White Paper on Methods for Assessing Ecological Risks of Pesticides with Persistent, Bioaccumulative and Toxic Characteristics

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LIST OF DEFINITIONS

Assessment endpoints: An explicit expression of the environmental value that is to be protected, operationally defined by an ecological entity and its attributes. For example, salmon are valued ecological entities; reproduction and age class structure are some of their important attributes. Together "salmon reproduction and age class structure" form an assessment endpoint.

Bioaccumulation: The net accumulation of a chemical in an organism from all possible exposure routes (respiration, diet, dermal) and sources (soil, air and diet) (Spacie *et al*. 1995; USEPA 2003, 2007b).

Bioconcentration: For aquatic organisms, the net accumulation of a chemical in an organism that results from direct contact with water only, such as through gill membranes or other external surfaces (USEPA 2003, 2007b). Bioconcentration excludes chemical accumulation from other exposure routes and sources such as ingestion of organisms and sediment. Although not routinely defined for terrestrial (air-breathing) organisms, an analogous measure of bioconcentration would be the net accumulation of a chemical that results from direct contact with air or soil only, such as through respiration or dermal uptake.

Bioaccumulation Factor (BAF): For aquatic organisms, the ratio of the concentration of a chemical in tissue to its concentration in water, in situations where both the organism and its food are exposed (USEPA 2003). For terrestrial organisms, an analogous measure of a BAF would be the ratio of the concentration of a chemical in tissue to its concentration in air (or soil), in situations where both the organism and its food are exposed. BAFs >1 indicate that the concentration/accumulation in the organism is greater than that of the medium from which the chemical was measured.

Bioconcentration Factor (BCF): For aquatic organisms, the ratio of the concentration of a chemical in tissue to its concentration in water, in situations where the organism is exposed via water only. For terrestrial organisms, an analogous measure of a BCF would be the ratio of the concentration of a chemical in tissue to its concentration in air (or soil), in situations where the organism is exposed via air or soil only. BCFs >1 indicate that the concentration/accumulation in the organism is greater than that of the medium from which the chemical was measured.

Biomagnification: The increase in concentration of a chemical in the tissue of organisms along a series of predator-prey associations, primarily through the mechanism of dietary accumulation.

Biomagnification factor (BMF): The ratio (unitless) of the concentration of a chemical in a predator organism at a particular trophic level to the concentration of the chemical in the tissue of its prey organism at the next lowest trophic level for a given water body and chemical exposure.

Conceptual Model: A written description and visual representation of predicted relationships between ecological entities and the stressors to which they may be exposed.

EC_{50}: The concentration of a chemical that is estimated to produce a specific effect in 50% of the test organisms.

Ecological Risk Assessment: The process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors.

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA): The statute that authorizes the US Environmental Protection Agency to register pesticides for use in the United States.

LC_{50}: The concentration of a chemical that is estimated to kill 50% of the test organisms.

LD_{50}: The dose of a toxicant that will kill 50% of exposed test organisms within a designated period of time. The lower the LD_{50}, the more toxic the compound.

Lines of evidence: Information derived from different sources or by different techniques that can be used to describe and interpret risk estimates. Unlike the term "weight of evidence," it does not necessarily imply assignment of quantitative weightings to information.

Lowest Observed Adverse Effect Level (LOAEL): The lowest dose in a toxicity study resulting in adverse effects.

No Observed-Adverse-Effect-Level (NOAEL): Refers to the highest tested dose of a substance that has been reported to have no harmful (adverse) effects to exposed test organisms.

No-Observed-Adverse-Effect-Concentration (NOAEC): The highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered adverse or precursors of adverse effects.

Problem Formulation: The process for generating and evaluating preliminary hypotheses about why ecological effects have occurred, or may occur, from human activities. It provides the foundation for the entire ecological risk assessment. Early in problem formulation, objectives for the risk assessment are refined. Then the nature of the problem is evaluated and a plan for analyzing data and characterizing risk is developed. The products of problem formulation are assessment endpoints that adequately reflect management goals and the ecosystem they represent, conceptual models that describe key relationships between stressor(s) and assessment endpoint(s), and an analysis plan.

Registrant: A pesticide manufacturer that has registered a pesticide product pursuant to the provisions of FIFRA.

Registration: Formal listing with EPA of a new pesticide before sale or distribution. EPA is responsible for pre-market licensing of pesticides on the basis of data demonstrating no unreasonable adverse health or environmental effects when applied according to approved label directions.

Risk Characterization: A phase of ecological risk assessment that integrates the exposure and stressor response profiles to evaluate the likelihood of adverse ecological effects associated with exposure to a stressor. Lines of evidence and the adversity of effects are discussed.

Risk Description: Following the preparation of the risk estimate, risk assessors interpret and discuss the available information about risks to assessment endpoints. Risk description includes an evaluation of the lines of evidence supporting or refuting the risk estimate(s) and an interpretation of the significance of the adverse effects on the assessment endpoints.

Risk Estimation: The process of integrating exposure and effects data and evaluating any associated uncertainties.

Sediment Dynamics: processes related to sediment transport into and within an aquatic ecosystem, including (but limited to): soil erosion, settling, resuspension and burial of sediment mass.

Steady State. A condition reached by a system when rates of chemical movement between phases and reactions within phases are constant so that concentrations of the chemical in the phases of the system are unchanged over time. A system at steady state is not necessarily at equilibrium; steady-state conditions often exist when some or all of the phases of the system have different activities or fugacities for the chemical.

Toxicity Reference Value (TRV): Estimate of a dose or concentration of a pesticide that is associated with a specific effect. For example, LC_{50} and LD_{50} values are common toxicity reference values used to assess acute risks, and NOAEC and NOAEL values are common toxicity reference values used evaluate chronic risks.

Trophic Transfer: The transfer of a chemical from prey species to a predator species via dietary exposure.

List of Acronyms

BAF: Bioaccumulation Factor
BCF: Bioconcentration Factor
BMF: Biomagnification Factor
BMP: Best Management Practice
BSAF: Biota-sediment Accumulation Factor
CUP: Current use pesticide
EC: Effective Concentration
EEC: Estimated Environmental Concentration
EFED: Environmental Fate and Effects Division of the Office of Pesticide Programs
EPA (USEPA): United States Environmental Protection Agency
FIFRA: Federal Insecticide, Fungicide, and Rodenticide Act
FOC: Fraction organic carbon
HUP: Historical use pesticide
K_{OA}: Octanol-Air partition coefficient
K_{OW}: Octanol-Water partition coefficient
LC: Lethal Concentration
LD: Lethal Dose
LOC: Level of Concern
NOAEC: No-Observed-Adverse-Effects-Concentration.
OPP: Office of Pesticide Programs under the Office of Pollution Prevention and Toxic Substances
OPPTS: Office of Pollution Prevention and Toxic Substances of the US Environmental Protection Agency
SOC: Semivolatile organic chemical
TRA: Toxicity Residue Approach
TRV: Toxicity reference value
CBR: Critical body residue

1. EXECUTIVE SUMMARY

The Office of Pesticide Programs (OPP) within the US Environmental Protection Agency (the Agency) has encountered a number of ecological risk assessment issues associated involving pesticides with combined persistence (P), bioaccumulative (B), and toxic (T) characteristics (collectively referred to as PBT). These risk assessment issues have arisen principally because the historical suite of assessment tools, methods and data have not been specifically designed to address certain aspects of pesticides with PBT profiles. To address these issues, the Agency has, on a case-by-case basis, considered and employed refinements to its available tools, methods as the science supporting such assessments has advanced.

The Agency has developed this White Paper for the meeting with the FIFRA Scientific Advisory Panel (SAP or Panel) on PBT-related ecological risk assessment issues. It describes the current approach and recent improvements to the tools, methods and data which have been used to evaluate the ecological risk of pesticides with varying PBT characteristics. Components of four case studies with unidentified pesticides are used to illustrate: (1) the analyses employed in those assessments; (2) the risk assessment issues that have arisen; and (3) the evolving tools, methods and data that are being considered at this time. Advice from the SAP is being requested on whether the Agency's approach to addressing the PBT issues and its use of additional methods are consistent with the available science and are appropriate for further development and integration into the Agency's risk assessment process.

The Agency considers this SAP peer review as an initial step in a process for making refinements to its ecological risk assessment practices for addressing pesticides with PBT profiles. Over the next few years, the Agency plans to return to the SAP for additional review of specific methods and tools related to each topic area. However, the Agency will use the comments from this 2008 SAP meeting to support ecological risk assessments in its ongoing registration and re-registration program.

Specifically, the Agency is seeking comments on its approach to addressing the issues identified in **Table 1.1**. A discussion of each of the issues follows the table.

Table 1.1. Current Challenges Associated with Ecological Risk Assessment of Pesticides with PBT Characteristics

Topic Area	Current Risk Assessment Issue
Environmental Persistence	1. Quantifying exposure to combined parent and degradation products 2. Interpreting predicted or measured exposure concentrations that exceed solubility 3. Interpreting degradation half lives when dissipation processes dominate 4. Quantifying long-term exposure (multi-year carryover) in soils, sediment and pore water
Sediment Dynamics	1. Understanding the importance of sedimentation processes on pesticide bioavailability in the context of model agricultural pond systems

Topic Area	Current Risk Assessment Issue
	2. Identifying and quantifying the principal processes related to sediment dynamics in these systems 3. Identifying appropriate methods for modeling these processes for OPP/EFED aquatic exposure assessments
Bioaccumulation	1. Quantifying pesticide exposure via the aquatic food web 2. Interpreting and integrating results from lab-, field-, and model-based bioaccumulation methods 3. Assessing bioaccumulation potential in terrestrially-based food webs
Long Range Transport	1. Establishing relationships between near-field pesticide loadings and far-field pesticide concentrations 2. Understanding the applicability and reliability of available models for screening long-range transport potential
Toxicity	1. Estimating combined toxicity of parent and degradation products 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.

1.1 ENVIRONMENTAL PERSISTENCE ISSUES

Assessing Total Residues of Concern

Assessing exposure to parent and degradation products is a principal issue for many ecological risk assessments, but is especially important for pesticides with high environmental persistence. Three methods have been applied for assessing the combined aquatic exposure to parent and degradation products (termed "total residues of concern") of pesticides with PBT characteristics. These methods are: (1) the formation/decline kinetics method, (2) the residue summation method, and (3) the total residue method. Each method has its strengths and weaknesses (**Table 1.2**) which are explored in this White Paper.

Table 1.2. Strengths and Weaknesses of Methods to Address Total Residues of Concern

Method	Strengths	Weaknesses
Formation /Decline Kinetics (FD)	• Provides separate exposure time-series for each parent and degradation product • Incorporates residue formation and decline kinetics	• Requires complete chemical property data on degradates, which is generally not part of the standard data set provided to the Agency
Residue Summation (RS)	• Provides separate exposure time-series for each parent and degradation product • Does not require calculation of complicated formation of decline kinetics	• Requires fate data for parent and degradates • Kinetics of residue formation are not addressed (assumes instantaneous formation of degradates on the day of application)

Method	Strengths	Weaknesses
Total Residue (TR)	• Most simplified approach • Can be applied with most data sets	• Does not provide separate time-series for each parent and degradation product • Kinetics of residue formation/decline are not addressed • Assumes similar fate properties among parent and degradates

Assessing Solubility Issues

In some cases, predicted or measured concentrations of certain example pesticides with PBT characteristics have exceeded the aqueous solubility limit reported from laboratory studies. Questions on the most appropriate interpretation of concentrations that exceed solubility have subsequently arisen. In these cases, two methods have been applied for interpreting predicted concentrations that exceed aqueous solubility. Both assume that laboratory-measured estimates of chemical solubility are reasonable approximations of aqueous solubility limits under field conditions.

Method 1: Assumes the amount of chemical above the measured aqueous solubility is not biological available (e.g. exists as a precipitate). The assumed precipitate is ignored in the exposure assessment.
Method 2: Assumes that at concentrations exceeding solubility, the chemical is temporarily biologically unavailable to biota until the aqueous concentrations drop below the solubility limit where it is then re-dissolved up to the solubility limit.

Interpreting Degradation Half Life Data

Another issue associated with assessing environmental persistence is the interpretation and application of half life data for pesticides with high environmental partitioning (high K_{OC}) but low volatility. In these cases, the chemical concentration in a mixed water/sediment system used for assessing biotic metabolism (biotransformation) will reflect strongly its dissipation (partitioning to sediment organic carbon) in addition to any degradation that may occur. For persistent, high K_{OC} compounds for which hydrolysis and volatilization processes are negligible, end result will be rapid dissipation from the water column with simultaneous accumulation in sediment. For these pesticides, the Agency believes that the half life reflecting the degradation of the compound in the total sediment/water system (i.e., the Total System Half Life) is a more appropriate representation of the degradation rate in water or sediments compared to the half life determined from individual media (water or sediment). This approach avoids 'double counting' the dissipation (environmental partitioning) processes when applying degradation rates derived from mixed water/sediment systems to its water quality model, which includes environmental partitioning.

Quantifying Long-Term Accumulation

The exposure assessments in the example pesticide case studies indicate that long-term (year-to-year) accumulation in environmental compartments such as soil and sediment can be

substantial. For quantifying long-term accumulation potential in soils and sediments, the capabilities of PRZM/EXAMS were explored. These capabilities have not been routinely applied in EFED ecological risk assessments. In the context of a 'field level' exposure scenario, these case study results demonstrate that:

1. The PRZM model can be used to describe long-term accumulation of pesticides in soils, which may provide useful exposure information for assessing pesticide movement in terrestrial ecosystems, and
2. The PRZM/EXAMS models can provide estimates of long-term pesticide accumulation in sediment and pore water, which would provide useful information for evaluating potential risks to benthic organisms.

These case studies also indicate that modeled time periods required to reach steady state often exceed the duration of most laboratory and field studies, thus suggesting a potential limitation in these studies for highly persistent pesticides.

1.2 SEDIMENT DYNAMICS

The temporal and spatial distribution of pesticides with PBT characteristics in aquatic ecosystems is expected to be influenced substantially by processes governing sediment particle delivery to (and transport within) water bodies (i.e., sediment dynamics). For these compounds, soil erosion is usually a major source of pesticide loading into aquatic ecosystems. Once in an aquatic ecosystem, processes such as settling, resuspension, and burial of sediment particles can affect the distribution of pesticides in the water column-, pore water-, and suspended- and benthic-sediment compartments. Sediment dynamics can also influence pesticide bioavailability within these compartments, due to pesticide sorption on particulate organic carbon and complexation with dissolved organic carbon.

Currently, OPP's aquatic exposure modeling framework incorporates pesticide delivery to a standard pond from soil erosion and runoff using the Pesticide Root Zone Model (PRZM). In this modeling framework, only the pesticide mass delivered from soil erosion and runoff is considered for delivery to an aquatic ecosystem (i.e., the mass of soil and volume of runoff predicted by PRZM are not considered). Pesticide transport between the water column and the benthic region within the standard pond is modeled using the Exposure Analysis Modeling System (EXAMS) based on a set of lumped parameters that are designed to reflect the combined effect of multiple transport processes (e.g., diffusion, setting and resuspension). The current modeling framework does not consider pesticide burial in the benthic area, a process by which pesticide is rendered permanently unavailable for biological interaction due to accumulating sediment. Without consideration of burial processes, the current modeling framework likely represents an effective screen for pesticide exposure assessment in both lentic (static) and lotic (flowing water) systems. The sensitivity of the current modeling framework to different assumptions regarding pesticide transport within the standard pond is explored in this White Paper. Other models that explicitly incorporate processes related to sediment dynamics are also reviewed. The Agency is seeking input from the SAP on the strengths and limitations of its current aquatic modeling framework for pesticides with PBT characteristics in the context of

sediment dynamics. The Agency is also interested in feedback on processes and modeling approaches it should consider for potentially incorporating sediment dynamics in refined aquatic exposure assessments.

1.3 BIOACCUMULATION

Accounting for Trophic Transfer

Chemical exposure to aquatic organisms via the diet (i.e., trophic transfer) can be important for some persistent, highly hydrophobic organic chemicals (i.e., log $K_{OW} > 5$) that are not readily metabolized and excreted by biota. Historically, the bioaccumulation potential of pesticides has been evaluated using laboratory-measured bioconcentration factors (BCFs). Although BCF studies have certain strengths, they do not account for chemical exposure via trophic transfer. This limitation can lead to underestimating pesticide bioaccumulation potential and subsequent exposure and risk to aquatic organisms and their predators. Recent refinements have been incorporated into several ecological risk assessments to account for trophic transfer of pesticides in aquatic food webs. These refinements include the use of laboratory-based feeding studies, field studies, and food web bioaccumulation models. Examples provided in the White Paper demonstrate the application of each of these approaches for incorporating trophic transfer potential into the overall aquatic bioaccumulation assessment of pesticides. Although for many pesticides the BCF is expected to represent an adequate measure of bioaccumulation potential, use of refined methods that incorporate trophic transfer potential is needed in certain cases.

Integrating Multiple Bioaccumulation Assessment Methods

Methods for estimating the aquatic bioaccumulation potential of chemicals include laboratory experiments (e.g., bioconcentration and trophic transfer studies), field experiments (outdoor mesocosm studies), monitoring studies, and food web bioaccumulation models. Each of these approaches has different strengths and limitations. Laboratory bioconcentration studies, by far the most commonly submitted data for pesticide registration, provide useful data on pesticide uptake and elimination kinetics under controlled conditions and incorporate in vivo metabolism by the study organism. However, as described previously, they do not routinely incorporate exposure via the diet. Experimental studies conducted in the field account for dietary exposure (trophic transfer) but may not reflect long-term (multi-year) bioaccumulation potential of highly persistent pesticides due to their relatively short exposure duration. Field studies also tend to be time and resource intensive and are not routinely conducted. Monitoring studies have an advantage in that long-term bioaccumulation potential can often be assessed under natural conditions; however, these studies are rarely conducted, often lack adequate characterization of exposure concentrations, and require pesticide release to the environment. Food web bioaccumulation models have been used by the Agency for characterizing bioaccumulation potential of organic chemicals (e.g., for deriving water quality criteria; USEPA 1995; 2000, 2003). These models can be particularly useful in overcoming the limitations of laboratory and field studies, including the assessment of long-term bioaccumulation potential; distinguishing the importance of water, sediment and dietary exposures; and being readily integrated with existing water quality models. Food web bioaccumulation models, however,

contain a number of important assumptions which require careful evaluation regarding their contribution to uncertainty in bioaccumulation predictions and subsequent risk estimation.

The example pesticide bioaccumulation assessments described in this White Paper demonstrate application of three of the four types of bioaccumulation methods (laboratory studies, field experiments, bioaccumulation models). Collectively, the application of these approaches in the example pesticide assessments indicates the need to consider multiple lines of evidence based on different bioaccumulation methods for effectively evaluating pesticide bioaccumulation potential.

Assessing Terrestrial Bioaccumulation

Exposure assessments conducted by OPP for terrestrial vertebrates typically involve characterizing pesticide dietary uptake from direct deposition on food items within the treated field. These assessments are generally considered to provide estimates of potential risks from relatively short-term exposures to peak pesticide residues. However, exposure of terrestrial animals to pesticides may also result from pesticide volatilization, drift, runoff and subsequent bioaccumulation in terrestrial food webs that inhabit 'non-target' sites (i.e., areas adjacent to or near pesticide-treated fields). Currently, risks associated with the potential bioaccumulation of pesticides in terrestrial food webs is not directly assessed, and the extent to which these risks may be greater than those estimated from direct deposition on food items is not clear.

Empirical methods for assessing pesticide bioaccumulation potential in terrestrial organisms are generally lacking in typical pesticide submissions, although some studies may provide insights into terrestrial bioaccumulation potential (metabolism studies in terrestrial organisms). Recently, a number of food web bioaccumulation models have been developed for application to terrestrial ecosystems. Some of these models suggest that certain compounds with moderate K_{OW} values but high K_{OA} values may be prone to biomagnification in terrestrial food webs (but not aquatic food webs). The Agency is interested in feedback from the SAP on the need for evaluating terrestrial bioaccumulation potential and methods that can be readily applied in the near term.

1.4 LONG-RANGE TRANSPORT

Addressing Far-field Pesticide Loading

Long-range atmospheric transport of certain historically used pesticides (HUC) such as lindane has been documented (Barrie et al., 1992). The occurrence of example Pesticide 2 and its primary degradate in remote regions distant from application sites has also been documented based on monitoring data. Although pesticide monitoring data are useful for documenting the occurrence of long-range transport, these data do not enable *a priori* screening of long-range transport before it actually occurs. Furthermore, establishing the relationship between near-field pesticide loadings and far-field pesticide concentrations is often very difficult based on monitoring data alone. Such relationships between near-field loadings and far-field exposure are needed to evaluate the impact of risk mitigation options on long-range transport potential.

Several multi-media environmental fate and transport models have been developed specifically to screen for long-range transport potential of chemicals (Fenner et al., 2005). Outputs from some models include estimates of Overall Persistence (Pov) and Characteristic Travel Time (CTD). OPP is interested in obtaining input from the SAP on the extent to which such models can be effectively used to screen for long-range transport potential in addition to their relative strengths and limitations.

1.5 TOXICITY

Toxicity of Parent and Degradate Mixtures

Assessment of the combined toxicity of parent and degradate mixtures will depend on the availability of toxicity, fate and mode of action data for the individual mixture components. In situations where the exposure assessment can be conducted on individual mixture constituents (e.g., Formation/Decline and Residue Summation methods), and toxicity data are available for each constituent that indicate a similar mode of action, the combined toxicity and risk of the mixture can be assessed via assumptions of additivity. In cases where separate exposure assessments could not be conducted for each mixture constituent (e.g., total residue method), assumptions regarding the combined toxicity of the mixture would have to be made (e.g., assumed to be as toxic as the most toxic constituent). OPP is seeking SAP input on these and other methods for assessing the combined toxicity of mixtures of parent and degradates that are predicted from aquatic exposure assessments.

Addressing Multiple Exposure Routes

As described previously, exposure of aquatic organisms via the diet can be important for some highly hydrophobic organic chemicals. Currently, dietary exposure is not routinely considered in laboratory aquatic toxicity data submitted to the Agency for pesticide registration. The use of a tissue residue approach (TRA) appears to offer promise for being able to use data from existing laboratory studies to address toxicity resulting from aqueous multiple exposure routes (water and diet). One of the example pesticide case studies demonstrates this approach using critical body residues (CBR), which may involve either predicted or measured residue-effect relationships, with the latter being the preferred approach. Although a number of refinements to the CBR method are available in the scientific literature (e.g., second-order toxicokinetic processes, stochasticity, and multi-compartment modeling), the ability to apply these more sophisticated methods with existing data submitted to the Agency would likely be limited. The Agency is seeking input from the SAP on these or other approaches for assessing aquatic toxicity from multiple chemical exposure using data typically available for pesticide registrations.

1.6 PATH FORWARD

The next steps (or "path forward") for incorporating refinements to OPP's ecological risk assessment (ERA) process to address PBT-related issues will largely be framed by the outcome of this SAP meeting. Pending the results from this SAP meeting, it is expect that detailed

reviews of methods pertaining to specific topic areas (e.g., persistence, sediment dynamics, bioaccumulation, toxicity, long-range transport) would be conducted during future SAP and other external peer review mechanisms. Therefore, providing a detailed proposal on the specific refinements to the OPP/EFED ERA process is considered premature at this time.

It is possible, however, to describe how certain elements of the problem formulation process are being considered for refinement in order to facilitate a more systematic approach for evaluating PBT-related issues in future pesticide ecological risk assessments. These potential refinements do not reflect a major alteration of the problem formulation process. Rather, they reflect steps to identify: (1) situations where PBT-related risk assessment issues may be important to consider in an ecological risk assessment, and (2) which PBT-related risk assessment issues need to be addressed.

As an initial screen, OPP is considering the use of National and International PBT/LRT criteria for identifying when PBT/LRT-related risk assessment issues may need to be evaluated in pesticide ecological risk assessments (**Table 1.3**). These screening criteria would be used in conjunction with information on a pesticide's physicochemical properties, environmental persistence, bioaccumulation potential, toxicity and long-range transport potential to determine whether or not PBT/LRT-related risk assessment issues described herein should be addressed in problem formulation portion of the risk assessment. Importantly, these criteria would be used in conjunction with available data in a strength of evidence approach to trigger additional data evaluation for defining which PBT/LRT issues need to be addressed in the risk assessment.

Table 1.3. National and International Screening Criteria for Classifying Chemicals According to PBT and LRT Characteristics

Attribute	Property or Data	Criteria
Persistence	Half-life in soil	>2 mo to >1 yr.
	Half life in water	>2 mo. to >6 mo.
	Half life in sediment	>2 mo. to >1 yr.
	Half life in air	$\geq$ 2 d to $\geq$ 5 d
Bioaccumulation	BCF or BAF	> 1000 to > 5000 L/kg (wet wt.)
	Log K_{OW}	> 5
Toxicity	Acute LC_{50} / EC_{50} Chronic NOAEC Potential to impact human health or the environment	< 1 ppm <0.01 to <0.1 ppm Best professional judgment
Long-Range Transport	Monitoring data Environmental fate properties and/or model results	- Measured levels at locations distant from sources that are of potential concern - Monitoring data indicating LRT and potential transfer to a receiving environment may have occurred via air, water or migratory species - Demonstrated LRT potential via air, water or migratory species and potential transfer to a receiving environment at locations distant from the sources. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days

Source: Appendix A.

If the aforementioned screening process suggested that PBT and/or LRT-related issues may need to be addressed during the ecological risk assessment, the problem formulation process would proceed as usual, but with an emphasis on identifying those PBT/LRT-related issues would likely need to be addressed in the conceptual model and analysis plan for the risk assessment. Formulating a conceptual model and analysis plan that addresses PBT-specific attributes would be informed by a series of risk assessment questions. Examples of such risk assessment questions are shown in **Table 1.4**.

Table 1.4. Example Risk Assessment Questions to be Considered During Problem Formulation For Addressing PBT and LRT Issues

Issue	Risk Assessment Question
Environmental Persistence	
1. Environmental Fate	*Which environmental compartments is the pesticide likely to persist?*
2. Environmental Degradates	*To what extent does the formation of environmental degradates contribute to the exposure of vulnerable ecological receptors? How similar are the fate properties of the parent and degradate compounds?*
3. Solubility	*Do predicted aqueous concentrations exceed aqueous solubility?*
4. Long-term Accumulation	*Is long-term accumulation (i.e., year-to-year carryover) expected to occur?*
5. Degradation Kinetics	*How important are dissipation processes in the interpretation of degradation half life data from laboratory or field studies? If important, how will degradation half lives be determined for exposure modeling purposes?*
Sediment Dynamics	
1. Model Sensitivity/ Uncertainty	*How sensitive are the risk assessment findings to model assumptions regarding the treatment of sediment dynamics?*
Bioaccumulation-Related Questions	
1. Exposure Routes	*How important is exposure through the diet and sediments for estimating bioaccumulation in aquatic organisms?*
2. Environmental Degradates	*How do the bioaccumulation potentials of parent and degradation products compare?*
3. Metabolism	*To what extent is bioaccumulation affected by pesticide metabolism in biota? What are the likely pesticide metabolites in aquatic organisms?*
4. Bioavailability	*How important are abiotic and biotic factors in affecting pesticide bioaccumulation in aquatic food webs?*
5. Steady State	*How long does it take for pesticide concentrations to reach steady-state accumulation in organisms*?
6. Critical Exposure Period	*What exposure period(s) is (are) considered most appropriate for estimating risk to sensitive ecological receptors? (e.g., weeks, months, year?)*
7. Multiple Lines of Evidence	*To what extent are aquatic bioaccumulation predictions by various methods (lab measurements, field measurements, model predictions) in agreement/disagreement? Can differences in bioaccumulation predictions be adequately explained?*
8. Terrestrial Ecosystems	*To what extent is bioaccumulation potential in terrestrial ecosystems a concern?*
Long-Range Transport	
1. Monitoring data	*What evidence exists on pesticide movement to remote locations distant from areas of pesticide application? What is the potential for adverse effects at these levels?*
2. LRT Potential	*What do physicochemical data and available environmental models suggest regarding the potential for long-range transport?*
Toxicity-Related Questions	
1. Ecological Receptors of Concern.	*What are the most sensitive ecological receptors and where do they occur in the environment?*
2. Dietary Exposure	*How important is dietary exposure to interpreting the results of laboratory toxicity studies?*

Issue	Risk Assessment Question
3. Parent vs. Degradate Toxicity.	*How similar is the toxicity of parent and degradatess? Are they likely to have the same mode of action?*
4. Steady-state	*Is steady-state accumulation likely to be achieved in chronic toxicity tests? Do reproductive studies allow sufficient time to adequately characterize maternal transfer?*
5. Bioavailability	*How much are toxicity test results likely to be affected by bioavailability differences across studies? Has the bioavailability of the pesticide been adequately characterized in the studies (e.g., centrifugation when concentrations approach or exceed solubility)?*

It is expected that the ability of the risk assessor to address the PBT/LRT-related risk assessment questions in **Table 1.4** will vary considerably from issue to issue. In some cases, relevant data may not be available to address a particular question, and thus simplifying assumptions or additional data may be required. In other cases, the available science underlying a particular risk assessment question may not be fully developed or might be evolving significantly. Specific methods for addressing many of the questions in **Table 1.4** will be informed by current and future SAP reviews.

2. INTRODUCTION

2.1 PURPOSE OF THIS SCIENTIFIC ADVISORY PANEL MEETING

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) is the statute that authorizes the US Environmental Protection Agency (Agency or US EPA) to register pesticides for sale or distribution in the United States. Before a pesticide can be registered in the United States, the Office of Pesticide Programs (OPP) conducts an ecological risk assessment to evaluate the potential risks posed by the pesticide to non-target organisms. The Agency may also conduct an ecological risk assessment after the initial registration when new uses are proposed, new data become available, or in response to statutory requirements for the periodic review of existing registrations.

Depending on the nature and level of potential risks identified, ecological risk assessments can vary from simple, screening level assessments with bounding assumptions to highly complex analyses. In general, the ecological risk assessment that is conducted uses risk quotients based on ratios of estimated environmental concentrations (EECs) to measured toxicity endpoints for various taxa. The tools, methods, and data that are routinely used in these ecological risk assessments have improved over time as the state of the science evolved.

Pesticides with combined persistence (P), bioaccumulative (B), and toxic (T) characteristics (collectively referred to as PBT) have represented particular challenges to the risk assessor, primarily because the historical suite of available assessment tools, methods and data have not been specifically designed to address the unique set of risk assessment issues associated with these pesticides. Over the past several years, the Agency has considered and employed a number of tools, methods and data in four of its ecological assessments to address PBT-related ecological risk issues. As the science behind the risk assessment of pesticides with PBT characteristics has evolved, so have the number and types of tools, methods and data being considered by the Agency in its pesticide risk assessments.

The purpose of this FIFRA Scientific Advisory Panel (SAP) meeting is to solicit comments from the Panel on the Agency's current approach and on the tools, methods and information for evaluating the ecological risks of pesticides with varying PBT characteristics. The Agency is also asking the SAP to provide recommendations for improving its approach for evaluating pesticides with PBT characteristics. Using case studies, the Agency has developed this White Paper describing the types of tools, methods and information which have been used to evaluate the ecological risk of four pesticides with varying PBT characteristics. Components of the assessments conducted for these four pesticides, which are not identified but referred to by generic names, illustrate: (1) the analyses employed in those assessments; (2) the risk assessment issues that have arisen; and (3) the evolving tools, methods and data that are being considered at this time. Advice from the SAP is being requested on whether the Agency's approach to addressing the PBT issues and its use of additional methods are consistent with the available

science and are appropriate candidates for further development and integration into the Agency's risk assessment process.

The Agency considers this SAP peer review as an initial step in a process for making refinements to its ecological risk assessment practices for addressing pesticides with PBT profiles. Over the next few years, the Agency plans to return to the SAP for additional review of specific methods and tools related to each topic area. However, the Agency will use the comments from this 2008 SAP meeting to support ecological risk assessments in its ongoing registration and re-registration program.

Specifically, the Agency is seeking:

1. An independent review of the need to modify the suite of tools, methods and information traditionally used by the Agency to address issues with assessing ecological risks of pesticides with PBT characteristics. Some of these issues include:

- Assessing non-aqueous routes of exposure of aquatic organisms (i.e., dietary uptake),
- Assessing aquatic organism toxicity from dietary exposure,
- Addressing lack of steady-state accumulation in standard laboratory toxicity tests,
- Incorporating factors that affect pesticide bioavailability and bioaccumulation (*e.g.,* organic carbon, lipid fraction, food web structure), and
- Addressing the challenges associated with the ecological risk assessment of compounds with extremely low water solubility or with potential PBTs having unknown or complex degradate pathways.

2. An independent review of refinements made to the ecological risk assessment methodologies of four example pesticides with varying PBT characteristics, including the suite of methods, models and data used to characterize the risk.

3. Advice on how the Agency should modify its problem formulation process for future ecological risk assessments involving pesticides with PBT characteristics, including:

- The process for identifying (screening) pesticides for potential PBT concerns (i.e., available data, triggers and assumptions regarding total residues of concern),
- The scope of risk assessment issues that the Agency should consider for pesticides with combined PBT attributes, and
- The existing suite of alternative models, methods and data the Agency should consider for addressing issues related to pesticide persistence, bioaccumulation and toxicity.

4. Advice for prioritizing the development of new models, methods, and information for addressing PBT issues (*e.g.,* bioaccumulation in terrestrial food webs, assessment of long range transport), which would become the subject of future, topic-specific SAP reviews.

2.2 ORGANIZATION OF THIS WHITE PAPER

This White Paper includes nine chapters and several appendices. The executive summary (Chapter 1) is followed by an introduction (Chapter 2) which includes: 1) the purpose of this SAP meeting, 2) how this White Paper is organized, 3) a summary of key risk assessment challenges involving pesticides with PBT characteristics, 4) the charge to the SAP, and 5) an overview of the OPP ecological risk assessment process for pesticides and current FIFRA data requirements. The body of this White Paper includes five chapters, each of which is focused on a specific topic related to assessing ecological risks of pesticides with PBT characteristics. Chapter 3 discusses issues and methods for assessing environmental persistence, Chapter 4—sediment dynamics, Chapter 5—bioaccumulation, Chapter 6—long-range transport, and Chapter 7—toxicity. Chapter 8 provides the conclusions and a proposed "path forward" that reflect the Agency's current thinking on how it might systematically refine its ecological risk assessment process for evaluating pesticides with PBT characteristics. The document concludes with Chapter 9, the bibliography, followed by the appendices.

2.3 RISK ASSESSMENT CHALLENGES ASSOCIATED WITH PESTICIDES WITH PBT CHARACTERISTICS

The characteristics of chemicals with PBT characteristics have been defined by various national and international institutions using numeric criteria pertaining to environmental persistence, bioaccumulation, and toxicity. A summary of the ranges of these PBT criteria are provided in **Table 2.1** along with values for four example pesticides that are being discussed in this White Paper.

Table 2.1. Selected National and International Criteria for Persistence, Bioaccumulation and Toxicity in Relation to Four Example Pesticides

Property	Process	Criteria(*)	Example Pesticide			
			1	2	3	4
Persistence	Half-life in soil (days) [1]	> 60 d to > 365 d	1,336	1,124	134 (47-205)	228 (187-287)
	Half life in water (days) [2]	> 60 d to > 180 d	*Hydr:* 11-19	Stable	408	Stable
			Met: 2,671	2,248	>100	186
			Phot: Stable	1.8	4.6	3
	Half life in sediment (days) [3]	> 60 d to > 365 d	382	2,004	>378	1,110
	Half life in air [4]	$\geq$ 2 d to $\geq$ 5 d	1.3 d.	Several years	0.3 d.	0.3 d.
Bioaccumulation	BCF or BAF [5]	>1000 to >5000 (L/kg wet wt.)	1,000 –3,000	960-1,100	2,100 – 7,300	27,000
	Log K_{OW}	> 5	3.55 – 4.78	4.8 – 5.3	4.4 – 5.1	8.1
Toxicity	Acute LC_{50} / EC_{50} [6]	< 1000 ug/L	0.1 & 5.8	56 & 12	1.79 [7]	500 & 1

	Chronic NOAEC [6]	<10 to <100 ug/L	0.01 & 0.11	13 & 18	1.79 [7]	49 & 1.4

(*) Ranges of numeric criteria reflect different institutional policies, regulations, and treaties regarding PBT classification. Sources: are provided in **Appendix A**.

[1] **Half Life in Soil** = 90th percentile (range) of aerobic soil metabolism half lives. Pesticide 1 half life calculated using total residues of concern (TROC) for parent isomer 1 (t½= 35-67 days) + isomer 2 (t½= 104-265 days) + a stable degradate. Pesticide 2 half life calculated using TROC for parent (t½= 77-189 days) + four stable degradates.

[2] **Half Life in Water:** *Hydr* = t½ for hydrolysis at pH 7; *Met* = t½ for aerobic aquatic metabolism using total system half life; *Phot* = t½ for aquatic photolysis (considered applicable only to shallow, clear water bodies). In absence of data for aerobic aquatic metabolism, t½ is estimated as 2X aerobic soil metabolism half life.

[3] **Half Life in Sediment =** t½ for anaerobic aquatic metabolism using total system half life. In absence of data, t½ is estimated as 2X anaerobic soil metabolism half life.

[4] **Half Life in Air** estimated using EPI SUITE; V4.02 noting that evidence of long range transport of pesticide 1 suggests longer half-life than estimated by EPI SUITE (i.e. longer than 1.3 days).

[5] Based on measured BCFs or BAFs for fish. Pesticide 4 BCF estimated from uptake and elimination rate constants.

[6] First toxicity value is for most sensitive fish, second value is the most sensitive invertebrate.

[7] Assumed toxicity value at limit of solubility.

In general, the Agency has found that chemicals with PBT profiles that conform to the criteria in **Table 2.1** present a number of risk assessment challenges for which many standard test and risk assessment methods are not well suited (USEPA, 2005). For example:

- **Toxicity from the Diet:** Chemical bioaccumulation through the aquatic food web can become an important exposure route for chemicals with PBT profiles. Standardized aquatic toxicity tests do not adequately address dietary exposure because the organisms are usually not fed in acute toxicity tests. In chronic toxicity tests, the organisms are usually fed a clean diet. If diet is an important route of exposure, this practice can render standard toxicity tests poor predictors of aquatic toxicity when the diet is an important route of exposure.

- **Chronic Toxicity**: Chemicals with PBT profiles often require long time periods to reach steady state accumulation in organisms (i.e., >28 days). Exposure durations of standard chronic tests are often 28 days or less. Furthermore, standard chronic tests protocols may not reflect the extent maternal transfer of these chemicals that would be expected during multi-generational exposure. Therefore, effects observed in these studies may underestimate toxicity that would result from long-term exposures in the environment.

- **Food Web Bioaccumulation:** Bioconcentration factors (BCFs) derived from standard bioconcentration tests of fish reflect chemical accumulation from water exposure only. For chemicals with PBT profiles, environmental exposure through the aquatic food web can be a major route of chemical uptake. In these situations, BCFs can significantly underestimate chemical bioaccumulation (uptake from water, food and sediments) by aquatic organisms and lead to underestimating risk.

- **Bioavailability:** Often, chemicals with PBT characteristics are highly hydrophobic and therefore, their bioavailability can be altered substantially by environmental factors and test conditions (*e.g.,* particulate and dissolved organic carbon, lipid content of organisms). This can lead to apparent inconsistencies among laboratory and field studies

when results are not corrected for bioavailability differences (not typically performed in most assessments). In addition, chemicals with PBT characteristics often have low water solubility which can lead to complications in the design and interpretation of environmental fate and effects studies.

- **Multi-year Exposures (Carry Over):** For highly persistent chemicals (with long environmental half-lives on the order of >1 year), increasing exposure from applications across multiple growing seasons and years can become a concern. Standard water quality/fate models are well suited to address pesticide 'carry over' in terms of abiotic compartments (water, sediment), but do not address long-term bioaccumulation from multi-year exposures. Food web bioaccumulation models are available, however, based on the Organization for Economic C-Operation and Development (OECD) survey (OECD 2002; 2005). They are not routinely used for pesticide registration across OECD member countries.

- **Bioaccumulation in Terrestrial Food Webs:** Compared to aquatic food webs, terrestrial food web bioaccumulation models are relatively new and have not been widely applied by the regulatory community. Recent studies suggest that certain persistent chemicals with moderate to high octanol-air partition coefficients (K_{OA}) may biomagnify substantially in terrestrial food webs (*e.g.,* Kelly et al., 2007; Kelly and Gobas, 2003) and thus, exposure via this route is potentially underestimated using the Agency's current methods.

- **Potential for Long-Range Transport:** It is widely known that some chemicals with PBT profiles can be subject to long-range transport via atmospheric processes. The ability to quantify and model the potential for long-range transport of chemicals is currently an evolving area of research for which additional risk assessment guidance is needed.

2.4 CHARGE TO THE SCIENTIFIC ADVISORY PANEL

The Agency provides the following charge to the SAP regarding ecological risk assessment of pesticides with PBT characteristics. This charge is informed by the Agency's past experience with assessing ecological risk of selected pesticides with varying PBT profiles and its desire to systematically refine and improve its ecological risk assessment process to address PBT-related issues in future pesticide assessments.

2.4.1 Topic-Specific Questions

Assessing Environmental Persistence

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.
- 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?
- 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.

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 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.

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, bank erosion) would be most important to consider in static ponds? Which processes would be most important in flowing water systems?

Assessing Bioaccumulation Potential

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.

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.

Assessing Toxicity

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.

Assessing Long-Range Transport

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.

- 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).

2.4.2 Cross-Cutting Questions

8. **PBT Risk Assessment Issues:** In this White Paper, the Agency describes a number of issues associated 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

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's 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.

Future PBT-Related Refinements

10. 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 need to be addressed
    - On the priority for developing new models, methods, and information for addressing PBT issues.

2.5 OVERVIEW OF THE ECOLOGICAL RISK ASSESSMENT PROCESS FOR PESTICIDES

This section provides a brief overview of the ecological risk assessments OPP conducts to identify those pesticides not likely to pose a risk to ecological resources. These assessments focus on the pesticide active ingredient and are intended to serve as a conservative screen

through the use of conservative exposure assumptions and the most sensitive species tested. In some cases, a more refined assessment may be needed, which could include the probabilistic models that were developed in OPP's initiative to refine the ecological assessment process for pesticides (http://www.epa.gov/oppefed1/ecorisk/).

Generally, these assessments follow the Agency's "Guidelines for Ecological Risk Assessment" (USEPA, 1998; **Figure 2.1**). For further information on the assessment process for pesticides, refer to the "Overview of the Ecological Risk Assessment Process in the Office of Pesticide Programs, US Environmental Protection Agency, Endangered and Threatened Species Effects Determinations" (USEPA, 2004).

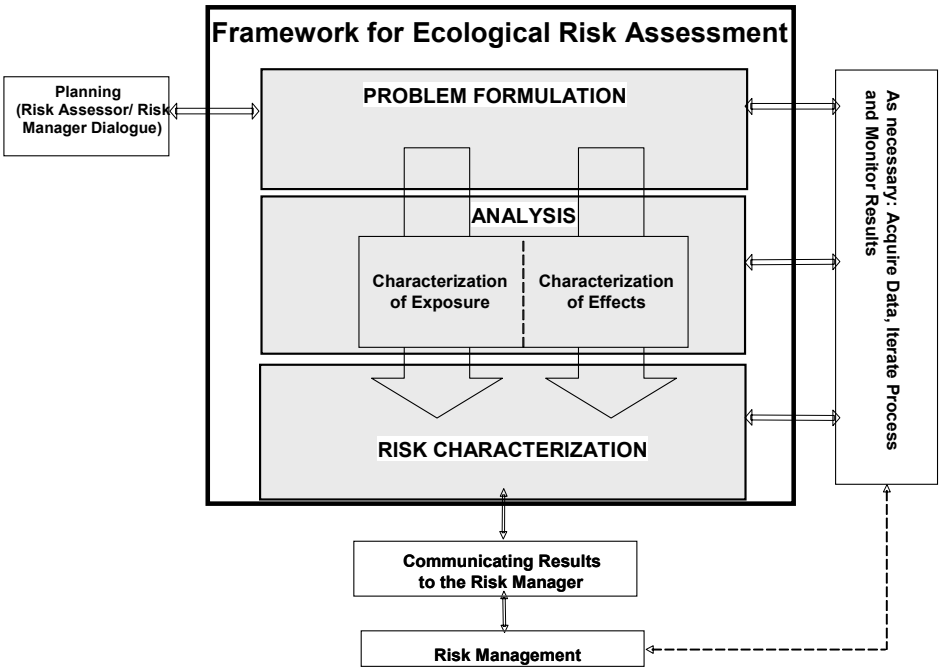


Figure 2.1. USEPA's Framework for Ecological Risk Assessment (USEPA, 1998)

2.5.1 Problem Formulation

Scientists assessing the environmental risk from pesticides begin with problem formulation, which provides the foundation for the assessment. Pesticide chemical characteristics are used to evaluate the nature of the chemical stressor and label information is used to characterize the use of the pesticide. The pesticide chemical characteristics that are considered may include the chemical class, empirical formula, molecular mass, vapor pressure,

Henry's Law Constant, solubility in water, Log K_{OW}, and PK_a/PK_b. Environmental fate and transport data for a pesticide are also considered, including persistence and mobility, major degradation pathways, routes of dissipation and degradation products.

The pesticide label information from proposed and/or existing labels includes instructions for use, application rates, use restrictions, and hazard statements. This information is used to characterize the pesticide use and is critical for determining input parameters for exposure models, evaluating the magnitude of exposure, and identifying geographic locations where non-target species are most likely to be exposed. The use characterization also allows the risk assessors and risk managers to focus the risk assessment on specific use patterns that are representative of a larger variety of use patterns. As a result, modeling and assessment resources can be focused on scenarios that reasonably represent the highest exposure potential among a suite of use scenarios.

During problem formulation, assessment endpoints, based on the goals of the proposed regulatory decision, are identified. For pesticides, the assessment endpoints are generally reduced survival and reproductive impairment for aquatic and terrestrial species from direct acute and chronic exposures to pesticides. Additional assessment endpoints, such as habitat modification and indirect effects (*e.g.,* reduction in prey base) are considered for Federally listed threatened and endangered species (listed species). In addition, a conceptual model and preliminary risk hypotheses are prepared during problem formulation.

Figure 2.2 portrays a generic conceptual model of pesticide sources, exposure routes, ecological receptors, and assessment endpoints routinely considered in the ecological risk assessment process in OPP. As depicted by this figure, sources and pathways of pesticide exposure commonly assessed include direct deposition on food items inhabiting the treatment site, runoff and erosion from fields to surface water, off-site (near field) spray drift and leaching to ground water. Exposure via volatilization and subsequent inhalation of pesticide by terrestrial animals is addressed in refined risk assessments and has been used to evaluate inhalation exposure from fumigant pesticides. In addition, dermal exposure may be evaluated as well on a case-by-case basis. Similarly, long-range (far field) atmospheric transport is not currently modeled, but is evaluated on a case-by-case basis using monitoring data (**Chapter 6**).

Risk to aquatic organisms is routinely assessed by comparing estimated exposure concentrations in water (pore water) with water-column acute and chronic toxicity reference values (*e.g.,* LC_{50}, NOAEC). Adverse effects resulting from aquatic organism exposure to pesticide-contaminated prey (i.e., trophic transfer) is currently assessed on a case-by-case basis.

For terrestrial animals, pesticide exposure and risks are commonly assessed via direct deposition of the pesticide on forage items (grasses, insects) inhabiting the treatment area and subsequent ingestion by terrestrial vertebrates.

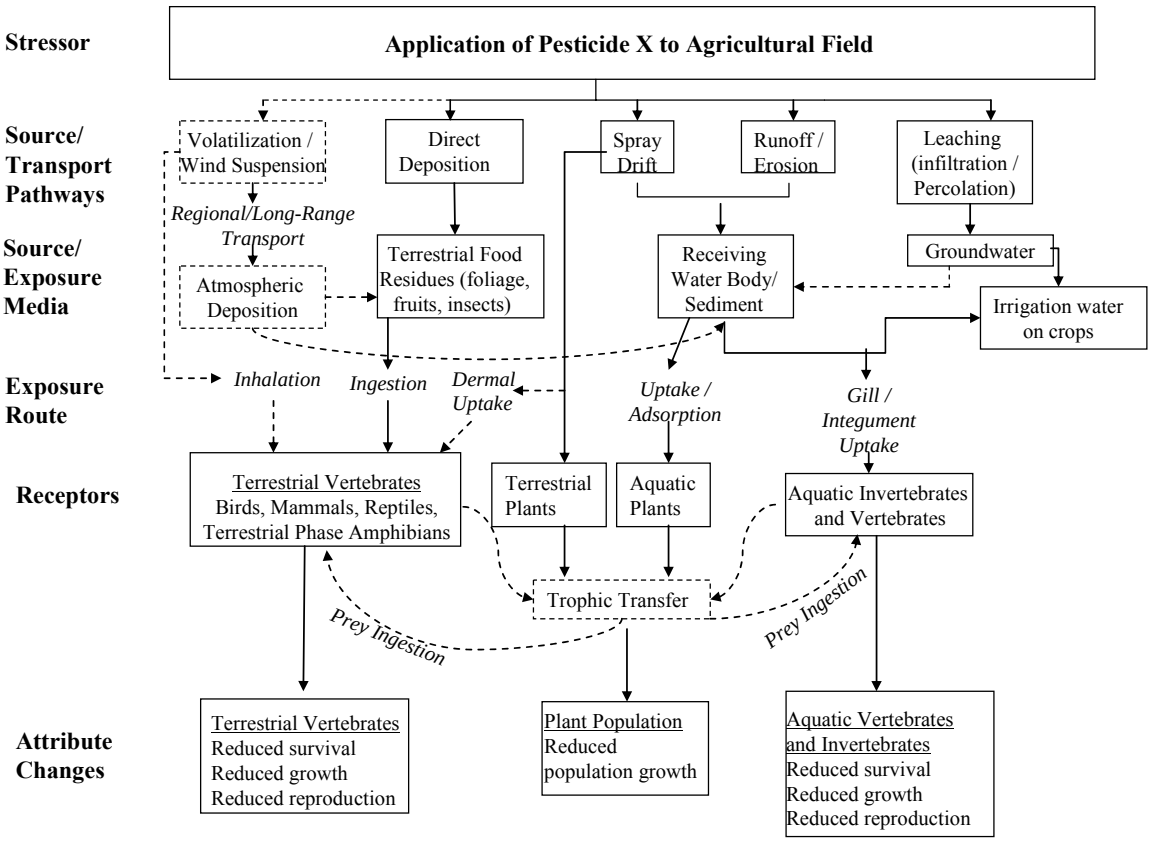


Figure 2.2. Generic Conceptual Model of Pesticide Ecological Risk Assessment by OPP
(Dashed sources and pathways are not routinely modeled by OPP/EFED)

Finally, problem formulation concludes with an analysis plan, which summarizes the process for analyzing the data, conducting the assessment and characterizing the risk. It also includes the identification of data gaps, which are addressed in the risk assessment as a source of uncertainty.

2.5.2 Exposure Characterization

The exposure characterization describes the potential or actual contact or co-occurrence of a pesticide with the receptors. Exposure is characterized through the use of computer models and the evaluation of environmental fate and monitoring data. As part of the development of the exposure profile, the environmental fate and transport of the active ingredient, and in some cases its degradates, in the environment is characterized. The analysis identifies the major routes of degradation, such as hydrolysis or photolysis, and evaluates persistence and mobility in aquatic and terrestrial environments. The potential for off-site movement, such as runoff to surface water, leaching into ground water or partitioning into air through volatilization or drift, is described in the exposure characterization. In addition, the mobility of the pesticide, its potential to sorb to soil particles and sediment, and its bioaccumulation potential should be considered and the primary dissipation pathways identified. Underlying the exposure characterization is a

discussion of the assumptions and limitations of analysis, confidence in the data, geographic variation, the effects of management practices and the value of additional data.

If available, pesticide monitoring data from a variety of sources are also evaluated to provide context to the aquatic exposure modeling. Monitoring data are often available for currently registered pesticides from a variety of sources. Typically, pesticide monitoring data from the United States Geological Survey's (USGS) National Water Quality Assessment (NAWQA) program are incorporated into ecological risk assessments. One common limitation of monitoring data is that the data are not necessarily targeted to detect maximum environmental concentrations of a particular pesticide. Therefore, the concentrations detected are not necessarily representative of the peak concentrations of that pesticide that may be occurring in the field.

The exposure characterization provides a synthesized interpretation of all available exposure information. This may include modeling and monitoring data; field study residue data or other field study information; residue data available from the appropriate health effects studies; and GIS analysis. It also reconciles the relationship between the modeling and monitoring data and considers other routes of exposure besides dietary, if the data are available. For example, dermal and inhalation exposure may be considered for terrestrial organisms in addition to dietary exposure which is routinely evaluated.

Exposure Characterization: Aquatic Organisms

Computer models that simulate the fate of pesticides in the environment are used to calculate EECs in surface water. These EECs are based on laboratory environmental fate and transport data and are used to evaluate pesticide exposure to aquatic organisms such as fish, invertebrates, and plants. In model simulations, a pesticide is represented by input parameters describing the physical, chemical, fate and transport properties of the pesticide. EECs are used to evaluate pesticide exposure to aquatic organisms such as fish, invertebrates and plants.

A two-tiered aquatic exposure assessment process is used to predict EECs in surface water and is based on estimating runoff from a watershed moving into a static surface water body. **Table 2.2** provides a summary of the key characteristics, including the limitations and assumptions, of each tier.

Table 2.2. Summary of the Key Characteristics of the Two-Tiered Aquatic Exposure Assessment Process

Tier	Model	Construct of Model	Scenario	Input Parameters	Duration of Exposure Concentrations	Limitations and Assumptions
I	GENEEC2	Meta-model of PRZM/EXAMS simulation for Mississippi cotton scenario	Single high runoff event for 10 ha field draining into a small farm pond	Application rate Application method Spray drift Solubility Soil/sediment: water partitioning Photolysis in water half-life Hydrolysis half-life Aerobic soil metabolism half-life Aerobic aquatic metabolism half-life	Peak 4 day average 21 day average 60 day average Annual average	No sediment consideration No residue accumulation potential No residue volatilization No simulation for degradation product formation and decline.
II	PRZM/ EXAMS	Mechanistic models using site-specific weather and soils	Multi-year daily time runoff events for 10 ha field draining into a small farm pond	Application rate Application method Pesticide timing Crop growth conditions Spray drift Depth of pesticide incorporation Solubility Vapor pressure Henrys Law Constant Soil:water partitioning coefficients Vapor pressure Photolysis in water half-life Hydrolysis half-life Aerobic soil metabolism half-life Aerobic aquatic metabolism half-life Anaerobic aquatic metabolism half-life	1 in 10 year concentration for Peak 4 day average 21 day average 60 day average Annual average	Residue accumulation is possible. Residue volatilization from field is not explicitly considered.

For Tier I, the Generic Estimated Exposure Concentration model (GENEEC2 v.2.0; August 1, 2001) is used to estimate pesticide concentrations from a single high runoff event. It should be noted that GENEEC2 does not provide a daily time series of concentrations or an estimate of the sediment and sediment pore water concentrations. Thus, the Tier I model has limited capability to assess compounds with PBT characteristics. Because of the conservative nature of the Tier I GENEEC model for compounds that do not have PBT characteristics, if the levels of concern (LOC) for risk to aquatic organisms are not exceeded, this generally provides evidence of minimal risk from the pesticide use. However, if the LOC is exceeded, additional refinement using Tier II models is warranted. (See **Section 2.5.4** for more information on LOCs.)

For Tier II surface water exposure assessments, the Pesticide Root Zone Model (PRZM; v3.12.2; May 2005 and Exposure Analysis Modeling System (EXAMS; v2.98.04.06; April 2005) models are used. The PRZM model estimates pesticide runoff and leaching and considers site-specific properties. It provides a daily output of pesticide runoff concentrations, runoff volumes, and eroded sediment for the EXAMS model. EXAMS is used to simulate degradation and dissipation in the standard pond environment and provides a fixed environment scenario for water quality, flow rates, dimensions, evaporation, etc. EXAMS output provides a daily time series of concentrations in the water column, sediment, sediment pore water, and biota. The 1 in 10 year concentrations for peak, 21-day average, and 60-day average are used as the aquatic exposure endpoints. This modeling process considers site specific climate and soils data. Model simulations are generally conducted using 30 years of daily weather data. Additionally, the model considers time-dependent agronomic management practices associated with the pesticide use.

Resulting EECs are based on aqueous exposure concentrations in the water column of the pond environment. These EECs are compared to acute and chronic toxicity data for aquatic animals and plants to derive risk quotients (RQs). If RQs exceed LOCs from the Tier II assessment, then additional refinements may be conducted to characterize the potential risk.

Exposure Characterization: Terrestrial Animals

Exposure to terrestrial animals is estimated using a series of tables based on a database of actual measured pesticide residue values on plants and insects. These tables are referred to as the Kenaga nomogram as modified by Fletcher (Hoerger, and Kenaga, 1972; Fletcher et al., 1994). The nomogram relates food item residues to pesticide application rate. A computer model is then used to simulate degradation and/or dissipation of residues on foliar surfaces and insects. The result is dietary-based EECs for different food items that are consumed by birds and mammals. The residue concentration is also converted to a daily oral dose based on fractions of avian or mammalian body weight consumed daily.

For granular, bait, and treated seed applications, estimation of loadings of pesticide per unit area (*i.e.,* LD_{50}/ft^2) are calculated at the time of application and no modeling of degradation or dissipation is conducted.

Exposure Characterization: Non-target Plants

The non-target terrestrial plant exposure assessment is based on the TerrPlant model (v1.2.2, December 26, 2006). This model estimates exposure concentrations from sheet runoff, channel runoff, and spray drift from a treated field. For the terrestrial plant exposure assessment, the model assumes a field/edge of field area ratio of 1 to simulate sheet runoff of pesticide onto adjoining terrestrial environments. For semi-aquatic plant exposure assessment , the model assumes a field/semi-aquatic area ratio of 10 to simulate channel runoff into adjoining semi-aquatic environments from the pesticide treated field. Magnitude of pesticide concentrations in runoff is dependent on pesticide solubility, application rate, and soil incorporation depth. Spray drift contributions are 1% of the application rate for ground sprays and 5% of the application rate for aerial, airblast, or spray chemigation methods. The model is suitable for single application events and makes estimates involving multiple pesticide applications an issue of potential importance for persistent compounds.

Exposure Characterization: Spray Drift

In more refined assessments, which may include the evaluation of mitigation measures such as spray drift buffer zones, the models AgDRIFT and AGDISP can be used to assess exposures of aquatic and terrestrial habitats to pesticides transported from the target area through spray drift. AgDRIFT (v2.01; May 24, 2001) is used to simulate spray drift movement from ground, aerial and spray blast applications. In addition, AGDISP (v8.13; December 14, 2004) can be used to simulate aerial and ground applications using the Gaussian far-field extension. AgDRIFT and AGDISP are spray droplet physics-based models capable of predicting the spectra and deposition of spray droplets over unite areas. The model are not necessarily suitable for use in evaluating other forms of pesticide aerial transport or deposition to terrestrial or aquatic habitiats.

2.5.3 Effects Characterization

The effects characterization evaluating potential acute and chronic effects to the receptor uses a surrogate species approach. Toxicological data generated from surrogate test species, such as a Mallard Duck *(Anas platyrhynchos)* or Bobwhite Quail *(Colinus virginianus)* and a passerine species, are intended to be representative of broad taxonomic groupings and are used to extrapolate to potential effects on birds, terrestrial-phase amphibians and reptiles, unless taxa-specific data are available through the open literature or other sources. The test species are selected based on their ability to thrive under laboratory conditions and are not intended to be representative of the most sensitive species.

Within each of these taxonomic groupings, acute and chronic endpoints are selected from the available test data on aquatic and terrestrial receptors. The selection is made from the most sensitive species tested within that taxonomic grouping. Data sources for the effects characterization include registrant-submitted studies and published literature studies. The typical test species that are often used as surrogate species for taxa of concern are identified in **Table 2.3.**

Table 2.3. Test Species Typically Evaluated For Assessing Potential Ecological Effects Of Pesticides

Taxonomic Group	Surrogate Species
Freshwater fish[1]	Bluegill sunfish (*Lepomis macrochirus*) Rainbow trout (*Oncorhynchus mykiss*) Fathead minnow (*Pimephales promelas*)
Freshwater invertebrates	Water flea (*Daphnia magna*) Midge (*Chironomus riparius*)
Estuarine/marine fish	Sheepshead minnow *(Cyprinodon variegatus)*
Estuarine/marine invertebrates	Mysid shrimp *(Americamysis bahia)* Eastern oyster (*Crassostrea virginica)*
Non-vascular aquatic plants	Green algae (*Pseudokirchneriella subcapitatum*) Blue-green algae (*Anabaena flos-aquae*) Freshwater diatom (*Navicula pelliculosa*) *M*arine diatom (*Skeletonema costatum*)
Vascular aquatic plants	Duckweed (*Lemna gibba*)
Birds[2]	Mallard Duck (*Anas platyrhynchos*) Bobwhite Quail (*Colinus virginianus*) Passerine species
Mammals	Laboratory rat (*Rattus norvegicus*)
Insects	Honey bee (*Apis mellifera L.*)
Terrestrial plants[3] – monocots	Corn (*Zea mays*) Oat (*Avena sativa)* Ryegrass (*Lolium perenne)* Onion (*Allium cepa)* Barley (*Hordeum vulgare)* Sorghum (*Sorghum vulgare)*
Terrestrial plants[3] – dicots	Soybean (*Glycine max*) Cucumber (*Cucumis sativus)* Sugar beet (*Beta vulgaris)* Oilseed rape (*Brassica napus)* Sunflower (*Helianthus annuus)* Tomato (*Solanum esculentum)* Radish (*Raphanus sativus)*

[1] Freshwater fish may be surrogates for aquatic-phase amphibians.
[2] Data are required on one passerine species and either one waterfowl species or one upland game bird species
[3] Guidelines require: 1) 4 species of two families of monocots, of which one is corn; and 2) 6 species of at least four dicot families, of which one is soybeans.

The effects characterization describes the available toxicity data and includes toxicity endpoints for aquatic and terrestrial animals and plants. The acute measures of effect for animals are the median lethal dose (LD_{50}), median lethal concentration (LC_{50}), and the median effects concentration (EC_{50}). Endpoints for chronic measures of exposure for listed and non-listed animals are the no-observed-adverse-effect level/concentration (NOAEL/NOAEC). The NOAEC is used to evaluate potential effects to listed plants, while the EC_{25} and EC_{50} are used to evaluate potential effects to non-listed terrestrial and aquatic plants, respectively.

The toxicity testing scheme is tiered and is based on the use and toxicity of the pesticide active ingredient. Depending on the results of studies conducted at a lower level, testing can progress from basic laboratory tests at the lowest level to applied field tests at the highest level. Other effects data may also be available, and professional judgment is used to determine whether and how available data on other toxicity endpoints can be included in the risk assessment.

2.5.4 Risk Characterization

Risk characterization, which is the final phase of the ecological risk assessment, consists of two major components: risk estimation and risk description. As stated previously, the Agency uses a deterministic approach or a point estimate to estimate risk to nontarget organisms from exposure to a stressor. In this approach, referred to as the risk quotient (RQ) method, the RQ is calculated by dividing a point estimate of exposure (EEC) by a point estimate of effects. The results are then compared to the Agency's Level of Concern (LOC), the Agency's threshold value used to interpret the risk quotient. The potential risk to non-target organisms is analyzed, and a determination is made regarding the need for regulatory action. Methods for deriving RQs for acute and chronic exposures to specific taxa as well as the corresponding LOCs are in **Table 2.4.**

Table 2.4. Agency Risk Quotient (RQ) Metrics and Levels of Concern (LOC) Per Risk Class

Risk Class	Risk Description	RQ	LOC
Aquatic Animals (fish, amphibians and invertebrates)			
Acute	Potential for effects to non-listed animals from acute exposures	Peak EEC/LC_{50} or EC_{50}[1]	0.5
Acute Restricted Use	Potential for effects to animals from acute exposures Risks may be mitigated through restricted use classification	Peak EEC/LC_{50} or EC_{50}[1]	0.1
Acute Listed Species	Listed species may be potentially affected by acute exposures	Peak EEC/LC_{50} or EC_{50}[1]	0.05
Chronic	Potential for effects to non-listed and listed animals from chronic exposures	60-day EEC/NOAEC (fish)	1
		21-day EEC/NOAEC (invertebrates)	
Terrestrial Animals (mammals, birds, amphibians, reptiles)			
Acute	Potential for effects to non-listed animals from acute exposures	EEC[2]/LC_{50} (Dietary)	0.5
		EEC/LD_{50} (Dose)	
Acute Restricted Use	Potential for effects to animals from acute exposures Risks may be mitigated through restricted use classification	EEC[2]/LC_{50} (Dietary)	0.2
		EEC/LD_{50} (Dose)	
Acute Listed Species	Listed species may be potentially affected by acute exposures	EEC [2]/LC_{50} (Dietary)	0.1
		EEC/LD_{50} (Dose)	
Chronic	Potential for effects to non-listed and listed animals from chronic exposures	EEC [2]/NOAEC	1
Plants			
Non-Listed	Potential for effects to non-target, non-listed plants from exposures	EEC/ EC_{25} or EC_{50}	1
Listed Plant	Potential for effects to non-target, listed plants from exposures	EEC/ NOAEC	1
		EEC/ EC_{05} [3]	

[1] LC_{50} or EC_{50}.
[2] Based on upper bound Kenaga values.
[3] EC_{05} is used in place of a NOEC if a NOAEC value is not established.

Risk description interprets the risk estimation by providing an evaluation of the lines of evidence supporting or refuting the risk estimates, interprets the relevancy of the lines of evidence to assessment endpoints, and discusses the field studies, incident data, monitoring data, and modeling data. The risk description also describes the likely effects, such as acute mortality

or chronic reductions in growth, reproduction or survival, in those cases where the LOCs were exceeded. The extent to which open literature was used to support the association between EECs and effects should also be addressed. Potential food chain effects and uncertainties related to the risk estimates are described, and a comparison of the laboratory data and field data, if available, is made. Finally, the risk description includes a review of the adequacy and quality of data as well as a description of the degree of variability and type of uncertainty.

2.6 OVERVIEW OF CURRENT FIFRA DATA REQUIREMENTS

Under FIFRA sections (3)(c)(1)(F), (3)(c)(2)(B), the Agency is authorized to require data to support the proposed registration application of a pesticide, to request additional data on currently registered products. Under FIFRA (6)(a)(2), registrants must report data indicating any adverse effects associated with a registered product. CFR 40, Part 158 describes the type and number of data that the Agency needs to determine the potential risks of a pesticide to nontarget organisms. These data include product and residue chemistry, environmental fate, mammalian toxicology, aerial drift evaluation, terrestrial and aquatic plant and animal toxicity data. A summary of selected FIFRA-required environmental fate and ecological effects studies that have particular relevance to PBT risk assessment issues is provided in **Appendix B**.

3. ASSESSING ENVIRONMENTAL PERSISTENCE

3.1 INTRODUCTION

The exposure assessment in the FIFRA aquatic risk assessment is routinely focused on estimating pesticide concentrations in the water column. There is, however, no routine analysis of exposure concentrations in air, soil, sediment, or sediment pore water. Soil, sediment and air exposure assessments are conducted only when there is evidence, either through environmental fate data, modeling, or monitoring data, of pesticide occurrence in the sediments/soils and/or air.

OPP conducted risk assessments on four pesticides with characteristics comparable to persistent, bioaccumulative, and toxic compounds. For these pesticides, assessment of pesticide exposure potential in sediment, pore water and/or air was considered necessary for estimating ecological risk. During the conduct of these risk assessments, OPP encountered several challenges associated with interpreting and quantifying environmental fate and exposure of pesticides exhibiting high persistence, high soil/sediment sorption coefficients, and low solubility. Major risk assessment challenges with the four example pesticides are as follows:

- Estimation of exposure concentrations for total residues of concern (TROC);
- Prediction and interpretation of exposure concentrations above the water solubility;
- Interpretation of degradation half-lives in soil and aquatic systems when sorption is an important route of dissipation; and
- Quantification of exposure concentrations for long-term accumulation in soil, sediment, and associated pore water.

Each of these issues is discussed in the ensuing sections of this White Paper. An overview of the environmental fate properties for the four pesticides is presented immediately below to provide context to the identified environmental fate and transport assessment issues.

3.2 OVERVIEW OF ENVIRONMENTAL FATE DATA FOR EXAMPLE PESTICIDES

As discussed earlier, a suite of environmental fate and transport studies, as listed in 40 CFR Part 158, are submitted by registrants to support pesticide registrations for specific use patterns. Additional studies also may be required to address unique environmental fate properties of the pesticide (*i.e.*, volatilization and bioaccumulation). Environmental fate and transport data include: physiochemical properties; rates and routes of abiotic/biotic degradation; partitioning and mobility in soil; volatilization from soil; bioconcentration in fish; and dissipation under actual field use conditions. These environmental fate data, in addition to use information from pesticide labels, are used in models to predict the exposure concentrations of the pesticides and their degradation products in aquatic and terrestrial environments. Below is a summary of the environmental fate data and use information for the four example pesticides. These data are

used to illustrate issues and challenges in addressing environmental persistence in exposure assessments.

3.2.1 Pesticide 1 Environmental Fate and Transport Data and Use Information Summary

Pesticide 1 is used as an insecticide on a variety of fruits, vegetables, cereals, and cotton (**Table 3.1**). It is a mixture of two isomers with a ratio of 30:70 isomer 1: isomer 2. The isomers exhibit different environmental fate profiles; isomer 1 is less persistent than isomer 2 in soil and aquatic environments (**Table 3.2**). Both isomers exhibit vapor pressures and Henry's Law Constants comparable to semi-volatile pesticides. Additionally, the isomers degrade to form a common toxic and persistent degradation product (68% formed) in soil. Data suggest that this degradate product is more persistent than the parent.

Table 3.1. Representative Application Rate for Pesticide 1

Crop	Application Type	Date of First Application	Maximum Single Application Rate (lbs ai/A)	Minimum Interval (days)	Maximum Number of Applications	Maximum Annual Total (lbs ai/A)
Cotton	Aerial	June 1	0.15	14	3	1.2
Tomato	Aerial	June1	3.00	36	3	9.0

Table 3.2. Representative Environmental Fate Data for Pesticide 1

Model Parameter	Value			
	Isomer 1	Isomer 2	Degradation Product	Total Residues of Concern
Aerobic Soil Metabolism Half-life	57 days[1]	208 days[1]	Stable	1,336 days[1]
Aerobic Aquatic Metabolism Half-life	114 days[2]	416 days[2]	Stable	2,671 days[2]
Anaerobic Aquatic Metabolism Half-life	286 days[3]	382 days[3]	240 days	382 days[3]
Aqueous Photolysis Half-life	Stable	Stable	Stable	Stable
Hydrolysis Half-life	19 days	11 days	19 days	19 days
Koc	10,600L/kg-OC[4]	13,500L/kg-OC[4]	10,600L/kg-OC[5]	10,600L/kg-OC[5]
Molecular Weight	406.9 g/mole	406.9 g/mole	422.9 g/mole	406.9 g/mole

Model Parameter	Value			
	Isomer 1	Isomer 2	Degradation Product	Total Residues of Concern
Water Solubility	530 µg/L	280 µg/L	330 µg/L	530 µg/L
Vapor Pressure	$3X10^{-6}$ torr	$7.2 X 10^{-7}$ torr	No Value	$7.2 X 10^{-7}$ torr
Henry's Law Constant	$3.03E^{-5}$ atm-m^3 mol^{-1}	$1.38E^{-6}$ atm-m^3 mol^{-1}	$1E^{-10}$ atm-m^3 mol^{-16}	$1.38E^{-6}$ atm-m^3 mol^{-1}

1- Estimated 90% percentile of the mean half-life; for the total residue of concern, half-lives were for the total of isomer 1+ isomer2 +degradate
2- Estimated 2X aerobic soil metabolism half-life
3- Estimated 2X anaerobic soil metabolism half-life
4- Represent mean value
5- Assumed to be equal to parent
6- Assumed to be non-volatile

Exposure modeling was conducted to establish estimated environmental concentrations (EECs) for the individual isomers as well as for the total residues of concern (TROC= isomers + degradation product). TROC modeling was conducted because the toxic degradation product is persistent and has similar toxicological profile as the parent. **Figure 3.1** illustrates an example of the degradation pattern of Pesticide 1 in an aerobic soil metabolism study. The high persistence of the toxic degradation product is expected to extend the residual effect of this pesticide.

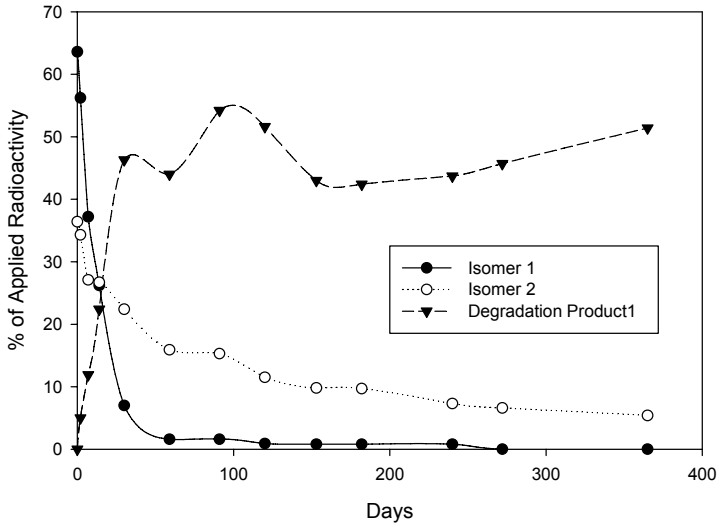


Figure 3.1. Degradation Pattern of Pesticide 1 in an Aerobic Soil Metabolism Study

3.2.2 Pesticide 2 Environmental Fate and Transport Data and Use Information Summary

Pesticide 2 is used as a fungicide on turf, peanuts, cole crops, potatoes, and cotton **(Table 3.3)**. This pesticide degrades to form 4 toxic degradation products. Important routes of degradation for Pesticide 2 are photolysis in water and anaerobic soil metabolism **(Table 3.4)**.

Volatilization is expected to be an important route for off-site movement for the parent and degradation products because of their large Henry's Law Constants (10^{-7} to 10^{-4} atm-m^3 mol^{-1}).

Table 3.3. Representative Application Rates and Methods for Pesticide 2

Crop	Application Type	Date of First Application	Maximum Single Application Rate (lbs ai/A)	Minimum Interval (days)	Maximum Number of Applications	Maximum Annual Total (lbs ai/A)
Cotton	In-furrow	April 20th	2	N/A	1	2
Potatoes	Granular	May 20th	25	NA	1	25
Cabbage	Ground Spray	August 15th	30	N/A	1	30
Turf	Ground Spray	Nov. 15th	32	N/A	1	32.7

Table 3.4. Representative Environmental Fate Data for Pesticide 2

Model Parameter	Value	
	Parent	Total Residues of Concern
Aerobic Soil Metabolism Half-life	189 days	1,124 days[1]
Aerobic Aquatic Metabolism Half-life	378 days[2]	2,248 days[2]
Anaerobic Aquatic Metabolism Half-life	9 days	2,004 days[3]
Aqueous Photolysis Half-life	2.5 days	1.83 days
Hydrolysis Half-life	Stable	Stable
Koc	6,470 L/kg-OC[4]	6,470 L/kg-OC*
Molecular Weight	295.3 g/mole	295.3 g/mole*
Water Solubility	440 µg/L	440 µg/L*
Vapor Pressure	1.13 X 10-4 torr	1.13 X 10-4 torr*
Henry's Law Constant	$4.42E^{-5}$ atm-m^3 mol^{-1}	$4.42E^{-5}$ atm-m^3 mol^{-1}*

1- Estimated 90% percentile of the mean half-life; for the total residue of concern, half-lives were for the total of parent +degradation products
2- Estimated 2X aerobic soil metabolism half-life
3- Estimated 2X anaerobic soil metabolism half-life; for the total residue of concern, half-lives for the anaerobic soil metabolism were calculated for the total of parent +degradation products
4- Represent mean value
*- Assumed to be equal to parent compound

PRZM/EXAMS modeling was conducted to establish EECs for the parent alone and total residues of concern which includes the parent and four degradation products.. The TROC modeling approach was conducted because the degradation products have similar toxicological profiles and are expected to have the same mode of toxicity as the parent compound to non-target aquatic organisms**. Figure 3.2** illustrates an example of the degradation pattern of Pesticide 2 in an aerobic soil metabolism study. The formation of numerous persistent, toxic degradation products is expected to extend the residual effect of this pesticide 2.

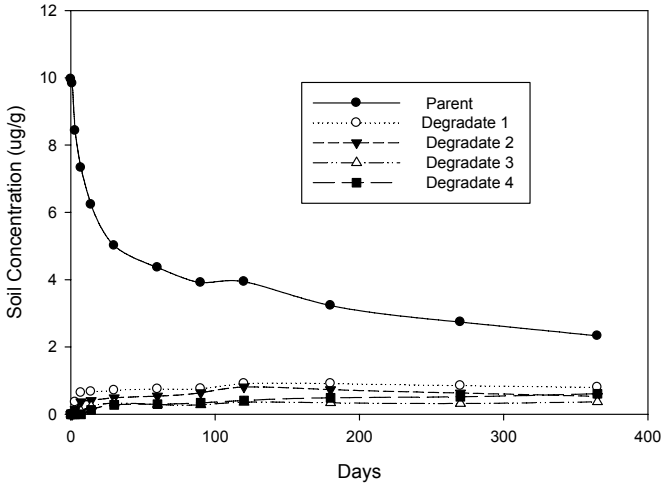


Figure 3.2. Degradation Pattern of Pesticide 2 in an Aerobic Soil Metabolism Study

3.2.3 Pesticide 3 Environmental Fate and Transport Data and Use Information Summary

Pesticide 3 is proposed to be used as an insecticide on potatoes, leafy vegetables, fruiting vegetables, and cotton **(Table 3.5)**. This pesticide has two isomers with an isomeric ratio of 12:1. The isomers have similar environmental fate and toxicological properties. The important route of degradation for Pesticide 3 is photolysis in water **(Table 3.6).** There are no major degradates of concern. PRZM/EXAMS modeling was conducted to establish EECs for the parent compound alone.

Table 3.5. Representative Application Rates and Methods for Pesticide 3

Crop	Application Type	Maximum Single Application Rate (lbs ai/A)	Minimum Interval (days)	Maximum Number of Applications	Maximum Annual Total (lbs ai/A)
Potatoes	Aerial/Ground Spray	0.25	7	4	1
Cole Crops	Aerial/Ground Spray	0.25	7	4	1
Fruiting Vegetable	Aerial/Ground	0.25	7	4	1
Cotton	Aerial/Ground Spray	0.25	7	4	1

Table 3.6. Representative Environmental Fate Data for Pesticide 3

Model Parameter	Value
	Parent
Aerobic Soil Metabolism Half-life	134 days[1]
Aerobic Aquatic Metabolism Half-life	268 days[2]
Anaerobic Aquatic Metabolism Half-life	378 days[3]
Aqueous Photolysis Half-life	4.6 days
Hydrolysis Half-life	408 days
Koc	30,753 L/kg-OC[4]
Molecular Weight	506.4 g/mole
Water Solubility	1.79 µg/L
Vapor Pressure	9.3×10^{-11} torr
Henry's Law Constant	3.4×10^{-8} atm m^3 mol^{-1}

1- Estimated 90% percentile of the mean half-life
2- 2X aerobic soil metabolism half-life
3- >378 days (Assumed to be 378 days)
4- Represent mean value

3.2.4 Pesticide 4 Environmental Fate and Use Information Summary

Pesticide 4 is proposed to be used as an insecticide on cotton, tobacco, lettuce, cole crops, peppers, turf, grapes, and apples **(Table 3.7)**. The major route of degradation is photolysis in water **(Table 3.8)**. There are no major degradates of concern. PRZM/EXAMS modeling was conducted to establish EECs for the parent compound alone.

Table 3.7. Representative Application Rates and Methods for Pesticide 4

Crop	Application Type	Date of First Application	Maximum Single Application Rate (lbs ai/A)	Minimum Interval (days)	Maximum Number of Applications	Maximum Annual Total (lbs ai/A)
Cotton	Aerial	June 1	0.15	14	8	1.2
Tobacco	Aerial	July 1	0.2	14	6	1.2
Lettuce	Aerial	April 1	0.2	14	6	1.2
Cabbage	Aerial	January 1	0.2	14	6	1.2
Pepper	Aerial	October 1	0.2	14	6	1.2
Turf	Ground	May 1	0.381	14	6	2.29
Grape	Ground	August 1	0.381	14	6	2.29
Apple	Airblast	June 1	0.381	14	6	2.29

Table 3.8. Representative Environmental Fate Data for Pesticide 4

Model Parameter	Value
Aerobic Soil Metabolism Half-life	228 days[1]
Aerobic Aquatic Metabolism Half-life	186 days[1]
Anaerobic Aquatic Metabolism Half-life	1,110 days[2]
Aqueous Photolysis Half-life	3 days
Hydrolysis Half-life	Stable
Koc	1,241,000 L/kg-OC[3]
Molecular Weight	491.1
Water Solubility	0.15 µg/l
Vapor Pressure	2.05×10^{-7} torr
Henry's Law Constant	4.95×10^{-10} atm m^3 mol^{-1}

1- Estimated 90% percentile. of the mean half-life
2- Estimated 3X single value for aerobic aquatic metabolism half-life which is > 370 days
3- Represent mean value

3.3 INTEGRATED ENVIRONMENTAL FATE ASSESSMENT

The Subdivision N environmental fate data suggest common routes of dissipation (degradation + movement) among the example pesticides **(Table 3.9)**. The data clearly illustrate that photolysis in water is the most rapid route of degradation for Pesticides 2, 3, and 4. Additionally, abiotic hydrolysis and microbial-mediated degradation in soil and aquatic environments are degradation pathways for individual isomers of Pesticide 1. Toxic degradation products for Pesticide 1 and 2, however, are persistent in soil and aquatic environments. A

common environmental fate property among the example pesticides is a high organic carbon: water partitioning coefficient. Sorption on soil and sediment is expected to control the environmental behavior of these pesticides. Volatilization is a pathway for off site movement of Pesticide 1 and 2 because of their moderate vapor pressure and Henry's Law Constants.

Table 3.9. Summary of Dissipation Pathways for Example Pesticides

Routes of Dissipation	Parent 1	Parent 2	Parent 3	Parent 4
(1) Degradation				
Hydrolysis	√			
Photodegradation in Water		√	√	√
Aerobic Degradation in Soil	√			
Anaerobic Degradation in Sediment		√		
(2) Movement				
Sorption	√	√	√	√
Volatilization	√	√		

√= Indicates Important Dissipation Pathway

3.4 PBT-RELATED CHALLENGES AND ISSUES

3.4.1 Addressing the Combined Exposure to Parent and Degradation Products

As described in the Overview document[1] and discussed briefly in the preceding chapter, exposure characterizations conducted in support of pesticide regulatory decisions typically provide a quantitative analysis of the critical environmental fate and transport properties of the pesticide active ingredient. However, there are situations where degradates occur in significant amounts and/or are of significant toxicological concern. In such situations, exposure characterizations would include a quantitative or qualitative analysis of the risk implications from organism exposure to these degradates in addition to the parent compound. For example, DDT degrades to form persistent and toxic degradation products DDE and DDD.

The Agency's risk assessment guidance instructs risk assessors to clearly and concisely describe the nature of the stressors evaluated in the risk assessment. This includes documentation of the potential significance of degradates in the risk assessment of pesticides. For ecological risk assessments, concern for pesticide degradation products is determined based on their known or expected toxicity. Degradates of similar toxicity to their parent compound are of concern if they account for at 10% of the applied amount. Degradates more toxic than the parent compound are generally of concern when detected at any concentration. Consideration is

[1] USEPA 2004. Overview of the Ecological Risk Assessment Process in the Office of Pesticide Programs, U. S. Environmental Protection Agency. Endangered and Threatened Species Effects Determinations. Office of Prevention, Pesticides and Toxic Substances, Washington, DC. http://www.epa.gov/espp/consultation/ecorisk-overview.pdf

also given to whether the mode of action underlying degradate toxicity is similar to that underlying parent toxicity.

Pesticides with persistent toxic parent and degradation products require special consideration in exposure assessments. The prolonged persistence of the pesticide residues increases the potential risk of exposure and toxicity to both aquatic and terrestrial organisms. Additionally, it complicates exposure assessment because of the potential for year-to-year carryover of residues in soils and sediments.

OPP has employed various modeling strategies for predicting exposure concentrations of total residues of concern (TROC) in aquatic environments **(Table 3.10)**. These modeling strategies are not routinely considered in terrestrial exposure assessments. The modeling strategies include:

(1) Residue Summation (RS method): This modeling strategy requires summation of individual residues of concern concentrations to represent the TROC. Application rates for degradation products need to be adjusted to account for molecular weight ratios of degradate to parent and the normalized maximum percentage of degradation product formed. This method requires environmental fate data for individual residues. It also requires manual post-processing of data for estimating 1-in-10 year exposure concentrations. This method cannot be used to estimate temporal occurrence of degradation products.

(2) Simultaneous Formation/Decline Kinetics (FD method): This strategy is the preferred method for estimating concentrations of TROC. The strategy requires estimation of simultaneous formation and degradation rate constants for parent and degradation products. The method requires environmental fate data for individual residues. Application rates of the pesticide and its degradation products do not require any correction or normalization to account for formation and decline of the degradation products. A major advantage of this method is the estimation of temporal occurrence of degradation products.

(3) Total Residue (TR method): This modeling strategy requires an assumption that all residues of concern have similar physical, chemical, and partitioning characteristics. Application rates for the parent pesticide are used to represent the total mass loading of pesticide and its degradation product. This modeling approach does not consider temporal occurrence of degradation products.

Table 3.10. Overview of Modeling Approaches for Assessing Environmental Concentrations of Total Residues of Concern

Attributes	Residue Summation	Simultaneous Formation/Decline	Total Residue
Individual Residues Considered	Yes	Yes	No
Physicochemical Properties Considered	Individual Compounds	Individual Compounds	Most Conservative from known residues
Degradation Half-lives	Individual Compounds	Individual Compounds	Cumulative Residue

Attributes	Residue Summation	Simultaneous Formation/Decline	Total Residue
Partitioning Coefficients	Individual Compounds	Individual Compounds	Most conservative from known residues
Application Rate	Application rate is proportionally distributed for all residues	Application Rate of Parent	Application Rate of Parent
PRZM/EXAM Modeling	Model Simulation for Individual Residues	Model Simulation for Parent and Degradation Product	Model Simulation for Total Residue
Data Management	Summation of Daily Time Series for Individual residues for calculation of exposure endpoints	PRZM/EXAMS Output	PRZM/EXAMS Output
Simulated EEC	1-in-10 year	1-in-10 year	1-in-10 year
Major Limitation	Require environmental fate data for degradation products Does not account for the time of formation	Requires a kinetic analysis of degradation pathways from parent to degradation products	Assume all residues have similar physical, chemical, and partitioning characteristics; does not account for time of formation
Level of Effort	Moderate	High	Moderate

Although the simultaneous formation/decline kinetic modeling strategy is the preferred method for estimation of TROC concentrations, this method is highly dependent on the ability to describe the formation and degradation kinetics of degradation products. To that end, the method requires environmental fate data for the toxic degradation products. Another important consideration is the ability to integrate these data into PRZM/EXAMS model simulations. In light of these issues, alternative modeling strategies have been employed to estimate TROC concentrations. The total residue approach or the residue summation approach has been employed depending on the availability of data for estimation of TROC concentrations.

The different methods for assessing exposure of TROC will be illustrated using Pesticide 1 and Pesticide 2. These example pesticides were selected because they form persistent and toxic degradation products. PRZM/EXAMS models were used to provide time series for calculation of 1-in-10 year aquatic exposure concentrations. The 1-in-10 year exposure concentrations were calculated using linear regression for interpolation. These model simulations were conducted using the EXPRESS (Version 1.03.02) model platforms. The EXPRESS model platform was used because it allows for simulation of simultaneous formation and degradation kinetics of degradation products.

3.4.1.1 Total Residues of Concern Assessment for Pesticide 1

Pesticide 1 is composed of two isomers that degrade at different rates to form one common degradation product that has toxicity similar to that of the most toxic parent isomer. **Figure 3.3** illustrates this typical degradation pattern. It clearly shows isomer 1 degrades rapidly to form the persistent degradation product.

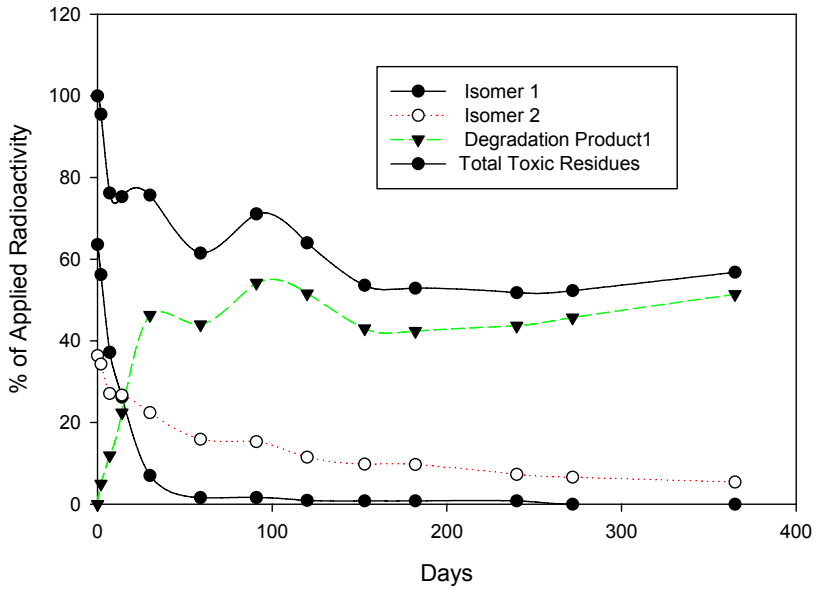


Figure 3.3. Pesticide 1 Degradation Pattern in an Aerobic Soil Metabolism Study

Common PRZM/EXAMS input parameters are used for conducting the three TROC modeling strategies for Pesticide 1. The fate and transport parameters used in these simulations were presented earlier in **Table 3.1** and **Table 3.2**. Other common input parameters are shown in **Table 3.11**.

Table 3.11. Pesticide Application and Agronomic Practices Used in PRZM/EXAMS Simulation

Scenarios	Chemical Application Method (CAM)	Application Efficiency	Number of Applications	Spray Drift (% of App Rate)	Application Dates
FL tomatoes	Aerial (CAM=2)	0.95	3	0.05	June 1

CAM= Chemical application method in PRZM simulations (Refer to PRZM Manual). For example, CAM 2 is a foliar applied pesticide.

Uses of different parameter and/or needed changes to these parameters are included in the following description of the methods. **Appendix C** contains detailed PRZM input and output files for all simulations associated with the three procedures for the TROC assessment of pesticide 1.

(1) The Residue Summation Method (RS method)

This method requires assignment of an application rate for the individual residues of Pesticide 1. These rates are included in **Table 3.12**. The application rates for the individual residues were normalized according to the percentage of residue detected in aerobic soil metabolism studies and the molecular weight ratio of degradate and parent compounds.

Table 3.12. Recalculation of Application Rates for Residue Summation Method for Pesticide 1 and it's Degradation Product

Compounds	Application Rate of Parent (lbs/A)	Aerobic Metabolism Study (Normalized %)	Molecular Ratio: Degradate /Parent	Application Rate (lbs/A)[1]
Isomer 1	3	0.48	1	1.433
Isomer 2	3	0.18	1	0.532
Degradation Product	3	0.35	1.039	1.076

1= Application Rate (lbs/A) = Parent Application Rate (lbs/A)*Max normalized Percent in Aerobic Soil Metabolism Study * Molecular Ratio

(2) The Simultaneous Formation/Decline Kinetics Method (FD method)

This method requires that PRZM/EXAMS modeling to be conducted using a single parent-daughter kinetic model for individual isomers. Additionally, the method requires an analysis to estimate the simultaneous formation and decline first-order rate constants. Subdivision N aerobic soil metabolism data were used in the analysis which was conducted in accordance to the generalized metabolism map (**Figure 3.4**).

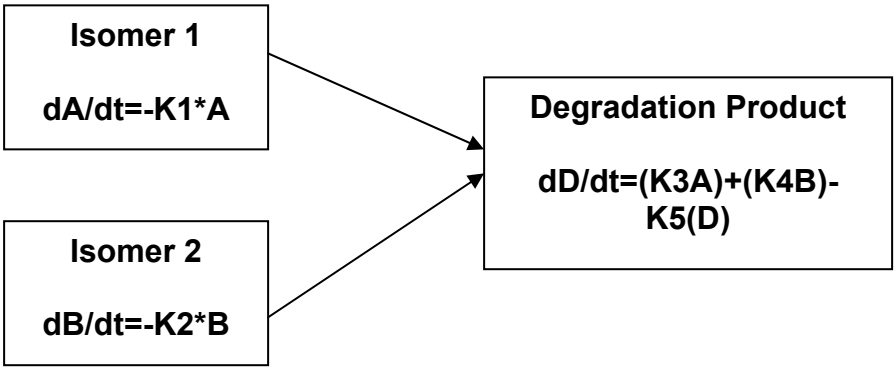


Figure 3.4. Schematic of Simultaneous Formation / Decline Kinetics Approach for Pesticide 1
(Note: Analytical equations for the degradation pathway are included in Appendix C)

(A= Isomer 1 Concentration; B= Isomer 2 Concentration; D= Degradation Product Concentration; K1 and K2= 1st Order Degradation Rate for Isomer 1 and Isomer 2; K3 and K4= 1st Order Formation Rate of Degradation Product from Isomer 1 and Isomer 2; and K5= 1st Order Degradation Rate for the Degradation Product)

The differential equations were solved to provide simultaneous formation and decline first-order rate constants **(Table 3.13)**.

Table 3.13. Rate Constants Describing Degradation of Pesticide 1 and Formation of the Toxic Degradation Product Using Simultaneous Formation / Decline Kinetics

Compound	First-Order Degradation Rate (day-1)	First-Order Formation Rate (day-1)	Half-Life (days)	Relative Fraction on Origin of Degradation Product
Isomer 1	-0.069033	NA	10.94	NA
Isomer 2	-0.007579	NA	91.45	NA
Degradation Product formed from Isomer 1	NA[1]	0.050344		0.729
Degradation Product formed from Isomer 2	NA	0.000179		0.0238

1-Not applicable because model development required constraining no degradation of Degradation Product.

The model estimated concentrations are shown in **Figure 3.5.**

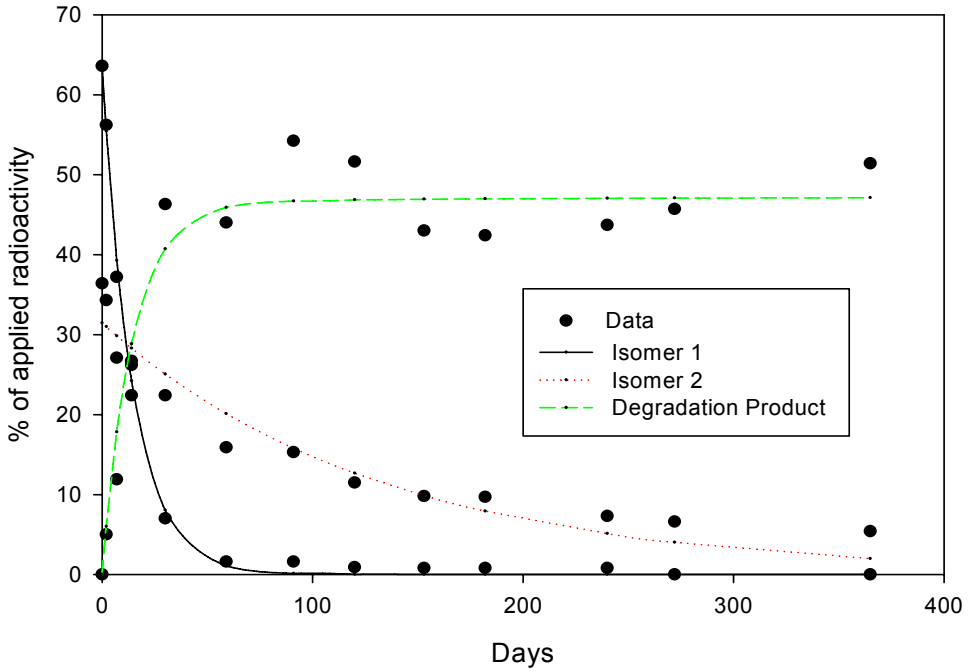


Figure 3.5. Model Simultaneous Degradation of Pesticide 1 and Formation of the Toxic Degradation Product Using Simultaneous Formation Decline Kinetics

The kinetic analysis indicates that isomer 1 contributes 72.9% in the formation of the toxic degradation product (**Table 3.14**). In contrast, isomer 2 contributes only 2.4% to this formation. Therefore, the formation rate of the degradation product is directly related to the shorter half-life for Isomer 1 in soil.

Table 3.14. Contribution Fraction of Pesticide 1 Isomers to Formation of Degradation Product

Parent Metabolite Model	Fraction Degradation Product from Parent	Source
Isomer A→ degradation product	0.729	Derived
Isomer A→ degradation product	0.02	Derived

PRZM/EXAMS simulations were conducted using the application rate of the parent without corrections. However, derived data were also used including: half-lives and fractions of degradation product formed from each isomer.

(3) The Total Residue Method (TR method)

This method calls for executing PRZM/EXAMS simulation using the application rate of the parent and fate and transport data assigned to the total residues of concern.

(4) Comparison of Total Residue Modeling Methods for Pesticide 1

The 1-in-10 year EECs for the three TROC modeling approaches are shown in **Table 3.15**. Although the modeling strategies produce comparable EECs, the TR Method produced the most conservative EECs for pesticide 1 among the various modeling strategies.

Table 3.15. Comparison of 1 in 10 year EECs for Pesticide 1 using Various TROC Modeling Strategies

Modeling Approach	Concentration (µg/L)				
	Peak	21-Day Average	60-Day Average	90-Day Average	Annual Average
Residue Summation (RS Method	32.63	13.03	9.17	8.21	5.54
Simultaneous Formation/ Degradation Kinetics (FD method)	38.10	15.17	10.67	9.52	6.44
Total Residue (TR Method)	48.02	20.22	14.5	13.41	9.46

Because the simultaneous formation/decline kinetic approach(FD method) is the preferred TROC modeling approach, time series of daily water concentrations for the various TROC methods were compared to the time series of daily water concentrations for the TROC using the FD method (**Table 3.16**). These data indicate the residue summation method (RS) accounts for 99% of concentration predicted using the FD method. In contrast, the total residue method accounts for only 58% of the FD method.

Table 3.16. Mean Percentage of Total Residues of Concern Estimated Using the FD Method Relative to RS and TR Methods for Pesticide 1

Compared Modeling Approach	Mean % of TR Method [3]
Residue Summation (RS Method)[1]	99%
Total Residue (TR Method)[2]	58%

1 (FD method/RS method)*100

2 (FD method/TR method)*100

[3] Based on a 30-year Simulation with the FL Tomato Scenario

Figure 3.6 illustrates a three-year time series of water column concentrations in the small pond scenario for different TROC modeling approaches. The time series' clearly illustrate that information on temporal occurrence of the degradation product is lost using the TR method.

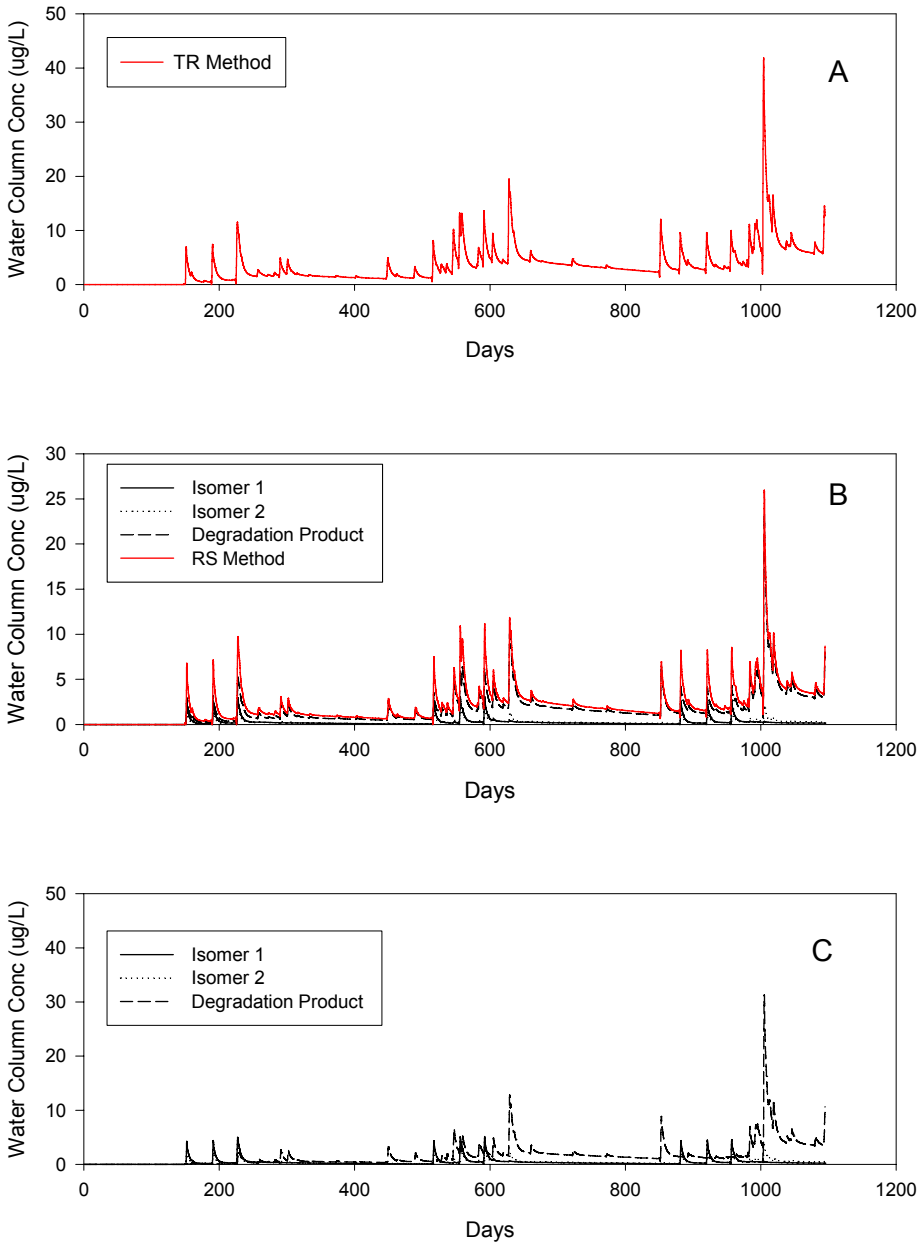


Figure 3.6. Time Series of TROC Modeling Strategies for Pesticide 1
(A = Total Residue; B=Residue Summation; C=Simultaneous Formation Decline Kinetics)

3.4.1.2 Total Residue of Concern Assessment for Pesticide 2

Pesticide 2 degrades to form 4 degradation products. **Figure** 3.7 illustrates the typical parent degradation pattern with formation/decline of toxic degradation

products. It clearly shows that parent compound degrades rapidly to form four persistent degradation products at low concentrations relative to the parent.

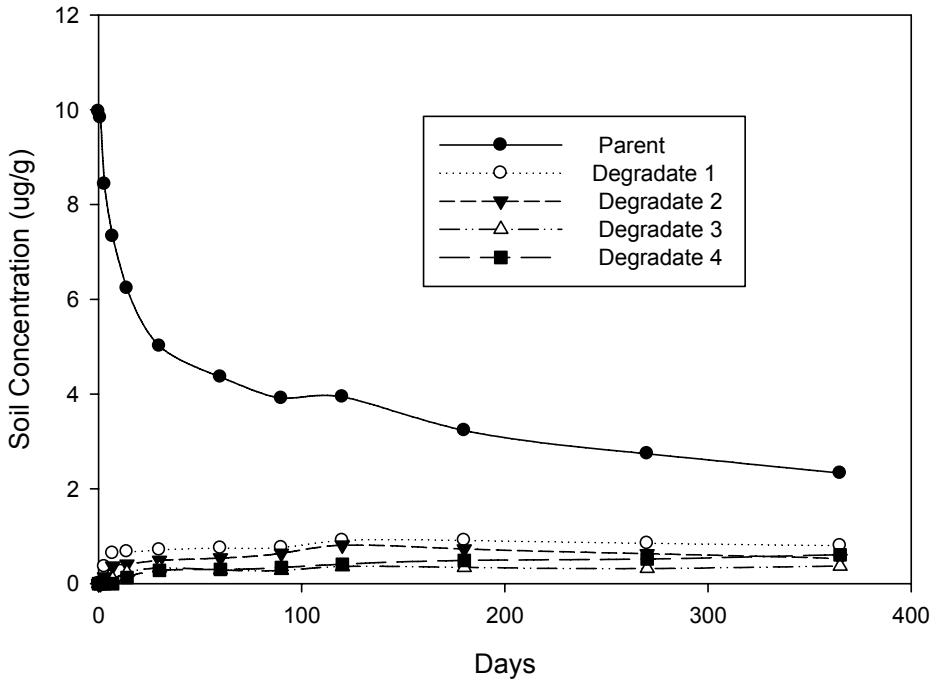


Figure 3.7. Degradation Profile of Pesticide 2

Only two approaches were conducted for assessing the total residues of concern for pesticide 2. Resultant 1-in-10 year EECs for this Pesticide are shown in **Table 3.17**. As expected, the TR modeling approach produced similar but higher EECs than the parent compound. The most pronounced differences in EECs are associated with time-averaged concentrations. These differences can be explained by the residual effect from the high persistence of the degradation products of this pesticide.

Table 3.17. Comparison of 1 in 10 year EECs for Pesticide 2 using the TR Modeling Strategy.

Modeling Approach	Concentration (µg/L)				
	Peak	21-Day Average	60-Day Average	90-Day Average	Annual Average
Parent	17.76	6.75	3.09	2.07	0.78
Total Residue	19.05	7.81	4.53	3.67	2.37

Further evaluation of the PRZM/EXAMS time series indicates the daily parent concentration accounts for 17% of the daily TR concentration over a 30-year time series comparison. The 1-in-10 year peak concentration of the parent accounts for 93% of the TR concentration. In contrast, the 1-in-10 year annual concentration of the parent accounts for only 33% of the TR concentration.

Figure 3.8 illustrates a time series of water column concentrations for Pesticide 2 and its total residues. The cumulative residual effect of the persistent degradation products can be seen in the prolonged tailing of concentrations from year to year.

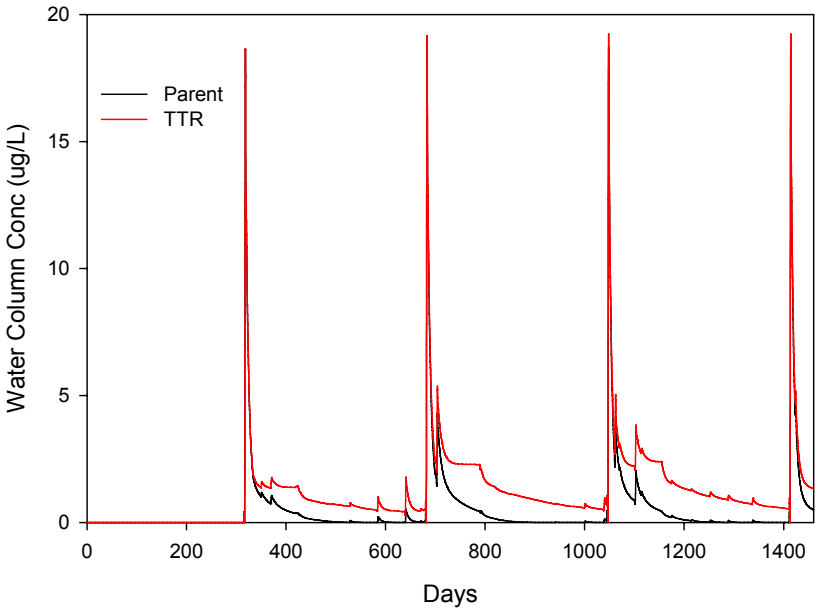


Figure 3.8. Time Series Comparison for the Pesticide 2 TROC Modeling Strategies

3.4.1.3 Conclusions from Application of Total Residues of Concern Approaches

The TROC modeling strategies illustrate each strategy has advantages and disadvantages in the prediction of aquatic exposure concentrations for pesticide risk assessments. The goal is to be as accurate as possible without underestimating exposure. Ideally, the simultaneous degradation/formation kinetic approach (FD Method) could be applied to all situations. However, this approach requires a comprehensive kinetic analysis. More importantly, the ability to use simultaneous kinetic rate constants in PRZM/EXAMS modeling is dependent on the complexity of degradation pathways. For situations of complex degradation patterns or in the absence of critical environmental fate data, OPP has employed the total residue modeling approach (TR Method) or residue summation modeling approach (RS Method) as an first approximation method for estimating TROC.

The TR Method was the most conservative exposure modeling approach regardless of the example pesticide. Although the total TR method is conservative, it provides a consistent approach for capturing residual effects of persistent degradation products. This method, however, requires a simplifying assumption that all TROC have similar chemical, physical, and partitioning characteristics. Additionally, this method does not provide any information on temporal occurrence of pesticide degradation products.

The residue summation (RS Method) and the total residue method (TR) are approximations to the simultaneous formation and decline kinetic (FD) method. These methods require consideration of environment fate properties of individual pesticide residues. The RS Method requires modification of application rates to account for the maximum percent of degradation product formed and the molecular weight ratio of degradate and individual degradation products. As stated previously though, this method does not provide any information on temporal occurrence patterns because it is assumed all residues are applied at maximum concentrations at the time of application.

The FD Method provides the ideal simulation method because it eliminates the need to manipulate application rates and it eliminates a need to assume that all the residues of concern have similar chemical, physical, and partitioning characteristics. Additionally, the FD Method provides an indication of temporal occurrence patterns of individual residues. However, this approach requires an ability to solve linear differential equations for calculation of formation and degradation kinetics; therefore, it does not lend itself to a standard modeling strategy. It is noted that the latter limitation could be overcome by using standardized software. Unfortunately, most data sets are not of sufficient quality to allow accurate estimation of the formation rate for degradates.

3.4.2 Addressing Exposure of Compounds with Low Water Solubility

Pesticides with PBT characteristics are generally neutral-organic compounds with very low water solubilities, high octanol: water partitioning coefficients (K_{OW}), and high sorption coefficients to organic carbon, sediment, and soil.

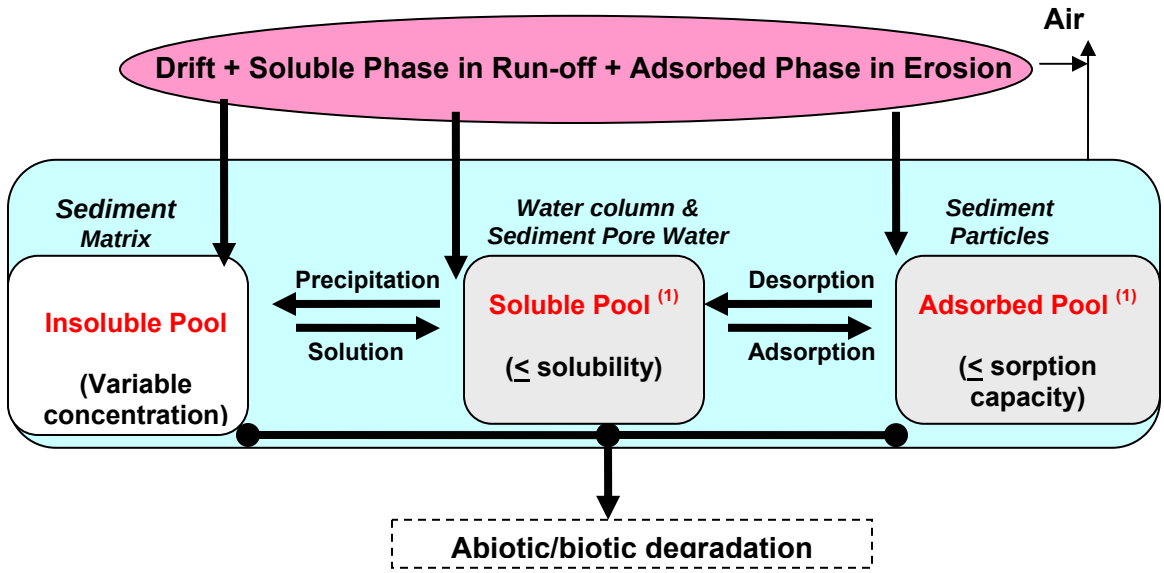
Environmental fate and ecotoxicity studies on such compounds are difficult to perform because of the inability to solubilize sufficient pesticide mass for testing. Subdivision N guidelines allow the use of 1% co-solvent in the environmental test conditions. The introduction of a co-solvent, however, might introduce bias as to the representativeness of experimentally-derived sorption coefficients for pesticides in natural waters or soil solution. The presence of co-solvent increases the tendency of the pesticide to stay in the dissolved phase and lowers the measured K_d. This results in concluding that the pesticide is less bound in the environment.

3.4.2.1 Interpretation of Predicted Concentrations That Exceeded Aqueous Solubility

To address these issues in the context of aquatic systems, OPP has developed a conceptual model that illustrates OPP's understanding of the chemo-dynamics for high K_{OC} or K_d / low solubility pesticides in the aquatic environment (**Figure 3.9**). This diagram represents a three-phase system in which pesticide is distributed among soluble, insoluble (precipitate) and adsorbed phases.

In the aquatic environment, environmental fate and transport processes are considered in the water column, sediment, biota, and sediment pore water. Pesticides can move off-site to surface water through spray drift, runoff, or on entrained sediments in runoff waters (erosion).

Because these pesticides have high soil sorption coefficients, they are expected to move from the application site through erosion. Spray drift may be an important off-site transport process as well for aerial applied pesticides. Once in the surface water, the pesticide can equilibrate with suspended sediments, dissolved organic carbon (DOC), bed sediments, and biota.



(1) EXAMS currently model soluble and adsorbed pools, but not the insoluble (precipitate) pool.

Figure 3.9. Conceptual Model of High K_{OC} or K_d / Low Solubility Pesticide Equilibria in an Aquatic System

For low solubility compounds, PRZM/EXAMS modeling can predict peak EECs in the water column and sediment pore water that exceed the water solubility of the pesticide active ingredient. **Figure 3.10** illustrates estimated water column concentrations for example Pesticide 4 exceeding the chemical's water solubility.

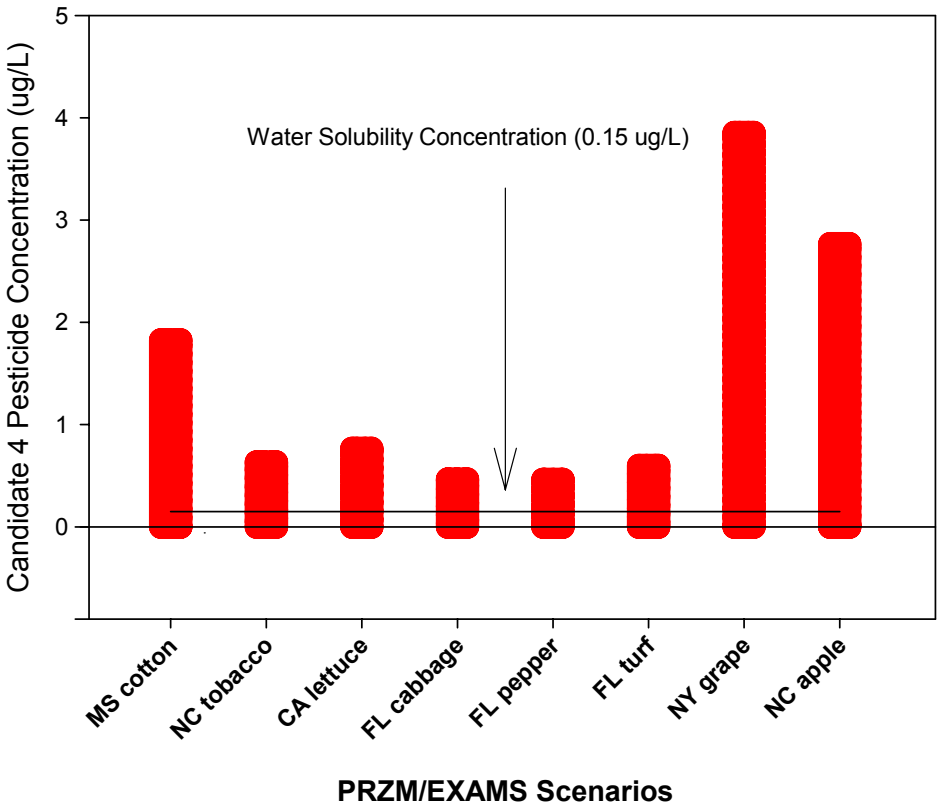


Figure 3.10. PRZM/EXAMS EECS in the Water Column for Pesticide 4

PRZM/EXAMS modeling suggests potential excursions of EECs above the water solubility for Pesticide 4. Early versions of EXAMS model were designed to limit the pesticide concentration in the water column to 50% of the pesticide water solubility. This modeling constraint was employed to maintain linear sorption processes (Burns, 2002). More recent versions of EXAMS (Version 2.98.04.06), however, allow pesticide water concentrations to exceed the pesticide solubility. The PRZM model does not utilize the water solubility of a pesticide as a bounding concentration in soil solution or runoff.

Given the current limitations of the EXAMS model in relation to predicted pesticide concentrations that exceed aqueous solubility (*i.e.*, addressing 2 of the 3 phases depicted in **Figure 3.9**), the general practice in OPP has been to constrain the predicted EECs in water to the limit of solubility measured for the pesticide active ingredient[2]. This approach has been adopted because PRZM and EXAMS models are not designed to account for the environmental fate and transport effects from precipitation of a solid phase of the pesticide. This approach essentially assumes:

[2] In one case (pesticide 4), OPP allowed for peak concentrations to exceed water solubility based on field data suggesting dissolved concentrations could exceed laboratory-measured solubility.

1. Predicted concentrations above solubility are not biologically available (*i.e.*, they exist as a precipitate and are not subject to dissolution).
2. Solubility limits measured for pesticide active ingredients in the laboratory are representative of pesticide solubility in the environment (*i.e.*, the model agricultural pond).
3. The formation of a pesticide precipitate does not alter environmental fate processes such as sorption and degradation.
4. The water solubility is the maximum estimated environmental concentration in water.

OPP acknowledges that assumptions on the pesticide concentrations at the water solubility limit can contribute to uncertainty in its ecological exposure assessment. Although environmental concentrations of pesticides are not expected to exceed their water solubility, there may be certain conditions in the field (*e.g.*, temperature, pH, and presence of naturally-occurring ligands in surface water) that might enhance aqueous solubility relative to laboratory measurements. Furthermore, as illustrated in **Figure 3.9**, chemical precipitates may serve to enhance pesticide concentrations due to dissolution when concentrations drop below solubility, thus contributing to the soluble (dissolved) pesticide pool.

Another option for addressing solubility limit concerns in aquatic exposure assessment involves modeling the formation and dissolution of precipitate chemical. This approach is used by the AGRO water quality model (CEMC, 2007), which OPP is currently evaluating. Specifically, the AGRO model assumes that predicted chemical concentrations above the solubility limit exist in a precipitate (non-bioavailable) form. When predicted concentrations of chemical drop below solubility, dissolution of the chemical precipitate is assumed to occur up to the solubility limit. The result is that excess chemical above the solubility limit is gradually assumed to dissolve over time as predicted concentrations drop below solubility.

3.4.2.2 Interpretation of Measured Concentrations That Exceeded Aqueous Solubility

OPP has also encountered situations where measured concentrations of dissolved (filtered) pesticides applied in fate or effects studies exceed solubility. For example, an evaluation of mesocosm studies for pesticide 4 indicates the water solubility was exceeded for short durations (**Figure 3.11 a & b)** at the time of application. Specifically, dissolved concentrations of Pesticide 4 (as determined by filtration) exceeded the water solubility limit of 0.15 µg/L for 5- to 10-days after application. The exceedance of water solubility, however, was not observed for the remaining duration of the mesocosm studies. These data suggest that long-term pesticide concentrations were predominately controlled through sorption on sediment.

Although the solubility limit was apparently exceeded at the time of application, it is not clear, based on filtered samples alone, whether or not Pesticide 4 was present entirely in a dissolved form or also present as a precipitate and/or suspension. OPPTS test guidelines (OPPTS 850.1000) specify centrifugation of samples when concerns exist regarding solubility (and hence bioavailability) of the test chemical in aquatic laboratory studies. Filtration is also acceptable if appropriately validated. In the absence of co-solvents at effective concentrations, OPP generally considers the bioavailability of pesticide concentrations exceeding aqueous

solubility in aquatic studies to be suspect, unless samples are properly centrifuged and/or filtration methods are validated in terms of separating dissolved from precipitated chemical.

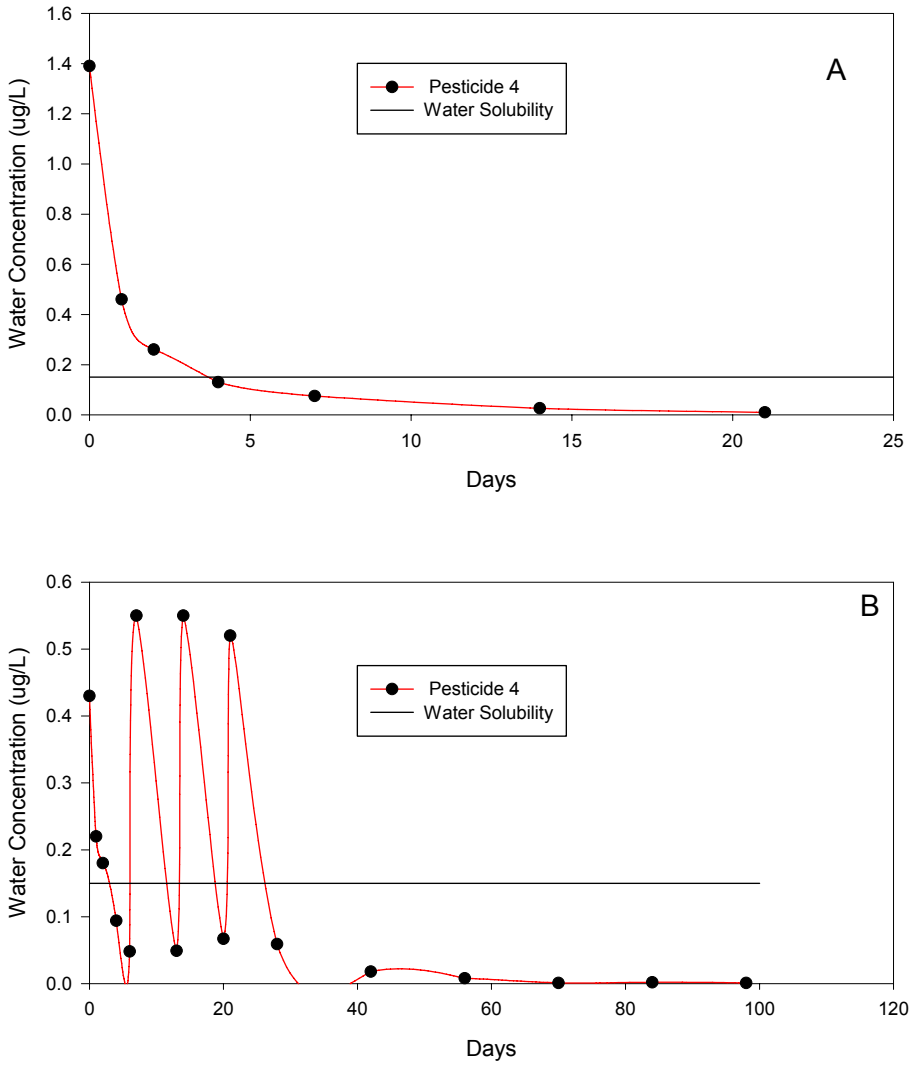


Figure 3.11. Dissolved (Filtered) Water Column Concentrations of Pesticide 4 in Registrant Submitted Mesocosm Studies

3.4.3 Interpretation and Application of Degradation Rates from Laboratory Studies

Another common challenge with low solubility pesticides with high sorption coefficients is the ability to differentiate degradation and adsorption processes. This is an important issue for

selecting the proper half-lives for use in exposure modeling and characterization of environmental fate processes.

Below is an example of "hockey stick" pattern in the water phase of an aquatic metabolism studies for Pesticide 3 (**Figure 3.12**).

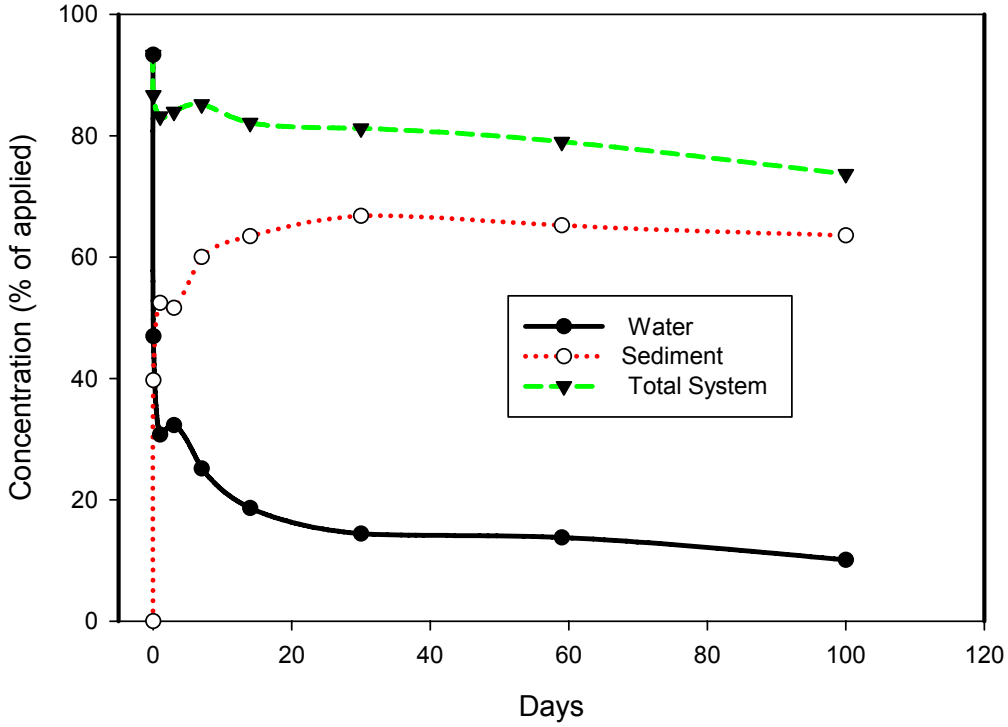


Figure 3.12. Concentrations of Pesticide 3 in the water column, sediment, and total system of aerobic aquatic metabolism studies

The abrupt hockey stick decline pattern of the pesticide in the water column indicates rapid sorption of the pesticide to the sediment. Further evaluation of the data indicates the total system half-lives were consistently greater than the estimated half-lives in the water column (**Table** 3.18). These data suggest the rapid residue decline in the water column is more dependent on the sorption rather than degradation.

Table 3.18. Comparison of Pesticide 3 Residue Decline Half-Lives in Aquatic Metabolism Studies

Study	Water Half-life (days)	Total System Half-life (days)
UK Sediment/Lake Water	0.1	>100
UK Sediment/Pond Water	0.1	>100
SD Sediment/Pond Water	0.3	>100
SD Sediment/Lake Water	0.03	> 378

OPP/EFED input parameter guidance for surface water modeling recommends the use of total system pesticide half-life from laboratory soil and aquatic metabolism studies. This recommendation is made because OPP surface water quality models already account for pesticide dissipation processes (volatilization, sorption) and thus, use of an observed half-life in water would amount to "double counting" the dissipation processes. Additionally, the use of single process half-life (*e.g.*, water column or sediment) is not recommended because simultaneous processes of sorption and degradation cannot be differentiated in estimating of the degradation half-life. The use of field dissipation half-lives in modeling is not recommended because they represent multiple processes including leaching, runoff, and degradation (USEPA and Health Canada, 2006).

3.4.4 Quantification of Exposure Concentrations for Long Term Accumulation in Soil and Sediment

3.4.4.1 Persistence Evaluation of Pesticide 1 in Soil

Soil metabolism half-lives for the example pesticides indicate there is sufficient persistence in soil for the parent compound or the total residues of concern to warrant concern for year-to-year carryover of residues (soil metabolism half lives ranging from 134 days to > 1000 days; **Section 3.2)**. By way of illustration, this section presents an overview of OPP's persistence evaluation of Pesticide 1 in soil that led to concern for year-to-year carryover. The issue of pesticide accumulation in soil is not routinely evaluated in the terrestrial exposure assessment.

PRZM simulations were conducted to evaluate the potential for accumulation of Pesticide 1 and its degradation product in soil. Total soil concentrations for pesticide 1 were simulated according to the application conditions and PRZM input parameters described in **Table 3.1** and **Table 3.2**.

Results indicate there is no substantial year to year accumulation in the PRZM time series for the parent isomers of Pesticide 1 (**Figure 3.12** and **Figure 3.13**). The toxic degradation product concentration, however, shows year-to-year accumulation in soil. This is not unexpected because the degradation product is stable in aerobic soil metabolism studies. Similar soil accumulation patterns in soil can be predicted for the total residues of concern (parent isomers plus degradate) of Pesticide 1. Mass balance analysis indicates 36 to 57% of applied residue using the TR method or the residue summation method accumulated in soil during a 5 year simulation period (**Table 3.19**). Most of the accumulation was due to the formation of a stable toxic degradation product; approximately 91% of formed degradation product continued to accumulate over a 5-year simulation period.

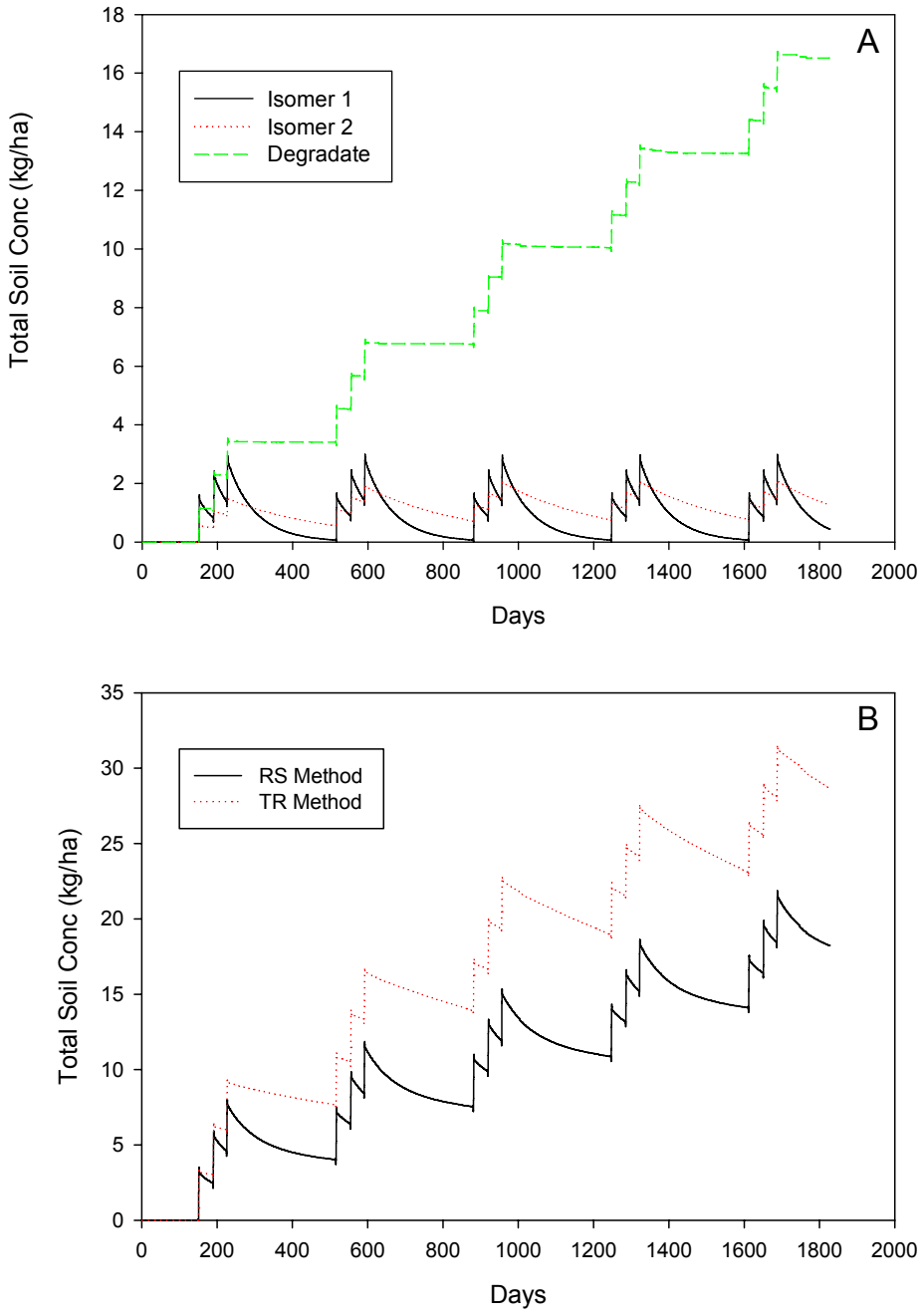


Figure 3.13. PRZM Time Series for Total Soil Concentration of Pesticide 1 Residues in a FL Tomato Scenario (A= Individual Residues from RS Method; B= RS and TR Methods)

Table 3.19. PRZM Simulated Accumulation of the Pesticide 1 and its Toxic Degradation Product in Soil

Description	Total Applied or Formed During 5 year Simulation (kg/ha)	Soil Concentration After 5 year Simulation (kg/ha)	Percent of Applied that Accumulated
Pesticide 1 Isomer 1	24.1	0.4	1.7%
Pesticide 1 Isomer 2	8.9	1.3	14.6%
Pesticide 1 Degradation Product	18.1	16.5	91.2%
Pesticide 1 Residue Summation	50.4	18.2	36.1%
Pesticide 1 Total Residues of concern	50.4	28.7	56.9%

For pesticide 1, the PRZM modeling suggests year-to-year accumulation of the toxic degradation product, but not the parent compound. This residue accumulation is expected to prolong exposure in terrestrial environments. Although ecological risks associated with pesticide accumulation in soil are not currently assessed by OPP on a routine basis, this analysis suggests that PRZM-based soil accumulation modeling might be useful tool for assessing ecological risks from long-term soil accumulation in terrestrial environments.

3.4.4.2 Persistence Evaluation of Pesticide 4 in Sediment and Sediment Pore Water

Anaerobic and aquatic metabolism half-lives for the pesticides indicate there is sufficient persistence in water/sediment systems to warrant concern for year-to-year carryover of residues (half-lives ranging from >100 days to >2200 days for total residues of concern; **Section 3.2**). The issue of pesticide accumulation in sediment is not routinely evaluated in the aquatic exposure assessment.

Pesticide 4 is expected to accumulate in sediments because of its extremely high K_{OC} (average value = 1,241,000 ml/g) and high persistence ($t_{1/2}$=1,110 days). The potential for accumulation in sediment was quantified using PRZM/EXAMS. PRZM/EXAMS input parameters for this assessment are shown in **Table 3.7** and **Table 3.8.**

Representative PRZM/EXAMS scenarios were used to quantify pesticide 4 accumulation in sediment with an organic carbon fraction (FOC) of 0.04. **Table 3.20** shows descriptive statistics for single-year maximum concentrations of pesticide 4 in sediment and pore water over a 30-year use period.

Table 3.20. Descriptive Statistics for Single Year Maximum Pesticide 4 Concentrations in Pore Water and Sediment for Representative PRZM/EXAMS Scenarios

Scenarios	Pore Water µg/L		Sediment mg/kg	
	Min	Max	Min	Max
Apple	0.007	0.136	0.359	6.75
Cabbage	0.002	0.022	0.104	1.11
Grape	0.007	0.257	0.370	12.7
Lettuce	0.004	0.052	0.222	2.6
Cotton	0.016	0.091	0.798	4.54
Pepper	0.002	0.024	0.079	1.19
Tobacco	0.002	0.033	0.116	1.65
Turf	0.001	0.012	0.056	0.61

Additional analysis was conducted to evaluate the accumulation potential in sediment (**Figure 3.14 and Figure 3.15**) and pesticide enrichment of pore water (**Figure 3.16**) in the representative PRZM/EXAMS scenarios. **Figure 3.14** shows time series of pesticide 4 concentrations in sediment over a 30-year use period. Similar accumulation trends were observed for pesticide 4 concentrations in benthic microbes and pore water. As indicated in **Figure 3.14**, pesticide 4 concentrations in sediment typically increased for approximately 15 years, then leveled off to apparent steady-state concentrations. One exception to this is evident in the NY grape scenario, where pesticide 4 concentrations in sediment were estimated to be highest at the last application, with an apparent increasing trend throughout the simulation.

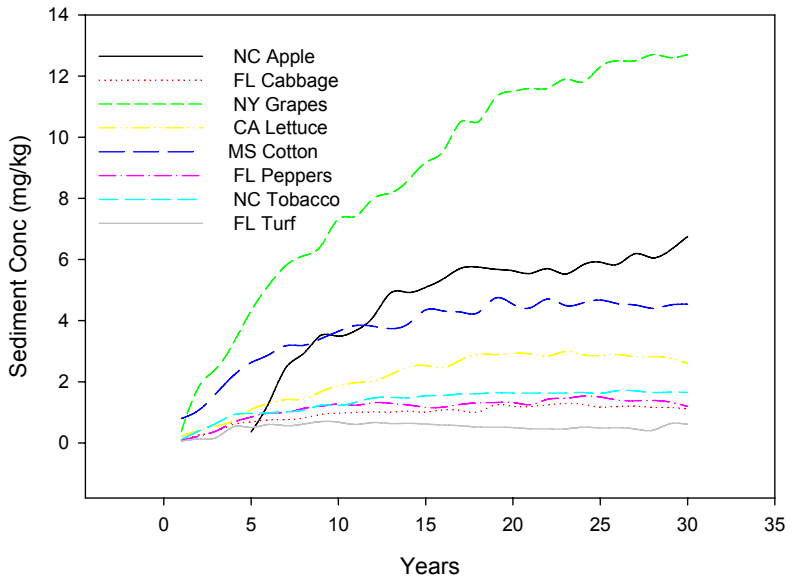


Figure 3.14. PRZM/EXAMS Predicted Accumulation in Sediment for Representative PRZM/EXAMS Scenarios for Pesticide 4

Further analysis of the time series was conducted using mean and associated standard deviations for pesticide 4 concentrations among representative scenarios. This approach was used to simplify interpretation of the different accumulation curves for individual

PRZM/EXAMS scenarios. Sediment concentrations accumulated for approximately the first 15 years of use; thereafter, the concentration reached a plateau of approximately 3 mg/kg (**Figure 3.15**).

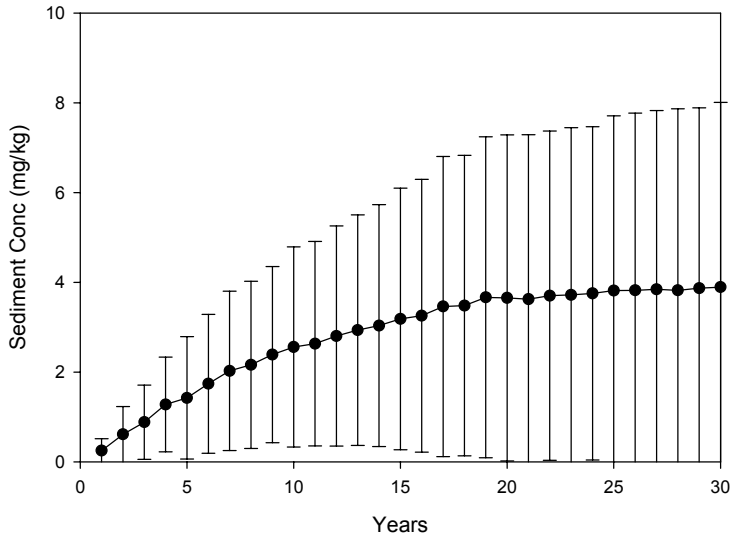


Figure 3.15. PRZM/EXAMS Predicted Mean Sediment Concentration (Standard Deviation) for Representative PRZM/EXAMS Scenarios with Pesticide 4

As expected, sediment pore water concentrations of pesticide 4 followed a similar accumulation curve as the estimated sediment concentration. Sediment pore water concentrations accumulated for approximately the first 15 years of use; thereafter, the concentration reached a plateau of 0.060 µg/L (**Figure 3.16**).

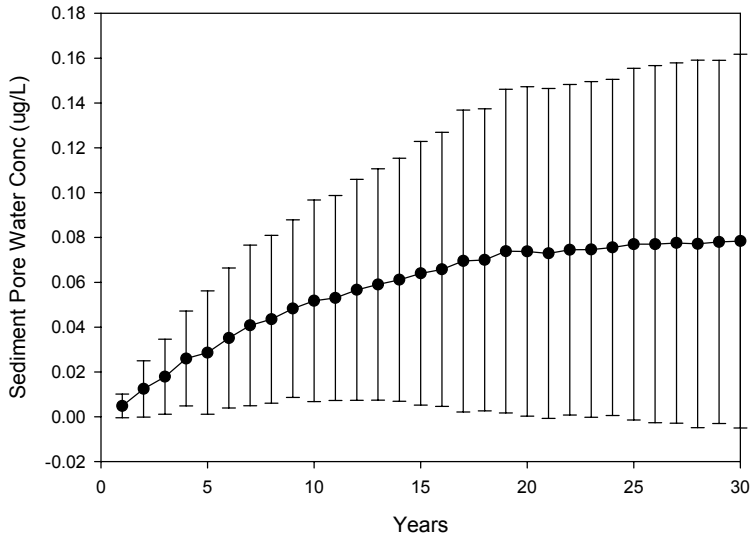


Figure 3.16. PRZM/EXAMS Predicted Mean Sediment Pore Water Concentration (Standard Deviation) for Representative PRZM/EXAMS Scenarios with Pesticide 4

Preliminary analysis on the impact of the fraction of organic carbon (FOC) in sediment showed a substantial dependence on partitioning among the sediment, benthic microbial organisms, and pore water. As expected, an increase in FOC above 0.04 in benthic sediment caused an increase the sediment concentration (**Figure 3.17**).

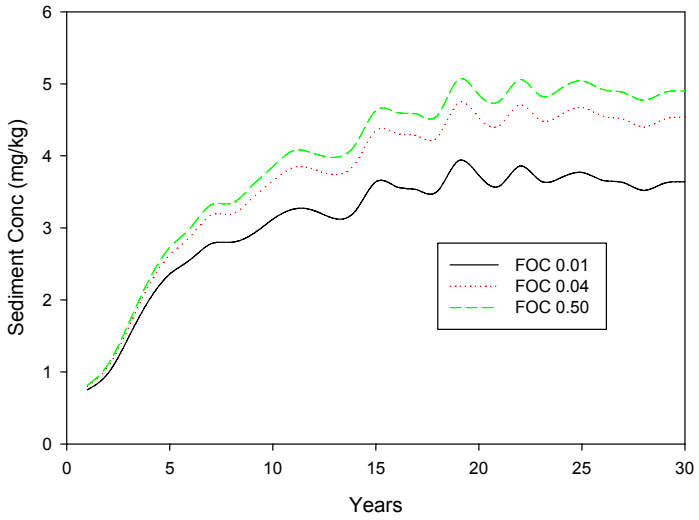


Figure 3.17. PRZM/EXAMS Predicted Pesticide 4 Accumulation in Sediment for the MS Cotton Scenario

The impact of FOC in benthic sediment on concentrations in pore water showed a higher sensitivity to change than observed for the Pesticide 4 bound on benthic sediment (**Figure 3.18**). The estimated concentrations in pore water were inversely related to the FOC in benthic sediment. As such, there is a decrease in concentration in pore water when there is an increase in the FOC in benthic sediment, which is consistent with equilibrium partitioning assumptions in EXAMS for calculating pore water concentrations.

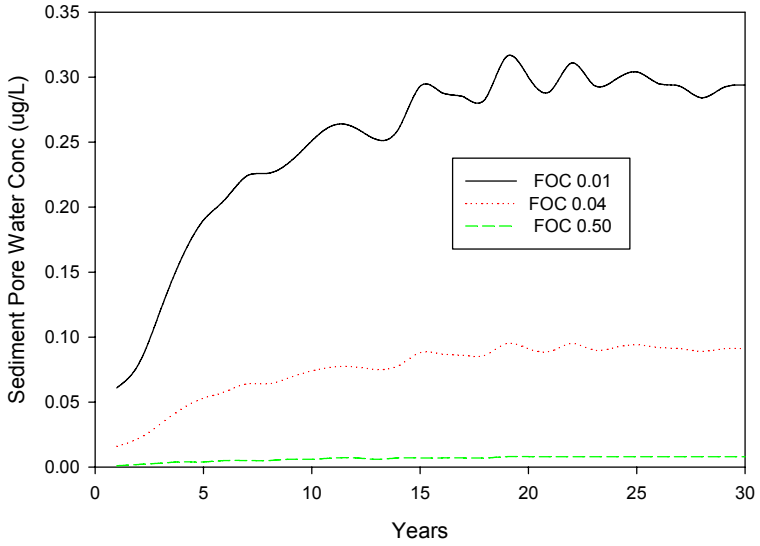


Figure 3.18. PRZM/EXAMS Predicted Pesticide Enrichment of Pore Water of Pesticide 4 for the MS Cotton Scenario

Although sediment exposures are not routinely assessed by OPP, PRZM/EXAMS modeling provides the capability for predicting pesticide concentrations in sediment, sediment pore water, and benthic organisms. PRZM/EXAMS modeling indicates year-to-year accumulation of pesticide 4 in the sediment. The extent of accumulation is expected to be highly dependent on the assumptions used in the modeling scenario. Typically, the small pond is a static pond receiving runoff water and eroded sediment from a 10-ha watershed. The modeling does not account for the amount of eroded sediment or runoff water entering the pond. Instead, it assumes daily pulse loadings of the cumulative pesticide mass in runoff water and on eroded sediment. In the static water body, there is assumed to be a 50% mass partitioning between the water column and sediment prior to pesticide sorption on sediment. Several modeling assumptions control the calculation of pesticide concentrations in sediment. These factors include:

1.) The pesticide concentration in sediment is not directly dependent on the amount of eroded sediment from the runoff scenario. This assumption does not address the impact of sediment burial.
2.) The degradation processes in the sediment are assumed to be controlled by microbial processes under anaerobic conditions. This assumption does not consider the impact of surface sediments with aerobic conditions.
3.) The sediment is assumed to have a percent organic carbon content of 4%. This assumption does not consider the variability of organic carbon contents in sediment.
4.) Equilibrium partitioning is assumed between the sediment pore water and sediment particles.

For pesticide 4, the PRZM modeling suggest year-to year accumulation in sediment and sediment pore water. This residue accumulation is expected to prolong exposure in benthic organisms and their consumers (see **Chapter 5** for discussion of bioaccumulation). These data illustrate PRZM/EXAMS modeling can be a useful tool for identifying long-term persistence issues of pesticides in sediments.

4. SEDIMENT DYNAMICS AND PESTICIDE TRANSPORT IN AQUATIC ECOSYSTEMS

4.1 INTRODUCTION

In aquatic ecosystems, pesticides with PBT characteristics are expected to partition strongly to sediment particles and potentially accumulate over time in benthic sediments due to their long persistence in the environment. Therefore, consideration of the processes that affect the delivery and distribution of sediment-sorbed pesticide in aquatic ecosystems is relevant to exposure assessments involving these compounds. Specifically, processes related to sediment dynamics are expected to affect the distribution of pesticide mass between water and sediment compartments as well as the bioavailability of a given mass of pesticide within these compartments. For the purposes of this White Paper, the term "sediment dynamics" is used to represent processes of sediment transport into and within an aquatic ecosystem. These processes include (but are not limited to): soil erosion, sedimentation, resuspension and burial of sediment mass which are described further in **Section 4.2**.

As part of its 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 pesticide concentrations in small ponds and also are protective of small first- and second-order streams that receive runoff-containing pesticide residues from many fields during the period following pesticide applications.

OPP believes that the farm pond is not only important as a surrogate for flowing water, but that both natural and constructed ponds are an important resource which themselves require protection. They are used not only for recreation and also serve as habitat for aquatic organisms (e.g. fish), reptiles, mammals, and birds (e.g. waterfowl). A recent land cover inventory using satellite imagery indicates there may be as many as 9 million ponds in the United States (Renwick, et al., 2005).

Currently, the OPP approach for modeling pesticide transport in a static aquatic ecosystem accounts for movement of pesticide mass between the water column and benthic region based on a set of "lumped" parameters. These parameters are intended to implicitly account for pesticide mass transfer in a static aquatic ecosystem due to sediment dynamics processes, such as diffusion, settling, resuspension and other processes that tend to mix the sediment layer. The current OPP modeling approach does not include inflow of sediment mass (through soil erosion from a field) to the water body which could lead to burial of pesticide mass through deposition. OPP is seeking SAP input on the current OPP approach for modeling pesticide movement between the water column and the benthic region as well as the strengths

and limitations of simulating burial of a pesticide by sediment in the standard pond as a process by which a pesticide would be made permanently unavailable to aquatic organisms.

The purpose of this chapter is to explore the potential influence of sediment dynamics on pesticide transport in aquatic ecosystems and how these processes relate to OPP's current aquatic exposure modeling approach. Topics specifically related to pesticide degradation have been discussed in Chapter 3 and are not the focus of this chapter. The following discussion begins with a conceptual model that depicts the relationship between sediment dynamics and pesticide transport within aquatic ecosystems (**Section 4.2**). The relationship of OPP's current aquatic exposure modeling approach to this conceptual model is described in **Section 4.3**, along with its assumptions, strengths and limitations. Lastly, descriptions of how other models address sediment dynamics processes are provided in **Section 4.4**.

4.2 CONCEPTUAL MODEL OF PESTICIDE TRANSPORT AND SEDIMENT DYNAMIC PROCESSES

A conceptual model depicting the relationship of sediment dynamic processes and pesticide transport in a static (*i.e.,* lentic) aquatic ecosystem is shown in **Figure 4.1**. Potential sources of pesticides to aquatic ecosystems include runoff and spray drift from treatment sites as well as wet and dry deposition. Within these sources, pesticides may be dissolved in water (*i.e.,* in runoff or rainwater entering the ecosystem) or sorbed to particles (*e.g.,* soil particles eroding from the field, dry deposition). Once in an aquatic ecosystem, the pesticide is expected to re-partition in the direction of thermodynamic equilibrium with the surrounding media. Loss of pesticide mass in the water column may result from volatilization and a multitude of degradation processes (*e.g.,* hydrolysis, photolysis, biotransformation). These degradation processes have been discussed earlier in Chapter 3 and are not shown in **Figure 4.1** since the intent of this figure is to depict pesticide transport. Pesticide mass in the water column can be transported to and mix with benthic sediments through various processes, including settling (*i.e.,* deposition), resuspension, bioturbation and diffusion. Deposition of sediments to the upper portion of the benthic area can lead to burial of pesticide mass sorbed to the sediment. In this Chapter, "pesticide burial" is considered a process by which pesticide mass in a portion of the benthic layer is considered permanently unavailable for interaction within an aquatic ecosystem (*i.e.,* not bioavailable) as a result of deposition and accumulation of sediment. The term "bioavailable" refers the amount of chemical that is available for absorption across (or adsorption onto) biological membranes of organisms.

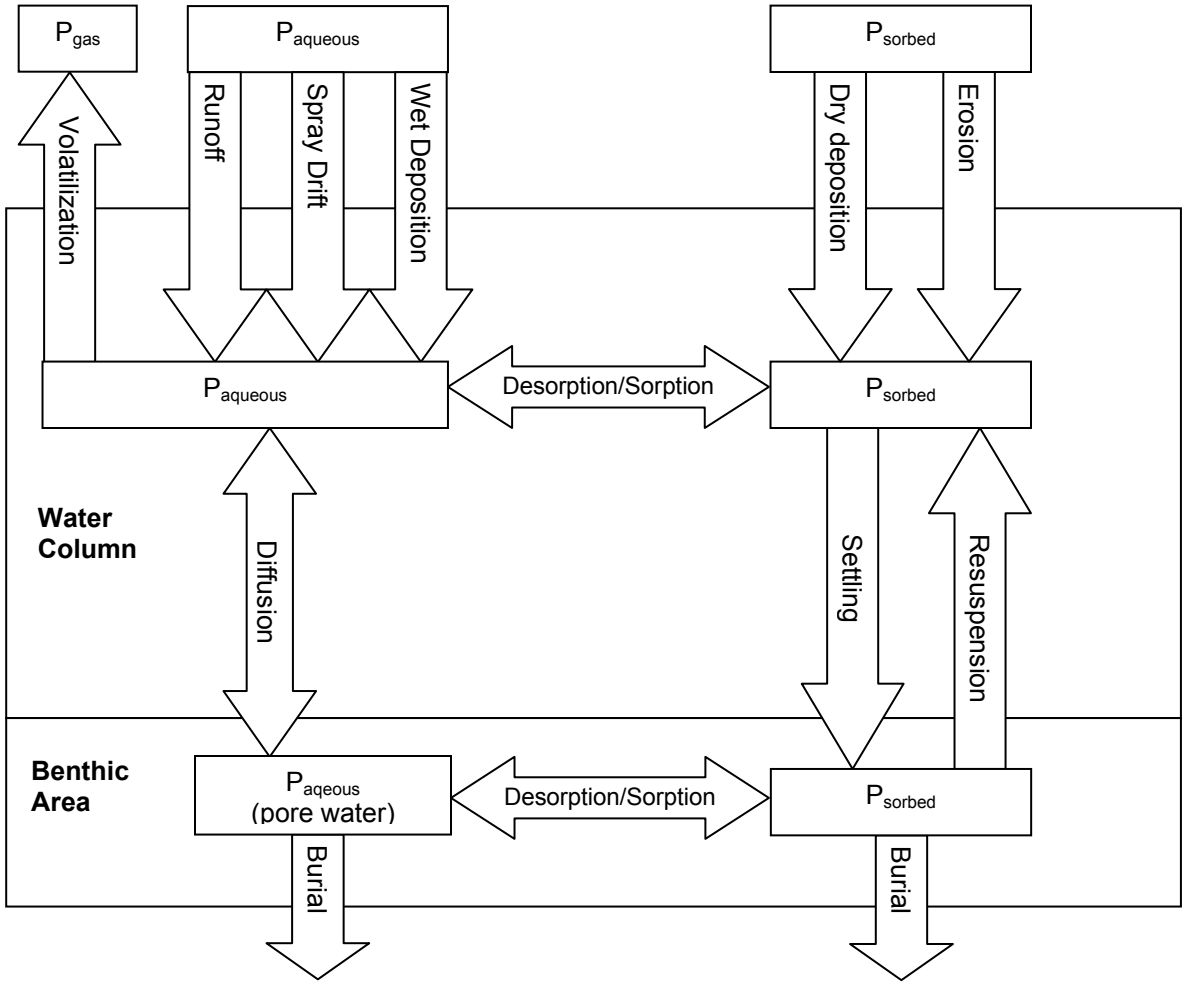


Figure 4.1. Conceptual Model of Pesticide Transport Within A Lentic Aquatic Ecosystem. Arrows represent movement of mass from one phase (*i.e.,* sorbed or aqueous) or region to another. Aquatic ecosystems are conceptualized as comprising a water column and a benthic region. In this figure, P_{aqeous}=aqueous mass of pesticide; P_{sorbed}= sorbed mass of pesticide; and P_{gas}= gaseous mass of pesticide.

Characteristics of the pesticide are expected to influence the transport of the pesticide within the aquatic ecosystem. The pesticide's hydrophobicity/affinity for organic carbon influences the distribution of chemical between aqueous and sorbed phases within the water column or benthic area. The characteristics of pesticides with PBT profiles indicate a strong tendency to be sorbed to sediment and thus, a significant potential to be affected by processes related to sediment dynamics.

The recently completed Lake Michigan Mass Balance Project (LMMBP) illustrates the importance of sediment dynamics for highly hydrophobic and persistent compounds (*e.g.,* PCBs). This effort involved extensive modeling of atmosphere, major tributaries, sediments, water column and biota during 1994-1995. Multimedia, mass balance modeling frameworks were applied to evaluate the primary source and loss categories for each pollutant and to forecasts under various loading scenarios. The average masses of total PCBs presented in the water column and the surficial sediments (0-1 cm) of Lake Michigan during 1994-1995 were

1,216 kg and 13,085 kg, respectively. The overall PCB mass balance indicates a net loss of PCBs is occurring in Lake Michigan, with volatilization and deep sediment burial being the primary gross loss processes. Internal PCB loading from sediment resuspension was significant, indicating the importance of considering internal contaminant cycling processes. Model forecasts indicate the PCB mass in the surficial sediment is large and could support PCB concentrations in the water column for "a very long time." A conceptual process diagram involving an inventory of PCB movement in Lake Michigan is depicted in **Figure 4.2**. While very different in scale from OPP assessments (see **Figure 4.3**. below), the underlying processes related to sediment dynamics and pesticide transport are similar (USEPA, 2006).

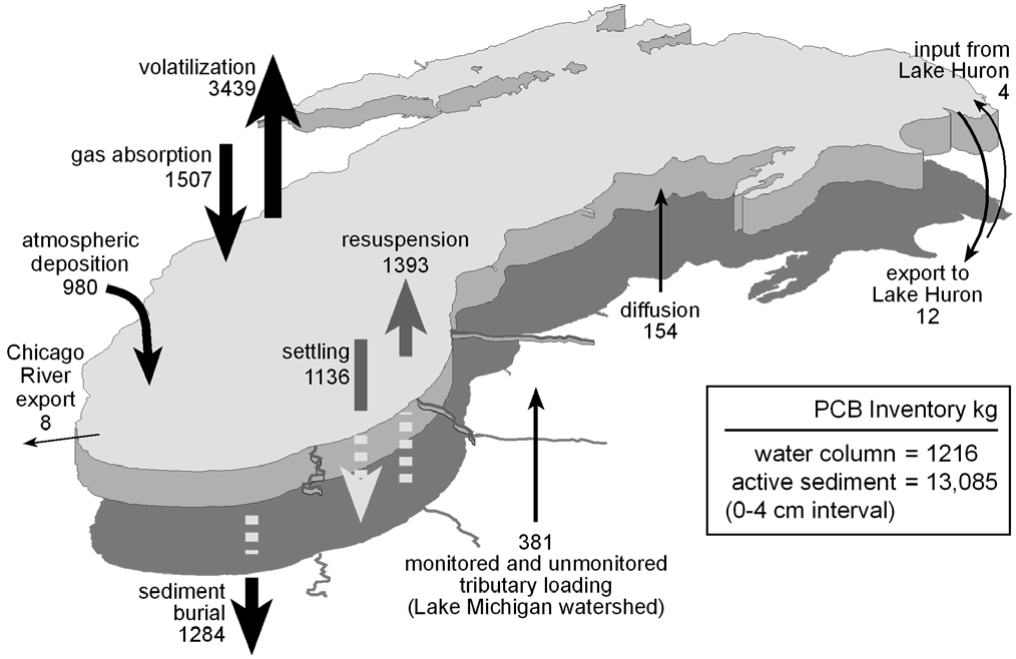


Figure 4.2. Process Diagram: Lake Michigan Mass Balance Project (Source: USEPA, 2006).

4.2.1 Pesticide Transport to Aquatic Ecosystems from Eroding Soil

Due to their high K_{OC} values, pesticides with PBT characteristics are likely to be sorbed to soil and carried into aquatic ecosystems via soil eroding from treatment sites. The quantity of pesticide mass (sorbed to soil) entering aquatic ecosystems is therefore impacted by factors related to erosion of the soil from the field. Specifically, the mass of eroded soil entering the aquatic ecosystem can vary based on several factors. These include:

- erosivity of the rain (as a function of the energy and intensity of rainfall events),
- erodibility of the soil (as a function of soil texture and content of organic mater)
- protection from raindrop impact provided to the soil by the growing crop,
- slope and slope length of the site exposed to rainfall, and
- management practices (terraces, contour cultivation, reduced tillage, crop residues, etc).

PRZM3 uses a variant of the Universal Soil Loss Equation (USLE) to estimate the mass of eroded soil associated with each stormwater runoff event. The USLE was developed by the USDA Natural Resources Conservation Service (NRCS) through statistical analyses of many plot-years of rainfall, runoff, and sediment loss data from many small plots located around the United States (Wischmeier and Smith, 1978).

The USLE equation is designed to represent annual average soil erosion losses at a specific field. The equation has been modified in order to provide storm-by-storm estimates of soil erosion losses that can be use in computer modeling.

PRZM3 provides the option of using any one of three of these USLE modifications to estimate soil erosion. These are the Modified Universal Soil Loss Equation (MUSLE) as developed by Williams (1975), MUST and MUSS (Williams 1995:933 in (Singh 1995)). The MUSS modification of USLE which was selected as the most appropriate for OPP/EFED PRZM modeling is as follows:

$$\text{MUSS,} \qquad X_e = 0.79\ (V_r\ q_p)^{0.65} A^{0.009} K\ LS\ C\ P$$

where,

X_e = the event soil loss (metric tonnes day),

V_r = volume of daily runoff event (mm),

q_p = peak storm runoff rate (mm/h),
A = field size (ha),
K = soil erodability factor (dimensionless),
LS = length-slope factor (dimensionless),
C = soil cover factor (dimensionless), and
P = conservation practice factor (dimensionless).

Typical values of soil erosion for different land uses are presented in **Table 4.1** (Boyd, 1995).

Table 4.1. Representative Rates of Erosion for Selected Land Uses*

Land Use	Erosion (metric tonnes ha^{-1} yr^{-1})
Forest	0.034
Grassland	0.34
Cropland	6.8
Harvested forest	17.0
Construction	68.0

* Source: Boyd, 1995

In all aspects of monitoring, modeling, or prediction of non-point source management, the scale is important to accurately estimating soil erosion into water bodies. The mass or eroded soil per area decreases with increasing land area due to redeposition within the field. Understanding the dynamics of scale is vital to the ability to estimate erosion from varying sizes of field as well as to extrapolate useful management principles that will apply to larger areas.

4.2.1.1 Sediment Enrichment

The concept of the sediment enrichment ratio (SER) is quite important to understanding the impact of chemical loss from fields. The SER is defined as:

$$SER = \frac{\textit{Chemical Concentration in Transported Sediment}}{\textit{Chemical Concentration in Soil}}$$

The process of surface erosion tends to be selective towards fine particles and organic matter both of which also selectively sorb pesticide. Consequently, the particle size characteristics of material eroded at the source is progressively changed towards finer particles through deposition of the coarser fraction (e.g. sand-size material). Because of the chemically enriched nature of fine particles due to the large surface area of clay-size sediment, the concentration of chemicals that are associated with sediment (hydrophobic pesticides, etc.) increases as the impoverished sand-size fraction is lost during down-field transport. This results in an increasing proportion of the chemically enriched fine (silt-clay) fraction. Organic mater to which pesticide is adsorbed is also preferentially eroded due to its low density and tendency to float.

4.2.2 Pesticide Transport within Aquatic Ecosystems

A number of characteristics of an aquatic ecosystem are also expected to influence pesticide transport within that system. The composition of solids present in the water column (*e.g.,* organic carbon and clay content) can influence pesticide sorption. For hydrophobic chemicals, increases in the organic carbon content of particles in the water column result in increases in the mass of a chemical sorbed to the particles. Hydrological and biological features of the aquatic system can cause mixing of sediment and resuspension of particles, thus moving pesticide sorbed to the sediment. For example, the effects of floating-leaved, submerged and emergent macrophytes on sediment resuspension and internal phosphorus loading were studied in the shallow Kirkkojaervi basin by placing sedimentation traps among different plant beds and adjacent open water and by sediment and water samples. All the three macrophytes considerably reduced sediment resuspension compared with non-vegetated areas (Horppila and Nurminen, 2005).

Settling characteristics of soil particles depend on their size, shape, mass and density. Thus, deposition rates of suspended sediment-sorbed pesticide would also be expected to vary according to sediment composition. As particles settle due to gravity, the suspended sediment concentration is reduced from its initial, post-storm level and turbidity decreases beginning at the surface and moving downward as progressively smaller and smaller particles settle out of the water column. Larger particles settle more quickly followed by the fine silt and clay size fractions of the soil carrying with it pesticide that has sorbed to it. Settling velocities in quiescent (still) water as a function of particle density and diameter is presented in **Table 4.2**.

Table 4.2. Settling Velocities of Particles Based on Stokes Law

Particle Class	Particle Diameter (mm)	Velocity (m/day) based on particle density (g/cm^3)			
		1.8 g/cm^3	2.0 g/cm^3	2.5 g/cm^3	2.7 g/cm^3
Fine sand	0.2	380	470	710	800
	0.05	94	120	180	200
Silt	0.05	94	120	180	200
	0.02	15	19	28	32
	0.01	3.8	4.7	7.1	8.0
	0.005	0.94	1.2	1.8	2.0
	0.002	0.15	0.19	0.28	0.32
Clay	0.002	0.15	0.19	0.28	0.32
	0.001	0.04	0.05	0.07	0.08

Source: WASP7 Training course: http://www.epa.gov/athens/wwqtsc/html/wasp.html.

Resuspension of bottom sediment in a static pond (i.e., without significant inflow/outflow) most likely results from turbulence caused by largely by wind action and the activity of aquatic and benthic dwelling and burrowing animals (bioturbation). Organic sediment in ponds originates primarily from plankton. According to Boyd (1993), there is usually not enough turbulence in small ponds to maintain high concentrations of soil particles in suspension; plankton is the main source of turbidity. Turbulence due to resuspension in static ponds of less than one meter depth is not likely (Rodney and Stephan, 1987). Biotic and wave-induced resuspension, however, near the bottom of a pond or lake remains a significant cause of mixing of pesticide between water column and the benthic layer even if resuspended particles do not reach the surface.

Resuspension of bottom sediments in flowing streams is due largely to shear forces caused by the flowing water, although wind action and bioturbation also have some impact. Computation of bottom shear stresses is an integral part of the sediment transport processes in lotic systems. The impact of flow may vary depending on the level of cohesiveness of the sediments. Both resuspension and deposition mechanisms depend upon the shear stress induced at the sediment-water interface. The bed armoring processes may be due to the sorting of particle sizes based on flow and may lead to decreased detachment of particles resulting from normal flow.

Permanent burial of sediment is much more likely in a static water body than in a flowing stream, in which sediments are resuspended and carried downstream. Low flow conditions result in less shear stress on bed sediment resulting in increased deposition and burial of underlying sediments. High flow conditions result in greater shear stress on bed sediment resulting in increased scouring of bottom sediment. Frequency of burial and resuspension and downstream transport of suspended material are directly related to the frequency of high and low flow conditions.

4.3 OPP'S STANDARD APPROACH FOR MODELING PESTICIDE TRANSPORT IN STATIC WATER BODIES

As indicated in Section 2 of this White Paper, OPP uses the electronically linked PRZM and EXAMS models to simulate pesticide fate and transport for use in aquatic ecological exposure/risk assessments. (Carsel, et.al, 1984, 1985; Burns et al. 1982, Burns and Cline 1985, Burns 2000). EXAMS is parameterized to represent a farm pond (termed *standard pond*) to follow the movement and transformation of pesticides into and within aquatic ecosystems. The standard pond receives pesticide mass inputs from PRZM, which simulates an agricultural site where a pesticide is applied. A conceptual model depicting the configuration of the treatment sites (represented using PRZM) and the standard pond (represented using EXAMS) is depicted in **Figure 4.3**. The ultimate goal of this approach is to generate aquatic EECs for use in ecological risk assessments of pesticides.

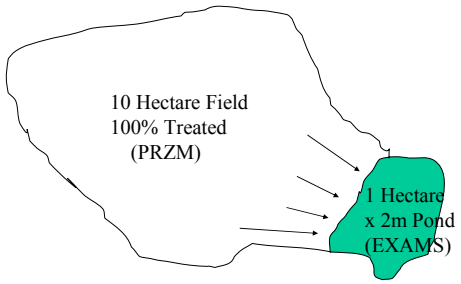


Figure 4.3. Land-to-Water Configuration for OPP/EFED Aquatic Ecological Exposure Assessment.

PRZM simulations use 30 years of measured, site-specific, daily weather data that are parameters of standard scenarios intended to represent pesticide use sites (*e.g.,* a field growing cotton in Mississippi). Simulations involve crop-specific and soil-specific inputs to represent the treatment site. Pesticide-specific inputs, such as fate and transport characteristics, application rates and methods are also used. Among other parameters, PRZM simulations generate 30 years of daily estimates of:

(1) pesticide mass dissolved in runoff,
(2) pesticide mass sorbed to eroded soil,
(3) volume of water running off of the field, and
(4) mass of soil eroding off of the field.

The standard pond scenario used by OPP considers only 2 of these PRZM outputs—the daily aqueous pesticide mass and the daily sorbed pesticide mass. The pesticide mass is treated independent of the volume of water running off of the field and the mass of soil eroding from the field. The volume of water and the mass of soil leaving the PRZM field are not accounted for in the standard pond scenario (**Figure 4.4**).

The standard pond also receives pesticide mass through spray drift, which is generally based on default assumptions (*i.e.,* 1% of application rate for ground applications and 5% for

aerial), but will also use the spray drift estimates from the AgDRIFT or AgDISP models (**Figure 4.4**).

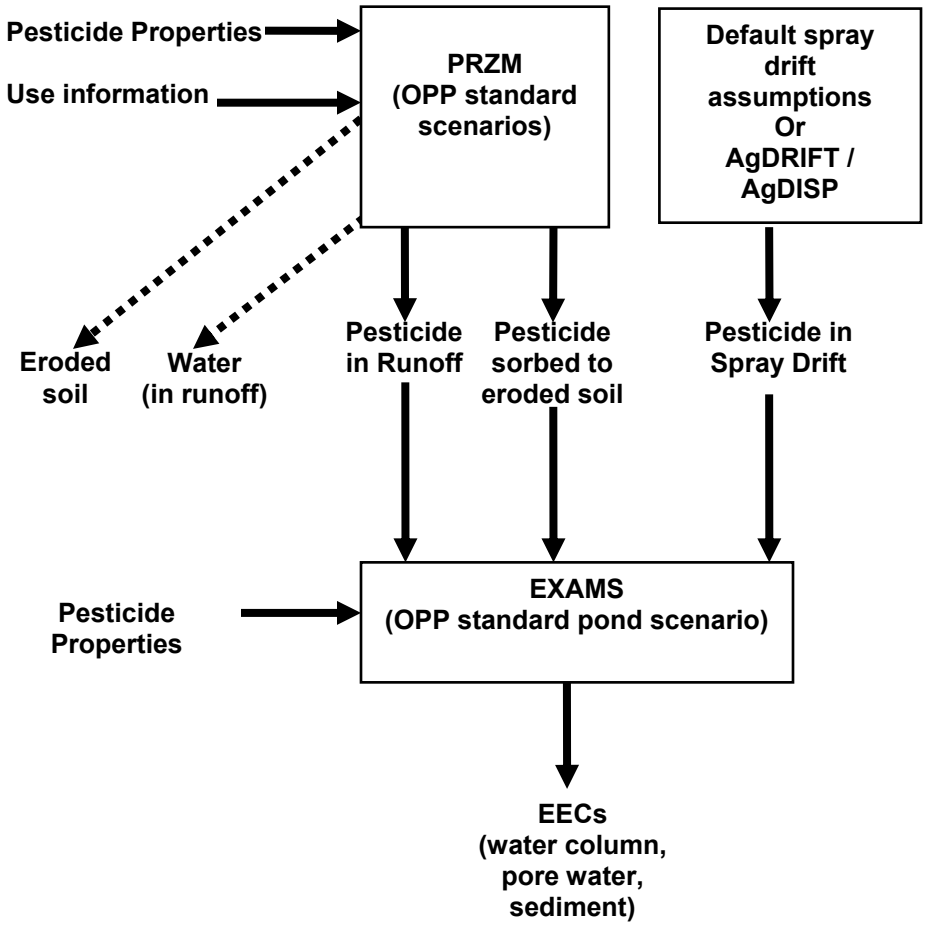


Figure 4.4. Diagram of OPP/EFED Aquatic Ecological Exposure Modeling Scheme.
(Dashed lines represent PRZM outputs that are not included as inputs to the Standard Pond.)

It should be noted that EXAMS and the OPP standard pond scenario are not synonymous. The OPP standard pond scenario is a set of defined parameters (*e.g.*, water volume, suspended sediments, sediment properties) intended to represent rural agricultural ponds. It is assumed by OPP that EECs generated from this scenario are conservative representations of expected pesticide concentrations in farm ponds and in small first- and second-order streams that receive storm water runoff containing pesticide residues from many fields during the period following pesticide application (http://www.epa.gov/scipoly/sap/meetings/1998/july/1part5.pdf). EXAMS is the modeling system that defines the equations used to model the transport and transformation of chemicals, including pesticides, within the aquatic system parameterized by the user (Burns et al. 1982, Burns and Cline 1985, Burns 2000).

Figure 4.5 depicts the conceptual model associated with OPP's approach for modeling pesticide transport in aquatic systems using the standard pond. OPP's standard pond approach for modeling pesticide transport in aquatic systems is generally consistent with the conceptual model depicted in **Figure 4.1**, with some exceptions. Specifically, the grey arrows of this

conceptual model depict portions of the original conceptual model (**Figure 4.1**) that are not included in OPP's modeling approach.

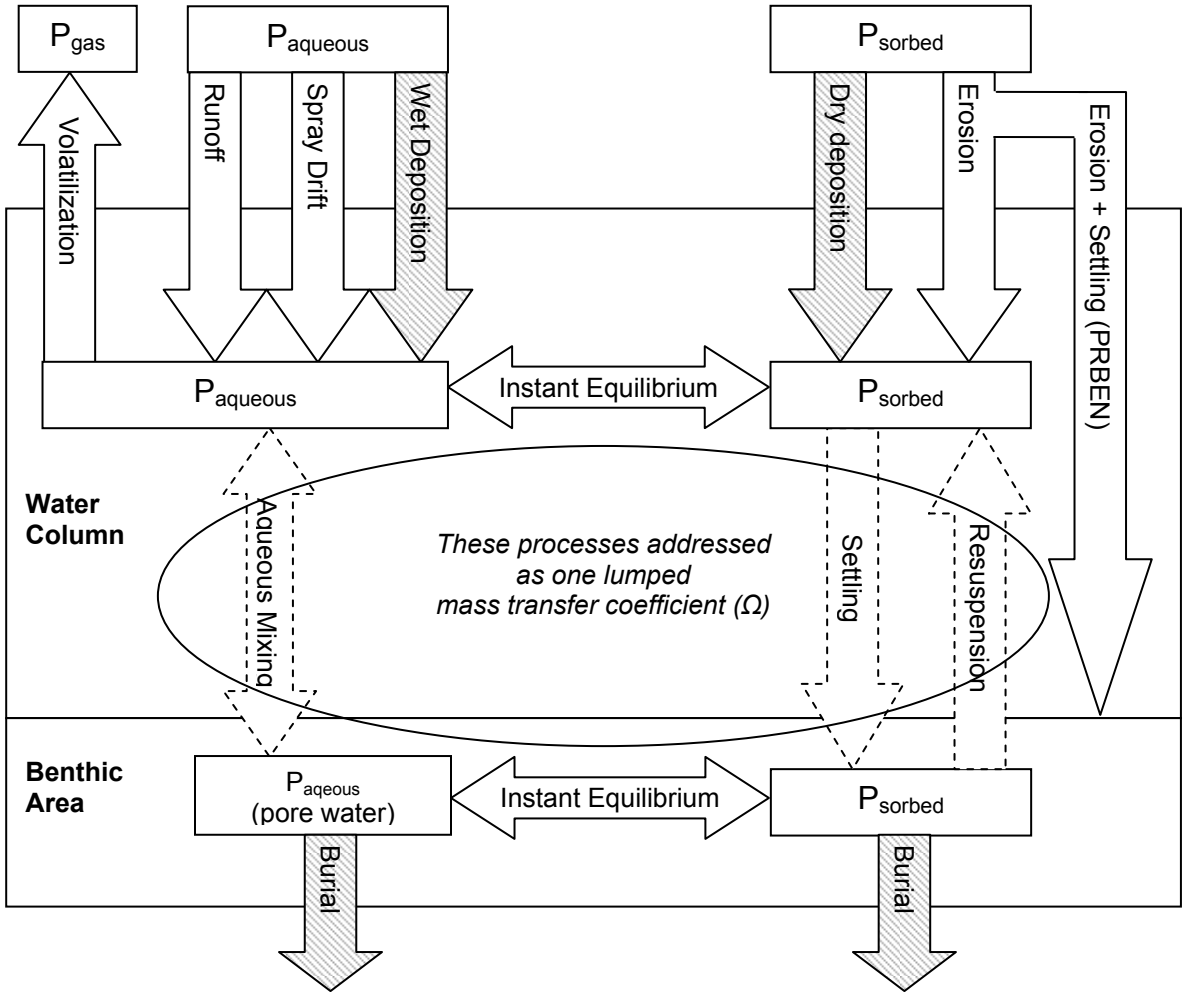


Figure 4.5. Conceptual model of OPP Standard Pond Scenario for Depicting Pesticide Transport (P). Arrows represent movement of pesticide mass from one phase (*i.e.*, sorbed or aqueous) or compartment to another. In this figure, P_{aqeous}=aqueous mass of pesticide; P_{sorbed}= sorbed mass of pesticide; and P_{gas}= gaseous mass of pesticide.

As shown in **Figure 4.5**, the standard pond scenario is represented by 2 compartments - the water column and the benthic area. It is assumed that the standard pond remains at a constant volume of water, where inflow from rainfall and storm water runoff is equal to losses from evaporation. It is also assumed that there is no loss of water (and with that, pesticide mass) through seepage. The composition and concentration of the suspended sediments, dissolved organic carbon (DOC) and biota in the water column remain constant. Also, the volume of water and mass of sediments in the benthic compartment remain constant.

Pesticide inputs are received by the standard pond as dissolved in storm water runoff, adsorbed to eroding soil entrained in storm water runoff, and deposition from spray drift from

pesticide applications. The OPP approach does not include pesticide input to the standard pond through wet and dry deposition. The OPP approach accounts for pesticide loss from the water column through volatilization and degradation.

Aqueous pesticide which enters the standard pond in runoff (from the agricultural field simulated using PRZM) and spray drift instantaneously mixes and equilibrates with the entire water column. In EXAMS, it is assumed that sorbed pesticide mass that enters the aquatic ecosystem is distributed instantaneously between the water column and the benthic compartment (where it will subsequently undergo equilibrium partitioning within each compartment). This initial distribution of sorbed pesticide mass is accomplished via the PRBEN parameter, which assigns a set proportion of the incoming sorbed pesticide mass to the benthic compartment of the aquatic environment. In the OPP standard pond, PRBEN is set to 0.5, which effectively distributes 50% of the incoming sorbed pesticide mass to the benthic compartment and the remaining 50% of the sorbed mass to the water column of the standard pond. This distributing of sorbed pesticide mass between the water column and benthic component of the standard pond is intended to account for settling of incoming soil particles that take with them sorbed pesticide mass.

Pesticide mass in the water column of the standard pond can sorb to suspended sediments and biota and can complex with dissolved organic carbon (DOC) also present in the water column. Concentrations of suspended sediment, biota and DOC are set to constant values throughout the 30 year simulation of the exposure scenario modeled using the standard pond (See **Table 4.3**).

The OPP approach does not involve modeling sediment dynamics (transport of eroded soil mass within the pond). This approach involves modeling transport of the mass of the pesticide itself. The OPP approach is intended to represent movement of pesticide mass as affected by sediment dynamics. However concentrations of suspended solids, DOC, and the benthic mass transfer coefficient are assumed to remain constant. In case of pesticides with low limit of solubility, it is important to note that pesticide mass entering the water column may exceed the measured solubility of the pesticide[3].

Within the water column, pesticide mass is distributed between aqueous and sorbed/complexed phases according to partitioning coefficients that are based on the K_{OC} of the pesticide being modeled, as well as parameters related to the standard pond environment. EECs in the water column are calculated by multiplying the total mass of the pesticide in the water column by the fraction of freely dissolved pesticide mass in the water column ($f_{W1;}$ Equation 4.1 and **Table 4.3**) and dividing that mass by the volume of the water column. The resulting EECs are used to represent exposures (through respiratory uptake) of aquatic organisms to the pesticide in the water column. This approach assumes that the mass of pesticide that is freely dissolved is bioavailable to aquatic organisms.

[3] Modeled EECs are then compared to the solubility of the pesticide and EECs above solubility are set to the solubility limit.

Equation 4.1 $$f_{w1} = \frac{v_1}{\left(m_{sed\_1}K_{sed\_1} + m_{bio\_1}K_{bio\_1} + m_{DOC\_1}K_{DOC\_1} + v_1\right)}$$

Table 4.3. Parameters Used to Determine the Freely Dissolved Fraction of Pesticide in the Water Column of the Standard Pond

Symbol	Description	Value/Calculation (in standard pond)	Units
F_{OC}	Fraction of organic carbon in suspended sediment	0.04	none
K_{OC}	Organic carbon partition coefficient	Pesticide specific	m^3/kg
K_{sed_1}	linear isotherm partitioning coefficient for suspended sediments, this is a set parameter in EXAMS	$F_{OC}*K_{OC}$	m^3/kg
K_{bio_1}	linear isotherm partitioning coefficient for biota, this is a set parameter in EXAMS	$0.436*\left(\frac{K_{oc}}{0.35}\right)^{0.907}$	m^3/kg
K_{DOC_1}	linear isotherm partitioning coefficient for dissolved organic carbon (DOC), this is a set parameter in EXAMS	$0.2114*K_{OC}$	m^3/kg
m_{sed_1}	Mass of suspended sediment in water column	600*	kg
m_{bio_1}	Mass of suspended biota (*e.g.*, plankton) in water column	8*	kg
m_{DOC_1}	Mass of DOC in water column	100*	kg
v_1	volume of water in water column	20,000*	m^3

*The concentrations of suspended sediment, biota and DOC in the water column are 30, 0.4 and 4 mg/L, respectively.

When concentrations of DOC, biota and suspended sediments are kept constant, the freely dissolved fraction of pesticide mass in the water column (*i.e.,* f_{W1}) decreases with increasing K_{OC} (**Figure 4.6**). This indicates that as K_{OC} increases, water column EECs decrease. For example pesticides 1, 2 and 3, the majority (*i.e.,* >90%) of the total mass of present in the water column of the standard pond is freely dissolved. In the case of pesticide 4 which has a much higher Koc, the majority (75%) of the mass of the pesticide in the water column is sorbed to suspended solids and biota or complexed to DOC in the water column (**Table 4.4**).

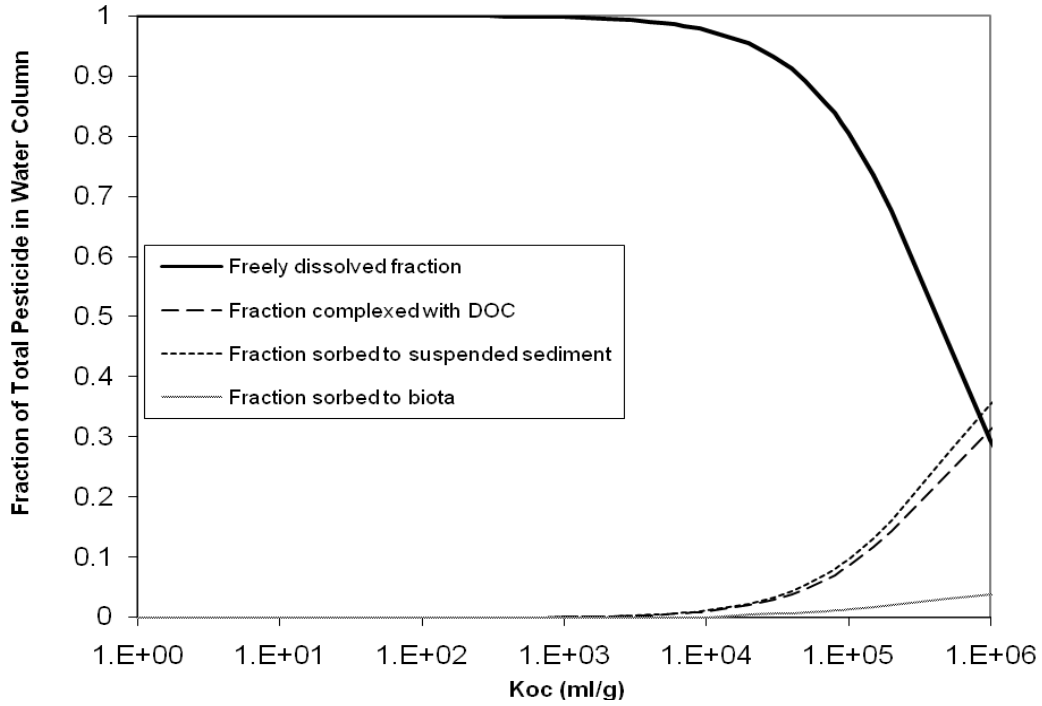


Figure 4.6. Calculated Fraction of Pesticides in the Water Column of the Standard Pond in Different Phases as a function of K_{OC}.

Table 4.4. Calculated Freely Dissolved Fraction of Example Pesticides In The Water Column of the Standard Pond.

Pesticide #	K_{OC} (mL/g)	f_{W1}
1	1.06-1.35 x 10^4	0.97
2	6.47 x 10^3	0.98
3	3.08 x 10^4	0.93
4	1.24 x 10^6	0.25

Two EECs can be calculated to represent pesticide exposures to aquatic organisms in the benthic compartment - pore water EECs and sediment EECs. Pore water EECs are calculated by multiplying the total mass of the pesticide in the benthic compartment by the fraction of freely dissolved pesticide mass in the pore water ($f_{W2;}$ Equation 4.2; **Table 4.5**) and dividing that mass by the volume of the pore water.

Equation 4.2. $$f_{w2} = \frac{v_2}{\left(m_{sed\_2}K_{sed\_2} + m_{bio\_2}K_{bio\_2} + m_{DOC\_2}K_{DOC\_2} + v_2\right)}$$

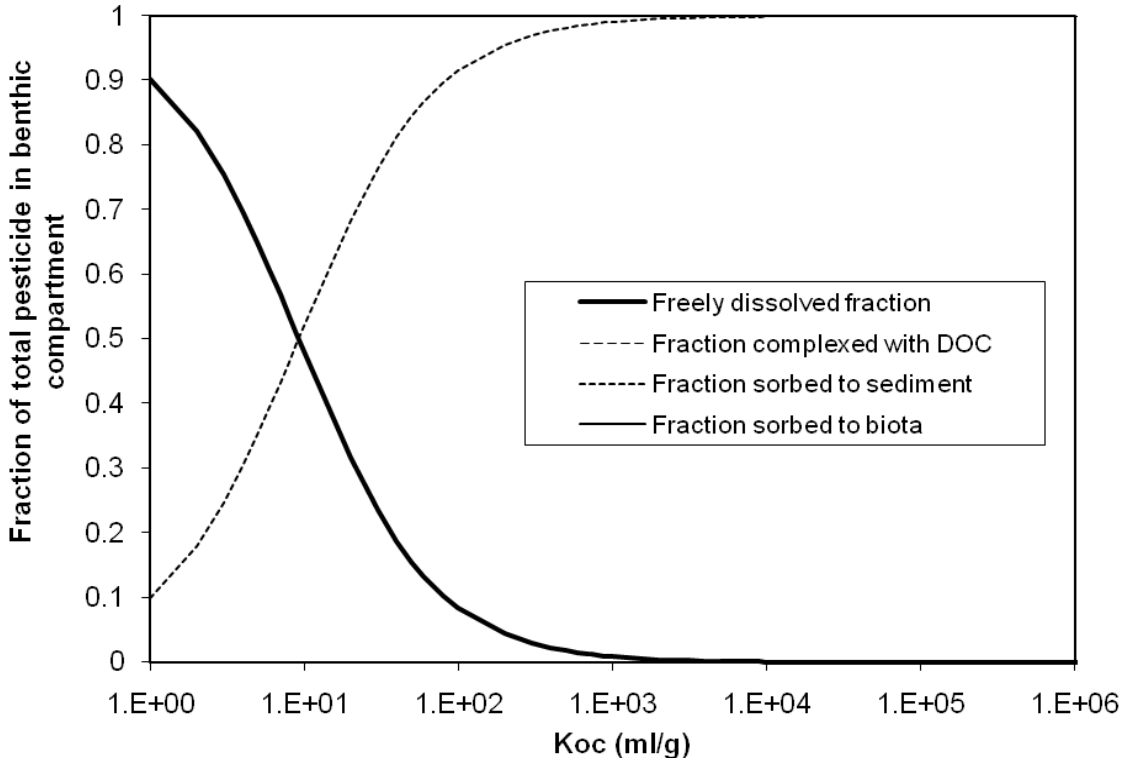
Table 4.5. Parameters Used to Determine the Freely Dissolved Fraction of Pesticide in Pore Water of the Standard Pond

Symbol	Description	Value/Calculation (in standard pond)	Units
F_{OC}	Fraction of organic carbon in sediment	0.04	None
K_{OC}	Organic carbon partition coefficient	Pesticide specific	m^3/kg
K_{sed_2}	linear isotherm partitioning coefficient for suspended sediments	$F_{OC}*K_{OC}$	m^3/kg
K_{bio_2}	linear isotherm partitioning coefficient for biota	$0.436*\left(\frac{K_{oc}}{0.35}\right)^{0.907}$	m^3/kg
K_{DOC_2}	linear isotherm partitioning coefficient for dissolved organic carbon (DOC)	K_{OC}	m^3/kg
m_{sed_2}	Mass of sediment	675,183	kg
m_{bio_2}	Mass of biota (*e.g.,* plankton) in benthic area	0.06	kg
m_{DOC_2}	Mass of DOC in benthic area	1.25	kg
v_2	volume of water in benthic area	250 *	m^3

*Note: the volume of the entire benthic area (including the volumes of both the water and the solids) is 500 m^3.

Sediment EECs are calculated by multiplying the total mass of the pesticide in the benthic compartment by the fraction of pesticide mass sorbed to the sediment and then divided by the mass of the sediment. Such EECs are typically normalized to the organic carbon fraction in sediment to address bioavailability differences associated with sediment organic carbon of different sediments.

When concentrations of DOC, biota and sediments are kept constant, the freely dissolved fraction of pesticide mass in the benthic area pore water (*i.e.,* f_{W2}) decreases with increasing K_{OC}. With K_{OC} >20 mL/g, the majority of the pesticide mass is sorbed to the sediment, with a minor fraction (<$1.0x10^{-4}$) of the overall pesticide mass complexed to DOC or sorbed to biota present in the benthic compartment (**.Figure 4.7**). For example pesticides 1-4, the majority (*i.e.,* >99.9%) of the total pesticide mass is not present in the pore water of the benthic compartment, but rather sorbed to the sediment (**Table 4.6**).



.**Figure 4.7. Calculated Fractions of Pesticide in the Benthic Compartment of the Standard Pond in Different Phases as a function of K_{OC}.**

Table 4.6. Calculated Fractions of Example Pesticides Freely Dissolved in Pore Water and Sorbed to Sediment.

Pesticide #	Koc (mL/g)	freely dissolved (f_{W2})	sorbed to sediment
1	1.06-1.35 x10^4	0.00069-0.00087	~1.0
2	6.47 x 10^3	0.0014	~1.0
3	3.08 x 10^4	0.0004	~1.0
4	1.24 x 10^6	7.5 x10^{-6}	~1.0

EXAMS does not have specific mechanistic inputs for the individual components that are responsible for mass transfer from the water column to the benthic region (*e.g.*, settling, resuspension, diffusion, aqueous mixing). Instead, EXAMS lumps these processes into one mass-transfer coefficient representing the movement of pesticide mass between the water column and the benthic compartment. This coefficient is intended to represent all means of pesticide exchange between the water column and benthic compartment of the standard pond. It is assumed that this includes exchange through the aqueous-phase (*i.e.*, diffusion, hydrologic mixing) as well as by mixing of sediments between the two compartments (*i.e.*, through settling and resuspension). The mass transfer of pesticide between the water column and the benthic compartment of the standard pond relies upon variables specific to the environment rather than to the pesticide being modeled.

As a simplified analysis, consider a persistent chemical (neglecting the degradation components of the equation). In this case, EXAMS treats mass transfer to the benthic region by Equation 4.3. In this equation, c_1 is the water column aqueous concentration, c_2 is the benthic pore water concentration, and Ω is a system-dependent mass transfer coefficient that can be further decomposed as depicted in Equation 4.4 (SAP, 2004). In Equation 4.4, the $K_{tranfer}$ parameter is the fundamental (geometry-independent) mass transfer coefficient. In the OPP standard pond, the parameters in equation 4.4 have the values presented in **Table 4.7**. Note that the aqueous concentrations in equation 4.3 are used only as a surrogate driving force and do not imply aqueous-only transport.

Equation 4.3. $$\frac{dc_2}{dt} = \Omega(c_1 - c_2)$$

Equation 4.4. $$\Omega = K_{transfer}\frac{A}{V_{T2}}$$

Table 4.7. Parameters Used to Determine the Mass Transfer Coefficient (Ω) B**etween the Water Column and Benthic Compartment of the Standard Pond.**

Symbol	Description	Value (in standard pond)	Units
A	Surface area of boundary between water column and benthic compartment	10,000	m^2
$K_{Transfer}$ *	water column to benthic transfer coefficient	8.17×10^{-9}	m/s
V_{T2}	total volume of the benthic compartment (including the volumes of both the water and the solids)	500	m^3

*This parameter is depicted in the EXAMS manual (USEPA, 2004) as DISP/CHARL. It is combined here because of the inseparability of these two parameters.

4.4 EVALUATION OF OPP'S STANDARD AQUATIC MODELING APPROACH IN RELATION TO SEDIMENT DYNAMICS

The main assumptions OPP's standard aquatic modeling approach in relation to the potential influence of sediment dynamics on exposure estimates for pesticides with PBT characteristics are shown in **Table 4.8**. These assumptions and their potential effects to exposure modeling of pesticides with PBT characteristics are further explored below.

Table 4.8. Current Assumptions of the Standard OPP Aquatic Exposure Modeling Approach in Relation to Sediment Dynamics

Assumption	Strength and Limitation in Relation to Sediment Dynamics
Bioavailability is most closely related to freely dissolved pesticide concentration in water. Within sediment and water compartments, equilibrium exists between freely dissolved, DOC and POC-sorbed chemical	Reflects current state of the science regarding bioavailability of non-ionic organic chemicals. However, current OPP modeling approach assumes constant DOC and POC concentrations, which would be influenced by sediment dynamics if it was explicitly modeled.
Environmental parameters of the standard pond are static (*e.g.,* water volume, suspended sediment concentrations, sediment volume).	This enables computational efficiency and comparability across scenarios and pesticides. However, if sediment dynamics were explicitly modeled, spatial and temporal variation in water volume, suspended sediment concentration and sediment volume would be expected. This would likely add substantial complexity to current modeling approach.
No inflow/outflow to the standard pond	Provides an effective screen for evaluating pesticide risks in a variety of aquatic ecosystems. However, pesticide mass that would be transported 'down stream' in flowing systems is not removed. If pesticide mass were removed via flowing water or sediment flow, the accumulation of the pesticide in the aquatic system would be less than that of the current OPP approach.
Initial distribution of sorbed pesticide mass assumed to instantaneously partition between sediment layer (50%) and water column (50%), where it is then subject to equilibrium partitioning within these compartments	There is a wide range of potential values that could be assigned to this initial distribution parameter (PRBEN). The value of 0.5 reasonably falls within the range of available values.
Pesticide transport between the water column and the benthic compartment (*i.e.,* settling, re-suspension, diffusion) of the standard pond are represented by a single lump mass transfer coefficient.	The mass transfer coefficient does not consider the independent impacts of resuspension, sedimentation, and diffusion on the transfer of pesticide mass between the water column and benthic compartment of the standard pond. Uncertainty exists on parameterization of parameters to individually represent sedimentation, resuspension, and diffusion.
Pesticide mass is not permanently removed from the standard pond due to burial.	Provides an effective screen for evaluating pesticide risks in a variety of aquatic ecosystems. However, if pesticide mass were removed via burial, estimated accumulation of the pesticide in the aquatic system would be less than that of the current OPP approach.

4.4.1 Bioavailability

As discussed above, the freely dissolved fraction of pesticide in the water column and in the pore water are used for EECs representing pesticide uptake in aquatic organisms through respiration. This implies that the fraction of pesticide that is freely dissolved is bioavailable to aquatic organisms through respiration, while the fraction that is sorbed is not bioavailable. The chemical mass associated with DOC and suspended sediments in the water column is assumed to be in equilibrium with the chemical mass that is freely dissolved in the water column. Therefore, any additions or removal of chemical from any of the three phases (*i.e.,* freely dissolved chemical, chemical associated with DOC, and chemical associated with suspended sediments) will cause a re-equilibration of the chemical among the three phases. Due to the equilibrium conditions among these three phases, the chemical concentration in the water column expressed

using any of the three phases, individually or in combination, is indicative of the chemical concentrations in the other water column phases for a given set of ecosystem conditions.

It is also understood that pesticide mass that is sorbed to sediments is bioavailable to biota through consumption of sediments (with sorbed pesticide mass). Pesticide mass contained within aquatic organisms (that have bioconcentrated or bioaccumulated the pesticide) is also bioavailable to higher level biota through consumption of lower level biota (that are contaminated with the pesticide). The topic is discussed in the bioaccumulation chapter of this White Paper.

4.4.2 Static Environmental Parameters

The OPP approach for modeling pesticide transport between the water column and the benthic area of the standard pond involves the mass transfer coefficient ($K_{transfer}$) in combination with the PRBEN parameter. This approach is intended to track the pesticide mass transport, not the transport of solids (*i.e.,* sediments) to which the pesticide is sorbed. The proportion of pesticide mass being exchanged between the water column and benthic area is constant in the OPP modeling approach, regardless of time, PRZM scenario or the pesticide being modeled. There is the potential for uncertainty in this approach, since soil loads into a pond would be expected to vary over time based on variable runoff events, and over space. This can be illustrated by examining predicted runoff of PRZM scenarios (**Figure 4.8**). Differing soil loads into the pond could lead to differing suspended sediment and DOC concentrations in the pond over time and space, and with that, differing settling rates over time and space of pesticide mass sorbed to suspended sediments.

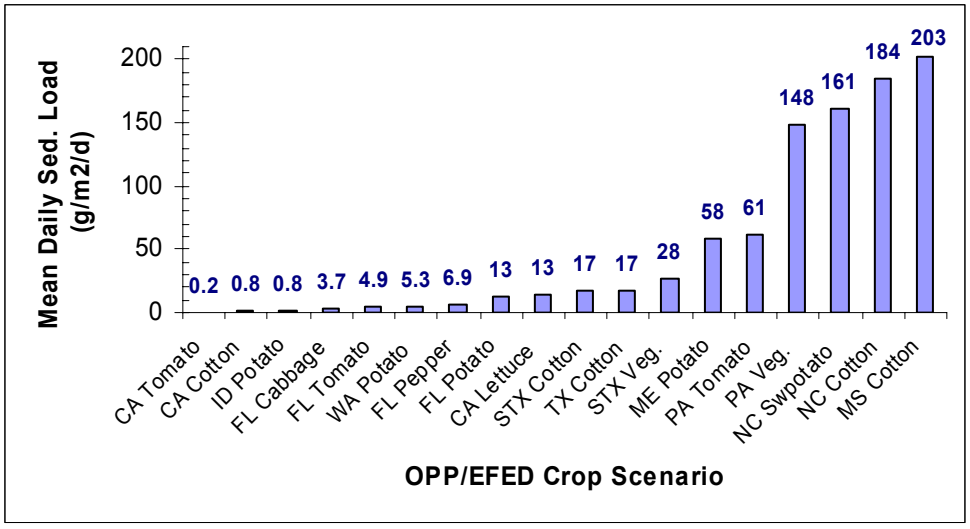


Figure 4.8. Mean daily soil erosion (resulting in sediment loads) from various PRZM scenarios.

The freely dissolved fraction of pesticide in the water column estimated using the standard pond is related to the concentrations of suspended sediments, DOC and biota as well as the fraction of organic carbon of the suspended sediments (Equation 4.1). Depending upon the

K_{OC} of the pesticide, the values of these parameters can influence the freely dissolved fraction of pesticide in the water column and thus, affect the EEC. One limitation of the standard pond scenario is that the values of these parameters are not varied, but constant throughout the 30 year simulation period. There is uncertainty in this approach because it would be expected that differing soil loads into the pond over time and space would lead to different concentrations of suspended sediments and DOC over time. Decreases in concentrations of suspended sediment and DOC result in increases in the freely dissolved fraction of pesticides with $K_{OC} > 10^3$ mL/g in the water column (**Figures 4.9 and 4.10**, respectively). By the same token, increases in concentrations of suspended sediment and DOC would result in decreases in the freely dissolved fraction of pesticide in the water column. Therefore, the concentration of suspended sediments and DOC in the water column can affect EECs used for generating RQs and for estimating bioaccumulation of the pesticide in the aquatic food web.

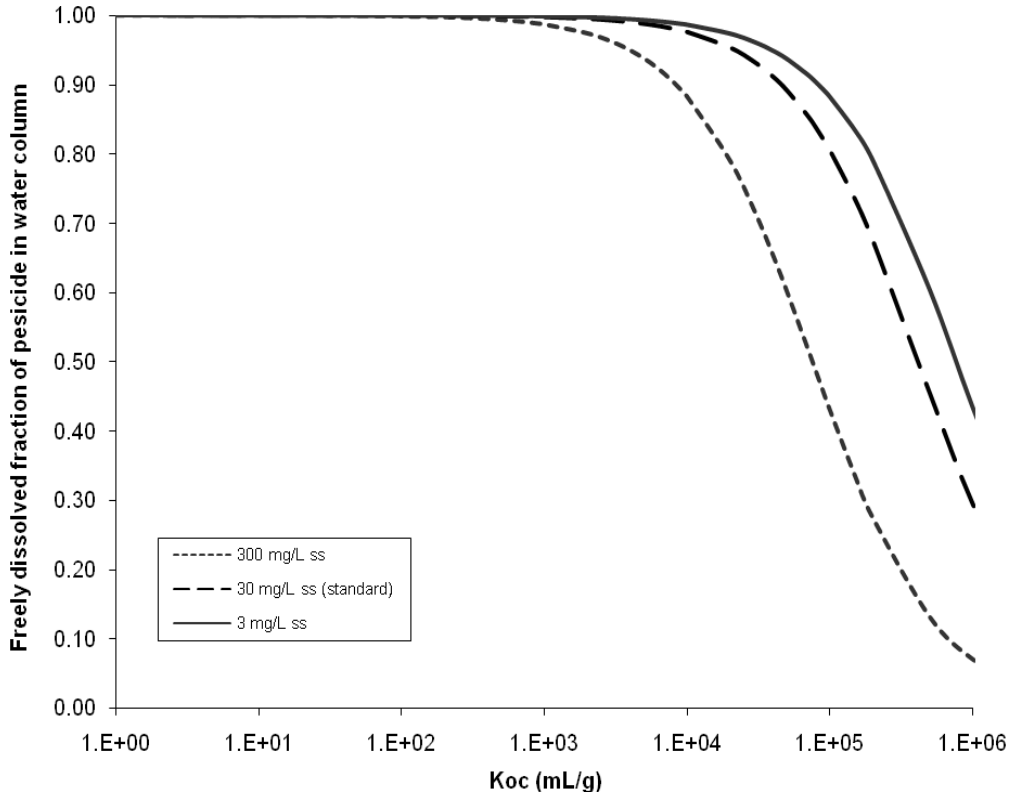


Figure 4.9. Freely Dissolved Fraction of Pesticide in Water Column at Different K_{OC} and Suspended Sediment (Ss) Concentrations. (Concentrations of DOC and biota (5 and 0.4 mg/L, respectively), are consistent with the standard pond.)

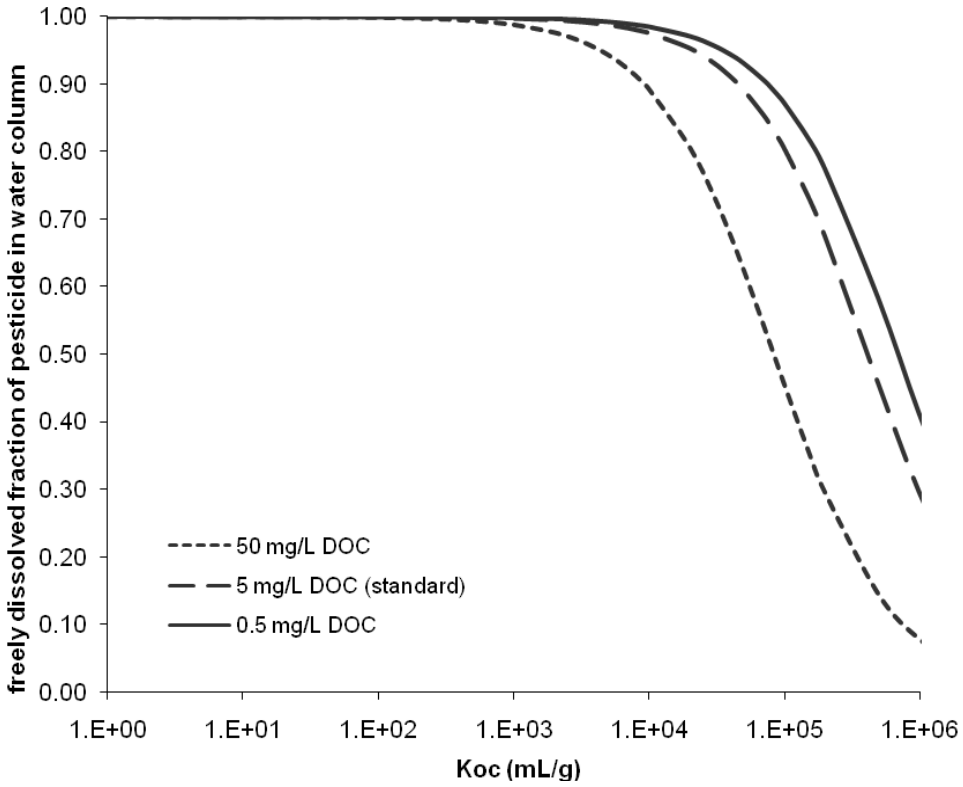


Figure 4.10. Freely Dissolved Fraction of Pesticide in Water Column at Different K_{OC} and DOC Concentrations. (Concentrations of suspended sediment and biota (30 and 0.4 mg/L, respectively), are consistent with the standard pond).

According to NAWQA data for streams, suspended sediment concentrations range 1-281 mg/L, with an average of 13 mg/L and a median of 2 mg/L (n=771). DOC data available from USGS for flowing waters and lakes range 0.05-30 mg/L, with median and average values of 3.0 and 4.1 mg/L, respectively (n=811). These data indicate that concentrations of suspended sediments and DOC can vary by orders of magnitude. These data also indicate that the values used to represent concentrations of suspended sediment and DOC in the standard pond (*i.e.,* 30 and 5 mg/L, respectively) are representative of the median and average values observed in the environment.

4.4.3 EXAMS Parameter *PRBEN*

According the EXAMS manual: "The parameter PRBEN controls EXAMS' treatment of sediment-borne materials. When PRBEN is zero, all sediment-borne materials are equilibrated with the water column upon entry into the system. When PRBEN is 1.0, all sediment-borne materials are routed directly to the benthic zone. PRBEN has a default value of 0.5, based on the observation that, in general, about 50% of sorbed chemical is usually labile, and about 50% recalcitrant, to rapid re-equilibration in water."

Chemical sorption to soil is often described as having a fast-equilibrating component and slow-equilibrating component. The slow equilibrating fraction (*i.e,* the part that appears to not equilibrate instantaneously) can range widely. Pignatello and Xing (1996) gave a limited review of some studies with slow fractions ranging from 0.14 to 0.94. Based on these values, a reasonable value for the PRBEN parameter could range anywhere between 0 and 1. It is these slow fraction values that could be conceived to be an estimate as a starting point for determining a value for PRBEN, as these fractions would be relevant to representing the mass of sorbed pesticide incoming to the pond that would remain sorbed to soil and be transported to the sediment via settling of soil/suspended sediment.

The K_{OC} of a chemical can be used to explore reasonable proportions of pesticide mass that would be expected to desorb from incoming soil/suspended sediment to reach equilibrium within the water column. **Figure 4.11** depicts the fraction of pesticide expected to be sorbed to 30 mg/L of suspended sediments in the water column (this is the set concentration of suspended sediments in the standard pond) with consideration of varying K_{OC} values. For pesticides with high Koc values, such as pesticide 4, a value of 0.5 for PRBEN appears to be a reasonable approximation. This exploration does not include the changing mass of suspended sediment that would come with the incoming load of eroded soil as well as other factors that would affect the equilibration of incoming pesticide mass within the water column (*e.g.,* characteristics of eroded soil); however, the approach is intended to explore whether or not soil-associated pesticide mass could come to equilibrium once it enters the water column.

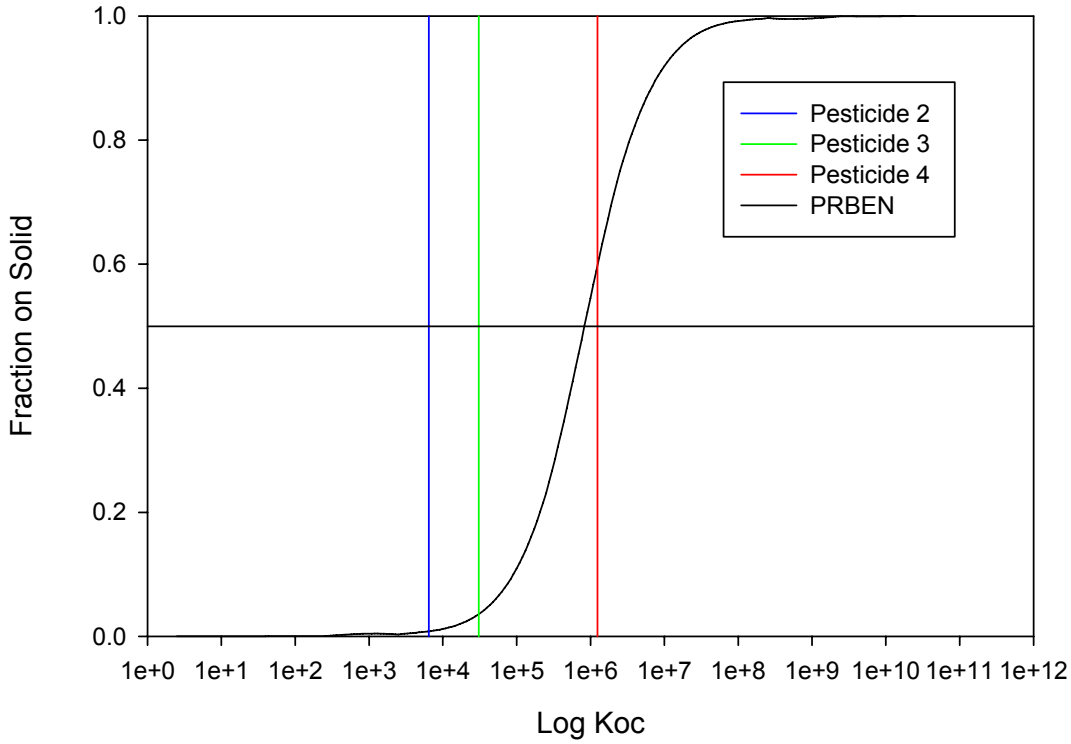


Figure 4.11. Fraction of pesticide sorbed on 30 mg/L suspended sediment for different K_{OC} values.

4.4.4 Mass Transport Coefficient

The water column to benthic area transfer coefficient ($K_{transfer;}$ Equation 4.4; **Table 4.7**) is set to a value of 8.17 x 10^{-9} m/s in the standard pond. Data available from empirical studies suggest that this value can vary by orders of magnitude. Schwarzenbach et al (1993) report a value of 2 x 10^{-6} m/s, while Worman (1995) reports a value of 5 x 10^{-5} m/s. Analysis of studies submitted to the Agency indicated that $K_{transfer}$ describing pesticide movement in aquatic systems throughout the country ranged 10^{-5} to 10^{-10} m/s (Schnier 2008). Although there is wide variability in the range of estimates of $K_{transfer}$, the value used in the OPP standard pond is within that range. Whether a change in $K_{transfer}$ will increase or decrease EECs is chemical dependent; however, in any case, increasing $K_{transfer}$ will serve to decrease the concentration differences between pore water and water column will decrease. The effect on EECs is uncertain.

4.4.5 Pesticide Burial

As indicated above, the standard pond does not include burial of pesticide mass within the benthic compartment. Although sediment burial of chemicals may occur in some natural water bodies, temporarily covered pesticide mass may be re-exposed in natural systems due to water turbulence and to bioturbation caused by animals in the benthic compartment (*e.g.,* fish and sediment dwelling or borrowing species). Since temporarily covered pesticide mass could be re-exposed in natural systems, inclusion of the process of burial in prediction of pesticide concentrations within an aquatic system is not conservative. Therefore, the process of burial is not used in OPP's standard pond used to estimate pesticide exposure concentrations in baseline risk assessments. The process of burial of chemical mass is not explicitly included in the EXAMS model.

As indicated in the EXAMS manual (USEPA, 2004), EXAMS can be used to model loss of pesticide mass from the benthic compartment by using a first-order rate constant. In order to explore the impact of burial on estimates of pesticide exposures in the water column and benthic area of the standard pond, a first order rate coefficient was estimated by assuming that sediment burial is equal to the sediment residence time. Sediment residence time in this case was estimated by dividing the average daily sediment inflow rate by the mass of the sediment in the benthic compartment. The MS cotton scenario was selected to determining the average daily sediment inflow rate because it represents a PRZM scenario with a high soil erosion rate (see Figure 4.8). The resulting half-life in the benthic area due to burial is 222 days. This half-life is expected to represent a higher burial rate compared to what would be derived using other PRZM scenarios.

The impacts of incorporation of burial into aquatic modeling (modifying the standard pond) on 1 in 10 year EECs of pesticides 3 and 4 are shown in **Tables 4.9 and 4.10**, respectively. As expected, sediment burial lowers the 1 in 10 year EECs, with a greater effect on EECs of pesticide 4 as compared to those of pesticide 3. For this exercise, soil erosion from the MS cotton scenario was used to determine the half-life used to simulate burial. As noted above, this scenario was selected to represent a high end burial rate. Therefore, effects to EECs due to

incorporation of burial would be less pronounced if soil erosion rates from other PRZM scenarios (*e.g.,* CA cotton) were used. Since no limitations were placed on aqueous solubility for these example pesticides, the potential impact of solubility limitations on the effect of burial was not quantified.

Table 4.9. Estimated 1 in 10 year EECs for Pesticide 3 in the MS Cotton Scenario[(1)].

Estimated Environmental Concentrations	**1 in 10 year Concentration**			
	Peak	**21-day average**	**60-day average**	**Annual Average**
Water Column Concentration (µg/L)				
Non-Burial	5.358	1.716	1.405	1.036
Burial	5.109	1.456	1.093	0.731
Percent Reduction	**4.6**	**15.2**	**22.2**	**29.4**
Pore Water Concentration (µg/L)				
Non-Burial	0.944	0.930	0.894	0.780
Burial	0.706	0.695	0.665	0.531
Percent Reduction	**25.2**	**25.3**	**25.6**	**31.9**
Sediment Concentration (mg/kg)				
Non-Burial	1.166	1.147	1.099	0.960
Burial	0.868	0.855	0.818	0.653
Percent Reduction	**25.6**	**25.5**	**25.6**	**32.0**

(1) EECs assumed no limit to solubility for this exploratory analysis.

Table 4.10. Estimated 1 in 10 year EECs for Pesticide 4 in the MS Cotton Scenario[(1)].

Estimated Environmental Concentrations	**1 in 10 year Concentration**			
	Peak	**21-day average**	**60-day average**	**Annual Average**
Water Column Concentration (µg/L)				
Non-Burial	1.827	0.620	0.565	0.527
Burial	1.504	0.245	0.186	0.133
Percent Reduction	**17.7**	**60.5**	**67.1**	**74.8**
Pore Water Concentration (µg/L)				
Non-Burial	0.094	0.093	0.093	0.089
Burial	0.027	0.026	0.025	0.021
Percent Reduction	**71.3**	**72.0**	**73.1**	**76.4**
Sediment Concentration (mg/kg)				
Non-Burial	4.661	4.640	4.602	4.429
Burial	1.318	1.288	1.230	1.048
Percent Reduction	**71.7**	**72.2**	**73.3**	**76.3**

(1) EECs assumed no limit to solubility for this exploratory analysis.

4.5 SEDIMENT DYNAMICS REPRESENTED BY OTHER FATE AND TRANSPORT MODELS

The following is a short description of the sediment dynamics portions of several pesticide fate and transport models which simulate one or more sediment dynamics processes. The models described below are (in alphabetical order): AGRO, AnnAgNPS, ECOMSED, HSPF/SPSM, PRZM/RivWQ, SWAT and WASP. The sediment handling capabilities of these

seven models are compared in **Table 4.11**. Listing of these models here does not indicate official USEPA endorsement of their use. The scale of many of these models is quite different in scale from the current EFED exposure assessment modeling scenario and many are basin-scale or watershed-scale flowing water models. Although EFED has recently completed an evaluation of three of these models, no decision has been made as to their use. For a complete comparison, see: http://www.epa.gov/scipoly/sap/meetings/1998/july/matrix.htm.

Table 4.11. Comparison of Sediment Handling Capabilities of Selected Models *

Model Capabilities	(PRZM)/ AGRO	AnnAgNPS	ECOMSED	HSPF/ NPSM (BASINS)[1]	PRZM/ RivWQ	SWAT (BASINS)[1]	WASP
Overland Erosion (USLE, Onstad-Foster, SLOSS)	√	√			√	√	
Sediment deposition	√	√	√	√	√	√	√
Distribution of sediment size		√	√	√		√	√

*See Model User's Manual and Technical Descriptions
√ - Model is capable of simulating indicated parameter.
[1.] The SWAT and HSPF models are included in the USEPA BASINS shell (Lahlou, et.al., 1996)

Three flowing water models were recently evaluated by OPP/EFED at the request of a July 1998 SAP advisory group (Parker, et.al, 2007). They are presented below in the following sections: (4.5.4) HSPF / NPSM (Hydrological Simulation Program – FORTRAN / Non-point Source Model), (4.5.5) PRZM – RivWQ (Pesticide Root Zone Model / Riverine Water Quality) Model, and (4.5.6) Soil Water Assessment Tool (SWAT). Also presented to this SAP meeting was the AnnAGNPS model which was judged at the time to need further development before EFED evaluation. The materials presented to the SAP members can be viewed at: http://www.epa.gov/scipoly/sap/meetings/1998/july/1part5.pdf. HSPF and SWAT are included in the EPA BASINS shell. A feature-by-feature comparison of the four models can be viewed at: http://www.epa.gov/scipoly/sap/meetings/1998/july/matrix.htm. These models are briefly described below.

4.5.1 AGRO

The Canadian Environmental Modeling Centre's AGRO modeling system is a MicroSoft Excel® based application that combines a water quality model with a food web model to estimate exposure to aquatic species from pesticides in a user-defined water body. A major feature of this system is its capability to incorporate dynamic functionalities which allow the user to introduce changing environmental and emission conditions so that the fate and bioaccumulation results of numerous chemicals can easily and efficiently be compared.

This system can be run in dynamic mode which uses daily input of water, sediment, and pesticide from predicted daily mass loadings generated by version PRZM (version 3.12) (Suárez, 2006). Daily loading and emission values from PRZM are then used to generate predicted daily pesticide concentrations in the water column, benthic pore water and benthic sediment of the water body.

The water quality model component of the AGRO modeling system is the Quantitative Water, Air, Sediment Interaction (QWASI) Fugacity model developed by Mackay et al. at the Canadian Environmental Modelling Centre (Mackay, Joy and Paterson (1983), Mackay, Paterson and Joy (1983), Webster Lian and Mackay (2005), Mackay and Diamond (1989)). The QWASI model is based on a single receiving water body of user-defined size and depth with an active sediment layer. This model is run in dynamic mode which includes daily input of water from field runoff, dissolved pesticide in field runoff, eroded sediment, pesticide sorbed to eroded sediment, pesticide emissions resulting from application drift and rainfall.

An earlier version of AGRO (ver. 1.2.6, May 16, 2008) modeled sediment deposition, resuspension and burial via a set of fixed daily rates ($g/m^2/d$). These sedimentation parameters were set independent of spatial and temporal differences in estimated sediment delivery to the pond. Sediment burial was the difference between deposition and resuspension.

A more recent version of AGRO (ver. 1.2.8b, July 18, 2008) considers spatial and temporal heterogeneity in PRZM-predicted erosion rates to the pond by incorporating daily soil erosion predictions from PRZM specific to each crop scenario. This version has not been evaluated by EFED.

4.5.2 AnnAGNPS (Annualized Agricultural Non-point Source Model)

Overland erosion of sediment is determined using RUSLE (Renard et al., 1997) and was modified to work at the watershed-scale in AnnAGNPS (Geter and Theurer, 1998). Sediment-transported nutrients and pesticides are also calculated and equilibrated within the stream system. Sediment is subdivided into 5 particle size classes (clay, silt, sand, small aggregate, and large aggregate). Particle sizes are routed separately in the stream reaches.

A daily mass balance adapted from GLEAMS (Leonard et al., 1987) is computed for each pesticide. AnnAGNPS allows for any number of pesticides, each with their own independent chemical properties. Each pesticide is treated separately, independent equilibration is assumed for each pesticide. Major components of the pesticide model include foliage wash-off, vertical transport in the soil profile, and degradation. Soluble and sediment adsorbed fractions are calculated for each cell on a daily basis.

The methods used to route sediment, nutrients, and pesticides through the watershed are outlined in Theurer and Cronshey (1998) and briefly discussed here. Peak flow for each reach is calculated using an extension of the TR-55 graphical peak discharge method (Theurer and Cronshey, 1998). Sediment routing is calculated based upon transport capacity relationships using the Bagnold stream power equation (Bagnold, 1966). Sediments are routed by particle size

class where each particular size class is deposited, more entrained, or transported unchanged depending upon the amount entering the reach, availability of that size class in the channel and banks, and the transport capacity of each size class. If the sum of all incoming sediment is greater than the sediment transport capacity, then the sediment is deposited. If that sum is less than the sediment transport capacity, the sediment discharge at the downstream end of the reach will include bed and bank material if the user has indicated that it is an erodible reach. Nutrients and pesticides are subdivided into soluble and sediment attached components for routing. Attached P is further subdivided into organic and inorganic. Each nutrient component is decayed based upon the reach travel time, water temperature, and an appropriate decay constant. Soluble nutrients are further reduced by infiltration. Attached nutrients are adjusted for deposition of clay particles. Equilibrium concentrations are calculated at both the upstream and downstream points of the reach. A first-order equilibration model is used.

4.5.3 ECOMSED

The development of ECOMSED has its origins in the mid 1980's with the creation of the Princeton Ocean Model (Blumberg and Mellor, 1987) and its version for shallow water environments – rivers, bays, estuaries and the coastal ocean and reservoirs and lakes- named ECOM (Blumberg, 1996). In the mid 1990s, concepts for cohesive sediment resuspension, settling and consolidation (Lick, et al., 1984) were incorporated within the ECOM modeling framework. During the last several years, ECOMSED was enhanced to include generalized open boundary conditions, tracers, better bottom shear stresses through a submodel for bottom boundary layer physics, surface wave models, noncohesive sediment transport, and dissolved and sediment-bound tracer capabilities.

The ECOMSED model is capable of simulating the transport and fate of suspended sediments, dissolved tracers and neutrally-buoyant particles in estuarine and coastal ocean systems. A wide variety of problems concerning water optics and spill tracking can be studied using the model due to the various options built into ECOMSED. Capabilities of the model include: (1) runtime computed (internal) or pre-computed (external) hydrodynamics; (2) cohesive and non-cohesive sediment transport; (3) sediment-bound tracer transport (conservative or first-order decay); (4) dissolved tracer transport (conservative or first-order decay); (5) neutrally buoyant particle tracking; and (6) inclusion of wind wave effects on hydrodynamics and sediment transport.

The transport and fate of cohesive and non-cohesive sediments can be simulated with ECOMSED. Resuspension, deposition and transport of cohesive sediments, which are composed of clays, silts and organic material, are simulated using the SED module. The suspended transport of non-cohesive sediments, i.e., fine sands, is calculated using the van Rijn procedure (van Rijn, 1984). The effects of bed armoring due to particle-size heterogeneity can also be included in non-cohesive sediment transport simulations.

4.5.4 HSPF / NPSM (Hydrological Simulation Program – FORTRAN / Non-point Source Model)

HSPF is a comprehensive package for simulation of watershed hydrology and water quality for both conventional and toxic organic pollutants. (Bicknel, et.al, 1985, 1996; Chen, Y.D., et.al., 1995; Donigian, A.S., Jr., and N.H. Crawford, 1976). HSPF incorporates watershed-scale ARM and NPS models into a basin-scale analysis framework that includes fate and transport in one dimensional stream channels. It is the only comprehensive model of watershed hydrology and water quality that allows the integrated simulation of land and soil contaminant runoff processes with In-stream hydraulic and sediment-chemical interactions. The result of this simulation is a time history of the runoff flow rate, sediment load, and nutrient and pesticide concentrations, along with a time history of water quantity and quality at any point in a watershed. HSPF simulates three sediment types (sand, silt, and clay) in addition to a single organic chemical and transformation products of that chemical.

The HSPF/NPSM sediment procedures are common to both the PERLND and IMPLND modules, and sediment delivery algorithms that compute the amount of sediments eroded from a field and delivered to a watershed outlet are available in both these modules. The major components of the sediment modules include sediment or soil build up, etachment, transport, and scouring. The erosion calculation is based upon the Universal Soil Loss Equation. The erosion processes includes sediment carrying capacity of the flow, runoff energy, and adsorption/desorption of dissolved pesticides and other pollutants. Hydraulic (Stream) Routing- The transport of surface waters in rivers and streams is simulated in the HYDR module. The major components of this module are single layer flow which is completely mixed, unidirectional flow, flow routing by the kinematic wave or storage-routing method where the conservation of momentum is not considered, function tables for the depth-volume-discharge relationship for each reach, the use of precipitation and evaporation data, and the calculation of outflow, depth, volume, surface area, and selected additional variables. Inflow parameters are tributaries, point sources, and nonpoint source flows. The BASINS implementation features flows generated for each reach, capabilities to delineate sub-watersheds, and final flows and loads calculated at the most downstream reach in the watershed.

4.5.5 PRZM / RivWQ (Pesticide Root Zone Model / Riverine Water Quality Model)

Terrestrial components of the watershed, including the application and dissipation of the pesticides in agricultural fields, were simulated using the Pesticide Root Zone Model, PRZM version 3.12 (Carsel et al., 1998). The fate of pesticides in the aquatic system was simulated using the pesticide transport model for riverine environments, RIVWQ version 2.12 (Williams et al., 1999).

RIVWQ is an explicit finite-difference model that can accommodate tributary systems, non-uniform flow, and mass loadings anywhere along the model system (Williams et al., 1999). Model geometry is based on the link-node approach in which the simulated system is divided into a number of discrete volumes (nodes or junctions), which are connected by flow channels (links). Dynamic constituent transport is a combination of advective flows and dispersion

processes. Dispersion processes, including constituent mixing as a result of backwater and flow reversals, are lumped together into a single diffusion coefficient. Chemical constituent mass balance is calculated within each node and can accommodate dilution, advection, volatilization, partitioning between water and sediment, degradation in water and sediment, burial in sediment, and resuspension from sediment. RIVWQ can simulate up to five chemicals, including metabolites. A sediment transport routine that contains the ability to simulate bed scour is also included. RIVWQ simulates water and chemical mass balance. Water mass balance accounts for conservation of mass from time varying discharges. The model can simulate up to five chemical/metabolites.

Chemical input parameters include water-sediment partition coefficient, degradation rate in water, degradation rate in sediment, mixing velocity (diffusion), and rate of volatilization. Geometric input includes node number, incremental drainage area to node, link volume, length, hydraulic radius, and dispersion coefficient. Sediment properties include initial suspended sediment settling velocity, resuspension velocity, porosity of bed sediment, and bulk density of bed sediment.

4.5.6 SWAT (Soil Water Assessment Tool) Model (Version 2005)

As a watershed model, SWAT simulates pesticide loadings from multiple land use and management areas within a basin and routes the pesticides through aquatic ecosystems. SWAT has been extensively validated across the U.S. for stream flow and sediment yields (Arnold et al, 1999). Some validation of SWAT nutrient simulation has been completed (Santhi et al, 2001; Saleh, 2000; Engel et al., 1993; Alexander, 2001). Many of the pesticide algorithms included in SWAT are drawn from CREAMS (Knisel, 1980), a model developed to simulate the impact of land management on water, sediment, nutrients, and pesticides leaving the edge of a field. The GLEAMS model (Leonard et al, 1987) is a field scale model evolved from the original CREAMS to simulate pesticide ground water loadings, and EPIC (Williams et al, 1984) a field scale model evolved from the original CREAMS to simulate the impact of erosion on crop production. GLEAMS has had considerable validation of pesticides at the field scale (Knisel et al, 1993). SWAT was developed to scale the field non-point source modeling to watershed and river basin scales (Neitsch et al, 2002a). Although SWAT contains GLEAMS algorithms for simulating edge-of-field pesticide loadings, a rigorous validation of pesticides at the basin scale has not been previously attempted. The SWAT model is supported by the U.S. Department of Agriculture (USDA) and builds on 30 years of non-point source modeling within the USDA.

SWAT was developed to simulate watershed processes and the impact of land and water management on water quality. The model operates on a daily time step (infiltration can be simulated sub-hourly and flood routing can be simulated hourly) and allows a basin to be subdivided into grid cells or natural subwatersheds which are further divided into hydrologic response units (HRUs). HRUs are sets of disconnected units in a sub-basin with the same soil and land use. For each HRU, hydrology, weather, sedimentation, soil temperature, plant growth, nutrient cycling, pesticide cycling and agricultural management are simulated. The primary considerations in model development were to stress (1) land management, (2) water quality loadings, (3) flexibility in basin discretization, and (4) continuous time simulation. The model

integrates hydrology, soil erosion, plant growth, and nutrient/pesticide cycling with off-site processes such as channel erosion/deposition, pond and reservoir processes, groundwater flow and climate variability. The model has been validated against measured stream flow and water quality parameters across the U.S. (Arnold et al, 1999).

The equations used to model the movement of pesticide in the land phase of the hydrologic cycle were adopted from GLEAMS. Processes affecting pesticide movement within the HRUs include foliar and soil degradation, foliar wash off, infiltration, leaching, soluble transport by surface runoff and lateral flow, and sorbed transport by sediment. While an unlimited number of pesticides may be applied to individual HRUs, only one pesticide may be simulated at a time through the channel network due to the complexity of the processes simulated. The total pesticide load in the channel is partitioned into dissolved and sediment-attached components. While the dissolved pesticide is transported in runoff, the pesticide attached to sediment is affected by sediment transport and deposition processes. The major in-stream processes simulated by the model for pesticides are settling, burial, resuspension, volatilization, diffusion and transformation.

Land management scenarios that can be simulated include cropping rotations, timing and amounts of fertilizer, manure, pesticides and irrigation applications as well as timing and mixing of tillage operations. At the end of a growing season, the accumulated biomass can be removed as yield or left on the soil surface as residue.

4.5.7 WASP (Water Quality Analysis Simulation Program)

The Water Quality Analysis Simulation Program, WASP7 (Di Toro et al. 1983, Ambrose et al. 1988, Wool et al. 2001) is a general dynamic mass balance framework for modeling contaminant fate and transport in surface waters. Based on the flexible compartment modeling approach, WASP can be applied in one, two, or three dimensions with advective and dispersive transport between discrete physical compartments, or "segments." WASP provides a selection of modules to allow the simulation of conventional water quality variables as well as toxicants.

WASP is designed to permit substitution of different water quality kinetics code into the program structure to form different water quality modules. Two classes of modules are provided with WASP. The toxicant WASP modules combine a kinetic structure initially adapted from EXAMS (Burns et al. 1982) with the WASP transport structure and simple sediment balance algorithms to predict dissolved and sorbed chemical concentrations in the water and underlying sediment bed. The eutrophication WASP module combines a kinetic structure initially adapted from the Potomac Eutrophication Model (Thomann and Fitzpatrick 1982) with the WASP transport structure to predict nutrients, phytoplankton, periphyton, organic matter, and dissolved oxygen dynamics.

WASP Transport Options A body of water is represented in WASP as a series of discrete computational elements or segments. Environmental properties and chemical concentrations may vary spatially among the segments. Each variable is advected and dispersed among water segments, and exchanged with surficial benthic segments by diffusive mixing. Sorbed or

particulate fractions may settle through water column segments and deposit to or erode from surficial benthic segments. Within the bed, dissolved variables may migrate downward or upward through percolation and pore-water diffusion. Sorbed variables may migrate downward or upward through net sedimentation or erosion. Advective water column flows directly control the transport of dissolved and particulate pollutants in many water bodies.

Overview of WASP Sediment Transport. Sediment size fractions, or solids types, are simulated using the TOXI program. Simulations may incorporate total solids as a single variable, or, alternately, represent from one to three solids types or fractions. The character of the three solids types is user-defined. They may represent sand, silt, and clay, or organic solids and inorganic solids. The user defines each solid type by specifying its settling and erosion rates, and its organic content. WASP6 performs a simple mass balance on each solid variable in each compartment based upon specified water column advection and dispersion rates, along with special settling, deposition, erosion, burial, and bed load rates. Mass balance computations are performed in benthic compartments as well as water column compartments. Bulk densities or benthic volumes are adjusted throughout the simulation. The user can vary all solids transport rates in space and time. There are, however, no special process descriptions for solids transport. Erosion rates, for example, are not programmed as a function of sediment shear strength and water column shear stress. Consequently, the TOXI sediment model should be considered descriptive, and must be calibrated to site data.

Water Column Transport. Sediment and particulate chemicals in the water column may settle to lower water segments and deposit to surficial bed segments. Velocities and surface areas in transport fields 3, 4, and 5 describe settling, deposition, and scour rates in WASP6. Particulate transport velocities may vary both in time and in space, and are multiplied by cross-sectional areas to obtain flow rates for solids and the particulate fractions of chemicals. Settling velocities should be set within the range of Stoke's velocities corresponding to the suspended particle size distribution.

WASP Sediment Loading. Sediment loading derives primarily from watershed erosion and bank erosion. These can be measured or estimated by several techniques, and input into each segment as a point source load. For some problems, long-term average sediment loads can be calculated using the Universal Soil Loss Equation (Wischmeier and Smith, 1978). A useful treatment of this process is given by Mills et al. (1985). This technique works poorly for short term or inherently dynamic problems because much of the sediment loading occurs during a few extreme storm or snow melt events. If available, suspended sediment data at local gaging stations can be extrapolated to provide areawide-loading estimates. Alternatively, daily runoff loads can be simulated with a watershed model and read in directly from an appropriately formatted nonpoint source-loading file.

WASP Sediment Bed. The bed sediment plays an important role in the transport and fate of water quality constituents. Sediment-sorbed pollutants may be buried in the bed by deposition and sedimentation, or they may be released to the water column by scour. In WASP6, the movement of sediment in the bed is governed by one of two options. In the first option, bed segment volumes remain constant and sediment concentrations vary in response to deposition and scour. No compaction or erosion of the segment volume is allowed to occur. In the second

option, the bed segment volume is compacted or eroded as sediment is deposited or scoured. Sediment concentration in the bed remains constant. In both options chemical may be transported through the bed by pore water flow and dispersion.

The Constant Bed Volume Option--The first bed option, referred to as the constant volume option, allows the sediment concentration of the bed to change according to the net flux of sediment. Bed segments are located in reference to the rising or falling bed surface. The rate at which the bed rises or falls is represented by a sedimentation velocity input in flow fields 3, 4, and 5 for each sediment size fraction. Sediment in the bed is added through deposition and lost through scour and sedimentation. It should be noted that under the constant volume option WASP6 does not require a balance of sediment fluxes into and out of a bed segment. The user should, therefore, take care that deposition, scour, and sedimentation velocities reflect the intended mass flux of sediment in the bed. The constant volume option also has a provision for a movable upper bed layer. This layer is modeled by specifying a total advective flow rate (flow field one) between upper bed segments. Thus, when a flow rate Q_{ij} is specified from upper bed segment j to upper bed segment i, the sediment, pore water, and chemical in j are transported to i. To maintain a mass balance in segment i, a similar flow rate should be specified out of i. This option allows for the lateral transport of sediment across the upper bed, and can be used to represent bed load transport.

The Variable Bed Volume Option--The second bed volume option, referred to as the variable bed volume option, allows bed volumes to change in response to deposition and scour. Two types of bed layers are assumed: an upper uncompacted layer, and one or more lower compacted layers. When deposition exceeds scour, the upper layer increases in volume as the surface of the bed rises. After a period of time, the added volume of upper bed compresses and becomes part of the lower bed. When scour exceeds deposition, the volume of the upper layer decreases as the surface of the bed drops. When the upper layer erodes completely, the next layer of bed is exposed to scour.

This sedimentation time step is input by the user and will generally be much larger than the simulation time step. As sediment and sorbed chemical settle from the water column, the top bed segment increases in volume, sediment mass, and chemical mass. Sediment concentrations remain constant. The volume of the upper bed continues to increase until the end of the sedimentation time step. At this time, the volume of the upper bed that has been added by net deposition is compressed to the density of the lower bed. Since the porosity of the uncompressed bed is greater than the porosity of the compressed bed, pore water and dissolved chemical are squeezed into the water column. During compression, the lower bed segments rise to include the compressed portion of the upper bed. The volumes and sediment concentrations of these lower bed segments remain constant. A portion of the bottom bed segment is buried out of the network, however, as bed segments rise in response to sedimentation. Thus, chemical mass in the lower bed is added through compression of the upper bed, and lost through sediment burial. After compression, the top bed segment returns to its original predeposition volume. Sediment and chemical concentrations in the upper bed are not changed by compaction. In the lower beds, segment volumes and sediment concentrations are unchanged. Chemical mass from the compacted portion of the bed is added to the lower bed, and chemical mass in the bottom bed segment is buried out of the model network.

As sediment and sorbed chemical erode from the bed, the top bed segment decreases in volume, depth, chemical mass, and sediment mass. Its density remains constant. When the sediment mass in the top bed layer equals zero, then segment renumbering is triggered. All the properties of the remaining bed segments, including chemical concentration, remain unaffected by renumbering. The new top bed segment, for example, has the same depth, volume, and sediment and chemical concentration as the old second bed segment. A new bottom bed segment is created with the same physical properties as the other bed segments. Its chemical concentration, however, is zero. Renumbering and creation of a new bottom segment completes the WASP6 erosion cycle (or time step). As a consequence of the way the variable bed volume option treats sedimentation, certain constraints are imposed on the bed segment properties defined in the input data set. The density (or sediment concentration) of a top bed segment must be less than or equal to the density of the lower bed segments within a vertical stack. Since the compaction routine implicitly handles sedimentation, no sedimentation velocities to lower beds may be specified in the sediment transport fields. Finally, the user must simulate sediment as a state variable in order to use this option. Sediment is a state variable in the toxics program, but not the eutrophication program.

5. ASSESSING BIOACCUMULATION

5.1 BACKGROUND

5.1.1 Role of Bioaccumulation in Pesticide Ecological Risk Assessments

For a number of chemicals (e.g., certain banned pesticides and industrial chemicals including DDT, dieldrin, toxaphene, PCBs), exposure of non-target aquatic and terrestrial organisms via the process of bioaccumulation has been well documented (e.g., USEPA, 2002; Giesy et al., 1994; Gilbertson et al., 1991; Tillit et al, 1992). In aquatic ecosystems, *bioaccumulation* refers to chemical accumulation through all relevant routes of exposure (e.g., respiratory and dermal uptake from water, ingestion of contaminated food and sediment) whereas *bioconcentration* refers to chemical accumulation directly through water exposure only. *Biomagnification*, a term often used in context with bioaccumulation, refers to the chemical accumulation through diet whereby chemical concentrations increase in successive trophic levels. Ecological risks from pesticide bioaccumulation in aquatic and terrestrial ecosystems may result from direct accumulation from abiotic media (water, soil, air) or from accumulation in an organism's diet.

The characteristics of many non-ionic organic compounds which lead to concerns over bioaccumulation in aquatic food webs generally include:

- high hydrophobicity (typically log Kow > 5),
- high environmental persistence,
- high toxicity to non-target organisms, and
- limited biotransformation (metabolism) in organisms to less toxic and/or rapidly eliminated forms.

For such chemicals, available data and bioaccumulation models indicate that exposure through the diet can be important in determining chemical residues in aquatic organisms (e.g., Russell et al., 1999; Fisk et al., 1998; Oliver and Niimi, 1983, 1988; Niimi, 1985; Swackhammer and Hites, 1988; Gobas, 1993; Burkhard, 1998; Arnot and Gobas, 2004). Furthermore, methods that measure bioconcentration alone can substantially underestimate organism exposure to these chemicals because dietary exposure and trophic transfer are not addressed (**Figure 5.1**).

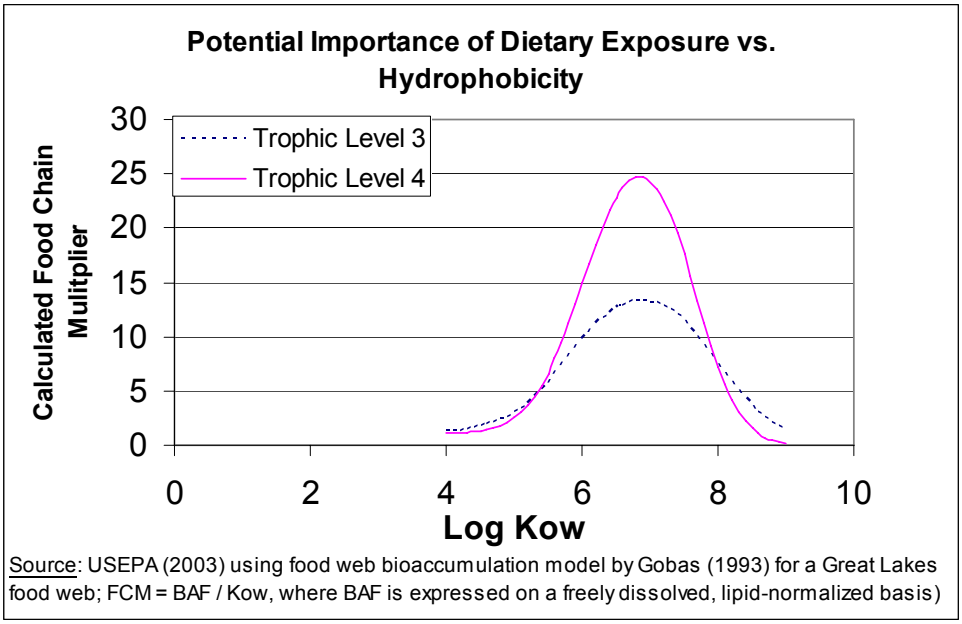


Figure 5.1. Estimated Impact of K_{OW} on Dietary Exposure for Poorly Metabolized, Hydrophobic Organic Chemicals

(Source: USEPA, 2003 using food web bioaccumulation model by Gobas, 1993 for a Great Lakes food web; FCM = BAF / K_{OW}, where BAF is expressed on a freely dissolved, lipid-normalized basis)

For terrestrial food webs, concerns have also been raised over potential biomagnification of chemicals with moderate hydrophobicity (as measured by K_{OW}) but high octanol-air partitioning (as measured by K_{OA}; Kelly et al., 2007). Furthermore, the bioaccumulation potential of some types of organic chemicals may not be readily predicted by classic lipid:water partitioning (e.g., Perfluorooctanesulfonic acid [PFOS], Perfluorooctanoic acid [PFOA]).

In general, the primary goal of the bioaccumulation assessment is to assess the extent to which a pesticide (including its degradates) is likely to accumulate in vulnerable ecological receptors or their diet. Vulnerable ecological receptors are those at greatest risk from bioaccumulation routes of exposure, such as through a combination of high sensitivity and high exposure potential via bioaccumulation.

5.1.2 Current Agency Practice

Historically, OPP has assessed the aquatic bioaccumulation potential of pesticides primarily through the use of a bioconcentration factor (BCF). A BCF represents the ratio of the chemical concentration in an organism (whole body or specific tissue) to the concentration in water[4] and is measured in laboratory studies. Currently, the most commonly submitted data related to a pesticide's bioaccumulation potential include:

- A BCF study for a fish species (typically bluegill sunfish; OPTTS Guideline 850.1730)

[4] BCFs are usually determined to reflect steady state accumulation and can also be derived based on the ratio of the uptake rate constant (K_u) to the elimination rate constant (K_e), assuming a first order, single compartment model.

- A BCF study for oyster (typically the eastern oyster; OPTTS Guideline 850.1710)
- The n-octanol-water partition coefficient (K_{OW}).

The methods listed above do not account for potential exposure to pesticides through the aquatic diet, since they are based on laboratory studies of bioconcentration. As a result, the Agency has been considering alternative methods for addressing pesticide bioaccumulation that incorporate dietary exposure. Similarly, the USEPA Office of Water has recently revised its assessment of bioaccumulation for deriving water quality criteria to protect human health in order to address non-aqueous routes of exposure by aquatic organisms (USEPA 2000, 2003). The Office of Water methodology incorporates a combination of laboratory, field and model-based methods for estimating the bioaccumulation potential of non-ionic organic chemicals.

The science underlying the assessment of pesticide bioaccumulation in terrestrial ecosystems has not evolved to the extent that it has for aquatic ecosystems. As a result, pesticide bioaccumulation in terrestrial-driven food webs has typically not been incorporated into past OPP ecological risk assessments. Assessment of terrestrial organism exposure to pesticide currently relies on estimates of dietary exposure through forage items that have been in direct contact with the applied pesticide (e.g., foliage and small insects residing in the pesticide application area). At this time however, OPP does not have specific data requirements or sufficiently vetted models to estimate pesticide bioaccumulation in terrestrial ecosystems.

5.1.3 Chapter Purpose and Overview

The purpose of this section is to summarize the Agency's current thinking on how the assessment of pesticide bioaccumulation potential can be improved in the context of its ecological risk assessments. **Section 5.2** describes the major issues associated with assessing the bioaccumulative potential of pesticides. **Section 5.3** then describes current approaches for assessing the bioaccumulation potential of a pesticide in aquatic ecosystems. Examples of how these methods have been applied in recent Agency risk assessments are described in **Section 5.4**. An overview of available methods for assessing the bioaccumulative potential of pesticides in terrestrial ecosystems is provided in **Section 5.5.** As described in the Charge to the SAP (**Section 2.4**), the Agency seeks comment on the alternative methods being considered for assessing pesticide bioaccumulation potential in both aquatic and terrestrial ecosystems and on approaches it has used in previous pesticide ecological risk assessments.

5.2 BIOACCUMULATION ASSESSMENT QUESTIONS

Based on the Agency's prior experience in assessing the bioaccumulation potential of chemicals in various regulatory programs (e.g., Office of Water Ambient Water Quality Criteria, Superfund), several common assessment questions have emerged as being important to consider in the problem formulation step of an ecological risk assessment (ERA). These bioaccumulation assessment questions help to define the scope and outcome of the bioaccumulation assessment and the methods that are most suitable for application. A summary of these assessment questions and their relevance to OPP's ERA process is provided in **Table 5.1**

Table 5.1. Risk Assessment Questions Relevant to Evaluating the Bioaccumulation Potential of Pesticides

Assessment Question	Relevance to Pesticide Ecological Risk Assessment
1. Chemical Fate. *Based on the properties of this chemical, is it likely to be transported to aquatic habitats? To terrestrial habitats? Is it likely to persist in these habitats?*	Defines the likelihood of a chemical to reach aquatic and/or terrestrial habitats and persist within them.
2. Ecological Receptors of Concern. *What are the primary ecological receptors of concern?*	Determines the scope of the bioaccumulation assessment.
3. Exposure Routes. *How important are biotic exposure routes (e.g., diet) for bioaccumulation of a pesticide?*	Influences the utility of BCF studies for bioaccumulation assessment
4. Bioavailability. *To what extent are abiotic and biotic factors likely to affect pesticide bioavailability and bioaccumulation?*	Important for interpreting the results from different studies (and models) used for assessing bioaccumulation
5. Metabolism. *To what extent is bioaccumulation affected by pesticide metabolism by biota?*	Helps determine the utility of modeling approaches (which typically assume no in vivo metabolism) for predicting pesticide bioaccumulation.
6. Degradates. *Are any pesticide degradation products likely to contribute to bioaccumulation and toxicity?*	Defines the chemical stressors of concern.
7. Steady State. *How long does it take for pesticide concentrations to reach steady-state accumulation in organisms*?	Helps determine the applicability of short-term bioaccumulation and toxicity studies for assessing long-term bioaccumulation and toxicity potential.
8. Multiple Lines of Evidence. *To what extent are bioaccumulation predictions by various methods (lab measurements, field measurements, model predictions) in agreement/disagreement? Can differences in bioaccumulation predictions be adequately explained?*	Important for understanding the applicability and uncertainty associated with different bioaccumulation assessment methods.
9. Critical Exposure Period. *What exposure period(s) is (are) considered most appropriate for estimating risk to sensitive ecological receptors? (e.g., weeks, months, year?)*	For dynamic bioaccumulation modeling, helps to define the time period over which to average chemical concentrations in tissue for comparing against toxicity benchmarks.

If a pesticide has the potential to bioaccumulate in aquatic or terrestrial ecosystems, it should be considered in the conceptual model for an ecological risk assessment (e.g., **Figure 2.2**). As stated previously, OPP has historically assessed bioaccumulation in aquatic ecosystems only. This has been done primarily through the use of a BCF which is derived from laboratory tests and considers accumulation (in fish) from direct water exposure only.

5.3 METHODS FOR ASSESSING AQUATIC BIOACCUMULATION

OPP is aware of many different types of methods that are available for assessing the bioaccumulation of pesticides in aquatic ecosystems. Generally, aquatic bioaccumulation methods can be categorized into four broadly defined groups: laboratory-based experimental studies, field-based experimental studies, field-based monitoring studies and model-based bioaccumulation assessments. The relative strengths and limitations of each type of method is summarized in **Table 5.2** and discussed in more detail in the ensuing sections.

Table 5.2. Strengths and Limitations of Various Methods for Assessing Chemical Bioaccumulation in Aquatic Ecosystems

Bioaccumulation Assessment Approach	Strengths	Limitations
Laboratory-Based Experimental Studies	• Accounts for chemical metabolism by the accumulating organism • Steady-state bioconcentration can be determined directly • Test methods are standardized	• For bioconcentration tests, chemical uptake from contaminated diet or sediment is not addressed • For bioconcentration tests, chemical metabolism by food chain organisms is not incorporated • Bioavailability conditions may differ substantially in the laboratory vs. field
Field-Based Experimental Studies	• Accounts for chemical uptake from food, sediment, and water (bioaccumulation) • Accounts for chemical metabolism by all organisms in the food chain • Greater environmental realism compared to laboratory exposures	• Bioaccumulation estimates reflect attributes of the experimental design (food chain, bioavailability, exposure conditions, etc) which may differ from real world exposures • Exposure duration might not account for pesticide 'carry over' from multi-season and multi-year applications • Relative importance of water vs. dietary exposure is difficult to distinguish
Field-Based Monitoring Studies	• Accounts for chemical uptake from food, sediment, and water (bioaccumulation) • Accounts for chemical metabolism by all organisms in the food chain • Most environmental realism compared to laboratory and microcosm exposures	• Requires pesticide release to the environment (i.e., unlikely to have data for new pesticides) • Adequately characterizing chemical exposure can be difficult, expensive • Relative importance of water vs. dietary exposure is difficult to distinguish
Model-Based Bioaccumulation Assessments	• Readily applied and adapted to different exposure scenarios • Long-term (multi-year) pesticide 'carry over' can be assessed • Relative importance of water dietary exposure pathways can be distinguished	• Chemical metabolism by organisms is usually difficult to incorporate • Most models are limited to nonionic organic chemicals • Model predictions depend on accuracy of input data and modeling assumptions

5.3.1 Laboratory-Based Experimental Studies

Test guidelines developed by OPPTS are available for several types of laboratory-based experimental studies from which bioconcentration (uptake from water only) or bioaccumulation (uptake from water, food and/or sediment) can be measured. In addition, other Agency protocols

for laboratory-based experimental studies are available from which bioconcentration or bioaccumulation can be assessed. A list of these laboratory-based studies is shown in **Table 5.3**.

Table 5.3. Laboratory-Based Experimental Methods for Assessing Bioconcentration or Bioaccumulation

Test Guideline	Title [(1)]	Test Description/Scope
OPPTS 850.1710	**Oyster BCF**	• Used to determine bioconcentration by bivalve mollusks (preferably the Eastern Oyster, *Crassostrea virginica*). • Uptake period lasts from 4 to 28 days (depending on estimated time to steady state); depuration period lasts 14 days. • Results include the BCF, uptake rate constant, and depuration rate constant (water exposure only)
OPPTS 850.1730	**Fish BCF**	• Used to determine chemical bioconcentration by freshwater and estuarine fish. A variety of test species are recommended, including warm and coldwater fish. • Uptake period lasts from 28 days to 60 days (depending on estimated time to steady state); depuration period lasts half the uptake phase duration. • Results include the BCF, uptake rate constant, and depuration rate constant (water exposure only)
OPPTS 850.1850	Aquatic Food Chain Transfer	• Specific test design is study specific, but can include one or more species from a variety of taxonomic groups (e.g., fish, crustaceans, insect larvae, mollusks). • Results are study-specific, but can include assessment of a trophic transfer factor (i.e., chemical concentration in an organism divided by concentration in their diet) for estimating dietary uptake.
OPPTS 850.1900 OPPTS 850.1925	Generic Freshwater Microcosm Test Site-specific Aquatic Microcosm Test	• Organisms occupying one or more trophic levels and environmental compartments (e.g., algae, microinvertebrates, macroinvertebrates) are exposed to the test chemical in laboratory vessels. • Generic tests reflect artificially constructed assemblages whereas site-specific tests reflect naturally occurring assemblages at a specific site. • Results consist of chemical fate and effects on aquatic organisms, including bioaccumulation in food chain organisms.

Test Guideline	Title [1]	Test Description/Scope
ORD/OW Test Guideline	Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates (Second Edition)	• Bioaccumulation test involves the freshwater oligochaete, *Lumbriculus variegatus,* exposed for 28 days artificial or natural sediments. • Results include the BAF, uptake and elimination rate constants (if depuration is measured).

[1] Studies in bold text are commonly conducted for pesticide registration, other studies are relatively rare.

Laboratory-based methods are generally conducted under controlled conditions which tend to minimize the influence of confounding variables on experimental results. Furthermore, chemical exposure and bioaccumulation can be well controlled and characterized. Because chemical concentrations are actually measured, any chemical metabolism by test organisms is addressed.

Laboratory-based methods also have some important limitations. First, aquatic BCF tests do not incorporate chemical exposure via the diet. This can lead to a substantial underestimation of bioaccumulation potential, particularly for poorly-metabolized chemicals with Kow > 5.0 (Fisk et al., 1998; Arnot and Gobas, 2004, USEPA, 2003). Second, water quality factors affecting chemical bioavailability often differ substantially between the laboratory and the natural environment. Lastly, while aquatic microcosm studies may improve the environmental realism compared to bioconcentration studies, they are typically conducted for relatively short exposure durations (e.g., several weeks to months) and may not reflect any pesticide "carry over" that might occur between growing seasons involving highly persistent pesticides (e.g., long-term build up in sediments).

5.3.2 Field-Based Experimental Studies

Field-based experimental studies for assessing bioaccumulation include medium and large-scale mesocosm studies, the latter of which were prominent in the late 1980s and early 1990s but are rarely conducted for current pesticide registration submissions given the study expense and extent of variability associated with the results. Currently, OPPTS has one test guideline available for field studies (OPPTS 850-1950: *Field Testing for Aquatic Organisms*). In theory, such experimental field studies combine some of the strengths of laboratory studies (replication, multiple treatment levels, controled chemical exposures) with the environmental realism of natural (or near-natural) ecosystems. Although designed with the primary goal of assessing the effects of pesticides on aquatic organisms under field conditions, these experimental field studies do not typically involve measurement of pesticide residues in biota but do include measurements in abiotic media. While estimates of bioaccumulation could be obtained from these studies, study procedures would have to be modified to include residues in biota. Because entire food webs are exposed, chemical uptake from water, diet and sediments (in addition to chemical metabolism by biota) could be incorporated into bioaccumulation estimates.

As discussed with laboratory-based studies, field-based studies of bioaccumulation typically do not incorporate the potential for pesticide 'carry over' from year to year.

Experimental field studies are also typically resource intensive and costly to conduct compared to laboratory studies and thus, are usually reserved when uncertainty caused by lab-to-field extrapolations is important to address in the risk assessment. They also may not represent the most vulnerable environments to pesticide exposure. Lastly, while chemical uptake from multiple uptake routes is addressed, distinguishing the relative importance of these exposure pathways is typically difficult to determine.

5.3.3 Field-Based Monitoring Studies

Field-based monitoring studies are distinguished from field-based experimental studies by the degree to which chemical exposures are controlled and the use of naturally occurring aquatic ecosystems. Such studies typically involve uncontrolled studies of chemical bioaccumulation in aquatic biota in one or more aquatic ecosystems. Chemical exposure is not manipulated *per se*, rather site(s) are selected for targeted monitoring of chemical concentrations in biota and abiotic media. Among the types of bioaccumulation studies summarized in **Table 5.2**, field-based monitoring studies contain the greatest degree of environmental realism. However, they often lack the depth of information on environmental exposure compared to laboratory or field-based experimental studies, which can be a major source of uncertainty when attempting to derive bioaccumulation factors (USEPA, 2003; Burkhard, 2003). Furthermore, results from field monitoring studies reflect site-specific factors that influence chemical bioaccumulation, which can be difficult to extrapolate to other ecosystems without a clear understanding of the exposure conditions in the study. As discussed with field-based experimental studies, field-based monitoring studies are far less common compared to laboratory-based studies.

5.3.4 Model-based Bioaccumulation Assessments

Model-based bioaccumulation assessments refer to the use of mathematic models for describing the processes and relationships underlying chemical bioaccumulation. Many such models exist, some of which are shown in **Table 5.4**

Table 5.4. Selected Models Used to Estimate Chemical Bioaccumulation by Aquatic Organisms

Model	Description	Example Application
Arnot and Gobas (2004); Gobas (1993)	Fugacity-based bioaccumulation model for nonionic organic chemicals.	USEPA Water Quality Criteria (USEPA 1995, 2000, 2003) PCBs and pesticides in the Great Lakes, Hudson River, Bayou D'Indie, LA
BASS	Physiologically-based bioaccumulation model for fish and other aquatic organisms; incorporates fish bioenergetics, chemical toxicity, predator/prey interactions	Lake Hartwell, SC, (USEPA 1994; Barber 2006)

Thomann et al 1992	Equilibrium-partitioning based model of chemical bioaccumulation	PCBs in Lake Ontario
AQUATOX	Chemical fate and effects model	PCBs in Lake Ontario (Park et al 2008)
Level I, II, and III Fugacity models (Mackay, 1991)	Used to predict general behavior of chemicals in the environment, including bioaccumulation	Risk screening for new industrial chemicals (e.g., USEPA's Pre-Manufacture Notice program)

The use of mathematical models for assessing bioaccumulation offers a number of distinct advantages over empirically-based methods. First, such models are readily applied with relatively modest resource requirements. The impact of various model assumptions can be explicitly evaluated in the context of the risk assessment outcome. Furthermore, such models can be run for long time periods (in a dynamic mode) and thus, can evaluate the temporal aspects of pesticide bioaccumulation (i.e., year-to-year carry over). Lastly, the source and relative importance of different pesticide exposure routes can be explicitly evaluated with the use of bioaccumulation models (e.g., uptake from water vs. diet).

Despite the strengths of aquatic bioaccumulation models, they contain a number of limitations which should be carefully understood and evaluated when assessing pesticide bioaccumulation. Typically, these models are parameterized assuming that chemical metabolism by aquatic biota is zero or negligible, due to a lack of reliable information on metabolism rates *in vivo*. However, differences between model and experimental-based estimates of bioaccumulation can vary dramatically, in part due to chemical metabolism and/or bioavailability differences in aquatic biota. Further, such models require numerous assumptions regarding environmental and organism conditions, which may introduce uncertainty in the bioaccumulation assessment.

5.4 EXAMPLE BIOACCUMULATION ASSESSMENTS

This section contains a summary of the Agency's assessment of bioaccumulation potential of three example pesticides. Consistent with the previous section on environmental persistence, these example pesticides are referred to as: Pesticide 1, 3 and 4.

These three pesticides were selected because they reflect the Agency's use of 'refined' methods for assessing aquatic bioaccumulation potential (i.e., information and methods that extend beyond the use of an aquatic BCF). Within each of the example pesticide summaries below, the primary goal is to illustrate:

1. The type of data that was available to OPP for assessing pesticide bioaccumulation potential,
2. How OPP refined its methods to address bioaccumulation-related issues, and
3. How bioaccumulation potential was ultimately incorporated into the ecological risk assessment

In providing these examples to the SAP, OPP recognizes that the types of methods used to assess bioaccumulation potential differ somewhat across chemicals. Since these assessments were conducted over the course of several years, these differences not only reflect nuances in the quantity and quality of available bioaccumulation data, but also some evolution in OPP's understanding of bioaccumulation assessment issues and the methods available for addressing these issues.

Consistent with the charge to the SAP, the Agency seeks feedback on the extent to which the refinements used to assess bioaccumulation potential (*i.e.*, methods beyond BCF) reflect the state of the science and whether conclusions regarding bioaccumulation potential are supported by the methods and data discussed.

5.4.1 Bioaccumulation Assessment for Pesticide 1

As described in **Section 3.2.1**, Pesticide 1 is used as an insecticide on a variety of fruits, vegetables, cereals, and cotton (**Table 3.1**). The parent compound is composed of two isomers with an isomeric ratio of 30% isomer 1 (P1) and 70% isomer 2 (P2). The isomers exhibit different environmental fate profiles; isomer 1 is less persistent than isomer 2 in soil and aquatic environments. Both isomers exhibit vapor pressures and Henry's Constants comparable to moderately volatile pesticides. Additionally, the isomers degrade to form a toxic and persistent degradation product in soil and aquatic environments (i.e., degrade D1).

A review of K_{OW} values for Pesticide 1 indicates that its two isomers and primary degradate are moderately hydrophobic (log K_{OW} of 3.55 to 4.78; **Table 5.5**). Measured values of K_{OC} indicate a propensity to partition to organic carbon (mean K_{OC} values ranging from 10,600 to 13,500 L/kg-OC). These properties, combined with the persistence of the parent and degradate in the aquatic environment, (**Section 3.2.1**), suggest that Pesticide 1 and its degradate, D1, will readily partition to suspended and bed sediments.

Table 5.5. Summary of Bioaccumulation-Related Fate Parameters for Pesticide 1

Parameter	Value	Study Notes and Interpretation (Source)
Log K_{OW}	3.55 – 4.78 **(*1)**	Suggestive of moderate bioaccumulation potential, dietary exposure could be significant, although it is not expected to be a dominant exposure route.
K_{OC}	10,600 – 13,500 L/kg-OC (parent isomers)	Indicates chemical partitioning to suspended and bed sediments likely to be important

(*1) Range of measured Kow values reported for Pesticide 1 isomers (P1, P2) and its primary degradate of concern (degradate D1).

5.4.1.1 Summary of Bioaccumulation Data for Example Pesticide 1

Bioconcentration in Fish. Several studies of varying quality were available in the peer reviewed literature on the bioconcentration of Pesticide 1 by fish (**Table 5.6**). Specifically, bioconcentration data were identified and reviewed for seven species of fish, including sheepshead minnow (*Cyprinodon variegatus)*, zebra fish (*Brachydanio rerio)*, yellow tetra

(Hyphessobrycon bifasciatus), striped mullet *(Mugil cephalus),* pinfish (*Lagodon rhomboids),* long whiskers catfish (*Mystus gulio),* and spot *(Leiostomus xanthurus*). Considering the unscreened data at "face value," the reported BCF values for fish ranged from approximately 20 to 11,600 (L/kg wet wt.). With the exception of one species (yellow tetra), BCFs were less than 3,000 for the remaining six fish species. Once these data were screened for quality, however, only two studies remained that were considered to provide the most reliable estimates of Pesticide 1 bioconcentration in fish. The mean BCF values derived from these two studies ranged from 1,146 L/kg wet wt. for the sheepshead minnow (Study 1) and 2,755 L/kg wet wt. for striped mullet (Study 2). These studies met screening criteria of:

1. Documenting the stability of the test compound in water via use of measured concentrations in water and flow-through conditions.
2. Documenting (or likely providing sufficient time to achieve) steady state accumulation in test organisms for BCFs calculated using the ratio method.
3. Quantifying concentrations of at least the two separate parent isomers in tissue and water.
4. Exposing organisms to test material below levels expected to cause adverse effects on test organisms
5. Exposing organisms only to Pesticide 1 (and not other chemical or biological stressors).

Table 5.6. Summary of Bioconcentration Studies for Pesticide 1 in Fish

Chemical (formulation/ % ai) (*1)	Species	Study Design (*2)	Exposure Duration (Exposure Conc. µg/L)	BCF Method (*3)	Avg. BCF/ (BAF)	Range [SD] BCF/ (BAF)	N	Reference
Studies Meeting Quality Screening Criteria								
64% P1 / 36% P2 (TG/ 98%)	Sheepshead minnow *(Cyprinodon variegatus)*	FT / M / WB	28 d (5 levels, ~0.05-5.5)	Ratio, P1+ P2	**1,146** (*4)	318-2963	9	Study 1
70% P1 / 30% P2 (TG, ai NR)	Striped mullet *(Mugil cephalus)*	FT / M / WB	28-d (1 level, 0.035 ± 0.006)	Ratio, P1+ P2+ D1	**2,755**	NR	5	Study 2
Studies Not Meeting Quality Screening Criteria								
2:1 P1 / P2 (TG/97%)	Zebra Fish *(Brachydanio rerio)*	SR / U / WB	21 d (1 level, 0.3)	Kinetic, P1+ P2+ D1	2,650	[441]	3	Study 3
2:1 P1 / P2 (TG/97%)	Yellow Tetra *(Hyphessobrycon bifasciatus)*	SR / U / WB	21 d (1 level, 0.3)	Kinetic Ratio P1+P2+ D1	11,583 (*5) 5,670	[2361] ---	3 3	Study 4
70% P1 / 30% P2 (TG, ai NR)	Striped Mullet *(Mugil cephalus)*	FT / M / WB	96-h (3 levels, 0.36-0.49)	Ratio, P1+ P2+ D1	1,115	1000-1344	3	Study 2
	Spot *(Leiostomus xanthurus)*	FT / M / WB	96-h (3 levels, 0.05-0.31)	Ratio, P1+ P2+ D1	780	620-895	3	

Chemical (formulation/ % ai) (*1)	Species	Study Design (*2)	Exposure Duration (Exposure Conc. µg/L)	BCF Method (*3)	Avg. BCF/ (BAF)	Range [SD] BCF/ (BAF)	N	Reference
	Pinfish (Lagodon rhomboids)	FT / M / WB	96-h (2 levels, 0.15-0.26)	Ratio, P1+ P2+ D1	1,173	1046-1299	2	
% P1 & P2 NR	Striped mullet *(Mugil cephalus)*	FT / M / Muscle	10-d (3 levels, 0.13- 1.25)	Ratio	18.4	18.1-18.6	3	Study 5
	Catfish *(Mystus gulio)*	FT / M / Muscle	10-d (3 levels, 0.2- 1.95)	Ratio	17.1	16.6-17.5	3	

(*1) P1 = parent isomer 1; P2 = parent isomer 2; D1 = degradate 1; TG = technical grade; ai = active ingredient; NR = not reported.
(*2) FT = flow through; R = static renewal; S = static; M = measured exposure conc.; U = unmeasured exposure conc. WB = whole body.
(*3) Ratio method = ratio of tissue to water concentration; Kinetic method = ratio of uptake to elimination rate; All BCFs are expressed on a wet weight basis.
(*4) Average BCFs reported here are calculated from 9 acceptable tests reported by the authors and from treatments with no statistically significant effects on survival or growth relative to controls.
(*5) Kinetic-based BCF is questionable because elimination half-life derived from K2 is not consistent with observed data. A 21-d BCF (ratio method) of 5670 is calculated based on parent and degradate (P1, P2, D1).

A summary of these studies is provided below.

Study 1: Sheepshead Minnow. Study 1 involved an interlaboratory comparison of the early life stage toxicity of Pesticide 1 (technical grade, 98% ai) to the sheepshead minnow. Although this study was not designed to assess bioconcentration *per se*, Pesticide 1 residues were measured in fish at test termination (day 28). Of the 14 Pesticide 1 tests conducted by 7 laboratories, 9 were considered acceptable by the authors based on control survival, variability in exposure concentrations and adherence to ASTM protocols. Continuous flow-through Pesticide 1 exposures began with embryos and continued through 28 days. Concentrations of Pesticide 1 (isomers 1 and 2) were measured in exposure chambers and in fish from 5 treatments and two controls (negative and unspecified solvent control). In accordance with ASTM and OPP guidelines on bioconcentration studies, BCFs reported in **Table 5.6** were calculated only from treatments without significant effects on survival and growth relative to controls (*i.e.*, organism stress can alter accumulation kinetics and BCFs). Using data from treatments without adverse effects, the mean BCF across all 9 acceptable tests was 1,146 (L/kg w.w.) and ranged by about a factor of 10 across laboratories (approximately 300 to 3,000).

Several limitations of this study should be considered when interpreting these bioconcentration results. First, the existence of steady-state conditions could not be absolutely confirmed since only one measurement of Pesticide 1 residues was made at test termination. However, if biological half lives in larval sheepshead minnow are similar to those reported for other adult fish (on the order of a few days), steady-state conditions would have been reached in the study. Second, the BCFs reported are based on parent compound only (Pesticide 1 isomers)

and do not include the primary degradate (D1). To the extent that the D1 degradate was formed by larval fish, the BCFs reported would underestimate the total residue accumulation of Pesticide 1 and its primary degradate. Lastly, the fish used in the study were by design, actively growing throughout the exposure period. Thus, the phenomenon known as 'growth dilution' could have occurred thereby reducing the magnitude of BCF values compared to non-actively growing fish. Aside from these limitations, this study has a number of strengths including the use of flow-through conditions, rigorous QA on the analytical chemistry, and measured concentrations in water with acceptable temporal variability.

Study 2: Striped Mullet. Bioconcentration and depuration of Pesticide 1 (70:30 P1:P2) were studied using a 28-d flow through exposure with juvenile striped mullet (Study 2 in **Table 5.6**). Mullet were exposed in duplicate aquaria (n = 100/aquarium) to nominal concentrations of 0.008 and 0.08 µg/L Pesticide 1. Residues (n=5) were collected over time for analysis in addition to water concentrations. Recovery of spiked residues was 85% (results not corrected). Pesticide 1 (P1, P2, D1) was not detected in water or tissue at the 0.008 µg/L treatment (DL 0.01 ppb in water, 0.01 ppm in tissue). In the 0.08 µg/L treatment (mean measured concentration of 0.035 µg/L), accumulation was rapid in the first 48 hours, reaching 0.056 ppm total Pesticide 1 (P1, P2, D1) where it remained at or below this level until day 22. On day 22 and 28, tissue concentrations of total Pesticide 1 increased from 0.065 to 0.097 ppm. The vast majority of Pesticide 1 residues in tissue was present as the metabolite, D1. The whole body BCF calculated on day 28 was 2,755, which might not reflect steady-state conditions. Depuration of Pesticide 1 residues was rapid, with no Pesticide 1 measured in mullet tissues after 2 days.

The only major limitation identified with the 28-d bioconcentration study with striped mullet is uncertainty in whether the 28-d BCF reflects steady-state conditions. Pesticide 1 concentrations in edible tissues increased throughout the exposure period while those in whole body increased initially, leveled off, then increased again by approximately 50% on day 22 and 28. Increases in tissue concentrations could reflect a reduction in growth rate of juvenile fish, however, no information was presented regarding growth of organisms. This bioconcentration study has several strengths, including measurement of chemical concentrations in tissue and water, use of flow-through exposures at sublethal concentrations, and measurement of both Pesticide 1 isomers and its principle degradate (D1).

Bioconcentration in Invertebrates. Bioconcentration studies with aquatic invertebrates were available for five species of invertebrates and included the blue mussel (*Mytilus edulis),* grass shrimp, (*Palaemonetes pugio),* oyster, (*Crassostrea madrasensis)*, clam, (*Katelysia opima)* and red swamp crayfish, (*Procambarus clarkii).* Based on the studies presented in **Table 5.7**, the bioconcentration of total Pesticide 1 residues by aquatic invertebrates appears to be lower than those reported for fish, ranging from about 1.9 to 600 (L/kg w.w.). However, none of the bioconcentration studies with invertebrates met the quality screening criteria described above and thus, results should be interpreted with caution.

Table 5.7. Summary of Bioconcentration Studies for Pesticide 1 in Invertebrates

Chemical (formulation/ % ai) (*1)	Species	Study Design (*2)	Exposure Duration (Exposure Conc. µg/L)	BCF Method (*3)	Avg. BCF/ (BAF)	Range [SD] BCF/ (BAF)	N	Reference
70% P1 / 30% P2 (TG, ai NR)	Grass shrimp *(pugio)*	FT / M / WB	96-h (5 levels, 0.16-1.75)	Ratio, P1+ P2+ D1	175	81-245	5	Study 2
Mixture of 7 pesticides, % P1 & P2 NR	Blue Mussel *(Mytilus edulis)*	S / M / WB	7 d (1 level, 2.1➔0.14)	Ratio	600	NR	NR	Study 6
% P1 & P2 NR	Blue Mussel *(Mytilus edulis)*	FT / U / WB	122-d (3 levels, 100-1000)	Ratio, P1+ P2	12	8-17	3	Study 7
% P1 & P2 NR	Oyster *(Crassostrea madrasensis)*	FT / M / Foot	10-d (3 levels, 0.14- 1.41)	Ratio	60	42-70	3	Study 5
	Clam *(Katelysia opima)*	FT / M / Foot	10-d (3 levels, 0.14- 1.41)	Ratio	46	30-61	3	
Pesticide 1 (NR)	Crayfish *(Procambarus clarkii)*	NR / U / WB	56-d (100)	Ratio, , P1+ P2+ D1		≤ 1.9(*4)	---	Study 8

(*1) P1 = parent isomer 1; P2 = parent isomer 2; D1 = degradate 1; TG = technical grade; ai = active ingredient; NR = not reported.
(*2) FT = flow through; R = static renewal; S = static; M = measured exposure conc.; U = unmeasured exposure conc. WB = whole body.
(*3) Ratio method = ratio of tissue to water concentration; Kinetic method = ratio of uptake to elimination rate; SS = steady state. All BCFs are expressed on a wet weight basis.
(*4) BCF value from this study is highly suspect due to irregular accumulation patterns and study design problems.

Bioaccumulation Studies. Bioaccumulation studies (i.e., those that included exposure to multiple uptake routes) were available for three invertebrates, including the mussel (*M. galloprovincialis)*, Eastern oyster, (*C. virginica)*, and the water flea, (*Daphnia magna*;**Table 5.8**). Bioaccumulation factors calculated for the eastern oyster and *D. magna* based on total residues of Pesticide 1 (isomers 1 & 2 and degradate D1) are approximately 600 L/kg. Based on a short-term (24 h) exposure, uptake of Pesticide 1 from food (contaminated algae) by *D. magna* was considered negligible compared to uptake from the water column. These studies, however, represent short-term exposure periods (24 – 96 h) and may not reflect long-term bioaccumulation potential of Pesticide 1.

Table 5.8. Summary of Aquatic Bioaccumulation Studies with Pesticide 1

Species	Study Location/ Design	Analytes	Water Conc. (µg/L)	Sediment Conc. (µg/kg)	Tissue Conc. (ug/kg w.w)	BAF [BSAF]	N	Reference
Mussel *(Mytilus galloprovincialis)*	Black Sea (4 coastal stations)	D1	<0.01	< 0.01-25	<0.01-0.08	[0.059]	4	Study 9
Oyster *(Crassostrea virginica)*	Mesocosm (96-h, 70:30 α:β)	P1 + P2 + D1	3 levels; 0.18➔0.06 0.52➔0.12 3.0➔0.29	ND (< 32)	35-606	637 ± 189	3	Study 10
Green alga *(Pseudokirch-neriella subcapitatum)*	Microcosm (24-h TG 2:1 α:β)	P1 + P2 + D1	100	NA	53.6 (*1)	536(*1)	---	Study 11
Water flea *(Daphnia magna)*	Microcosm (24-h TG 2:1 α:β)	P1 + P2 + D1	100 (*2) 100 (*2)+food food only	NA	65.6(*1) 62.4(*1) 1.68(*1)	656(*1) 624(*1) 16.8(*1)	---	

(*1) Tissue concentrations and BCF converted from dry wt to wet wt. assuming 80% water fraction in tissue.
(*2) Water concentrations based on nominal values.

5.4.1.2 Bioaccumulation-Related Assessment Issues for Pesticide 1

The bioaccumulation assessment approach for Pesticide 1 was informed by the following considerations and findings.

Environmental Fate. The use profile for Pesticide 1 (variety of fruits, vegetables, cereals, and cotton) suggests that pesticide drift, runoff and erosion into aquatic ecosystems is a potential concern. In aquatic ecosystems, the environmental fate profile (summarized in **Section 3.2.1** suggests that Pesticide 1 (isomers P1, P2, and degradate D1) will likely partition to organic matter such as suspended and bed sediments (Koc = 10,600 – 13,500L/kg-OC) and will and persist for relatively long periods of time (biotic metabolism half lives ≥ 114 days

Exposure Routes. At log K_{OW} values of 3.55 to 4.78, available aquatic food web bioaccumulation models suggest that dietary exposure of aquatic organisms to poorly metabolized organic chemicals would not likely be a dominant concern, although at the high end of this K_{OW} range, dietary exposure can begin to become significant (e.g., (**Figure 5.1;** Arnot and Gobas, 2004, Fisk et al., 1998).

Ecological Receptors of Concern. The primary focus of the bioaccumulation assessment of Pesticide 1 was the potential impacts on piscivorous wildlife through acute and chronic dietary exposure, due to their high exposure potential at the top of the aquatic food web. Relevant toxicity data for Pesticide 1 (mixture of P1 and P2 isomers) for surrogate species (lab rat for mammals, bobwhite quail and mallard for birds) are shown in **Table 5.9.**

Table 5.9. Toxicity of Pesticide 1 to Mammals and Birds

Species	Endpoint	Value(*1)
Laboratory rat	LD_{50}	**10 mg/kg-bw**
(*Rattus norvegicus)*	NOEC	**15 mg/kg-diet**
Northern bobwhite quail	LC_{50}	**805 mg/kg-diet**
(Colinus virginianus)	NOEC	60 mg/kg-diet
Mallard duck	LD_{50}	**28 mg/kg-bw**
(Anas platyrhynchos)	LC_{50}	1053 mg/kg-diet
	NOEC	**30 mg/kg-diet**

(*1) Bold values indicate toxicity endpoints used for risk estimation.

***In Vivo* Metabolism.** Available evidence from the bioconcentration, toxicity and monitoring studies for Pesticide 1 indicates that the metabolite, D1, is the dominant metabolite concern and is of similar acute toxicity to birds and aquatic organisms. Therefore, although *in vivo* metabolism of Pesticide 1 is known to occur to a significant extent, both the parent isomers (P1 & P2) and primary degradate (D1) are of toxicological concern.

Time to Reach Steady State. Some studies indicate the depuration of Pesticide 1 and its metabolite (D1) by fish appears to be relatively rapid, with half lives ranging from 2-6 days for zebra fish, yellow tetra, and striped mullet (Study 3, Study 4, and Study 2, respectively in **Table 5.6**). It is noted that in two studies, calculated half lives in fish (approx. 2 days) appear inconsistent with observed accumulation in tissue (i.e., steady-state accumulation was not observed after 21 and 28 days in yellow tetra and striped mullet, respectively when in theory, it should have been reached by 7 days based on depuration rates for these two species; Study 3 and Study 2). This inconsistency suggests that Pesticide 1 accumulation by fish might be more complex than the assumption of simple first order kinetics, at least in some cases.

Information on the depuration of Pesticide 1 by invertebrates was only available for the blue mussel, *M. edulis*. In one study, a depuration half life of 33.8 hours (approximately 1.5 days) was reported for blue mussel (Study 6; **Table 5.7**), while a second long-term study suggested a depuration half-life on the order of two weeks for this species (Study 7). As noted previously, these two studies did not meet the study quality criteria and thus, depuration half lives are considered uncertain.

5.4.1.3 Bioaccumulation Assessment Methods for Pesticide 1

The aquatic bioaccumulation assessment for Pesticide 1 focused on the use of an aquatic food web bioaccumulation model for estimating exposure and subsequent risk to piscivorous wildlife. This model, (KABAM or **K**ow-based **A**quatic **B**io**A**ccumulation **M**odel), is intended for use as a screening-level model for estimating bioaccumulation potential of hydrophobic organic pesticides in freshwater aquatic food webs and subsequent risks to mammals and birds via consumption of contaminated aquatic prey. The model is represented in spreadsheet form and is based on the aquatic food web bioaccumulation model published by Arnot and Gobas (2004). This model and its precursor, (Gobas 1993) have been used extensively by USEPA for

assessing bioaccumulation in the development of water quality criteria for nonionic organic chemicals (USEPA, 1995; 2000, 2003). The primary bioaccumulation assessment questions of interest included:

- *To what extent do food web models predict bioaccumulation of Pesticide 1 and its primary degradate by aquatic organisms and how do these compare to measured data?*
- *What is the relative contribution of diet and water uptake routes to predicted concentrations in biota?*
- *What are the potential risks to piscivorous wildlife from exposure to concentrations of Pesticide 1 in aquatic biota?*

For comparative purposes, the bioaccumulation assessment approach also considered empirical data on Pesticide 1 (e.g., BCF values in **Table 5.6** that met data quality screening objectives) for estimating concentrations of Pesticide 1 in biota. Comparison of model and data-derived estimates of bioaccumulation is considered important for evaluating model assumptions and predictability.

Model Inputs and Assumptions.

Detailed information on input parameters and risk calculations are presented in **Appendix D**. Only a brief summary of input parameters and assumptions is provided below.

- **Food Web Structure:** A simple aquatic food web was assumed consisting of phytoplankton, zooplankton, filter feeding invertebrates, benthic feeding invertebrates, small and medium-size forage fish and piscivorous fish. Feeding preferences are defined in **Table 1 of Appendix D** and basically consist of higher trophic level organisms consuming various fractions of organisms at lower trophic levels based on typical feeding ecology for organism groups.
- **Exposure Concentrations.** Pesticide 1 concentrations in water were assumed to range from 0.1-5 ppb (total chemical) based on 60-d average concentrations predicted from PRZM/EXAMS for different crop exposure scenarios (**Table 4 of Appendix D**). Freely dissolved concentrations in pore water were assumed equivalent to overlying water based on PRZM/EXAMS modeling of pore water concentrations.
- **Chemical Properties.** The log K_{OW} of Pesticide 1 was assumed to range between 3.55 and 4.78 based on reported data for P1 and P2 isomers of Pesticide 1 (**Table 3 of Appendix D**). A mean K_{OC} of 13600 was used (range: 10000-16000) based on the range from individual studies (**Table 2 of Appendix D**). Chemical metabolic rate by biota was set to zero. Although Pesticide 1 can be metabolized to the degradate 1 (D1) by biota, available data indicates this degradate is of comparable acute toxicity as the parent isomers (P1 and P2). Thus, the assumption of chemical metabolic rate of zero is considered reasonable.
- **Organism Characteristics.** Lipid fraction of organisms ranged from a mean of 0.5% for phytoplankton to a mean of 6% in piscivorous fish (**Table 2, Appendix D**). All organism physiological parameters were used as defined by Arnot and Gobas (2004).
- **Ecosystem Characteristics.** Ranges of values assumed for total organic carbon in sediment and water, suspended solids concentrations, oxygen saturation and temperature were based on information from NAWQA as shown in **Table 2 of Appendix D**.

The Arnot and Gobas model was run using a Microsoft® Excel spreadsheet and Monte Carlo simulations (10,000 trials of randomly selected parameters) using Crystal Ball 2000. Assumptions regarding distribution types and variance parameters are provided in **Table 2 of Appendix D**.

5.4.1.4 Model Output: Tissue Concentrations & Biomagnification

Predicted mean concentrations of Pesticide 1 in aquatic organism tissues are shown in **Table 5.10**. Results indicate that mean predicted concentrations in tissues range form about 1.3 ppm in phytoplankton to 4.7 ppm in top piscivorous fish (wet weight basis). To evaluate biomagnification, however, tissue concentrations must be converted to a lipid weight basis. When this is done, it appears that biomagnification of Pesticide 1 is not significant, as the calculated biomagnification factors (BMF) are near or below unity. Predicted BMF values near or below unity also occur when comparing lipid-normalized concentrations in tissue determined at higher percentiles of the distribution (e.g., 75th and 90th percentiles, lipid-normalized data not shown).

Table 5.10. Mean Predicted Concentrations and Biomagnification Factors (BMFs) of Pesticide 1

Taxonomic Group	Mean Lipid Fraction	Mean Predicted Concentration (ug/kg w.w.)	Mean Predicted Concentration (ug/kg-lipid)	Mean Predicted BMF (lipid basis)
Phytoplankton	0.005	1,279	255,800	---
Zooplankton	0.02	1,280	64,000	0.25
Benthic feeding inverts	0.02	1,282	64,100	0.65
Filter feeding inverts	0.02	1,411	70,550	0.51
Small forage fish	0.06	3,346	55,767	0.84
Medium forage fish	0.06	3,447	57,450	0.87
Piscivorous fish	0.06	4,682	78,033	1.38

Details on model inputs, assumptions and outputs are provided in Appendix D.
BMF values calculated as the lipid-normalized concentrations in the predator divided by lipid-normalized concentrations in its diet, weighted according to feeding preferences in Table 1 of Appendix D. Lipid-equivalent concentrations in sediments determined by normalizing to sediment OC fraction * 0.35 per Seth et al. (1999) assuming negligible lipids in sediments.

Based on an average EEC in water of 2.5 ug/L predicted for the crop scenarios (**Table 4 of Appendix D**) and measured BCFs of 1,100 to 2,800 L/kg wet wt (**Table 5.6**), predicted concentrations in fish tissue would vary between 2,700 and 7,000 ug/kg wet wt for total residues of Pesticide 1. These values are similar to mean predicted concentrations of Pesticide 1 in tissue for fish (3,300 to 4,700 ug/kg wet wt.; **Table 5.10**) using the Arnot and Gobas (2004) methodology.

5.4.1.5 Model Output: BCFs and BAFs

Mean bioconcentration and bioaccumulation factors predicted from the model simulations are shown in **Table 5.11**. Bioconcentration factors were estimated by considering Pesticide 1 uptake through respiratory processes only while bioaccumulation factors considered

both respiratory and dietary pathways. Again, the similarity in predicted BCF and BAF values indicates that the contribution of the diet to chemical accumulation is minimal, which is consistent with the moderate hydrophobicity of Pesticide 1. For fish, predicted BCF values range from about 1,000 (mean, wet weight basis) to about 2,400 (90th percentile, wet weight basis).

Table 5.11. Mean and 90th Percentile BCFs and BAFs Predicted for Pesticide 1

Taxonomic Group	Mean Lipid Fraction	Mean Predicted BCF (L/kg w.w.)	Mean Predicted BAF (L/kg w.w.)	90th Percentile Predicted BCF (L/kg w.w.)	90th Percentile Predicted BAF (L/kg w.w.)
Phytoplankton	0.005	499	499	1,079	1,079
Zooplankton	0.02	496	500	1,077	1,089
Benthic feeding inverts	0.02	525	530	1,122	1,132
Filter feeding inverts	0.02	515	585	1,102	1,239
Small forage fish	0.06	1,196	1,308	2,553	2,885
Medium forage fish	0.06	1,184	1,353	2,527	3,049
Piscivorous fish	0.06	1,127	1,806	2,365	4,282

Details on model inputs, assumptions and outputs are provided in Appendix D.

Comparison of Empirical and Model-based BCFs

Model-predicted BCFs for fish range from approximately 1,100 to 2,500 L/kg-wet wt., for the mean and 90th percentile estimates, respectively (**Table 5.11**). These values are remarkably close to measured BCFs for sheepshead minnow and striped mullet (1,100 and 2,800 L/kg wet wt., respectively), which are derived from highest quality studies, **Table 5.6)**. This suggests that the model is providing reasonable predictions of BCFs and BAFs for Pesticide 1.

5.4.1.6 Risk Estimation for Piscivorous Wildlife for Pesticide 1

In order to assess risks to mammals and birds consuming aquatic organisms associated with predicted Pesticide 1 concentrations in aquatic organisms, several species were selected, including mink *(Mustela vison)*, river otter *(Lutra canadensis)*, belted kingfisher *(Ceryle alcyon)*, herring gull *(Larus argentatus)*, osprey *(Pandion haliaetus)*, mallard duck *(Anas platyrhynchos)*, great blue heron *(Ardea herodias)* and bald eagle *(Haliaeetus leucocephalus)*. Information on species ecological and physiological characteristics (dietary composition, body weights, food consumption rates, drinking water rates, etc) is provided in Appendix D. Pesticide 1 toxicity data used in this comparison are shown in **Table 5.9.**

Following standard OPP avian and mammalian risk assessment practices, risk quotients (RQ) were calculated using exposures expressed on an ingested dose basis (mg/kg-bw/d) and a dietary basis (mg/kg-diet). Exposure concentrations in the diet of piscivorous wildlife were predicted using an aquatic food web bioaccumulation model as described previously in this section and in Appendix D. The RQ values are then compared to Agency Levels of Concern (LOC) for determination of potential risk.

For acute exposures, RQ values associated with mean predicted concentrations in aquatic biota exceed the Agency acute risk LOC (0.1) for one of the eight species modeled (river otter, **Table 5.12**). Although the dose-based RQs are based on the same toxicity value within birds and mammals, differences in RQs reflect differing food and water intake rates relative to body weights across the different species. At higher percentiles of predicted exposure concentrations, exceedences of the acute risk LOC also occur mink and belted kingfisher. Although the acute LOC of 0.1 and the restricted use LOC of 0.2 is exceeded for these species, all RQ values are less than 0.4, indicating the magnitude of risk is likely to be sensitive to modeling assumptions. Calculated RQ values resulting from chronic exposure to predicted Pesticide 1 concentrations in aquatic biota are shown in **Table 5.13**. Results indicate RQ values are all below the Agency's LOC of 1.0 for chronic risks.

Table 5.12. Predicted RQ Values for Piscivorous Mammals and Birds Exposed to Pesticide 1 Through Acute, Dose-based Exposures

Organism	Mean	SD	25th %	75th %	90th %
Dose-Based					
Mink	0.07	0.08	0.02	0.09	**0.18**[1]
River otter	**0.15**[1,2]	0.25	0.04	**0.20**[1,2]	**0.39**[1,2]
Belted kingfisher	0.08	0.08	0.02	**0.11**[1]	**0.20**[1,2]
Herring gull	0.03	0.05	0.01	0.04	0.07
Osprey	0.03	0.03	0.01	0.03	0.07
Mallard duck	0.02	0.02	0.01	0.03	0.05
Great blue heron	0.02	0.02	0.01	0.03	0.05
Bald eagle	0.01	0.02	<0.01	0.02	0.03

[1] Exceeds LOC (0.1) for acute exposures to listed animals.
[2] Exceeds the endangered species LOC of 0.1 and the restricted use LOC of 0.2.
All parameters varied according to Table 2 in Appendix D. All dietary-based RQ values for birds are <0.01.

Table 5.13. Predicted RQ values for mammals and birds exposed to Pesticide 1 through chronic, dose- and dietary-based exposures

Organism	Mean	SD	25th %	75th %	90th %
Dose-Based					
Mink	0.03	0.03	0.01	0.04	0.08
River otter	0.06	0.11	0.02	0.08	0.16
Dietary-based					
Mink	0.04	0.04	0.01	0.05	0.09
River otter	0.37	0.61	0.10	0.49	0.95
Belted kingfisher	0.01	0.01	<0.01	0.01	0.02
Herring gull	0.03	0.04	0.01	0.04	0.07
Osprey	0.04	0.04	0.01	0.05	0.09
Mallard duck	0.02	0.02	0.01	0.02	0.04
Great blue heron	0.05	0.05	0.01	0.07	0.12
Bald eagle	0.07	0.11	0.02	0.09	0.17

All parameters varied according to Table 2 in Appendix D. Chronic, dose-based RQs are not calculated for birds due to lack of appropriate data.

5.4.1.7 Conclusions from Aquatic Bioaccumulation Assessment with Pesticide 1

The empirical and model-based estimation of the bioaccumulation potential of Pesticide 1 in aquatic food webs support the following conclusions.

1. Dietary exposure to Pesticide 1 (and its primary degradate) does not appear to be a dominant exposure pathway for aquatic organisms, as indicated by similarity in predicted BCF and BAF values and BMF values that are generally less than 1.

2. The similarity in measured and modeled BCFs supports the notion that the Arnot and Gobas (2004) food web bioaccumulation model can be used to produce reasonable bioaccumulation predictions for Pesticide 1.

3. Risks to piscivorous birds and mammals from exposure to Pesticide 1 via drinking water and the aquatic diet are relatively modest, with mean RQ values exceeding the Agency's level of concern for acute risk for Listed species (0.1) and restricted use (0.2) for one of seven modeled species. No exceedence of chronic levels of concern was indicated by this analysis.

5.4.2 Bioaccumulation Assessment for Pesticide 3

As described in **Section 3.2.3**, Pesticide 3 is used as an insecticide on potatoes, leafy vegetables, fruiting vegetables, and cotton. This pesticide has two isomers with an isomeric ratio of 12:1. The isomers have similar environmental fate and toxicological properties.

5.4.2.1 Summary of Bioaccumulation Data

Table 5.14 provides a summary of the bioaccumulation profile for Pesticide 3. A brief summary of the BCF and BAF studies follows this table.

Table 5.14. Bioaccumulation Profile for Pesticide 3 Based on Registrant Submitted Data

Parameter	Value	Study Notes and Interpretation (Source)
Log K_{OW}	**5.1** (isomer 1, 92%) **4.4** (isomer 2, 8%)	Suggestive of high bioaccumulation potential, dietary exposure may be significant
Koc	**30,753** L/kg-OC (parent isomers)	Indicates chemical partitioning to suspended and bed sediments likely to be important
BCF (42d constant laboratory exposure, bluegill sunfish)	• **7,325** L/kg wet wt. (whole fish) • **106,000** L/kg lipid	• Time to reach 90% steady state estimated at 48d • Transformation products in fish tissue estimated <0.1% of total radioactive compound
BCF (zebra fish, 2-4 pulses at 7d intervals, enhanced lighting)	Maximum BCFs (L/kg wet wt.) • **2,402-5,015** (whole fish)	• BCFs based on measured concentrations associated with maximum tissue residues• significant uncertainty in BCFs due to highly variable exposure concentrations • enhanced lighting may have resulted in greater chemical degradation due to photolysis
BAF (18 in. deep outdoor mesocosms; 2-4 pulses at	Maximum BAFs (L/kg wet wt.) • **2,133-4,079** (fathead minnow) • **4,549- 20,022** (snails)	• BAFs based on time weighted average water conc. at or near occurrence of peak tissue conc. • measured conc. in water exceeded water solubility

7-d intervals, 77-91 d study duration)	• **1,772-3,127** (mussels) • **396-2,188** (sowbug) • **437-820** (periphyton)	of 1.79 ug/L up to 10X • minor amounts of transformation products were reported • fish were fed "clean" food during the study

Bioconcentration in Bluegill Sunfish. The bioaccumulation of Pesticide 3 was studied in bluegill sunfish (*Lepomis macrochirus*) at nominal concentrations of 0.040 and 0.400 µg/L under flow-through conditions. At both the low and high dose treatment levels, the chemical residues accumulated in the fish tissues, with maximum concentrations in fish tissue occurring on day 42 (the last day of the exposure period). A maximum bioconcentration factor (BCFs) of 7,325 L/kg wet wt. was calculated for whole fish. Based on uptake and elimination kinetics, 90% steady state was estimated at 48 ± 5.6 days (BIOFAC modeling program). Therefore, BCFs may have been underestimated somewhat since steady state was not reached. Two transformation products were isolated from the water and the fish tissues but these were minor, occurring at ≤0.1% of the total radioactive residues in the fish tissues. Depuration was relatively slow as it took 56 days of depuration for the [^{14}C]residues in the fish to decrease by ≥85% of maximum.

Bioconcentration in Zebrafish. The bioconcentration potential of Pesticide 3 was studied in a non-guideline study using zebrafish (*Danio rerio*) in a static, artificial sediment/water system for approximately 232 days. Two separate groups of near mature zebrafish were exposed to two and four weekly applications (7-day interval) of the pesticide to the overlying water at nominal concentrations of 5.0 µg a.i./L. Based on time-weighted averages of measured water concentrations, maximum estimated bioconcentration factors (BCFs) based on total radioactive residues in fish were 2,402 and 2,515 L/kg wet wt. for the treatment groups treated with two and four applications of 5.0 µg a.i./L, respectively. Due to study design limitations, uptake and elimination kinetics were not quantitatively evaluated.

Bioaccumulation in Outdoor Mesocosms. The aquatic dissipation and bioaccumulation of Pesticide 3 was also studied using an outdoor freshwater mesocosm experiment using three different treatment designs:

- Study I: 2 applications of 2 ug/L 7 days apart
- Study II: 2 applications of 20 ug/L 7 days apart
- Study III: 4 applications of 2 ug/L 7 days apart

Residues of Pesticide 3 and two of its transformation products were measured periodically in water, sediment and seven aquatic species: fathead minnows (*Pimephales promelas*); snails (*Lymnea stagnalis*); pond mussels (*Anodonta cygnea*); zebra mussels (*Dreissena polymorpha*); sowbugs (*Asellus aquaticus*); and two aquatic plants (*Myriophyllum spicatum* and periphyton *Potamogeton crispus;* **Figure 5.2**). Pesticide concentrations in water peaked at each application and declined rapidly until the next application, which appears likely to have resulted from dissipation processes (e.g., partitioning to sediments) and possibly degradation process (photolysis due to the shallow depth).

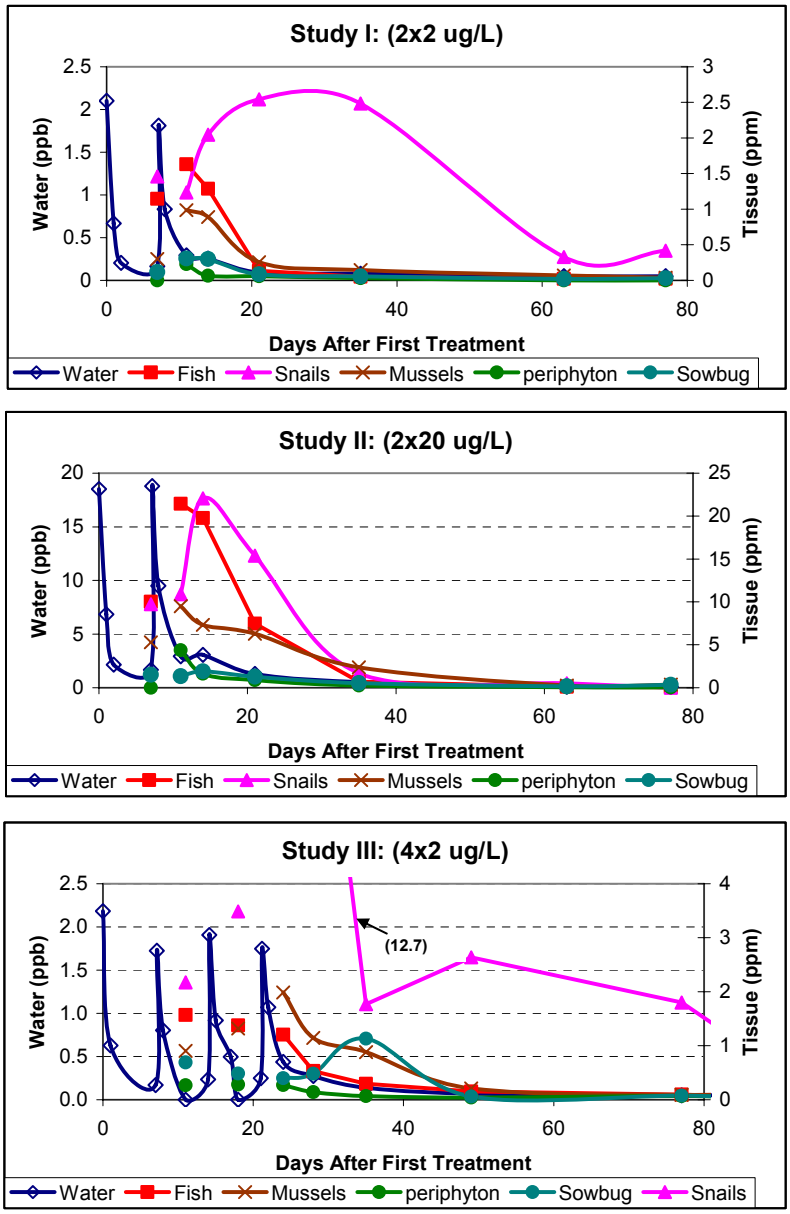


Figure 5.2. Results from a Mesocosm Study with Pesticide 3

The reported peak concentrations in fish, snails, mussels, aquatic sowbugs, periphyton, and macrophytes were 21.4, 22.0, 11.3, 1.9, 4.4, and 2.6 ppm, respectively. Peak concentrations in fish occurred within 4 days following an application, while those for mussels, snails, and sowbugs occurred within 3-14 days (**Figure 5.2**). Metabolites were measured but were minor fractions of the parent compound. Due to fluctuating concentrations in the water column, BAFs were calculated based on a time-weighted average of measured concentration up to the point of the measured concentration in tissue. Maximum BAFs occurred on or near the point of peak concentrations in tissue and ranged from approximately 2,100-4,100 L/kg in fish, 4,500-20,000 in snails, and 1,700 to 3,100 in mussels. It should be noted that because water concentrations in study III greatly exceeded solubility and samples were not centrifuged prior to analysis, the bioavailability of Pesticide 3 in water is considered uncertain. Furthermore, the shallow nature of

these systems (approx 18 in deep) may have resulted in enhanced rates of photolysis relative to deeper, natural ecosystems where light penetration is significantly reduced at greater depths.

5.4.2.2 Bioaccumulation Assessment Issues with Pesticide 3

The bioaccumulation assessment approach for Pesticide 3 was informed by the following key issues and findings.

Environmental Fate. The use profile for Pesticide 3 (aerial and ground application on agricultural crops such as cotton, leafy vegetables, potatoes) suggests that pesticide drift, runoff and erosion into aquatic ecosystems are likely. In aquatic ecosystems, the environmental fate profile (summarized in **Section 3.2.3**) suggests that Pesticide 3 will likely partition to organic matter such as suspended and bed sediments (Koc = 30,753 L/kg-OC) and will and persist for relatively long periods of time (biotic metabolism and hydrolysis half lives > 100 days). The dominant degradation pathway is expected to be photolysis (half life = 4.6 days). However, for agricultural ponds with typical turbidity (e.g., total suspended solids of 30 mg/L), photolysis is only considered important at or near the water surface due to light attenuation at greater depths. Given its propensity to partition and persist in aquatic sediments (anaerobic aquatic metabolism half life > 378 days), concern was raised for potential year-to-year "carryover" of Pesticide 3 that might result from successive pesticide applications over multiple years.

Ecological Receptors of Concern. The primary focus of the bioaccumulation assessment of Pesticide 3 was the potential impacts on piscivorous wildlife through dietary exposure, owing to their likely exposure at the top of the aquatic food web and sensitivity to Pesticide 3. Reproductive effects on bobwhite quail were found to be the most sensitive endpoint, with the NOAEC and LOAEC identified as 7.6 and 15 ppm in the diet, respectively, based on seizures and spasms in chicks.

Exposure Routes. At log K_{OW} values of 4.4 to 5.1, available aquatic food web bioaccumulation models suggest that dietary exposure of poorly metabolized organic chemicals can be a significant contributor to the bioaccumulation of Pesticide 3 by higher trophic level aquatic organisms (e.g.**, Figure 5.1,** Arnot and Gobas, 2004, Fisk et al., 1998).

***In Vivo* Metabolism.** Available evidence from the bioconcentration and bioaccumulation studies indicates that in vivo metabolism by fish is not a dominant concern, with degradation products occurring at low levels relative to the parent compound (e.g., < 1% in the bluegill bioconcentration study).

Time to Reach Steady State. Based on the accumulation kinetics from water-only exposure to bluegill, the time to reach 90% steady state accumulation is estimated to be 48 days (**Table 5.14**). This suggests that concentrations of Pesticide 3 in fish will be somewhat temporally 'dampened' relative to water column concentrations, which is supported by data from the aquatic mesocosm study (**Figure 5.2**).

5.4.2.3 Bioaccumulation Assessment Methods for Pesticide 3

Although the bioconcentration and bioaccumulation data presented in **Table 5.14** could have been used directly to estimate Pesticide 3 concentrations in fish tissue, these data were considered limited in several aspects:

- The potential for trophic transfer (biomagnification) was likely underestimated due to lack of dietary exposure in bioconcentration tests and experimental design limitations of the mesocosm study (i.e., potentially enhanced photolysis due to shallow depth and only a single season of pesticide exposure).
- In field settings, the persistence of Pesticide 3 may lead to greater bioaccumulation compared to the laboratory and mesocosm studies due long-term (multi-year) pesticide accumulation in sediments.
- The bioavailability of Pesticide 3 in field settings may differ substantially from the laboratory and mesocosm studies.

Given the limitations identified with the available bioconcentration and bioaccumulation data for Pesticide 3, the OPP/EFED supplemented these data with the use of a food web bioaccumulation model (Arnot and Gobas, 2004; Gobas, 1993). Use of a food web bioaccumulation model was considered advantageous because trophic transfer and the potential impact of long-term pesticide accumulation in sediments could be directly assessed. As discussed previously, the Arnot and Gobas model, including its precursor (Gobas, 1993), have been used extensively by EPA's Office of Water for estimating the bioaccumulation of nonionic organic chemicals for deriving human health and wildlife criteria (USEPA, 1995; 2000, 2003). Although originally developed and applied to the Great Lakes ecosystem for modeling PCBs and selected pesticides, these models have been successfully applied to other ecosystems including the Hudson River, Fox River/Green Bay, and Bayou D'Indie, Lousiana (USEPA, 2003; Burkhard, 2003). The Arnot and Gobas (2004) model was selected for estimating pesticide bioaccumulation in OPP because it has been published in peer-reviewed literature, it has been improved upon since its original publication (Gobas 1993), and the 1993 version of the model has already been used by EPA for regulatory purposes (USEPA, 1995; 2000; 2003). The original Gobas (1993) model is generally accepted by the scientific community (Burhkard, 1998) as a reasonable approach method for estimating bioaccumulation of hydrophobic organic compounds in aquatic systems.

Two dominant issues emerged during the course of the bioaccumulation modeling and dialogue with the registrant as potentially influential on the bioaccumulation and ecological risk assessment results:

1. Can a steady-state bioaccumulation model provide reliable estimates of pesticide bioaccumulation under highly variable environmental exposures?
2. How do model predictions respond to different assumptions regarding sediment dynamics?

In order to address these bioaccumulation-related assessment issues, the following three modeling approaches were applied using OPP's standard agricultural pond system:

1. PRZM/EXAMS + Arnot and Gobas (2004) food web model (steady state mode)
2. PRZM/EXAMS + Arnot and Gobas (2004) food web model (dynamic mode)
3. "AGRO" (CEMC 2007), (dynamic mode, includes sediment dynamics)

Modeling Approach 1 & 2: PRZM / EXAMS / Arnot & Gobas

Modeling approach 1 and 2 involved assessing the aquatic bioaccumulation of Pesticide 3 using the PRZM, EXAMS and Arnot & Gobas models. The Arnot & Gobas model was run in both a steady state and dynamic mode (**Figure 5.3**).

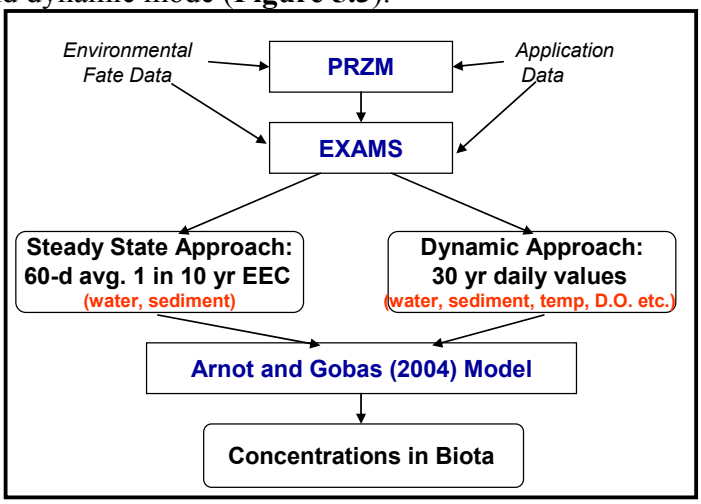


Figure 5.3. Bioaccumulation Modeling Approach Using PRZM/ EXAMS/Arnot & Gobas Models for Pesticide 3

The components of modeling approaches 1 & 2 are as follows:

- **Estimating Pesticide Loads to the Pond.** EPA's PRZM model was used to estimate daily pesticide loads resulting from runoff and soil erosion to the standard agricultural pond. Simulations were run for representative crop scenarios, soil characteristics, application rates, and weather data over a 30-yr period.

- **Estimating Pesticide Concentrations in the Pond**. The daily concentrations of Pesticide 3 in water and sediment resulting from pesticide spray drift, runoff and erosion were then estimated using EPA EXAMS model parameterized for the standard, EFED agricultural pond. For several crop scenarios, predicted concentrations of Pesticide 3 in water exceeded its solubility, raising concerns regarding the bioavailability of predicted pesticide concentrations. In these situations, dissolved concentrations were "capped" at the limit of solubility (1.79 ppb).

- **Estimating Pesticide Concentrations in Biota (Steady State).** For the steady-state version of the Arnot and Gobas model, a 60-d average estimated environmental concentration (EEC) with 1 in 10 year return interval was selected for input to the a spreadsheet version of the food web bioaccumulation model developed by Arnot and

Gobas (2004). The 60-d average was selected to reflect the critical period required for Pesticide 3 to reach steady state accumulation in birds and the subsequent maternal transfer in eggs (approximately 30-60 days). The predicted concentration of Pesticide 3 corresponding to the 60-d average, 1 in 10 year EECs (water, sediment) was then compared to the chronic dietary toxicity endpoint for birds (NOAEC = 7.6 ppm).

- **Estimating Pesticide Concentrations in Biota (Dynamic).** For the dynamic version of the Arnot and Gobas model, daily values of water, sediment and relevant water quality parameters (e.g., dissolved oxygen, temperature) were used as input to produce a prediction of pesticide concentrations in aquatic forage items over 30 years. The 60-d average, 1 in 10 year EEC of the tissue concentrations was then calculated for comparison with the chronic dietary toxicity endpoint for birds (NOAEC = 7.6 ppm).

Modeling Approach 3: "AGRO" (PRZM / QWASI / Arnot & Gobas)

The modeling approach using the AGRO modeling system followed a similar process as described above for approaches 1 and 2, except for the bioaccumulation modeling which was only run in the dynamic mode **(Figure 5.4).**

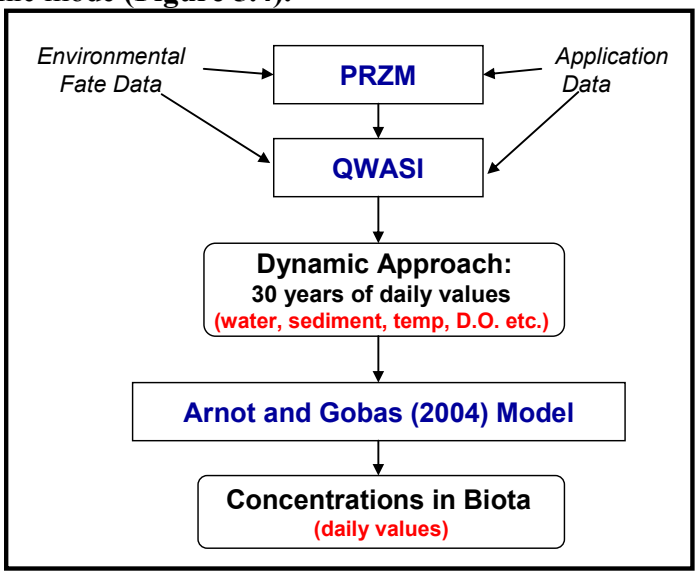


Figure 5.4. Schematic of AGRO Aquatic Bioaccumulation Modeling System

The Canadian Environmental Modelling Centre'AGRO modeling system is a MicroSoft Excel® based application that combines a water quality model with a food web bioaccumulation model to estimate exposure to aquatic species from pesticides in a user-defined water body (CEMC, 2007). The components of modeling approach 3 (AGRO) are as follows:

- **Estimating Pesticide Loads to the Pond.** Identical to approaches 1 and 2, the AGRO modeling system uses EPA's PRZM model to estimate daily pesticide loads to the standard agricultural pond based on representative crop scenarios, soil characteristics, application rates, weather data over a 30-yr period.

- **Estimating Pesticide Concentrations in the Pond**. In contrast to modeling approaches 1 and 2, estimates of the resulting daily concentrations of pesticide 3 in water and sediment were produced using the "Quantitative Water, Air, Sediment Interaction" (QWASI) Fugacity model developed by Mackay et al. at the Canadian Environmental Modelling Centre (Mackay, Joy and Paterson (1983), Mackay, Paterson and Joy (1983), Webster Lian and Mackay (2005), Mackay and Diamond (1989)). The QWASI model was parameterized to the same standard agricultural pond as used for approaches 1 and 2 above. One important difference in the functionality of QWASI vs. EXAMS is the inclusion of sediment dynamics (e.g., deposition, resuspension, burial) which affects the amount of pesticide in the dissolved phase that is available for bioaccumulation in organisms. Another difference involves the treatment of pesticide concentrations predicted in excess of solubility. QWASI contains an numeric algorithm to account for the mass of pesticide in excess of solubility (presumed to be in a precipitate form), which is then converted to dissolved pesticide as concentrations drop below solubility.

- **Estimating Pesticide Concentrations in Biota.** The AGRO modeling system uses the same food web bioaccumulation model as approaches 1 and 2 (Arnot and Gobas, 2004) for estimating pesticide concentrations in aquatic biota. Based on 30-years of daily concentrations in biota, the 60-d average, 1 in 10 year EEC of the tissue concentrations was calculated for comparison with the chronic dietary toxicity endpoint for birds (NOAEC = 7.6 ppm).

5.4.2.4 Bioaccumulation Modeling Inputs: Approaches 1, 2 & 3

For the purposes of this illustration, a brief summary of key input parameters for the three bioaccumulation modeling approaches is provided in (**Table 5.15**). OPP considers a detailed review of the input parameters and model algorithms used to predict bioaccumulation is considered beyond the scope of this SAP consultation. Pending the outcome of this consultation, OPP expects to bring its refined bioaccumulation assessment modeling framework to the SAP for detailed review in the future.

As described previously, the primary differences between the PRZM/EXAMS / Arnot & Gobas modeling approach and AGRO modeling system (PRZM/ QWASI/Arnot & Gobas) reside in the functionality and parameterization of the water quality models (EXAMS vs. QWASI). Among the more important differences in the water quality models are:

- the treatment of sediment dynamics (incorporated in QWASI but not EXAMS)
- the treatment of pesticide degradation (EXAMS uses separate processes whereas QWASI uses a lumped parameter for water and sediment half lives)
- suspended sediment organic carbon (set to 4% in EXAMS and 6.7% in QWASI)

Although QWASI is designed to simulate inflow and outflow of surface water to and from the pond, it was set to a negligible flow rate to minimize differences from the standard parameterization of the EXAMS model, which assumes any inflow is offset by evaporation.

Table 5.15. Key Input Parameters Used for Bioaccumulation Modeling with Pesticide 3

Parameter	Value	Model Applicability			
		PRZM	EXAMS	QWASI	A&G
Log Kow	5.1	✓	✓	✓	✓
Koc	30,753 L/kg OC	✓	✓	✓	✓
Solubility	1.79 ppb	✓	✓	✓	
Application Rate/Frequency	0.25 lb a.i./A; 1X yr (Cotton) 0.25 lb a.i./A; 2X yr (Potato)	✓	✓	✓	
Degradation Half Lives:					
- hydrolysis	stable (pH 7&9)	✓	✓		
- photolysis	Soil: 54 d; Water: 4.6 d	✓	✓		
- aerobic aquatic metabolism (1)	268 d		✓	✓	
- anaerobic aq. metabolism (2)	Stable		✓	✓	
Pond Characteristics:					
- volume/area	2 x 10^6 L / 10,000 m^2		✓	✓	
- depth of water/sediment	2m / 5 cm		✓	✓	
- TSS	30 mg/L		✓	✓	
- bed sediment OC	4%		✓	✓	
- suspended sediment OC	4% (6.7% for QWASI)		✓	✓	
- inflow/outflow	(set to negligible flow)			✓	
- sediment deposition, burial, resuspension	80/40/40 g/m^2			✓	
Food Web Characteristics:	**% Lipid (Feeding Pref.)**				
- phytoplankton	0.5% (N/A)				✓
- zooplankton	2% / (100% phytoplankton)				✓
- benthic inverts.	2% / (100% sediment)				✓
- forage fish A & B	5% / (50% benth.,50% zoopl.)				✓
- piscivorous fish	4% / (50% f. fish A, 50% f. fish B)				✓

5.4.2.5 Results for Bioaccumulation Modeling Approach 1: (PRZM / EXAMS / Arnot & Gobas—Steady State)

Based on PRZM/EXAMS modeling described previously, dissolved water and sediment EECs were calculated as the 60-d average concentration with a 1 in10 year return frequency for different crop scenarios **(Table 5.16)**. The EECs for the crop scenarios shown in **Table 5.16** span the concentration range predicted in piscivorous fish (up to four) for each crop type (cotton, potato, tomato). EECs in water for the three crop scenarios receiving the greatest pesticide load exceeded the solubility limit for Pesticide 3 and were capped at 1.79 ug/L.

Table 5.16. 60-d Average EECs Used for Steady State Bioaccumulation Modeling

Crop Scenario	Dissolved Concentration (ug/L)	Concentration in Sediment (ug/kg dry wt.)
CA Cotton	0.673	675
MS Cotton	1.790 *	2593
ID Potato	1.382	1386
FL Potato	1.790 *	3080
CA Tomato	0.945	939
FL Tomato	1.790 *	2125

* concentration capped at the limit of solubility.

The 60-d EECs from **Table 5.16** were used to predict steady-state concentrations of Pesticide 3 in aquatic biota **(Figure 5.5)** using the Arnot and Gobas (2004) bioaccumulation model described previously. Results indicate pesticide concentrations predicted in piscivorous fish exceed the avian dietary NOAEC (7.6 ppm) in all six crop exposure scenarios (by up to 5X) and exceed the avian LOAEC (15 ppm) in five of the six crop scenarios (by up to 2X), indicating a potential risk to piscivorous birds. Concentrations in zooplankton and benthic invertebrates approached the avian NOAEC in the three scenarios with the highest pesticide loadings (MS Cotton, FL Potato, FL Tomato) and were well below the NOAEC in the other three crop scenarios.

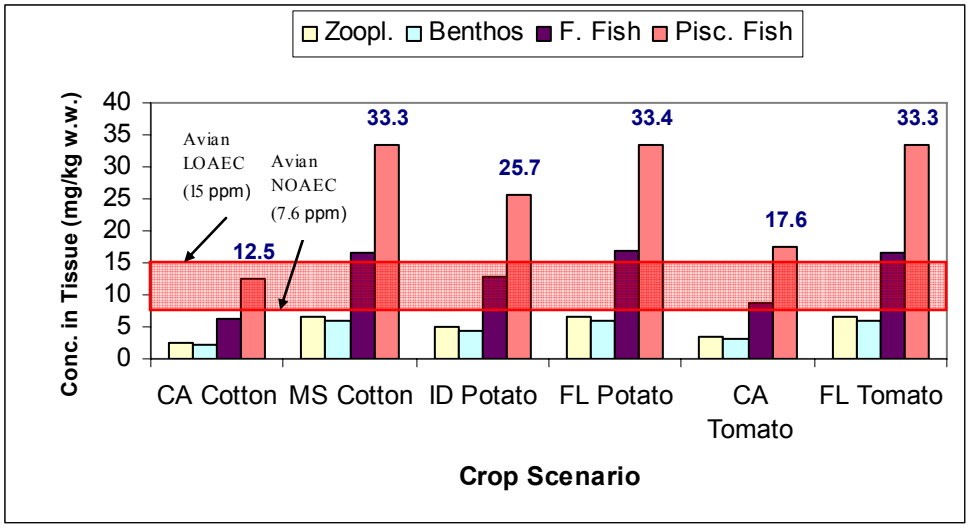


Figure 5.5. Steady State Bioaccumulation Modeling Results for Pesticide 3

In order to evaluate the potential for biomagnification of Pesticide 3, tissue concentrations of biota among successive trophic levels were first normalized for lipid fraction. Comparison of lipid-normalized pesticide concentrations accounts for differential bioaccumulation due to variation in lipid fraction alone and thus enables a more accurate assessment of biomagnification, which is determined by processes related to dietary uptake. Examination of lipid-normalized concentrations (**Figure 5.6**) suggests no apparent biomagnification by forage fish from their prey (zooplankton and benthic invertebrates); however, there appears to be a potential for biomagnification by piscivorous fish from their prey (forage fish), with a biomagnification factor of approximately 2.5.

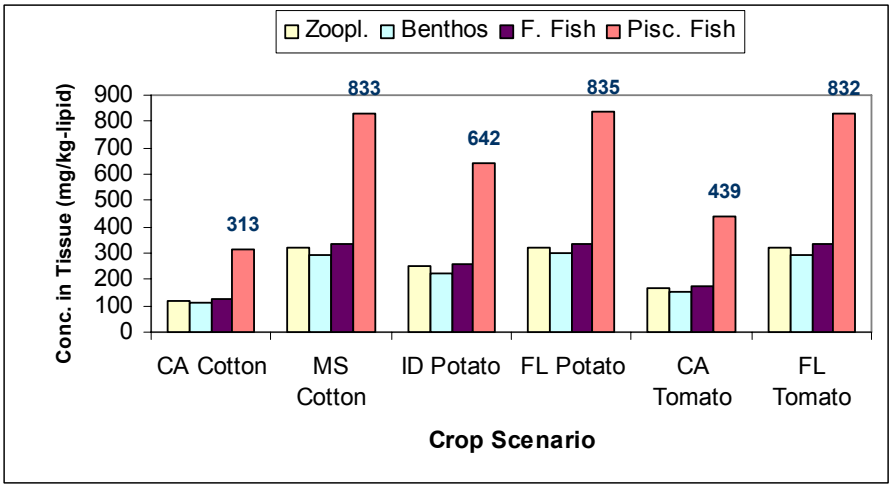


Figure 5.6. Lipid-Normalized Concentrations of Pesticide 3 in Aquatic Biota

5.4.2.6 Bioaccumulation Modeling Results for Approach 2

Dynamic bioaccumulation modeling enables variation in pesticide concentrations in tissue to be directly assessed as a function of time-variable exposure concentrations and water quality (temperature, dissolved oxygen, etc.). Results from the dynamic bioaccumulation modeling with Approach 2 (PRZM / EXAMS / Arnot & Gobas) for the two cotton scenarios (CA Cotton and MS Cotton) are shown in **Figure 5.7**.

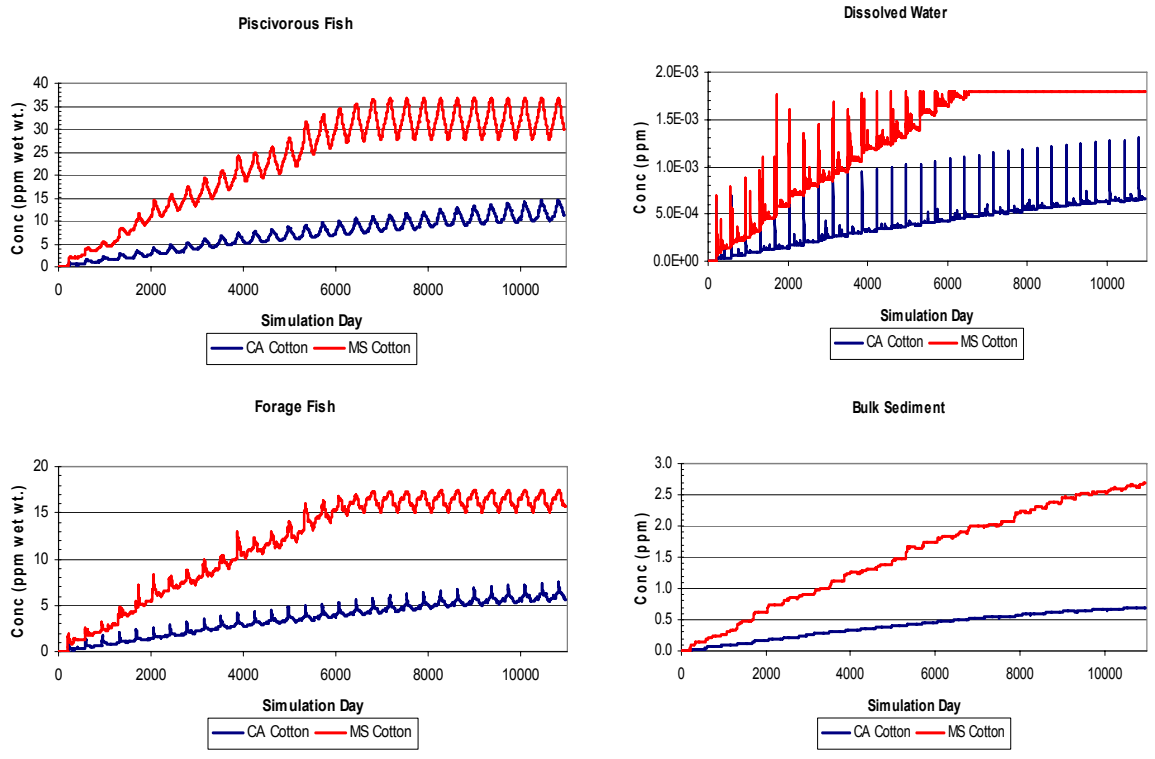


Figure 5.7 Dynamic Bioaccumulation Modeling Results for Pesticide 3 Using Approach 2

The following observations were drawn from the bioaccumulation modeling results presented in **Figure 5.7.**

- **Water Concentrations**. Dissolved concentrations of Pesticide 3 reflect a seasonal periodicity of pesticide loads to the pond (seasonal spikes) and a gradual increase over the course of the 30-yr simulation. For MS cotton (i.e., the high loading cotton scenario), concentrations in water increased to the limit of solubility (1.79 ppb) by approximately day 6000, at which point they were equated to the solubility limit under the assumption that concentrations above the solubility limit would be in a precipitate form and not bioavailable. Concentrations from CA cotton (the low pesticide loading cotton scenario) did not reach the solubility limit.

- **Sediment Concentrations.** Concentrations of Pesticide 3 in sediment (dry weight) displayed a gradual increase over the entire 30-yr simulation period and never reach a plateau. This pattern is likely a function of the assumed persistence of the compound in sediments (half life > 378 days, therefore assumed to be 'stable' in sediment) and the treatment of the sediment layer in EXAMS. Specifically, the sediment layer is modeled as a fixed volume and mass with no incorporation of sediment loads to the pond (i.e., only chemical that is sorbed to sediment is considered by EXAMS). Furthermore, sediment dynamics within the pond is not considered (e.g., deposition, resuspension, burial, etc.)

- **Biota Concentrations.** Similar to the temporal profile of pesticide 3 in the water column, concentrations in biota display a seasonal periodicity that is linked to pesticide application and rainfall events (**Figure 5.7**). For MS cotton, concentrations in piscivorous fish reach a plateau near day 6000 (roughly 16 years) with peak concentrations reaching approximately 36 ppm (wet weight), nearly 5X the avian NOAEC. This likely reflects the corresponding plateau in dissolved water concentrations caused by limiting concentrations at the limit of solubility. For the CA cotton scenario, predicted concentrations in piscivorous and forage fish never reach a plateau, again which mirrors the pattern in dissolved water concentrations. The temporal 'dampening' in predicted pesticide concentrations in biota related to those in the water column is greater for piscivorous fish compared to forage fish. This is expected given their higher position in the food web and slower accumulation kinetics.

Based on the dynamic modeling results, EECs of Pesticide 3 in tissue were calculated from the maximum annual 60-d average concentrations in biota with a 1 in 10 year return interval (i.e., the same averaging period and return interval used for calculating exposure-based EECs used in the steady-state bioaccumulation modeling). Results from the calculated EECs in tissue are shown in **Figure 5.8**.

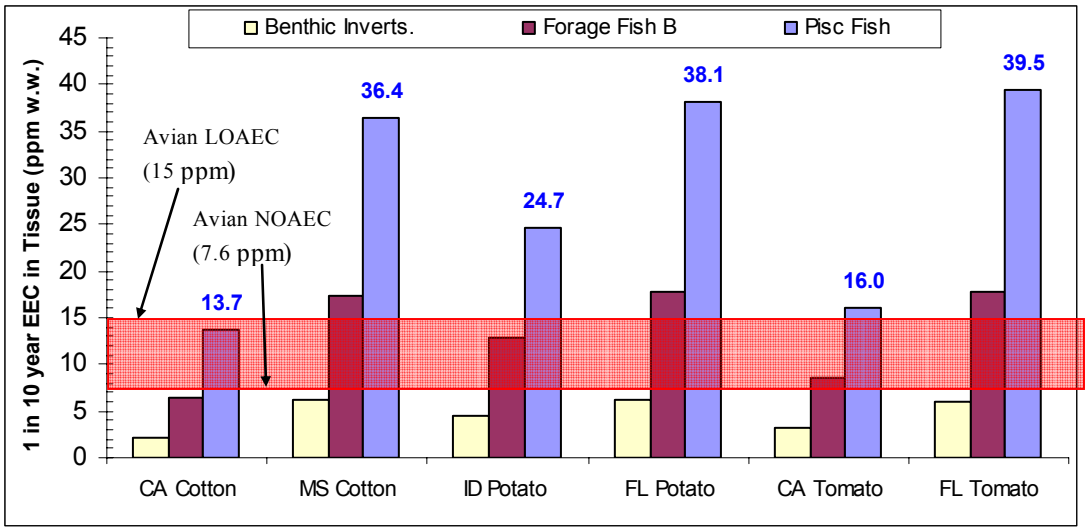


Figure 5.8 Tissue-Based EECs for Pesticide 3 Using Bioaccumulation Approach 2

Comparison of the EECs predicted using the steady state and dynamic bioaccumulation modeling with PRZM/EXAMS/Arnot and Gobas (Approaches 1 & 2, respectively) indicates predictions are very similar (**Table 5.17**). This suggests that steady-state bioaccumulation modeling can provide useful predictions of bioaccumulation potential even with highly dynamic exposures, provided proper consideration of the averaging period associated with water and sediment concentrations is made. This same concept (i.e., selecting the proper time period over which to average water and sediment concentrations) was also recommended for designing field studies to assess measured bioaccumulation factors (Burkhard, 2003) and incorporation of BAFs into the derivation of ambient water quality criteria (USEPA, 2000; 2003).

Table 5.17. Predicted Concentrations of Pesticide 3 in Piscivorous Fish Using Approaches 1 and 2

Crop Scenario	Approach 1: Tissue-Based EEC Using Steady State Model (mg/kg wet wt.)	Approach 2: Tissue-Based EEC Using Dynamic Model (mg/kg wet wt.)
CA Cotton	12.5	13.7
MS Cotton	33.3	36.4
ID Potato	25.7	24.7
FL Potato	33.4	38.1
CA Tomato	17.6	16.0
FL Tomato	33.3	39.5

5.4.2.7 Bioaccumulation Modeling Results for Approach 3 (PRZM/QWASI/Arnot & Gobas)

Results from the modeling of Pesticide 3 using Approach 3 (i.e., PRZM / QWASI / Arnot & Gobas as represented by AGRO) indicate substantially different concentration profiles using similar inputs and the same crop exposure scenarios (**Figure 5.9**). Specifically, the overall amplitude of the peak concentrations in piscivorous and forage fish are typically below the screening toxicity benchmark of 7.9 ppm. Furthermore, unlike the EXAMS modeling used in Approach 2, dissolved water concentrations do not indicate a year to year carry over and

sediment concentrations reach a plateau at or around 5000 days. The overall lower amplitude and duration of peak concentrations observed with Approach 3 translate into lower EECs compared to those derived using Approach 2 (**Figure 5.8 vs. Figure 5.10).** Specifically, tissue-based EECs using Approach 3 are at least a factor of 6 lower than those from Approach 2.

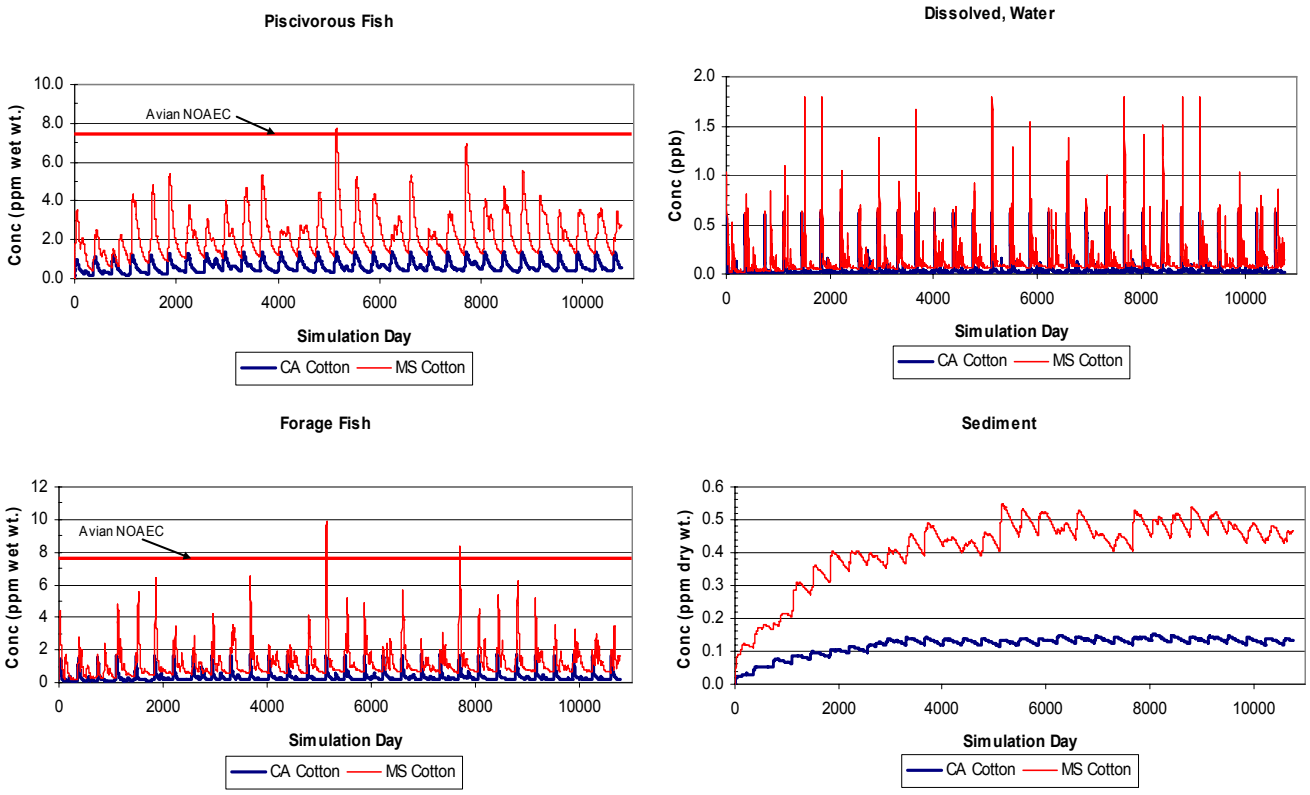


Figure 5.9. Pesticide 3 Modeling Results using Approach 3 (PRZM/QWASI/Arnot & Gobas)

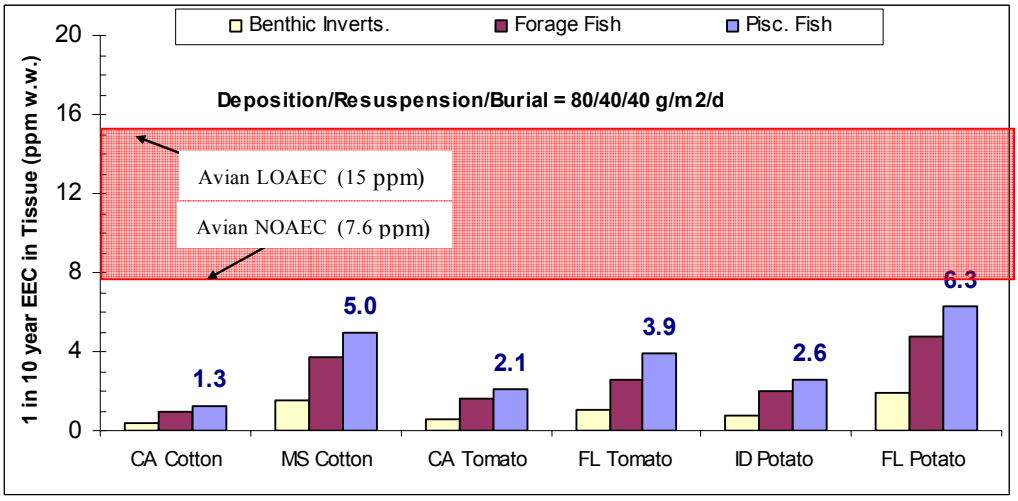


Figure 5.10. Tissue-Based EECs for Pesticide 3 Determined from Bioaccumulation Approach 3

A sensitivity analysis indicates the dominant factor explaining the difference between the results for Approaches 2 and 3 is the incorporation of sediment dynamics in the QWASI model of Approach 3 (80, 40, and 40 g/m^2/d for sediment deposition, burial, resuspension, respectively). The 80 g/m^2/d rate selected for deposition was based on the central tendency of PRZM-predicted soil erosion estimates for the 18 applicable crop scenarios for Pesticide 3 (**Figure 5.11**). Burial and resuspension rates were based on an assumption that 50% of the deposited sediment would be subject to burial and resuspension each day.

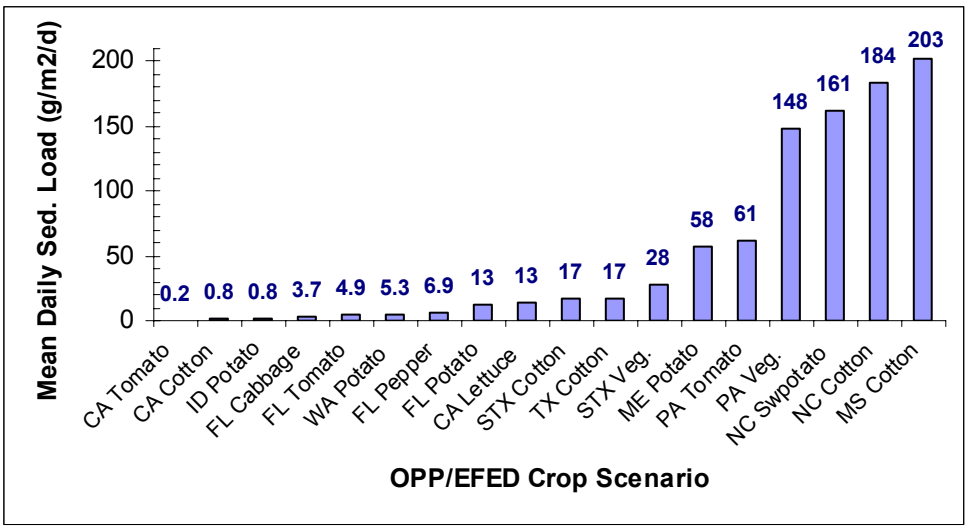


Figure 5.11. Mean Daily PRZM-predicted Soil Erosion for 18 Crop Scenarios

Within the context of Approach 3, sensitivity analysis indicates that the rates of deposition, burial and resuspension have a substantial impact on predicted concentrations in fish. For example, when alternate rates of deposition, resuspension and burial (50, 40 and 10 g/m^2/d) were chosen, the resulting tissue-based EECs increased by a factor of two compared to the 80/40/40 g/m^2/d rates, respectively (**Figure 5.12**).

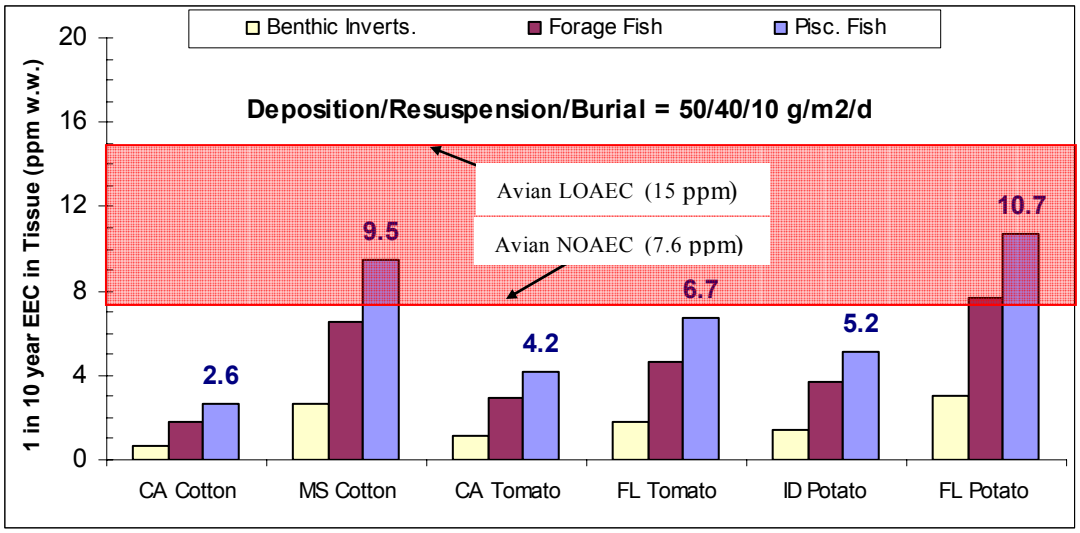


Figure 5.12. Effect of Alternate Assumptions Regarding Rates of Deposition, Resuspension and Burial (50/40/10 g/m2/d) on Tissue-based EECs for Pesticide 3

When daily average soil loadings calculated from PRZM are used for sediment deposition rates (i.e., values shown in **Figure 5.11**), greater differences are seen in predicted concentrations in biota (**Figure 5.13**). Based on the predicted concentration in piscivorous fish, different ordering of scenarios is also apparent. This reflects the regional differences in PRZM-predicted sediment loadings to the pond.

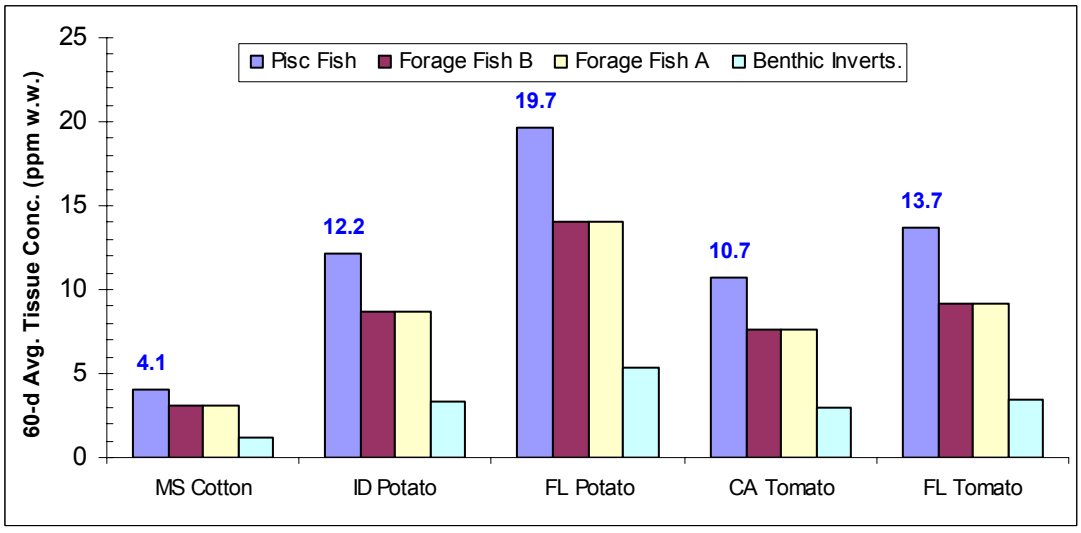


Figure 5.13. Effect of Alternate Assumptions Regarding Rates of Deposition, Resuspension and Burial (PRZM Values) on Tissue-based EECs for Pesticide 3

Currently, OPP/EFED is evaluating a revised version of the AGRO modeling system (Version 1.2.8f) that incorporates temporal and regional variability in soil erosion to the pond based on daily soil erosion estimates from PRZM. This version is viewed as a more realistic expression of high temporal and spatial variability that exists in soil erosion across different agricultural regions. Nonetheless, the above questions are still applicable to this or any other model being considered for addressing the potential impact of sediment dynamics on pesticide bioaccumulation. OPP invites SAP comments on these and other issues associated with incorporation of sediment dynamics in pesticide aquatic bioaccumulation modeling.

5.4.3 Bioaccumulation Assessment for Pesticide 4

As described in **Section 3.2.4,** Pesticide 4 is a new insecticide proposed for a number of uses including indoor greenhouse ornamentals and a number of agricultural commodities (e.g., cotton, vegetables, and tobacco). Chemical 4 is unique in its physicochemical properties and in the type of data that have been submitted to the Agency. It has very low solubility (0.15 ug/L), high hydrophobicity (log Kow of 8.1), high K_{OC} (1,200,000), and high bioconcentration factor (estimated steady state BCF = 27,000 L/kg wet weight), which suggests that when the chemical enters water, it will predominantly partition to the sediment (organic carbon) and biota (lipid) phases.

This section discusses the following:

- the available data used to evaluate bioaccumulation for Chemical 4;
- methods used to estimate accumulation (body burdens) in organisms exposed to Chemical 4; and
- methods used to evaluate potential risks to animals that may consume organisms that have accumulated Chemical 4.

Only the quantitative bioaccumulation analysis for fish is presented in this white paper. A comparable analysis was also performed for aquatic and benthic invertebrates using submitted accumulation studies (**Table 5.19**). However, the accumulation assessment in fish and invertebrates used the same basic approaches as further described in Section 5.4.3.3.

5.4.3.1 Summary of Available Bioaccumulation Data for Chemical 4

Table 5.18 provides a summary of the bioaccumulation profile for Pesticide 4. Available bioaccumulation data for Pesticide 4 included laboratory studies, microcosm/mesocosm studies, and modeling data. Studies that were submitted in support of registration for Pesticide 4 that are not typically available for risk assessment include: (1) short-term and long-term accumulation studies in sediment organisms (oligochaetes); (2) dietary accumulation study in fish; and (3) mesocosm study that evaluated accumulation and toxicity in benthic invertebrates. Studies are available in addition to those presented in **Table 5.18;** however, only studies that have been used to quantify bioaccumulation potential are included in **Table 5.18**.

Table 5.18. Summary of Bioaccumulation Data for Pesticide 4

Study Type	Organism	Summary and Interpretation
Log K_{OW}	8.1 (±1)	Suggestive of high bioaccumulation potential, dietary exposure is expected to be significant relative to water exposure
Koc	1,200,000 (average value)	Indicates chemical partitioning to suspended and bed sediments likely to be important
Water exposure 49-Day BCF study	Fish – Bluegill sunfish	Whole fish BCF was **>16,000** L/kg w.w. (estimated steady state BCF was approximately **27,000** L/kg w.w). **Uptake constant**: 515/day to 600/day **Depuration constant**: 0.022/day to 0.023/day Depuration half-life was approximately 30 days
Dietary exposure BAF. 56-Day exposure and 56-day depuration.	Fish – Rainbow Trout	Trout were fed oligochaetes that contained 0.92 mg/kg pesticide. Resulting mean measured tissue levels in the trout were 0.1 mg/kg. Apparent steady state was reached within the first 7 days of exposure.
Spiked Sediment Study with 28-Day Accumulation Period	Oligochaetes	**BSAF**: approximately 5.7 **Uptake constant:** 0.00453/day **Depuration constant**: 0.0142/day (however, it is uncertain if depuration occurred in the study because chemical levels at the last exposure day were equivalent to levels at the last day of depuration).
Spiked sediment study with 56-day accumulation period	Oligochaetes	**BSAF:** 1.1 **Uptake half-life:** Not calculated; apparent steady state reached by the first body burden measurement **Depuration half-life:** 50 days (kd: 0.0138/day; depuration was primarily due to growth dilution).
98-Day outdoor mesocosm study	Sediment and sediment organisms	Addition of 0.65 ppb a.i. to overlying water (4 applications, 7-day intervals) resulted in oligochaete and chironomid body burden levels of up to approximately 10,000 ppb. The highest residue levels in chironomids occurred at the last day of the study. Residue levels in other biota were somewhat lower.

5.4.3.2 Bioaccumulation Assessment Issues

The bioaccumulation assessment approach for Pesticide 4 was informed by the following key issues and findings.

Environmental Fate. The proposed use profile for Pesticide 4 (aerial and ground application on agricultural crops) suggests that pesticide drift, runoff and erosion into aquatic ecosystems is a potential concern. In aquatic ecosystems, the environmental fate profile (summarized in **Section 3.2.4**) suggests that Pesticide 4 will likely partition to organic matter such as suspended and bed sediments (Koc = 1,200,000 L/kg-OC) but will persist for relatively long periods of time (biotic metabolism and hydrolysis half lives > 100 days). The most rapid degradation pathway is expected to be photolysis (half-life 4.6 days). However, for agricultural ponds with typical turbidity (e.g., total suspended solids of 30 mg/L), photolysis is only considered important at or near the water surface due to light attenuation at greater depths. Given its propensity to partition to and persist in aquatic sediments (anaerobic aquatic metabolism half life > 1000 days), concern was raised for potential year-to-year "carryover" of Pesticide 4 that might result from successive pesticide applications over multiple years.

Ecological Receptors of Concern. The focus of the aquatic bioaccumulation assessment of Pesticide 4 included:

(1) Aquatic invertebrates via pesticide exposure from sediment, water and diet,
(2) Fish via pesticide exposure from water and diet, and
(3) Piscivorous wildlife through dietary exposure.

Exposure Routes. At log K_{OW} values of approximately 8, available aquatic food web bioaccumulation models suggest that dietary exposure of poorly metabolized organic chemicals can be a significant contributor to the bioaccumulation of Pesticide 4 by higher trophic level aquatic organisms (Arnot and Gobas, 2004, Fisk et al., 1998).

***In Vivo* Metabolism.** Available evidence from the bioconcentration and bioaccumulation studies indicates that *in vivo* metabolism by fish occurs (with depuration half lives of approximately 30 days), but appears to be considerably lower in invertebrates.

Time to Reach Steady State. Based on the accumulation kinetics from water-only exposure to bluegill, the time to reach 90% steady state accumulation is estimated to be approximately 100 days. This suggests that concentrations of Pesticide 4 in fish will not approach steady state within the time frame of the available guideline aquatic toxicity studies.

5.4.3.3 Empirically-Based Bioaccumulation Assessment

For estimating Pesticide 4 bioaccumulation in aquatic food webs, multiple lines of evidence were considered that reflect the availability of different bioaccumulation assessment methods (e.g., measured vs. modeled data) and availability of data that are not typically available for risk assessment such as an oral bioaccumulation study in fish. Careful consideration of a variety of approaches for assessing bioaccumulation was critical because each approach contains different strengths and limitations. Importantly, information derived from different bioaccumulation assessment approaches can be used in a complementary manner for improving the applicability of bioaccumulation assessments. For example, bioaccumulation models can assist in the interpretation and application of laboratory or field-based bioaccumulation estimates, and conversely, laboratory and field-based studies can be used to validate and improve model-based bioaccumulation estimates.

Modeling was conducted using methodology similar to those described previously for Example Chemicals 1 and 3 (Arnot and Gobas, 2004; Gobas, 1993). Methods that may be used to evaluate bioaccumulation using bioaccumulation studies and modeling are described below. A summary of the types of studies available to assess accumulation is presented in **Table 5.19**. This chapter discusses accumulation assessment methods for fish. A comparable assessment may also be performed in invertebrates. Details of the invertebrate assessment are not included in this white paper; however, available accumulation data in invertebrates are provided in **Tables 5.19 and 5.20**.

Table 5.19. Application of Empirical Bioaccumulation Studies for Pesticide 4

Taxonomic Group / Bioaccumulation Pathway	Study Type	Study Utility/Comment
Fish / water exposure	49-day lab study	Study used to estimate fish body burden

		from water exposure.
Fish / dietary exposure	56-day lab study	Study used to estimate fish body burden from dietary exposure. Rainbow trout were fed contaminated oligochaetes and were kept in non-treated water.
Sediment invertebrates / sediment exposure	28- and 56-day spiked sediment studies	Studies used to estimate benthic invertebrate body burden from exposure to contaminated sediments.
Sediment invertebrates / water (drift) exposure	98-day spiked water mesocosm study	Studies used to estimate benthic invertebrate body burden from exposure to spray drift. Chemical 4 was added to mesocosms 4 times with 7-day intervals.

(1) Laboratory Accumulation Studies in Fish

In fish, laboratory studies were used to evaluate bioaccumulation potential from both dietary and water column exposures. The contribution of body burden in fish from exposure to contaminated water was estimated using a 49-day spiked water bioconcentration study in bluegill using the following equation (Newman, 1995).

$$C_t = k_u \times C_l \frac{(1 - e^{-ke \times t})}{k_e}$$

C_t = concentration in the fish at time t
C_l = concentration in water associated with the LC50
k_u = uptake rate constant
k_e = depuration rate constant
t = time (days)

The analysis was conducted using water exposure EECs from PRZM/EXAMS and kinetics parameters from the water exposure bioconcentration study in bluegill sunfish. Although an analysis was performed using PRZM/EXAMS estimated EECs, the available data suggest that EECs are likely to be reduced to levels that are at or below the water solubility limit of Pesticide 4 within several days after it enters the water. Therefore, the water solubility of the chemical was ultimately used to estimate fish body burdens from water exposure, which resulted in a steady state tissue body burden of 4,000 µg/kg (4 mg/kg) as shown in **Table 5.20**.

Table 5.20. Estimated Tissue Concentration of Pesticide 4 in Fish from Contaminated Water

Range of 60-Day Surface Water EECs (µg/L)	Resulting Fish Body Burden (60-Day Exposure Duration, µg/kg / steady state estimate)
0.15 (solubility limit)	3,000 / 4,000 Used in Risk Estimation
0.1 – 0.6 (all uses)	2,000 / 2,700 to 12,000 / 16,000

Fish body burden from dietary exposures were estimated using an oral bioaccumulation study in rainbow trout and were added to the water exposure body burden. A biomagnification factor of approximately 0.11 was observed in that study where trout were fed oligochaetes that contained approximately 1 ppm of Pesticide 4. The lipid normalized BMF was 0.067 with a mean lipid content of 2.1% in fish and 1.4% in oligochaetes. Steady state was reached prior to the first analytical measurement of body burden; therefore, uptake kinetics rate constants could not be derived for dietary exposures. Fish tissue residues for use in risk assessment were calculated using the following Equation:

> Body burden in fish = lipid normalized BMF x (concentration in dietary food item / lipid content in food) x lipid content of assessed fish

Estimated fish body burden from dietary exposures are presented in **Table 5.21.** Total estimated body burden is also presented and was calculated by adding body burdens from water exposure and dietary exposures.

Table 5.21. Estimated Concentrations of Pesticide 4 in Fish Via Water and the Diet

Range of Estimated Pesticide 4 Levels in Food (mg/kg)[a]	Estimated Fish Body Burden from Dietary Exposure (mg/kg) [b]	Total Body Burden Dietary + Water Exposure (mg/kg)[c]
12 to 38	1.3 to 4.2	5.3 to 8.2

[a] Dietary values based on estimated body burdens in oligochaetes based on empirical studies.
[b] Body burden from dietary uptake estimated using a lipid-normalized BMF of 0.067
[c] Body burden from water exposure was calculated assuming steady state at the water solubility limit of 0.15 µg/L, which results in 4 mg/kg being added to the dietary body burden.

Only the analysis for fish is presented. However, a comparable analysis could also be performed for aquatic and benthic invertebrates using data from BCF and BSAF (biota-sediment accumulation factor) studies. For Pesticide 4, benthic invertebrate body burdens were estimated using data from short-term and long-term spiked sediment bioaccumulation studies and from a spiked water mesocosm study. The BSAF values from spiked sediment laboratory studies were used to estimate body burden from exposure to contaminated sediment, and the spiked water mesocosm study was used to estimate body burden from exposure to contaminated water (spray drift). The two exposure routes were evaluated separately because dramatic differences in accumulation were observed between the sediment and water exposure studies. Details of this analysis are not included as part of this white paper, but the principles are equivalent as those described for fish.

5.4.3.4 Modeling-Based Bioaccumulation Assessment

Pesticide tissue residues were also estimated for fish, benthic invertebrates, and other aquatic organisms using methodology from Arnot and Gobas (2004). This model was previously described in **Section 5.4.1.** The K_{OW} of Pesticide 4 is outside the range of well studied chemicals; therefore, there is considerable uncertainty in estimating its behavior and accumulation potential within an organism. Therefore, kinetics data obtained from oral and submersion bioaccumulation/ bioconcentration studies in fish and benthic organisms submitted

by the registrant were incorporated into the estimates where applicable. However, accumulation potential was evaluated with and without incorporation of kinetics parameters from laboratory studies to evaluate the sensitivity of accumulation estimates to incorporation of the kinetics parameters. The estimations assumed a log Kow of 8.1 and Pesticide 4 levels in surface and pore water of 0.15 µg/L, which is the solubility limit of the chemical. Note that this modeling exercise was a screen in that selected model inputs were chosen to produce high-end estimates of body burden. Uptake and depuration parameters in addition to ecosystem parameters from the submitted studies used to estimate body burden are listed in **Appendix D.**

In addition to biological parameters, ecosystem characteristics may also impact estimated body burden. Abiotic characteristics used for this assessment are defined in **Appendix D**. A brief explanation of the rational for the selection of the parameters is also provided in the appendix. Values for abiotic parameters were typically selected from national water quality data available from the NAWQA program (USGS, 2006).

(1) Modeling Results

Initially, body burdens were estimated without entering Pesticide 4 specific kinetics data (listed in Appendix D) from submitted accumulation studies (kinetics values were estimated from log Kow). The resulting estimations are in **Table 5.22**.

Table 5.22. Estimated Concentrations of Pesticide 4 in Using Default Parameterization of an Aquatic Food Web Model

Component	Estimated Residue Level (µg/kg, whole organism)	Lipid or Organic Carbon Fraction	Lipid Normalized Estimated Residue Level (µg/kg, lipid)
Sediment (in solid)	7,000	4%	175,000
Phytoplankton	200	0.5%	40,000
Zooplankton	1,000	2%	50,000
Benthic Invertebrates	100,000	2%	5,000,000
Filter Feeders	15,000	2%	750,000
Small Forage Fish	90,000	6%	1,500,000
Medium Forage Fish	100,000	6%	1,700,000
Piscivorous Fish	200,000	6%	3,300,000

Notes: Food web model based on Arnot and Gobas (2004). Ecosystem parameters defined in Appendix D.

The estimated body burdens in **Table 5.22** are considerably higher than those estimated using the empirical data presented in **Section 5.4.3.3**, particularly in higher trophic level organisms. These initial model runs based on estimated kinetics values do not account for metabolism by aquatic organisms or potential reductions in absorption due to the large size of Pesticide 4. In comparing the empirical kinetics values with those calculated using the Arnot and Gobas (2004) methodology, a striking difference in some the elimination constants is apparent.

The depuration constant observed in the water exposure BCF study in bluegill was 0.02, which is approximately 1000 fold higher than the k_2 value estimated using the Arnot and Gobas (2004) methodology and is approximately 16-times higher than the sum of k_2, k_e, and k_g (elimination/depuration from gills, fecal matter, and growth). This means that the empirical data indicates that Pesticide 4 is eliminated much faster than the modeling estimates indicate. This higher gill elimination rate determined from the empirical data may reflect metabolism of Pesticide 4 by fish. Incorporating the depuration rate constant of 0.023 and setting all other depuration and growth dilution constants to 0 dramatically reduces the estimated body burdens in fish (**Table 5.23**). All other elimination constants were set to zero because a total depuration rate constant is being used from the water exposure study. In addition, the depuration rate constant observed in an oral accumulation study is approximately 300-fold higher than the fecal elimination constant (ke) predicted using the Arnot and Gobas (2004) methodology and is approximately 50 fold higher than the sum of the elimination constants from the gills (k_2), digestive system (k_e), and growth (k_g). Incorporating the depuration rate constant of 0.067 and setting all other depuration and growth dilution constants to 0 also dramatically reduces the estimated body burdens in fish (**Table 5.24**).

The impact on fish tissue levels from incorporating the depuration constants from each exposure route (dietary and respiration) were evaluated separately from each other by assuming that all other elimination pathways are negligible (set to 0 in the model). Therefore, this screening analysis may result in high-end exposures because multiple elimination routes are likely to contribute to elimination of the pesticide in fish for each exposure route. The combined effect of incorporating both rate constants was not quantified.

Table 5.23. Estimated Concentrations of Pesticide 4 in Fish Using Measured K1 and K2 rate Constants with an Aquatic Food Web Model

Taxonomic Group	Estimated Body Burden (µg/kg, whole fish)	Lipid Normalized Body Burden Based on 6% Lipid (µg/kg, lipid)
Small Forage Fish	2400	40,000
Medium Forage Fish	1700	28,333
Piscivorous Fish	170	2,833

Notes: Food web model based on Arnot and Gobas (2004). Ecosystem parameters defined in Appendix D. A depuration rate constant value of 0.023 day^{-1} and an uptake rate constant of 600 day^{-1} were incorporated into the body burden estimation.

Table 5.24. Estimated Concentrations of Pesticide 4 in Fish Using a Measured Value for Measured K1 and Ke Rate Constants with an Aquatic Food Web Model

Taxonomic Group	Estimated Body Burden (µg/kg, whole fish)	Lipid Normalized Body Burden Based on 6% Lipid (µg/kg, lipid)
Small Forage Fish	840	14,000
Medium Forage Fish	600	10,000
Piscivorous Fish	25	418

a An uptake rate constant of 600 day^{-1} was incorporated into the body burden estimation as a k1 value, and the depuration rate constant of 0.067 was incorporated as a ke based on the oral bioaccumulation study. All other elimination and growth constants were set to 0.

A similar exercise could also be performed for benthic invertebrates by incorporating uptake and depuration kinetics into modeling.

5.4.3.5 Summary of Body Burden Estimates Using Various Methods

In conclusion, multiple methodologies were used to estimate fish tissue concentrations of Pesticide 4. Comparison of these methods indicates that the two methods that relied solely or partially on empirical data produced similar results. The analysis demonstrates the value of carefully evaluating model assumptions. These data are summarized in **Table 5.25.**

Table 5.25. Comparison of Estimated Concentrations of Pesticide 4 in Fish and Benthic Invertebrates Using Different Methodologies.

Method	Maximum Fish Tissue Estimate (µg/kg)
Empirical Accumulation Factors From Water an Diet	8,000
Model-based Estimates Using Empirically-derived Accumulation Kinetic Constants *	2,400
Model-based Estimates using Default Accumulation Kinetic Constants	200,000

* Based on Arnot and Gobas model (Appendix D) and measured K1 of 600 day $^{-1}$ and K2 of 0.023 day $^{-1}$

5.4.3.6 Evaluating Potential Dietary Risks from Bioaccumulation of Chemical 4

For evaluating potential risk to birds and mammals that may consume aquatic organisms, maximum-predicted concentrations of Pesticide 4 using the methods (except the default parameterization of the Arnot and Gobas model) were compared to available dietary toxicity reference values (**Table 5.26**). Dietary RQs indicate that the acute or chronic LOCs were not exceeded for birds or mammals, despite the high Kow and high persistence of Pesticide 4. This finding reflects reduced bioaccumulation potential as determined from empirical and model-based bioaccumulation methods that were supplemented with measured parameters for accumulation kinetics. This evaluation demonstrates the utility in carefully evaluating model assumptions and collecting additional data to resolve model uncertainties.

Table 5.26. Dietary RQs Used To Estimate Potential Risk To Birds And Mammals From Consumption Of Aquatic Animals

Taxomonic Group Consumed	Estimated Levels in Food (mg/kg)	Birds		Mammals
		Acute Dietary RQ (LC50: 1308 ppm)	Chronic Dietary RQ (NOAEC: 157 ppm)	Chronic Dietary RQ: NOAEC: 200 ppm
Fish	8	0.006	0.05	0.04
Aquatic Invertebrates	38	0.029	0.24	0.19

5.5 ASSESSING TERRESTRIAL BIOACCUMULATION

Currently, OPP assesses risks of pesticide exposures to non-target, terrestrial animals that consume contaminated plants and insects on application sites. This approach, which involves the T-REX model (USEPA, 2006), simulates exposures through dietary uptake within one year of the pesticide application. T-REX does not account for pesticide exposures to non-target animals through dermal contact or inhalation exposure. Although OPP has other tools available to refine risks to non-target terrestrial animals exposed to pesticides through inhalation and dermal contact (i.e. the Terrestrial Investigation Model), these exposure pathways are generally not incorporated into baseline assessments. In addition, T-REX does not account for bioconcentration or bioaccumulation of pesticides within food items of terrestrial animals. Pesticide concentrations estimated within one year of applications to crops on a treatment site may not be protective of pesticide concentrations on vegetation adjacent to treatment sites that have been receiving pesticide mass through spray drift over multiple years of applications, assuming the pesticide is persistent in the terrestrial environment. The extent to which T-REX estimates of exposures to non-target terrestrial animals on treatment sites is expected to relate to exposures to these animals resulting from bioaccumulation on non-target sites is unknown.

Pesticide bioaccumulation in terrestrial ecosystems has rarely been incorporated into past ecological risk assessments conducted by OPP. At this time, OPP does not have specific data requirements or sufficiently vetted tools to estimate pesticide bioaccumulation in terrestrial ecosystems. . Current OPP pesticide data requirements and tool development efforts have been focused on identifying potential bioaccumulation of pesticides in aquatic ecosystems. These data do not typically lend themselves to evaluating bioaccumulation of pesticides in terrestrial ecosystems.

The scientific literature reports detections of pesticides in non-target terrestrial plants, suggesting that these pesticides have concentrated in terrestrial plants and have the potential to bioaccumulate in terrestrial food webs. Terrestrial bioaccumulation monitoring studies generally include historical use pesticides (HUPs) that are no longer in use in the United States (*e.g*. DDT, aldrin, heptachlor, dieldrin). Some current use pesticides (CUPs), such as endosulfan, trifluralin, triallate, chlorpyrifos and dacthal, have been detected in terrestrial plants in non-target areas (Kelly *et al*. 2007, Landers *et al.* 2008). Little monitoring data are available for terrestrial bioaccumulation of CUPs, since these pesticides are rarely included as analytes in terrestrial bioaccumulation studies.

Monitoring studies which suggest that pesticides could bioaccumulate in terrestrial ecosystems indicate a need to evaluate bioaccumulation in terrestrial ecosystems. Monitoring data are useful for characterizing environmentally relevant concentrations of a pesticide. However, these data have limited utility for OPP because: 1) they do not allow for the connection between specific pesticide applications and observed concentrations; 2) monitoring data are not generally targeted to detect high-end concentrations of a pesticide in the environment; 3) monitoring data are available for a limited number of CUPs; and 4) monitoring data are only useful for chemicals that are already in use and cannot be used to identify the bioaccumulation potential of a new chemical that has not previously been released into the

environment. In order to assess and prevent pesticide bioaccumulation and associated risks in terrestrial ecosystems, there is a need to identify suitable simulation models and types of data that would serve this purpose.

The text below includes a generic conceptual model depicting terrestrial bioaccumulation and discusses models available in the literature that assess bioconcentration or bioaccumulation of chemicals in terrestrial ecosystems. Potential data needs for assessing the bioaccumulation of pesticides in terrestrial habitats will be influenced by the specific model, but are generally discussed below.

5.5.1 Conceptual Model for Bioaccumulation of Pesticides in Terrestrial Organisms

Once a pesticide is in the air, it can be transported to non-target terrestrial ecosystems through air movements. These non-target sites could be at different spatial locations in relation to the pesticide application site (*i.e*. near field or hundreds of miles away). In the air, a pesticide can be present as a gas, dissolved in water in the air or sorbed to particulates suspended in the air. While in the air, a pesticide may be degraded by direct photolysis, or by the action of atmospheric oxidants (ozone, hydroxyl radicals, nitrate radicals). **Figure 5.14** presents a simple conceptual model where a pesticide present in the air can be deposited onto soil and terrestrial organisms (plants and animals). Once a pesticide is deposited onto a terrestrial habitat, plants can bioconcentrate that pesticide through uptake from direct deposition and through the soil. Animals can bioaccumulate the pesticide through uptake of the pesticide from the air (inhalation) and through consumption of plants or other animals containing the pesticide. Although not depicted in **Figure 5.14**, pesticide mass within an organism can be lost via elimination and metabolism.

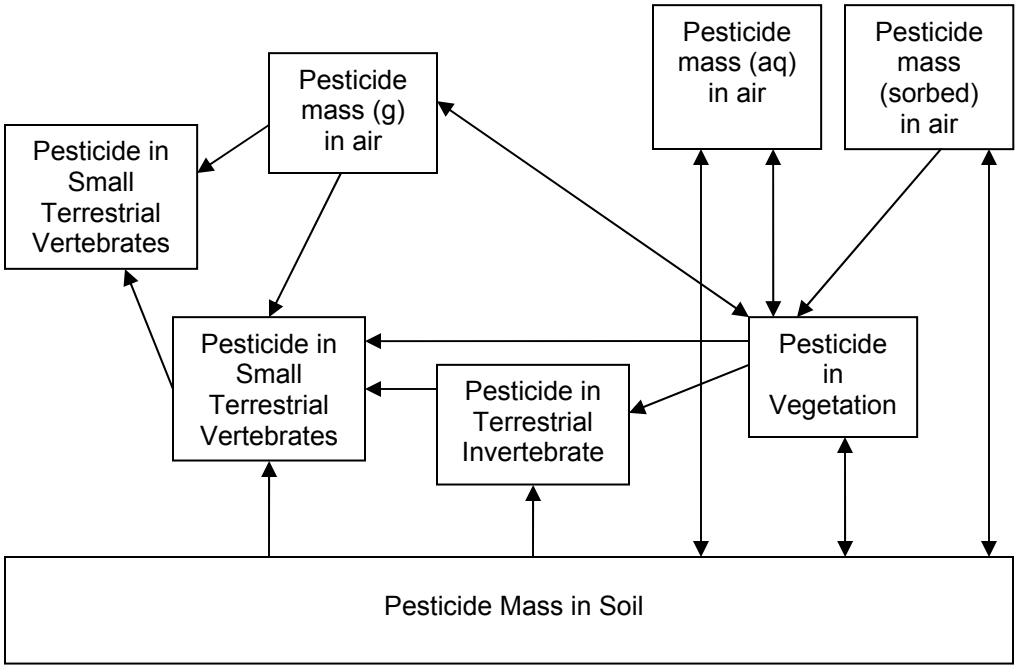


Figure 5.14. Conceptual Model Depicting Pesticide Deposition and Bioaccumulation in a Terrestrial Ecosystem. (Arrows represent movement of pesticide mass from one compartment to another)

Plants represent a logical beginning point for considering terrestrial bioaccumulation because of their crucial roles within ecosystems as food sources, their relatively large amount of biomass compared to other organisms in ecosystems, their stationary locations within habitats and their contact with air and soil. As indicated in **Figure 5.14,** plants can uptake chemicals from 1) air, 2) precipitation, 3) dry deposition and 4) soil. Plants can bioconcentrate a chemical through all of these transport pathways, although the relative contributions of the pathways to the overall bioconcentration will likely be disproportionate and will depend upon the chemical's characteristics (*i.e*. vapor pressure, hydrophobicity, solubility).

Volatile and semivolatile organic chemicals (VOCs and SOCs, respectively) would be expected to partition from air to plants. Plant tissues likely to concentrate organic chemicals include: lipids, cutin (Welke *et al*. 1998; Moeckel *et al*. 2008) and lignin. Since leaf surfaces are composed of cutin, organic chemicals would be expected to adsorb to the leaf surface from air or precipitation. Welke *et al*. (1998) derived partition coefficients between tomato cuticles and air for over 30 VOCs and indicated that these values could be correlated with the boiling point, vapor pressure and octanol-air partition coefficient of the chemical. Moeckel *et al.* (2008) indicated that partitioning of PCBs from air into plant cuticles was dependant upon the chemical's octanol-air partition coefficient (K_{OA}) as well as inherent plant characteristics, with different uptake for different plant species. Chemicals present in rainwater, fog or snow would be deposited on plants as the precipitation contacts plant surfaces. K_{OW} values would likely correlate plant uptake of pesticides from precipitation (Kelly and Gobas 2003). Hydrophobic organic chemicals would be expected to be sorbed to particulates present in the air. Plants would be exposed to these particulate-bound chemicals through deposition of contaminated particulates. Plants can also uptake chemicals from the soil. Chemicals can be present in pore water or sorbed

to soil particulates. This process of chemical uptake is exploited in cases where phytoremediation is used to "clean up" contaminated soils using plants that translocate chemicals from soil to above ground plant tissues.

Researchers have noted differences in bioconcentration of SOCs by various plant species (Bohme *et al*. 1999; Komp and McLachlan 1997). These differences could be attributed to specific characteristics of plant species including: lipid content, leaf surface area, overall plant surface area, cuticle thickness, and root zone mass. As part of the consideration of terrestrial bioconcentration and bioaccumulation models, the factors that lead to interspecies differences in bioconcentration in plants need to be identified. These factors can then be appropriately represented in simulation models.

Once within a plant, a chemical can be translocated to different plant tissues. This is a concern for modeling bioaccumulation because translocation could result in higher or lower chemical exposures to animals consuming plants, based on the part of the plant animals consume. In addition, chemicals can be lost from the plant due to metabolism to chemicals not of concern, or due to volatilization or evapotranspiration from plant surfaces.

Terrestrial animals can also bioconcentrate chemicals from contacting soil, drinking water, breathing air or sorption of a chemical to the animal's skin (from particulates, precipitation or air). Terrestrial animals bioaccumulate chemicals from consuming plants with the chemical or preying on animals containing tissue residues of the chemical. Similar to what occurs in plants, the chemical could be lost from animal tissue due to metabolism to degradates not of concern. The chemical could also be lost through respiration or elimination of wastes.

5.5.2 Existing Terrestrial Bioaccumulation Models

There are several simulation models reported in the scientific literature that estimate bioconcentration and bioaccumulation of persistent organic chemicals, including pesticides, in terrestrial organisms. Several fugacity-based models estimate the partitioning of organic chemicals from air to vegetation (Riederer 1990, Trapp and Matthies 1995, Tolls and McLachlan 1994), from soil to vegetation (Chiou *et al*. 2001) and from water to vegetation (Riederer 1990). Models are also reported in the literature for describing the bioaccumulation of chemicals in terrestrial animals consuming plants and other animals (Kelly and Gobas 2003, Armitage and Gobas 2007). These models are also fugacity based and rely on chemical characteristics to estimate chemical concentrations in plant and animal tissues. They require an estimate of the concentration of the modeled chemical in the environment. A summary of the inputs and outputs of selected terrestrial bioaccumulation models is provided in **Table 5.27**.

Table 5.27. Summary of Selected Terrestrial Bioaccumulation Models

Source	Ecosystem component	Necessary chemical-specific parameters	Transport pathway	Outputs
Reider 1990	Plant (broadleaf)	K_{OW} K_{CW} solubility (aqueous) vapor pressure	Air (gas) → Plant Air (precipitation) → Plant	- Concentration of chemical in different leaf tissues - Chemical bioconcentration from air to vegetation
Tolls and McLachlan 1994	Plant (grass)	Molecular mass Molar volume Henry's Law Constant (H) K_{OW} Enthalpy of vaporization	Air (gas) → Plant	Concentration of chemical in different leaf tissues
Chiou et al. 2001	Plant	K_{POM} K_{OC}	Soil Pore Water → Plant	Concentration of chemical in plant
Trapp and Matthies 1995	Plant	K_{OW} K_{AW}	Soil → Plant Air (gas) ↔ Plant Air (precipitation) → Plant	Concentration of chemical in plant
Kelly and Gobas 2003	Lichen Caribou Wolf	Vapor pressure K_{OA}	Air (gas) → Plant Air (precipitation) → Plant Plant → Caribou Air (gas) → Caribou Air (gas) → Wolf Caribou → Wolf	- Concentration of chemical in lichen - Concentration of chemical in caribou - Concentration of chemical in wolf - Biomagnification factors
Armitage and Gobas 2007	Earthworm Shrew	K_{OW} K_{OA}	Soil ↔ Earthworm Soil → Shrew Earthworm → Shrew	- Concentration of chemical in earthworms - Concentration of chemical in shrew - Biota Soil Accumulation Factors
K_{CW} = cuticle-water partition coefficient K_{POM}= plant-organic matter partition coefficient				

Based on modeling results of work by Kelly and Gobas (2003), Armitage and Gobas (2007) and Kelly *et al*. (2007), these researchers concluded that biomagnification in terrestrial food chains could be linked to K_{OA}. They concluded that chemicals that do not metabolize within organisms and have high K_{OA} ($>10^5$) and $K_{OW} > 10^2$ have the potential to bioaccumulate and biomagnify in terrestrial food chains. Two of the example pesticides discussed in this white paper (Pesticides 1 and 2) are semi volatile and persistent in air and therefore, have the potential to move through the air from target sites to non-target terrestrial habitats. Based on the estimated K_{OA} values of Pesticides 1 and 2 ($10^{8.6}$ and $10^{7.4}$, respectively), the results of these researchers indicate that these two pesticides have the potential to biomagnify in terrestrial ecosystems.

Considering the conclusions of Kelly and Gobas (2003), Armitage and Gobas (2007) and Kelly *et al.* (2007) regarding the utility of K_{OA} in predicting biomagnification in terrestrial habitats, OPP's current reliance on K_{OW} to predict bioaccumulation in aquatic habitats does not necessarily extend to predict bioaccumulation in terrestrial habitats. For example, a chemical that has a low Log K_{OW} (*i.e.* <4) may not be considered to be of concern for aquatic bioaccumulation. But if that chemical has a Log K_{OA} >5, it may biomagnify in terrestrial ecosystems.

5.5.3 Current Terrestrial Bioaccumulation-Related Data Requirements

OPP requires several studies that can provide insight for the bioaccumulation potential of a pesticide in terrestrial organisms. For example, OPP receives data that can be used to determine whether or not a chemical can be expected to metabolize within plants and livestock (guidelines 860.1300 and 860.1480). Such data can also be gleaned from mammalian bioassays (*e.g*., 2-generation rat reproduction study). Although not designed with the intent of quantifying bioaccumulation *per se*, these data on *in vivo* metabolism have direct relevance for assessing bioaccumulation potential because they provide an understanding of pesticide metabolism by plants and mammals. Metabolism is important for assessing bioaccumulation because as the metabolism rate of a chemical increases, its bioaccumulation potential decreases (assuming that this chemical is metabolized to degradates that are not of concern). Lack of understanding of the magnitude and nature of *in vivo* metabolism by organisms is a major source of uncertainty in both aquatic and terrestrial bioaccumulation modeling.

OPP also reviews monitoring data on the occurrence of pesticides in the environment, which may include terrestrial food webs. Such studies can provide insight to the spatial extent and magnitude of accumulation of a pesticide by terrestrial organisms. As discussed previously, these studies are often much less common than those involving aquatic food webs and are typically limited in the characterization of exposure concentrations--- a component needed for assessing the relative magnitude of bioaccumulation or bioconcentration potential.

As shown in **Table 5.27**, the K_{OA} of a chemical can be used in the context of available models for estimating bioaccumulation in terrestrial food webs (Kelly and Gobas, 2003; Armitage and Gobas, 2007; Kelly *et al*., 2007). Experimental measurements of K_{OA} are not routinely required for pesticides at this time, but could be required on a case-by-case basis or estimated using quantitative structure activity relationships (QSARs), such as those in the

KOAWIN portion of EPISUITE v.3.20 (USEPA, 2007a). K_{OA} can also be calculated using the K_{OW} and Henry's Law constant of a chemical.

6. ASSESSING LONG-RANGE TRANSPORT

6.1 INTRODUCTION

Pesticides can enter the atmosphere through spray drift, volatilization from the soil surface and/or wind erosion of soil particles. They can enter surface water via spray drift, runoff, and erosion during or shortly after their application and via wet or dry atmospheric deposition following longer periods after their application. Once entered into a transport media such as air or water, a pesticide has the potential for long-range transport (LRT) from its point of release to a remote region, typically hundreds of miles distant from its use site, provided the pesticide persists. Long-range transport may also occur through successive events of short-range deposition and revolatilization of the compound. The long-range transport potential (LRTP) of chemicals can be predicted from their intrinsic properties such as volatility, water solubility, adsorption/desorption, and their longevity in various media, usually expressed as the degradation half-lives. Monitoring data are considered to provide the most reliable evidence of long-range transport. In the past, OPP has utilized publicly available reports and open literature to characterize the long-range transport of some semi-volatile persistent compounds. However, the following issues have emerged that are likely to be important considerations toward characterizing long-range transport of pesticide during risk assessment.

- Current OPP risk assessment methods are based on near-field exposure. To address regional and global distribution of persistent chemicals, OPP would likely rely on existing scientific methods and the implementation of international standard criteria.

- Monitoring data can provide definitive evidence of LRT of substances, but these data have limitations for providing quantitative estimates of chemical loading to various environment media from specific uses. In other words, establishing the relationship between near field loadings and far-field concentrations is typically highly uncertain. Since there are uncertainties related to loading, the determination of environment exposure from LRT can only be addressed qualitatively. Furthermore reliance on monitoring data alone does not provide a mechanism to screen chemicals for LRT potential prior to their release to the environment.

- Due to the complexity of inter-media mass transfer and the multitude of dissipation processes involved, the scientific basis for understanding the global fate has not yet been fully established. However, a number of multimedia models have emerged to provide screening assessments of environmental persistence and long-range transport. Application of available screening models is critical in determining LRTP of pesticides, specifically for new chemistries.

These issues are considered important because addressing them helps to define the scope of LRT assessment and the methods that are most suitable. Therefore, the scientific aspects of LRTP, the challenges and methods associated with characterizing the LRTP of pesticides are

reviewed and presented in the following sections. Also, brief descriptions of existing international and regional treaties to address LRTP of these compounds are included. Case studies of two example pesticides are presented to illustrate a screening-level characterization of the LRTP using existing models. In addition, overall environmental persistence (Pov) and LRTP of selected chemicals were estimated using a screening tool.

6.2 REGIONAL AND GLOBAL REGULATORY EFFORTS ON LONG-RANGE TRANSPORT OF CHEMICALS

Persistent organic pollutants (POPs) are a class of organic chemicals exhibiting the combined properties of persistence, bioaccumulation, toxicity (PBT), and long-range environmental transport. Although not all definitions of PBTs include a specific LRT criterion, many do have a criterion for persistence in the atmosphere, which to a large extent determines the potential for LRT. The propensity of long-range transport of POPs and PBTs has prompted national, regional and international efforts to prohibit, restrict, or reduce the production and commerce of certain POPs and PBTs described below.

6.2.1 National efforts

The United States has taken a leading role to reduce and/or eliminate the release of persistent chemicals on both a local and regional basis. At local level, the EPA is engaged in a variety of initiatives on PBT chemicals. Examples of EPA's proactive efforts include EPA's PBT program to coordinate action regarding these pollutants (www.epa.gov/pbt), the Toxics Release Inventory (TRI) PBT reporting requirements under the Emergency Planning and Community Right-To-Know Act (EPCRA) (www.epa.gov/tri/pbtrule.htm), the prioritization accorded PBT parameters when evaluating new chemical notifications under the Toxic Substances Control Act (TSCA).

To address LRT of semi-volatile persistent chemicals, OPP has used registrant-submitted and open literature monitoring data and modeling results to characterize the exposure and LRT of substances. However, Registrant generated ecotoxicity data were not designed to address potential effects on native species of remote regions, which leads to uncertainty in determining potential pesticide risks due to exposure via LRT. Furthermore, registrant-submitted environmental fate data may not be relevant to the environmental conditions of remote regions.

Current OPP-approved models are not capable of estimating pesticide exposure from various uses beyond the near-field environment. Potential mechanisms of transport of pesticides to and from the atmosphere, such as secondary volatilization and condensation, wind erosion of soil, and wet and dry depositions, can only be discussed qualitatively. FIFRA does not specifically address characteristics PBT pesticides and the issue has not been resolved of whether concern exists based on the sheer persistence and long-range transport of a chemical apart from any hazard determination. However, the distribution of a chemical over a regional or global scale and the issue of global loading should be characterized even if the law does not specify it as a restriction. Since FIFRA provides limited regulatory options specifically for pesticide with PBT characteristics, in the past, OPP has severely restricted the use of this type of chemicals or encouraged registrants to withdraw their products voluntarily from the market based on adverse

effects on human health and environmental risks. However, for new pesticides, there is no mechanism under the current FIFRA to characterize presumptive PBT profile of new substances.

6.2.2 Regional Efforts

In 1993, Canada, Mexico, and the United States established the Commission for Environmental Cooperation (CEC) under the North American Agreement on Environmental Cooperation (NAAEC) to address transboundary environmental concerns, help prevent potential trade and environmental conflicts, and promote the effective enforcement of environmental law. The NAAEC complements the environmental provisions of the North American Free Trade Agreement (NAFTA). Under the auspices of the NAAEC, Mexico, Canada, and the United States have developed a regional initiative on the sound management of chemicals. This initiative was formally adopted in October 1995. Under this initiative, the CEC can develop Regional Action Plans, which identify activities that reduce or eliminate risks from chemicals of concern. The CEC has already established such plans for PBTs such as PCBs, DDT, and chlordane and is developing an action plan for dioxins, furans, and hexachlorobenzene.

In 1997, Canada and the United States signed an agreement entitled "Virtual Elimination of Persistent Toxic Substances in the Great Lakes". This agreement is based on the "Revised Great Lakes Water Quality Agreement" of 1978 and covers a range of organochlorines, Polycyclic Aromatic Hydrocarbons (PAHs) and other POPs/PBTs as well as certain compounds containing metals such as mercury, cadmium, lead and tin. Although the focus of the treaty is on reducing pollution of the Great Lakes by point source emissions from within the United States and Canada, long range transport from worldwide sources is also considered explicitly. The strategy sets long-term goals to promote reductions in toxic substance emissions.

6.2.3 Global Efforts

In 1998, the United States signed a legally binding protocol with other member nations (including European countries, Canada, and Russia) of the United Nations Economic Commission for Europe (UNECE) on POPs under the Convention on Long-Range Transboundary Air Pollution (LRTAP). This agreement seeks to eliminate production and reduce emissions of POPs in the UNECE region and addresses a list of 16 substances that have been singled out according to established risk criteria. The listed substances comprise eleven pesticides, two industrial chemicals and three by-products/contaminants. Elements from the LRTAP POPs protocol were used in negotiations for the Stockholm Convention discussed below.

In 2001, the United States signed the Convention on POPs in Stockholm, Sweden. This agreement is much broader than the UNECE POPs protocol since it also includes many non-European and developing nations. The Stockholm Convention was signed by 151 nations in May 2001 and has been subsequently ratified by 115 nations as of January 2006. Canada and Mexico are parties to the Convention and the United States has signed, but not ratified the Stockholm Convention. Additional information on the Stockholm Convention can be found at the URL: www.pops.int. Under the Convention, countries commit to reduce and/or eliminate the production, use, and/or release of the 12 POPs of greatest concern to the global community and

the signatores further agree to establish a mechanism by which additional chemicals may be added to the Stockholm Convention in the future. This treaty established the following criteria to screen potential long-range transport of a chemical:

- Measured levels of the active substance in locations distant from the sources of its release that are of potential concern;
- Monitoring data showing that long-range environmental transport of the active substance, with the potential for transfer to a receiving environment, may have occurred via air, water or migratory species; or
- Environmental fate properties and/or model results that demonstrate that the active substance has a potential for long-range environmental transport through air, water or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For an active substance that migrates significantly through the air, its half-life in air should be greater than two days.

The United States along with 71 other countries and the European Community also have signed the Rotterdam Convention on the Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals and Pesticides in International Trade, building on a 10-year-old voluntary program. The PIC Convention identifies pesticides and industrial chemicals of concern, facilitates information sharing about the risks associated with these chemicals, and provides countries with an opportunity to make informed decisions about whether the chemicals should be imported. Some of the POP/PBT substances are already on the PIC list.

6.3 MECHANISMS OF LONG-RANGE TRANSPORT

Specific physicochemical properties of pesticides that are critical to understanding their movement through the abiotic and biotic environment include water solubility, vapor pressure (VP), Henry's Law constant (H), dissociation constant (pK_a), partition coefficients including octanol-air (K_{OA}) and octanol-water (K_{OW}), and the sorption coefficients of soil and sediment (K_{OC}). These properties are responsible for a chemical's propensity to move from one environmental compartment to another and influence its susceptibility to additional abiotic and biotic degradation processes. Transformation or degradation reactions such as biodegradation, hydrolysis, and photolysis in various media are important, however, they may also result in degradation products that are more persistent and/or toxic than the parent. The dissipation and degradation rates in various media will vary depending on the physicochemical characteristic of a compound. Detailed discussion of these properties for the selected pesticides can be found in **Section 3.2.**

The physicochemical properties of a compound as well as agricultural practices, application methods and meteorological conditions influence the movement of pesticides into various environmental media or compartments and dictate LRTP. The inter-media mass exchange processes between air, water (fresh and marine), soil, and sediment, and the transformation in these media under spatially and temporally variable environmental conditions play key roles in controlling the fate and dissipation of a compound (Mackay et al., 2006). **Figure 6.1** depicts a simple conceptual model of LRT, which includes the transport mechanisms of compounds from a use site into various environmental media. Various transport media are

further divided into recognized subcompartments (Mackay et al. 2006) such as aerosol particles in air, snow and ice, vegetation (both below and above ground) and suspended particles or colloids in water. In most cases, environmental partitioning is dominated by the abiotic media (Roden, 1999 and Mackay et al. 2006, thus assessments of chemical fate often focus on how the mass of a chemical partitions between the abiotic media.

The atmosphere is the most mobile of the environmental media and as such, air is a major mode for LRT. Once airborne, pesticides may move into the upper atmosphere for more widespread regional, and possibly transcontinental (global) distribution **(Figure 6.1**). Also, pesticides may reversibly deposit on terrestrial surfaces close to the application site and still be transported over large distances, even global scales, through successive cycles of deposition and re-emission as result of temperature, precipitation, and latitude differences known as "global distillation or fractionation" (Wania and Mackay, 1996). However, for non-volatile substances, transport along rivers and through the ocean currents could result in regional redistribution of persistent chemicals. Furthermore, in specific cases, migratory animal species and drifting ice can play roles in the LRT of chemicals. Researchers have concluded that the contribution volume of biotic media for LRT is usually small relative to abiotic media (Mackay et al. 2006).

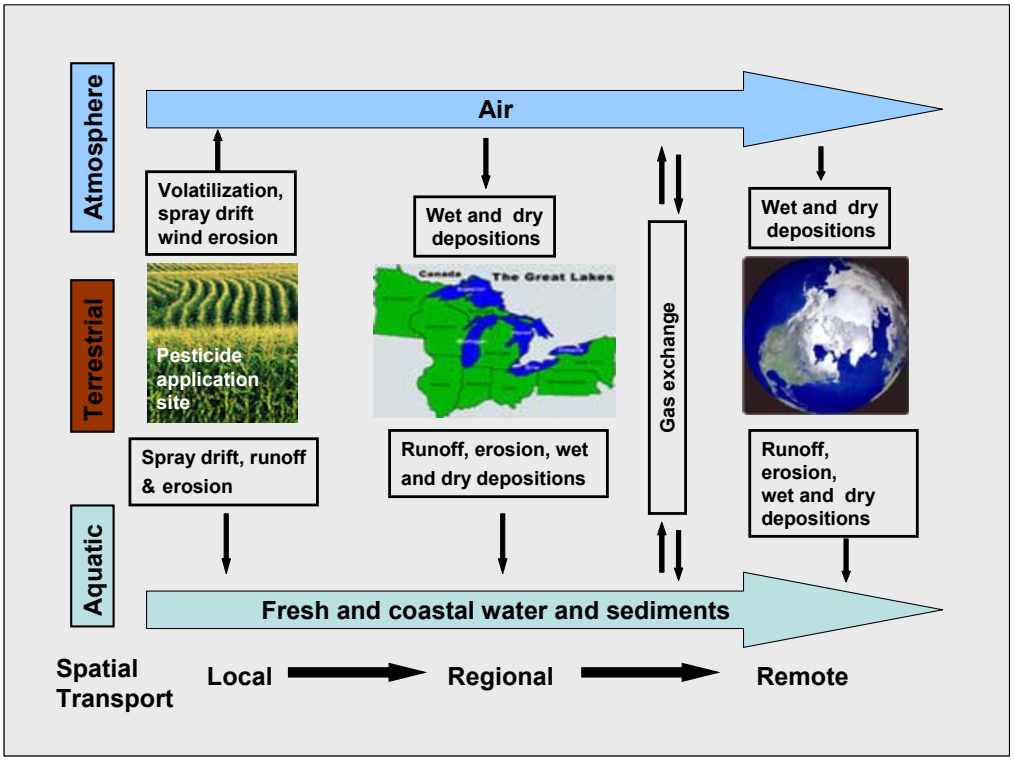


Figure 6.1. Conceptual Model Depicting Long-range Transport Potential of Persistent Substances

Wania and Mackay (1993) hypothesized that the physicochemical properties of chemicals and certain factors characterizing cold climates, contribute to the lasting spatial distribution of many persistent chemicals. Generally, emissions to and releases from each environmental media will differ for each chemical. Robust transport equations exist in most cases to describe inter-media transport processes, but there is uncertainty about specific input parameter values for these

multi-media models. In general, for most non-polar chemicals, the key media that control persistence have been identified. Partitioning and transport processes that are essential components of any mass-balance model can be expressed by using fairly robust and reliable equations (Klecka et al., 1998). However, researchers are continuing to work in resolving the uncertainties associated with predictions of transport and partitioning at global scale for multimedia modeling. While many of these models have been parameterized, there is considerable uncertainty in the appropriate input values.

6.4 AVAILABLE METHODS FOR ADDRESSING LRT ISSUES

6.4.1 Monitoring Studies

Many monitoring studies have shown that PBT chemicals are subject to LRT (Hargrave et al., 1998; Iwata et al., 1993; Barrie et al., 1992). Monitoring of biological samples (Ockenden et al., 1998; Barrie et al., 1992; Muir et al., 2002; Norstrom et al., 1988) has provided evidence that these chemicals are prone to bioaccumulation as well. Monitoring of PBTs is recognized as an essential tool in the evaluation of persistence and LRT. Measured levels of PBT chemicals in remote locations distant from use sites can unambiguously satisfy the long-range transport criterion. Many other international treaties as well as some national or regional regulations discussed earlier, also include monitoring data as a measure of the ability of a substance to undergo LRT. Thus, the physicochemical and environmental fate properties coupled with monitoring data represent a matrix of information used to characterize whether a compound should be classified as a PBT and has LRTP. The obvious limitation to this approach is that monitoring data would not likely exist for newer chemistries being considered for registration.

6.4.2 Modeling Approaches to determine LRTP

In order to understand the long-range transport potential of a compound, it is necessary to consider if multimedia environmental partitioning and degradation processes can substantially remove the substance. In response, a number of multimedia models have emerged. Detailed information on the development of multimedia models and their significance can be found in Wania and Mackay (1999).

The most widely used multimedia models (fugacity level I, II, and III) are the mass-balance Mackay-type compartment models (McKone and MacLeod, 2003). The Level III model is more complex and realistic than Level I and Level II models. The Level III model estimates the steady-state of a chemical between a number of well-mixed compartments which are not at equilibrium. This model also assumes a simple, evaluative environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, and sediment. This model gives a more realistic description of a chemical's fate including the important degradation and dissipation losses and intermediate transport processes.

Recently, a Level-IV model has been used to evaluate persistent chemicals (Sweetman et al, 2002 and McKone and MacLeod, 2003). The Level-IV model is a dynamic model, which is

an extension of the preceding steady-state (level I, II, and III) models that comprise the equilibrium criteria model. According to Sweetman et al. (2002), the Level IV model is particularly suited for describing the long-term (multiyear or multi-decade) behavior of known persistent chemicals that have accumulated in soils and sediments, and the model can identify new chemicals that have the potential to accumulate in soils and sediments over long periods of time and result in long recovery times.

During recent years, researchers have developed several multimedia models that compute numerical indicators for overall persistence (*P*ov), which account for degradation half-lives in individual media, environmental partitioning, and a model-specific measure for the long-range transport potential. Both the scientific and the regulatory communities have identified multimedia models as valuable tools for providing additional insight in screening assessments of environmental persistence and long-range transport (Roden et al., 1999 and Klecka et al., 2000).

A number of multimedia models are available for calculating *P*ov and LRTP for chemicals. Each model differs in construct, parameterization, and definitions of metrics. Detailed information on nine publicly available models (ChemRange, ELPOS, CalTOX, SimpleBox, Impact 2002, CEMC LIII and LII, Globo-POP, and BETR North America) can be found in **Table 1** and **2** in Fenner et al. (2005). All models except Globo-POP assume steady-state conditions (level III). Fenner et al. (2005) used a set of 3175 fictitious chemicals with a broad range of partition coefficients and degradation half-lives to evaluate the above models' performance in calculating Pov and LRTP. Rankings of the fictitious chemicals according to Pov and LRTP are relatively similar across the models evaluated and are largely determined by the chemical properties. The authors also identified the domains of chemical properties outside of which the models were likely to result in significantly different results, and they provided guidance to select the appropriate model to evaluate Pov and LRTP for chemicals with unusual chemical properties.

For LRT modeling, it has been demonstrated that a chemical's persistence in the transport medium (air or water) strongly governs the travel distance (Rodan et al., 1999; Klecka et al., 2000). Several comparative studies (Fenner et al., 2005; Scheringer et al., 2004) have concluded that most models predict similar rankings of LRTP values for sets of chemicals encompassing widely varying physico-chemical properties. The Organization for Economic Co-operation and Development (OECD) expert group developed a screening tool to estimate *P*ov and LRTP. The OECD Tool is a consensus model of environmental fate and transport for organic chemicals. The tool can be freely downloaded from the OECD website (http://www.oecd.org/document/17/0,3343,en_2649_34373_40754961_1_1_1_1,00.html). Results from the Tool do not estimate exposure in the environment but provide results to compare with pre-classified POPS according to their environmental persistence and potential for LRT.

6.5 CASE STUDIES FOR LONG-RANGE TRANSPORT

Of the 4 pesticides discussed at this SAP, the LRTP of 2 pesticides was characterized in OPP's ecological risk assessments. These pesticides were Pesticide 1 and Pesticide 2.

6.5.1 Pesticide 1

Pesticide 1 consists of two enantiomers (parent isomer "P1" and "P2"). Technical grade Pesticide 1 typically consists of a mixture of the two enantiomers in the ratio 30:70 (P1:P2). The P1 isomer is more volatile and dissipative, while the P2 isomer is generally more adsorptive and persistent. Both P1 and P2 can be oxidized to the principal degradate (D1) via biotic metabolism. The D1 degradate is of comparable acute toxicity to its parent, but it is more persistent than the parent. Estimated half-lives for the combined toxic residues (P1+P2+D1) range from several months to several years. The semi-volatile property of Pesticide 1 enables it to be transported through vapor and spray drift to multiple media, while its moderate adsorptive and persistence properties enable it to stay in the environment for an extended period. Pesticide 1 can be transported via runoff to surface water bodies or via dust dispersion to atmosphere and as a result redeposit to different areas.

Monitoring studies suggest that residues of Pesticide 1 volatilize and continue to recycle in the global system through a process of migration and redeposition via wet and dry depositions as well as air-water exchange in the northern Hemisphere. Local and regional monitoring data indicate that Pesticide 1 is moving through various environmental media such as air, water, and sediment. However, these data likely under-represent actual field residues, since monitoring efforts are mostly non-targeted. Data from non-targeted monitoring also pose uncertainties in spatial and temporal distributions of Pesticide 1 residues in relation to Pesticide 1 use. Because of the volatility of Pesticide 1 and its propensity to partition into air (high K_{OA}) and its resistance to degradation in the atmosphere, coupled with the persistence of degradate 1 (D1), total residues of this compound (P1, P2 isomers plus degradate D1) have been documented to travel considerable distances from known use sites.

The occurrence of Pesticide 1 in remote regions like the Great Lakes (Sun *et al.,* 2003 and 2006), Arctic (Hung et al., 2002), and mountainous areas of Western states (McConnell et al., 1998; Blais et al., 1998; Carrera et al., 2002) are well documented. Dust dispersion and translocation also contribute to atmospheric loading of Pesticide 1 as adsorbed phase onto suspended particulate matter, but this process does not appear to be as major a contributor as volatilization.

6.5.2 Pesticide 2

Pesticide 2 is a moderately volatile compound that can be expected to dissipate through volatilization; however, this route of dissipation from the soil is minimized for many uses by incorporation of the pesticide into the soil at application. Volatilization, however, is likely to be a more significant route of dissipation of the parent and degradate (D1) when Pesticide 2 is not incorporated. This will occur when the pesticide is applied as a foliar spray or is applied by chemigation (through overhead sprinkler irrigation. It has been observed that Pesticide 2 may volatilize more from moist or saturated soils relative to dry ones due to decreased adsorption in the wetter soils Large Henry's Law constants for the Pesticide 2 degradates D1, D2, D3 and D4 (on the order of 10^{-7} to 10^{-4} atm-m^3-mol) indicate that volatilization may also be an important environmental fate process for these compounds.

Although OPP is not able to quantify the extent to which Pesticide 2 will undergo long-range atmospheric transport once the pesticide has volatilized from a treatment site, this mechanism of transport is expected to constitute a route of exposure for non-target animals distant from use sites. Based on its vapor pressure ($1.13x10^{-4}$ mmHg @25^{o}C), Pesticide 2 will exist almost exclusively in the vapor phase in the atmosphere. The photo-oxidation half-life for Pesticide 2 in the vapor phase is estimated to be several years, so degradation in the atmosphere is expected to be negligible. Thus, the volatility of Pesticide 2 coupled with its likely persistence once in the atmosphere make long-range atmospheric transport of Pesticide 2 likely.

The potential for long-range atmospheric transport is supported by monitoring studies that involved Pesticide 2 reported in the open literature. 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. The presence of D1 in the environment is most likely a result of the use of Pesticide 2. The detection of Pesticide 2 in the atmosphere over areas in which the pesticide was not used along with detections of D1 in the arctic is evidence of the possibility for long-range transport of the compound and its degradates of concern.

6.5.3 LRT and Pov Modeling

The "OECD Pov and LRTP Screening Tool" (version 2.0) is utilized in evaluating the Pov, LRTP and transfer efficiency (TE). The OECD Tool requires estimated degradation half-lives in soil, water and air, and partition coefficients between air and water and between octanol and water as chemical-specific input parameters to calculate metrics of Pov and LRTP. Pov is derived from the degradation rate constants in soil, water and air to provide overall degradation. The resulted Pov value represents the characteristic time for disappearance of a chemical after releases in various media have been stopped and the overall degradation rate is determined by the disappearing of chemical from a medium (Scheringer et al., 2006). The CTD represents the potential of a chemical to be transported over long distances in air or water. In the OECD Tool, the CTD is the distance at which the concentration of chemical decrease to 37% due to transport of chemical by a constant flow of air (wind speed of 0.02 m/s) or water (ocean water circulation speed of 0.02m/s (Scheringer et al., 2006).

Transfer efficiency is a dimensionless metric of potential for atmospheric transport and deposition of parent compound in terrestrial and aquatic environments of a remote region (Wegmann et al., 2007). It is a ratio between the depositional flux (mol/day) in remote region and emission flux from the source area. A high TE value indicates an "optimal" transport condition from the source region to remote depositional region.

The OECD Tool is used in evaluating the Pov and LRTP for 3 known PBT chemicals and 4 pesticides with characteristics comparable to PBTs using chemical specific degradation half-lives in soil, water, and air as well as two partition constants, the K_{ow} and $K_{Aw.}$ Table 6.1 provides input parameters used in the OECD Tool.

Table 6.1. Physicochemical and environmental fate properties used as input for estimating overall persistence and long-range transport potential using the OECD Tool

Name of Chemical	Molecular Weight g/mole	Log K_{ow} [a]	Log K_{Aw} [a]	Half life in Air (hrs)	Half life in Water (hrs)	Half life in Soil (hrs)
p.p' DDT [b]	345.5	6.39	-3.34	170	5500	17000
Aldrin[b]	364.9	4.94	-3.38	2.86	2670	3830
Endrin[b]	380.9	5.44	-3.11	12.72	78840	29070
Pesticide 1 (isomer P1)	406.9	4 .74	-2.58	48[c]	2736[d]	1368[e]
Pesticide 1 (isomer P2)	406.9	4.78	-3.45	48[c]	9072[d]	4992[e]
Pesticide 2	295.3	4.64	-2.75	22560[f]	4320[d]	4536[e]
Pesticide 3	506.4	5.10	-5.87	6.5[g]	2400[d]	3216[e]
Pesticide 4	491.1	8.10	-5.09	7.2[g]	4464[e]	5472[e]

[a] Maximum reported value
[b] Input parameters for these chemical are based on the Reference chemicals data in the OECD Tool.
[c] Reported half-life in air for pesticide 1 (TOXNET, http://www.toxnet.nlm.nih.gov/)
[d] The half-life in water based on PRZM/EXAM inputs
[e] Half-life in air based on measured value of similar structure of pesticide 2. Determined half-life is based on 2nd order degradation half-life (Brubaker and Hites, 1998)
[f] Represents the 90th %-ile confidence bound on the mean half-life
[g] Half-life in air based on EPISUITE estimate

Modeling Results

Although there are considerable uncertainties in the environmental fate properties of the selected chemicals under consideration, the results indicate that these chemicals except pesticide 1-isomer P1 have Pov and LRTP properties similar to those of several known POPs (*p,p'* DDT, aldrin and endrin) presented in **Table 6.2**. Pesticides 1 and 3 have comparable or higher LRTP estimates (CTD or TE) than aldrin and endrin. Pesticides 2 and 4 have comparable or higher LRTP estimates than all three known POPs. All pesticides under consideration for PBT have higher TE estimates than those for aldrin and endrin. Pesticide 2 has very high TE value. TE values greater than 100% are possible since some chemicals may undergo several cycles of deposition and revolatilization during their residence time in the environment (Wagmann et al., 2007).

Results from the OECD Tool do not indicate absolute loading of pesticides in the environment but help to compare the inherent characteristics with reference POP pesticides according to their overall persistence, transfer efficiency (TE), and characteristic travel distance (CTD).

Table 6.2. Overall persistence and characteristic travel distances generated using the OECD Tool

Chemicals	Overall Persistence (Pov) (Days)	Characteristic Travel Distance KMs (Miles)	Transfer Efficiency (%)
Reference POP Pesticides			
p.p' DDT	1010	2530 (1572)	5.17
Aldrin	225	206 (128)	0.003
Endrin	1556	515 (320)	0.04
Example Pesticides			
Pesticide 1 (isomer P1)	81	950 (704)	0.28
Pesticide 1 (isomer P2)	308	915 (569)	0.69
Pesticide 2	599	33849 (21033)	457
Pesticide 3	193	246 (153)	0.14
Pesticide 4	329	2496 (1551)	9.65

7. ASSESSING TOXICITY

7.1 INTRODUCTION

OPP conducted risk assessments on four pesticides with characteristics comparable to persistent, bioaccumulative, and toxic (PBT-like) chemicals. From these risk assessments, OPP identified issues associated with interpretation and quantification of aquatic toxicity due in part to properties including high persistence, high bioaccumulation potential, high soil/sediment sorption coefficients, low solubility, and formation of toxic degradation products. These chemical characteristics are typical for many persistent, bioaccumulative chemicals and suggest that the dominant route of environmental exposures is controlled by the extent of sorption on sediment and soil and accumulation in aquatic organisms. Chemicals that partition primarily to soil and sediments present unique challenges to interpretation of aquatic toxicity studies because guideline toxicity studies submitted in support of registration derive toxicity reference values (TRVs) (e.g., LC50s) based on exposure in water and not on sediment/soil sorbed residues. This may limit interpretation of TRVs and hence potential risks from chemicals that partition out of the water phase.

The following topics related to interpreting toxicity assessments of persistent, bioaccumulative pesticides are discussed in this Section:

1. Estimating toxicity of pesticides with degradation products of toxicological concern (**Example pesticides 1 and 2)**; and
2. Quantifying and applying TRVs to account for multiple exposure routes and lack of steady-state conditions in aquatic environments (**Example pesticides 3 and 4**).

The objectives of this section are to: (1) provide an overview of potential issues in assessing the toxicity of pesticides that are persistent and bioaccumulative and that form toxic degradation products; (2) discuss methods used in the past to evaluate the toxicity of such chemicals; and (3) seek scientific input from the SAP on methods that may be considered for further development when evaluating the toxicity of persistent and bioaccumulative chemicals. Consistent with the previous chapters, specific pesticide examples are provided to illustrate methods that may be used to meet the challenges in evaluating the toxicity of such chemicals. These examples are only discussed in the context of presenting general issues associated with evaluating the toxicity of persistent, bioaccumulative pesticides.

7.2 ASSESSING TOXICITY: DEGRADATE TOXICITY AND TOTAL RESIDUES

7.2.1 Summary of Data Requirements

A summary of toxicity data on pesticide active ingredients that are typically submitted to the Agency to fulfill data requirements under 40CFR Part 158 is summarized below. Subsequent sections in this chapter discuss how available toxicity data may be used to evaluate the toxicity of persistent, bioaccumulative pesticides and pesticides that form degradation products of

concern. Additional details on the data requirements are discussed in **Section 2 and Appendix B** Effects data requirements typically include acute and chronic toxicity studies of fish and aquatic invertebrates in freshwater and saltwater environments, acute and chronic studies of birds, mammals and terrestrial invertebrates (pollinators), and studies in terrestrial and aquatic plants. Additional studies may also be required on a case-by-case basis. For example, acute and chronic studies in sediment-dwelling (benthic) organisms may be required for pesticides that may partition to and persist in sediment. Additional bioaccumulation studies may also be submitted if such data are important to support risk conclusions (see Section 7.4. for an example). Guideline studies typically evaluate the toxicity of the technical grade active ingredient (TGAI), although studies on degradates and formulated end products may also be required on a case-by-case basis.

Data sources that may be used to evaluate potential toxicity of degradation products include registrant-submitted and open literature studies. Also, toxicity data from structurally related compounds, and toxicity estimates using structure activity relationships (SAR) may also be used to evaluate the potential toxicity of parent and degradation products in the absence of available studies. Estimates of toxicity using SAR or surrogate chemicals are not used to satisfy guideline data requirements and are typically used to evaluate uncertainty associated with data gaps until acceptable studies are obtained. A more detailed discussion of the data requirements is provided in **Section 2 and Appendix B**

7.2.2 Methods Used to Evaluate Toxicity of Multiple Residues of Concern

Section 3.4.1 describes procedures used to estimate potential exposures when one or more degradates are expected to be of toxicological concern. This section summarizes methods that may be used to estimate toxicity of a pesticide that forms multiple residues of concern.

During the problem formulation stage of the risk assessment, degradates of concern are identified. Degradates of concern may be defined either on a toxicity or exposure basis. Major degradates are typically presumed to be of toxicological concern until data are submitted that indicate otherwise. It is also determined if the degradates and parent may possess the same mode of action. Degradates may be of concern regardless of the mode of action or presumed mode of action; however, the method used to estimate TRVs for the residues of concern depends on assumptions regarding additivity or independence.

Based on this evaluation and on the available environmental fate and effects data, a decision is made regarding the method used to estimate potential aquatic exposure and toxicity of the residues of concern. If a similar mode of action is expected for all the residues of concern, then co-exposures to degradates and parent may be evaluated together. However, specific degradates of concern may be evaluated separately if the expected environmental fate or toxicological profile is expected to be substantially different than the other residues of concern.

If the determination is made that degradates may have the same mode of action as the parent, then co-exposures to degradates + parent may be estimated using methods described in Chapter 3 and include:

- **Residue Summation (RS method):** Requires summation of individual residues of concern concentrations to represent the TROC. This method cannot be used to estimate temporal occurrence of degradation products;

- **Simultaneous Formation/Decline Kinetics (FD method):** Preferred method for estimating concentrations of TROC. A major advantage of this method is the estimation of temporal occurrence of degradation products; and

- **Total Residue (TR method):** Requires an assumption that all residues of concern have similar physical, chemical, and partitioning characteristics. This modeling approach does not consider temporal occurrence of degradation products.

The choice of method may depend on several factors including the availability of environmental fate and effects data for the parent and its toxic degradation products. A detailed discussion of these exposure methods is presented in **Section 3.4.1.**

Once exposure concentrations for the parent and its degradates of concern are derived, these values are compared to available acute and chronic toxicity data to determine the potential risks of ecological effects resulting from exposures to the parent and its degradates. An assumption implicit in estimating a single exposure concentration for the parent compound plus its degradates regardless of the method (*i.e.,* residue summation, total residue, simultaneous formation/decline kinetics) is that all the chemicals included in the residues of concern have a similar mode of action. Aquatic toxicity studies typically available for use in risk assessment do not provide insight into the mode of action for a pesticide. Therefore, risk assessors typically rely on the structural similarity to the parent to determine whether the degradate may be acting through a similar mode of action.

A tiered approach may be used to initially describe the toxicity of the residues of concern. The risk assessor may initially select the most conservative (lowest) TRV available across all residues of concern to represent the toxicity of the mixture as a conservative assumption. However, the assessor may also make alternative assumptions of toxicity in an attempt to bracket potential risks. For example, the assessor may choose a TRV from the most toxic and least toxic residue of concern to evaluate the sensitivity of risk conclusions to the choice of a TRV, or the assessor may choose a TRV from the expected predominant residue of concern. However, RQs are typically calculated initially using the most sensitive TRV across all residues of concern. Factors considered when choosing or characterizing a toxicity value for use in risk estimation may include quality of data, where and when the most toxic degradate forms, how much of it is expected to form in the environment, and stability of the most toxic residue.

In cases where the data are sufficient to allow for an estimation of exposure to each degradate, then the toxicity reference value of the mixture can be further refined. For example, RQs can be calculated for each of the residues of concern and summed. This is equivalent to use of a concentration addition model where EECs of all residues of concern are added together to predict toxicity, and differing potencies are taken into account by converting chemical concentrations to an equitoxic dose, such as toxic units (TUs) or toxicity equivalence factors

(TEFs), which convert all residues to one residue concentration. Alternatively, risk quotients (RQs) can be calculated and summed for each residue of concern. Concentration addition is often used when the constituents are known or assumed to act through the same or similar mode of action (USEPA, 2008b). However, Newman (2004) reported that applying concentration addition models to mixtures that contain numerous residues of concern could result in an upward bias in predicted toxicity. The toxicity equivalence method is described in detail in U.S. EPA (2008b).

Also, in cases where the toxicity of one or more degradates is expected to be different than the other residues of concern, then such degradates may be evaluated separately from the other chemicals identified as residues of concern. However, a default assumption of additivity is used in cases where the mode(s) of action cannot be determined for the various residues of concern.

There are several uncertainties associated with estimating toxicity of multiple residues for assessing the potential risks of a pesticide and its degradates. For example, reliable estimates of toxicity may not be available for all degradates that form in the environment, resulting in uncertainty in the toxicity of the degradates relative to the parent. This is especially true when numerous degradates may be formed in the environment and resulting toxicity values rely on estimated values. However, data may be requested to further characterize potential toxicity of degradates that are identified as a potential concern.

Section 7.2.3 below describes how the toxicity of degradates of concern were evaluated in ecological risk assessment of two example pesticides. Only the toxicity evaluation is discussed in this Section. Methods that may be used to evaluate potential exposures to degradates are described in **Section 3.4.1.**

7.2.3 Example Pesticides Used to Illustrate Total Residues of Concern Approach

7.2.3.1 Example Pesticide 2

Toxicity data used to assess potential risks to aquatic organisms from exposure to Pesticide 2 and its degradates of concern are discussed below. On an acute exposure basis, Pesticide 2 and some of its degradates are considered highly toxic (defined as LC_{50} = 100 -1000 ppb) to very highly toxic (defined as LC_{50} <100 ppb) to aquatic organisms on an acute exposure basis. Four degradates were identified as toxic degradates of concern for aquatic organisms (summarized in **Table 7.1).** Laboratory studies were not available to allow for a comparison of toxicity in all cases. Therefore, toxicity estimates using structure-activity relationships (SAR) were utilized and are also presented in **Table 7.1**. Toxicity estimates using SAR were generated using ECOSAR[5] (Version. 0.99h) for fish and aquatic invertebrates.

[5] USEPA. 2008. Ecological Structure Activity Relationships (ECOSAR). http://www.epa.gov/oppt/newchems/tools/21ecosar.htm

Table 7.1. Comparison of Measured and Estimated Acute Toxicity Values for Pesticide 2

Chemical	Fish		Aquatic Invertebrates	
	EPIWIN LC_{50} value (ug/L)	**Range of measured LC_{50} values across all species tested (ug/L)**	**EPIWIN LC_{50} value (ug/L)**	**Range of measured EC_{50}/LC_{50} values across all species tested (ug/L)**
Parent	311	100-7900	410	12-770
Degradate of concern 1	1593	**56**	432	300
Degradate of concern 2	174	140-800	234	160-230
Degradate of concern 3	803	95-442	1086	50-450
Degradate of concern 4	56	NA	79	NA

NA = not available

The total residues of concern for Pesticide 2 were defined as parent plus 4 degradates of concern as listed in **Table 7.1**). Structural analysis suggested that an assumption of additivity is reasonable. Data in **Table 7.1** suggest that the most sensitive LC50 value in fish for the degradates is within a factor of approximately 2 of the parent compound. Toxicity values are also comparable for each residue of concern within the same fish species tested. Sufficient data were not available to allow for a comparison of the toxicity of Pesticide 2 and its degradates within a given species of aquatic invertebrates. However, toxicity reference values for the degradates of concern for aquatic invertebrates are within the range available for the parent pesticide.

Assuming similar toxicity and similar mode of action for the degradates and parent, the toxicity value that may be used to estimate potential risks would be the most sensitive toxicity value across all the residues of concern (parent or degradate). For pesticide 2, the most sensitive TRV would be 56 ug/L for fish and 12 ug/L for aquatic invertebrates. As previously discussed, however, alternative TRVs may be used to explore the choice of a TRV on potential risks. For example, Table 7.2 indicates that the EEC for the total residues of concern is comprised predominantly (approximately 90%) of the parent chemical. Therefore, given that the toxicity of the parent and degradates are similar, use of the LC50 for the parent appears to be reasonable to represent the toxicity of the mixture. However, RQs were calculated using the most sensitive and least sensitive LC50 value to bracket potential risks (**Table 7.2**), and potential risk concerns were similar regardless of the LC50 value used in the analysis.

EECs were estimated for parent only and for total residues of concern in **Section 3.4.1**. The toxicity values for fish (**Table 7.2**.) were compared to the EECs from **Section 3.2.1**. to derive RQs for Pesticide 2, which are summarized in **Table 7.2**. The parent only method compares EECs and TRVs for the parent, and the total residues of concern method compares EECs for the total residues to the most sensitive TRV across the residues of concern. The acute toxicity analysis for fish (aquatic vertebrates) is presented; however, a comparable analysis could also be performed in aquatic invertebrates and for chronic exposures to aquatic organisms.

Table 7.2. Summary of Aquatic Organism RQs for Pesticide 2

EEC Derivation Method	Peak EEC	LC50, Fish	RQ, Fish
Parent Only	230 ug/L	100 ug/L	2.3
Total Residues of Concern	260 ug/L	56 ug/L 140 ug/L	4.6 1.9

In some cases, degradates form that are considerably different than the parent pesticide in their anticipated fate or toxicological profile. Potential risks from exposure to such a degradate may be quantified separately from the other residues of concern if sufficient data are available to allow for an estimation of the formation and decline of the degradate. Alternatively, potential risks from exposure to such a degradate may be discussed qualitatively if sufficient data are not available to allow for an estimation of exposure or toxicity.

7.2.3.2. Example Pesticide 1

In the assessment of Pesticide 1, a single degradate was identified as a major transformation product in some environmental fate studies; this degradate is structurally similar to the parent compound. Open literature studies suggested that the degradate could be of similar toxicity as parent and this was subsequently confirmed by registrant-submitted studies. Thus, the available data suggest that Pesticide 1 and its degradate are of similar toxicity **(**Table 7.3**)**.

Table 7.3. Aquatic Toxicity Data Comparison for Pesticide 1 and its Degradate of Concern

Chemical/Toxicological Property		Value
Solubility		300 ug/L
Log Kow		5
BCF		Up to 2400 L/kg w.w. (edible tissues)
Toxicity Values Used for RQ Calculations in Freshwater Aquatic Organisms	Fish LC50	Parent: 0.8 ug/L (rainbow trout) 2 ug/L (bluegill) Degradate: 4 ug/L (bluegill)
	Invertebrate LC50	Parent: 5.8 ug/L Degradate: No data
	Fish ELS NOAEC	Parent: 0.11 ug/L Degradate: No data
	Invertebrate Chronic NOAEC	Parent: 0.07 ug/L Degradate: No data

Direct comparison of the acute toxicity of Pesticide 1 and its degradate of concern within the same species (bluegill) indicates that the degradate is about equally toxic as the parent compound (i.e., within a factor of 2). Comparison among two decapod crustaceans (grass shrimp and mysid shrimp) indicates the acute toxicity of parent and the degrade are within a factor or approximately 6. Therefore, toxicity endpoints used to represent the total residues (parent + degradate) for risk estimation for aquatic organisms would be based on data on the parent pesticide. However, as noted in **Table 7.4**, the predominant component of the EEC is the degradate. Therefore, alternative approaches may be used to characterize the potential toxicity of the residues of concern (parent + degradate).

As described in **Section 3.4.1**, EECs were calculated using several methods for Pesticide 1 and its degradates. RQs were derived using each of the methods and are presented in **Table 7.4**. The toxicity reference value for Pesticide 1 would be the same for each exposure method because the structures of the parent and the degradate were similar and the toxicity of the parent and degradates in the available studies were comparable. However, further characterization of the components of the EEC derived using the formation/decline kinetics method was performed to account for the difference in potency of the parent and degradate. Risk conclusions were similar for each exposure method. Only the acute assessment in fish is presented in **Table 7.4**; however, an equivalent analysis for aquatic invertebrates and for chronic exposures could also be performed. It is clear from this analysis though that risk estimates can range considerably (RQs range from 30 – 60 when all residues of concern are considered) depending on the methods used to estimate toxicity and exposure.

Table 7.4. Comparison of RQs Based on 1 in 10 year EECs for Pesticide 1 Using Various Modeling Strategies

Modeling Approach	EEC (µg/L)	Acute TRV	Acute RQ
	Peak	Fish	Fish
Residue Summation	33	0.8	41
Total Residues of Concern	48	0.8	60
Formation/Decline Kinetics – Total	38	0.8	48
Formation/Decline Kinetics – Parent	9	0.8	11
Formation/Decline Kinetics – Degradates	32	1.6	20
Formation/Decline Kinetics – Concentration Addition			31 (RQ addition)

7.3 CHALLENGES IN EVALUATING AQUATIC TOXICITY AND RISK FOR PERSISTENT, BIOACCUMULATIVE CHEMICALS FROM WATER EXPOSURE TOXICITY STUDIES

Chemicals that bioaccumulate substantially in aquatic organisms typically have high log K_{ow} values, high organic carbon partition coefficients (K_{oc}), low water solubility values, and high bioconcentration factors (BCF). Therefore, the required water exposure-based toxicity studies described in **Section 2** of this white paper have limitations in quantifying the toxicity of bioaccumulative compounds to aquatic organisms. Issues discussed in this chapter include the following:

- Limitations in toxicity estimates due to their inability to account for potential importance of non-water exposure routes including diet and maternal transfer;
- Limitations in toxicity estimates due to insufficient study durations to achieve chemical steady-state in test organisms.

Each of these issues is described below. In addition, potential assessment methods that address these issues are discussed in **Section 7.4.**

7.3.1 Potential Importance of Alternate Exposure Routes

Guideline studies for aquatic organisms evaluate acute and chronic toxicity resulting from exposure of fasted animals in treated water. However, bioaccumulative chemicals may be found as residues in forage items (*i.e*., aquatic plants and animals) of aquatic organisms; therefore, dietary exposure may also be a potentially important exposure route under more natural conditions. For hydrophobic nonionic organic chemicals with Log Kow values of 4 or greater, available data indicate that exposure through the diet can become important in determining chemical residues in aquatic organisms (e.g., Russell et al., 1999; Fisk et al., 1998; Oliver and Niimi, 1983, 1988; Niimi, 1985; Swackhammer and Hites, 1988), and, therefore, could significantly impact exposure and toxicity.

The relative significance of each exposure pathway (water vs. diet) is influenced by a number of factors including: (1) bioaccumulation potential; (2) partitioning characteristics (e.g. octanol-water, organic carbon); and (3) solubility. Uptake via respiration and direct contact as well as consumption of chemical residues in dietary items represent plausible exposure routes for bioaccumulative compounds. For example, preliminary modeling using Arnot and Gobas (2004) as described in **Section 5** suggests that neglecting dietary exposures for aquatic organisms could result in an underestimation of potential exposure to and risks from pesticide exposure, as estimated by whole tissue body burden, by a factor of approximately 5 for chemicals with a log K_{ow} of 5. The contribution of diet to potential risks increased with increasing Log Kow for chemicals that are poorly metabolized in the organism.

In addition to dietary exposure, compounds that accumulate in the lipid stores of exposed organisms may be transferred from exposed maternal parents to their offspring at toxicologically significant levels. The development of eggs in oviparous species involves the transfer of glycolipoproteins (*e.g*. vitellogenin) from maternal tissues to eggs. The maternal transfer of these lipid-rich compounds to developing eggs can also involve transfer of lipid soluble contaminants as well given the capacity for glycolipoproteins to serve as carrier proteins.(Russell et al., 1999). For many compounds there is negligible biotransformation in eggs because phase I and phase II enzymes are not yet active (Kleinow et al., 1999). A substantial collection of maternal transfer data was published by Russell et al. (1999), which combined existing data with the results of field studies on Lake Erie to determine maternal transfer and egg accumulation of 44 hydrophobic organic chemicals in nine species of fish, herring gulls, and the common snapping turtle. They suggested that embryos and maternal organisms are expected to be exposed to equivalent effective internal concentrations. Chemicals with high Kow can be expected to have slow uptake kinetics (kinetics can be confirmed or evaluated using available BCF studies). As a result, organisms, especially embryos, in the standard early life-stage testing protocol would be expected to have much lower tissue burdens than would occur if there were maternal exposure of the parent fish (resulting in maternal transfer of chemical), as would expected under field application of the chemical.

Consideration of this phenomenon is especially important when evaluating the suitability of various chronic toxicity test protocols involving fish for the evaluation of lipophilic compounds that are highly bioaccumulative in nature. Currently, the Agency has protocols for

both a fish early life stage toxicity test (OPPTS Guideline 850.1400[6]) and a fish full life cycle toxicity test (OPPTS Guideline 850.1500[7]). Under the fish early life stage protocol, fertilized eggs are placed in the test solution and monitored for hatchability and embryonic/larval development. In the full life cycle study, adult fish are exposed to test solution, and the adults along with their progeny are followed for effects. The early life stage study cannot account for the potential for toxicologically significant maternal transfer of a pesticide from exposed maternal adults since the study does not include the maternal adult. There is concern that endpoints derived from early life-stage tests may underestimate the potential hazards for bioaccumulative compounds; therefore, life-cycle studies that expose fish continuously from one life stage to the same life stage of the next generation are more useful for characterizing potential exposure and toxicity and hence risks for bioaccumulative chemicals. Consequently, early life stage studies are of limited utility in ecological risk assessment for chemicals with bioaccumulation potential.

7.3.2 Insufficient Study Duration to Achieve Steady-State

Water-based estimates of toxicity in the standard acute assays (48- or 96-hours) are problematic for bioaccumulative compounds because these compounds typically have high log K_{ow} values and slower uptake kinetics. **Figure 7.1** illustrates BCF as a function of time and Kow based on the assumption of a single compartment, first order kinetic model. **Figure 7.1** suggests that steady state is not approached by 96 hours for poorly metabolized neutral organic chemicals with high Log Kow values. For example, time to reach 90% steady state observed for Pesticide 4 in the submitted water exposure BCF study was approximately 100 days. Therefore, internal dose (body burden) is not likely to have approached steady state within the duration of the toxicity studies for Pesticide 4.

[6] USEPA. 1996 Ecological Effects Test Guideline 850.1400 Fiah Early-Life Stage Toxicity Test. EPA 171-C-96-121. http://www.epa.gov/opptsfrs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-1400.pdf

[7] USEPA. 1996. Ecological Effects Test Guideline 850.1500. Fish Life Cycle Toxicity Test. EPA 121-C-96-122. http://www.epa.gov/opptsfrs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-1500.pdf

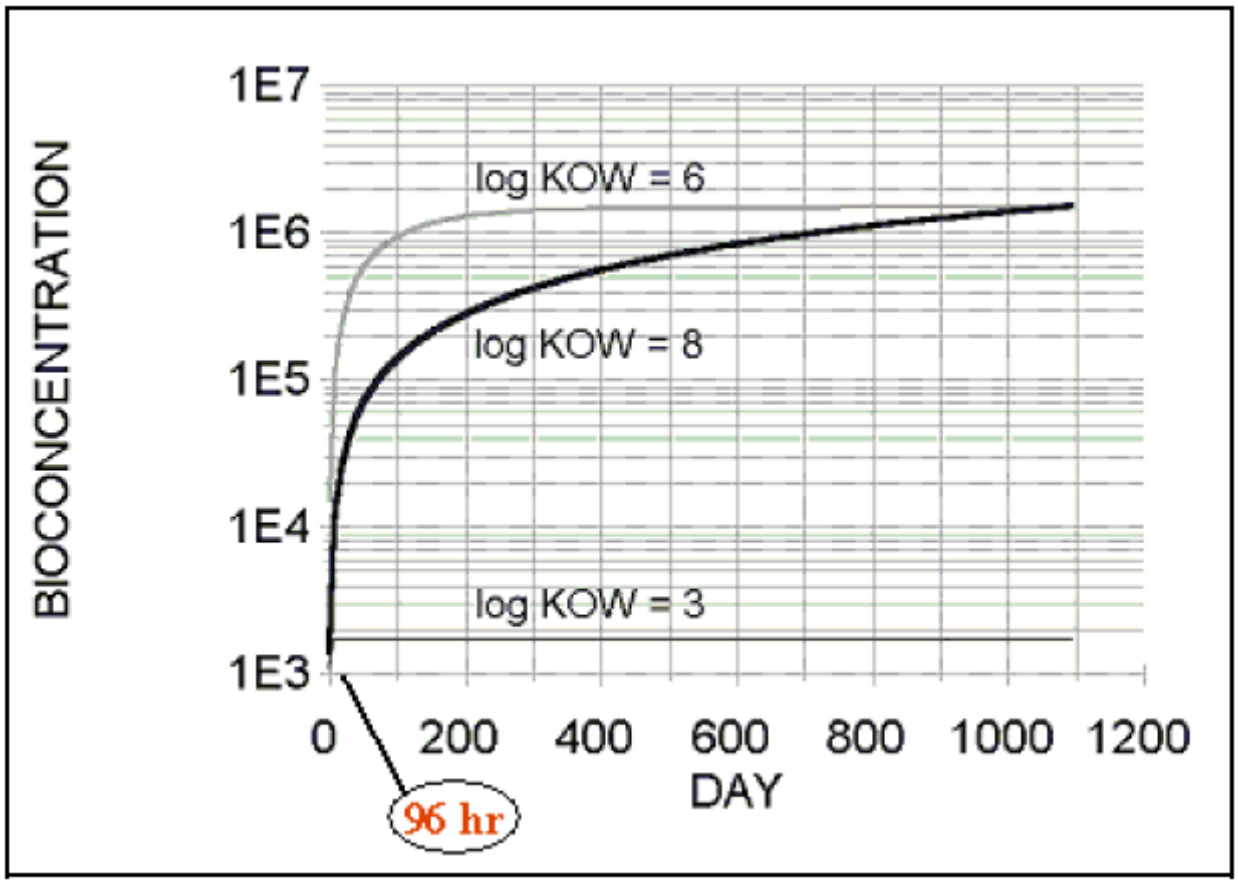


Figure 7.1. Bioconcentration as a function of time and K_{OW}
Figure obtained from http://www.epa.gov/waterscience/models/aquatox/technical/techdoc.pdf

If the allotted exposure duration of the studies is inadequate for achieving *in situ* steady-state, then the resulting water-based toxicity estimates may underestimate the toxicity of the compound because lower water concentrations may have resulted in higher body burdens had the study duration been extended to achieve steady state. In these instances, the utility of short-term toxicity studies to inform risk assessments may be limited, and the degree to which the toxicity estimates are influenced by the toxicokinetics (i.e., rates of uptake, distribution, metabolism, and elimination) of the chemical in the test species rather than the inherent toxicity of the compound is uncertain. Consequently, reliable cross-chemical and cross-species comparisons of toxicity may not be possible based on short-term water column exposure-based toxicity values. Possible alternative methods to evaluate aquatic toxicity of bioaccumulative compounds are described in **Section 7.4**.

7.4 USE OF A TISSUE RESIDUE APPROACH FOR ADDRESSING PBT-RELATED ISSUES

7.4.1 Introduction

An alternative to the use of water exposure-based expressions of toxicity would be the use of tissue-based toxicity estimates. The "tissue-residue approach" references toxicological data in terms of tissue concentrations in the exposed organisms. Chemical concentrations in tissues are commonly referred to in the literature as critical body residues, lethal body burdens, or tissue residues as opposed to concentrations in ambient media (water, sediment).

7.4.1.1 Why Use a Tissue-based Approach for Bioaccumulative Chemicals?

The concept of expressing toxicological data for aquatic organisms on the basis of tissue or whole body concentrations is not new (e.g., Könemann, 1981; Veith et al. 1983; McCarty, 1986; Cook *et al*., 1989; 1993; McCarty and Mackay, 1993) and a substantial body of literature has evolved around this approach. Use of a tissue residue approach for risk assessment of bioaccumulative chemicals has been advocated as an improvement for the prediction of toxicity to organisms in the environment (Friant and Henry, 1985; McCarty, 1986; Cook et al., 1987; Van Hoogen and Opperhuizen, 1988; Cook et al., 1991; McCarty, 1991; McCarty et al., 1991; Tas *et al*., 1991; Landrum *et al*., 1992; and McCarty and MacKay, 1993). Additionally, a recent SETAC workshop was held on the scientific foundation and application of the tissue-based approach for toxicity assessment (Meador et al., 2007). The approach has also been proposed for use in deriving aquatic life criteria for bioaccumulative chemicals (USEPA, 2005; Sappington et al., 2006).

The primary benefit for using a tissue-based approach for bioaccumulative chemicals is that it accounts for multiple routes of exposure (*e.g*., diet, sediment, water) for risk estimation purposes. However, the correlation of body residues to toxic effects (residue-based dose) has other advantages over using an exposure-based approach (*i.e*., water or food concentrations that cause toxic effects). As outlined by McCarty and MacKay (1993), these advantages include the following: (1) bioavailability is explicitly considered; (2) accumulation kinetics are considered, which reduce the confounding effect of exposure duration when interpreting results; (3) uptake from food (as distinct from water) is explicitly considered; (4) toxic potencies are expressed in a less ambiguous manner, facilitating identification and investigation of different modes of toxic action; (5) effects of metabolism on accumulation are considered; and (6) experimental verification can be more readily determined between laboratory and field. A major limitation in this approach, however, is that residue-based toxicity data are not widely available.

For organic chemicals exhibiting a narcotic mode of action, the lethal tissue residue or body burden concept has its foundations in the early development of quantitative structure activity relationships (QSARs) involving octanol-water partition coefficients (K_{ow}), bioconcentration, and acute toxicity (Veith et al., 1979; Veith et al. 1983; McCarty 1986).

Extending this approach to deriving tissue-based "RQs" for bioaccumulative chemicals would consist of two primary components: (1) estimating toxicity; and (2) estimating exposure.

In the tissue residue approach, both toxicity and exposure are derived in terms of body burden. Below, an overview of these two components as they pertain to aquatic life and aquatic-dependent wildlife is presented. A case study is also presented for an example pesticide.

7.4.2 Method Used to Estimate Toxicity of Bioaccumulative Pesticides to Aquatic Life Using the Tissue Residue Approach

Ideally, critical body residues (CBRs) could be measured in current acute and chronic guideline toxicity tests and these could in turn provide information on body burden/effect. When such data are available and are of sufficient quality, they would be used directly to determine CBRs. However, CBRs are not typically available in submitted toxicity studies. Although provisions exist in the Agency guidelines for the submission of separate studies to evaluate the accumulation potential of a compound in the aquatic environment (OPPTS 850.1710[8], 650.1730[9], 850.1850[10]), these studies have a limited capacity to couple the evaluation of toxicity and bioaccumulation potential because they are not designed to evaluate toxic effects. Nonetheless, there is utility in estimating body burdens that are associated with toxic effects. One approach involves applying available kinetics data from water exposure bioconcentration studies to water concentration TRVs. The following equation has been used to estimate body burden from water exposure toxicity values (Newman, 1995):

$$\textbf{EQ 7-1: } LD50\ (C_t) = k_u \times C_1 \frac{(1 - e^{-ke \times t})}{k_e}$$

C_1 = concentration in water associated with the most sensitive LC50 or NOAEC
k_u = uptake rate constant
k_e = depuration rate constant
t = time (exposure duration of toxicity study

Equation 7-1 assumes first-order uptake and depuration kinetics based on constant exposure. The assumption of first order kinetics may be tested using the available BCF study if more than one concentration was used.

There are a number of uncertainties in estimating CBRs using Equation 7-1 which are highlighted in the case study (Pesticide 4) below. For example, BCF studies are often available for only one species of fish. However, the most sensitive toxicity study may use a different species. Using kinetics data from a species other than the most sensitive tested species may underestimate toxicity and risk. Also, use of co-solvents is common practice for toxicity and bioconcentration studies on hydrophobic chemicals. Use of different co-solvents and different

[8] USEPA. 1996 Ecological Effects Test Guideline 850.1710. Oyster BCF. EPA 712-C-96-127. http://www.epa.gov/opptsfrs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-1710.pdf
[9] USEPA. 1996 Ecological Effects Test Guideline 850.1710. Fish BCF. EPA 712-C-96-129. http://www.epa.gov/opptsfrs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-1730.pdf
[10] USEPA. 1996 Ecological Effects Test Guideline 850.1710. Aquatic Food Chain Transfer. EPA 712-C-96-133. http://www.epa.gov/opptsfrs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-1850.pdf

species across the bioconcentration and toxicity studies could also result in an uncertain estimate of a tissue-based TRV. In addition, differences in fish characteristics such as age, size, and lipid content or water characteristics could influence uptake and depuration of the test chemical. Also, the amount of bioavailable chemical could be substantially different across studies depending on the water chemistry parameters used in the studies.

Critical body residues estimated using kinetics information from the water exposure BCF study and the LC50 may be confirmed by laboratory studies that directly relate body burden with a toxic effect.

Use of the body burden approach assumes that a specific toxic effect is related to total body concentration regardless of duration of exposure. It is recognized that other types of models have been proposed that account for toxicity time course such as a damage recovery model described by Lee et al. (2002). However, given the data that are typically available for risk assessment and resource constraints, the critical body residue methodology described in this section was chosen in the evaluation of the example pesticide.

In addition, to account for lack of steady state being achieved during the acute toxicity studies, a longer-term (e.g., 12-day fish LC50, but duration may depend on kinetics of the assessed chemical) study could be requested.

7.4.3 Pesticide 4 – Use of the Tissue Residue Approach

Of the four example pesticides described in this paper, Pesticide 4 had the highest BCF and Koc and lowest aqueous solubility limit. Therefore, the potential for dietary exposure to contribute to significant exposures and risks is considered greatest for this pesticide. Therefore, Pesticide 4 is used as an example for evaluating potential toxicity and risk to aquatic organisms resulting from multiple exposure routes. The analysis is described below. Pesticide 4 highlights some of the challenges and uncertainties for some chemicals that may be associated with estimating critical body burdens based on toxicity reference values when measured tissue-based dose-response data are not available. Relevant physicochemical properties of Pesticide 4 used to estimate CBRs are in **Table 7.5**.

Table 7.5. Selected Chemical and Toxicological Properties on Pesticide 4 Used to Estimate Tissue Based Toxicity Values

Property	Numerical Value	Comment
Log Kow:	8.1	--
Koc	1,241,000 mL/g	Average value
Molecular Weight	490 g/mole	--
Water Exposure BCF estimated at steady state:	27,000 L/kg w.w. (16,000 L/kg after 49 days)	K_u: 520 per day k_e 0.02 per day

K_u=uptake rate
k_e=elimination (depuration) rate

Physical-chemical properties illustrated in the preceding table may be used to estimate CBRs and body burden EECs as described below.

The LC_{50} for Pesticide 4 is 500 ug/L and is above the water solubility limit of the chemical. Pesticide 4's apparent water solubility was enhanced by use of a co-solvent, which introduces uncertainty in the CBR estimation. For example, some fraction of Pesticide 4 may have been sequestered in the co-solvent (added at a concentration of 0.1 mL/L). Therefore, the amount of freely dissolved or bioavailable test substance is unknown. An assumption of 100% bioavailability was initially made; however, alternative assumptions of bioavailable fractions were also explored. The CBR is directly proportional to the amount of bioavailable chemical in the test system.

Based on information in **Table 7.5**, CBRs may be estimated from the available water toxicity studies and the aquatic bioconcentration studies using Equation 7-1 (Newman, 1995).

EQ 7-1: $$C_t = k_u \times C_1 \frac{(1 - e^{-ke \times t})}{k_e}$$

C_1 = concentration in water associated with the LC50; 500 μg/L (LC50)
k_u = uptake rate constant; 520 μg/kg fish per μg/L water per day
k_e = depuration rate constant; 0.02 day^{-1}
t = time (days); 4 days (duration of a fish toxicity study)

Based on Equation 7-1 and inputs listed above, the resulting CBR would be 990 mg/kg-fish (approximately 2 mMoles/kg). In the acute study in rainbow trout, the probit dose-response slope was shallow (probit slope = 1.6). One possible explanation for the shallow dose-response curve is that the amount of bioavailable chemical did not increase in the water proportional to the total mass of chemical was added to the water. Mortality occurred at all concentrations tested in the acute study. At the lowest measured test concentration of 110 μg/L, 25% mortality occurred after 72 hours of exposure. Using Equation 7-1, exposure at 110 μg/L for 72 hours is associated with a whole fish body burden of approximately 160 mg/kg (0.3 mMoles/kg). CBRs of 0.3 to 2 mM/kg are within the range of CBRs for acute and chronic effects reported for chemicals with narcosis as a mode of action by McCarty and Mackay (1993).

Body burden associated with reduced fry survival (most sensitive endpoint) in an early life-stage study in rainbow trout was also calculated using Equation 7-1. All inputs were equivalent to those used to estimate CBR from the acute toxicity study, except that the water concentration was assumed to be at the NOAEC of 49 μg/L, and the duration was presumably 45 days. The resulting CBR was 710 mg/kg. The lowest CBR of 160 mg/kg was chosen for use in risk estimation; however, confirmatory data that associate body burden with toxicity are currently being generated.

There is considerable uncertainty in the CBRs derived above given issues with the study designs, particularly given that the study evaluated concentrations that were considerably above the water solubility limit of the chemical. Therefore, exploration of how various assumptions affect potential risks was performed, and confirmation of the CBRs via testing was requested, but studies that associated body burden with effects in fish have not yet been completed.

Methods used to estimate CBRs will depend on the available data. For example, CBRs were derived in aquatic invertebrates using a microcosm study that associated body burden with toxic effects (abundance). Microcosm studies that evaluate both accumulation and effects are seldom available, and they often are limited in their utility. However, the aforementioned study identified a particularly sensitive species (*Asellus aquaticus*) and determined measured tissue resides that were associated with an approximately 50% reduction in abundance of *A aquaticus* and effects in other sediment dwelling organisms. Effects were associated at test levels that resulted in tissue concentrations in *A. aquaticus* of 137 ug/kg and higher. Effects persisted throughout the study duration of approximately 3 months. CBRs in other species were higher than 137 ug/kg. Therefore, a CBR for sensitive invertebrates of 137 ug/kg may be used to calculate risk quotients. RQs were also calculated based on CBRs for other invertebrates derived from the same mesocosm study (**Table 7.6**). In the absence of a study that evaluated both accumulation and effects, an approach comparable to the approach described for fish may be used to estimate a CBR in invertebrates.

This critical body burden may then be compared with tissue-based EECs derived using methodology presented in **Section 5** for an estimation of potential risks. Tissue based EECs would also account for accumulation that may occur from multiple exposure routes. RQs based on the CBR approach are presented in **Table 7.6** below.

Table 7.6. Tissue-based Risk Quotients for Fish and Benthic Invertebrates for Pesticide 4

Taxonomic Group	Exposure Value	Toxicity Value (mg/kg-org)	RQ
Fish [a]	8 mg/kg-fish	160	0.05
Sediment Invertebrates [b]	38 mg/kg-org	0.137 3 - 10 5 - 10	280 3.8 - 13 3.8 - 7.6

[a] Water column invertebrates are not included in this table because accumulation data in daphnids are under review; however, the analysis would be equivalent to the methods used to estimate potential risks to fish.

[b] Three toxicity values for benthic invertebrates are presented: (1) 137 µg/kg (0.137 mg/kg) represents measured body burdens associated with toxicity for the most sensitive invertebrate tested (*Asellus. aquaticus*) although levels that produced no effects have not been tested in this species); 4000 µg/kg represents an approximate LOAEC for chironomids (NOAEC = 3000 µg/kg) and oligochaetes (NOAEC = 5000 µg/kg).

8. CONCLUSIONS AND PATH FORWARD

The previous chapters highlighted a number of risk assessment challenges that OPP/EFED has encountered for pesticides with high persistence, bioaccumulation, toxicity, and long-range transport potential, based on similarity to national or international PBT screening criteria. A recapitulation of these risk assessment challenges is provided in **Table 8.1.** In addition, the previous chapters summarize the methods and approaches taken by OPP/EFED to address these challenges in several recent ecological risk assessments.

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

Topic Area	Current Risk Assessment Issue
Environmental Persistence	1. Quantifying exposure to combined parent and degradation products 2. Interpreting predicted or measured exposure concentrations that exceed solubility 3. Interpreting degradation half lives when dissipation processes dominate 4. Quantifying long-term exposure (multi-year carryover) in soils, sediment and pore water
Sediment Dynamics	1. Understanding the importance of sedimentation processes on pesticide bioavailability in the context of model agricultural pond systems 2. Identifying and quantifying the principal processes related to sediment dynamics in these systems 3. Identifying appropriate methods for modeling these processes for OPP/EFED aquatic exposure assessments
Bioaccumulation	1. Quantifying pesticide exposure via the aquatic food web 2. Interpreting and integrating results from lab-, field-, and model-based bioaccumulation methods 3. Assessing bioaccumulation potential in terrestrially-based food webs
Long Range Transport	1. Establishing relationships between near-field pesticide loadings and far-field pesticide concentrations 2. Understanding the applicability and reliability of available models for screening long-range transport potential
Toxicity	1. Estimating combined toxicity of parent and degradation products 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.

The purpose of this chapter is two fold: First, to summarize the conclusions and "lessons learned" from the previously described ecological risk assessments regarding PBT-related challenges (**Section 8.1**), and second, to provide some insight for how OPP/EFED perceives its 'path forward' with respect to formally modifying its ecological risk assessment process

specifically to address pesticides with varying PBT characteristics (**Section 8.2**). This latter purpose will be highly dependent on the outcome of the SAP meeting and recommendations made by the SAP panel. Nonetheless, it is considered fruitful to share the Agency's current thinking regarding the overall path forward for review and comment by the SAP panel. Furthermore, it is noteworthy that the extent to which methods have been developed and applied to address the risk assessment challenges outline in **Table 8.1** varies widely. Some methods are relatively well developed (e.g., assessing exposure associated with total residues of concern and aquatic bioaccumulation) while others appear much less developed with respect to their scientific basis and/or regulatory application (e.g., terrestrial bioaccumulation, predicting long-range transport potential).

8.1 CONCLUSIONS FROM EXAMPLE PESTICIDE ASSESSMENTS

8.1.1 Environmental Persistence Issues

Assessing Total Residues of Concern

Assessing exposure to pesticides from both the parent compounds and their degradation products of concern is an important component of many OPP ecological risk assessments, including those for pesticides with PBT characteristics. **Section 3.4.1** describes three methods that have been applied for assessing the combined aquatic exposure to parent and degradation products (i.e., termed "total residues of concern or TROC). These methods include: (1) the formation/decline kinetics or FD method, (2) the residue summation or RS method, and (3) the total residue (TR) method.

Based on these examples, the ability to apply these methods appears largely determined by the physicochemical and toxicological nature of the parent compound and its degradates as well as the availability of environmental fate and toxicity data. Among the three available methods, the FD method would generally be preferred because it enables separate time series to be defined for the parent pesticide and each of its degradation products of concern. However, this method requires complete data on chemical properties of the degradates which may not be available at the time of the assessment, and is not often provided as part of the standard data set received by OPP from registrants. The RS method does not require calculation of complicated formation decline kinetics, but still requires fate properties for the parent and degradate compounds. The RS method also employs the simplifying assumption of instantaneous formation of the degradates on the day of pesticide application (i.e., degradation kinetics are not incorporated). The TR method is the most simplified approach among the three and requires the least amount of data for application. This method can generally be applied with the data most often available to risk assessors. Physicochemical data on individual degradates is considered desirable, but not absolutely required if assumptions regarding similarity in environmental fate behavior among the parent and degradate compounds are supported. However, the TR method does not enable separate time series to be characterized for parent and degradates which has a bearing on comparison to toxicity values.

Addressing Solubility Issues

Regarding interpretation of predicted concentrations that exceed aqueous solubility, two methods have been explored to date by OPP. The first is to assume that any amount of chemical above the measured aqueous solubility is not biological available (e.g. exists as a precipitate). This assumed precipitate could be ignored or added to the sediment chemical load. The second method involves the assumption that at concentrations exceeding solubility, the chemical is temporarily biologically unavailable, until such time that aqueous concentrations drop below the solubility limit where it is then re-dissolved up to the solubility limit (i.e. temporary chemical sink). Both of these approaches depend on the assumption that laboratory-measured estimates of chemical solubility are reasonable approximations of aqueous solubility limits under field conditions. It is noted, however, that for certain pesticides higher aqueous solubility might occur in the field resulting from effects of inert compound in the formulation as well as from naturally occurring organic compounds.

Interpretation of Degradation Half Life Data

Another issue encountered in prior assessments has been the interpretation and application of environmental half life data for compounds with high environmental partitioning (e.g., high Koc) but low volatility. In these cases, the concentration of a chemical in a mixed water/sediment system will reflect strongly its movement (partitioning to sediment organic carbon) in addition to any degradation (transformation) that may occur. For persistent, high Koc compounds (i.e., when hydrolysis and volatilization are minor degradation pathways), the end result will be rapid movement form the water column with simultaneous accumulation in sediment.

For these compounds, OPP/EFED believes that the half life reflecting the degradation of the compound in the total sediment/water system (i.e., the Total System Half-Life) is a more appropriate representation of degradation rate in water or sediments compared to the half life determined from individual media (water or sediment). Although individual degradation rates within each environmental compartment would be ideal, the rapid movement of compound between the water and sediment compartments in these laboratory fate studies does not enable such degradation rates to be determined separately from the adsorption process. Furthermore, because the OPP/EFED approach for estimating pesticide exposure concentrations in aquatic systems directly accounts for chemical movement processes (e.g., volatilization, partitioning onto organic carbon), application of half lives that reflect dissipation or the combined effect of movement and degradation processes would amount to "double counting."

Quantifying Long-Term Accumulation in Soils and Sediments

The exposure assessments from the example pesticides indicate that long-term (year-to-year) accumulation in environmental compartments such as soil and sediment can be substantial. In the context of a 'field level' exposure scenario, the PRZM model can be used to describe long-term accumulation of pesticides in soils, an exposure pathway that is currently not evaluated by OPP/EFED. Such concentration estimates in soil could, in the future, provide information for assessing pesticide movement in terrestrial ecosystems (e.g., soil➔earthworm➔bird/mammal).

The combined PRZM/EXAMS models can be used to model long-term pesticide accumulation in sediment, issues of the impact of assumptions regarding sediment dynamics notwithstanding. Importantly, these models demonstrate that time periods that often exceed those of laboratory and field studies are required to assess long-term accumulation potential of highly persistent pesticides.

8.1.2 Sediment Dynamics

The temporal and spatial distribution of pesticides with PBT characteristics in aquatic ecosystems is expected to be influenced substantially by processes governing sediment particle delivery to (and transport within) water bodies (i.e., sediment dynamics). For these compounds, soil erosion is usually a major source of pesticide loading into aquatic ecosystems. Once in an aquatic ecosystem, processes such as settling, resuspension, and burial of sediment particles can affect the distribution of pesticides in the water column-, pore water-, and suspended- and benthic-sediment compartments. Sediment dynamics can also influence pesticide bioavailability within these compartments, due to pesticide sorption on particulate organic carbon and complexation with dissolved organic carbon.

Currently, OPP's aquatic exposure modeling framework incorporates pesticide delivery to a standard pond from soil erosion and runoff using the Pesticide Root Zone Model (PRZM). In this modeling framework, only the pesticide mass delivered from soil erosion and runoff is considered for delivery to an aquatic ecosystem (i.e., the mass of soil and volume of runoff predicted by PRZM are not considered). Pesticide transport between the water column and the benthic region within the standard pond is modeled using the Exposure Analysis Modeling System (EXAMS) based on a set of lumped parameters that are designed to reflect the combined effect of multiple transport processes (e.g., diffusion, setting and resuspension). The current modeling framework does not consider pesticide burial in the benthic area, a process by which pesticide is rendered permanently unavailable for biological interaction due to accumulating sediment. Without consideration of burial processes, the current modeling framework likely represents an effective screen for pesticide exposure assessment in both lentic (static) and lotic (flowing water) systems. The sensitivity of the current modeling framework to different assumptions regarding pesticide transport within the standard pond is explored in this White Paper. Other models that explicitly incorporate processes related to sediment dynamics are also reviewed. The Agency is seeking input from the SAP on the strengths and limitations of its current aquatic modeling framework for pesticides with PBT characteristics in the context of sediment dynamics. The Agency is also interested in feedback on processes and modeling approaches it should consider for potentially incorporating sediment dynamics in refined aquatic exposure assessments.

8.1.3 Bioaccumulation Issues

Accounting for Dietary Exposure

It has been established that chemical exposure to aquatic organisms via the diet can be important for highly hydrophobic organic chemicals (i.e., Log Kow > 5) which are not readily metabolized and excreted by biota (e.g., Russell et al., 1999; Fisk et al., 1998; Oliver and Niimi, 1983, 1988; Niimi, 1985; Swackhammer and Hites, 1988; Gobas, 1993; Burkhard, 1998; Arnot and Gobas, 2004). For such chemicals, current measures of bioconcentration in laboratory tests may substantially underestimate bioaccumulation potential in aquatic organisms, particularly those occupying higher trophic levels. Although field studies (e.g., microcosm, mesocosm) do have the capacity to incorporate pesticide exposure via dietary uptake, these studies are not routinely available for most pesticides and may underestimate long-term (year-to-year) bioaccumulation. Food web bioaccumulation models have been used in both the research and regulatory communities for assessing chemical bioaccumulation potential resulting from water, sediment and dietary exposures (USEPA, 1995; 2000; 2003; USACE 200X, Barber 2006; Park et al 2008; Thomann et al 1992). Such models can be particularly useful in overcoming limitations associated with laboratory and field-based experimental studies, including the assessment of long-term bioaccumulation, distinguishing the importance of water, sediment and dietary exposures, and being readily integrated with existing water quality models.

For Pesticide 1 (Log Kow 3.5-4.7), model estimates indicate that chemical accumulation in aquatic organisms through the diet does not appear to be a dominant exposure pathway for top trophic level fish,. Predicted BCFs using this model are consistent with measured BCF values, thus supporting the predictability of the Arnot and Gobas food web model for Pesticide 1. Marginal contribution of the diet to the bioaccumulation of Pesticide 1 is also consistent with current understanding that chemical uptake via water is expected to dominate for non-ionic organic chemicals with Log Kow values in the range of 4 or less. For Pesticide 3 (log Kow = 5.1), chemical accumulation through the aquatic diet appears to be significant, with predicted BAFs for piscivorous fish exceeding the laboratory-measured BCF for bluegill by about a factor of 3. For Pesticide 4 (Log Kow = 8.1), model predictions of bioconcentration using the Arnot and Gobas (2004) model were not consistent with laboratory measured data. This finding prompted the collection of additional data on the dietary bioavailability of Pesticide 4. These data, in combination with measured values for uptake and elimination rate constants, were used to re-parameterize the bioaccumulation model to reflect the lower bioavailability and/or potential metabolism of Pesticide 4 by aquatic biota.

Integrating Multiple Bioaccumulation Assessment Methods

The assessment of the bioaccumulation potential of Pesticide 4 clearly demonstrates the value of incorporating multiple lines of evidence for assessing bioaccumulation and carefully evaluating model assumptions. Although most food web bioaccumulation models enable incorporation of rate constants for in vivo metabolism, availability of in vivo metabolism data is relatively sparse and extrapolation from in vitro metabolism studies involves considerable uncertainty. Therefore, the bounding assumption of no metabolism is often applied. In cases where default assumptions regarding metabolism are made, bioconcentration estimates should be

evaluated against reliable measured data. When discrepancies occur, careful evaluation of the source of the discrepancies should be conducted. In some cases, difference may reflect an artifact of the experimental design of empirical bioconcentration or bioaccumulation studies. In other cases, model assumptions may be violated. Use of a 'hybrid approach' such as incorporating measured parameters in a portion of the food web model used for Pesticide 4 represents a potentially useful approach for integrating the results of multiple approaches for assessing aquatic bioaccumulation potential.

Assessing Terrestrial Bioaccumulation

Exposure assessments conducted by OPP for terrestrial vertebrates typically involve characterizing pesticide dietary uptake from direct deposition on food items within the treated field. These assessments are generally considered to provide estimates of potential risks from relatively short-term exposures to peak pesticide residues. However, exposure of terrestrial animals to pesticides may also result from pesticide volatilization, drift, runoff and subsequent bioaccumulation in terrestrial food webs that inhabit 'non-target' sites (i.e., areas adjacent to or near pesticide-treated fields). Currently, risks associated with the potential bioaccumulation of pesticides in terrestrial food webs is not directly assessed, and the extent to which these risks may be greater than those estimated from direct deposition on food items is not clear.

Empirical methods for assessing pesticide bioaccumulation potential in terrestrial organisms are generally lacking in typical pesticide submissions, although some studies may provide insights into terrestrial bioaccumulation potential (metabolism studies in terrestrial organisms). Recently, a number of food web bioaccumulation models have been developed for application to terrestrial ecosystems. Some of these models suggest that certain compounds with moderate K_{OW} values but high K_{OA} values may be prone to biomagnification in terrestrial food webs (but not aquatic food webs). The Agency is interested in feedback from the SAP on the need for evaluating terrestrial bioaccumulation potential and methods that can be readily applied in the near term.

8.1.4 Assessing Long Range Transport

Long-range atmospheric transport of certain historically used pesticides (HUC) such as lindane has been documented (Barrie et al., 1992). The occurrence of example Pesticide 2 and its primary degradate in remote regions distant from application sites has also been documented based on monitoring data. Although pesticide monitoring data are useful for documenting the occurrence of long-range transport, these data do not enable *a priori* screening of long-range transport before it actually occurs. Furthermore, establishing the relationship between near-field pesticide loadings and far-field pesticide concentrations is often very difficult based on monitoring data alone. Such relationships between near-field loadings and far-field exposure are needed to evaluate the impact of risk mitigation options on long-range transport potential. Several multi-media environmental fate and transport models have been developed specifically to screen for long-range transport potential of chemicals (Fenner et al., 2005). Outputs from some models include estimates of Overall Persistence (Pov) and Characteristic Travel Time (CTD). OPP is interested in obtaining input from the SAP on the extent to which such models

can be effectively used to screen for long-range transport potential in addition to their relative strengths and limitations.

8.1.5 Assessing Toxicity

Assessment of the combined toxicity of parent and degradate mixtures will depend on the availability of toxicity, fate and mode of action data for the individual mixture components. In situations where the exposure assessment can be conducted on individual mixture constituents (e.g., Formation/Decline and Residue Summation methods), and toxicity data are available for each constituent that indicate a similar mode of action, the combined toxicity and risk of the mixture can be assessed via assumptions of additivity. In cases where separate exposure assessments could not be conducted for each mixture constituent (e.g., total residue method), assumptions regarding the combined toxicity of the mixture would have to be made (e.g., assumed to be as toxic as the most toxic constituent). OPP is seeking SAP input on these and other methods for assessing the combined toxicity of mixtures of parent and degradates that are predicted from aquatic exposure assessments.

As described previously, exposure of aquatic organisms via the diet can be important for some highly hydrophobic organic chemicals. Currently, dietary exposure is not routinely considered in laboratory aquatic toxicity data submitted to the Agency for pesticide registration. The use of a tissue residue approach appears to offer promise for being able to use data from existing laboratory studies to address toxicity resulting from aqueous multiple exposure routes (water and diet). One of the example pesticide case studies demonstrates this approach using critical body residues, which may involve either predicted or measured residue-effect relationships, with the latter being the preferred approach. Although a number of refinements to the CBR method are available in the scientific literature (e.g., second-order toxicokinetic processes, stochasticity, and multi-compartment modeling), the ability to apply these more sophisticated methods with existing data submitted to the Agency would likely be limited. The Agency is seeking input from the SAP on these or other approaches for assessing aquatic toxicity from multiple chemical exposure using data typically available for pesticide registrations.

8.2 PATH FORWARD: POTENTIAL REFINEMENTS TO PROBLEM FORMULATION FOR PESTICIDES WITH PBT CHARACTERISTICS

The next steps (or "path forward") to incorporating refinements to OPP's ecological risk assessment process for addressing these and other PBT-related issues will largely be framed by the outcome of this SAP consultation. Pending the outcome of this SAP consultation, it is expect that detailed reviews of methods pertaining to specific topic areas (e.g., persistence, sediment dynamics, bioaccumulation, toxicity, long-range transport) would be conducted during future SAP meetings. Therefore, a detailed proposal on the specific refinements to EFED's ERA methods is considered premature at this time.

It should be noted, however, that past experience gained from the pesticide risk assessments within OPP and chemical risks assessments outside of OPP has provided insight on

how the overall problem formulation process might be refined to improve ecological risk assessments of pesticides with PBT characteristics. These refinements do not reflect a major alteration of the problem formulation process. Rather, they reflect steps to identify:

1. Situations when PBT-related risk assessment issues may be important to consider in an ecological risk assessment, and
2. Which of these PBT-related risk assessment issues may need to be addressed.

As described in **Section 2.5** and in USEPA's Guidelines for Ecological Risk Assessment (USEPA, 1998), problem formulation is an early but critical step in the ecological risk assessment process. Problem formulation tends to be an iterative process involving the integration of available information to define the overall scope and plan for conducting the risk assessment.

This section describes potential refinements to the problem formulation process that that OPP/EFFED is considering for identifying when potential PBT risk assessment issues should be addressed. This section also provides a series of PBT-related risk assessment questions that are designed to inform the scope and analysis plan involving pesticides with PBT characteristics.

8.2.1. Identification of PBT-Related Risk Assessment Issues

The next steps (or "path forward") for incorporating refinements to OPP's ecological risk assessment (ERA) process to address PBT-related issues will largely be framed by the outcome of this SAP meeting. Pending the results from this SAP meeting, it is expect that detailed reviews of methods pertaining to specific topic areas (e.g., persistence, sediment dynamics, bioaccumulation, toxicity, long-range transport) would be conducted during future SAP and other external peer review mechanisms. Therefore, providing a detailed proposal on the specific refinements to the OPP/EFED ERA process is considered premature at this time.
Therefore, providing a detailed proposal on the specific refinements to the OPP/EFED ERA process is considered premature at this time.

It is possible, however, to describe how certain elements of the problem formulation process are being considered for refinement in order to facilitate a more systematic approach for evaluating PBT-related issues in future pesticide ecological risk assessments. These potential refinements do not reflect a major alteration of the problem formulation process. Rather, they reflect steps to identify: (1) situations where PBT-related risk assessment issues may be important to consider in an ecological risk assessment, and (2) which PBT-related risk assessment issues may need to be addressed.

As an initial screen, OPP is considering the use of National and International criteria for classifying chemicals according to their PBT and LRT characteristics for identifying when PBT/LRT-related risk assessment issues may need to be evaluated in ecological risk assessments (**Table 8.2**). These screening criteria would be used in conjunction with information on a pesticide's physicochemical properties, environmental persistence, bioaccumulation potential, toxicity and long-range transport potential to determine whether or not PBT/LRT-related risk assessment issues described herein should be addressed in problem formulation portion of the risk assessment. Importantly, these criteria would be used in conjunction with available data in a

strength of evidence approach to trigger additional data evaluation for defining which PBT/LRT issues need to be addressed in the risk assessment.

Table 8.2. National and International Screening Criteria for Classifying Chemicals According to PBT and LRT Characteristics

Attribute	Property or Data	Criteria
Persistence	Half-life in soil	>2 mo to >1 yr.
	Half life in water	>2 mo. to >6 mo.
	Half life in sediment	>2 mo. to >1 yr.
	Half life in air	$\geq$ 2 d to $\geq$ 5 d
Bioaccumulation	BCF or BAF	> 1000 to > 5000 L/kg (wet wt.)
	Log K_{OW}	> 5
Toxicity	Acute LC_{50} / EC_{50} Chronic NOAEC Potential to impact human health or the environment	< 1 ppm <0.01 to <0.1 ppm Best professional judgment
Long-Range Transport	Monitoring data	Measured levels at locations distant from sources that are of potential concern Monitoring data indicating LRT and potential transfer to a receiving environment may have occurred via air, water or migratory species
	Environmental fate properties and/or model results	Demonstrated LRT potential via air, water or migratory species and potential transfer to a receiving environment at locations distant from the sources. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days

Source: Appendix A.

If the aforementioned screening process suggested that PBT and/or LRT-related ecological risk assessment issues may be encountered during the assessment, the problem formulation process would proceed as usual, but with an emphasis on identifying those PBT/LRT-related issues would likely need to be addressed in the conceptual model and analysis plan for the risk assessment. Formulating a conceptual model and analysis plan that addresses PBT-specific attributes would be informed by a series of risk assessment questions. Examples of such risk assessment questions are shown in **Table 8.3.**

Table 8.3. Example Risk Assessment Questions to be Considered During Problem Formulation For Addressing PBT and LRT Issues

Issue	Risk Assessment Question
Environmental Persistence	
1. Environmental Fate	*Which environmental compartments is the pesticide likely to persist?*
2. Environmental Degradates	*To what extent does the formation of environmental degradates contribute to the exposure of vulnerable ecological receptors? How similar are the fate properties of the parent and degradate compounds?*
3. Solubility	*Do predicted aqueous concentrations exceed aqueous solubility?*
4. Long-term Accumulation	*Is long-term accumulation (i.e., year-to-year carryover) expected to occur?*
5. Degradation Kinetics	*How important are dissipation processes in the interpretation of degradation half life data from laboratory or field studies? If important, how will degradation half lives be determined for exposure modeling purposes?*

Issue	Risk Assessment Question
Sediment Dynamics	
1. Model Sensitivity/ Uncertainty	*How sensitive are the risk assessment findings to model assumptions regarding the treatment of sediment dynamics?*
Bioaccumulation-Related Questions	
1. Exposure Routes	*How important is exposure through the diet and sediments for estimating bioaccumulation in aquatic organisms?*
2. Environmental Degradates	*How do the bioaccumulation potentials of parent and degradation products compare?*
3. Metabolism	*To what extent is bioaccumulation affected by pesticide metabolism in biota? What are the likely pesticide metabolites in aquatic organisms?*
4. Bioavailability	*How important are abiotic and biotic factors in affecting pesticide bioaccumulation in aquatic food webs?*
5. Steady State	*How long does it take for pesticide concentrations to reach steady-state accumulation in organisms*?
6. Critical Exposure Period	*What exposure period(s) is (are) considered most appropriate for estimating risk to sensitive ecological receptors? (e.g., weeks, months, year?)*
7. Multiple Lines of Evidence	*To what extent are aquatic bioaccumulation predictions by various methods (lab measurements, field measurements, model predictions) in agreement/disagreement? Can differences in bioaccumulation predictions be adequately explained?*
8. Terrestrial Ecosystems	*To what extent is bioaccumulation potential in terrestrial ecosystems a concern?*
Long-Range Transport	
1. Monitoring data	*What evidence exists on pesticide movement to remote locations distant from areas of pesticide application? What is the potential for adverse effects at these levels?*
2. LRT Potential	*What do physicochemical data and available environmental models suggest regarding the potential for long-range transport?*
Toxicity-Related Questions	
1. Ecological Receptors of Concern.	*What are the most sensitive ecological receptors and where do they occur in the environment?*
2. Dietary Exposure	*How important is dietary exposure to interpreting the results of laboratory toxicity studies?*
3. Parent vs. Degradate Toxicity.	*How similar is the toxicity of parent and degradatess? Are they likely to have the same mode of action?*
4. Steady-state	*Is steady-state accumulation likely to be achieved in chronic toxicity tests? Do reproductive studies allow sufficient time to adequately characterize maternal transfer?*
5. Bioavailability	*How much are toxicity test results likely to be affected by bioavailability differences across studies? Has the bioavailability of the pesticide been adequately characterized in the studies (e.g., centrifugation when concentrations approach or exceed solubility)?*

It is expected that the ability of the risk assessor to address the PBT/LRT-related risk assessment questions in **Table 8.3** will vary considerably from issue to issue. In some cases, relevant data may not be available to address a particular question, thus simplifying assumptions or additional data may be required. In other cases, the available science underlying a particular risk assessment question may not be fully developed or might be evolving significantly. Specific methods for addressing many of the questions in **Table 8.3** will be informed by current and future SAP reviews.

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APPENDIX A. Summary of National and International PBT Criteria

ORGANIZATION and POLICY[1]	PROPERTY		
	Persistence	Bioaccumulation	Toxicity
U.S. EPA, Office of Environmental Information[2]	Half-life ≥ 2 months in soil, sediment or water OR Half-life ≥ 2 days in air	BAF/BCF ≥ 1,000	Professional judgment based on level of risk
UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP)[3]	Half-life > 2 months in water; > 6 months in soil or sediment; or otherwise sufficiently persistent to be of concern	BAF/BCF > 5000 or Log Kow > 5	Potential to affect human health and/or the environment adversely
UNEP POPs/CEG Framework (Stockholm Convention)[4]	Half-life > 2 months in water; >2 or 6 months in soil or sediment; or other evidence that substance is sufficiently persistent to be of concern	BCF/BAF > 5000 or Log Kow > 5; or evidence that substance with significantly lower BCF/BAF is of concern, e.g.,due to high toxicity/ecotoxicity; or monitoring data in biota indicating sufficient bioaccumulation to be of concern	Toxicity characteristics indicating potential damage to human health or the environment.
Environment Canada Toxic Substances Management Policy (June 1995)[5]	Half-life ≥2 days air; ≥6 months water/soil; ≥ 1 year in sediment	BAF or BCF >5000 or Log Kow >5	CEPA toxic (Defined at the following URL: http://www.ec.gc.ca/CEPARegistry/gene_info/CEPA_TOXIC.pdf)
ICCA[6]	Half-life ≥ 6 months in water, ≥ 1 yr in soil/sediment, or ≥ 5 days air	BCF ≥ 5,000 or Log Kow between 5 and 7.5, MW<700 and substance is not metabolized	Expert judgment that effects[7] are expected to occur at the concentrations observed in the environment

1. Other U.S. and International criteria are consistent with criteria presented in this table
2. Office of Environmental Information. Federal Register: October 29, 1999 (Volume 64, Number 209). Rules and Regulations. Page 58665-58753. On-line at http://www.epa.gov/fedrgstr/EPA-WASTE/1999/October/Day-29/f28169.htm
3. United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP) (Ref. 54); PTBs (February 1996)) http://www.unece.org/env/lrtap/
4. United Nations Environmental Programme http://www.chem.unep.ch/pops/default.html
5. Environment Canada Toxic Substances Management Policy (June 1995)
6. International Council of Chemical Associations http://www.icca-chem.org/
7. Effects include acute aquatic lethality, subchronic and chronic aquatic toxicity, acute wildlife toxicity, oral/dermal/inhalation toxicity in mammals in birds, carcinogenicity, mutagenicity, teratogenicity, reproductive toxicity, neurological toxicity, and immune system effects

APPENDIX B. RELEVANT ENVIRONMENTAL FATE AND ECOLOGICAL EFFECTS STUDIES REQUIRED UNDER FIFRA

The following tables summarize the data requirements for assessing ecological effects for aquatic and terrestrial animals (**Tables B.1 and B.2**) and environmental fate (**Tables B.3**) that are relevant to assessing risks of pesticides with PBT characteristics.

Table B.1. Relevant Aquatic Animal Toxicity Testing Requirements for FIFRA Pesticide Registration

Test Guideline	Title[(1)]	Study Type/Scope
850.1075	**Fish acute toxicity test, freshwater and marine**	• Required (outdoor uses); Conditionally required (indoor uses) • 96-hr, water only exposure • Common test species: bluegill sunfish, rainbow trout
850.1010	**Acute toxicity freshwater invertebrates**	• Required (outdoor uses); Conditionally required (indoor uses) • 48-hr, water only exposure • Common test species: waterflea
850.1025 850.1035 850.1045 850.1055 850.1075	**Acute toxicity estuarine and marine invertebrates**	• Required (outdoor uses); Conditionally required (indoor uses) • 48-96-hr, water only exposure • Common test species: oyster, mysid shrimp, penaeid shrimp,
850.1300 850.1350	**Invertebrate full life cycle**	• Freshwater inverts: required (outdoor uses); Conditionally required (indoor uses) • Saltwater inverts: conditionally required (outdoor uses) • 21-d (waterflea); 28-d (mysid shrimp) • water + incidental dietary exposure
850.1400	**Fish early-life stage: Fresh, estuarine, marine**	• Freshwater fish: required (outdoor uses); conditionally required (indoor uses). • Saltwater fish: conditionally required (outdoor uses) • 28-32-d post hatch (warmwater fish); 60-d post hatch (salmonids), • water + incidental dietary exposure • Common test species: fathead minnow, rainbow trout, Atlantic silverside
850.1500	Fish full life cycle	• Conditionally required (outdoor uses) • Egg to egg exposure (duration varies by species) • water + incidental dietary exposure • Common test species: fathead minnow, sheepshead minnow

. Test Guideline	Title[(1)]	Study Type/Scope
850.1900 850.1925 850.1950	Generic Freshwater Microcosm Test Site-specific Aquatic Microcosm Test Simulated or actual field testing	• Conditionally required (outdoor uses) • Organisms occupying one or more trophic levels and environmental compartments (*e.g.,* algae, microinvertebrates, macroinvertebrates) are exposed to the test chemical in laboratory (microcosm) or outdoor (mesocosm) vessels. • Conditionally required for outdoor uses • Results consist of chemical fate and effects on aquatic organisms, including bioaccumulation in food chain organisms. • Water and dietary exposure can be assessed
850.1735 850.1740	**Acute whole sediment invertebrate (fresh and saltwater)**	• Conditionally required (outdoor uses) • 10-28 days; Common test species: *Hyalella, Chironomus*, *Leptochirus, Mysidopsis, Ampilisca.* • Overlying water, pore water, bulk sediment, incidental dietary exposure
ORD/OW Test Guideline	**Chronic whole sediment invertebrate (fresh and saltwater)**	• Conditionally required (outdoor uses) • 28-65 days; Common test species: *Hyalella, Chironomus*, *Leptochirus, Lumbriculus.* • Overlying water, pore water, bulk sediment, incidental dietary exposure

[(1)] Studies in bold are commonly submitted as part of most outdoor pesticide registrations, those not in bold are rarely submitted.

Table B.2. Relevant Terrestrial Animal Toxicity Testing Requirements for FIFRA Pesticide Registration

test Guideline	Title[(1)]	Study Type/Scope
850.2100	**Avian oral toxicity**	• Required (outdoor uses) • Single dose, oral exposure, 14-d observation • Common test species: bobwhite quail, mallard, 1 passerine species
850.2200	**Avian dietary toxicity**	• Required (outdoor uses) • 5-d dietary exposure, 3-d observation • Common test species: bobwhite quail, mallard
850.2300	**Avian reproduction**	• Required (outdoor uses) • Dietary exposure, ≥ 10 weeks prior to egg laying➔ 2 weeks post hatch • Common test species: bobwhite quail, mallard
870.1100	**Acute oral - rodent**	• Required (outdoor uses) • Single, oral dose, 14-d observation • Common test species: rat, mouse
870.3100	**90 day oral- rodent**	• Required (outdoor uses) • 90-d oral exposure • Common test species: rat, mouse
870.4100	**Chronic oral - rodent**	• Required (food uses) • 12 months, dietary exposure • common test species: rat, mouse
870.3800	**Reproduction and fertility effects**	• Required (food uses) • 2-generation reproduction study, oral exposure • Common test species: rat

test Guideline	Title[1]	Study Type/Scope
850.2400	Wild mammal toxicity	• Conditionally required (outdoor uses) • Variable experimental design, higher tier study
850.2500	Simulated or actual field testing	• Conditionally required (outdoor uses) • Variable experimental design, higher tier study
850.3020	**Honeybee acute contact toxicity**	• Required (terrestrial uses) • Single dose, contact LD50 study • Honeybee

[1] Studies in bold are commonly submitted as part of most outdoor pesticide registrations, those not in bold are rarely submitted.

Table B.3 Relevant Environmental Fate Testing Requirements for FIFRA Pesticide Registration

Test Guideline	Title[1]	Study Type/Scope
835.2100	**Hydrolysis**	• Required (Terrestrial, Aquatic, Greenhouse, Forestry, Residential Outdoor uses); Conditionally required (Indoor use) • Assesses abiotic hydrolytic transformations of chemicals in aquatic systems at pH values normally found in the environment (pH 4 – 9)
835.2240	**Photodegradation in water**	• Required (Terrestrial, Aquatic, Forestry uses) • Determines photolytic stability of pesticide (and photoproducts) in water when exposed to sunlight
835.2410	**Photodegradation on soil**	• Required (Terrestrial, Forestry uses); • Determines photolytic stability (persistence) of pesticide (and photoproducts) on soil exposed to sunlight.
835.2370	Photodegradation in air	• Conditionally required (Terrestrial, Greenhouse, Forestry, Residential Outdoor uses) • Assesses photolytic stability (persistence) of pesticide and photoproducts in the vapor phase
835.4100	**Aerobic soil metabolism**	• Required (Terrestrial, Greenhouse, Forestry, Residential Outdoor uses); Conditionally required (Aquatic use) • Determines transformation rates of pesticide and degradation products in the aerobic soil environment to which plants and soil organisms may be exposed
835.4200	**Anaerobic soil metabolism**	• Required (Terrestrial use) • Determines transformation rates of pesticide and degradation products in the anaerobic soil environment to which plants and soil organisms may be exposed

Test Guideline	Title[(1)]	Study Type/Scope
835.4300	**Aerobic aquatic metabolism**	• Required (Terrestrial, Aquatic, Forestry uses); • Determines the following in the aerobic aquatic environment: the transformation rates of a pesticide and its degradation products in a water-sediment system and in the water and sediment compartments; the mineralization rate of the pesticide and/or its transformation products and mass balance (when ^{14}C-labeled test substance is used); the distribution of the test substance and its transformation products between the two phases.
835.4400	**Anaerobic aquatic metabolism**	• Required (Terrestrial, Aquatic, Forestry uses); • Determines the following in the anaerobic aquatic environment: the transformation rates of a pesticide and its degradation products in a water-sediment system and in the water and sediment compartments; the mineralization rate of the pesticide and/or its transformation products and mass balance (when ^{14}C-labeled test substance is used); the distribution of the test substance and its transformation products between the two phases
835.1230	**Adsorption/desorption**	• Required (Terrestrial, Aquatic, Greenhouse, Forestry, Residential Outdoor uses); • Estimates the adsorption/desorption behavior of a substance on various soils as a function of soil characteristics (*e.g.,* organic carbon content, clay content, soil texture, and pH)
835.1240	**Soil column leaching**	• Required (Terrestrial, Aquatic, Greenhouse, Forestry, Residential Outdoor uses); • Assesses the relative mobility of the pesticide and its degradates through columns packed with the various soils
835.1410	Volatility – laboratory	• Conditionally required (Terrestrial, Greenhouse uses) • Determines the rate of volatilization and the resulting air concentration under confined conditions.
835.8100	Volatility – field	• Conditionally required (Terrestrial, Greenhouse uses) • Provides realistic estimates of volatility when the pesticide is applied as it is intended to be used.
835.6100	**Terrestrial field dissipation**	• Required (Terrestrial, Residential Outdoor uses); Conditionally required (Aquatic, Forestry uses) • Determines the extent of pesticide residue dissipation under actual use conditions at various locations. Accounts for pesticide loss as combined result of chemical and biological degradation (*e.g.,* hydrolysis, photolysis, microbial transformation) and physical dissipation (*e.g.,* volatilization, leaching, plant uptake).

Test Guideline	Title[1]	Study Type/Scope
835.6200	Aquatic (sediment) field dissipation	• Required (Aquatic use); Conditionally required (Terrestrial use) • Quantifies the extent of pesticide residue dissipation and mobility under actual use conditions. Accounts for pesticide loss as combined result of chemical and biological degradation and environmental partitioning processes.
835.6300	Forestry field dissipation	• Conditionally required (Forestry use) • Quantifies the extent of pesticide residue dissipation and mobility in forestry sites
850.1730	**Accumulation in fish**	• Required; Conditionally required (Terrestrial, Aquatic, Forestry, Residential Outdoor uses) • Determine uptake and depuration rate constants and bioconcentration factors for fish exposed to a test chemical in aqueous solution, and identify and quantify major degradates in fish at steady state

[1] Studies in bold are commonly submitted as part of most outdoor pesticide registrations, those not in bold are rarely submitted.

APPENDIX C. Supporting Material for Chapter 3: Environmental Persistence

PART 1: Addressing the Combined Exposure to Parent and Degradation Products

Analytical Solution for Simultaneous Formation and Decline Kinetics for Pesticide (Derivation was conducted by Dr. R. David Jones)

Differential Equations **Integrated First-Order Equations**

Isomer 1 (*Degradation*)

$dA/dt = -k1A$ **$A = A_o e^{-k1t}$**

where: dA= Δ Isomer 1 Concentration (µg/L)
d t= Δ time (days)
k1= degradation rate for isomer 1 ($days^{-1}$)
A= Isomer 1 Concentration (µg/L)

where: A= Isomer 1 Conc (µg/L)
A_o= Isomer 1 Conc @ time 0
k1= degradation rate for isomer 1 ($days^{-1}$)
t= time (days)

Isomer 2 (*Degradation*)

$dB/dt = -k2B$ **$B = B_o e^{-k2t}$**

where: dB= Δ Isomer 2 Concentration (µg/L)
d t= Δ time (days)
k1= degradation rate for isomer 1 ($days^{-1}$)
B= Isomer 2 Concentration (µg/L)

where: A= Isomer 2 Conc (µg/L)
A_o= Isomer 2 Conc @ time 0
k1= degradation rate for isomer 1 ($days^{1}$)
t= time (days)

Degradation Product (*Formation Rate-Degradation Rate)*

$dD/dt = k3A + k4B - k5D$

where: dD= Δ Degradation Product Concentration (µg/L)
dt= Δ time (days)
k3= formation rate of degradate from Isomer 1 (days-1)
k4= formation rate of degradate from Isomer 2 (days-1)
k5= degradation rate of degradate (days-1)
D= Degradation Product Concentration (µg/L)

1. Using the above equations with substitution, the following equation is derived.

$dD/dt = k3(A_o e^{-k1t}) + k4(B_o e^{-k2t}) - k5D$

2. Rearrange to the standard form for 1st order linear differential equation (y' + Py=Q)

$dD/dt + k5D = k3(A_o e^{-k1t}) + k4(B_o e^{-k2t})$

so: $y' = dD/dt$
$y = D$
$P = K5$
$Q = k3(A_o e^{-k1t}) + k4(B_o e^{-k2t})$

3. The solution for a 1st order linear differential equation is in the form:

$$\mathbf{Y = e^{-I} \int Q e^{I} + C e^{-I}}$$

where: C= integration constant
$I = \int P dt = K5t$

Therefore, the following equation can be derived.

$$\mathbf{D = e^{-K5t} \int (K3 e^{A_0 - K1t} + K4Boe^{-K2t}) e^{K5t} dt + Ce^{-K5t}}$$

$$\mathbf{D = e^{-K5t} (K3A_0 \int e^{(K5K1)t} dt + K4B_0 e^{(K5K2)} dt + Ce^{-K5t}}$$

$$\mathbf{D = e^{-K5t} [(K2A_0/K5-K1)e^{K5-K1t} + (K4B_o/K5-K2)e^{K5K2t}) + Ce^{-K5t}}$$

$$\mathbf{D = Ce\text{-}K5t + K2Ao/(K5-K1)\, e^{-K1t} + K4Bo/(K5-K2)e^{-(K2+K5)t}}$$

3. To calculate integration C0 would set D=0 at t=0 so

$$\mathbf{0 = C_0 + K3Ao/(K5-K1) + K4Bo/(K5-K2)}$$

Solving for C_0

$$\mathbf{C_0 = -(K3Ao/K5-K1 + K4Bo/K5-K2)}$$

Used EXCEL Solver to solve for rate constants

APPENDIX C:

PART 2: PRZM/EXAMS INPUT AND OUTPUT SUMMARY FOR EXAMPLE PESTICIDES

(Due to large size, these data are provided under separate cover).

APPENDIX D. Supporting Data for Chapter 5: Bioaccumulation

PART 1. Probabilistic Bioaccumulation Analysis for Example Pesticide 1

Model Description

This appendix describes the bioaccumulation modeling assessment of Pesticide 1 in aquatic food webs. Specifically, aquatic bioaccumulation and subsequent risk to piscivorous wildlife were estimated using a spreadsheet model being development by OPP/EFED. This model (KABAM or **K**ow (based) **A**quatic **B**io**A**ccumulation **M**odel) is intended for use as a screening-level model for estimating bioaccumulation potential of hydrophobic organic pesticides in freshwater aquatic food webs and subsequent risks to mammals and birds via consumption of contaminated aquatic prey. KABAM is composed of two parts:

1. a bioaccumulation model that estimates pesticide concentrations in aquatic organisms, and
2. a risk component that translates exposure and toxicological effects of a pesticide into risk estimates for mammals and birds consuming contaminated aquatic prey.

The bioaccumulation portion of KABAM is based on a steady-state, food web bioaccumulation model published by Arnot and Gobas (2004). This model was originally published in 1993 by Gobas and was modified by Arnot and Gobas (2004). As described by Arnot and Gobas (2004), bioaccumulation is estimated using a chemical's octanol-water partition coefficient (K_{OW}) to estimate uptake and elimination constants through respiration and diet of aquatic organisms in different trophic levels. Pesticide concentrations in aquatic organisms are calculated for different levels of an aquatic food web through diet and respiration.

In the risk component of the model, pesticide concentrations in aquatic organisms are used to estimate dose- and dietary-based exposures and associated risk quotients to mammals and birds consuming aquatic organisms. The methods used in the risk component of KABAM are consistent with the EPA wildlife factors handbook (USEPA 1993) and with EFED's current modeling approach for assessing risks to terrestrial-feeding mammals and birds, as implemented in the T-REX model (version 1.3.1; USEPA 2006). At this time, KABAM is undergoing QA/QC within EFED.

Model parameterization

The bioaccumulation model used in assessing risks of Pesticide 1 this assessment uses the same equations published by Arnot and Gobas (2004) for predicting the concentration of tissues of aquatic organisms. Tissue residues are first calculated at the lowest level of the aquatic food chain (phytoplankton). Concentrations of Pesticide 1 residues are then calculated for zooplankton, including consideration that

the diet of zooplankton includes phytoplankton, which contain Pesticide 1 residues. Tissue residues are then calculated for the taxonomic groups at higher trophic levels based on their diets of organisms from lower trophic levels. The equations, their parameters and associated assumptions are described in Arnot and Gobas (2004).

Parameter definitions and abbreviations are consistent with those published by Arnot and Gobas (2004) in order to ensure consistency with the publication and transparent methodology used in this assessment. Ecosystem specific input parameters, such as organism body composition, temperature, and trophic level diets, see **Tables 1 and 2**.

In order to understand the distribution of possible residue of Pesticide 1 in aquatic organisms, a probabilistic-based analysis was conducted whereby parameters were assigned distributions and assumptions of ranges, means and standard deviations. From this, a Monte Carlo simulation was carried out using Crystal Ball 2000. In this simulation, 10,000 trials randomly selected parameters and predicted Pesticide 1 residue concentrations in organisms.

Table 1. Diets of biota of the model ecosystem.

	% Diet for:					
Organism in diet	**Zoo plankton**	**Benthic Invertebrates**	**Filter Feeder**	**Small Forage Fish**	**Medium Forage Fish**	**Piscivorous Fish**
sediment	0.0%	100.0%	33.0%	0.0%	0.0%	0.0%
phytoplankton	100.0%	0.0%	33.0%	0.0%	0.0%	0.0%
zooplankton	0.0%	0.0%	34.0%	33.0%	33.0%	0.0%
Benthic invertebrates	0.0%	0.0%	0.0%	33.0%	33.0%	0.0%
filter feeder	0.0%	0.0%	0.0%	34.0%	34.0%	0.0%
small forage fish	0.0%	0.0%	0.0%	0.0%	0.0%	50.0%
Medium forage fish	0.0%	0.0%	0.0%	0.0%	0.0%	50.0%
piscivorous fish	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Table 2. Parameters and Associated Assumptions Used for Estimating Tissue Concentrations, BCF and BAF Values of Pesticide 1.							
Para-meter	**Parameter Description**	**Trophic Level**	**Distribution**	**Mean**	**SD**	**Range**	**Data Source**
A	constant related to the resistance to pesticide uptake through the aqueous phase of plant	Phytoplankton	set value	$6.0x10^{-5}$	N/A	N/A	Arnot and Gobas 2004
B	constant related to the resistance to pesticide uptake through the organic phase of plant	Phytoplankton	set value	5.5	N/A	N/A	Arnot and Gobas 2004
C_{SS}	concentration of suspended solids	All	lognormal	$3.0\ E^{-4}$	$3.0\ E^{-3}$	$1.0\ E^{-6}$ to $2.0\ E^{-1}$	NAWQA 2006
C_{WTO}	total pesticide concentration in water column above the sediment	All	uniform	N/A	N/A	0.1-5.0	PRZM/EXAMS, 60 day values (see **Table 4**)
C_{WDP}	freely dissolved pesticide concentration in pore water	All	uniform	N/A	N/A	0.1-5.0	Assumed to be equivalent to aqueous concentrations.
K_{OC}	Organic carbon partition coefficient	All	lognormal	13600	2600	10000-16000	
Log K_{OW}	Octanol-water partition coefficient	All	uniform	N/A	N/A	3.55-4.78	**Table 3**
m_p	fraction of respiratory ventilation that involves pore-water of sediment	Phytoplankton	set value	0	N/A	N/A	Arnot and Gobas 2004
		Zooplankton	set value	0	N/A	N/A	
		Benthic Inv.	set value	0.05	N/A	N/A	
		Filter Feeders	set value	0.05	N/A	N/A	
		Sm. Forage Fish	set value	0	N/A	N/A	
		Med. Forage Fish	set value	0	N/A	N/A	
		Piscivores	set value	0	N/A	N/A	
OC	percent organic carbon in sediment	All	lognormal	1.40%	2.50%	0.01-50%	NAWQA 2006
S	oxygen saturation in water column	All	lognormal	83%	33%	0-100%	NAWQA 2006
T	temperature	All	lognormal	14	7.9	0-100	NAWQA 2006
V_{LB}	lipid fraction of organism	Phytoplankton	lognormal	0.50%	0.10%	0.01-1%	Arnot and Gobas 2004
		Zooplankton	lognormal	2.00%	0.20%	0.5-3.5%	Arnot and Gobas 2004
		Benthic Inv.	lognormal	2.00%	0.20%	1.0-3.0%	Arnot and Gobas 2004

		Filter Feeders	lognormal	2.00%	0.20%	1.0-3.0%	Arnot and Gobas 2004
		Sm. Forage Fish	lognormal	6.00%	0.60%	1.0-10.0%	Arnot and Gobas 2004
		Med. Forage Fish	lognormal	6.00%	0.60%	1.0-10.0%	Arnot and Gobas 2004
		Piscivores	lognormal	6.00%	0.60%	1.0-10.0%	Arnot and Gobas 2004
V_{NB}	NLOM (Non Lipid Organic Matter) fraction of animals, NLOC (Non Lipid Organic Carbon) of plants	Phytoplankton	set value	6.50%	N/A	N/A	
		Animals	set value	20%	N/A	N/A	Arnot and Gobas 2004
V_{WB}	water content of the organism	All	N/A	N/A	N/A	N/A	
W_B	wet weight of the organism at t	Phytoplankton	N/A	N/A	N/A	N/A	
		Zooplankton	lognormal	1E-07	1.00E-08	0.00000001 - 0.000001	Arnot and Gobas 2004
		Benthic Inv.	lognormal	0.00001	0.000001	0.000001 - 0.0001	Arnot and Gobas 2004
		Filter Feeders	lognormal	0.0001	0.00001	0.00001 - 0.001	Arnot and Gobas 2004
		Sm. Forage Fish	lognormal	0.01	0.001	0.001-0.1	Arnot and Gobas 2004
		Med. Forage Fish	lognormal	0.1	0.01	0.01-1.0	Arnot and Gobas 2004
		Piscivores	lognormal	1	0.1	0.1-10.0	Arnot and Gobas 2004
X_{TOC}	concentration of TOC in water	All	lognormal	4.43E-06	9.2E-06	0.0000001 - 0.00084	NAWQA 2006
β	proportionality constant expressing the sorption capacity of NLOM or NLOC to that of octanol	Phytoplankton	set value	0.35	N/A	N/A	Arnot and Gobas 2004
		Animals	set value	0.035	N/A	N/A	Arnot and Gobas 2004
ε_L	dietary assimilation rate of lipids	Zooplankton	lognormal	72%	7.20%	55-85%	Arnot and Gobas 2004
		Benthic Inv.	lognormal	75%	7.50%	15-96%	Arnot and Gobas 2004
		Filter Feeders	lognormal	75%	7.50%	15-96%	Arnot and Gobas 2004
		All Fish	lognormal	92%	9%	50-99%	Arnot and Gobas 2004
ε_N	dietary assimilation rate of NLOM	Zooplankton	lognormal	72%	7.20%	55-85%	Arnot and Gobas 2004
		Benthic Inv.	lognormal	75%	7.50%	15-96%	Arnot and Gobas 2004
		Filter Feeders	lognormal	75%	7.50%	15-96%	Arnot and Gobas 2004
		All Fish	lognormal	60%	6%	40-80%	Arnot and Gobas 2004
ε_W	dietary assimilation rate of water	All	set value	25%	N/A	N/A	Arnot and Gobas 2004

σ	efficiency of scavenging of particles absorbed from water	Filter Feeders	set value	100%	N/A	N/A	Maximum Assumption

Available data supported use of a range of values for K_{OW} of Pesticide 1 (**Table 3**).

Table 3. Log K_{OW} Values for Pesticide 1 Isomers and Its Primary Degradate.

Chemical	Measured Log K_{OW}	Estimated Log P *
Isomer 1 (P1)	3.55-4.74	3.50
Isomer 2 (P2)	3.62-4.78	3.50
Degradate 1 (D1)	3.66	3.64
* By K_{OW}Win		

Based on the total residue method described in Section 3, EECs for the combined parent and degradate compounds of Pesticide 1 were determined for seven applicable crop scenarios. These EECs were used to define the range of the distribution of water concentrations shown in Table 1.

Table 4. 60-day average Aqueous EECs (µg/L) of Pesticide 1 Generated by PRZM/EXAMS Using the Total Residue Method.

Crop	Total Pesticide 1 EEC (P1 + P2 + D1 in ug/L)	Aqueous EEC for Pesticide 1 Degradate (D1) in ug/L
Apples	0.24	0.13
Cotton	2.5	1.38
Lettuce	1.3	0.69
Pecan	3.8	2.09
Potato	1.6	0.89
Tobacco	1.8	0.97
Tomato	4.9	2.68

Calculation of BCFs and BAFs

Bioconcentration Factors (BCFs) and Bioaccumulation Factors (BAFs) are calculated according to **Equations 1 and 2**, where C_{BR} is the amount of pesticide in the tissue of the organism with respect to intake and excretion through respiratory processes, C_B is the total pesticide concentration in the tissue of the organism taken up through respiration and ingestion, and C_{WTO} is the amount of pesticide present in the water column.

$$Equation\ 1. \quad BCF = \frac{C_{BR}}{C_{WTO}}$$

$$Equation\ 2. \quad BAF = \frac{C_B}{C_{WTO}}$$

Calculation of Dose and Diet-based Risk Quotients for Pesticide 1

In order to assess risks to mammals and birds consuming aquatic organisms which have bioaccumulated Pesticide 1, several species were selected, including mink, river otter, belted kingfisher, herring gull, osprey, mallard duck, great blue heron and bald eagle.

Species body weight data (in kg) are consistent with the Wildlife Exposure Factors Handbook (USEPA 1993). Food intake values for mink, herring gull, osprey, great blue heron and bald eagle were taken from data cited in USEPA 1993. Food ingestion rates were estimated for otter (mammal equation) mallard duck and kingfisher (bird equation). Food ingestion rates (FI) were estimated by **Equations 3 and 4**, where FI is calculated in kg dry food/kg-bw day and Wt is animal body weight in kg. FI rates were converted from food dry weight/kg-bw day to food wet weight/day by assuming the diet of river otter and belted kingfisher includes food of 75% water by weight. The FI rate for mallard duck was converted from food dry weight/kg-bw day to food wet weight/day by assuming the diet of mallard duck includes food of 80% water by weight (USEPA 1993).

$$Eq.3 \quad FI = \frac{0.0687 * Wt^{0.822}}{Wt} \quad (mammals)$$

$$Eq..4 \quad FI = \frac{0.0582 * Wt^{0.651}}{Wt} \quad (birds)$$

Drinking water intakes (DW) for mammals and birds are calculated based on the **Equations 5 and 6** (USEPA 1993); where BW represents the body weight (in kg) of the animal for which the drinking water intake is being assessed. Resulting units of DW are L/day.

$$Eq.5 \quad DW = \left(0.099 * BW^{0.09}\right) \quad (mammals)$$

$$Eq.6 \quad DW = \left(0.059 * BW^{0.67}\right) \quad (birds)$$

Dose-based (mg/kg-bw day) and dietary-based (ppm or mg/kg-diet day) EECs are estimated assuming that pesticide intake is a function of the amount of pesticide contained in the food and drinking water of an animal. The pesticide concentration in food is based on the concentration of pesticide in the prey items and the percent of each prey item in the diet of the animal. Mink, belted kingfisher, great blue heron, and osprey consume 100% forage fish. River otter, herring gull and bald eagle are assumed to consume 80% forage fish and 20% piscivorous fish. Mallard ducks are assumed to consume 34% phytoplankton, 33% zooplankton and 33% benthic invertebrates (USEPA 1993).

The dose-based EEC is calculated by **Equation 7**. The pesticide intake through food is calculated by multiplying the percent of each prey item ($\%_{Prey}$) by the pesticide tissue residue concentration for that prey item (C_{Bprey}). The sum of the pesticide residues ingested through food is converted into units of mg pesticide/kg food. This value is then

multiplied by the food intake (in units of kg/kg-bw day) for a resulting value in units of mg pesticide/kg-bw day. The pesticide intake through drinking water is calculated by multiplying the concentration of the pesticide in water (C_{WTO}, which is in units of mg/L) by the water intake (DW, units of L/d) and dividing by the bodyweight. This results in units of mg pesticide/kg-bw day. The sum of pesticide intake through diet and through drinking water is the dose-based EEC.

$$Eq.7 \quad Dose-based \quad EEC = \sum \left(\%_{Prey} * C_{Bprey}\right) * FI + \frac{C_{WTO} * DW}{BW}$$

The dietary-based EEC is calculated by **Equation 8**. Pesticide intake through food is calculated by multiplying the percent of each prey item ($\%_{Prey}$) by the pesticide tissue residue concentration for that prey item (C_{Bprey}). The sum of the pesticide residues ingested through food is converted into units of mg pesticide/kg food. This value is then multiplied by the food intake (in units of kg food/kg-bw day) and animal body weight (kg-bw) for a resulting value in units of mg pesticide/day. The pesticide intake through drinking water is calculated by multiplying the bioavailable concentration of the pesticide in water (C_{WTO}) (which is in units of mg/L) by the water intake (DW, units of L/d). This results in units of mg pesticide/day. The sum of pesticide intake through diet and through drinking water is the dietary-based EEC.

$$Eq.8 \quad Dietary-based \quad EEC = \sum \left(\%_{Prey} * C_{Bprey}\right) * FI * Wt + \left(C_{WTO} * DW\right)$$

Available dose-based toxicity values are adjusted for the weights of the animal tested (e.g. laboratory rat and mallard duck or bobwhite quail) and of the animal for which the risks are being assessed (e.g. mink, bald eagle, etc.). These adjustments are made according to the equations below (USEPA 2006), where: AT = adjusted toxicity value; LD_{50} or NOAEL = endpoint reported by toxicity study; TW = body weight of tested animal (350g rat; 1580g mallard or 178 g Northern bobwhite quail); AW = body weight of assessed animal; x = Mineau scaling factor (default value of 1.15 used) (**Equations 9 and 10**).

$$Eq.9 \quad AT = \left(LD_{50} \text{ or } NOAEL\right)\left(\frac{TW}{AW}\right)^{0.25} \quad (mammals)$$

$$Eq.10 \quad AT = LD_{50}\left(\frac{AW}{TW}\right)^{(x-1)} \quad (birds)$$

Dose-based EECs are divided by adjusted toxicity values to derive RQ values. Dietary-based EECs are divided by available toxicity values to derive RQ values. RQ values are then compared to Agency levels of concern (LOCs) for non-listed and listed mammals and birds.

Estimated concentrations of total Pesticide 1 (P1+P2+D1)in aquatic organisms range from 10^2 to 10^4 µg/kg across different trophic levels Although concentrations (wet

weight basis) increase from lower to higher trophic levels (**Table 5**), when expressed on a lipid normalized basis, they do not display increases with increasing trophic level.

Table 5. Predicted concentrations of Total Pesticide 1 in aquatic organism tissues at different trophic levels.

Trophic Level	Prediced Concentration of Total Pesticide 1 in Tissue (ug/kg wet wt)				
	Mean	SD	25th %	75th %	90th %
Phytoplankton	1,279	1,290	383	1,739	3,233
Zooplankton	1,280	1,307	376	1,742	3,237
Benthic Invertebrates	1,282	1,271	399	1,749	3,188
Filter Feeders	1,411	1,588	407	1,857	3,476
Small Forage Fish	3,346	3,755	950	4,477	8,461
Medium Forage Fish	3,447	3,684	960	4,648	8,856
Piscivorous Fish	4,682	20,306	1,051	5,860	11,925

Table 6. Predicted BCF values of Pesticide 1 at different trophic levels.					
Trophic Level	Mean	SD	25th %	75th %	90th %
Phytoplankton	499	369	191	729	1,079
Zooplankton	496	370	190	720	1,077
Benthic Invertebrates	525	413	197	761	1,122
Filter Feeders	515	403	196	741	1,102
Small Forage Fish	1,196	887	467	1,737	2,553
Medium Forage Fish	1,184	867	462	1,726	2,527
Piscivorous Fish	1,127	805	457	1,627	2,365

Table 7. Predicted BAF values of Pesticide 1 at different trophic levels.					
Trophic Level	Mean	SD	25th %	75th %	90th %
Phytoplankton	499	369	191	729	1,079
Zooplankton	500	375	190	726	1,089
Benthic Invertebrates	530	421	199	765	1,132
Filter Feeders	585	577	204	816	1,239
Small Forage Fish	1,308	1,080	477	1,889	2,885
Medium Forage Fish	1,353	1,093	476	1,960	3,049
Piscivorous Fish	1,806	5,439	515	2,511	4,282

Toxicity data for exposures of Pesticide 1 to mammals and birds are available in **Table 8**. The resulting RQs are in **Tables 9 and 10**. The acute risk RQs indicate that residues of Pesticide 1 in fish tissues have the potential to be of concern to some mammals and birds, although the exceedence of Agency's LOCs are relatively modest and occurred for three species at the 90th percentile predictions (Table 9). The chronic risk RQs

(dose and diet-based) did not exceed the Agency LOC of 1.0 even at the higher percentiles of model predictions (Table 10).

Table 8. Summary of toxicity of Pesticide 1 to mammals and birds. Bold indicates parameters used for RQ derivation.		
Species	**Endpoint**	**Value (ppm)**
Laboratory rat (Rattus norvegicus)	LD_{50}	**10**
	NOEC*	**15**
Northern bobwhite quail (Colinus virginianus)	LC_{50}	**805**
	NOEC	60
Mallard duck (Anas platyrhynchos)	LD_{50}	**28**
	LC_{50}	1053
	NOEC**	**30**

Table 9. Predicted RQ values for mammals and birds exposed to Pesticide 1 through acute, dose-based exposures. All parameters varied according to Table 10. All dietary-based RQ values for birds are <0.01.					
Organism	**Mean**	**SD**	**25th %**	**75th %**	**90th %**
Dose-Based					
Mink	0.07	0.08	0.02	0.09	**0.18[1]**
River otter	**0.15[1]**	0.25	0.04	**0.20[1]**	**0.39[1]**
Belted kingfisher	0.08	0.08	0.02	**0.11[1]**	**0.20[1]**
Herring gull	0.03	0.05	0.01	0.04	0.07
Osprey	0.03	0.03	0.01	0.03	0.07
Mallard duck	0.02	0.02	0.01	0.03	0.05
Great blue heron	0.02	0.02	0.01	0.03	0.05
Bald eagle	0.01	0.02	<0.01	0.02	0.03
[1] **Exceeds LOC (0.1) for acute exposures to listed animals.**					

Table 10. Predicted RQ values for mammals and birds exposed to Pesticide 1 through chronic, dose- and dietary-based exposures. All parameters varied according toTable10.					
Organism	**Mean**	**SD**	**25th %**	**75th %**	**90th %**
Dose-Based					
Mink	0.03	0.03	0.01	0.04	0.08
River otter	0.06	0.11	0.02	0.08	0.16
Dietary-based					
Mink	0.04	0.04	0.01	0.05	0.09
River otter	0.37	0.61	0.10	0.49	0.95
Belted kingfisher	0.01	0.01	<0.01	0.01	0.02
Herring gull	0.03	0.04	0.01	0.04	0.07
Osprey	0.04	0.04	0.01	0.05	0.09
Mallard duck	0.02	0.02	0.01	0.02	0.04
Great blue heron	0.05	0.05	0.01	0.07	0.12
Bald eagle	0.07	0.11	0.02	0.09	0.17

PART 2: Supporting Bioaccumulation Data For Example Pesticide 4

Table 11. Uptake and depuration parameters used to calculate pesticide tissue residue (C_B) for single trophic levels for Chemical 4

Symbol	Definition	Organism	Calculated Value	Empirical Value[a]	Comment	Data Source(s) for Empirical Data
k_1 (L/kg*d)	rate constant through respiratory area (i.e. gills, skin)	Small fish	460	515 - 600	Empirical value is an accumulation constant from a water exposure BCF study in juvenile bluegill sunfish	Fish Water Exposure BCF Study
		Medium fish	210			
		Piscivorous fish	92			
		Sediment organisms	5179	Not estimated	Spiked sediment studies were insufficient to determine uptake through the respiratory area; however, mesocosm study suggests that uptake via the water column is rapid. However, an uptake constant of 0.00453 per day was reported in a spiked sediment study (see k_D)	Accumulation studies in benthic invertebrates included
k_2 (d^{-1})	rate constant for elimination of the pesticide through the respiratory area (i.e. gills, skin)	Small fish	0.000055	0.022 - 0.023	Empirical value is a depuration constant from a water exposure BCF study in juvenile bluegill sunfish	Water Exposure BCF Study
		Medium fish	0.000024			
		Piscivorous fish	0.000011			
		Benthic Invertebrates	0.001524	Not estimated	Available data are not sufficient for estimating respiratory elimination coefficients.	Accumulation studies in benthic invertebrates included
k_D (kg food/(kg org*day)	rate constant for uptake through ingestion of food and water	Small fish	0.003061	Not estimated because steady state was reached by the first measurement	Uptake rate constants were not estimated from the available oral bioaccumulation study because steady state appears to have been achieved by the first measurement of body burden.	Dietary Exposure Study in Trout
		Medium fish	0.002167			
		Piscivorous fish	0.001534			
		Benthic Invertebrates	0.008627	0.00453	Rate constant is a total uptake constant obtained from a 28-Day accumulation study that presumably encompasses uptake from multiple exposure routes.	
k_E (d^{-1})	rate constant for elimination of the pesticide through excretion of contaminated feces	Small fish	0.000201	0.067	0.067 is the total depuration constant after oral exposure, and may not represent a true ke. However, the oral bioaccumulation study did suggest that the predominant depuration pathway occurs via fecal elimination, although other elimination pathways were not quantified.	Dietary Exposure Study in Trout
		Medium fish	0.000142			
		Piscivorous fish	0.000174			
		Benthic invertebrates	0.000280	Calculated value used	Available data are not sufficient for estimating elimination coefficients for specific pathways; however, a total depuration constant of 0.014	

Symbol	Definition	Organism	Calculated Value	Empirical Value[a]	Comment	Data Source(s) for Empirical Data
					per day was reported.	
k_M (d^{-1})	rate constant for pesticide metabolic transformation	All	Not calculated	Not determined	Total depuration half lives were used to estimate elimination. Therefore, the Km was set to zero; however, metabolism is presumably incorporated into the other elimination rate constants (K_2 and K_E).	Elimination and depuration constants
Kg	Growth dilution	All fish and benthic invertebrates	Not presented	0	Contribution from growth that occurred in the submitted studies was included in the total depuration kinetics estimates. Therefore, growth dilution was set to 0 because growth dilution was included in the depuration constant.	None used

[a] Empirical values may encompass multiple elimination pathways; therefore, they were not used to directly replace the associated rate constant in the table for modeling purposes, but may be used in place of several rate constants as described in Section 5.

Table 12. Abiotic Characteristics of the Ecosystem Used to Estimate Body Burden for Pesticide 4

Characteristic	Value	Range Reported in USGS (2006)	Basis
TOC (kg OC/L)	1.20E-06	Mean: 4.4E-6 Std Dev: 9.2E-6	Lower TOC results in higher C_B values. Therefore, 25th percentile of NAWQA data for organic carbon in water was used (n=25084). Mean is $4.4x10^{-6}$, 10th percentile is $0.4x10^{-6}$, 75th percentile is $5.2x10^{-6}$.
% oxygen sat	83%	Mean: 83% Std Dev: 33%	The mean value from NAWQA data was used (n=8066). Mean = 82.5%.
Water Temperature (^oC)	17*C	Mean: 14 ^oC Std Dev: 7.9 ^oC	The influence of water temperature on C_B is dependant upon log K_{OW}. The maximum estimated body burden occurs at a temperature of 17 degrees centigrade for a chemical with a log Kow of 8.1 in the model. The 75th percentile of NAWQA data on water temperature (n=77,669) is 19.8 degrees Centigrade.
Concentration of suspended solids (kg/L)	3.04E-04	Mean: 3E-4 Std Dev: 3E-3	The influence of the concentration of suspended solids on C_B is dependant upon log K_{OW}. For high log K_{OW} chemicals, higher concentration of suspended solids results in lower C_B values. Therefore, the 25th percentile of $1.2 x10^{-5}$ of NAWQA data was used. The mean (n=23,924) was 3.04E-04, and the 75th percentile was $1.2E10^{-4}$.
Sediment OC (%)	4%	Mean: 1.4% Std Dev: 2.5%	4% was used to be consistent with EXAMS, which also approximates a 95th percentile (mean + 1 std dev).
Source of NAWQA data: USGS 2006.			