas that may be distantly removed from the treated field.

Irrigation with return flow to surface waters may also require development of new aquatic exposure scenarios and modeling tools. Tile drainage systems may not be captured in the fate and transport modeling scenarios described in the White Paper. Application of the pesticide in many fields over multiple years may also require development of a new aquatic exposure scenario. The Agency should systematically examine current agricultural practices to identify other exposure scenarios that will be needed to assess PBT pesticides.

Modeling at a range of details from the large scale environmental compartmental modeling approach to assess the overall mass balance to more detailed multiple compartment modeling systems representing organisms that partition P&B chemicals (e.g., liver and/or lipid) and organisms that feed selectively on "parts" (e.g., seeds or liver). Separating the mass balance component of the assessment from the food chain and food web dynamics may be appropriate given the range of modeling complexity needed to assess this class of chemicals.

Consideration of the issue of bound residues and implications for determination of persistence and bioavailability also needs to be expanded on. Although the White Paper discussed the effect of particulate and dissolved organic carbon on the bioavailability of PBT pesticides, in the linked PRZM-EXAMS model neither of these entities is dynamically modeled. Fixing the volume of the sediments, water volume, suspended sediments, particulate and dissolved organic carbon in the models may result in model behavior that is not representative of the aquatic system.

Scale issues

For this class of chemicals, the temporal scale may significantly influence the picture of risk. It may be 20 + years before we know if a PBT chemical is a problem and if the assessment does not consider the long term fate then we may miss important impacts. The biggest problem with PBT chemicals is that the benefit and risk are separated in time and space. This is a social aspect of the risk assessment process. Humans are very good at accepting short term gains at the expense of long term consequences. Lessons from the early-mid 20th century provide guidance on how important this is. It needs to be acknowledged and considered that the primary difference for PBT chemicals is the shift in risk both spatially and temporally.

Areal scale of use and areal scale of the assessment (i.e. moving away from a field scale assessment) are both important factors that need to be considered. These were not explicitly included as assessment issues discussed although they can have a profound effect on the results of the risk characterization. Further discussion would be needed to determine what the appropriate scale for assessment should be. It may be necessary to move to a completely different modeling approach that covers a much larger scale in time and space for this class of chemicals.

Please comment on the need for the Agency to incorporate refinements in the tools and methods it uses to assess ecological risks of these compounds.

Moving from the Agency's standard assessment to a PBT&LRT based assessment will definitely require refinements and the extent of refinement will vary depending on a range of external factors (policy) that are beyond the scope of this review, but also on factors that are specific to this class of chemicals as indicated in the previous section. The extent of refinement will differ depending on the particular issue to be addressed. What is proposed and demonstrated in the White Paper is a leap forward for the Agency and the refinements that have been considered are rooted in the science. In some cases, approaches are already in use by other groups in EPA or in other jurisdictions (e.g. states, countries) and the OPP/EFED should take advantage of this expertise and experience. Regardless of the path chosen by the Agency to assess these chemicals, the Panel strongly encourages them to base their advances, refinements and changes on the best available science and to make all practical efforts to verify any new/revised approach to the fullest extent possible.

At least one of the presentations (Dr. Gobas) suggested a pathway for developing and using models that include a number of well defined steps such as evaluation, calibration and applications. This philosophy is not new to the modeling community but given the issues facing OPP with regards to pesticides with PBT characteristics it is strongly recommended that the Agency re-visit the overall model development process and follow a balanced and systematic path in responding to this issue. The USEPA's Council for Regulatory Environmental Models (CREM) prepared a report within the past few years that has been reviewed by the Science Advisory Board on the overall process for developing, testing and using regulatory environmental models within the EPA. The OPP should consult this document because it highlights many of the suggestions that some members of this Panel have provided regarding model development and application and balancing the needs for relevance with the issue of model complexity and uncertainty.

The long-term accumulation of the PBT pesticides in soil and sediments will present new challenges in the use of the Agency's traditional aquatic models – PRZM, EXAMS, and Express – and terrestrial models. These models need to estimate concentrations of the residues of concern not only for the water column (as done at present) but also for soil, sediments, sediment pore water and terrestrial compartments and organisms both on and off-site. Long-term accumulation of PBT pesticides in environmental media due to combined carry-over from previous years will need to be addressed by the models. The model results presented on pages 63 to 67 of the White Paper are based on continued annual application of the PBT as well as persistence of the PBT material already applied. Running the model for the same duration while only applying the PBT pesticide during the first year would provide a way to examine the persistence of the pesticide without the confounding effect of additional applications.

Soils with high erosive and runoff potential are used in the model along with the regional meteorological data that maximizes precipitation in the growing area of the crop. Likewise, the scenario used to estimate soil concentrations also incorporates conservative assumptions designed to estimate maximum exposure in soil. Reliance on these two extremes may cause the Agency to miss other areas where PBT pesticides may persist and accumulate in agricultural environments and in areas that are well beyond the range typically considered in pesticide assessments. In short, the consideration of spray drift as the primary off-site transport process will not capture the potential for accumulation in the Great Lakes and/or Arctic regions.

Identifying the perhaps unexpected environments where pesticide accumulation could occur will be crucial in characterizing the risks associated with these pesticides. Linking the air, water and terrestrial models and using representative application and agricultural production scenarios could point out new areas of concern. Use of good agricultural practices, such as implementation of buffers or conservation tillage, in exposure scenarios may identify unexpected places where exposure may occur near application sites. Currently the aquatic and terrestrial scenarios, run separately, may not consider the deposition and possible accumulation of a PBT pesticide in a grassy buffer strip between the treated field and a water body. Total accountancy between air, water and terrestrial models with respect to PBT residues should be examined. In fact, the balance of mass in the predictive models for PBT&LRT chemicals is critical to understand the impact of potential feedback mechanisms and transport process in the environment.

New approaches to estimate the effect of PBT pesticides on food webs were suggested to address the bioaccumulation of these substances. The comparison between these approaches suggested that the modeling approaches had the advantage of being less costly in terms of time and resources than the laboratory or field mesocosms or monitoring studies. It is strongly recommended that the Agency commit additional resources to identifying appropriate data sets to be used for validation of the new food web models.

Mechanisms that reduce the concentration of PBT pesticides in organisms should be explicitly considered as well as those processes that increase the concentration. Metabolism or excretion of PBT pesticides within the organisms in the food web affects the concentrations predicted in biota (Pesticide 4 p. 144 {White Paper}). Estimating the parameters necessary to run the food web models requires more data than usually available. Validation of these models is essential to increase confidence in their use.

The fact that this particular class of chemicals presents hazards on a very different scale than pesticides without PB&LRT characteristics is illustrated by the difference in models that have been developed to assess these chemicals. While short lived chemicals that are not highly mobile in the atmosphere (relatively low volatility) have led to models like PRZM/EXAMS or PRZM/AGRO, and the high volatility chemicals that are relatively short lived have led to the development of detailed air dispersion models like ISCST3 or AERMOD (among other), chemicals with relatively high mobility and longer half-lives in the environment have been the basis of multimedia mass balance models like ChemCAN, SimpleBox, CalTOX and TRIM.FaTE (among others). The features in these mass balance models that may be lacking in the other modeling approaches are the ability to conserve mass (mass balance), the inclusion of feedback mechanisms (multimedia compartmental), the ability to consider spatial scale in the assessment (near-field, far-field, regional, continental, global) and the ability to consider temporal scale at a level which is relevant to persistent chemicals (i.e. the full lifecycle of the product).

Agency Charge

9) Example Pesticide Assessments

In this White Paper, the Agency provides examples of how it has assessed the environmental persistence, bioaccumulation, toxicity and long-range transport of several unidentified pesticides using refinements to its ecological risk assessment methods. Given the data available, as illustrated in the pesticide examples provided in the White Paper, please comment on:

- Whether the Agency has used these data appropriately to the fullest extent possible in assessing ecological risks of pesticides with PBT characteristics
- Methods it has used to characterize environmental persistence, bioaccumulation, toxicity and long-range transport potential of the example pesticides.

Panel Response

Some of the Panel members recognized and acknowledged that the proposed approaches and methods used for the example pesticides represent a significant change to the current approach to ecological risk assessment. There was general consensus that the Agency appears to be on the right path towards being able to better assess pesticides with PBT characteristics, although there remain many details still to be addressed or worked out.

Further, the Agency should be commended for offering real chemicals as case studies to illustrate the challenges related to PBT&LRT chemicals and to explore the tools and methods that are currently available for both screening and assessing these chemicals. The examples were informative and useful. In general, the examples demonstrate a willingness in the OPP/EFED to adapt their standard modeling approach in response to the unique challenges presented by this class of chemicals. For example, the Agency is clearly interested in improving the way their current models include sediment dynamics to improve the models applicability to POPs. However, the Agency's interest in improving or adapting the existing field scale assessment models assumes that these types of models are the appropriate next step in assessing chemicals that are flagged as PBT&LRT by screening tools.

Finally, the Panel stated that there also need to be a dialogue between risk assessors and risk managers to ensure that the results are a) fulfilling the needs of the risk managers and b) interpretable and understandable by the risk managers, including the degree of variability and uncertainty.

- ***Whether the Agency has used these data appropriately to the fullest extent possible in assessing ecological risks of pesticides with PBT characteristics***

A couple of Panel members thought that the question was slightly loaded. Given what EPA had to work with, the Agency provided a good outline of the process and results of analyses.

Two aspects need to be considered in responding to this question; first the registrant submitted data; and second the other data/information which is used to help characterize the risk (e.g. non-chemical specific model inputs, assumptions).

With respect to the registrant submitted data, for the most part it appears that the Agency attempted to use the data provided. Without understanding or having access to the context of the data used, it is difficult to judge if it has been used to its full potential. There were few cases, where faced with a range of values, rather than choose a single conservative input, they performed their analyses with values bracketing the range to understand impacts on outputs. However, there were more cases where only one value was chosen when multiple values or ranges were available (e.g. Kow for pesticide 4). In a tiered approach, the use of conservative values is often used in earlier tiers to help focus on areas where further characterization of hazard or risk is needed, providing an efficient way of proceeding with a risk assessment. However, it needs to be noted that this needs to be balanced with understanding the range of potential hazard or risk which should be part of the risk characterization.

With respect to other types of information/data which is used to help characterize risk, and specifically the non-chemical specific data which are used in models, input values are often used which are based on empirical data. The extent to which certain inputs values are fixed is model and context dependent. Information on the reasoning for fixing certain values should be presented, as well as the basis for choice of particular values, and the potential impact on modeling results (i.e. model sensitivity) should be apparent. To some extent the White Paper partially covers these for certain issues, for example the fixed input values for suspended sediments in the model farm pond scenario (based on NAQWA data), or for PRBEN input parameter in EXAMS. In other cases, it is not discussed. It should be acknowledged that this particular SAP was not specifically intended to address these types of questions.

- ***Methods it has used to characterize environmental persistence, bioaccumulation, toxicity and long-range transport potential of the example pesticides.***

With respect to methods and approaches, when examined across the issues discussed, several common themes emerge which from a scientific perspective may affect, to varying degrees, the ultimate acceptability and interpretation of proposed approaches. When considering further work, these topics should be considered.

These include:

- Characterization of uncertainty/variability of models
- Identification of assumptions for models, methods or approaches
- Assessment of model performance (can be addressed through mining of data on historical use PBT pesticides)
- Understand model sensitivity to key parameters
- Suitability of existing studies/protocols for use in assessment of PBT pesticides
- Suitability of existing data requirements for use in assessment of PBT pesticides
- Incorporation of scenarios/models that go beyond field scale assessment and/or that are representative of different receiving ecosystem scenarios
- Consideration of appropriate temporal scales
- Definition of tiered approaches where applicable

As an overarching issue which needs to be considered in the interpretation of existing data and potentially also for study protocol modification or development, the Agency should include a greater consideration of the effects of temperature on the risk assessment of PBT pesticides. Panel discussions highlighted where temperature affects physical chemical properties (water solubility, vapor pressure, Henry's Law Constant, Koa), LRT processes and potential, chemical persistence, the biology of organisms and bioenergetics (lipid content, respiration rates, feeding rates) and chemical kinetics such as uptake and elimination rate constants.

There are logical links between the models and methods proposed for consideration (e.g. EPISUITE - PRZM – EXAMS – QWASI or PRZM-AGRO). EPA needs to be cautious about building a house of cards through the chaining/compounding of uncertainty in models. At some point the resulting uncertainty may render the results less than ideal for making decisions.

To provide context to the response of this question the response roughly follows the topics and issues outlined in Table 8.1 of the White Paper.

Environmental Persistence

Combined Exposure - The use of a progressively more refined approach depending on data availability is logical. The three methods described are generally scientifically acceptable. The Agency will want to ensure that in the future transformation studies are conducted to allow use of Formation Decline method (i.e. are designed to allow for determination of kinetic rate constants for parent and transformation products). In general, if total residue (TR) or residue summation methods (RS) are to be used, there is a need to better understand variability between results from using different methods. This could be addressed through the mining of existing available data.

Aqueous Solubility – Proposed changes to models to incorporate "precipitate" compartment appear scientifically sound. Other methods (e.g. hockey stick) might also be considered as a fix (see Q3 response). This issue needs additional work to better understand differences between laboratory and field solubility and potential impacts in differences on a) interpretation of toxicity data and b) results of modeling (could be addressed through data mining). In addition, the assumption of only freely dissolved chemicals being bio-available is a key assumption in the interpretation of study data and the use of modeling results which may require further investigation.

Degradation half-lives – The Panel generally agreed that a whole system half-life is good for characterization of overall persistence in aquatic ecosystems.. This is vital information in understanding how pesticides behave once released into the environment. It is generally agreed to be an artifact of the study design. From a risk assessment perspective it is generally regarded as a conservative approach when distribution will be dominated by adsorption to suspended matter or the sediment (i.e. high Koc or Log Kow >5). It might be appropriate for use in an initial tier assessment. The Agency should also consider the possibility of revising the experimental design so that ambiguity is eliminated in data interpretation and parameters generated may be useful for fate and transport modeling.

Persistence in Soil/Sediment – The use of PRZM to examine year to year carry over in field soil is a science based, logical first step. The Agency may want to consider examining how this might be further refined (e.g. mimicking potential crop rotation) in subsequent tiers/refinements. The EPA could look at field dissipation studies results to help assess model performance for end of season carry over. Also modeling over different use scenarios for a given chemical could help characterize the variability.

For sediment, these issues need to be integrated with sediment dynamics & issue of burial and bioavailability, the key issue being burial which needs to be better defined before adjusting models and receiving water scenarios appropriately. This may include development of additional receiving water scenarios to adequately characterize the impact of differential sediment dynamics in different types of receiving water body scenarios (e.g. static and flowing).

Sediment Dynamics

It was generally agreed that incorporating sediment dynamics into modeling was necessary for the assessment of PBT pesticides. It is further noted that this issue is scientifically very complex as indicated by the breadth of subjects covered in the discussion and response to question 3.

Based on the scenarios presented by EPA, there was general agreement that burial was an important process to consider, but there were questions of the appropriateness of the rate of permanent burial used in the modeling, which represented a high erosion scenario. In addition, there is concern that what is buried has not disappeared, only temporarily out of circulation. Experience with PBT chemicals shows it can and will come back. For PBT chemicals, redistribution among and between environmental compartments is a key factor to be considered in problem formulation and risk assessment as it should inform the temporal and areal scale of the assessment (not only for sediments!).

Several Panel members suggested that, at least for PBT chemicals, serious consideration needs to be given to developing additional receiving water scenarios, including those for flowing water systems. This recommendation was evident in discussions of several of the charge questions.

Bioaccumulation

Aquatic – For aquatic systems an approach using of multiple lines of evidence has merit. Use of food web bioaccumulation models is consistent with what has been used elsewhere within EPA (e.g., Office of Water, etc) and appears to be scientifically supportable/reasonable. There is a need to settle which model is appropriate and determine appropriate scenario(s), then address the common issues listed above. EPA should consider that dynamic models may be appropriate for field scale assessments, but for far-field assessments steady-state may be appropriate for characterization of future potential contamination. For those chemicals which bioconcentrate is persistent, EPA should consider seeking additional data and the modification of existing protocols to help decrease uncertainty. For example, given the distinct possibility that bioaccumulative chemicals will not reach steady-state in the timeframes of standard protocols, there will be a need to rely on estimated rate constants (k1 and k2) to get BCFs. This means there will need to be some effort exerted on refining sample effort and timing. In addition, for larger animals, it may be necessary to measure residues in multiple compartments/tissues. (e.g., liver).

As with most of these issues, a tiered approach to assessment of bioaccumulation should be developed.

Terrestrial – Currently EPA has only some proposed potential screening methods for consideration of terrestrial bioaccumuation. Some potential models for risk assessment have been identified but additional work is needed to determine their potential suitability for use in a regulatory context. In addition stronger links between aquatic and terrestrial models – (e.g., spiders eat emergent insects and birds eat spiders) will be needed to model bioaccumulation through interactions between terrestrial and aquatic systems.

Toxicity

The use of Tissue Residue Values (TRVs) in pesticide risk assessment of PBT active ingredients is consistent with the approach taken by other groups within EPA. The science behind TRVs is understood and is well characterized in supporting documentation provided by EPA. There was a challenge identified for work on chronic toxicity issues and using TRA. This is especially important when considering the potential need to have population level effects as assessment endpoints.

The focus of toxicity discussions was on the use of Tissue Residue Values or critical body residues to alleviate some of the issues related to the interpretation of toxicity data for PBT pesticides (e.g. multiple exposure routes, exposure times) and in order to more effectively use and interpret waterborne exposure studies for chemicals which will likely have diet as the primary exposure pathway. The use of Toxicity Units (TUs) and Toxicity Equivalence Factors (TEFs) approaches were mentioned in the White Paper but not in the questions. The assumption of additivity needs some support when considering these approaches. This is especially important if there are co-applications of different pesticides. Criteria or guidance on when it is appropriate to use the assumption of additivity may be needed.

There is a need for EPA to consider modification of existing study protocols to incorporate the requirement for tissue residues, and possibly the development of dietary exposure studies for aquatic organisms. For toxicity tests which incorporate measured residues in test organisms, questions need to be addressed regarding which dose in test is used to measure body residues? How often are measurements needed (at end only or during interim times)? EPA may need to consider modifying the data requirement to allow ET50 type experiments and measuring residue levels at different times. In addition there is a need to clarify which organisms to sample (e.g., dead, moribund, alive) and if tissue specific sampling is needed.

LRTP

For consideration of the potential for long-range transport of pesticides, several existing models were identified and available for classification/screening. All are well rooted in science (e.g., OECD model, GloboPop, Wania et al., 2006) and some are already used in other jurisdictions. There was general consensus that existing models are suitable for screening and a tiered approach for screening has been suggested by the Panel. Assumptions and data use (like upper 90%tile or mean values as data inputs for models) would need to be clearly specified.

If using the OECD model, the Panel suggested the EPA should consider using in Monte Carlo mode or using a range of input values for parameters to assess variability in LRT potential. The Agency might also consider developing a comparison set of pesticides based on past historically used pesticides (e.g. chlordane, lindane, endosulfan, DDT/DDE, etc) and existing chemicals which are known not to be subject to LRT in order to provide context to results.

Consideration should be given to including Koa and Kwa as additional data requirements as these are important inputs for screening models. The Agency will need to investigate availability of protocols for Koa/Kwa to ensure data is consistent and scientifically sound.

With respect to assessment of far-field concentrations, suggestions were made on how to link near-field applications with far-field through the consideration of using existing data on historically used pesticides as the basis to develop transport models for estimating input/loadings to far-field systems.

When moving beyond a screening level assessment, using the current assessment approach with the available data would not provide an accounting of the chemical mass or the specific hazards that are captured by the OECD screening tool. At a minimum, the data needs to support an assessment that estimates how much of the applied mass is transferred to the pond, how much remains/accumulates on the application site and how much is lost by other transfer/transformation pathways. This information would then need to be scaled to represent the expected use rate of the product being considered. This information is particularly important for determining the mass that is transferred from all of the different applications sites to the local areas (urban/agricultural interface), region and global scale. Consideration to using a nested multimedia mass balance modeling approach is necessary to assess the hazards/risks posed by chemicals that are flagged by the OECD tool. These nested mass balance modeling approaches are available and the existing data set seems adequate to supporting such a modeling assessment. Further exploration in this area may be warranted.

Additional Considerations

The Agency should expand the aquatic fate-transport modeling scenarios to include a flowing water and estuarine scenario in addition to the agricultural pond. While not specifically addressed in the White Paper, it is clear that the Panel felt it is important to expand the toolbox of receiving water scenarios. It is also important to include a modeling scenario that will address the application of a PBT pesticide to multiple fields over multiple years. The persistent nature of these pesticides, coupled with their ability to move long distances from the application site, makes it likely that low concentrations of PBT pesticides applied each year to different fields will result in accumulation of the pesticides in regional water bodies receiving drainage from many agricultural areas.

Linking the air, water and terrestrial models and while using application and realistic agricultural production scenarios could point out new areas of concern. Use of good agricultural practices, such as implementation of buffers or conservation tillage, in exposure scenarios may identify unexpected places where exposure may occur. For example, currently the aquatic and terrestrial scenarios, run separately, may not consider the deposition and possible accumulation of a PBT pesticide in a grassy buffer strip between the treated field and a water body. Total accountancy between air, water and terrestrial models with respect to PBT residues should be examined.

For LRT potential, if the Agency follows the EPA Office of Research and Development (ORD) approach of ecosystem services, where their value of services is inversely proportional to human density, then there are issues within FIFRA that need to be addressed.

Consideration in the overall development of risk assessment approaches for PBT chemicals to issues/treaties/laws dealing with trans-boundary effects or with PBT chemicals in general. The question must be asked and considered if the Agency needs to be concerned about existing treaties/accords etc which may influence what needs to be characterized and how it is characterized (e.g. UNECE POPs, Stockholm Convention, etc).

The Agency should use existing data from PBT pesticides that have previously been registered – and possibly no longer are in use – to evaluate the current methods of identifying exposures of concern. If the Agency's current exposure assessment practices do not identify these older, cancelled products as problematic, the current practices need revision. Performing these case studies with the older products will increase confidence that the current practices can also be applied to PBT pesticides and will identify the types of deleterious effects associated with PBT pesticides. The data collected in the FIFRA-required environmental fate and ecological effects tests could be used to verify that the models are correctly calculating some of the internal variables used in the model.

Agency Charge

10) Future PBT-Related Refinements

The Agency is considering refinements to its problem formulation process to improve the ecological risk assessment of pesticides with PBT characteristics, as outlined in Chapter 8 of the White Paper. In particular, please comment on:

- The Agency's proposed process for identifying (screening) pesticides for potential PBT risk assessment issues that need to be addressed.
- The priority for developing new models, methods, and information for addressing PBT issues.

Panel Response

As a first step, the criteria listed for identifying persistence, bioaccumulation potential and toxicity (in Table 8.2, National and International Screening Criteria for Classifying Chemicals According to PBT and LRT Characteristics) appear to be reasonable.

Meeting the criteria for a particular attribute will help the Agency identify where it should focus its efforts.

As many of these criteria are broad ranges, the Agency may want to evaluate the lower end of these ranges and analyze the sensitivity of models and/or whether some of these criteria may need to be modified.

As an alternate screening criterion, as suggested by one Panel member, can the Agency identify a Level 3 fugacity model that could provide an overview of distribution to various media? This alternate model would provide a more informed means of investigating persistence and would allow the Agency to determine which compartment should be the focus of additional investigations or modeling efforts.

The relevance of using acute toxicity for bioaccumulation and persistence is not clear as a criterion for these screening chemicals. The major toxicity concerns with persistent and/or bioaccumulative chemicals are typically sub-lethal effects resulting from chronic exposure. Considering chronic studies are available from data packages for registration, alternative screening criteria could be developed.

The Agency should consider adding Koa or use one of the screening type models discussed.

One of the Panelists also provided several comments regarding risk assessment associated with the LRT issue. Long-range transport can in part be viewed as being similar to what happens in a chromatography column where the chemical signal peak broadens with time or distance and you also get a dilution effect with distance. This results in chemical loadings to ecosystems tending to be lower with distance from source (although another Panelist mentioned the unique character of the Arctic that might break with this pattern) and the signal is less variable over time (i.e., peaks flatten out). At some distance (not sure how far, and also depends on chemical properties) the use of a steady-state bioaccumulation modelling approach becomes a reasonable Tier I strategy for evaluating bioaccumulation potential. Assuming that one uses the same generic pond and food web scenario as a LRT receptor, these steady-state models will yield the same BAFs for organisms which would just have to be scaled to the chemical loading to yield predicted concentrations. Regions closer to the source with greater temporal variability in loadings would still require dynamic modeling.

Regarding the adaptation of the Wania "Arctic Contamination Potential" modelling approach, a Panelist indicated that there is no reason this approach could not be adapted to "receptor regions" other than the Arctic to evaluate the transport potential between source regions and areas of interest such as The Great Lakes.

Again considering long range transport, one of the Panelists indicated that if we follow the ORD approach of ecosystem services, where their value of services is inversely proportional to human density, then there are issues within FIFRA that need to be addressed.

As an overarching issue, one of the Panelists suggested that the USEPA should include a greater consideration of the effects of temperature on the risk assessment of PBT pesticides. Discussion over the week highlighted this where temperature affects physical chemical properties (water solubility, vapor pressure, Henry's constant, Koa), LRT processes and potential, chemical persistence, the biology of organisms and bioenergetics (lipid content, respiration rates, feeding rates) and chemical kinetics such as uptake and elimination rate constants.

On the priority for developing new models, methods, and information for addressing PBT issues (See Revised Table 8.1 (below)):

Table 8.1 Current Challenges Associated with Ecological Risk Assessment of Pesticides with PBT Characteristics.

Topic Area	Current Risk Assessment Issue	Comments	Priority
Environmental Persistence:	1. Quantifying exposure to combined parent and degradation products	Look across a larger group of chemicals to see how the results differ from TR or RS to FD	MEDIUM
	2. Interpreting predicted or measured exposure concentrations that exceed solubility	a) Need additional research to understand differences between laboratory solubility and apparent solubility in "real water"; note – this is not an issue if CBR is used	HIGH
		b) Develop a better understanding of the importance to incorporate transfer kinetics to support a precipitate compartment in the model	MEDIUM
	3. Interpreting degradation half lives when dissipation processes dominate	a) Experimental artifact needs to be resolved; could be resolved through modified data requirements.	MEDIUM
	4. Quantifying long-term exposure (multi-year carryover) in soils, sediment and pore water	a) Covered with existing models	Not applicable
		b) Assessing model performance in estimation of sediment concentrations	MEDIUM

Table 8.1 Current Challenges Associated with Ecological Risk Assessment of Pesticides with PBT Characteristics (cont.).

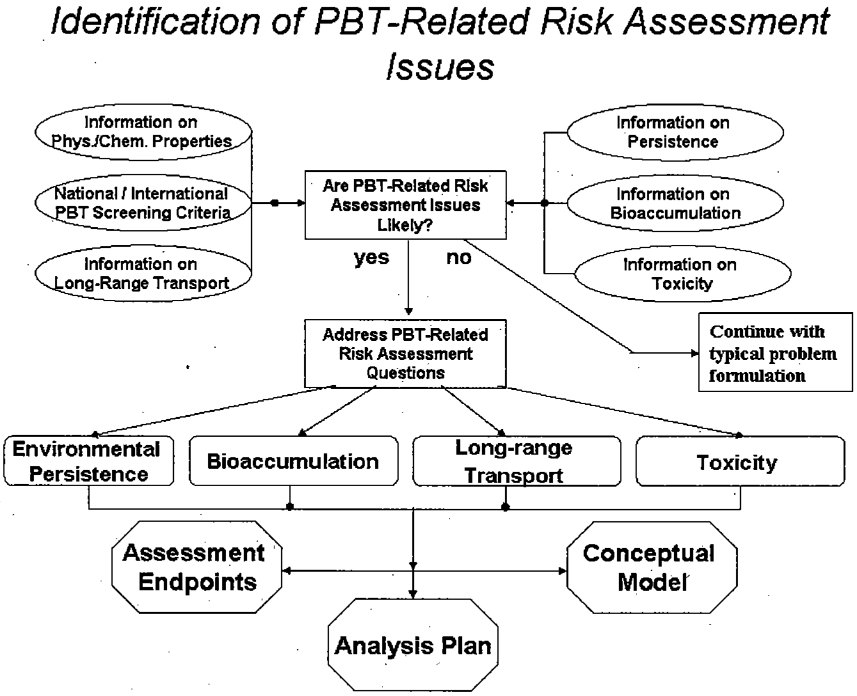
Topic Area	Current Risk Assessment Issue	Comments	Priority
Sediment Dynamics	1. Understanding the impact of sedimentation processes on pesticide bioavailability in the context of model agricultural pond systems	a) May depend on modeling approach	LOW
	2. Identifying and quantifying the principal processes related to sediment dynamics in these systems	a) Need a better understanding of sedimentation/burial/influent bioperturbation rates b) Development of additional receiving water scenarios	HIGH HIGH/MEDIUM
	3. Identifying appropriate methods for modeling these processes for OPP/EFED aquatic exposure assessments	a) Assess existing models beyond PRIZM/EXAMS and AGRO	LOW
Bioaccumulation	1. Quantifying pesticide exposure via the aquatic food web	a) Relative to other pathways, well-characterized; need to develop tiered approach	HIGH
	2. Interpreting and integrating results from lab-, field-, and model-based bioaccumulation methods	a) Assess model assumptions and performance (sensitivity analysis); b) Incorporate biomagnifications tests and models	HIGH HIGH
	3. Assessing bioaccumulation potential in terrestrially-based food webs	a) Identify all existing models for assessing bioaccumulation b) Explore/assess existing models to better understand implications of and magnitude of terrestrial bioaccumulation	HIGH MEDIUM
	4. Explore the links between terrestrial and aquatic bioaccumulation	a) Assess model performance b) Consideration of additional terrestrial links to model	MEDIUM MEDIUM

Table 8.1 Current Challenges Associated with Ecological Risk Assessment of Pesticides with PBT Characteristics (cont.).

Topic Area	Current Risk Assessment Issue	Comments	Priority
Long Range Transport	1. Establishing relationships between near-field pesticide loadings and far-field pesticide concentrations	a) It may be possible to resolve this issue by following current literature (i.e., this issue is being investigated in other venues); or, explore the possibility of using existing data on POP or LRD pesticides (e.g., chlordane, DDT/DDE, etc.) to establish this relationship b) Needs to be a dialogue within Agency with regards of how to translate long-range transport into risk estimates	MEDIUM MEDIUM
	2. Understanding the applicability and reliability of available models for screening long-range transport potential	a) As a screening tool, the existing models are appropriate; develop tiered approach b) Integrate existing models	MEDIUM MEDIUM
Toxicity	1. Estimating combined toxicity of parent and degradation products	a) For any toxicity assessment (esp., TRA) the toxicity of the individual metabolites needs to be addressed. Protocols should also consider including carrier influence on bioavailability, bioaccumulation and toxicity b) Examine the possibility of modifying test protocols to obtain residue levels in tissues	MEDIIUM MEDIUM
	2. Assessing toxicity due to multiple exposure routes and steady-state conditions, both of which may not be adequately evaluated in standardized laboratory toxicity tests.	a) Assess the performance of different models for estimating CBR when measured residues are not available and/or field methods to evaluate multiple exposure routes & steady-state conditions	MEDIUM

The Panel also discussed the role of modeling in directing risk assessments for all pesticides and in particular its use for PBT chemicals. As part of the Agency presentation on refinements to problem formulation Figure 1 below was presented. One Panel member indicated that the role of modeling seemed to be peripheral to the process, whereas the complexity of the issues discussed seemed to suggest the need for a much more formal role for models.

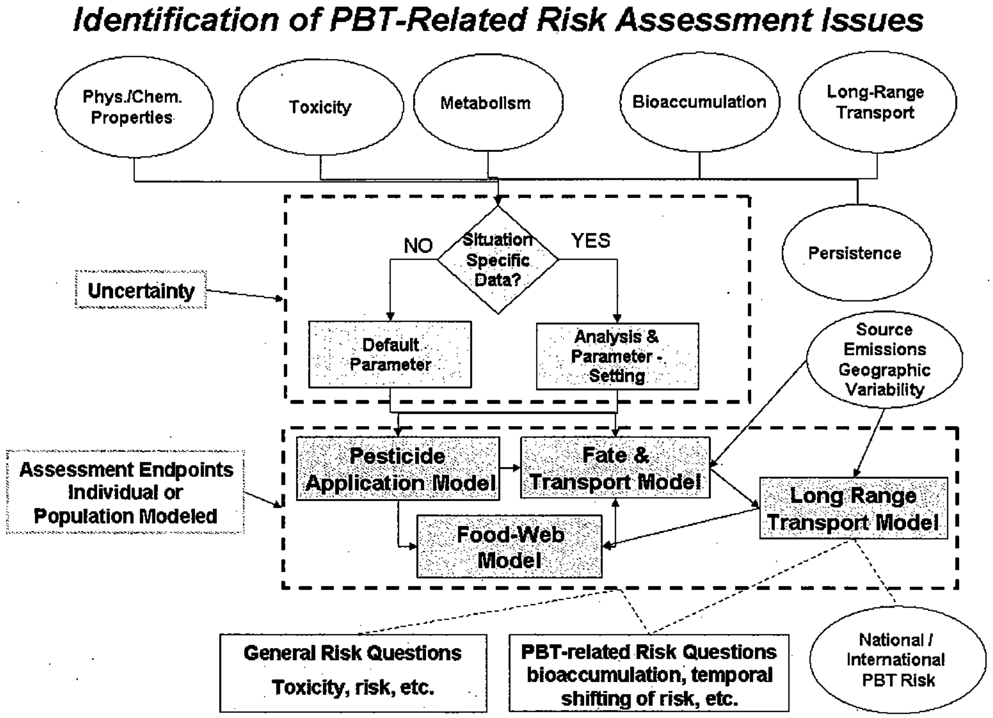
Figure 10.1 Agency view of the PBT issues development process



The Panel pointed out that models can serve a number of roles, including

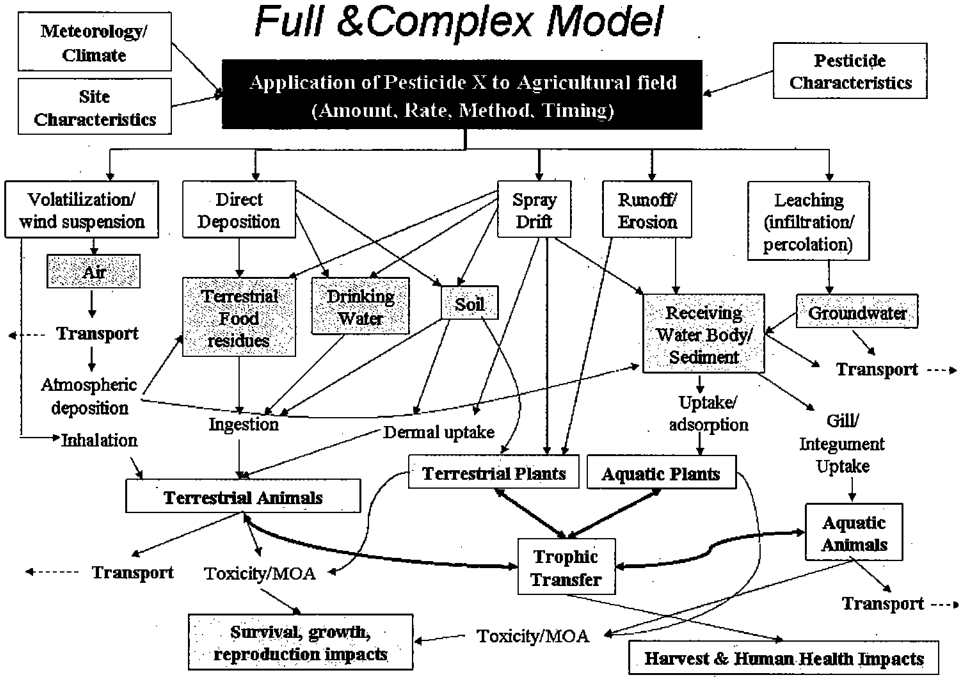
- integrator of what we know.
- leveler for comparisons.
- means of gaining insight into expected effects.
- focus for data analysis/ collection.

Figure 10.2 Modified view of the role of modeling in identifying risk assessment issues for PBT chemicals



In Figure 10.2 the problem formulation process can be viewed as a three part process. In the first stage, what information is available on physical/chemical properties, toxicity, metabolism, bioaccumulation, long-range transport and persistence is collected and a decision is made as to whether it can be used to replace default parameters needed for input to the models. In addition, the uncertainty on these parameter estimates can be quantified. In the second stage the assessment endpoints are identified. In the final stage, the model is modified to accommodate the specific assessment endpoints.

Figure 10.3 Proposed full complex model framework



An attempt at a full complex model framework was provided by one Panel member and was discussed by the full Panel (see Figure 10.3). It was pointed out by this one Panel member that what EPA seems to do in risk assessments is to build models specifically for each assessment in what can be called a forward approach, that is, components are added as needed to a core model. This was seen in how AGRO was added to the EXAMS and PRZM models. An alternative approach was suggested. This approach, referred to as a backward approach, has assessments starting with the full and complex model. At the problem formulation stage of an assessment, components are subtracted from the full model once it is determined they are not needed to address the selected target endpoints. In addition, the full model can be used to illustrate why certain paths/processes/sinks are not important. In this process, subtracting becomes one of the main tasks of the problem formulation. The full model framework becomes something like a checklist for the assessment.

The Panel discussed this proposal for a radical change in the use of models in risk assessment and the approach to selecting the appropriate model for an assessment. The Panel felt that no one model would likely satisfy all situations or all scientists. The Panel debated how one might define the initial complexity of the model, what constraints would have to be placed on the model, the role of experimental data in defining model complexity. Many Panelists felt that when EPA asks for a model or in general when a model is developed, it must be done in the context of the purpose to which the model is to be used and the accuracy to which predictions are needed. In addition, components which do not add significantly (<10% of explained variability) to the predictions should not be included. Extremely accurate or extremely realistic models may not be particularly useful to EPA for risk assessments. Other Panelists felt that it was not necessary to build the most complex model, but models which might prove useful for the broadest class of situations. In addition, how are risk assessors to know the full importance of certain processes unless they are examined within the context of the full and complex model? The growth in use of models by scientists in general should be reflected in the future practices of EPA risk assessors.

One Panelist indicated that the approach being discussed sounded a lot like the FRAMES-3MRA (Multi-media, Multi-pathway, Multi-receptor Risk Analysis) modeling approach being developed by EPA-ERD. This system has been used in assessing risks for Hazardous Waste Identification Rule (HWIR) in the EPA Office of Solid Waste (http://www.epa.gov/athens/research/projects/3mra/index.html).

From the risk assessor view, models are simply mathematical representations of reality, a tool which aids the risk assessor in characterizing concentrations and toxicity, and explore relationships, to do the job simply and efficiently. Other types of models, for example, mesocosm models allow us to experiment, measure, and produce the data against which the models are validated. The goal is to find a balance between the two approaches, ensuring that we don't make the wrong decisions, support making decisions within the framework of uncertainty.

The Panel discussed how to ensure a return on the efforts needed to create consolidated models. Current model building is to link current model components. Such linked models typically lack key feedbacks links. Some Panel members suggested caution in how the models are grown. There was discussion about the necessity when assessing PBT chemicals to utilize fully coupled models because the links and feedback are more important than is typical. Others suggested that building such complex models may not be very practical. Models often take on a life of their own. Users don't understand how they work. For this same reason there is often need for in-house control of the model development.

Some Panelists were more comfortable with an experimental approach, Models make them uncomfortable. There was a feeling that current fate models do a decent job of prediction but models to predict effects often cannot approach the accuracy and information collected in experiments.

The Panel discussed the need to incorporate time and space dimensions into these models. Terrestrial ecosystems tend to be spatially larger and operate on a different time scale than is typical for pond systems; hence there is a discontinuity between models of the two. In many assessments, the spatial or aerial scale extent is never explicitly specified. In addition, since models have to be bounded at some point, the importance of processes that predict net losses of the chemical must be examined. Time scales from 2 weeks to 200 years may have to be modeled.

Finally, two Panelists noted that there are lessons to be learned from the early-mid 20th century regarding the importance of long term ecological consequences from the use of PBT pesticides. Thus, some of the problems associated with evaluating the risks from PBT pesticides may have been considered previously. One Panelist also emphasized the global transport characteristics of PBT pesticides and suggested that the traditional methods for risk assessment may be inadequate.

This panelist noted that to evaluate the risk associated with a PBT pesticide, a higher level of scientific scrutiny and data generation may be needed.

REFERENCES

Ackerman, L.K., Schwindt, A.R., Simonich, S.L.M., Koch, D.C., Blett, T.F., Schreck, C.B., Kent, M.L., Landers, D.L. 2008. Atmospherically deposited PBDEs, pesticides, PCBs, and PAHs in Western U.S. National Park fish: Concentrations and consumption guidelines. Environ. Sci. Technol. 42:2334-2341.

AMAP, 2004. AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. xvi +310 pp.

Armitage, J.M., and Gobas, F.A.P.C. 2007. A terrestrial food-chain bioaccumulation model for POPs. Environ. Sci. Technol. 41:4019-4025.

Arnot, J.A. 2008. Assessing the exposure, hazard and risk of organic chemicals. PhD Dissertation, Environmental and Life Sciences Graduate Program, Trent University, Ontario Canada. 434p.

Arp, H.P.H., Schwarzenbach, R.P., Goss, K-U. 2008. Ambient gas/particle partitioning. 1: Sorption mechanisms of apolar, polar, and ionizable organic compounds. Environ. Sci. Technol (in press).

Arp, H.P.H., Schwarzenbach, R.P., Goss, K-U. 2008. Ambient gas/particle partitioning. 2: The influence of particle source and temperature on sorption to dry terrestrial aerosols. Environ. Sci. Technol. 42:5951–5957.

Atkinson, R., Guicherit, R., Hites, R.A., Palm, W-U., Seiber, J.N., de Voogt, P. 1999. Transformations of pesticides in the atmosphere: a state of the art. Water, Air, Soil Pollut. 115:219-243.

Bailey, R., Barrie, L.A., Halsall, C.J., Fellin, P., Muir, D.C.G. 2000. Atmospheric organochlorine pesticides in the western Canadian Arctic: Evidence of transpacific transport. J. Geophys. Res., [Atmos.] 105:11805–11811.

Barron M.G., Hansen, J.A., Lipton J. 2002. Association between contaminant tissue residues and effects in aquatic organisms. Rev Environ Contam Toxicol 173:1-37.

Beckvar, N., Dillon, T., Reed, L. 2005. Approaches for linking whole-body fish tissue residues of mercury or DDT to biological effects thresholds. Environ. Toxicol. Chem. 8:2094-2105.

Berner, R.A. 1980. Early diagenesis-a theoretical approach. Princeton University Press, Princeton, NJ.

Bidleman, T.F., and Leone, A.D. 2004. Soil-air exchange of organochlorine pesticides in the southern United States. Environ. Pollut. 128:49-57.

Bidleman, T.F., Leone, A.D., Wong, F., Van Vliet L, Szeto, S., Ripley, B.D. 2006. Emission of "legacy" chlorinated pesticides from agricultural and orchard soils in British Columbia, Canada. Environ. Toxicol. Chem. 25:1448-1457.

Boudreau, B.P., and Jorgensen, B.B. (eds.). 2001. The benthic boundary layer-transport processes and biogeochemistry. Oxford University Press, Oxford, UK

Boudreau, B. P. 1997. Diagenetic models and their implementation; Modeling transport and reactions in aquatic sediments. Springer, Berlin.

Bosworth, W.S., and Thibodeaux, L.J. 1990. Bioturbation: a facilitator of contaminant transport in bed sediment. Environmental Progress 9:211-217.

Brandes, L.J., den Hollander, H., van de Meent, D. 1996. SimpleBox 2.0: a nested multimedia fate model for evaluating the environmental fate of chemicals. Home Page (http://www.rivm.nl/bibliotheek/rapporten/719101029.html).

Braune, B.M. and Norstrom, R.J. 1989. Dynamics of organochlorine compounds in Herring Gulls (Larus argentatus): III. Tissue Distribution and bioaccumulation in Lake Ontario gulls and Organochlorines in Lake Ontario. Environ. Toxicol. Chem. 8:957 968.

Breivik, K., Wania, F., Muir, D.C.G., Alaee, M., Backus, S., Pacepavicius, G. 2006. Empirical and modeling evidence of the long-range atmospheric transport of decabromodiphenyl ether. Environ. Sci. Technol. 40:4612-4618.

Bridges, T.S., and Lutz, C.H. 1999. Interpreting Bioaccumulation Data with the Environmental Residue-Effects Database. Dredging Research Technical Note EEDP-04-30, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, USA.

Brown, T.N., and Wania, F. 2008. Screening chemicals for the potential to be persistent organic pollutants: a case study of arctic contaminants. Environ. Sci. Technol. 42:5202-5209.

Buckman, A.H., Brown, S.B., Small, J., Muir, D.C., Parrott, J., Solomon, K.R., Fisk, A.T. 2007. Role of Temperature and Enzyme Induction in the Biotransformation of Polychlorinated Biphenyls and Bioformation of Hydroxylated Polychlorinated Biphenyls by Rainbow Trout (Oncorhynchus mykiss). Environ. Sci. Technol. 41:3856-3863.

Chiou, C.T. 2002. Contaminant Sorption to Soils and Natural Solids, Chapter 7 in Partition and adsorption of organic contaminants in environmental systems. John Wiley and Sons, Inc. New York, NY.

Collins, C., Fryer, M., Grosso, A. 2006. Plant uptake of non-ionic organic chemicals. Environmental Science & Technology 40:45-52.

Cowan, C.E., Mackay, D., Feijtel, T.C.J., van de Meent, D., Di Guardo, A., Davies, J., Mackay, N. 1995. The multimedia fate models: a vital tool for predicting the fate of chemicals, SETAC Press, Pensacola, FL.

Czub, G., Wania, F., McLachlan, M. 2008. Combining long-range transport and bioaccumulation considerations to identify potential arctic contaminants. Environ. Sci. Technol. 42:3704-3709.

Daly, G., Lei, Y.D., Teixeira, C., Muir, D.C.G., Castillo, L.E., Wania, F. 2007b. Accumulation of current-use pesticides in neotropical montane forests. Environ. Sci. Technol. 41:1118-1123.

Daly, G., Lei, Y.D., Teixeira, C., Muir, D.C.G., Wania, F. 2007a. Pesticides in western Canadian mountain air and soil. Environ. Sci. Technol. 41:6020-6025.

Daly, G., Wania, F. 2005. Organic contaminants in mountains. Environ. Sci. Technol. 39:385-398.

Dettenmaier, E., Doucette, W.J., Bugbee, B. 2008. Chemical hydrophobicity and plant root uptake. Environ. Sci. Technol. Publication Date (Web): December 10, 2008.

Di Toro, D.M., and McGrath, J.A. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. II. Mixtures and sediments. Environ. Toxicol. Chem. 19:1971-1982.

Di Toro, D.M., McGrath, J.A., Hansen, D.J. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue. Environ. Toxicol. Chem. 19:1951-1970.

Drouillard, K.G. and Norstrom, R.J. 2000. Dietary absorption efficiencies and toxicokinetics of polychlorinated biphenyls in blood plasma of ring doves following initial exposure to Aroclor mixtures. Environ. Toxicol. Chem. 19:2707-2714.

Drouillard, K.G., Fernie, K., Smits, J.E., Bortolotti, G.R., Bird, D.M., Norstrom, R.J. 2001. Bioaccumulation and toxicokinetics of 42 PCB congeners in American kestrels (Falco sparverius). Environ. Toxicol. Chem. 20:2514-2522.

Erickson, M.J., Turner, C.L., Thibodeaux, L.J. 2005. A field observation and modeling of dissolved fraction sediment-water exchange coefficients for PCBs in the Hudson River. Environ. Sci. Technol. 39:549-556.

Fenner, K., Scheringer, M., MacLeod, M., Matthies, M., McKone, T.E., Stroebe, M., Beyer, A., Bonnell, M., Le Gall, A.-C., Klasmeier, J., Mackay, D., van de Meent, D., Pennington, D., Scharenberg, B., Suzuki, N., Wania, F. 2005. Comparing estimates of persistence and long-range transport potential among multimedia models. Environ. Sci. Technol. 39:1932-1942.

Fisk, A.T., Norstrom, R.J., Cymbalisty, D.C., Muir, D.C.G. 1998. Dietary accumulation and depuration of hydrophobic organochlorines. Bioaccumulation parameters and their relationship with the octanol/water partition coefficient. Environ. Toxicol. Chem. 17:951-961.

Foreman, W.T., Majewski, M.S., Goolsby, D.A., Wiebe, F.W., Coupe, R.H. 2000. Pesticides in the atmosphere of the Mississippi River Valley, part II: air. Sci. Total Environ. 248:213-226.

Glaser, D., and Connolly, J.P. 2002. A model of *p,p'*-DDE and total PCB bioaccumulation in birds from the Southern California Bight. Continental Shelf Res. 22:1079.

Gobas, F.A. P.C., Kelly, B.C., Arnot, J.A. 2003. Quantitative structure activity relationships for predicting the bioaccumulation of POPs in terrestrial food-webs. QSAR Comb. Sci. 22:329-336.

Goolsby, D.A., Thurman, E.M., Pomes, M.L., Meyer, M.T., Battaglin, W.A. 1997. Pesticides and their metabolites in rainfall: origin, transport and deposition patterns across the southwestern and northeastern United States, 1990-1991. Environ. Sci. Technol. 31:1325-1333.

Gouin, T., Harner, T., Blanchard, P., Mackay, D. 2005. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes Basin. Environ. Sci. Technol. 39:9115-9122.

Gotz, C.W., Scheringer, M., MacLeod, M., Roth, C.M., Hungerbühler, K. 2007. Alternative approaches for modeling gas-particle partitioning of semivolatile organic chemicals: Model development and comparison. Environ. Sci. Technol.:41:1272-1278.

Gotz, C.W., Scheringer, M., MacLeod, M., Wegmann, F., Schenker, U., Hungerbühler, K. 2008. Dependence of persistence and long-range transport potential on gas-particle partitioning in multimedia models. Environ. Sci. Technol. 42:3690-3696

Hageman, K.J., Simonich, S.L., Campbell, D.H., Wilson, G.R., Landers, D.H. 2006. Atmospheric deposition of current-use and historic-use pesticides in snow at national parks in the western United States. Environ. Sci. Technol. 40:3174-3180.

Harner, T., Shoeib, M., Kozma, M., Gobas, F.A.P.C., Li, S. M. 2005. Hexachlorocyclohexanes and endosulfans in urban, rural, and high altitude air samples in the Fraser Valley, British Columbia: Evidence for trans-Pacific transport. Environ. Sci. Technol. 39:724-731.

Hendriks, A.J., Traas, T.P., Huijbregts, M.A.J. 2005. Critical body residues linked to octanol-water partitioning, organism composition, and LC_{50} QSARs: Meta-analysis and model. Environ. Sci. Technol. 39:3226-3236.

Hermanson, M., Isaksson, E., Teixeira, C., Muir, D.C.G., Compher, K.M., Li, Y-F., Igarashi, M., Kamiyama, K. 2005. Current-use and legacy pesticide history in the Austfonna Ice Cap, Svalbard, Norway. Environ. Sci. Technol. 39:8163-8169.

Hickie, B.E., Mackay, D., de Koning, J. 1999. Lifetime pharmacokinetic model for hydrophobic contaminants in marine mammals. Environ. Toxicol. Chem. 18:2622-2633.

Hinck, J.E., Norstrom, R.J., Orazio, C.E., Schmitt, C.J., Tillitt, D.E. 2009. Persistence of organochlorine chemical residues in fish from the Tombigbee River (Alabama, USA): Continuing risk to wildlife from a former DDT manufacturing facility. Environ. Pollut. 157:582-591.

James, R.R., and Hites, R.A. 1999. Chlorothalonil and dacthal in Great Lakes air and precipitation samples. J. Grt. Lakes Res. 25:406-411.

Jantunen, L.M., Wong, F., Bidleman, T.F., Stern, G.A. 2008. Air-water exchange of current-use pesticides in the Canadian Arctic. Presented at the Society for Environmental Toxicology and Chemistry meeting, Tampa Bay, FL, November, 16-20.

Jarvinen, A.W., and Ankley, G.T. 1999. Linkage of effects to tissue residues: Development of a comprehensive database for aquatic organisms exposed to inorganic and organic chemicals. Society for Environmental Toxicology and Chemistry. SETAC Press: Pensacola, FL.

Jaward, F.M., Zhang, G., Nam, J.J., Sweetman, A.J., Obbard, J.P., Kobara, Y., Jones, K.C. 2005. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. Environ. Sci. Technol. 39:8638-8645.

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A., Jones, K.C. 2004. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. Environ. Sci. Technol. 38:34-41.

Kelly, B.C., and Gobas, F.A.P.C. 2001. Bioaccumulation of persistent organic pollutants in lichen-caribou-wolf food chains of Canada's central and western Arctic. Environ. Sci. Technol. 35:325-334.

Killin, R.K., Simonich, S.L., Jaffe, D.A., DeForest, C.L., Wilson, G.R. 2004. Transpacific and regional atmospheric transport of anthropogenic semivolatile organic compounds to Cheeka Peak observatory during the spring of 2002. J. Geophys. Res., [Atmos.] 109, D23S15.

Klasmeier, J., Matthies, M., MacLeod, M., Fenner, K., Scheringer, M., Stroebe, M., Le Gall, A.C., McKone, T., Van de Meent, D., Wania, F. 2006. Application of multimedia models for screening assessment of long-range transport potential and overall persistence. Environ. Sci. Technol. 40:53-60.

Kurt-Karakus, P.B., Bidleman, T.F., Staebler, R.M, Jones, K.C. 2006. Measurement of DDT fluxes from a historically treated agricultural soil in Canada. Environ. Sci. Technol. 40:4578-4585.

Lassiter, R.R., and Hallam, T.G. 1990. Survival of the fattest: implications for acute effects of lipophilic chemicals on aquatic populations. Environ. Toxicol. Chem. 9:585-595.

Leistra, M., and van der Berg, F. 2007. Volatilization of parathion and chlorothalonil from a potato crop simulated by the PEARL model. Environ. Sci. Technol. 41:2243-2248.

Li, Y-F. 2001. Toxaphene in the United States. 1. Usage gridding. J. Geophys. Res. 106:17919-17927.

Li, Y-F., Bidleman, T.F., Barrie, L.A. 2001. Toxaphene in the United States. 2. Emissions and residues. J. Geophys. Res. 106:17929-17938.

Li, Y.F., Macdonald, R.W., Ma, J., Hung, H., Venkatesh, S. 2004. α-HCH budget in the Arctic Ocean: The arctic mass balance box model (AMBBM). Sci. Total. Environ. 324:115-139.

Lick, W. 2008. Sediment and Contaminant Transport in Surface Waters. CRC Press, Boca Raton, FL.

Ma, J., Daggupaty, S., Harner, T., Li, Y-F. 2003. Impacts of lindane usage in the Canadian prairies on the Great Lakes Ecosystem. 1. Coupled atmospheric transport model and modeled concentrations in air and soil. Environ. Sci. Technol. 37:3774-3781.

Ma, J., Venkatesh, S., Li, Y-F., Daggupaty, S. 2005. Tracking toxaphene in the North American Great Lakes Basin. 1. Impact of toxaphene residues in United States soils. Environ. Sci. Technol. 39:8123-8131.

Mackay, D. The Canadian Centre for Environmental Modelling and Chemistry (www.trentu.ca/academic/aminss/envmodel/)

MacLeod, M., Woodfine, D.G., Mackay, D., McKone, T., Bennett, D., Maddalena, R. 2001. BETR North America: A regionally segmented multimedia contaminant fate model for North America. Environmental Science and Pollution Research 8:156-163.

MacLeod, M., Bennett, D.H., Perem, M., Maddalena, R.L., McKone, T.E., Mackay, D. 2004. Dependence of intake fraction on release location in a multimedia framework: A case study of four contaminants in North America. Journal of Industrial Ecology 8:89-102.

MacLeod, M., Woodfine, D., Brimacombe, J., Toose, L., Mackay, D. 2002. A dynamic mass budget for toxaphene in North America. Environ. Toxicol. Chem. 21:1628-1637.

Majewski, M., and Capel, P. 1995. Pesticides in the atmosphere: distribution, trends and governing factors. Ann Arbor Press, Chelsea, MI.

Majewski, M.S., Desjardins, R., Rochette, P., Pattey, E., Seiber, J., Glotfelty, D.E. 1993. Field comparison of an eddy accumulation and an aerodynamic-gradient system for measuring pesticide volatilization fluxes. Environ. Sci. Technol. 27:121-128.

Majewski, M.S., Foreman, W.T., Goolsby, D.A., Nakagaki, N. 1998. Airborne pesticide residues along the Mississippi River. Environ. Sci. Technol. 32:3689-3698.

McCarty, L.S., and Mackay, D. 1993. Enhancing ecotoxicological modeling and assessment: Body residues and modes of toxic action. Environ. Sci. Technol 27:1719-1728.

McCave, I.N., Editor. 1976. The benthic boundary layer. Plenum Press, NY.

McKone, T.E., (http://eetd.lbl.gov/ie/ERA/caltox/index.html)

McKone, T.E., Maddalena, R.L. 2007. Plant uptake of organic pollutants from soil: Bioconcentration estimates based on models and experiments. Environ. Toxicol. Chem. 26:2494-2504.

Meador, J.P. 2006. Rationale and procedures for using the tissue-residue approach for toxicity assessment and determination of tissue, water, and sediment quality guidelines for aquatic organisms. Human and Ecological Risk Assessment. 12:1018-1073.

Meador, J.P., Sibley, T.H., Swartzman, G.L., Taub, F.B. 1998. Copper tolerance by the freshwater algal species Oocystis pusilla and its ability to alter free-ion copper. Aquatic Toxicology 44:69-82.

Meador, J.P., Taub, F.B., Sibley, T.H. 1993. Copper dynamics and the mechanism of ecosystem level recovery in a standardized aquatic microcosm. Ecological Applications 3:139-155.

Muir, D.C.G., Ford, C.A., Stewart, R.E.A., Smith, T.G., Addison, R.F., Zinck, M.E., Beland, P. 1990. Organochlorine contaminants in belugas, Delphinapterus leucas, from Canadian waters. Can. Bull. Fish. Aquat. Sci. 224:165-190.

Muir, D.C.G., Norstrom, R.J., Simon, M. 1988. Organochlorine contaminants in Arctic marine food chains: Accumulation of specific polychlorinated biphenyls and chlordane-related compounds. Environ. Sci. Technol. 22:1071-1079.

Muir, D.C.G., Teixeira, C., Wania, F. 2004. Empirical and modeling evidence of regional atmospheric transport of current-use pesticides. Environ. Toxicol. Chem. 10:2421-2432.

National Research Council. 1997. Contaminated sediments in ports and waterways-clean-up strategies and technologies. National Academy Press, Washington, DC.

Nichols, J.W., Larsen, C.P., McDonald, M.E., Niemi, G.J., Ankley, G.T. 1995. Bioenergetics-based model for accumulation of polychlorinated biphenyls by nestling tree swallows. (*Tachycineta bicolor*). Environ. Sci. Technol. 29:604-612.

Norstrom, R.J., and Letcher, R.J. 1997. Role of biotransformation in bioconcentration and bioaccumulation in: Biotransformation in Environmental Risk Assessment, Society of Environmental Toxicology and Chemistry (SETAC) -Europe Worskhop. D. Sijm, J. deBruin, P. de Voogt and P. de Wolf, eds. SETAC-Europe Pub., Brussels, Belgium, pp 101-113.

Norstrom, R.J., Clark, T.P., Enright, M., Leung, B., Drouillard, K.G., Macdonald, C.R. 2007. ABAM, a model for bioaccumulation of POPs in birds: validation for adult herring gulls and their eggs in Lake Ontario. Environ. Sci. Technol. 41:4339-4347.

Organization for Economic Cooperation and Development (OECD). 2001. Glossary of Statistical Terms. http://stats.oecd.org/glossary/detail.asp?ID=1558

Pozo, K., Harner, T., Lee, S-C., Wania, F., Muir, D.C.G., Jones, K.C. 2008. Seasonally-resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. Environ. Sci. Technol., accepted.

Pozo, K., Harner, T., Wania, F., Muir, D., Jones, K.C., Barrie, L.A. 2006. Toward a global network for persistent organic pollutants in air: Results from the GAPS study. Environ. Sci. Technol. 40:4867-4873.

Primbs, T., Wilson, G., Schmedding, D., Higginbotham, C., Simonich, S.M. 2008a. Influence of Asian and western United States agricultural areas and fires on the atmospheric transport of pesticides in the western United States. Environ. Sci. Technol. 42:6519-6525.

Primbs, T., Piekarz, A., Wilson, G., Schmedding, D., Higginbotham, C., Field, J., Simonich, S.M. 2008b. Influence of Asian and western United States urban areas and fires on the atmospheric transport of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and fluorotelomer alcohols in the western United States. Environ. Sci. Technol. 42:6385-6391.

Preuger, J.H., Gish, T.J., McConnell, L.L., McKee, L.J., Hatfield, J.L., Kustas, W.P. 2005. Solar radiation, relative humidity and soil water effects on metolachlor volatilization. Environ. Sci. Technol. 39:5219-5226.

Reible, D.D., Valsaraj, K.T., Thibodeaux, L.J. 1991. Chemodynamic Models for Transport of Chemicals from Bed Sediments, Chapter 3 in Handbook of Environmental Chemistry, Vol. 2 Part F, Reactions and Processes, O. Hutzinger(Ed.), Springer Verlag GmbH, Germany, pp. 185-228.

Reichman, R., Wallach, R., Mahrer, Y. 2000a. A combined soil atmosphere model for evaluating the fate of surface-applied pesticides. 1. Model development and verification. Environ. Sci. Technol. 34:1313-1320.

Reichman, R., Mahrer, Y., Wallach, R. 2000b. A combined soil atmosphere model for evaluating the fate of surface-applied pesticides. 2. The effect of varying environmental conditions. Environ. Sci. Technol. 34:1321-1330.

Risebrough, R.W., Huggett, R.J., Griffin, J.J., Goldberg, E.D. 1968. Pesticides: transatlantic movement in the northeast trades. Science 159:1233-1235.

Sadiki, M., and Poissant, L. 2008. Atmospheric concentrations and gas-particle partitions of pesticides: Comparisons between measured and gas-particle partitioning models from source and receptor sites. Atmos. Environ. 42:8288-8299.

Sauret, N., Wortham, H., Putaud, J.P., Mirabel, P. 2008. Study of the effects of environmental parameters on the gas/particle partitioning of current-use pesticides in urban air. Atmos. Environ. 42:544-553.

Scheringer, M., Jones, K.C., Matthies, M., Simonich, S., van de Meent, D. 2009. Multimedia partitioning, overall persistence, long-range transport potential of organic chemicals - Results from a SETAC Pellston Workshop. Integr. Environ. Assess. Managem. 5, in preparation.

Scholtz, M.T., and Bidleman, T.F. 2006. Modelling of the long term fate of pesticide residues in agricultural soils and their surface exchange with the atmosphere: Part I. Model description and evaluation. Sci. Total Environ. 368:823-838.

Scholtz, M.T., Voldner, E., McMillan, A.C., Van Heyst, B.J. 2002a. A pesticide emission model (PEM). Part 1. Model development. Atmos. Environ. 36:5005-5013.

Scholtz, M.T., Voldner, E., McMillan, A.C., Van Heyst, B.J. 2002b. A pesticide emission model (PEM). Part 2. Model evaluation. Atmos. Environ. 36:5005-5013.

Seba, D.B., and Prospero, J.M. 1971. Pesticides in the lower atmosphere of the northern equatorial Atlantic Ocean. Atmos. Environ. 5:1043-1050.

Shen, L., Wania, F., Lei, Y.D., Teixeira, C., Muir, D.C.G., Bidleman, T.F. 2005. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. Environ. Sci. Technol. 39:409-420.

Shen, L., Wania, F., Lei, Y.D., Teixeira, C., Muir, D.C.G., Bidleman, T.F. 2004. Hexachlorocyclohexanes in the North American atmosphere. Environ. Sci. Technol. 38:965-975.

Spencer, W.F., Singh, G., Taylor, C.D., LeMert, R.A., Cliath, M.M., Farmer, W.J. 1996. DDT persistence and volatility as affected by management practices after 23 years. J. Environ. Qual. 25:815-821.

Steevens, J.A., Reiss, M.R., Pawlisz, A.V. 2005. A methodology for deriving tissue residue benchmarks for aquatic biota: A case study for fish exposed to 2,3,7,8 tetrachlorodibenzo-p-dioxin and equivalents. Integrated Environmental Assessment and Management 1:142–151.

Su, Y., Hung, H., Blanchard, P., Patton, G.W., Kallenborn, R., Konoplev, A., Fellin, P., Li, H., Geene, C., Stern, G., Rosenberg, B., Barrie, L.A. 2008. A circumpolar perspective of atmospheric organochlorine pesticides (OCPs): Results from six arctic monitoring stations in 2000–2003. Atmos. Environ. 42:4682-4698.

Sun, P., Backus, S., Blanchard, P., Hites, R.A. 2006a. Temporal and spatial trends of organochlorine pesticides in Great Lakes precipitation. Environ. Sci. Technol. 40:2135-2141.

Sun, P., Blanchard, P., Brice, K., Hites, R.A. 2006b. Atmospheric organochlorine pesticide concentrations near the Great Lakes: temporal and spatial trends. Environ. Sci. Technol. 40:6587-6593.

Talbert, B., Thibodeaux, L.J., Valsaraj, K.T. 2001. Effectiveness of very thin soil layers in controlling chemical release from bed sediment. Environmental Progress 20:103-107.

Thibodeaux, L.J. 1996. Environmental Chemodynamics: Movement of chemicals in air, water and soil. Ch. 2 and 5. John Wiley and Sons, Inc., New York, NY.

Thibodeaux, L.J. 2005. Recent advances in our understanding of sediment-to-water contaminant fluxes: The soluble release fraction. Aquatic Ecosystem Health and Management 8:1-9.

Thibodeaux, L., and Mackay, D. 2007. The Importance of Chemical Mass-Transport Coefficients in Environmental and Geo-chemical Models. SETAC Globe 8: 29-31.

Thibodeaux, L.J., Valsaraj, K.T., Reible, D.D. 2001. Bioturbation driven transport of hydrophobic organic contaminants from bed sediment. Environmental Engineering Science. 18:215-223.

Thibodeaux, L.J., Reible, D.D., Valsaraj, K.T. 2001. Non-particle Resuspension Chemical Transport from Stream Beds, Chapter 7 in Chemicals in the Environment: Fate, Impacts and Remediation, Ed. R.L. Lipnick, R.P. Mason, M.L. Phillips, and C.U. Pittman, ACS Symposium Series 806. Washington, D.C.

Thibodeaux, L.J., and Bierman, V.J. 2003. The Bioturbation Driven Chemical Release Process. Environ. Sci. Technol. 37:253A-258A.

Thibodeaux, L.J. 2002. In situ capping design of a pyrite cinder pile in the St. Lawrence River for metal containment. Remediation 13:5-19.

Thoms, S.R., Matisoff, G., McCall, P.L., Wang, X. 1995. Models for Alteration of Sediments by Benthic Organisms. Project 92-NPS-2. Alexandria, VA: Water Environment Research Foundation.

Trapp, S. 2007. Fruit tree model for uptake of organic compounds from soil and air. SAR QSAR Environ. Res. 18:367-387.

Traas, T.P., van Wezel, A.P., Hermens, J.L.M., Zorn, M., van Hattum, A.G.M., van Leeuwen, C.J. 2004. Environmental quality criteria for organic chemicals predicted from internal effect concentrations and a food web model. Environ. Toxicol. Chem. 23:2518-2527.

Tuduri, L., Harner, T., Blanchard, P., Li, Y.-F., Poissant, L., Waite, D. T., Murphy, C., Belzer, W. 2006a. A review of currently used pesticides (CUPs) in Canadian air and precipitation: Part 1: Lindane and endosulfans. Atmos. Environ. 40:1563-1578.

Tuduri, L., Harner, T., Blanchard, P., Li, Y.-F., Poissant, L., Waite, D. T., Murphy, C., Belzer, W. 2006b. A review of currently used pesticides (CUPs) in Canadian air and precipitation: Part 2: Regional information and perspectives. Atmos. Environ. 40:1579-1589.

UNEP. 2001. Text of the Stockholm Convention on Persistent Organic Pollutants for adoption by the Conference of Plenipotentiaries. United Nations Environment Program, Geneva, Switzerland.

US ACOE. 1997. The Environmental Residue-Effects Database (ERED). Home Page http://el.erdc.usace.army.mil/ered/ United Stated Army Corps of Engineers, webdate: November 4, 1997.

US EPA 2008. The PCB Residue Effects (PCBRes) Database. United Stated Environmental Protection Agency, Washington, D.C. Home Page http://www.epa.gov/med/Prods_Pubs/pcbres.htm

Usenko, S., Landers, D., Appleby, P., Simonich, S.L. 2007. Current and Historical Deposition of PBDEs, Pesticides, PCBs, and PAHs to Rocky Mountain National Park, USA: Does the Continental Divide Make a Difference? Environ. Sci. Technol. 41:7235-7241.

Valsaraj, K.T., Thibodeaux, L.J., Reible, D.D. 1997. A quasi-steady-state pollutant flux methodology for determining sediment quality criteria. Environ. Tox. Chem. 16:391-396.

Waite, D.T., Cabalo, E., Chau, D., Sproull, J.F. 2007. A comparison of flux chambers and ambient air sampling to measure γ-hexachlorocyclohexane volatilisation from canola (*Brassica napus*) fields. Chemosphere 68:1074-1081.

Waite, D.T., Gurprasad, N.P., Sproull, J.F., Quiring, D.V., Kotylak, M.W. 2001. Atmospheric movements of lindane (γ-hexachlorocyclohexane) from canola fields planted with treated seed. J. Environ. Qual. 30:768-775.

Wania, F. 2003. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. Environ. Sci. Technol. 37:1344-1351.

Wania, F. 2006. Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic. Environ. Sci. Technol. 40:569-577.

Weber, J., Halsall, C.J., Muir, D.C.G., Teixeira, C., Burniston, D.A., Strachan, W.M.J., Hung, H., Mackay, N., Arnold, D., Kylin, H. 2006. Endosulfan and γ-HCH in the Arctic: an assessment of surface seawater concentrations and air-sea exchange. Environ. Sci. Technol. 40:7570-7576.

Wegmann, F., Cavin, L., MacLeod, M., Scheringer, M., Hungerbühler, K. 2009. The OECD software tool for screening chemicals for persistence and long-range transport potential. Environ. Model. Software 24:228-237 (in press).

Weisbrod, A.V., Sahi, J., Segner, H., James, M.O., Nichols, J., Schultz, I., Erhardt, S., Cowan-Ellsberry, C., Bonnell, M., Hoeger, B. 2009. The state of in vitro science for use in bioaccumulation assessments for fish. Environ. Toxicol. Chem. 28:86-96

Wilkinson, A. C.; Kimpe, L. E.; Blais, J. M. 2005. Air-water gas exchange of chlorinated pesticides in four lakes spanning a 1,205 meter elevation range in the Canadian Rocky Mountains. Environ. Toxicol. Chem. 24:61-69.

Wong, F., Alegria, H.A., Bidleman, T.F., Alvarado, V., Angeles, F., Galarza, A.A., Bandala, E.R., Hinojosa, I.C., Estrada, I.G., Reyes, G.G., Gold-Bouchot, G., Zamora, J.V.M., Murguía-González, J., Espinoza, E.R. 2008. Passive air sampling of organochlorine pesticides in Mexico. Environ. Sci. Technol., accepted.

Yao, Y., Harner, T., Blanchard, P., Tuduri, L., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F., Sverko, E. 2008. Pesticides in the atmosphere across Canadian agricultural regions. Environ. Sci. Technol. 42:5931-5937.

Yao, Y., Harner, T., Ma, J., Tuduri, L., Blanchard, P. 2007. Sources and occurrence of dacthal in the Canadian atmosphere. Environ. Sci. Technol. 41:688-694.

Zhang, L., Ma, J., Venkatesh, S., Li, Y-F., Cheung, P. 2008. Modeling evidence of episodic intercontinental long-range transport of lindane. Environ. Sci. Technol. (in press).