FIFRA SCIENTIFIC ADVISORY PANEL (SAP)

OPEN MEETING

SELECTED ISSUES ASSOCIATED WITH THE RISK ASSESSMENT PROCESS FOR PESTICIDES WITH PERSISTENT, BIOACCUMULATIVE AND TOXIC CHARACTERISTICS

U.S. ENVIRONMENTAL PROTECTION AGENCY

CONFERENCE CENTER- LOBBY LEVEL

ONE POTOMAC YARD (SOUTH BUILDING)

2777 South Crystal Drive

Arlington, Virginia 22202

OCTOBER 28, 2008

8:42 A.M.

FIFRA SCIENTIFIC ADVISORY PANEL

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October 28, 2008

**MS. CHRISTIAN:** Good morning. I am Myrta Christian and I will be serving as the designated federal official to the FIFRA Scientific Advisory Panel. I want to thank Dr. Heeringa for agreeing to serve as chair of the FIFRA Scientific Advisory Panel for this meeting. I also want to thank both the members of the panel and the public for attending this important meeting of the FIFRA SAP to consider selected issues associated with risk assessment process for pesticides with persistent, bioaccumulative, and toxic characteristics.

We appreciate the time and effort of the panel members in preparing for this meeting and taking time out of their busy schedules. The FIFRA SAP is a federal advisory committee that provides independent, scientific counsel and advice to the agency on pesticides and pesticide related issues regarding the proposed federal action on human health and environment. The FIFRA SAP only provides advice and recommendations to EPA. Decision making and implementation authority remains with the agency. As the DFO for this meeting, I serve as the liaison between the panel and the agency.

I am also responsible for issuing permission of the federal advisory committee as needed. As the designated federal official for this meeting, a critical responsibility is to work with the appropriate agency officials to ensure that all appropriate ethics regulations are satisfied. In that capacity, panel members are briefed with provisions of federal conflict of interest laws.

In addition, each participant has signed a standard government financial disclosure report. I, along with our deputy ethics officer for the office of pesticides and toxic substances and consultation with office of the general counsel have reviewed these forms to ensure all ethics requirements are met.

For members of the public requesting time to make a public comment, please limit your comments to five minutes unless prior arrangements have been made. For those who have not pre-registered, please notify either myself or another member of the SAP staff if you're interest in making a comment.

For presenters, panel members and public commentors, please identify yourself and speak into the microphone provided, since this meeting has been recorded. There is a public docket for this meeting.

All background material, questions posed to the panel by the agency and other documents related to this meeting are available in the docket. Overheads will be available in a few days.

Background documents are also available on the EPA website. The agenda lists contact information for such documents. At the conclusion of the meeting, the SAP will prepare a report as a response to questions posed by the agency, background material, presentations and public comment. The report serves as meeting minutes.

We anticipate the meeting minutes will be completed in the first 90 days. Again, I wish to thank the panel for their participation and I'm looking forward to both a challenging and interesting discussion over the next few days.

Finally, I just want to let you know that there is a big meeting tomorrow morning at 8:30 in this building. Therefore, the security line is expected to be longer than normal. Please plan accordingly. At this point, I would like to introduce Dr. Steven Heeringa, the Chair for the FIFRA Scientific Advisory Panel.

**DR. HEERINGA:** Thank you very much Myrta. I'd like to reiterate her thanks to the members of the panel, the EPA staff and to the public who've assembled here this morning and potentially throughout this week for a very important meeting on the topic on the selected issues associated with risk assessment process for pesticides with persistent bio-accumulative and toxic characteristics.

As indicated, I'm Steve Heeringa, acting chair of the FIFRA Science Advisory Panel, from the University of Michigan, I'm a statistician. My main role in these meetings over the next few days is to facilitate the scientific discussion and coordinate the exchange.

I'll turn now to some of the experts on the panel who've been assembled and I think it's a very large and diverse panel in terms of the expertise that's represented here. So if they would introduce themselves by name and affiliation, maybe just a short description of your background. I'll begin with Dan Schlenk.

**DR. SCHLENK:** Good morning, my name is Dan Schlenk. I'm a Professor of Aquatic Ecotoxicology at the University of California Riverside and my area of expertise is mode of action of pesticides and aquatic organisms.

**DR. POPE:** Good morning, my name is

Carey Pope. I'm a Professor of Toxicology at Oklahoma State University. My area of interest is insecticide toxicity.

**DR. PORTIER:** Good morning, my name is Ken Portier. I'm Director of Statistics at the American Cancer Society national home office in Atlanta. I'm a bio-statistician.

**DR. CHAMBERS:** I'm Jan Chambers. I'm in the College of Veterinary Medicine at Mississippi State University and my area is pesticide toxicology. I'm a member of the permanent panel.

**DR. BUCHER:** I'm John Bucher, I'm a toxicologist at NIEHS. I'm Associate Director of the National Toxicology Program and a member of the permanent panel.

**DR. DONNELLY:** I'm Casey Donnelly, I'm a Professor in the School of Rural Public Health at Texas A&M University and I work with complex mixtures.

**DR. ORIS:** I'm Jim Oris at Miami University in Ohio, a Professor of Zoology and an aquatic eco-toxicologist.

**DR. SIMONICH:** Good morning, I'm Stacie Simonich. I'm an Associate Professor at Oregon State University in the Department of Chemistry and also in the Department of Environmental and Molecular

Toxicology. My lab studies the trans-pacific and regional atmospheric transport of pesticides.

**DR. STEENHUIS:** I'm Dr. Steenhuis, from Cornell University. I'm a Professor down there in the Department of Biological and Environmental Engineering and I do transport experiments to see how this stuff moves.

**DR. THIBODEAUX:** My name is Louis Thibodeaux, I'm a Professor of Chemical Engineering at Louisiana State University. My area of expertise is chemical fate and transport in multimedia systems, with exclusion of groundwater.

**DR. MEHTA:** I'm Dr. Mehta from the University of Florida. I'm in coastal engineering and I work in areas of sediment transport and coastal hydrology.

**DR. MEADOR:** I'm James Meador from the Northwest Fisheries Science Center in Seattle, Washington. I'm an environmental toxicologist and my area of expertise is energetics and growth in salmon eggs.

**DR. NORSTROM:** Ross Norstrom, I'm retired from the Game and Wildlife Service, Adjunct Professor at Carlton University. My expertise is primarily bioaccumulation in crops and wildlife.

**DR. MADDALENA:** Good morning, I'm Randy Maddalena. I'm from Lawrence Berkeley National Lab. I'm an environmental chemist, some analytical chemistry, transport modeling is another area of interest.

**DR. LICK:** I'm Willy Lick, the University of California at Santa Barbara and I'm interested in sediment and contaminant transport in surface waters.

**DR. HICKIE:** My name is Brendan Hickie, I'm a Professor at Trent University in Ontario, Canada in the Environmental Science Program there. My area of research is bioaccumulation in aquatic and marine ecosystems.

**DR. GAN:** I'm Jay Gan from University of California Riverside. I'm a Professor in Environmental Chemistry. I work on transport mitigation of pesticides.

**DR. DOUCETTE:** I'm Bill Doucette, a Professor at Utah State University in the Department of Civil and Environmental Engineering and I have a background in environmental chemistry.

**DR. DELORME:** Good morning, I'm Peter Delorme. I'm a Senior Advisor in the Pest Management Regulatory Agency of Health Canada. My area of expertise is environmental risk assessment of pesticides.

**DR. BIDLEMAN:** Terry Bidleman from Environment Canada. Adjunct Professor from University of Toronto. Interested in long range transport and deposition of pops and currently used pesticides.

**DR. ABBOTT:** Linda Abbott, I'm a Regulatory Risk Analyst at USDA's Office of Risk Assessment and Cost-Benefit Analysis and my area of expertise is ecological modeling.

**DR. HEERINGA:** Thank you very much. Again, panel members, I look forward to working with you all over the next four days. At this point in time, I'd like to begin a set of introductory remarks from Frank Sanders, who is the Director at the Office of Science Coordination Policy to the EPA. Good morning Frank.

**DR. SANDERS:** Good morning, my name is Frank Sanders and I am the new office Director of the Science Coordination Policy. Under that office, we have responsibility for the management of the scientific advisory panel. Our Executive Secretary, Steve Knott, who over the years has done an outstanding job in working with the SAP and I'm sure we will continue that sort of focus and it's important we do that.

But I want to take a few minutes this morning to welcome you and thank you for taking the time to be here for this meeting. I am confident that you'll find it to be very interesting and productive that you'll hear from the environmental fate and effects division in the office of pesticide programs about this work on the assessment of ecological risk of pesticides with persistent, bioaccumulative, and toxic characteristics. I also want to take the time to thank the director, Donald Brady, and the scientific staff of EFED for all their efforts and initiatives in preparing for this meeting.

Before becoming the OSEP director, I spent most of my career in the office of pesticide programs and most recently as the division director of antimicrobials division. My background has been in the office of pesticides programs for a long time and I have witnessed some of the important decisions that were made by the SAP.

Let me give you an idea as to some of the things that I have been involved with over the years. I started out as a team leader in the insecticide-rodenticide branch and moved from there to become a section head of the insecticide-rodenticide section. And from there, I moved to become the branch chief of the science review branch.

And from there I became branch chief of the fungicide-herbicide branch and then to become the director of what we had at that time, program management and support division, and then to the anti-microbial division director and now the director of OSEP.

So, I've got a long history of working in the office of pesticide programs and had the pleasure and opportunity of dealing with many scientific issues, so I really understand the relevance of the decisions made by the SAP. The scientific advisory panel is held in a very high regard by the agency.

But the office of pesticides programs is the main peer-review mechanism for challenging scientific issues associated with pesticides. I know from my personal experience in the anti-microbial division how important it is to gain expert scientific advice on challenging issues that directly impact our ability to evaluate pesticides and ensure that they present no adverse risk to human health or the environment.

Most recently, AB brought issues related to efficacy of products to inactivate anthrax exposure to the SAP. In the not too distant past, we also brought issues related to wood treated with CCA and other preservatives to the SAP.

We value the SAP's advice and seriously consider its recommendations as we move forward with the risk assessment process undertaken before registering a pesticide product for use in the United States.

This is a very important process and to me, when I was division director of the anti-microbial division, one of the most important things for that division is to seek advice, particularly in areas that were controversial. And the advice that we received was very valuable in making regulatory decisions and I certainly appreciate the work that you will be doing here all this week.

As you engage this week in the discussion of PBT topics, be assured the agency is looking forward to getting new expert advice and recommendations to move forward with the evaluation of further risk assessments of pesticides with PBT characteristics.

Again, thank you for taking the time to come to evaluate and to think seriously about the issues that are going to be presented to you this week. Thank you again.

**DR. HEERINGA:** Thank you very much, Director Sanders, it's very nice to have you join us here. At this point, I'll turn to Doctor Steven Bradbury, who is the director of the special review and re-registration division within the office of pesticide programs at EPA. Good morning Steve.

**DR. BRADBURY:** Good morning. Good morning to the panel as well. I want to also thank Dr. Heeringa and the panel for your time over the next several days to meet with us to discuss the issues of this SAP. We really appreciate all the time and effort it takes to prepare for one of these meetings as well as the long hours you'll be putting in to help prepare the report for us which we'll be very excited to read and use that input as we move forward.

As you know, we have a very ambitious schedule set out for ourselves and for you as we go over the next several days and we'll be discussing a broad range of issues including persistence and bioaccumulation, sediment dynamics and how that can influence bioaccumulation estimates. As well as the issue of long range transport.

All in the context of performing

ecological and in some cases, human health risk assessments for chemicals that have varying characteristics with regard to persistence and bioaccumulation and long range transport. Clearly, we're not going to be able to resolve all the many uncertainties and issues that face this area of science.

But what we do hope to accomplish in this SAP is to present to you, through a white paper and presentations, an overview of where we're at in trying to address some of these issues. And to get feedback on two fronts. One area of feedback would be hearing insights and advice on how one can best use currently available information and currently available scientific methods for decisions about pesticide registrations, which I'll discuss in a bit, but how to make those decisions right now.

With the best available information and accepted scientific methods. I'm also looking forward to your insights and advice as we look forward into the future, in terms of what kinds of adaptations or methods of development can we look forward to in the future to further refine the capabilities of undertaking risk assessments for chemicals that have varying characteristics of persistence and long range transport bioaccumulation.

To help put this SAP in context, I want to spend a few minutes just describing some of the statutes in the United States that guide us as we do pesticide evaluations and make regulatory decisions with regard to pesticides. The two major statutes that oversee or drive out work- one is the federal insecticide, fungicide and rodenticide act, or FIFRA.

The other is the federal food, drug and cosmetic act, or FSDCA. FIFRA is the real over-arching statute, the driver in terms of how we lay out the work we do in the pesticide program.

And in the context of FIFRA, we're looking at dietary risks, we're looking at ecological risks, residential risks, occupational risks, as we make decisions about pesticide registrations. Now, in the case of dietary and drinking water exposure and residential risk, that's a risk-only standard.

And so we just take a look at the risk to make sure the risks do not exceed our reasonable certainty of no harm standard. In terms of ecological risk and occupational risk, it's a risk benefit decision that we make.

So we're looking at the risks associated with uses and we're looking at the benefits of those uses and our decision is ensuring that the risks don't exceed the benefits of the product. And so those are the FIFRA sorts of things, the over-arching statute. FSDCA is a statute that we followed in terms of setting tolerances for pesticides that can be in the dietary food chain for humans, and or in drinking water.

And so that aggregation is what drives FSDCA in looking at tolerances in food. And that aspect of our pesticide regulations does, in some ways, factor into some of the discussion today in terms of the potential for pesticides to get into dietary sources in the environment.

Maybe some fish or other components of the human diet. So we have these two statutes then that drive both the decisions we make on registering new insecticides and pesticides as well as a process to re-evaluate pesticides that are currently on the market.

Another act that was passed in the mid-90's is the food quality protection act which sort of helped integrate these two acts and put some things in context and added some more stringent risk assessment and risk management perspectives to the work we undertake.

The acts also lay out a strategy not

only towards proceedings on new chemicals, but also a process for looking at listed chemicals. Through FIFRA, we're required every fifteen years to re-evaluate pesticides that are on the market. So a process that's dealing with decisions about new pesticides that can come on the market as well as processes that are evaluating chemicals that are already on the market to ensure, over time, that our decisions are meeting current scientific and regulatory policies.

Of course, that evolves over time. I think another important backdrop to the work we do has to do with the throughput of work we do in a time frame in which those actions have to be undertaken. In the mid 2000's, 2004, and there was an update a couple of years later, congress passed the Pesticide Registration Improvement Act, PRIA.

And that act not only sets up schedules for fees that the registrants supply EPA to help do all this work, but it also sets up time frames in which decisions need to be made. So for example, a new pesticide, the EPA needs to make a decision in approximately 18-24 months from submission of the information to EPA. So we have a throughput that's set up and time frames that have to be addressed.

And we typically are evaluating 10-12 new active ingredients per year and many more chemicals are being evaluated in the context of new uses being added to existing registrations. Which also requires a human health and ecological risk assessment.

PRIA also sets a schedule for that 15 year cycle in terms of re-evaluating existing chemicals. About 2 or 3 weeks ago, we finished our first round of re-evaluation of pesticides and what we accomplished a couple of weeks ago was the re-evaluation of approximately 600 active ingredients that had been registered prior to 1984.

A year or so ago, we embarked on our second round of the re-evaluation program, which would turn registration review, now require that all the active ingredients be re-evaluated by 2022. Which translates to about 70 decisions per year to meet that schedule.

So you get a sense of the throughput that's associated with the activity we take. When you strive to ensure that as we make those risk assessments and form our risk management decisions, that we are, as best we can, taking advantage of currently accepted scientific methods and high quality data as we go forward.

As many members of the panel know, the underlying scientific basis of all these decisions has been greatly enhanced and enriched by meetings with the SAP over the years and years and years of the development of this program.

So insights, in terms of everything from what kind of bioassays are critical to interpret the potential risks of the pesticides to what kinds of tests are important to understand the fate and transport of chemicals and that influences the type of data the pesticide registrant generate to submit to the agency to support the decisions about registering a pesticide.

As well as getting feedback from the SAP on the various models and methods that the agency uses to evaluate this information and integrate that information into established estimates of exposure, understand potential effects and then put it together and make a risk assessment. Then any of the risk managers are making the ultimate regulatory decision about the product.

When we look back at where we've been and where we're going forward in this risk assessment, issues we're going to be talking about over the next few days, many of the scientific methods and bioassay techniques and the methods we use to integrate the information which was aided to a great degree from SAP input over the years, they tend to be based on chemicals whose half-lives may be in the range of hours to days.

So they typically tend to be chemicals that don't have a potential to bio-accumulate in aquatic food chains and food webs or terrestrial food webs. In general, they don't have a potential for long range transport.

So in essence, the problem formulation that typically drives an ecological risk assessment is based on chemicals with really short half-lives that degrade relatively quickly, don't have a long range transport potential, don't seem to have a potential to bio-accumulate.

Not surprising then, the underlying bioassays, for example, and some of the underlying methods in the models are built for time scales that say a field season or a bit beyond the field season in terms of the potential direct effect of the pesticide. Spatial scale tends to be at the scale of the field where the pesticide is applied and some off-field from spray drift or runoff that's affecting the habitat around the field.

But generally not focused, either the risk assessment or the risk management decision, on the spatial scale that could be miles and miles and miles from the site of application.

So where we've been has been risk management decisions supporting risk assessment decisions that are based on short lived chemicals, time scales of a year or so, spatial scales of an agricultural field and the surrounding habitat.

Recently though, in both the registration process, which is a process in which we evaluate new chemicals coming on the market, as well as some situations where we're doing our re-evaluation exercise, evaluations and looking at chemicals that are currently on the market, we've started to see some situations where we're looking at chemicals that in fact don't have short persistence and the fact persistence can be in the range of months to up to a year.

The same chemicals whose bioaccumulation potential is such that we would expect them to potentially bio-accumulate in aquatic food webs and terrestrial food webs. Also seeing chemicals with some characteristics that would suggest they do have the potential for long range transport.

And clearly, as chemicals with these kinds of characteristics come to bear, not only does that influence the kinds of tools and techniques that we use to undertake those risk assessments, it also changes the risk management framework, in terms of chemical scale and spatial scale we begin to start looking at things a bit differently and as risk managers, looking towards how that science will evolve to help support a risk management framework that's now somewhat different from the typical scenario that we're dealing with.

So as we go forward over the next several days, we'll be looking forward to your insight on these issues and again, in two contexts. One is through the white paper that you'll hear from the scientists in E-FED and the discussion you all will have, is to give us feedback on today's currently available methods and models.

Because as I have indicated before, we have many decisions to make every year and the statutes require those decisions to be made in a time sensitive manner.

So it's important to get some insights on what can we use today, what's the status of today's science and tools. In addition to getting feedback on what advances can we look for in the future, so that we can all use our resources and our talents effectively and efficiently in focusing on first-order, second-order, third-order challenges and uncertainties as we go into the future.

So again, I want to thank you all for the preparation before you got here and all the hard work you'll be doing while you're here. We certainly look forward to the feedback and the discussions over the next several days. Dr. Heeringa, I'll turn it back to you.

**DR. HEERINGA:** Thank you, Dr. Bradbury. Speaking for the panel, we look forward to engaging with the scientific staff, the EPA, in the discussion over the next few days. I appreciate your opening remarks. At this point in time, I'd like to turn to Dr. Donald Brady, who is the division director of the environmental fate and effects division, OPP, EPA.

**DR. BRADY:** Thank you very much. I'd also like to express my appreciation to the members of the panel for the work you're about to undertake and also right up front, to express my appreciation to the members of the E-FED scientific team who will, following me, begin to make the detailed presentations that pose the issues and the questions we've got set up here for you today.

So, just briefly from the standpoint of the ecological risk assessment process, EPA's pesticide ecological risk assessment process, which as been reviewed and supported by SAP's in the past, has been effective in assessing risks of pesticides to non-target organisms and the environment.

However, pesticides with combined persistent bio-accumulative and toxic characteristics have presented particular challenges because the methods, tools and data used in our current risk assessment process have some limitations in addressing pesticides with the characteristics.

In these situations, the office of pesticides programs has made the best use of available tools and methods from other parts of the agency and/or the scientific community.

So as you heard a minute ago, one of the reasons we're here today is to seek input from this panel on whether we've made the best use of the available data and methods for addressing those risk assessment issues in past assessments.

We're also seeking input on how best to proceed for future assessments involving pesticides with these characteristics.

In our white paper, we used case studies with four example generic pesticides to describe the analyses used. The evolving tools, methods and data being considered, and the issues that have arisen with older pesticides and new pesticides with these characteristics.

We have focused on methods and tools for addressing a number of the risk assessment uncertainties and have presented the program's approaches to refine the risk assessments and to highlight remaining challenges.

In this SAP, we also pose some questions related to long range transport. Some of those will also be addressed in a later SAP and Mr. Safkin will describe in his more detailed presentation exactly how those issues will fall out.

So in terms of the scientific challenges that we've raised before the panel today, one of the primary challenges we face concerns environmental persistence. For this topic area, we're seeking advice on how to quantify long term exposure to chemicals in soil, sediment and pore water. And how to quantify exposure to the combination of parent and degradation products.

Another challenge area concerns sediment dynamics, which has the potential to influence bioaccumulation. For this area, we are seeking advice on the appropriate methods and tools for identifying and quantifying the principle processes related to sediment dynamics. In the area of bioaccumulation, we are seeking comments on quantifying pesticide exposure in aquatic food webs and on assessing bioaccumulation potential in terrestrial based food webs.

One of the primary issues involved in long range transport is associated with establishing relationships between near field pesticide loadings and far field pesticide concentration.

So, we are looking forward to your advice on how to best to approach the problem formulation page on pesticides with some or all of these characteristics as well as how to best use today's available methods and models in characterizing risk in these situations.

In addition, we are interested in your thoughts on options for advancing current methods and models from the existing foundation of approaches developed by the EPA and the broader scientific community. So again, I'd like to thank you very much and that's it.

**DR. HEERINGA:** Thank you very much, Dr.

Brady. At this point we're going to begin a sequence of presentations by the EPA Scientific Staff from EFED who has contributed to the white paper and addressing a number of topics that were covered in that paper. These will be a series of presentations in which has about 30 minutes set aside for each of them including discussion.

I can tell you from experience there is a trend at the start of these sessions for the initial presentations, the discussions to go on longer. I don't want to cut things off, but we'll try to stay to the agenda schedule more or less. But without any further delay, do you want to introduce your staff.

**DR. BRADY:** Keith Sappington will discuss background and set the stage for the following presentations. So I'll let Keith do that.

**MR. SAPPINGTON:** Good morning. I'm going to talk about the issues associated with assessing ecological risks of pesticides with persistent bioaccumulation and toxic characteristics and I'm just going to provide a background of how we address these issues in the past and how our overall risk assessment process is perceived.

I'm going to talk about three areas. One is just to give an overview of our standard ecological risk assessment process. That is which pesticide sources, exposure pathways and ecological receptors we routinely consider.

As well as the typical effects and exposure assessment information that we generate as part of these assessments. I'm going to provide a brief introduction to the PBT related ecological risk assessment issues and introduce the example case studies which are outlined in the white paper.

The ecological risk assessment process that is used in the office of pesticides program closely follows the agency's risk assessment frame work and following risk assessment guidelines.

And I've provided a risk assessment frame work figure here. And this process proceeds in basically three steps. The first is a problem formulation phase and that is a lot of what we're focusing on in this SAP.

This is basically the planning phase of the risk assessment. In relation to our topic area, it is where we would first identify which PBT related issues that we have to be concerned about. And also the methods that are available to address these issues.

The problem formulation phase involves constructing a conceptual model that relates the sources ultimately to the risks to the organisms of concern. And this includes an explicit statement of the assessment endpoints which is the ecological receptors of concern and the attributes of those receptors.

Ultimately, an analysis plan is formulated, which is basically the blue print for the ecological risk assessment. The second step involves an analysis phase and that is where the exposure information is assembled. It usually proceeds in a predictive fashion, with environmental modeling, but also would consider monitoring data. And analysis of effects, this is where the effects profile is assembled.

Again, typically these are data that are generated in the laboratory using standard methods but on occasion we have information available from the field or field studies. The final step is the risk characterization and this is where those estimates of risk are generated by integrating the exposure and effects profiles and the risk estimation box that you see is where the quantitative risk estimate is determined.

Usually, this is done in a deterministic fashion, but when we have sufficient information, we can also do this in a probabilistic fashion using all the exposure information we have as well as the effects information. Such as the species sensitivity distribution.

The risk characterization or risk description step is important because that's where we discuss the uncertainties and sensitivities of the risk assessment to different assumptions and where we can bring in sort of non-standard models to the process to help inform the risk estimate.

And importantly, while this is presented in a sort of a linear fashion, there's quite a bit of iteration between these steps and there's the opportunity in the pesticides program to stop and request more information as part of this process. Although is always competing with the rigid time lines we have for making decisions.

Now I'm going to walk through a conceptual model that is in the white papers, it's very similar to the one presented there. And the point in doing this is to illustrate basically three things. One is what are the sources and exposure pathways we routinely consider in our risk assessment.

And then which ones are those that are not routinely considered that we address on a case by case basis and which pathways and sources are particularly a challenge with respect to pesticides with PBT characteristics.

So in terms of what we're trying to assess risks on, we have aquatic animals, plants, both terrestrial and aquatic, as well as terrestrial animals. And listed below the entities here are the assessment endpoints.

The reduction in survival growth and reproduction we're mostly concerned about. I'm going to start with the aquatic pathway. In terms of sources, we have pesticide spray drift, runoff and erosion. And we use environmental models to route these loads to a standard receiving water body, which generates concentrations and we're interested in pesticide uptake in aquatic plants as well as aquatic animals. And this is the water only phase. For PBT chemicals and sediments here, we also have to predict concentrations in sediments and that's particularly important based on their chemical properties.

We also consider leaching to groundwater and right now, this is evaluated or used to evaluate potential impacts on irrigated crops, when groundwater is used as a source water.

Obviously, there's a connection between

the groundwater and the surface water and this is not evaluated routinely in our models. In terms of terrestrial plants, we evaluate the risks associated with runoff and erosion potential as well as spray drift and for terrestrial animals we consider direct deposition on food items in the treated fields and evaluate this for pesticide ingestion from the food stuffs.

This is not bioaccumulation, it's the deposition or absorption of the pesticide to the food item, plants, small insects. There are other sources, obviously for terrestrial animals. Drinking water, as well as exposures due to soil and exposure routes include ingestion and dermal uptake. We have evaluated these pathways in the past, but these are not routinely done. And as shown in blue here, the soil is a compartment of particular concern with pesticides with PBT characteristics.

We also consider volatilization and exposure through the inhalation route. This is done less commonly, but we do this where it is of a concern on a case by case basis. For example, for pesticide fumigants with high volatilization rates. Now for pesticides with PBT characteristics, tropic transfer both in a terrestrial food web and the aquatic food web is a potential concern. This is not routinely evaluated now.

We have provided examples of where we have done it and that's one of the big reasons we're here today is to seek your input on this topic. Also, long range transport and atmospheric deposition are of concern in some cases. We do evaluate long range transport but it's largely from a retrospective fashion by looking and considering monitoring data. I'm going to talk briefly about the aquatic exposure assessment. Dr. Ron Parker, who will be presenting just after myself, will go into more detail.

But you'll see a theme with most of our assessment approaches. And that is using a tiered process. We have quite a number of substances due every year and a short amount of time to do them. And so when we can, we apply a screening process, so we can identify those pathways that really deserve most attention in the risk assessment.

And in that light, with the aquatic exposure assessment, we used a tier one model that's a screening model, called JANIK and that's used to screen out the aquatic exposure pathway from further consideration. If the pesticide fails that screen, then we move on to tier 2, which is the PRZM exam process, which is described more throughly in the white paper.

And again, Dr. Parker will be describing this. The scale of the assessment is important to consider. We are looking at the field scale assessment that considers spray drift, runoff, and erosion to a standard pond. We evaluate these parameters on a region specific basis because application, timing and rates, and soil characteristics as well as weather conditions vary on a regional basis.

So we have standard scenarios that vary by region and crop. The output from pesticide concentrations predicted in water, sediment, and fore water over a 30 year record, and that's to attempt to account for some of the inter-annual variability that might be expected over time. And then from this large amount of information, we distill it down into some statistics, that are then used to evaluate risk and these range from peak concentrations to a different averaging periods with a return interval of one and ten years.

On the terrestrial exposure assessment, I'm just going to talk about the spray applications. I mentioned this in the conceptual model, that we evaluate exposure from pesticides that adhere to food items, such a foliage, seeds, and insects. And the residues are estimated based on an empirical database that relates just the application rate to the residue concentration. We can simulate degradation usually as a first order process and exposures are expressed in terms of dietary concentrations and also converted to an ingested dose basis. We evaluate exposure two different ways.

On the effects assessment, typically for acute toxicity, we're looking at fresh estuarine marine organisms, common test species on the fresh water side are bluegill and rainbow trout for fish and daphnia and shrimp for invertebrates. Typical endpoints there are the LC-50 and the E.C.-50. The lethal concentration that effects half of the organism and the effective concentration that effects half the organism.

For chronic toxicity for fish, we most often get early life stage tests. These vary from 28 days to 60 days or even longer, depending on the species. For invertebrates, we receive a life cycle study and the endpoint from these tests are that no observed adverse effect concentrations as well as lowest observed adverse effect concentrations. More recently, we've been requiring sediment toxicity studies and these are done and conducted on a short term, ten day basis, as well as a chronic basis.

And the effects are indexed to bulk sediment concentrations as well as concentrations in fore water. Typical endpoints, I mentioned this earlier, are survival, growth, reproduction and development. We also consider on a case by case basis other endpoints that can be strongly related to these assessment endpoints. We feel these are the ones that are most closely tied to population level effects.

And again, field studies, usually in the form of mesocosm studies are occassionally available and some of those are described in the white paper. In terms of the assessment, usually when we distill this information down, we look within each taxonomic group with the most sensitive species.

Again, occasionally if we're in a data rich situation, we can actually look at the distribution of sensitivities across the species and actually describe that statistically and use that distribution as part of the risk estimation process.

For terrestrial organisms, for birds, we have three taxa, upland, game, species and more recently, we required a passerine species. For mammals, typically what we're looking at is information on a laboratory rat. Chronic toxicity, again for birds, we require information on two taxa, and for mammals it's usually a laboratory rat. And we're looking at similar endpoints, growth, survival, reproduction and development.

We also have information that is collected and evaluated as part of the agency's program on incidents that occur in the field. We have a database of this so we can refer to field incident data as sort of another line of evidence in the effects assessment. Characterization of risk usually proceeds with what is known as the risk quotient method and that's where the estimated environmental concentration, or EEC, is divided by the toxicity reference value to give us a quotient.

For acute risks, we usually base the exposure concentrations on peak values. For chronic, it depends on the species. It's 21 day average concentration for invertebrates and 60 days for fish and again, these are tied to a return frequency that's one in ten years.

We compare these risk quotient values to the agency's level of concern and this is just a table of the LOC values for assessing aquatic organism risk. For this point in my discussion, I'm going to outline the major PBT related ecological risk assessment issues and I'm going to start with environmental persistence.

One of the issues we have with addressing environmental persistence of pesticides with PBT characteristics is assessing exposure to both the parent and degradate products. This is not a question of whether we do this, but more a question of how we do it. And we have a range of methods that we can use, but our ability to use the more complex methods is often limited by the available information that we have.

So we have some surrogate approaches that are presented in the white paper and that we're seeking feedback on. We also have questions regarding interpreting the degradation kinetics that come from our standard studies, like our aquatic metabolism study. And some of the issues here occur when you have rapid partitioning occurring at the same time as your degradation rates and trying to distinguish where degradation is occurring in the system, in a water sediment system it can be a challenge. And interpreting that information for application to the exposure model. In some instances, our predicted concentrations from our aquatic exposure modeling can exceed the solubility limit that's generated using standard laboratory tests.

This raises questions about the bio-availability of those predicted concentrations. At least the concentrations are above the solubility limit. And there are a couple of methods that will be presented later today that will discuss how we interpret these concentrations and apply them in risk assessment. Assessing long term accumulation in soil and sediments is also a concern, particularly the potential for pesticide carryover over time, over multiple years. With regard to sediment dynamics, we are interested in better understanding the role of sediment dynamics on pesticide bio-availability in aquatic systems.

This can impact multiple aspects of the risk assessment. As Don mentioned, the bioaccumulation estimates as well as the toxicity assumptions and risks to organisms. We're interested in understanding sediment dynamics in the role of our standard agricultural ponds, but also in other aquatic systems that we might address down the road. The available methods for identifying and quantifying sediment dynamics, we're interested in your feedback on those.

And in particular, those which we can use now perhaps in the screening level sense, as well as those that would be appropriate for more refined assessments. Again, if we can save resources by using a screening level approach to identify whether sediment dynamics is important to the risk estimate, that's a very useful tool for us to have. And again, providing feedback, both in terms of what we can do now versus the future would be very, very helpful to us.

With regards to bioaccumulation, quantifying pesticide exposure via the aquatic food web is an issue of concern to us for these types of chemicals and we have presented different methods for doing that in the white paper. And we're interested in your feedback on how best to interpret and quantify bioaccumulations from these different methods.

Have we adequately characterized the relative strengths and limitations and have we, in the example case studies, integrated these methods appropriately. I will mention here that in terms of where we are in the process, again we're sort of in that problem formulation phase.

We expect to come back on some of these topics with more specific information about which models and which methods and sort of the exact process of marching through the risk assessment. But right no, we're looking for input, sort of more broadly on the types of methods that were appropriate here.

And also, this is an area, getting back to the conceptual model, I mentioned that we're not evaluating bioaccumulation in the terrestrial food web and there are some properties of compounds that suggest that bioaccumulation in terrestrial food webs may be important even when screening for aquatic bioaccumulations suggest they might not be.

So we're particularly interested in this aspect and view it as sort of an emerging area. Long range transport, the biggest challenge we have is relating near term pesticide loadings, sort of at the field scale level, to far field concentrations. And we're aware that there are methods out there for screening long range transport potential.

So these can be used in a prospective fashion, but right now the current state of the science is largely using monitoring information to infer long range transport. For toxicity, we're also looking at the toxicity of mixtures apparent in degradate compounds and toxicity resulting from multiple exposure routes, not just the water pathway, which is standard. In the aquatic toxicity test, anyway.

And I introduce the pesticide case studies, and the purpose for providing these in the white papers is to illustrate some of the refinements we've made on a case by case basis to our methods for addressing PDT related issues.

The focus here is on the methods, and not on the chemical specific issues, and that's one of the reasons why we did not name the pesticides. We're really interested in the process we used for determining and addressing these issues. The characteristics of the 4 case studies regarding hydrophobicity, there is a range of hydrophobicity there. Typically log KOW from 4 to 8, depending on the chemical in degradate. And they display high environmental persistence through either the parent or the degradate, and relatively high toxicity, and we have concerns on long range transport for 2 of the case studies.

And we brought these case studies to the SAP, because based on the national and international criteria that are established to classify compounds according to their persistent bioaccumulative and toxic characteristics, these raise flags that some of these issues regarding bioaccumulations and environmental persistence and toxicity would be of concern. And this table just provides a road map for your reference with regards to the white paper. The parent and degradate exposure are illustrated for pesticide 2. Solubility issues are for pesticide 3 and 4.

We have an example of the degradation kinetic output and how we interpret that in pesticide 3, and long term accumulation and sediment in soils are presented for pesticides 1 and 4, and these are all found in Chapter 3 of the white paper. For sediment dynamics we present information for how sediment dynamics may effect exposure concentrations for pesticide 4 as well as the bioaccumulations for pesticide 3. And in the white paper we provide examples, summary examples, of how we access bioaccumulation, aquatic bio-cumulation for pesticides 1, 3 and 4.

I mentioned already that long range transport is an issue for us with pesticide 1 and 2, as well as toxicity, assessing toxicity in both the parent and the degradate compounds. And then we provide an approach for addressing aquatic toxicity from multiple exposure out, particularly for the diet for pesticide 4, and that uses a tissue residue approach. And that's it.

**DR. HEERINGA:** Thank you very much, Mr. Sappington. At this point we have time for a few questions of clarification on this background and overview presentation. Panel members, any questions that you would like to raise at this point? I'm sure Keith will be here throughout the sessions if anything else comes up. Yes, Dr Doucette.

**DR. DOUCETTE:** Just one quick question. Measured versus estimated values, in certain situations when you are going through the assessment you've got the availability of both, ideally, you know, you've always got measured, but a lot of times you may have both, and if there is a conflict between the two how do you weight whether you are going to use a measured value or an estimated value if there is a large difference between them? Do you always go measured, or not?

**MR. SAPPINGTON:** I'll address that in the context of bio-cumulation, which is my background. I think it's important to understand the strengths and limitations of the method that's used to generate both estimates.

For example, you could have a scientifically valid measured bioaccumulation factor in the field, but if information suggests that the pesticide would be accumulating over long time periods, much longer than used in that study, then you could bring that into play, in terms of how you interpret that, and potentially weight or explain differences between what a model may predict for bioaccumulation versus a measured value.

And so I think it's really on a case by case basis which ones you use, because...and I'll go through this in the bio-cumulation presentation. Each of the methods has their strong points and their weak points, and we feel we really need to evaluate those in a final selection process.

**DR. HEERINGA:** Dr. Maddalena.

**DR. MADDALENA:** Yeah, just a quick question on the scope of your, I guess your problem. A dozen or so new active ingredients per year, 70 some new evaluations a year, of that batch, how many would fall into this PBT characteristic? Just to give me a sense of the workload that you are going to have in this area.

**DR. HEERINGA:** Dr. Bradbury, do you want to tackle that one?

**DR. BRADBURY:** Good question. With regard to the new active ingredients, that's even more difficult to project because we won't know what is going to come in till it comes in. But I think our sense in looking at some new active ingredients are that group of 10 or 12 gave us some sense that for a couple of chemicals at least, we had to deal with these issues and we felt it would be wise to have...use these two situations to expand our thinking in terms of risk management and risk assessment, so that we are prepared to take on anything that comes in the future with sound science and good decision making. With the existing chemical universe there are clearly some chemicals out there that we have dealt with.

We dealt with Indane some years ago, and went through a cancellation process for that. There are other chemicals that are you, you know, in Congress now that we are starting to take a look at. Some are being dealt with at the international level and at the national level.

So I wouldn't say that there is a large percentage of compounds, I mean some of the experiences I think...DDT, Aldrin, Dieldrin, Endorin, there was movement away from the kind of characteristics that lend chemicals to persist in bio-cumulation, because of the issues that society faced in looking through those structures.

But erythroids, you know, we are dealing with some issues in terms of maximum bioaccumulation, but what's going on in sediment...better understand that, both in Canada and here in the U.S. and some of the States have those issues too.

And again, I think it's to be prepared for taking on the re-evaluation of the tools in our toolbox, because we know right now as Keith described and Don described, not all the tools in the toolbox are quite tuned to this kind of issue. I think it's good to be prepared, we are going to have to deal with some of those problems.

**DR. HEERINGA:** Thank you. Dr. Norstrom.

**DR. NORSTROM:** Just a point of clarification. I noticed in the generic conceptual model here that you don't appear to have any direct update by terrestrial plants and soils. Maybe that's not relevant for PBT substances, but is that just an oversight, or ... you have it for aquatic plants but not for terrestrial.

**MR. SAPPINGTON:** You know the testing for which we evaluate threshold plants are emergent studies and vegetative vigor. And the product is applied as a fraction of the application rate, so it uses spray drift. But we also evaluate the using a screening level model called Tur Plant. The effect of runoff and steep runoff next to the field on plants. So maybe it needs to be included in the model, in the conception model.

**DR. NORSTROM:** Thanks.

**DR. HEERINGA:** Dr. Simonich, and Dr. Gan.

**DR. SIMONICH:** Staci Simonich, Oregon State University. I actually have 2 questions, the first is why isn't long range transport and atmospheric deposition to bodies of water considered in the conceptual model? For example, lakes and oceans.

**MR. SAPPINGTON:** Yeah, I think it clearly is a relevant process, and I think one of the challenges in putting any kind of generic conceptual model together is trying to make sense out of it when you are done. And that's exactly why I animated walking through the model. And so we could have another sort of line going over there. We tried to really emphasize generically the things that we do more commonly and those that we do not do more commonly. So, yes, in fact, in our assessment themselves we usually will have a conceptual model for terrestrial and aquatics separate because of all the details and the arrows running across on another...good point, I don't.

**DR. SIMONICH:** And my second question. Why would an aquatic toxicity test being conducted over the aqueous solubility of the chemical be acceptable?

**MR. SAPPINGTON:** The aquatic studies, with a number of these compounds solubility limit is extremely low. And my understanding is that this could present a challenge in actually conducting the study for making stock solution, which have to be at higher concentrations in the solution in order to expose the organisms to a range of concentrations and elicit effects.

We do have limit tests in which the registrants are required to test up to some particular limit, but they are expected to generate a toxicity value up to that limit. If it's above the limit, I think it's a hundred, I think for aquatic it's 100 milligrams. I'm not sure what the limit is, but we do have a limit which they can then just do a screening test, and not actually generate a dose response. But as part of the guidelines themselves we are expected to generate an actual dose response from a study.

**DR. HEERINGA:** I'd like to give Dr. Gann a chance to pose his question, and then we'll move on.

**DR. GANN:** The question is do you intend to address fully the sediment toxicity issues through this process as well? Because these chemicals are outside, the sediment toxicity would also be very important, you know, I just wanted to see if you plan to address this here or in the future?

**MR. SAPPINGTON:** Yeah, as I mentioned in the presentation, we more recently have been getting or acquiring sediment toxicity tests, and as part of our risk assessment process. And clearly they would be the compartment, major focus on sort of a mass balance basis for these compounds. And the type of comparisons that we would do would be comparing the direct toxicity through poured water or bulk sediment to those...to the end points that would come out of those toxicity tests. And as Steve mentioned, this is also an issue for other compounds like the pyrethroids, so yes, we are moving down the process of figuring out how best to use the sediment toxicity information that we have. But it is a measure of direct toxicity through the sediment organisms, not so much any exposure they may be getting through the food web, plankton, whatever. So yes, we are marching down that road.

**DR. HEERINGA:** Thank you very much, Mr. Sappington for that presentation, and at this point I would like to move on to the next presentation by Dr. Ronald Parker, also of the Environmental Fate and Effects Division. And panel members, if you have questions that...we'll have chances throughout this to get them answered, please hold them.

**DR. PARKER:** Thank you, and good morning. I'm going to be presenting a rapid overview of our current computer modeling methods that we use for aquatic ecological exposure assessment.

As Mr. Sappington pointed out, EFED does use a tiered modeling/monitoring system to assess these chemicals. The tiers are use to officially allocate resources to assessment efforts of varying complexities and potential risks. The tiers themselves represent a level of effort and therefore expense. Lower tiers require less time and effort, far less input data, and the higher tiers then require more time and effort and more data.

Each higher tier is somewhat less conservative than the previous tier that was completed before it. The lower tiers generally use conservative assumptions in lieu of site specific data, for some of the model inputs, and then in upper tiers we substitute more site specific data for some of those conservative assumptions. It is not a pass/fail system, but a pass, progress to the next higher tier system. And the higher tiers then are designed to resolve uncertainties that may have arisen during implementation of the lower tiers.

I'm going to provide a description of our tier 2 aquatic assessment procedure. In tier 2, we use the electronically linked US EPA PRZM and EXAM models. PRZM is an inter-field model, it simulates pesticide in storm water runoff using the edge of a pesticide treated agricultural field. EXAMS is a receiving model, electronically linked to PRZM, it simulates transport and fate within the water body which has received pesticide coming off the edge of the field from PRZM, from the runoff model.

This figure is a pictorial of our surface water modeling configuration. We assume runoff from a single pesticide treated agricultural field to a single static pond. The PRZM program simulates the hundred percent treated, 10 hectare field, providing runoff to the 1 hectare by 2 meter deep pond, which is then simulated by the exposure analysis modeling system, the EXAMS program.

Why do we simulate a farm pond? Two basic reasons, first the OPP static pond serves as a simple yet conservative surrogate for all surface water in the U.S.. Our assumption in that static pond is that inflow from runoff is exactly equal to the outflow from seepage plus evaporation. And I might add that we consider there is no chemical removal in that seepage from the pond. When compared with monitoring data, this single static pond has been shown to be appropriately conservative as a surrogate for other surface water.

We have noted however that if we add significant flow through that pond, which is an option within the EXAMS program, that it is no longer as useful as a conservative screen, and we do start seeing many times substantial monitoring values that are higher than what are predicted by our...in our pond.

The second major reason for using a farm pond is that the U.S. does have at least 2.6 million natural and constructed ponds. I've seen estimates of up to 8 to 9 million ponds, and so we believe that the pond itself is a significant ecological resource. They are resources in their own right, for wildlife conservation.

So, in other words, we thought this farm pond is a conservative screen for rivers and streams, which do receive runoff from multiple agricultural fields as a result of multiple rainfall events over a substantially sized watershed. PRZM has fairly simple hydrology. A simple water balance, inflow is equal to outflow plus any change in storage. Inflow comes from precipitation, snow melt and irrigation. Irrigation in many parts of the country, as you are well aware, is used to bring soil moisture up to field capacity.

Outflow is from evaporation and

transpiration from the field as well as runoff to our standard assessment pond, and percolation into the lake ozone and or into front water. PRZM runoff assumes Hortonian flow, assumes that that occurs when the precipitation rate exceeds the conductivity of the soil surface.

Runoff is typically delayed until infiltration produces saturation at that soil surface. The runoff estimation depends on the antecedent Moisture content of the soil and on the hydro logic root, on which I'll say more in a moment. And PRZM does use the NRCS proof number approach to relate runoff from the soil site to the soil type to land use, and in farm management practices that may be put into practice by the farmer or the grower.

PRZM is a scenario driven model. There are 2 basic inputs that go into PRZM, the first is the simulation data input file. That includes a wide variety of inputs. The pesticide environmental fate data, specific pesticide application timing, and application method information, field soil properties that typically a specific soil series in each of the input files. Cropping data, which includes growth rates, crop heights, rooting depths, fueled water body, geometry and also allows the user to select the type of output and units that are desired for output from the model.

The other input file is the weather data. That includes daily measured values for rainfall, for high and low temperatures measured at that site, for Pan evaporation. Total amount of wind, in some cases we have wind direction, for looking at spray drift and solar radiation. EFED uses approximately 80 standard scenarios. We also have additional special purpose scenarios, which are used for cumulative assessments for chemicals that would have a common mode of action, and sometimes for endangered species assessments.

There are 4 basic steps that we use in developing a new scenario for PRZM. First step is to identify the potential national usage area for the chemical that we are looking at developing. For example, a scenario for corn we would be looking at the central part of the United States where corn is grown, would be the likely area for developing a corn scenario, for obvious reasons.

Secondly, we select a location with high runoff, and the USGS Isobars For Runoff is an excellent resource for that. We can actually see where higher runoff area is, so for example, going back to our corn scenario, we see that if this central area of the country is the area where corn is grown, we would be more likely to have our scenario down in this part of the country, where we do have higher runoff.

Next, we look at the soils, again these are selected by the USDA Hydro Logic Group. USDA classifies all soil series. I think there are approximately 20,000 soil series in the United States, divided into 4 hydro logic classes. The A hydro logic group has the highest infiltration and the lowest runoff rates. D soils on the other end of the spectrum would have the highest runoff and lowest infiltration rates. So for selecting a higher runoff soil series we would typically select a C or D soil, as providing the most runoff.

We're also wanting to select a erosion soil series. We also use the hydro logic groups for that. A soils are typically sandy, and for that reason large soil particles are not highly erodible. D soils are more "clayee", and may adhere and therefore are frequently not highly erodible.

So for a high soil erosion we would typically select a D or a C soil. So the overall choice in looking at both runoff and erosion is likely to be a C soil which would then maximize both the runoff and the soil erosion, in order to provide a conservative assessment site.

The fourth step is to select weather. That is a fairly easy process once you have selected the soil series, we select the nearest weather station. We have roughly 320 weather stations for which we have daily...30 years of daily weather data. So we use that measured data from the National Weather Service. The reason we use multiple years of weather is to simulate the temporal distribution of concentrations at the assessment site.

A year or two of data may vastly underestimate or overestimate the overall amount of rainfall that you might be looking at. Looking at the exposure analysis modeling system, this is our farm pond configuration. It is a 1 hectare farm pond, 10,000 square meters, 2 meters depth of water, underlain by a sediment layer of 5 centimeters depth. That gives us a 20 million liter assessment area in which that 20 million liters obviously is then the denominator in our exposure assessment calculations.

EXAMS is also driven by inputs that are selected by EFED. Chemical specific inputs; with the molecular weight and solubility, also a number of degradation inputs; pH specific hydrolysis, aqueous photolysis, aerobic and anaerobic aquatic metabolism. Movement inputs within and around the aesthetic water body. Vapor pressure, and Henry's Law Constant are used to calculate volatilization, adsorption, desorption, obviously are used to determine how much of that pesticide is dissolved, and how much of it is orbed to the eroding soil.

Fixed inputs for all cropping scenarios don't change typically with the chemical. There are pond water chemistry inputs, pond sediment inputs. Go over those, as that's sort of the focus of what we are talking about today. The characteristics of a suspended sediment, the sediment biota, the organic carbon content of the sediment, both density and percent water. Benthic Biomass, Benthic Bacteria, and the population density of both, and then the dimensions of that Benthic layer, and then obviously the pond geometry.

There are site specific inputs as well. Monthly water temperature at each of the sites is based on the temperature in the PRZM input file. Solar radiation and wind are also site specific. Cloud cover on a historical basis, and latitude and longitude of that particular site. And possibly the most significant, or one of the most significant inputs then is the storm by storm dissolved in orbed pesticide masses that are predicted by the PRZM program and then go into the PRZM EXAMS, go into the EXAMS file.

EXAMS model reports the following concentrations. Ones that are specifically relevant to us are the maximum peak; which is used for acute risk assessment, the maximum of the 21 day running average values; which is used for the invertebrate chronic risk quotient, and the maximum of the 60 day average running values, which is used for the chronic risk assessment.

This is a graph of 10,500 and sum daily values coming out of EXAMS. This is 30 years of daily values, you can see that the spikes typically will be pesticides applied in the summer time. So every year, depending on the size of the rainfall events, you do have a spike.

What we do is to sort and rank all of those values and pick out, as I said, the maximum running average for each of the exposure concentration exposure durations of interest. These are ranked and plotted from highest to lowest, left to right on this graph, and if you look on the right hand side here, this 1 in 10 year line represents the value for each of these exposure durations that we would use in the risk assessment.

That was very quick, explaining a very complex system, are there any clarification questions that I can answer briefly at this point?

**DR. HEERINGA:** Thank you, Dr. Parker, I think Dr. Schlenk has an opening question.

**DR. SCHLENK:** Yeah, thanks for the presentation, very nice. I assume you are using the ponds system as a conservative worst case scenario approach, in terms of the type of exposure that you are going to model, as far as the risk assessment. Would that be correct?

**DR. PARKER:** Yeah, I think it isn't necessarily worst case, but it is designed as a high exposure scenario. We do see...once in a while you'll see monitored values that are higher than this pond, but typically it is a high exposure assessment.

**DR. SCHLENK:** My question actually deals more with residential use, particularly with some of the pyrethroids. We see that as actually being a little bit more of a worse case scenario in certain water bodies out in the west coast, at least in urban settings. And what I'm wondering, is can PRZMS or EXAMS be modified to implement sort of an urban runoff, or a urban deposition based exposure setting?

**DR. PARKER:** We have spent a lot of time discussing that. We have a PRZM scenario, which I don't believe we've used yet for...that would divide lawn areas from hard surfaces, and route them into a pond. I think our general feeling is that this would be somewhat simplistic for the typical urban runoff scenario, where you do have multiple holding ponds and multiple storm sewers.

And we've always had difficulty trying to estimate the inputs where you have hundreds or thousands of homeowners that may be applying on the day that Home Depot has a sale. It's very difficult to estimate whether we have no applications in a year, or 10. So the inputs are different or difficult. The PRZM EXAM scenario is somewhat simplistic for an urban situation, and that's an issue that we are looking at in various ways. So it could be done. My own feeling is that that's probably too simplistic for an urban setting.

**DR. HEERINGA:** Dr. Oris.

**DR. ORIS:** Excuse me, Jim Oris, from Miami University. Thanks for the nice overview of how this works, but if you could please, could you give us a very brief description of how you get from the time series information for EEC's to the exceedance probability graphs that you use for doing that 1 and 10 year return.

**DR. PARKER:** Okay, the EXAMS program itself predicts, produces a long output file that has concentration values in all of the inputs and all of the outputs for each of the 30 years, so that EXAMS output file has 30 sections. There is a, I think it's a table 20 in that...there are 30 table 20's in that output file, probably more information than you wanted. That includes the maximum running average for each of the durations of interest that we care about in each year. So we pick out the maximum value for each year, the maximum running 4 day window for each year, the maximum 21 day window for each year, and reports those in the file.

We then take those and rank them from the highest to the lowest, for each of those durations and then pick the 1 and 10 year, which typically is about the 4th largest of those annual values, which we use for risk assessment. So it isn't the highest of all of those 30 years, but it is a high value. We have in the past determined that that's the level at which we want to regulate using this pond.

**DR. ORIS:** So there's no uncertainty built into these exceedance probabilities? It's a deterministic measure?

**DR. PARKER:** It's deterministic. We know the highest year, and the lowest year, but we just use that 1 and 10 year value. We had that debate years ago; should we bee looking at the 95th percentile, or the 90th percentile? To be consistent with some of the other offices of EPA, we chose the 90th percentile. That's obviously a judgement call rather than a science call.

**DR. HEERINGA:** Dr. Portier, then Dr. Simonich.

**DR. PORTIER:** I just wanted to follow up on that. So the thirty years of rainfall that goes into the model, that's a natural 30 year sequence from site? There's no taking the years and rotate, and randomly..? That site hasn't observed a drought, a long drought for example, in that 30 year series. That long drought is not represented in the 1 and 10 year calculations?

**DR. PARKER:** Correct. That drought year would end up in the lowest concentration years, so it's typically only the high, only the wettest years that would be represented in that 1 and 10 year value.

**DR. HEERINGA:** Dr. Simonich.

**DR. SIMONICH:** Staci Simonich, Oregon University. I'm interested as to how the dissolved organic carbons in the suspended sediments and the organic carbon content values were selected, and if they're conservative for the ecosystem?

**DR. PARKER:** They were selected by our Office of Research and Development, when we started using the PRZM, the linked PRZM and EXAMS models back in '92 or '93, we worked with the developers of the models. The developers of the PRZM EXAMS models looking at what we were doing, looking through databases that were available at that point, and those were representative of the ponds that we were simulating. They're not designed specifically to be extremely high, or extremely low, so they're representative I guess, is the best word I can use, rather than meeting any sort of policy criteria.

**DR. HEERINGA:** Dr. Abbott.

**DR. ABBOTT:** Linda Abbott, USDA. Can the electronically linked PRZM and EXAMS be used to simulate an application of a pesticide to an area that has one curved number, perhaps one type of practice, followed by over land transport to another area that has a different curve number? Perhaps a different practice type, a non-cropped area?

**DR. PARKER:** That capability is available. I don't believe we have ever done that with our 10hectare field. We typically represent just one soil series and then that just has one curve. He have the capability of putting in up to 30 curve numbers per year, so if we wanted to simulate compaction of the soil as a result of tillage operations, we could do that, but we don't at this point.

**DR. ABBOTT:** Just to be clear, I don't mean in different times, using a different curve number or I mean two different physical areas, with one curve number in overland transport to another area that may be non crop before getting to the pond.

**DR. PARKER:** Yeah, we can do that, we've played with the model a little bit in terms of simulating infiltration into buffer areas, grass waterways. To my knowledge, we haven't used that for a risk assessment. The capability is there, if we wanted to do that.

**DR. HEERINGA:** Dr. Maddalena, and then Dr-

**DR. MADDALENA:** The effort that was made to decide what runoff soils and types you use, has there been any effort to see that just because a maximum amount of soil and water are transferred to the pond, that means the maximum amount of chemical will also be transported to the pond? In other words, the moving, the effecting media, which is the runoff soil in the water, have different characteristics at different sites. So they may actually carry more chemical, even with less water or particles are moving. Does that make sense?

**DR. PARKER:** Yeah.

**DR. MADDALENA:** Has that been looked at? Like a sensitivity analysis in this modeling system?

**DR. PARKER:** Well, the Koc, the binding coefficient of the chemical with the partition between the model loading soil and the model runoff coming out of the model and so the surface water concentration is pretty much fixed. I mean if we went to a different site and put another high exposure site the numbers could be different I suppose. Is that what your what you're asking?

**DR. MADDALENA:** Yeah, maybe I can look closer into the details of the model when I get a chance. I had another sort of simplistic question in the conceptual model that follows up on an earlier question. We keep coming back to the pond as the receiving body, but what if the house was actually the receiving, the end point of your assessment? What if chemicals moved from your site to the house and accumulated in the house, the built environment and not the pond necessarily. Is there a--

**DR. PARKER:** Into the house?

**DR. MADDALENA:** Urban environments tend to be moving into these agricultural regions at a phenomenal pace in a lot of places, and when you apply chemicals at a site I think we all agree they don't stay at that site. We're assuming here in this discussion that they move from the site to a pond, but there may be more important receiving environments that should be considered. I don't know, but is there a way to look at other off-site transports mechanisms to get accumulation in different environments such as a house for example? Tracking into a house of dust and materials. Or is that a different agency?

**DR. PARKER:** That's our health effects division, that typically looks at that. They do look at residential exposure from pesticides that would be applied to a lawn, pesticides that are used for tick sprays for cats and dogs; so they do that. We pretty much stick to the ecological questions.

**DR. HEERINGA:** Dr. Hickie.

**DR. HICKIE:** Just a question of organic carbon. If I gathered from you presentation there are 6 properties from the sediment in the water? Or do they change over the duration of the evaluation, and 30 years?

**DR. PARKER:** The organic carbon in the water bodies, in all of the water bodies, no matter what country it is are fixed valued. I suppose the limitation of that is that it might not always be the same as you went from site to site. It does allow us one thing that we are required to do and that is provide a level playing field for all of the chemicals that we assess, so there is one value I think of our standard pond is that we are accessing all chemicals on exactly the same criteria. So it is a fixed value.

**DR. HICKIE:** Okay, is there organic carbon coming in with runoff? I'm just wondering whether the model has any check for carbon subject as a balance.

**DR. PARKER:** There isn't organic carbon specifically coming in, but there is an organic carbon enrichment ratio in PRZM that adds...because a chemical can be preferentially absorbed to organic carbon, you do get more pesticide delivered because of that organic carbon content in the soil. So that it is a fixed.

**DR. HICKIE:** So that the pond does not have the potential for organic carbon content to gradually build up?

**DR. PARKER:** Correct.

**DR. HEERINGA:** Dr. Biddle man, and I think then we'll move to a break.

**DR. BIDLEMAN:** Terry Bidleman, Environment Canada. Is there an atmospheric component to either PRZM or EXAMs? If not, do you have a mechanism for dealing with volatilization losses?

**DR. PARKER:** Yes, there is volatilization predicted both in PRZM and in EXAMs based largely on the vapor pressure and the end result constant for both of the models.

**DR. BIDLEMAN:** Okay.

**DR. HEERINGA:** One final quick question-

**DR. SIMONICH:** Just to clarify on Harry's point. So it accounts for volatilization but not atmospheric deposition?

**DR. PARKER:** Correct.

**DR. HEERINGA:** Okay, at this point in the process I want to thank everybody for the pace which we have able to move in our coverage. Dr. Parker, thank you very much for that presentation. I'm sure if there are other questions that come up we will be able to come back to you. And I'll work on getting my hard and soft eyes for panel members, Simonich and Bidleman, Simonich and Bidleman, and see if I can manage that after the break. Let's take 15 minutes. I've got just short of 10:30 on my watch, so 10:45. These EPA clocks are company clocks, they're about 5 minutes slow here.

**(WHEREUPON** , a break was taken)

**DR. HEERINGA:** Okay panel members, if we could have a seat we'll get under way again. Welcome back everybody to the second half of our morning session on the EPA FIFRA Science Advisory Panel meeting on the topic of selected issues associated with the risk assessment process with pesticides, with persistent bioaccumulative and toxic characteristics. We are in the process of hearing a number of scientific presentations that center on the white paper prepared by the Environmental Fate and Effects division. And at this point in time Dr. Mohamad Ruhman is going to do a presentation on environmental persistence issues.

**DR. RUHMAN:** Thank you, Mr. Chairman. I'm going to present the environmental persistence issues. This paper was presented by me, but Dr. Hetrick is here and he is also a co-author with me. The presentation outline; first I'll introduce the subject, secondly, I'll illustrate four major issues for risk assessment challenges. For the fourth example, pesticides which we are dealing with.

The first one is how to estimate the environmental concentration for the total residue of concern. Because some of these pesticides do degrade into degradates, which are persistent. That's called the total residue of concern. Interpreting the predicted or measured environmental concentration, which is above the water solubility. If we get some measures above the water solubility, how we look at that.

Second thing is interpreting the degradation half lives with a compound which has a high sorption to the soil, which the four pesticides which we are dealing with have this characteristic.

And the last thing is to quantify the long term residue accumulation in soil and sediment. I'll come up with some conclusions through my thought. For environmental fate I will transfer there, you don't have it there in the hand out. It's actually a fate and transport processes. Those fate and transport processes close the dissipation of pesticide. We look at dissipation of pesticide here as 2 things. First degradation, and second is movement. For degradation, the processes are hydrolysis, photolysis and metabolism in different environmental compartments.

For movement, we look at things which cause movement, like vapor pressure or movement between phases, like absorption from one phase to another from water into the sediment. We get studies for all these, from these studies we can say that then pesticide is degrading or not degrading by hydrolysis or photolysis, and they are specific, like for hydrolysis, specific for hydrolysis instead of all the other processes. And for Photolysis is also strict for photolysis. But then aerobic soil linked up with, it's actually a combination of 2, metabolism and sometimes hydrolysis.

For our example, pesticides, we have 4 example pesticides that are here. Pesticide 1, Pesticide 2, Pesticide 3, and Pesticide 4. Pesticide 1 is 2 isomers and a common degradate, and this is TROC's total residue concerned. It's a degradate, isomer 1 and isomer 2. That's all of them together.

This is site 2, we have the parent and the total residue of concern because the parent also degrades into about 4 degradates, which is also of concern to us. For pesticide 3 and 4 only the parent is mainly of concern to us.

If you just ignore everything and look at the red numbers there, you can see that for the half life of these pesticides, either the isomers or the degradates or the parent or the degradates or the total thing is between 114 to  stable in almost all systems. These systems which I have, we look at the half life and different environmental compartments in order. We looked at the hydrolysis half life, which indicates to us if it's resistant or not. So here is stable, so it's resistant to hydrolysis.

This pesticide is resistant to hydrolysis. And photolysis same. Aerobic soil...for, for aerobic aquatic, look at the water ponds for the water. For the soil compartment look at the aerobic soil half life. For the sediment we look at the anaerobic soil half life. As you can see that everything is giving resistance, except there is some, as you can see here, there is no resistance for isomer 1 or isomer 2 in hydrolysis. So that indicates that the degradate is a little more persistent, although we don't have any data for it.

We look at the photolysis. At the photolysis you can see that this is side 2 and 3 and 4 are not persistent, but we are looking at...it's not persistent, it's specific environmental compartment where you have a clear water, and also very shallow water. So in most environments it's all the pesticides are persistent. If we look at the...in the soil the aerobic soil, we can see that it's all persistent except one of the isomers. But when we look at the pesticide 1, we look at the total residue of concern, because isomer 1 is a concern, isomer 2 is a concern, degradate and also the total. And you can see that it's persistent.

Here we can see that pesticide 2, parent is not persistent in an aerobic aquatic system, but if we look at it and the degradate with it, it's highly persistent So we can say that these pesticides are persistent in most environmental compartments.

I agree on example this pesticide 1 can be an example for pesticide 1 and 2. As you can see here, it has, parent has 2 isomers, that's 64% and 30, 40, 55, 70 percent, and isomer 1 degrades very quickly, as you can see here. Isomer 2 degrades rather quickly, but there is a common degradate forming, and this is the degradate forming, which is a common degradate from both pesticide, from isomer 1 and isomer 2, and this degradate when it forms, comes to a maximum and it flats out, so it's highly persistent. When you look at the system we look at the total there. The total amount which is left is highly persistent.

We look at another example for another pesticide, and this pesticide is pesticide 3. And you can see that the degradates of all the degradates are not that very highly important, not important. The most important, persistent chemical is the parent and you can see the parent is degrading not very quickly. It's persistent, and the DT 50 for this pesticide is about over 200 days.

Now we look at why are pesticides partitioned either into the soil or sediment, and they partition sometimes to the earth. That's pesticide 1 and 2. If we look at values on adsorption coefficient, the adsorption coefficient for all the pesticides and also their isomers or degradates are very high. Goes from 10,600 and carries it to 1.2 million, indicating that partitions into the soil and sediment, that's all of our pesticide. We look at which partition into the air.

We can see that here we look at the Henry's Law Constant and here is between 10 to the minus 6, 10 to the minus 5, pesticide 1, the isomers and also for pesticide 2, you have 10 to the minus 5, 10 to the minus 6. But the other, the degradate of pesticide 1 and pesticide 3 and 4 are not of concern to us when they partition into the air. That's a movement, a qualitative movement.

Now I'll go through the four major risk assessment challenges. The first challenge is to estimate the environmental concentration of the total residue of concern. That's the parent plus the degradates. Total residue of concern.

First I'll give you some definitions and I think some of them have been already given to you. Hour exposure is just by looking at the EEC or the expected estimated environmental concentrations, so exposure is synonymous with EECs.

So if you want to measure exposure using your EEC, which is estimated environmental concentration, we could give this estimated environmental concentrations as a daily concentration, which is a daily EEC, or a one in ten years EEC, that's what the bar graphs told you, it's a summary of what we have here which used data to get the 90th percentile. This actually is the one we used in our risk assessment.

I also use words like TROC which is the total residue of concern. That means the degradates and the parent that we, the parent sometimes too, like this is the side one isomer on isomer 2, and a common degradate. That's the total residue of concern.

The IROC, which is the individual residue of concern, meaning either isomer 1 or isomer 2 or degradate. The methods we use for estimating that exposure, EECs are three methods. The simulation for measuring the parameters are standard gold method and estimation of this, the results of that by the residue summation method or the total residue method.

I would just go through what issues we have to consider when choosing between these methods. We have to ask ourselves similar questions and do some analysis to our answers to see which one we could use.

First question is are data available to conduct scientific analysis? Do we have data available to do scientific analysis? Are data available for individual compounds? Is there data available for isomer 1 and isomer 2 and degradate, or just for all of them? Do we have data that supports similar toxicity or can we say that the whole isomer 1, isomer 2 and the degradate are having the same toxicity or are they different? So that give us, either we go this way or the other or use this method or the other.

Can we accept assumptions because each one of these has assumptions. Can we accept these assumptions, given case by case situation. Is the degradate from a fine application because the two method, the RS method and the TR method assumes that degradate forms at time of application which is not actually the case all the time, but epidemiologists know it takes care of the time of application, of the time of formation of the degradate.

The methods used to partition the application rate, how we do the partitioning of the application rate between the degradate and the parent. And the assumption of the total residue method where you get a physicochemical product before three or four chemicals which is an assumption in that. Is that acceptable or not?

I go through method by method how we do the execution of these methods. The first method, which should be our standard gold method is the formation of decline method and we estimate the simultaneous decline of isomer 1 and isomer 2, this is, all these three examples is for, this is side one which has an isomer 1 and an isomer 2 and a common degradate. So estimate the simulation of decline curve for the isomer 1 and isomer 2 which forms isomer common degradate 1 and isomer 2 also the common degradate 1.

From that we get a rate constant, we get the ratio between the formation rate of common degradate over the degradation rate of the isomer 1 and degradation rate of isomer 2. Then we execute two separate parent-daughter PRZM exam model. And we do modeling, we get parent to go like isomer 1 go into full degradate, isomer 2 go to the common degradate.

We have two, two things here. Actually if we have only one parent, the other we have two parents, we can use only one.

This mother runs with parent break, divided between two isomers according to the ratio in the, in the material, in the pesticide and each one produce daily EECs. We combine those daily EECs and from that we calculate or summarize it into the one in ten year EECs.

The second method is the RS method. Here we divide the application at the application timing between the three compounds, which is isomer 1, isomer 2 and degradate, and we use the surrogate for that is the aerobic size study, when we get how much of it, of isomer 1 and how much of isomer 2 and how much of the degradate and then add them up, if it comes to over a hundred, we normalize into a hundred and then we, we make corrections of the molecular weight so we divide the application at three all three.

Then we exclude freons for PRZM exam, which is the two isomer and the common degradate, and we combine the freons to get the EECs and then we summarize it, the one that's in here.

The last method is the TR method which is a simple method. Here we obtain only one set of physicochemical work. Although we have three chemicals we get one set of physicochemical. We, for the half lives it's probably as simple because we calculate the half life. We see how much is of the added material is for isomer 1 and isomer 2 and degradate, we add them up and then we recalculate the half life so we have a half life for the total residue of concern. And we execute a PRZM exam run and we produce the EECs and the one continues for only one run. Okay?

I want to compare these methods and I look in comparing these methods is the formation decline method, the residue summation method and the total residue method. I use attributes here to compare them.

First is the feasibility of using any one of those. For the feasibility I have, I use the, it's based on the availability of. If we have scientific data and also for fate data for each one of those members of the residue of concern, which is the IROC, the individual residue of concern fate data then I could use the FD method. If I have only the IROC for the fate data only then I can use the RS method. If I don't have either the scientific data nor the IRO fate data for the individual degradates, then I have to use the TR method.

The second attribute is when the method is recommended and this is based on the toxicity data. If we have different toxicities we use either the FD or the RS method, are approximated by the RS method. If we have similar toxicity, we could use the TR method. For the epidemiologist it has two unique strengths which doesn't have, appear in any one of those two. These two unique strengths that incorporate the formation of the kinetics and that accounts for timing of formation. These are simpler because it doesn't do that and also this is more simpler because you had only one run.

The assumptions you have here, list assumptions. The only assumption you have is that the kinetics go first order, but here you have to assume that the timing is okay to be at the beginning of the application so you have more assumption if you go this way from the epidemiological approximations.

And the required data and therefore we have high requirement for this epidemiological method and not only for that method. We could say that the RS and the TR method are actually an approximation to the FD method.

Method compare the outputs, the outputs we got from the FD and R method is different from that of the TR method. It's different because the FD and the R, RS method generate the EECs for the individual residues of concern, each one of them and also for the total, the TR method only for the total. So but both of them generates EECs and both of them we calculate whether the 90th percentile are the assimilation of the EEC or the daily EECs.

I give you an example of this, and you can see that I'm just giving only examples for sides one and two because we just said before that this is side four, three and four, our concern is only the parent. Here we have also degradate.

Daily EECs for assimilation, for this is side one and this is side two. For side one we use the scenario simulation, we squirted that tomato with three applications per year, as, as will be labeled. But on this side two, we used a simulation of Pennsylvania turf one application per year. We look at the output. As you can see here, the epidemiological is the red line. The RS method which is an approximation on the FD method is the black line and the TR method is the blue line.

As, if we look at the peak here we can see on the simulation here, I'm choosing to do for only two years but it goes also for 50 years and this is the concentration in parts per million. I want you to notice that our gold method is somewhere in between. That the TS, TR method which is the blue here is overestimating and the TR, the RS method is less estimating our gold standard.

The next thing is for, this is side two and I'm looking also at daily concentrations. and I'm just, I've choose to do only two years, but there's the third year. Here is the time and here is the concentration in EEC in parts per million.

We can see here in the peak, the main constituent of the peak is the parent, but if you go down here that the degradates become more important and you can see here and then right here, right here is the degradate is the main, is the one which is taking, which is reducing the concentration in the pond so the outlook for one in ten years EEC for pesticide one so these same simulations I'm going to just talk about the summary of these simulations.

As you can see here for, this is side one is one in ten year EECs. As I told you before, here is the EEC in parts per million. Here is the peak concentration, the 21 day concentration, this is the one in ten year concentration, 60 days concentration right here. Mr. Parker has told you about what this means.

As you can see here, you can differentiate between the constituents of the residue. That's the parent, that's, that was isomer 1, parent isomer 2, and here is the degradate and here is the degradate coming from isomer 1, and here is the small one of that degradate coming from isomer 2. So it actually gives you the epidemiologic method, gives you also the, what is contributing to the total and you can see the total. I want you to notice the total here is about 40 parts per million, parts per billion.

Okay, next. That's the RS method. It's giving the same thing but also it's less estimating. As you can see here, it's about 30 parts per billion is the peak and also the same goes for the annual and 60 day and the 21 days.

For the TR method, as I said before, we just get only one thing which is for total. It's a mixture of isomer 1, isomer 2, and common degradate. Only one concentration. As you can see here, it's overestimating the peak and also 21 day and the annual and as I can, I showed you before for, this is side 2, how the degradate is important to time. And the long term degradates are important. As you can see here, the peak mainly is, the contribution's coming from parent, and this is the amount of degradate, there's actually four degradate.

Going with time, the parent contribution is very little because the amount of degradates are important in determining. So we have to look at the total residue of concern because these degradates are of concern and would be of concern at the chronic time and it's a long term exposure. The second thing that it's interpreting, can be predicted or measured environmental concentration above is also significant.

The ability to measure solubility for the pesticides, we have, we can compare the two categories, this is sides one and too and this is sides three and four and there's about two, two, one to two order of magnitude and that's solubility. I guess this is sides one and two, between 500 and 440. This is side three is between 1.75 and .15 parts per billion. It's very non-significant.

To decide solubility in an aquatic environment is uncertain. Why? Because the solubility in the level of the water may not be reflective of what's in the actual ambient environment. Because you have temperature variation, you have pH, you have all these, you have all kinds of things in the environment of waters or natural waters. The possible effects of formulation also might reduce, might increase the solubility, and that's because you have some, what is the chemical phase in there, is it solid or liquid and also the additives, there's solvents and elements of fires with the formula.

So the message here is that it's not always, the limit of solubility from the lab is not always the case. Solubility in the environment is uncertain. Why the water solubility is an issue because of the problems in experimental variables. Experimental issues we have modeling issues. Experimental issues is that we are not able to solubilize enough material for testing and therefore it needs a cross over.

When you add a cross over, you introduce bias, you might mis-estimate the Kd and the Koc and also introduce cross over, there's uncertainty in the toxicity studies with the concentration I mentioned above the solubility limit because we have enough separation between those phases or not.

There's modeling issues. Our present exam has no bounding. It just assumes that solubility is okay, can go up, over the solubility limit of the compound.

What we do in interpreting, these are

more than values, we get more than values from codon. This one, this is side four, these are the concentrations which is the environmental concentrations which we have and you can see that's different scenarios, you get different concentrations and if you look at the solubility limit there, the solubility limit is there for this pesticide.

So all of our estimated, our estimated EEC's are above the solubility limit. So what we do, what we do is that we constrain, we constrain the predicted pesticide EEC in the water column to be absent, so we just say that the results of this exercise is that EECs in this compound is .15 micrograms per liter.

The second thing we get studies where you have like concentrations applications, this is a Meco positive study for pesticide four, you get concentration measured with time. You can see these are four applications. When the pesticide was applied one, two, three, four times, you can see the concentrations above the solubility limit. There is the solubility limit. Above it's here, here, it's about five days which is above the solubility limit.

For us when we look at an experiment like this, we just consider it to be a suspect unless it is validated. The validation is not to say that, okay, that was no precipitate forming here or give us the reason why this, all the precipitate is combined here. So we have to show that the precipitate is separated well from, in these, in these samples.

Our conceptual model for interpreting this water solubility is that when the pesticides come to an aquatic system which contains a sediment metrics, a water column of sediment per water or sediment particles. It comes through both soluble, insoluble phase or adsorbed phase. It just goes into three different bowls, the insoluble bowl, the soluble bowl, and the adsorbed bowl with air purity in between them as can be seen here and the adsorbed bowl is, we'll take that capacity as adsorption capacity of the sediment particles.

The soluble bowl should not be over the solubility, because if it's over the solubility, it goes into the insoluble bowl as precipitate. Right here. And if the solubility go, if the concentration go under the solubility here, then you get solution, you get to the soluble bowl. And the pesticide has to go through that to go, to be air absorbed.

In, in PRZM exam modeling, or EXAMS modeling mainly in the front, we just look at only the soluble bowl and the insoluble. We don't take care of the insoluble bowl.

The third thing which I'm going to talk about is interpreting degradation half-lives when it combines with high adsorption for soil and sediment constituents. Well, our example pesticides, the partition from water into the sediment, and they cause major concentrations to decrease in the water and increase in sediment.

The half lives calculated for either water or sediment is actually a function of two things: degradation and movement. Degradation in the water and sediment cannot be separated. We cannot separate how much was degraded in the water, how much was degraded in the sediment. But what we can do, we can know exactly how much degraded in the whole system, in the system as a whole.

I'll give you an example to that. That's pesticide 3, and you can see here that when the pesticide, this is the concentration first to apply and here is the time. The pesticide's up right here, applies to the water, it goes rather very quickly in the water. This is movement. Because if you look at the sediment, it's going up in this movement.

So it is, the process here is actually

movement of pesticide between the water column and the sediment.

But the degradation if you look, that's what we look at when we look at degradation. Degradation is the pesticide is not degrading very much. That's the amount in the total system. Okay?

The last thing I'm going to talk about is the quantification of long term residue accumulation in the sinus rhythms. Exposure assessment for our examined pesticide indicate that it required reach a long period for the steady state and this often exceeds the duration of most levels that is usually about a year. And that possible appearance of substantial long term accumulation because of that. Because the partition into the sediment and soil.

We can quantify this, the long term accumulation, maybe the other end of it, is by looking at results from our modeling, from PRZM and from lake PRZM exam. There is an example for quantification of pesticide long term accumulation pesticide 1 in soil. And these are results from PRZM. That's the total, here is the total concentration in kilogram per hector, and here is the data. As you can see, over 5.2 years, there is the accumulation, and that goes with the, these are applications. So it accumulates with time.

These are results from PRZM only.

If we look at residue exam, we have different scenarios, and different scenarios as Dr. Parker has told you, that gives you different things, depending on, on the site, which is a site specific. We have New York grapes, California lettuce, and Florida turf. As you can see here, that very little accumulation is evident in the turf, more accumulation in the California lettuce, but substantial accumulation is evident in the New York grapes.

In conclusion, examined pesticides, as I said before, either the pesticide itself or, and/or the degradates, which we call the total residue of concern, is considered persistent. We feel the formation of decline method or one of its, we look at the RS or the TR method as an approximation to the FD method. They can be used to estimate exposure concentrations. This we should look at it case by case. We always look to get all of them at the FD method, but we have to go look at case by case basis.

The choice will depend upon the data availability, if we have fate data and toxicity data, also the toxicity data and what kind of fate data and toxicity data. We analyze the situation and from that we can choose these methods. Observed and/or model predicted concentrations are expected to be at or below the limit of solubility. Therefore, if we get any values over that solubility from a, from our modeling, we just cap it at the solubility and if we observe concentrations above that solubility which is reported to us, we need validation for such results.

The last two things and conclusions is the aquatic metabolism studies are designed to differentiate degradation occurring, they are not designed to do that. They're designed to get the degradation in the whole system.

Adsorption from the water pond, because this adsorption from the water pond should be interpreted as, should not be interpreted as a degradation process, but it's actually a movement process from one phase to another. The total system half life should be used in modeling, especially in modeling we use Koc to account for the movement. We don't want to do double account, double counting.

And PRZM or link PRZM exam modeling can assist the long term exposure in threshold ecosystem like the soil and also in benthic compartments. As I show you.

Any questions?

**DR. HEERINGA:** Thank you very much, Dr.

Ruhman, I appreciate the way that you moved so crisply through this material and hit the high points from the white paper. I want to acknowledge your colleague, too, Dr. James Hetrick, Dr. James Hetrick welcome too, I want to make sure everybody gets acknowledged for their participation as panel members. I'm sure there are some questions of clarification with regard to this section of the white paper and this presentation. Dr. Delorme and then Dr. ...

**DR. DELORME:** Peter Delorme from Health Canada. You made mention for photolysis that it's really only important when water is shallow and clear so what is your definition of shallow water, do you have a specific depth or...

**DR. RUHMAN:** Well, it's, that's a good question. For me it's more clear water. I would assume something like 30 parts per million.

**DR. HETRICK:** I can say that in our standard pond that photolysis really doesn't, is not that critical of a dissipation process. I wouldn't want to hesi...I don't want to hesitate and say or give you any clear example what's considered shallow but a two meter deep pond with the characteristics of our standard farm pond, photolysis is really not that, in water is not really that important.

**DR. DELORME:** And, and just a followup. How do you guys determine what a degradative concern is, is it based on toxicity, is it based on persistence, is it based on both? I mean you haven't provided any criteria when you would consider a degradate a problem.

**DR. RUHMAN:** We have a process here, we have a committee called the ROC committee, where we just give them our degradates and they look at the, the degradate structure and see structural relationships and see if they...also they look at the degradates which indeed help a specific division and they look at also their studies which they have to see, but it's not actually an ecology problem, it's more like human health.

**DR. DELORME:** So it's, it's partly driven by human health, partly driven by environmental fate?

**DR. HETRICK:** There are many components of that. We have to confer with our toxicologists to insure that we're all on the same page as far as the, what the toxic residues are, that's number one, and that's in consultation not only with our eco toxicologists but also with our human health toxicologists.

In addition to that we look at the concentration of these degradation products that are formed in these metabolism studies. Generally if they're greater than ten percent of the applied, we consider them to be major degradation products and we tend to focus on them.

**DR. DELORME:** Thank you.

**DR. RUHMAN:** But even if the concentration is just ten percent and it's toxic, we think, we consider it to be.

**DR. HEERINGA:** Dr. Bidleman?

**DR. BIDLEMAN:** Terry, excuse me, Terry Bidleman, Environment Canada. I have a question about the statement, observed concentrations above the solubility limit are suspect until validated. The normal way of analyzing water samples is to pass them through a filter and a lot of stuff goes through the filter that is not truly dissolved, it is colloidal or it can be associated with dissolved humic materials and so there may be good reasons why those so called dissolved water concentrations are higher than the solubility limit, and I have a concern that discarding them may underestimate the true concentration.

**DR. RUHMAN:** Well, we have to, they have to just prove to us that there is a good separation between the two phases and concentration's not always good because also these pesticides actually the formulations are less than one micron.

And you know, if you get part of it going through the filter so you have, we have, it's actually it's an interesting standard where you have a certain force which you have centrifuge to get the rest of the precipitate that's forming to go down, especially in those pesticides where especially the concentration was very low.

**DR. HEERINGA:** Dr. Gan and then Dr. Maddalena.

**DR. GAN:** Well, my question also is similar to Terry's since in the real water samples you have a lot of DOM and, you know, we have, we have some model studies showing that DOM can enhance the solubility of these chemicals so maybe, you know, it's pretty typical I guess.

**DR. RUHMAN:** Well, I do, I agree with you. That's why I sit there and my conclusion that the solubility method which we do here, we always ask the respondent to give us some solubilities in metro waters but it doesn't come to us all the time but we do ask, we are, and especially also for formulations if the formulations can also enhance the solubility of the compound.

**DR. GAN:** I have one more question regarding degradation kinetics. You know, I, since that's one question that's charged to me and I want to know what's the purpose of getting these half life, is that for modeling as a parameter for modeling exercises or what's the use of this half life?

**DR. RUHMAN:** Well, the use of...you mean the half lives in the different compartments of the environment?

**DR. GAN:** That's right.

**DR. RUHMAN:** We use those for modeling, we don't actually only have one, one value as you can see there. That is, we, we have many values. Hopefully it's representative. We actually looked into that, it's representative of the areas where the pesticide is going to be applied, and they get similar soils, and from those similar soils, something, the half life would be low, some high, and so on, so we get the 90th percentile of that and we use it for modeling and also we use it for saying that the pesticide has persistence...

**DR. GAN:** No, I'm sorry. I was talking about, you know, the distinction between movement and degradation. I guess your purpose is to get a true half life and is the purpose of getting that half life for modeling or for some other purposes?

**DR. RUHMAN:** It's for modeling but for describing what's happening and why would we just do say that this pesticide does not stay long in the water column, it just, it just partitions into the sediment. So we qualify that, but for degradation which we use in modeling, we just use only degradation, how far for the total system because it's actually a reflection of the degradation not movement and the movement is taken care of by Koc which we enter into the modeling so the partitioning will happen, too. There, too. So we take care of that, too.

**DR. HEERINGA:** Dr. Maddalena, then Dr. Simonich.

**DR. MADDALENA:** Would it be possible to pull up slide, that 36 again that showed the three different scenarios on pesticide four and sediment. My question just to give you a heads up and this slide kind of points it out, I'm not quite sure this slide shows three different, I guess you would call it time and steady state or overall persistence, persistence overall.

**DR. RUHMAN:** Accumulation.

**DR. MADDELENA:** Well, accumulation but it may also, the uptake curves tend to reach steady state on, at different times, five years maybe, fifteen, maybe thirty years on the three different plots and if this is the same pond with the same sediment with the same loss processes, I would think it would reach steady state at the same time so there's something else changing in this system. Are these, this scenarios are very different as far as different ponds?

**DR. RUHMAN:** This is the concentration and the sediment, not the, the sediment of the entire pond.

**DR. MADDELENA:** Right, the receiving environment is the pond and the sediment is what you're tracking and it's reaching steady state at very different times so what's different about that sediment that makes that happen?

**DR. HETRICK:** Well, first off going back to Dr. Parker's presentation, each one of these scenarios you see a New York grape scenario, a California lettuce scenario and a Florida turf. Those are three different PRZM scenarios so they have different weather profiles that go along with those scenarios and so that's probably one of the driving forces as to why you see differences in the steady state conditions as to what's occurring in the pond.

**DR. MADDALENA:** Okay, so, so then, so that leads me to, I guess that makes my next question not very important. It looks to me like the yellow line, there's material going somewhere other than the pond and I was curious if you had a mechanism to figure that out but it may just be that the application is much different. Is there a way to figure out why the mass is there a, let me see. Can you link the mass applied to the mass that ends up in the sediment, in other words, and know what goes elsewhere?

**DR. HETRICK:** Yeah, you, you can do a mass balance on using a PRZM exams model. Yeah, you can do that.

**DR. RUHMAN:** The amount which is coming into the Florida turf, the run off is very little, so it takes less time, it takes less time to get to this steady state. And what's coming from California lettuce or what's coming from New York grapes, we, it's more run off.

**DR. HETRICK:** I just want to add something to this. In looking at these different scenarios, I was glad to see that the turf had the lowest runoff capacity compared to the other scenarios because if it had a higher sediment load compared to our, let's say our California lettuce or our New York grapes or Mississippi cotton, I'd be a little concerned and I would think that it wouldn't make sense, so at least in a categorical kind of a trying to rank these scenarios, it makes a little bit of sense that the turf is the lowest run off scenario.

**DR. MADDALENA:** Yeah, it makes sense but it also brings up the question where the material's accumulating. If it's still persistent in the environment, it's accumulating somewhere and you're just not catching it in the pond.

**DR. HETRICK:** Well, it could be in the field, too.

**DR. HEERINGA:** Dr. Simonich, we have a number of questions, and we'll work our way through them.

**DR. SIMONICH:** Staci Simonich, Oregon State University. It seems from your presentation that you're considering partitioning to the atmosphere through the Henry's law constant but I don't see where you're considering the atmospheric half life. For example, it's not listed in the table for the four pesticides.

**DR. RUHMAN:** Well, I don't want to say everything, so I left something for my, my colleague.

Actually we do, we look at the half life. According to national and international standards if it's more than two day, this was, so we do.

**DR. HEERINGA:** Go to Dr. Schlenk and then Dr. Norstrom.

**DR. SCHLENK:** Dan Schlenk, ACR. I had a question to sort of follow up on Terry's and Jay's question here on the organic, carbon organic matter component. That's a set value, right, in the PRZM exams model, that is not variable based on the different locations, is that correct?

**DR. RUHMAN:** That's correct, yeah, along with the sediment..

**DR. SCHLENK:** Is there....I'm just curious is there any mechanism or thought in the future to maybe better characterize that in terms of colloidal size or UM content to in terms of refinement of the model, is that something that's been looked at, or....

**DR. HETRICK:** I think if we get into more sophisticated, particularly in the sediment dynamics issues and looking at size fractions of sand silt, clay and different particle sizes, I think we might be able to handle that and I think Dr. Ambrose's talk on WASP will give us some insight into that.

**DR. HEERINGA:** Thank you. Dr. Norstrom.

**DR. NORSTROM:** Yes, from my experience doing some work around DDT, I know that anaerobic degradation in soils can sometimes be quite important especially if it's flooded. I wondered since you apparently have divided the world up into sediments and aerobic, and soils as aerobic whether you considered adding an anaerobic component?

**DR. RUHMAN:** I don't know, I did not put these, you know, the studies which we get is the one which, but we do look at anaerobic system. We have the guideline to do anaerobic soil, an anaerobic soil half life and usually most, most of the cases is less, it's more resistance.

In most of the cases which I looked at, there's more resistance there than in aerobic systems but the anaerobic aquatic gives you an idea also about what it would be in an aerobic system soil, soil system.

**DR. NORSTROM:** I would think it would be more important in specific site situations where you had flooded soils or very high moisture content.

**DR. RUHMAN:** This actually can be used in, we can use the PRZM example, LOEL rises.

**DR. HETRICK:** I think when we're doing our simulations, we're looking at conditions that are agronomic conditions where you have crop growth and you're looking at optimal crop growth. I would say under anaerobic conditions that wouldn't be the case. Not to discount the fact that that's not an important thing to consider, but the bottom line is, is that really we're looking at a situation where we're growing crops on it and if redox potential gets too low, crops don't survive.

**DR. HEERINGA:** Dr. Thibodeaux.

**DR. THIBODEAUX:** Thibodeaux, Louisiana State University. Back to the water solubility question, as I understand it there are really two questions. One is you're finding exceedances in using the exam PRZM model and you also, it's an analytical problem as well in both lab and field?

**DR. RUHMAN:** Yep.

**DR. THIBODEAUX:** All of those?

**DR. HEERINGA:** Dr. Oris and then Dr. Steenhuis?

**DR. ORIS:** Jim Oris, Miami University, could you give me an idea of how you define persistent, or is there a cut off or is it based on each individual characteristic or each individual situation, how do you define that?

**DR. RUHMAN:** I also am sorry because

some other people would say that but I'm going to say it anyway. What we do, we look at lines of evidence and actually we see, look at different lines of evidence of what is happening in the different compartments of the environment and the half life, and we use national/international to give us standards which is like over sixty days and over a few months, but just for our problem formulation to look, see how these compounds need some more concern about than other components where you don't have that, but we do look at it as a line of evidence for our analysis further. Get more, more in depth analysis of the compound

**DR. ORIS:** Okay, so that would be defined in the problem formulation for each individual compound?

**DR. RUHMAN:** Right, right.

**DR. ORIS:** Can I ask one more question?

**DR. HETRICK:** May I add to that? One of the concerns that we have is carry over from year to year and that's a consideration and an important consideration in looking at persistence.

**DR. ORIS:** So length of growing season would be important?

**DR. HETRICK:** Yes.

**DR. ORIS:** The other question I had

regards to the use of values above solubility. I can understand why you'd want to limit exposure levels to solubility levels but why wouldn't you account for residual pools of material in your estimation of degradation rates, because as the compound degrades, it may in it there's precipitate present or adsorbed material present, wouldn't it desorb or resolubulize?

**DR. HETRICK:** You're absolutely correct, and that, if you, that tracks right along with the way we believe our conceptual model is. The problem that we have is that we don't have that written into our EXAMS nor do we have it written in the PRZM into the code to take into account when you get an exceedance of a solubility that you get a precipitate form. Now there is a model that will be presented by, called Agro today that will give you some insight that where they have integrated that precipitation into the model and do exactly as you suggested.

**DR. HEERINGA:** Entertain just a few more questions, but Dr. Steenhuis has it.

**DR. STEENHUIS:** Tammo Steenhuis, you say that the FD method over predicts? And in order, I mean you choose a degradation rate in order to do this. How did you choose the degradation rate? I mean how are these degradation rates chosen?

**DR. RUHMAN:** We, we use the aerobic soil data to generate these because the pesticides may be going into the soil that probably a good thing to do. But...

**DR. STEENHUIS:** Why can you not choose the parameter in such a way that it doesn't over predict? You know, you ask later a question about what method is the best. It depends on how you choose the parameters. And it may, I mean...

**DR. RUHMAN:** Choosing the method is not only because it's a good method or a bad method, it's also if we have the data to support what we're going to do and most of the times we don't have data for the degradates.

**DR. HETRICK:** I don't know if that was a full answer, but I want to try to take a crack at that. Number one, is we recognize that the formation decline kinetics and that approach is the gold standard that we should be striving for but we're realistic in the sense that we don't always have the data to be able to do that and since we don't have the data and we're under time constraints where we can't do an extensive kinetic analysis and sometimes doing a kinetic analysis on four data points doesn't yield much.

So the bottom line is that we go through other methods and the other methods, one would be the total residue method and the other method would be the residue summation method, and we're seeking comment as to whether those approximations are reasonable approximations for the formation decline method.

**DR. HEERINGA:** Dr. Delorme, and then I'd like to move on.

**DR. DELORME:** Just following up on the questions with respect to solubility, you indicated that if you had, you would sometimes like to have data for real water so if you have that versus the distilled water, which one would you use?

**DR. RUHMAN:** I would be inclined to use the other one. The real water.

**DR. DELORME:** Thank you.

**DR. RUHMAN:** But then also you know, the real water is different from one place than...

**DR. HEERINGA:** Well, I would like to thank Dr. Ruhman and Dr. Hendrick, Dr. Hetrick for their contributions here. Panel members, I know there are probably residual questions that you want to ask and hopefully we'll have plenty of chance to ask them and certainly before we move on to charge questions. We'll have a general set of questions and I assume that all the members of your staff, Dr. Brady, are going to be here more or less for the duration so okay, at this point in time, I think before we do have lunch, I want to try to stay on at least the sequential schedule if not the chronological schedule or time schedule for this, and Dr. Brady, if you'd like to introduce the next segment.

**DR. BRADY:** Thanks very much, Dr. Heeringa. Next series of presentations which will bridge the lunch gap will discuss sediment dynamics so I'd just like to introduce them now and then we can move right into them. Dr. Parker from the Environmental Fate and Effects Division will discuss our current methods in EFED of modeling soil and sediment dynamics.

Following the lunch break, Dr. Donald Mackay from the Canadian Environmental Modeling Center at Trent University will provide an overview of the AGRO model. Dr. Frank Gobas from the School of Resource and Environmental Management at Simon Frasier University will discuss environmental fate and food led bio-cumulation models. I'd just like to note that Dr. Mackay and, Drs. Mackay and Gobas are presenting models developed independently from the EPA that were used to evaluate a specific pesticide that was undergoing an EPA risk assessment.

We in EPA looked at this modeling work, compared the results to our own modeling efforts and thought it would be worthwhile for Drs. Mackay and Gobas to share their work with this panel. Robert Ambrose from EPA's National Exposure Research Lab in EPA's Office of Research and Development will discuss sediment transport processes and finally to conclude, Dr. Parker will return and present on simulating sediment dynamics for pesticide aquatic eco-exposure assessments, so, we'll start with Dr. Parker.

**DR. HEERINGA:** Thank you very much, Dr. Brady. Dr. Parker, welcome back.

**DR. PARKER:** Well, thank you again. This is a continuation of the modeling presentation that we started earlier this morning concentrating specifically on the sediment dynamics question. The first question I suppose is why does EFED care about eroding soil and sediment dynamics? I've highlighted in red the portions of what we do that does apply specifically to the sediment dynamics question.

The sediment moves from a tree in sight to surface water in three main ways, dissolved in run off water, adsorbed to eroding soil, entrained in that same run off water and drifting in air during spray application and from redeposition of volatilized pesticides. I might say in that latter case that we do simulate spray drift, we have specific methods for and models for simulating spray drift and, but we do not simulate redeposition of volatilized pesticides back into any of the assessment water bodies.

Second point very relative to this SAP is that many of the pesticides with PVT characteristics are found largely in the adsorbed phase attached to soil particles in the field or sediment particles in the water body and so simulating soil pesticide requires also accurately simulating eroding soil which carries it from the field into that water body.

Each of our two main models simulate an important soil sediment transport process. The pesticide root zone model simulates the transport and fate of pesticide adsorbed to eroding soil from the treated field into the exposure assessment water body, in this case our standard farm simulation pond.

Soil eroding from the treated field is estimated by a modification of the universal soil loss equation which is I think the basic work horse of a lot of the edge of field models that simulate run off of pesticide from treated fields and then simulates pesticide degradation and movement within and between the lateral and the benthic model compartments in the

EXAMS model.

For people that may not be familiar with the universal soil loss equation, there are five or six main parameters that, that are used in that representation of soil erosion to estimate the total amount that the universal soil loss equation as it was originally formulated was based on around 10,000 plot years of field data from a standard plot which was done by the USDA Agricultural Research Service back in the, starting in the '50s and continuing I think on into the, on into the '70s, extensive data base of information on soil erosion. The main parameters used in estimating soil erosion are the erosivity of the rain as it falls on the eroding soil. Erosivity is the function of the energy of the rain and the intensity of the rainfall events in terms of millimeters per hour.

Second factor is the erodability of the soil itself which is a function of soil texture and the organic matter content of the soil. The third factor is the protection from the erosive impact provided by, provided to soil by the growing crop, that is a function that increases typically as the growing crop provides more protection from the soil.

A cotton sprout provides very little protection from raindrop impact but as that cotton crop grows, you may have a leaf area index of three or four and so by the time you have a full canopy of cotton in the field there's very little raindrop impact on that growing soil and the PRZM model does simulate that growing crop. We have crop protection, the C values for about every two weeks throughout the year representing each of the particular crops.

Next factor is the slope and the slope length of the specific site. That is obviously a site specific parameter based on the inclination, the slope of the field and the length of the slope that is exposed to the run off of that. And the last factor is the management practices implemented by the farmer or grower which would include terraces, contour plowing, reduced tillage, leaving proper residues in the field, all of which have specific values for reducing soil erosion.

The universal soil loss equation in its original form was predicted an annual average value over a, officially a 22 year, a 22 year simulation. That 22 year average value was not particularly useful in this kind of a model where you're needing to predict soil erosion on a storm by storm basis as you have rainfall events happening throughout the year and so Dr. Jimmy Williams at Texas A&M has modified the universal soil loss equation in several ways that can be used in this kind of a representation.

We currently use a modification called MUS. MUS is an acronym that has an acronym in it. MUS is the muscle which is another of the modifications, muscle for small water sheds and you can see that equation there on the screen if you look at the last few, where's my pointer, if you look at these last few factors here, they are four or five of the main USOE factors that are used in the USOE equation, and then these first factors are the ones that make it available on a daily basis for predicting soil erosion.

Within the EXAMS model partitioning two benthic sediment is a function of the process that is bringing the pesticide into the water body, pesticide, dissolved pesticide in the run off water is instantaneously partitioned between the water column the suspended sediment, the suspended biota and the benthic sediment based on the partition coefficient, either the Kd or the organic carbon normalized Koc can be used for that.

Adsorbed pesticide is a bit different. In the run off water it is initially routed among the four destinations: the water column, the suspended sediment, suspended biota and benthic sediment based on another's exam's parameter called the percent benthic or PR ben. The developers of this model have given a default value of point five and for all pesticides and we haven't seen a reason to change that so that is our default for the percent benthic for partitioning routing of the adsorbed pesticide and then it is after that is repartitioned based on the partition coefficient.

Spray drift partitions instantaneously, also the same as the dissolved portion between the water column, suspended sediment, biota, and the benthic sediment again completely based on the partition co-efficient and then once that's happening, all pesticide in the water body and in the benthic sediment zone are continuously repartitioned based on differential degradation within the water compartment and the sediment compartment.

So for example, if the pesticide in the sediment department, sediment compartment is degrading much more quickly then you would have a net movement from the water column to the sediment in order to maintain that, the initial Koc value.

Looking at enrichment ratios for organic matter and soil, I believe someone touched on earlier. Due to the large surface area of the fines, the silt and clay size fraction of the soil, these size fractions differentially sorb more pesticide than the larger size fractions.

Soil erosion also selectively erodes the finer soil particles and the organic matter so you have both of those happening at the same time, selective partition to the finer particles and organic matter and selective erosion of those same particles and so there is an enrichment process going on in between the field and the water body.

PRZM does use an organic carbon enrichment process to account for enrichment of the organic matter in the soil but does not have a sediment enrichment process to select for the finer erosion particles in the eroding soil. This is an important slide, this and the next one are two representations of the same scheme. If you look at the PRZM box on the OP standard scenarios on the upper left, you see that pesticide in run off goes directly into the exam's EFED standard pond.

The pesticide sorbed to eroding soil, the same goes directly to the standard pond but the eroded soil, which is also predicted by the mass of eroded soil which is also predicted by the PRZM program and the depth of run off water, which I guess becomes a volume by the time you know the area, are not read into the EXAMS pond so you, we do not have an accumulation of sediment from PRZM going into the exam's pond and we do not have eroded soil coming from PRZM going into the exam's pond.

This is a verbal representation of the same thing. There are four, well, there are many, many parameters that are estimated by PRZM but these four are estimated and go into the PRZM/ EXAMS transfer file but only the bottom two that the pesticide masses are the ones that actually, actually enter into EXAMs and so many of the questions that we are asking you to take a look at are based on this specific concept that the pesticide mass is moving into the pond but the mass of eroded soil and the volume of run off water are not routed into that pond.

The EXAMS, sediment dynamics EXAMS uses a lumped process to represent pesticide mixing between the water column and the benthic zone. Many models specifically represent individual processes.

The EXAMS has looked at, from discussions with the developers of EXAMS has looked at those processes and decided that this single lumped process is an adequate representation of that total process and so that is the representation which is in the EXAMS model.

That mass transfer coefficient represents sediment settling and resuspension. That represents any wave action within the pond that might cause resuspension or mixing within the bottom sediments, bioturbation caused by either lateral or benthic fauna that may be living in the pond, ranging from bacteria to muskrats and mink I suppose, and then all of these are represented by this mass transfer coefficient with the assistance of the percent benthic or PR ben parameter.

This is a general representation of the sediment dynamics processes which I think could be said to represent what happens in a large number of models that deal with sediment dynamics. You can look at these a little more closely at your leisure after the presentation. The area in the oval toward the bottom of this representation looks at the processes that are represented by our lumped mass transfer coefficient rather than representing each of those individually and then does not actually represent....does not actually represent variable.

From your white paper, if you look in chapter four which presents most of this information, there are two equations that represent what's actually happening with this mass transfer coefficient. This equation simply states that the change in the poor water concentration as a function of time is, can be expressed as the mass transfer coefficient times the difference in concentration between the benthic poor water concentration which is what's being predicted and the concentration, the aqueous concentration in the water column itself.

It should be noted in this case that the aqueous concentrations in this, in this equation are only used as a surrogate Dragon force and do not imply aqueous only transport from the water column to the benthic region. This equation then represents all of the causes of pesticide mixing between the water column and the benthic zones.

This is the way that this equation is implemented within the EXAMS program. Again, you can see, you can get more information in your white paper when you're looking at chapter four. The K transfer is the geometry independent water column to benthic mass transfer coefficient, which has a fixed value which you can see there on the right and then that's multiplied by the surface area of the boundary between the water column and the benthic compartment which is the same as our one hector pod so that's ten thousand square meters divided by the total volume of that benthic compartment which again is that ten thousand square meters times the five centimeter depth of sediment, giving us five hundred cubic meters of sediment to which all of the chemical is bound.

The percent benthic in EXAMS is the initial routing parameter, as I mentioned before, for incoming sorbed particles. What it actually represents is the routing of the labile portion of the field sorbed pesticide, that which comes off the field already sorbed as it mixes instantaneously into the water column and suspended sediments and the benthic sediment.

The EFED default PR ben value, as I pointed out, is zero point five for all pesticides meaning that fifty percent is initially routed, initially meaning day one, routed into the water column, and fifty percent is initially routed into the benthic sediments and suspended sediments and biota and then after that they are repartitioned, continuously repartitioned based on the sediment, based on the repartitioning on the partitioning coefficients.

The EXAMS manual describes a method to simulate permanent pesticide burial using a first order rate constant, but the manual also advises that for evaluation and screening purposes, it seems unwise to suppose that buried synthetic chemicals will never reappear.

EFED generally agrees with that cautionary advice and currently does not simulate buried pesticide. However, as an example specifically for this presentation to the panel, we did use the first order burial method as described in the EXAMS manual and using our example chemicals three and four to see what impact, see what impact that would meant, that would mean for those, for those chemicals and the next couple of slides you can see the results.

The Mississippi cotton cropping scenario is a scenario that produces a lot of sediment, and so we used that as sort of a high exposure case for looking at that. Here we, we compared the non-burial simulation with the burial simulation and looked at the percent reduction as the function of looking at that burial process.

The top row there looks at the water column concentration, that difference. The next row looks at the poor water concentration difference and the bottom row looks at the sediment concentration difference looking at this first order rate burial process for pesticide three, also looking at pesticide four and rather than forcing you to look at a lot of numbers and trying to figure out what's what, I actually put them on a single slide here so you can look at what the impact of that burial process does.

And as I say, this is not something that we normally do as part of our risk assessment process, but it came up in looking at how we simulate these specific pesticides where you do have a large amount of it that is sorbed to the pesticide, we looked at how that process might be represented within EXAMS if we were to do that and here you can see that the results that are from your, from the two previous, two previous slides summarized so you can see it.

I think the reason that the numbers are so much higher, reductions are so much higher in pesticide four is that the Koc of that particular compound is higher than the Koc of pesticide three.

So summarizing just this particular presentation, EFED uses the PRZM EXAMS model to estimate pesticide concentrations for ecological exposure assessments. PRZM uses the MUS modification of the universal soil loss equation to estimate soil erosion from the field into the water body.

PRZM simulates organic matter enrichment but not fine sediment enrichment in that process.

EXAMS uses a lumped mass transfer coefficient process to represent all mixing between the lateral and benthic model compartments and EFED does not currently use the first order process available in EXAMS to simulate pesticide burial.

**DR. HEERINGA:** Thank you again, Dr. Parker, and what I'd like to do is entertain questions for about 15 or 20 minutes and then we'll break for lunch. Dr. Thibodeaux.

**DR. THIBODEAUX:** Thibodeaux, Louisiana State University. From the water shed to the pond you said that particles, soil being eroded from the water shed were directed away from the pond, is that correct?

**DR. PARKER:** No, I may have said that, but I, they're, they're, it's actually the eroding soil is carried by the run off water from the water shed into the pond.

**DR. THIBODEAUX:** Could you go back to that slide?

**DR. PARKER:** I can. It is number...

**DR. HEERINGA:** Is it true that once it hits the pond it disappears though because it does not accumulate?

**DR. THIBODEAUX:** Nine, Number 9.

**DR. PARKER:** Which, which slide is that?

**DR. THIBODEAUX:** Number 9.

**DR. PARKER:** Slide Number 9?

**DR. THIBODEAUX:** Yeah, I'm looking at both of those dotted arrows, the one that says eroded soil and run off water...

**DR. PARKER:** Right, they, they are not used by the EXAMS program. They are in the, they could be, but we don't currently use them. The run off water and the eroding soil which are predicted by the PRZM program are not actually utilized in the EXAMS program.

It's only the sediment bound portion of the pesticide and the dissolved portion of the pesticide so it's just the two pesticide masses or three if you include spray drift, that actually enter the EXAMS pond and we don't actually simulate the soil as it flows into the pond or the volume of water as it comes off the water shed so the soil and the water are not simulated by EXAMS but the pesticide dissolved and sorbed to both are simulated by EXAMS.

**DR. THIBODEAUX:** So a follow up question. On those two dotted arrows that go to the left, do they contain any of the pesticide?

**DR. PARKER:** No.

**DR. THIBODEAUX:** Thank you.

**DR. PARKER:** All of the pesticide goes to the pond and the sediment and the water are ignored by EXAMS.

**DR. HEERINGA:** Yes, Dr. Mehta.

**DR. MEHTA:** Yeah, but that means that the burial effect is not simulated...

**DR. PARKER:** Correct, correct, we don't simulate burial, but that's one question that we're looking at.

**DR. HEERINGA:** Dr. Portier.

**DR. PORTIER:** Can you give me some idea of how sensitive the model is to the PR Ben? You chose that 50 percent split. I mean, if you're moving that a little bit does the model really react strongly to that?

**DR. PARKER:** The peak concentration on the first day reacts quite vigorously to that as you can imagine, because you're putting, if you're putting 90 percent of, if you assume that 90 percent of the pesticide is labile is going instantaneously into the sediment, then that peak concentration in the sediment is much higher, the peak concentration in the water is much lower. But after that initial routing, it's the Koc that then redistributes them based on that particular parameter. So for a sixty day simulation it really doesn't make much difference but if you're concentrating on that peak value it makes a big, it can make a big difference.

**DR. HEERINGA:** Dr. Schlenk.

**DR. SCHLENK:** Dan Schlenk, UC Riverside. Yeah, just to follow up on a question I asked in the earlier presentation, maybe you're trying to say it here and as far as PRZM simulates organic matter enrichment but not fine sediment enrichment, does that mean again the DOC that's in the pond is not being parameterized in terms of the model or is that even an issue, is that even considered in the model. Or are you just using just a total mass or concentration of DOC in the water at that particular point?

**DR PARKER:** The DOC does change with the incoming pesticide...

**DR. SCHLENK:** Okay, so like for example, so you're not using the eroded soil component, I see that, but in the water itself is there any size class differentiation of that DOC in the water column at all?

**DR. PARKER:** No.

**DR. SCHLENK:** In the inner model?

**DR. PARKER:** Correct.

**DR. SCHLENK:** Is it possible to do that in EXAMS?

**DR. PARKER:** EXAMS uses the three size fractions of the soil to based on some Wells and Bracken-Seeks regression equations to estimate both density and water holding capacity and so those are available to us, but the erosion process itself doesn't differentiate between them so we really don't know which size classes are injuring. We know the texture of the soil, the field soil, but beyond that, we don't have that information.

**DR. SCHLENK:** One final question, is there any way to estimate colloidal impact in terms of the water column?

**DR. PARKER:** No.

**DR. HEERINGA:** Dr. Delorme and Dr. Gan.

**DR. DELORME:** Just out of curi...Peter DeLorme from Health Canada. Just out of curiosity, where does the assumption of a first order process for burial come from? Is that based in science anywhere or is that just something somebody, one of the developers pulled out of the air? I know you're not using it, but I'm just curious as to where that assumption might have come from.

**DR. PARKER:** I'm guessing that Larry Burns when he was very active with the regulatory community and with us and at some point he did some playing with that to see if he could simulate burial. He, as you know, he passed away last November and so I can't ask him that anymore, but I'm guessing that came from Larry Burns. I don't know that there's more science behind it than...

**DR. DELORME:** So you don't know if it's based on any empirical data of any sort?

**DR. PARKER:** No.

**DR. DELORME:** And I have a...what was my second question? I can't remember.

**DR. HEERINGA:** You can come back to it. Dr. Gan?

**DR. GAN:** Just a question on your enrichment ratio of soil to organic matter, does that vary from soil to soil or do you have a fixed relationship and how important you think that will affect the ultimate fate and transport?

**DR. PARKER:** The organic matter is, comes from the data base of soil properties that we use for developing the, developing the scenarios and so it does, that is a function of the original organic matter in the soil and I don't know what the impact of that is, we've never looked at what the impact of that might be. I mean it's something we could do, but we have, up to this point we have not...

**DR. GAN:** So does the current PRZM address that process?

**DR. PARKER:** Yes, but not the, but not the sediment process.

**DR. HEERINGA:** Dr. Hickie and Dr. Doucette?

**DR. HICKIE:** Agricultural ponds are often enriched in nutrients from fertilizer use, does EXAMS take that into account in any way in terms of production of algae within the ponds?

**DR. PARKER:** No, there is a fixed value for the algae content of the pond. I think if you listen to Bob Ambrose's presentation this afternoon, they actually predict changing algal populations based on water temperature and solar radiation but it's a fixed value in our, in our pond.

**DR. HEERINGA:** Dr. Doucette.

**DR. DOUCETTE:** Bill Doucette. Have you considered looking at other ways of normalizing absorption other than just organic carbon, especially for certain classes of pesticides or types of pesticides where organic carbons may not be the dominant absorptive site?

**DR. PARKER:** If we had the data, we

would probably use specific surface as a, at least as an alternative for beaching the soils but that's not a parameter that we get from, as a potential input so the only inputs that the model accepts are the organic carbon normalized version of the Kd itself.

**DR. HEERINGA:** Peter, did you think of your second question?.

**DR. DELORME:** Yeah, Peter DeLorme. It came back to me. You used the high or a high erosion scenario when you did your burial so given that for one of the pesticides is around 20 percent, do you guys have an idea of where you would bring in burial? Like do you have any idea of criteria because if you look at this if it's a low erosion scenario or a medium, it may not have any effect. I'm just wondering how could you factor that into your sort of risk assessment or your tiered E, or have you given it much thought?

**DR. PARKER:** Well, with these high Koc compounds are something. I mean, we've looked at some prior neutroids, but are something that we weren't really dealing with in the beginning so that's something we want to look at. We're actually, in having a number of these compounds that we're starting to look at, we're looking at the parameterization for our early soil parameters to see if they are appropriately conservative to represent this class of compounds.

**DR. HEERINGA:** Okay, Dr. Parker, I'd like to thank you again for the presentation and addressing the questions. Panel members will have a chance to revisit questions to all of the presenters before we enter the charge questions. It's time I think we've all earned lunch, and I'm showing just a little bit before 12:25. Let's say we'll reconvene at 1:30 instead of 1:15 as shown on the agenda, so 1:30 and see everybody this afternoon.

**(WHEREUPON,** a recess was taken for lunch.)

**DR. HEERINGA:** Okay, let's find our seats, and we'll get underway. Thank you, everyone, and welcome back to the first day of our multi-day meeting of the FIFRA Science Advisory Panel on the topic of Selected Issues Associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative, and Toxic Characteristics.

Through the morning session, we heard a series of presentations linked to the white paper that was prepared by the Patent Effects Division, and at this point, before we move on with a...a presentation by Dr. Mackay, I would like to turn it back to Dr. Parker for just a few points of clarification, follow-up on this morning's discussion. Dr. Parker?

**DR. PARKER:** Thank you. Over the lunch hour, I received a little bit more information from a couple of my colleagues and answers to a couple of the questions this morning. In terms of the question on the first order...order burial rate using the EXAMS. EXAMS mathematically is a stirred reactor, behaves that way, and so the...the first order process lays down the sediment continuously, and as it enters the pond, it continuously...if it enters the pond continuously, it is automatically deposited continuously.

And the way that...the way that half-life value was calculated was to take the entire mass of sediment in each of the rainfall events over the 30-year period and divide that continuously on a...a moment-by-moment basis to...to develop that first order process which then lays down the...lays down the sediment in the pond.

On the question of organic matter in the soils and in the pond, the organic matter in the PRZM field is taken from the USDA data base which is the official record of that particular soil as it's used in...in the PRZM scenario, and in the EXAMS the...the DOC is fixed at 5 parts per million for all sites and all simulations. That doesn't...that doesn't vary.

It's not...that value is not a function of the organic matter in the soil.

And EXAMS has the capability of running flow through it. We just don't...don't choose to...to do that through the eco assessments. We do, as a matter of fact, run flow through...through the index reservoir for drinking water, human health drinking water assessments, because the level of concern in this for a bigger watershed is less. And so, we can still be conservative by running flow through that, but we don't use that for...for ecological risk assessments.

And we do have...we are working on developing a variable volume pond that is quite similar to the EXAMS pond except that it has the capability for the water level to raise and lower with evaporation and inflow, and that model will accept sediment on a day-by-day basis as it's...as it's produced from the flow.

Did I catch everybody's points? Okay, thank you.

**DR. HEERINGA:** Thank you very much. That's very helpful.

Before I move on, just one quick administrative note. With...with Myrta Christian's permission, I have a teaching obligation at the

University of Maryland early this evening, late afternoon, so I'm going to be stepping out part way through the afternoon session, and Dr. Bucher is going to be taking the chair for the balance of the afternoon. I'll be back tomorrow morning. So, I'm not running out. If you want to know where I'm going, there's that piece of information.

Okay, at this point in time, I'd like to recognize Donald Mackay. Is it Mackay? I was told it was Mackay...who is with the Canadian Environmental Modeling Center at Trent University, for an overview of the AGRO model for pesticides. Dr. Mackay?

**DR. MACKAY:** Thank you very much. I appreciate the opportunity to share some thoughts with you on the AGRO model. I will be talking about the water quality aspects, and my colleague, Frank Gobas' assignment will be looking at the food web.

A few comments. I...I was very much impressed by the white paper that was produced. It's a formidable document, and it certainly covers all the issues, and I compliment the EPA staff for producing it.

And I was equally impressed with the qualifications of the analysts. So, I think it's going to be a very useful event.

The focus here is on models for pesticides which are more PDT like in properties. I'm going to outline the evolution and the performance of the AGRO model and in doing so compare with EXAMS and then have some concluding thoughts or prejudices on desirable model features for your consideration.

Frank and I were given a task to develop a dynamic water quality aquatic food web bio-cumulation model for chemical III, and as you heard this morning, EFED defines a 10 hector field, a 1 hector pond, 2 meters deep with input by spray drift and soil erosion. We selected the QWASI, that's quantity of water-air sediment interaction model for the water and the IMA-Gobas model as the food web model, and we modified them for this purpose.

Our aim was to produce a realistic model, including all the relevant processes, and especially focusing on more hydrophobic substances.

A few words on hydrophobicity, because it's a very important concept here. To a physical chemist, hydrophobicity is fundamentally determined by the activity coefficient of the substance in water which is a measure of the force with which the water matrix is attempting to expel the...the solute molecule. It's not a very happy quantity to use directly. You can use water solubility, and for a liquid solute, water solubility is essentially the reciprocal of the activity coefficient. So, it's hydrophobic substances, some very high activity coefficients and very low water solubilities.

The best metric is octanal water partition coefficient which is essentially the ratio of the activity coefficient in water to activity coefficient in octanal, and because activity coefficients in octanal are generally quite constant, range from about 2 to 10, it's a very good indicator of the hydrophobicity, and it's generally accepted as such, and it is used, for example, to calculate the organic carbon water partition coefficient, and TOC is generally about a third of KOW. KOW is also important, because it's usually equated to the lipid water partition coefficient, and it is lipid water partition coefficient that is the major determinant of bio-cumulation.

The question then arises, is there a bright line cutoff for hydrophobicity versus non-hydrophobicity? And the short answer is no.

About a log KOW of 4, you're beginning to see hydrophobitic...hydrophobic character. Above 6, it is strongly hydrophobic, but so 5 is sort of a middle of the road number, and it, by coincidence, at a log KOW of 5, partitioning in a pond between the dissolved phase and the particulate phase is about equal, so that above 5, it is very important to include the chemical sorbed to water. And on page 82 of the white paper, it gives a nice example of this.

Hydrophobicity also affects the bioavailable fraction in water by partitioning not only the particles but the dissolved organic carbon, dissolved organic matter. It also controls the rates of respiratory and dietary uptake by fish, and roughly speaking, at a log KOW of 5, there are equal weights of uptake from respiration and dietary uptake. When you go to 6, it's about 90 percent from diet.

So, as you go to more hydrophobic substances, bioconcentration, that's uptake from water becomes less important. Frank KOW substances can also have very slow uptake and clearance times, long half-lives. And roughly speaking, at a log KOW of about 5, it takes about a week or so or maybe two weeks for the...the fish to take up the material, half of that is taken up by respiration.

So, 5 is sort of a good middle of the road number.

Just a little bit of history. I was

privileged in the 1970s to work with George Bachman and his colleagues at Athens, and he and his colleagues put together the EXAMS model. My particular responsibility was volatilization in that model. So I was completely familiar with EXAMS at that time, and essentially, I copied it and converted it into a fugacity format, and that became the QUASI model. So QUASI is really now sort of son of EXAMS, but in doing so, I introduced two major changes which I'll mention later.

So, the AGRO model is...there is the QUASI model. It leads into a food web model and into other deliberations, and the difference from the existing EFED model which we heard about this morning is that EXAMS replaces it. So, that is the AGRO shell and the models contained in it.

So, this is a picture of the QUASI model. There are a number of arrows in this, and each one has a D against it. That represents a process. There's an equation for that process. There are parameters go into it, and I draw your attention to four arrows between the water column and the surface sediment.

There is deposition of particles. There is resuspension of particles. There is diffusion from water to sediment or water and diffusion from sediment or water to the water column. And as Ron Parker described this morning, these four processes are all lumped in EXAMS, and I felt uncomfortable about that, and the reason was that when you go to very hydrophobic substances, the sediment deposition and resuspension processes become very much more important than the diffusion processes. In fact, you get to a KOW of 6, you can almost ignore sediment in water diffusion.

I also put in burial as a process, because I was mainly interested in having a model which would simulate conditions in the Great Lakes or areas of concern within the Great Lakes. But it has all the usual processes of inflow, exchange with the atmosphere...it also has deposition from the atmosphere which is irrelevant here...outflow, reaction in water, and reaction in sediment.

A key modeling principle, I think, is that if a process occurs naturally that affects more than a few percent of the substance's fate, you must include it in the model, but the relative importance of all these processes depends on the chemical's half-life and on its hydrophobicity and on its volatility. So, a fate model should be capable of treating a wide range of chemicals. At least, a user should be aware of any limitations that occur, and this is particularly the case with respect to hydrophobicity.

So, that's a list of all the processes which are included in the QUASI model. They are all treated as separate processes with a separate equation.

The model also includes partitioning between water and suspended matter and between core water and sediment. It can include the influence of dissolved organic matter, and it can include partitioning to microorganisms in fish and microphytes, as Frank will talk about.

It does not treat mixing in the water column. It treats the water column as well mixed, although there are directions which stratify the water column. And bioturbation can be included by increasing the diffusivity between the sediment and the water.

So, how do EXAMS and QUASI compare? Well, they both have inflow and outflow of volatilization. They both have degrading reactions. EXAMS does a much better job of treating reaction in that it will help the user obtain, for example, photolysis half-life, QUASI just asks for a half-life, and how you get it is your own business. EXAMS doesn't include sediment burial, QUASI does. And EXAMS, as Ron Parker explained, treats sediment water exchange as a bulk dispersive diffusive process and QUASI, there are four separate processes.

Some of the key parameters in the model, Koc, organic carbon partition coefficient. This is usually measured rather than derived from KOW, and the way in which it is measured normally is to measure Kd, that is, the whole solid to water partition coefficient, and then that is divided by the organic carbon content. So, any sorption to mineral matter is actually automatically included, and it's wrongly but actually attributed to organic carbon partitioning.

The degradation half-lives are usually measured. You can get field to pond transport from PRZM, which is an excellent model, and it is the deposition resuspension steps that are critical, and these deposition rates can be generic constant values, or they can be values based on local measurements or other sources as I'll discuss.

Sediment in water transport, I was going to present some material, and then, to my horror, I discovered that Willie Lick and Louis Thibodeaux were on this panel, and I know you're all putting together your Christmas wish lists of books to buy, so Willie Lick's book on sediment transport should be at the top of the list, followed by Louis Thibodeaux's Environmental Chemodynamics.

So, the actors...

**DR. THIBODEAUX:** Thanks for the plug.

**DR. MACKAY:** The invoice is in the mail. All I'll say is this, and I bow to these guys' greater knowledge of this. The deposition and resuspension rates depend on the size of the pond, the fetch, any flow rates of water, solids characteristic, wind speed, duration, depth, shielding, microphytes, benthic organisms, and so on. There has been an enormous amount of excellent work done on resuspension deposition in lakes like Lake Erie and estuaries, and Willie Lick has been the guru of this for many years.

We're dealing with relatively small ponds, and I think applying these lake correlations to ponds is not wise, because they're unlikely to be reliable. Functionally, for small ponds, the measurements are easy. The pond is accessible, and you can make deposition resuspension measurement. So, that is, I think, the ideal source of data for those purposes.

And one point is and it came up this morning in Mohammed Ruhman's discussion, if you have a pond, it's essential that the model have some mechanism for loss of chemical, because if there isn't, the chemical will build up and build up indefinitely. For example, if you apply copper ion as a pesticide, which I hope you never do, it will just runoff into the pond and build up until you have a deep blue pond of saturated copper ion. You must have exit processes or the model gets distorted results.

So, we went through essentially three volumes...three versions of the AGRO model. The first one, we had an integrative chemical, either steady state, X grams per hour, or a pulse of Y grams or repeated pulses, and we use this to validate that a mass balance was, in fact, achieved, and it worked.

We put in constant on what we thought was reasonable but user selectable values of the pond parameters, the transport parameters such as resuspension deposition rates, and you get tabular and graphical output, and Frank used that to calculate organism concentrations.

We discovered that the solubility in water may be exceeded, and this is a...a sketch of what you might get. The concentration in water will rise rapidly, usually as a result of spray drift, and then it falls fairly rapidly over a day or two. This is the dissipation process that Mohammed was talking about. And, of course, there is uptake and an increase in concentration in the sediment.

And it is very easy to exceed the solubility limit, especially with spray drift, because the solubility of these substances is in the microgram per liter range, and that really worried us. Oh, I'm going to skip that.

What is it that causes all the solubility? Well, it's hydrophobicity, a high log KOW, and it's also a high melting point, especially if the molecule has molecular symmetry. I mean, x-chlorobenzene is the classic example. It's something that's going to be a much more frequent issue with hydrophobic and high molecular weight pesticides. It's a problem that I think has to be addressed.

The white paper and this morning, they have strategies on how to address this problem. Exam allows the solubility to increase, and that kind of makes the problem go away. From a physical chemistry point of view, that's a little bit naughty, but it works.

AGRO goes through the process of allowing for a precipitate reservoir to form which can dissolve once the concentration in water falls below the solubility limit, and that, I think, is more rigorous. The precipitate just sits there in water. It doesn't deposit. It doesn't flow out. It doesn't react. Nothing happens to it.

It's not entirely a happy assumption, but it kind of works. So, that's what AGRO does.

So, what you get with AGRO is a picture of spikes of concentration corresponding to spray drift from an application followed by input by runoff or erosion from the field, and you have highly variable water concentration and buildup in the sediment which eventually decays, and over a year or two, this is repeated. You can look at it in terms of fugacity as well, and you get essentially the same picture.

That concentration pulse propagates into the food web, but it is very highly damped, and the reason for that is the pulse in the water column lasts a couple of days. The uptake time of the fish is measured in weeks. So, the fish never get close to the equilibrium value corresponding to the maximum concentration in the water column.

So, the fast sediment water transport reduces the high concentration. It's of short duration, and although the pulse propagates into the food web, the organism functionally is relatively slow to take it up compared to the pulse duration, so it is absolutely essential to apply a dynamic model. The worst thing you can do is take a peak concentration and then multiply it by a steady state bioconcentration or bio-cumulation factor.

This, actually, is the old canary in the coal mine philosophy. Steady state models are useful in places like the Great Lakes where you have chronic conditions, but for agricultural/agrochemical processes, you really need a dynamic version of both the water quality model and the food web model, and that's what AGRO seeks to do.

You can put in repeated pulses, and over a long period of time, you get results that are close to the steady state value, and as Frank will explain, you can get good agreement with mesocosm registration data. And the short-term water concentration is controlled largely by sediment deposition rather than reaction. So, measuring that dissipation rate gives you that rate, but it's difficult to get a reaction rate out of it, and I'll return to this later.

The reason is this. And for those of you who like mathematics, this is my attempt to do it. The differential equation for the water concentration is that, and there's a whole group of five processes which are reducing the water column concentration. There is flow, there is volatilization, there is deposition, there is diffusion, and there is reaction.

And the total might be a number like 120 units. It don't matter. Of that, perhaps 100 is deposition.

So, to try and extract an accurate value of 5 from that data is basically impossible, and this is just a restatement of the message that Dr. Ruhman gave you this morning.

AGRO then move to version 2 in which we had input from PRZM, and then version 3 in which input was again from PRZM, but particles of solids flowing from the field were now included in the deposition process. And this was discussed this morning.

So, that arrow in Ron Parker's diagram which went off to the left in...in AGRO, goes right into the pond. And this is important, because you increase the rate of deposition, and that reduces the concentration in the water column, reduces the bioavailability of the chemical, and it reduces the concentration.

And burial is now important. Because you're putting more particles into the water, they've got to go somewhere. They go to the sediment, and this results in burial. So, I'm convinced that it's important to include burial.

In the white paper, page 91, there's an example, and Ron Parker described it this morning, of a burial half-life of 222 days. That's a long time, it's a slow process, but what that means is every year, virtually all that sediment is buried and replaced. So, over 30 years, in fact, the pond fills up completely, and you no longer have a pond. So, although it's a slow process, it is very important, especially if the degradation rate in the sediment is very slow.

So, for accurate simulation of pond dynamics, it is essential to include burial, in my opinion, and I'm going to skip that.

So, ideally, I think, the model that should be used should simulate the real world as closely as possible. If you can simulate it, it is capable of validation, and I'd love to see a lot more effort into actually going out and measuring concentrations in real ponds and seeing if these models are producing results that in any way mimic reality, so validation is very important.

And if you...I understand completely the desire to apply regulatory conservatism to the results, but I think it should be applied to the results at the very end and not to the model processes. Don't remove a process from the model like burial because you think it's non-conservative. You can do that at the end if you wish.

So, PRZM gives flows of chemical and solids and water. I would argue you should include all of these three flows into the water, and putting sediment into the pond results in burial, and it results in faster deposition. Putting water into the pond, especially after severe storm events, increases the volume of the pond, it dilutes the contaminant, and it may result in outflow. And if you want, you can reduce the outflow to a very small number.

So, these are just some concluding thoughts for your consideration. I think it's important that the model include...includes all the relevant processes in a realistic manner with realistic parameter values, and it should be validated, if possible.

And I would urge you to strive for simplicity consistent with the need for a realistic simulation. A simple model is much more easily interpreted. It's much faster, and you must remember the likely accuracy.

If you can get within a factor of 2 or 3 of the real numbers, you're doing quite well in this game, in my opinion. So, don't worry if the result is 4.1 as distinct from 4.2. You'll never get that accuracy with these models.

And you can do sensitivity analysis and a combination of careful interpretation and Monte Carlo methods is I think the way to go. So, we favor a simple two-compartment sediment water model, and that's what we designed, with advice from EFED.

And un...in the white paper on page 93, there are other models. These and in EXAMS are excellent models. There's no doubt about it, but they're not designed for this purpose. And I would urge EFED to design their own model for their own purpose. Then, you're free of all the constraints of these other models.

And if it's a simple model, it can treat a pond, and it can treat a very gently flowing river. And it can treat the total residue degradation product issue which Dr. Ruhman talked about this morning, but there's no doubt that the...the formation degradation option, the FD version, is the way to go, and with a simple model, it's not all that difficult to include the formation and degradation of degradation products.

I'm going to skip the remark on OECD2. There are some difficult but not insurmountable problems with the concept of an overall system half-life, 'cause in a two-compartment system, you basically have at least two half-lives, one that occurs early on and one that occurs later.

Weaknesses of AGRO. AGRO does not take into account the pesticide mass that is in the food web. It assumes that the water column is not reduced by the transfer of chemicals into the food web. That could be included, but it's a conservative assumption.

We neglect deep or irreversible sorption into organic matter. Often it is found that after a long period of time, chemical sorbed to organic matter is very, very difficult to get out, and it's very non-bioavailable. We ignore the soil type or texture or drain size, mainly because we just didn't have the data to do it, and I think the input of soil solids and the input of water from PRZM will go a large way to alleviate the so-called solubility problem.

AGRO is a fugacity model. Some people don't like fugacity models, but you shouldn't be afraid of fugacity. Fugacity and concentration levels are fully inter-convertible. In fact, the EU's model in Europe which is widely used in the REACH program used to be a model called simple bogs, which was initially a fugacity model, and it was converted into a concentration model and Frank's bio-cumulation model can also be written...and we have done it...as a fugacity version.

In fact, EPA has a model called TRIM.FaTE which was not in the list which actually uses QUASI treatment of sediment and water exchange with a fugacity approach. So, don't get scared of fugacity.

So, I'd like to thank the people who supported our work at the modeling center. You're very welcome to visit our web site for newsletters, and we have all soil models, including models on long-range transport, and thank you for your attention.

**DR. HEERINGA:** Thank you, Dr. Mackay.

I'd like to give the panel an opportunity...I know we want to hear next from Dr. Gobas, but give the panel an opportunity for any questions of clarification or interchange with Dr. Mackay. Yes, Dr. Biddle man?

**DR. BIDDLE MAN:** Don, has AGRO been applied to estuaries, or do you see any special modifications that would be needed to apply it to estuaries?

**DR. MACKAY:** It has not been applied to estuaries, and it would require considerable modification. Estuaries are very tricky often because of salinity wedges and things like that, and it's just not suitable for that purpose.

**DR. HEERINGA:** Dr. Mehta?

**DR. MEHTA:** Yeah, when you talk about including burial would actually reduce the concentration in suspension, you know, if you had a substantially low enough say fine-grain sediment that was very quickly and to the point, you get inert settling, and so, that would mean that you would have to modify your settling velocity function also, because if you didn't do that, then it will, settling in it in that way could actually transport itself out rather than get it buried. So, all I'm saying is that if you include burial it could also involve, more refine some of the other processes.

**DR. MACKAY:** Yeah, you're absolutely correct. One of the tricky points is to define that deposition rate, and for very fine-grain sediments, it can be quite slow, but in EFED's use of EXAMS, there is no outflow at all, so that material just can't get out regardless of how fine it is.

**DR. HEERINGA:** Dr. Maddalena?

**DR. MADDALENA:** So a question, Don, about the...the, about the solubility limit issue that you brought up. I agree we need to, you can't just ignore that. In your conceptual model, do you just create a new compartment essentially at the pure phase, and if so, how do you regulate the...read the solution of that new phase as to solubility? Because it seems like you would just maximize your water solubility over the solid state.

**DR. MACKAY:** What happens is if, for example, you're applying pesticide on spray drift, let's say the solubility in water is 1 microgram per liter. Once you mix the pesticide into the water, you get 2 micrograms per liter. What then happens is the model reduces that 2 to 1, and it moves all of that chemical into another compartment that's called precipitated pesticide. And that sits there, and as reaction and other processes dissipate the chemical from the water column and the concentration drops, that precipitate dissolves and feeds the dissolved compartment and keeps it constant until the precipitate goes away completely.

So it's a kind of temporary storage reservoir for...that is essentially the model that Dr. Ruhman described this morning.

**DR. MADDALENA:** Okay, so I did...maybe I looked down with the chart, but it seems like the water solubility would be flat at that point.

**DR. MACKAY:** It would be, yeah. That...that...on that graph, that was the results we got before we...

**DR. MADDALENA:** Okay.

**DR. MACKAY:** ...put in the solubility.

**DR. MADDALENA:** Okay, so you didn't actually, it stayed until the reservoir is gone, and then it goes back to...

**DR. MACKAY:** Yeah. So, and now what it would do is it would go up, go along at a steady level, and then come down. I should have put that slide in, thanks.

**DR. HEERINGA:** Dr. Simonich?

**DR. SIMONICH:** Don, this question might be better asked of Frank, but let me throw it out. Have you...have you modeled amphibians yet in the food web model?

**DR. MACKAY:** That would be a question to ask Frank.

**DR. HEERINGA:** Hold that one. Dr. Norstrom?

**DR. NORSTROM:** Norstrom. Don, with extremely high log KOW substances that precipitate, do you think they will ever redissolve?

**DR. MACKAY:** That precipitate because you've exceeded the solubility?

**DR. NORSTROM:** Yeah.

**DR. MACKAY:** Yes, I think they will, because...because they're very sparingly soluble, the precipitated particles must be very, very small, and very, very small particles tend to have a large air to volume ratio. So, they dissolve fairly fast. I think so.

**DR. NORSTROM:** You know, I have a lot of concerns about kinetic phenomena for...for high log KOW compounds, because I think we've ignored that, but I'll bring that up maybe later in the panel discussion. But if it's very small, yes, I suppose it would. If it was large, however, they might lay there forever and never dissolve.

**DR. MACKAY:** Yeah, that's right. I don't really know what happens. I suspect a very small precipitate particle of pesticide would probably associate to some extent with the dissolved and particulate organic matter in the water column, and it might well sediment, but I didn't want to include that, because it's a sort of enhanced method of deposition that's a bit suspect.

**DR. HEERINGA:** Dr. Abbott and Dr. Thibodeaux and then...

**DR. ABBOTT:** I support your comments about the need to validate the model. I wonder if you could suggest a data set that could be adequate for validating, say, the redesigned PRZM that included burial and outflow, or would that data set have to be collected?

**DR. MACKAY:** I think, ideally, it has to be collected, but it's not, you know, rocket science to do that. I think there are data out there, and...and at least one or maybe two papers in the white paper that are cited that have data of this type, and because AGRO is flexible...you can usually change the volume, the area and the depth of ponds, and it's...I think it's highly likely that you can find data out there that would...could be used to our data, and, of course, our mesocosm data which are much more tightly controlled which can be bounced against the model.

**DR. HEERINGA:** Dr. Thibodeaux?

**DR. THIBODEAUX:** Don, it was a nice comparison between AGRO and EXAMS and cleared a lot of things up for me. Back to the solubility idea. It seems to me your way of accounting for it through a precipitate is really a mass routing rather than a process model. Is that correct?

**DR. MACKAY:** Yeah, Mm-hmm (indicating affirmatively).

**DR. HEERINGA:** Dr. Doucette?

**DR. MACKAY:** Well, it...it...it is my attempt to get at a process model, and it's...

**SPEAKER:** Good start.

**DR. MACKAY:** Thank you, yeah.

**DR. HEERINGA:** Dr. Doucette and then Dr. Hickie.

**DR. DOUCETTE:** Yeah, I was wondering, you mentioned this model ignores irreversible absorption or combining. Have you played around with the...the scenario within the model if you allowed that process to occur and what...what sort of results there would be? I mean, I realized you're trying to keep it conservative, but conservative is nice but not if it's not realistic all the time.

**DR. MACKAY:** I haven't played around with it, and the basic reason is I'm kind of lazy, because it means putting in all kinds of sorption kinetic, desorption kinetic expressions into the model, I was very reluctant to do. So, it's laziness.

**DR. DOUCETTE:** Could...could you do a simplification where you basically ignored the kinetics and...and just put a...a certain percentage into a...a compartment as a...as a removal mechanism?

**DR. MACKAY:** Yes, you can do that. In fact, it...we've done some work on soils and partitioning from soils to terrestrial invertebrates like worms, and in order to get the model to give the results, we have to put in a fudge factor which is the fraction of the total chemical in the soil which is bioavailable. And it can be something like 20 or 30 percent. And so, that addresses the problem that you raised, but I...I feel uncomfortable about it, because I don't know where to get those 20 or 30 percent.

**DR. HEERINGA:** We have a few more questions. Dr. Hickie and then Dr. Maddalena and then Dr. Delorme.

**DR. HICKIE:** Don, I have several, hopefully, short questions. One is I, earlier I asked about EXAMS and keeping track of carbon budget. Does AGRO do that?

**DR. MACKAY:** It doesn't, and if...if I was to continue to develop AGRO, I would want to, you know, keep track of the chemical, keep track of the water, keep track of the mineral and solids and keep track of the organic matter, because the organic matter is a vehicle for moving the chemical around, and it doesn't do that at the moment, and some years from now, I think that is definitely where to go.

**DR. HICKIE:** I...I'm particularly thinking of a potential issue of biodilution with algal growth and things of that sort.

**DR. MACKAY:** Absolutely.

**DR. HICKIE:** And the other one is AGRO has an input of...of the weather records over years and years. Does...does AGRO do that? I'm sorry. EXAMS has that. Does AGRO?

**DR. MACKAY:** The weather record goes into PRZM.

**DR. HICKIE:** Okay.

**DR. MACKAY:** And PRZM, then, gives you the runoff record. So, AGRO doesn't have the...

**DR. HICKIE:** I have just one last question. Is...these ponds are very shallow, so sediment incidence is very much wind driven, I would imagine?

**DR. MACKAY:** It probably is, and we use the ponds 100 meters across, and it's not a very long fetch, but...

**DR. HICKIE:** I...I'm just wondering about variability in winds and storm events and what effect that might have on the burial process.

**DR. MACKAY:** Yeah. Well, the whole sediment resuspension and deposition process is highly episodic, and it, you know, Willie Lick has been saying this for many years, and I'm sure the same things happens in...in these small ponds, and I...it should be characterized in some way.

**DR. HEERINGA:** Dr. Maddalena and then Dr. Delorme.

**DR. MADDALENA:** One more question on the PRZM. You taught AGRO to talk to PRZM, so I'm wondering if the flow, the invecting moving phase that comes from PRZM into AGRO, do you have any control over the fugacity capacity of that moving phase? I asked this question this morning but in...not in fugacity terms though.

**DR. MACKAY:** Sorry, Randy. The input to AGRO comes from...through the PRZM, and PRZM has got water and soil into your pond.

**DR. MADDALENA:** It does. Do you have control over the fugacity capacity of that water and soil, or is that just a single volt input in the model upstream?

**DR. MACKAY:** AGRO doesn't really care. All it wants to know is what mass of solids goes in, what mass of water goes in, and what mass of chemical goes in, and the fugacity capacity of the solids leaving AGRO, it's kind of taken into account by the adsorbed enhancement factor, whatever you actually get when you open in AGRO...in PRZM, but it...it could be.

**DR. HEERINGA:** Dr. DeLorme?

**DR. DELORME:** Thanks, Don, for enlightening me on fugacity once again. It's been a few years since I talked about it. Anyway, I have a couple of questions.

With respect to your statements on dynamic versus steady state models, although I can appreciate using a dynamic model for...for a farm pond, I think one of the issues that we face as regulators, when we look at the PBT substances, they don't stay where they're put, and when they move around, they are persistent. I mean, in the longer term, I think a steady state model in an area like the Great Lakes or in the Arctic may be appropriate for use in some of our regulatory risk assessments.

**DR. MACKAY:** Well, I...I...I think that a steady state model is...is quite appropriate for a system like the Great Lakes or the Arctic where you don't have intense spikes of input as you have in the vicinity of an agri pond.

**DR. DELORME:** So...but we may need to develop both kinds of...

**DR. MACKAY:** Yes, yes.

**DR. DELORME:** The other question I had is...and I'm not sure...might...might need to talk to...to Ron about it. I wasn't quite sure how EXAMS and how your model handle temperature. Certainly, in the northern states and in Canada, you have a significant part of the season when the water's frozen. That affects dynamics. You also have a...an effect on metabolism...metabolites, metabolic rate of the organisms that are going to degrade these things. So, I'm not quite sure.

You know, the studies we get are lab studies done at 20 degrees, but for a persistent compound, that could result in some changes to the dynamics of that system.

**DR. MACKAY:** AGRO does not include any temperature variation, and it certainly doesn't include any ice cover. It just assumes constant temperature conditions, and the properties it uses are the properties that are in...the user puts in and if the user thinks that these properties change with time then they've got to pretend that these changes.

Temperature is an important consideration. And here it's like in a secondary effect. And I think for evaluative purposes such as EFED is concerned with, maybe you can ignore it, but there certainly are differences from location to location and season to season.

**DR. DELORME:** And the final question I had with respect to your comment about apply regulatory conservatism to the result and not the model processes, as one of the people who...who would be looking at the results, I'm trying to figure out how I would do that. How can I apply conservatism to the results of the modeling rather than in the...in the formulation of the models themselves?

**DR. MACKAY:** Well, what I suggest is you run the model with outflow and with burial and get results, look at them, and the results will tell you how important these processes are, and then you can tweak them. You can reduce burial a little bit and see how that affects outflow. In fact, Arthur did that this morning, and that way, you can obtain a...an impression of the sensitivity of the final result to that process, but if you remove burial right at the beginning, you'll never know whether burial was important or not.

So, we play games with it, tweak it.

**DR. DELORME:** And then that's the answer you want, do the what if analysis.

**DR. MACKAY:** Exactly.

**DR. DELORME:** And see what the sensitivity relies on, and then you can include that in your risk characterization, and it's up to the risk managers then to take that information and make the decision. Okay.

**DR. MACKAY:** Exactly.

**DR. HEERINGA:** Let's have one more question from Dr. Thibodeaux, I believe. You pass? Okay, wanted to give you the opportunity for certain.

At this point, I'd like to thank you very much, Dr. Mackay. Very interesting presentation.

And appending to that is the next presentation by Dr. Frank Gobas who is with the School of Resource and Environmental Management at Simons Frazier University and talking on Application of Environmental Fate and Food Web Bioaccumulation Model for Assessing Ecological Risks of PBT Type Pesticides.

Dr. Gobas, welcome.

**DR. GOBAS:** Thank you very much, and thanks for inviting me to...to come to this...to this meeting. I...I'm sure I speak for Don as well. We...we greatly appreciate the opportunity to...to talk about something we all share, and that's an interest in...in PBT type substances.

And PBT substances are, of course, special. They are different from other chemicals in the sense that they are persistent, of course. They react slowly, perhaps not at all, and they also typically have high KOWs and/or high KOH which gives them high sorption coefficients which ostensibly cause them to sorb strongly to...to particulate matter, and they also have slow elimination rates because of those properties in biota, and as we've already talked about quite a bit, they have, in many cases, high melting points and...and low aqueous solubility.

And these characteristics themselves have profound effects in terms of how these chemicals behave and...and how you...how you should model them. And we've talked about the models, and here they are.

The...we have an existing model that Ron Parker talked about in...in...in detail which links the...the PRZM model to EXAMS, to a steady state food web model that includes the food web, and the model that Don talked about which was the QUASI model here, and that is part of the newer model which links PRZM to QUASI through a time dependent food web model and to...and to...and the...the food web model. And...and that is the model that...that we...we...we talked about.

And, oh, I'm pushing the wrong button. Is there any other button...oh, here we go. Now, the key thing about the slower reaction rates and persistence is that when you start looking at these models is you start to turn off certain rates, right, so Don, this is the...the...the...the sediment reaction rate, persistent...the chemical's persistence. We basically turn that one off. We turn this one off if the chemical is not per...is persistent in the water phase. If you...if the outflow of the chemical is slow or if you turn it off and that becomes no longer an exit route, if the chemical has high...or has a low Henry Law constant, then even that route becomes very small as well.

And then, you really end up in the system, and this will probably see in many of these pond systems, where there's really only one net loss rate that...that...that applies to that system, and that's the burial or the net deposition rate. And QUASI has that ability, of course, but EXAMS does not.

When we...when you start modeling, and when you compare the two models in terms of how they behave in dealing with inputs of...of...of pesticide, you start looking at two different situations. Is the EXAMS model here really, is it inputs of pesticide into the water column? 50 percent is then moved to the active sediment layer which is the sediment layer that interacts with the water phase, that...that connects with the water phase as well as to the biota living in that system?

And here, we've got the buried sediment and there is, of course, no arrow there, whereas in AGRO, you...you...you don't have that extra rate out. And that rate has an important impact, of course, on the...on the concentrations that you would calculate as a result of pesticide input into that pond system.

And this is an example. This is the EFED farm pond. Has constant sediment dynamics. What I'm showing you here is...is...is a 30-year simulation. Annual concentration estimates...these are the concentration sediments. And you can see what the difference in including that burial rate does in terms of the calculations. Right?

Over a 30-year period, you get substantially different estimates of concentrations in...in that system. Is not correspondingly related to the sediment. The water will really show you the same results. Right? Major differences.

Also, when you start to use real PRZM scenarios...and that's here shown for...for the Maine potato scenario...you still get the same kind of results. You see a constant accumulation in the EXAMS model, whereas the AGRO model really provides a lift to that maximum concentration which is totally controlled, really, by that net deposition rate or burial rate.

And this is another example. This is the California cotton scenario. And we can see that...that there are some...there are differences, but in all cases, there remain very big differences in concentration estimates between these two models.

This is the sensitivity analysis. Here, we look at the impact of the degree of burial on sediment concentrations over time, and basically, what I'm showing you here is the EXAMS output with no burial, AGRO with no burial, and you can see that with increasing burial rates, of course, there's a greater net loss of that substance from the system, and as a result, the concentrations really go down and also, tend to reach a maximum at a certain point in time rather than keep continuing to accumulate over time.

Another important aspect of modeling this processes of meta deposition is...is dealing with...oh, sorry. These...this is the sensitivity analysis of the biota. Of course, I've got to talk about biota. That's my job in this life.

This is the impact of...this is the analysis for burial rate on the...on the biological data, so these are now concentrations of Perciforous fish. Perciforous fish is a larger 1 kg fish higher up in the food web, and...and you can see how the concentrations in these fish really vary as a function of time and as a function of the burial rate, and, again, you can basically see that a higher degree of burial will give you lower concentration estimates. Right?

And the fish really respond to the water concentrations and the sediment concentrations, and whatever happens to those concentrations will have an immediate impact on the levels in them, in the food web.

And important aspect of...of dealing with these...modeling these net deposition rates is actually dealing with this active sediment layer. The active sediment layer is used by modelers to describe the amounts of sediment that interact with the water phase.

In many cases, that's hard to define, and it's really hard to state, you know, what depth should one choose in these models, what, you know, to what depth do chemicals still interact with the water phase and interact with the biological systems that live in that system as well.

So, that's a key...key issue in terms of how you...how you find and how you set an active sediment layer. So, what I'm giving you here is basically a sensitivity analysis on...on...on selecting these values.

Typically, what...what happens is that for fresh water systems, these rates or these thicknesses are a little bit smaller than the order, in the area of 5 to 10 cm. In marine systems, because of tidal actions, the active sediment layers are typically much larger in...in these fate models.

The impact of selection of these numbers is shown in here where I basically have shown you the concentrations in the sediment. This is pesticide 3 again, effects farm pond, these are the deposition parameters, 30-year simulation, and now I'm using different thicknesses of that active sediment layer.

And basically, what the active sediment...the thickness of the active sediment layer does, it determines the response time of the chemical concentration in sediment. The thicker the layer, the slower the response time.

And what it doesn't really do is it doesn't really change that maximum level, that steady state level, that if you were to take the simulation longer, that you would have achieved. That's fairly independent of the selection of that thickness.

This is the impact of this...the...the active sediment layer on the biological systems, these are concentrations in fish, and here we can see, again, that the thickness of the sediment layer has...has some effect on the concentration of the biota, but it is relatively small. That...that's good news, that in terms of selecting that parameter, the selection is not that sensitive or the...the concentration estimates that you derive is not that sensitive on the thickness of that layer except for the time response which is quite sensitive to that sediment thickness.

And these are, of course, all model simulations, and model simulations need to be compared with real data to see if we're on the right wavelength, and that's what I've tried to do here. And so here, now, we're...we're trying to see the behavior that's predicted in these models is actually realistic.

And we...we don't...I'll show you some examples later, but the example that I've shown here is...is...is...is an example for...is an example for a really big pond which is Lake Ontario, and where we basically have seen over the past an input of PCBs over the years in that, then followed by sharp declines in the PCB inputs over the years.

And what you tend to see in this...this little box here are really the concentrations in the sediments, and we can see how they have responded over time. They have gone up, and as soon as the loadings actually went down, soil concentrations went down. And the concentrations in these sediments were also...or these decline rates were also mimicked to a certain degree in the biological systems as well. So, concentrations in a number of fish species like rainbow snell, lake trout, and also perch species fell as a response to those declining sediment concentrations.

And I think that the...the point here is that when loadings go down in systems that I think are comparable...we're looking here at PCBs. They are persistent chemicals. Loss rates of...for Lake Ontario for outflow are low, and we...we basically have somewhat comparable situations that shows that when these loadings stop, the concentrations will drop.

I think that's important, because if you would...and the other point I was going to try to make here is after these concentrations drop, you tend to see a rate of concentrations decline, and they tend to follow the rate that you would expect from the net deposition rate of that system which, in this case here for...for Lake Ontario, is about 5.5 years. And in the end, what you're seeing is that when these loadings actually stop, the concentrations will start declining at rates that are comparable to the burial rate.

It's probably one of the best indications that we have that burial rates can control the central dynamics in, in this case, a big system like...like a lake.

And this is, of course, what you would expect from...from EXAMS if you did not have that burial rate and you did not have the loss rate through transformation and you have no loss rate through volatilization. And the only result that you're going to get is...is for something like...like that, and I think in the Lake Ontario example, the point is that we don't really see that.

The other aspect that I would like to spend a little bit of time about is...is about slow excretion rate of PBT substances. The slow elimination rate of chemicals have a very important effect in terms of modeling and controlling the behavior of chemicals in biological organisms.

Slow elimination rate basically means the chemicals reach steady state very, very slowing. So, in many cases, they don't reach steady state. And I think that's important to keep in mind when we're running these models, because the...the model that's often used to...to apply to the biological system is a steady state food web model. And for many of these PBT substances, you don't reach steady state.

For that reason, we...we have replaced that with a TINY TIMS model. And I think that can have a major impact on...in...in terms of what kind of concentrations you're going to see in...in the biological systems.

This is an example. This is pesticide number 3. Has a log KOW of 5. If you tried to put that in...in Perciforous fish, it's about a 1 kg lipid content of 6 percent, it takes about 189 days to get to 95 percent steady state, a half-life time of 44 days. Right?

And you can see that the elimination rate, of course, mimics that. The same kinetics apply to the elimination phase, in this case the elimination phase is largely controlled by gill elimination which is represented by this K2 value which is the largest elimination rate and...and the largest elimination rate constant of all the losses, which is gill elimination, fecal excretion, and roe. You can see for this particular chemical, elimination through the gills is controlling the time dynamics, but the time dynamics are slow, very slow.

When we go to a chemical with a log KOW of 8.1, pesticide 4, that uptake curve is even slower. Right? It takes more than 1000 days to...to get to steady state. Right? And the elimination kinetics which is actually quite interesting is actually no con...no longer controlled by...by this gill elimination which is K2. It's not controlled by fecal excretion either. It's really controlled by...by KG which is the growth rate of the animal. So, the elimination is really controlled by growth.

Now, that...that has important implications when you start exposing organisms to pulses of chemicals in water and...and sediments, and this is an example, pesticide 3. This is an actual scenario, Maine potato scenario. And the output is from PRZM, and what I'm showing you here are concentrations aim water over time, and this is at 168 days. These are four applications, and you can see how the water concentration responds through those four applications of pesticide 3.

Now, if you would run the steady state model to calculate the concentrations in the fish, this is what you would get for...for Perciforous fish. That's the 1 kg fish. You can see, of course, you know, the, the, the pulses in the water concentration are mimicked by similar pulses and in the concentrations in the fish.

However, the fish, of course, cannot respond to those concentrations that fast, and this is more the type of response that you would expect to see, and that's the time response given by...by...by a time dependent model. And you can see the differences are...are significant.

This is an example of now a 30-year simulation. Pesticide 3 again. PRZM linked to AGRO model. These are the concentrations in the water that you would expect to see over that 30-year simulation, and if you run the steady state model, you see the same pulses again, and you get this. If you run the time dependent model simulations, you get that. Right? And this is for a small fish.

If you do this for a bigger fish, these are the steady state concentrations. These are the concentrations of the time dependent model. And I put them on the same scale here so you can easily compare them.

You can see, of course, that there are major differences. And these differences can really make an enormous difference when you do the risk assessment. If this is your cutoff value that you're comparing these concentrations to, you can obviously see you're far below it, and if you run the steady state model, you get to see instances like...like this where you would, of course, exceed those threshold concentrations.

This effect that Don already talked about of this...this temporal effect in the food web where, basically, concentrations are dammed or cannot achieve their steady state values increases when you go up the food web. Basically, when you go from smaller to bigger organisms, this effect becomes greater. Also, when you increase the...the lipid content, this effect becomes bigger.

And also, when you go to higher KOW pesticide, this effect only becomes bigger. So, the effects that I've shown you so far for pesticide 3, has a log KOW of 5. This differences are much, much greater when you go to a chemical with a log KOW of 4.

And so far, again, I've talked about models. It's important to...to make sure that when we start using these models, that these models are reliable, and I think the best way to do that is actually by comparing the models to actual data. In this case, what I'm really concerned about is the temporal dynamics to how do these temporal dynamics that we're using in the...in the AGRO model and in the tem...in the food web model, how do they stack up, are they reliable so that you can make reliable calculations with...with your model.

I'll show you two levels of comparisons here. The one is for a...a comparison with laboratory studies, typical BCF stuff, the BCF test that you may be familiar with where you expose fish to chemical concentration in the water and in the water only, and you follow the concentrations in time in the water and in the organism, and you can use that then to calculate the rate constants, and those rate constants of uptake and elimination are telling you about the temporal response of the model.

So, what I'm going to do here is give you some examples of how these models fare. This is pesticide 3, bluegill sunfish, two exposure scenarios at different concentrations. These are the rate constants that we should look at. The uptake rate constant for pesticide 3, it's 380, 330, and this test more a calculation of about 366.

Elimination rate constant here, 0.04. 0.04, 0.056, and the steady state fairly comparable. Bioconcentration factor is fairly comparable and the steady state fairly comparable. So, it's a good example where...where we see a reasonable performance of the model calculations and in terms of providing us with estimates of rate constants.

This is pesticide 4. Pesticide 4 is interesting. Here, what we've basically done is we have performed the model, and by mimicking, really, the bioconcentration test, basically, we see the model coming up with a rate constant of 385. BCF study is 600.

Now, the total elimination rate constant is interesting, 'cause it's totally controlled by growth in the BCF test. So this is really a growth rate constant, controlled totally by the conditions of the test, and we've taken that number and compared that to the reported value, 0.023, and the BCFs are roughly the same. T95s are quite comparable.

I think when you look at the report, you'll see major differences between how...how the BCF results differ from...from the results of this model. It's largely because of this effect, growth, and we see...let me show you how important it can be.

There's a little lesson there. And these are really the growth data in the bluegill sunfish experiment. These animals were growing quite rapidly, from about 13g at the beginning of the test to about 130g...well, it would have been 130g in about 180 days. This fish would have been about 1.3 kg at the end of a year.

Typically, a fish cannot grow that fast, and these are the growth rates that are typically used in the model which are much smaller, more reflective of growth in the...in the field. And as a result, you get...you get enormous differences between the BCF results...and this is the model outcome for the BCF results...and field conditions. Right?

Here, you see this large amount of growth that totally controls the elimination rates. And growth also controls the elimination rate in the model, but that growth rate is much smaller.

And another lesson in here is really that when you start doing...running these BCF tests for chemicals with low KOWs of that magnitude, 8.1 in this case, you really start to measure the properties of the fish rather than the properties of the chemical, and you have to really watch out for that when you start using those results and using them to predict situations in the field.

This is the...the final part of the simulations. Here, what I'm going to show you is how these time dynamics of this food web, in this case, the food web bio-cumulation model, how it compares to the real data. What I'm doing here is basically taking the...the water concentrations and sediment concentrations in microcosm studies and using them as input to the food web bioaccumulation model to look...to estimate the time dynamics of that model, and then we're going to calculate the concentrations in various biota and then compare them to the observed values to see for any agreement.

These are the...the results. This is for macrophytes. This is what we predict, blue line. This is what is observed. And you may see a difference of where...we're actually really proud of this result. These are...or this is...this is not a logarithmic axis. These concentration differences are actually really small.

So when...and there...there's no fudging in this model. There's no calibration. So, we basically see a reasonable agreement of time dynamics between model and data.

These are crustaceans. I'll flip through them quite quickly so you get a bit of a feel for it. This is sea brown mussels. This is snails, and these are fish. And, in general, what you tend to see for this particular pesticide is a fairly good agreement in terms of time response, and I think that's...that's encouraging.

And I also tried to re...we...we also tried to fit here the...the combined model, so now we're looking at evaluating the time dynamics of the combined AGRO and food web model. Right? By taking the pesticide application, putting in the AGRO model, letting the AGRO model calculate the concentrations in fish and water. The biota picks it up, and then we calculate the concentrations in...in the food web to see how these models behave.

And pesticide 3, and the two models we're running here combined. There are two pesticide applications at 370 intervals, and we're comparing concentrations. And this is for water, and we can see how...how that behaves. And this is it for macrophytes. And we get a similar behavior, basically telling you that the...the AGRO model does a good job in predicting the time dynamics of concentrations in these microcosm studies.

So, we have a few con...conclusions. First, I think that we all agree that the very high persistence of these chemicals and the high sediment absorption coefficients of PBT substances create a strong linkage between the fate of the pesticide and the sediment. Right? And the sensitivity analysis that we...that I've shown you confirms that linkage, and it shows you that concentrations of these PBT type substances in water, sediment, and biota can be expected to be directly related to the magnitude of sediment deposition which is a key part of what controls the fate of the sediment.

Sensitivity analysis also shows that the thickness of the sediment layer affects the temporal response of the chemical concentrations but not so much the long time steady state response of the concentration.

The monitoring data, the little bit that we have, but I think there are some other examples that we can draw from, show that sediment dynamics play a key role in controlling temporal response of concentrations of PCBs in lakes and other persistent chemicals as well.

There are some good examples. Lake Ontario is a good one. Another one is in San Francisco Bay where you really can really see the effect of net sed...of net sediment deposition on the fate of the substance.

Including net deposition, therefore,

seems to be a logical next step to make the...the models, the environmental fate models, more realistic. I think this is especially important for PBT type substances, because they don't have an extra loss through reaction and transformation.

And EXAMS...or it can, as we've learned, include that process, but at the moment, I think in most applications, the sediment dynamics and especially net deposition is not included, and I think that can have major impact on the levels that you're going to calculate.

On the biological side, PBTs have slow excretion rates, require a long time to reach steady state. As a result, they don't really reach steady state quite often, especially in situations where the chemical is applied on an episodic basis, the pesticides.

The application of steady state bio-cumulation models to PBT type substances under conditions of time variable exposure concentrations may, therefore, produce unrealistic concentrations in...in...in...in wildlife.

Also...and this is something that I tried to put in and maybe I'll regret it, but I think we should exercise very great caution when using BCFs for PBT type substances in exposure assessment. I think that in many cases, we can make major errors using these BCF data in the risk assessment.

I've shown you the effect of growth. I haven't shown you the effect of dietary exposure which is a key...key exposure route for PBT type substances. It can further only increase the difference between the BCFs that you see in the test and the real values that are observed in the field, and we're really talking orders of magnitude here. So, we can make big mistakes there.

So, be very cautious or don't do it at all perhaps. Be careful in the use of these BCFs.

Finally, the model results for AGRO, I think, are encouraging. Temporal dynamics of the pesticides in...or pesticide 3, at least, and we also looked at two other pesticides. I don't have the data for you, but they...the model did fairly well in describing the temporal dynamics.

It's a flexible model as well, so it...it can be parameterized to represent varying degrees of net deposition, so if you want to parameterize it for a no net deposition environment, you can.

I don't think...AGRO, I think, will

improve exposure assessment of PBT and non-PBT substances. I think there is still some work that needs to be done in the parameterization of these net deposition rates. I think there is some uncertainty still there, what are the appropriate values to use.

And, finally, a...a...a...something we learned or we learned when we went through this exercise is that when you start doing the modeling, it's often interesting to do it in...in...in a two-step way where you verify and apply, and that's perhaps something I learned out of this exercise. Typically, what we're doing with our models is we parameterize them for the pesticide management scenarios, and we run the exposure analysis.

And this is maybe a...a very useful way as well. When you take that model and parameterize it for the field conditions that you've got data for and you test your model first with the data, you calibrate it, then produce a new model, a calibrated model which is again parameterized for your management scenario to do the exposure analysis.

This will allow you to deal with...with many processes that the model is poorly equipped for dealing with for certain chemicals, perhaps, that it is not truly designed for, or if you're dealing with metabolism and it's poorly characterized, there is a possibility to calibrate these models and then use the calibrated model for the actual management scenario.

I'll leave it there. Thank you for your interest.

**DR. HEERINGA:** Thank you very much, Dr. Gobas. I'm sure there are some questions, and we'll begin with Dr. Simonich.

**DR. SIMONICH:** Thank you, Frank. I have three questions. The first is, are amphibians included in your model?

**DR. GOBAS:** No. That's easy.

**DR. SIMONICH:** Should they be?

**DR. GOBAS:** Yes. This is a good one. No, I...I think you're absolutely right. It...it...I think we still see a lot of risk analysis are done for fish, and we're very good at...at...at...at making estimates for fish, but we often stop at fish, not necessarily, but in some cases, we do, and we should realize that there is much more out there than fish.

And especially for PBT substances, this is important, because for a...for the few examples that we have, we typically see examples of wildlife effects in...in higher trophic levels, not necessarily in fish, but in marine mammals, in birds, and amphibians, perhaps, as well. So, we should definitely broaden our horizons and include more organisms and...in...in our risk assessment methods.

**DR. SIMONICH:** Second question. On a slide on model sensitivity, it shows that EXAMS and AGRO with 0 percent burial deviate from each other after about 25 or 30 years.

**DR. GOBAS:** A little bit, yeah.

**DR. SIMONICH:** What would cause that?

**DR. GOBAS:** Well, these are really minor differences in...in...in how these models run. I don't know the exact answer to your question right now. We would have to look that up in...in more detail.

But these models are...are fairly similar in the way they behave, but there are some minor differences, for example, in the way sorption is calculated, the transfer of mass, for example, from the water phase into the benthic phase. That's set at a value of 0.5. In AGRO, it's calculated, and when we do the calculations, you know, the equivalent value is about 0.89, and that may be one of the factors that can cause these differences.

And...but the differences are minor enough that you can say that the models for the AGRO with no burial will produce...at least in that scenario that I showed...similar results as...as EXAMS.

**DR. SIMONICH:** And my last question, is...do you consider the soil...the half-life of the chemical in soil and how that chemical may be resuspended or released into the environment each year with piling? Because I think currently, we see some of the past PBT pesticides that are now banned, we still see them deposited in ecosystems each year, and, I think, in part, due to the persistence in the soil and the annual piling of soils in volatilization.

**DR. GOBAS:** My understanding is that PRZM takes that to...into account to a certain degree. So, there's runoff from the field into the pond in included, and in that calculation, weather conditions and changes in weather conditions...and...and Ron Parker really explained it well...are taken into account. So, that's really in the PRZM part.

Is that..did I answer your question?

**DR. SIMONICH:** Yes.

**DR. BUCHER:** Dr. Meador?

**DR. MEADOR:** I wasn't clear if bioturbation's part of your model.

**DR. GOBAS:** Well, bioturbation is really part of the resuspension process.

**DR. MEADOR:** So you, in a sense this is obviously more important than others and it will probably keep burial from going deeper, and the variants are really good about ...

**DR. GOBAS:** Yes.

**DR. MEADOR:** ...keeping the soil mix. So not only effluent water but actually it gives you a human variant.

**DR. GOBAS:** Absolutely.

**DR. MEADOR:** So, how do you...what's the parameter? How do you actually quantify that?

**DR. GOBAS:** That's a good point. That's why I had in my conclusions, you know, that still more attention is needed in characterizing what the appropriate resuspension rates are in ponds of this kind.

**DR. MEADOR:** Okay. It's really a physical process.

**DR. GOBAS:** Yes.

**DR. MEADOR:** Okay.

**DR. BUCHER:** Dr. Thibodeaux?

**DR. THIBODEAUX:** This question is directed both at Don and Dr. Gobas. Going back a few years, I have seen models go from what I call a thermodynamic base, and now we seem to be having problems, one of them exemplified by the fact that the solubility is limited. And also, I noticed on your models, there is a definite time shift kinetic-wise between sources and what ends up in the fish.

And you made the point blank statement that bioconcentration factors are getting us nowhere. Do you think the time is right for future emphasis on transport processes in these models?

And, for example, you keep bringing up the idea of particle deposition which...in your transport. It's not an equilibrium process. It's not a reaction process. As we move ahead...and, of course, we hear dynamics from every presenter's lips. We also see time series of concentrations.

So, the only question is, do you see maybe we should put...haven't we...haven't we arrived on partitioning? Do we need to do more on partitioning, or are we at the point of diminishing returns? Shouldn't the kinetics come forth, because it's plain to me at this time that's the things that need to be tended to.

And, by the way, bioturbation is not a deposition process.

**DR. GOBAS:** No, no, the resuspension process...

**DR. THIBODEAUX:** No, it's not that

either. Anyway, question to both you and Don on that point.

**DR. MACKAY:** My answer is yes.

**DR. THIBODEAUX:** The question is partitioning. You know, we've done partitioning. Everybody does partitioning. Very few people do transport kinetics. Is that maybe a blind spot that now needs to be fixed?

**DR. MACKAY:** Yeah, I think you're absolutely right. There is an enormous literature on basic solubility and thermodynamics and bioconcentration and so on, but over relatively short time periods and episodic inputs, it just doesn't apply, and kinetics is a mass transport in the sediment water process and into the fish and from the fish, it's very much kinetically controlled, and it's basically a mass transfer phenomenon and it has to be quantified.

**DR. GOBAS:** One instance, it does not achieve these equilibria in time, so it's the time course to these partition coefficients that is really controlling the...the concentration.

**DR. THIBODEAUX:** Kinetically controlled?

**DR. GOBAS:** Kinetically controlled.

**DR. THIBODEAUX:** And mobility controlled?

**DR. GOBAS:** Well, yes, yeah, and especially for these PBT substances, because they behave so slowly because of their properties. The release rates from organisms in particle is very, very slow which basically means that you do not get to see these equilibria ever being achieved. The environment changes too quickly.

**DR. THIBODEAUX:** I'm not saying that these parameters shouldn't be in the model, at least not at that valid concept except it's outdated now. Not outdated in the sense we don't need it, but the emphasis of research should move away from partitioning onto how fast, because my first law of chemodynamics is the only way you're going to get partitioning in any phase is to diffuse it from its source into that phase so that fusion and transport has to come before partitioning. Do you agree with that?

**DR. GOBAS:** Yeah, I would agree with it.

**DR. THIBODEAUX:** Thank you.

**DR. BUCHER:** Dr. DeLorme first, and then Dr. Norstrom.

**DR. DELORME:** Just a couple of questions, possibly clarifications. I think it...it's good to see this...this work and sort of have my eyes opened a little bit on what's going on out there with temporal courses and...and what not, but as an ecologist, I always wonder where do you bring in the ecological reality.

I think of something like a forage fish which may have a life span of two to three years maximum. You've got a...in some systems, you're going to have a lot of your chemical tied up in the biota, and that's going to cycle back and forth into the sediments and through the microbial populations, et cetera, et cetera.

I mean, the reality is the stuff just doesn't disappear if it's persistent. I mean, it's being slowly degraded. So, I mean, is there room for moving some of these things into the model at some future date?

**DR. BUCHER:** Before you answer that, could everyone speak into the microphones so that everyone in the room could hear, please?

**DR. GOBAS:** I don't exactly understand the question.

**DR. DELORME:** Well, okay, if you take a look at your...one of your slides, you looked at the...the bioconcen...or food web bio-cumulation model, and you've got, you know, it looks like for forage fish. Okay? Reality is, I mean, you're...you're stating a steady state isn't reached for hundreds of days in some cases.

**DR. GOBAS:** Right.

**DR. DELORME:** It might exceed the life span of some of these organisms.

**DR. GOBAS:** That's right. Yeah, that's correct.

**DR. DELORME:** And so, I mean...I mean, it's another consideration. You know, the biological component or compartment where the chemicals end up, I think, is an important component in the model to consider the dynamics of exchange not only to the sediment and the water but also between the biota and the sediment, et cetera, et cetera.

**DR. GOBAS:** Yeah, I fully agree. That...that's why we developed the time dependent food web model, yeah.

**DR. DELORME:** The other...the other point I have has to do with the amphibians. I think if we're going to look at amphibians, we have to look a redefining what our receiving water body is, because I don't think a 2 meter, 1 hector pond is, you know, appropriate. You have to bring in some ecological relevance there. Just as an aside.

**DR. BUCHER:** Dr. Norstrom?

**DR. NORSTROM:** Thanks so much for bringing this whole business of...of equilibrium partitioning and dynamics in. I've felt for a long time that it's extremely important to these processes. We're living in an era where everything that was happening with chemicals was fast compared with everything else, so we could get away with it, but in this particular case, we can't. So, for some of these chemicals, I think we have to be dealing with dynamic systems..

One of the things...

**DR. BUCHER:** Speak into the microphone, please.

**DR. NORSTROM:** All right. Well, as close as I can get to it without sort of swallowing it.

I presume that the reason for this rather short depuration half-life in the white paper on page 139 for chemical 4 is due to growth dilution. I had a question on that. I wondered how something with a KOW that high could be depurated into the half-life of 30 days, but that's the bluegill sunfish.

**DR. GOBAS:** Yes. It's growth dilution.

**DR. NORSTROM:** The...the other comment I'd like to make is that I don't know...I used to be a physical chemist in the dim distant past. Actually, it wasn't a Ph.D. then, but if I remember correctly, equilibrium constants like log KOW are actually ratios of rate constants, strictly speaking. They're not just ratios of concentrations at equilibrium.

And so, a partitioning constants in that sense can theoretically be dynamic, and we could have situations where two chemicals with the same log KOW would actually have very different rates of transfer between the two media. If the solubilities were different in the two, you could have different rates of transfer. Is that correct? I...I'm...sort of in my simplistic view of things, that's the way I would look at it.

**DR. GOBAS:** I...I think you can look at it both ways. At equilibrium, the weight of the flux in and the flux out become equal, and this was a cause and effect. I tend to look at it from a thermodynamic point of view. The equilibrium corresponds to equal chemical potential or equal fugacity in the two phases, but at the same time, the fluxes are equal.

So, it's just, I think, a different way of saying the same thing.

**DR. BUCHER:** Dr. Hickie?

**DR. HICKIE:** A couple of questions. One is does your dynamic food web model still use equilibrium partitioning into plankton?

**DR. GOBAS:** The...no, it's not.

**DR. HICKIE:** Okay. Second question, then, is in this model, you have one grouping of 1kg fish.

**DR. GOBAS:** Mm-hmm (indicating affirmatively).

**DR. HICKIE:** And you're running it for 30 years. Is it the same 1kg fish, or are you...are you reintroducing a new fish that has acquired some burden of contaminant before it joins the 1kg fish study?

**DR. GOBAS:** That's a...that's a good point. In this simulation, the answer is no. So, this was the same fish. You can do it and create new generations of fish.

**DR. HICKIE:** You're actually getting population turnover and...

**DR. GOBAS:** Yes. That was not done in this example, but you can, and we have done that.

**DR. HICKIE:** Okay. Third thing just comes back to sediments. You gave your example of the decline of PCBs in Lake Ontario suggesting back when you wrote that paper that the half-life was 5.5 years, and, really, since about 1985, that has stalled, it is virtually no change, so I'd just like to hear your comment on how sediment burial has come into play in explaining that.

**DR. GOBAS:** Well, the...I think the answer is that the...the loadings have not kept going down. So at a certain point, the loadings have put a lid on that going down of the concentration, and so, the example I've shown you is not ideal, but, of course, many...in most...most cases, the environment is not ideal to demonstrate some of these more theoretical points.

And all the data that...that...that...that were included in that study indicate that if the loadings would have continued to drop, that's the rate of decline in concentration that would have been expected. Initial decline was actually seen, but it didn't last long enough because of the loadings. The loadings didn't go down anymore.

**DR. NORSTROM:** In that then can you separate out the change in loadings from the rate of burial?

**DR. GOBAS:** Yes, yes, you can. In the model, you can, but the point of the example was to demonstrate that when...that when loadings stop, concentrations don't just stay the same forever. It's not a continuous accumulation. The system actually has ways of...of...of eliminating chemicals even when they are persistent ones, and the key one that was identified in that study and also in the study that Don did earlier on...on...on the same topic was that sediment burial is the key loss route for PCBs in that system.

**DR. NORSTROM:** Thank you.

**DR. BUCHER:** Dr. Maddalena?

**DR. MADDALENA:** Frank, thank you for...really, a lot of kudos for saying here's the model and in this last slide, here's how you use it. I...I appreciate that.

I wondered if you could elaborate just a little bit on what you mean by calibration. Specifically, I'm interested in is there a formal process that you like to use for your food web model, and if so, were the results that we saw that looked so nice, were they calibrated previously, or were they raw inputs and here's your output?

**DR. GOBAS:** No, what I've shown you is not calibrated. So, these are just...just the raw calculations, but in terms of getting to bio-cumulation issues, there's...the issue of metabolism is a really important one. Organisms in...in...in many cases, have the ability to metabolize chemicals. These rates can vary tremendously between the organisms or at various times of the year and under various conditions.

It's...it's not possible at this point, although we're making some progress lately, especially Joan Arnett who worked on this issue or wrote a thesis on this, but we're still not there in terms of calculating metabolic transformation rates of...of chemical in...in biota.

And that may be an issue for pesticides that are metabolized, since we do not have that capability to estimate what these metabolic rates are. The calibration step provides you with a way to take metabolism into account.

**DR. BUCHER:** Are there any other questions at this point?

(No response.)

**DR. BUCHER:** Okay, thank you very much for those presentations.

I think we'll move on now to the last presentation before the break. It's Dr. Robert Ambrose, Ecosystems Research Division, National Exposure Research Laboratory at ORD of EPA, on Sediment Transport Processes in Pesticide Models.

**DR. AMBROSE:** First, I want to say it's good to follow these previous two talents, I've followed the careers of Dr. Mackay and Gobas to some degree and hold them in high regard, and I particularly do want to say up front a couple of things. One, how you set up and use the model, I think, is more important than which model you choose or which processes happen to be explicitly represented in the models, because we often implicitly set up and use a model in...in the right way. If we have good process, we can still get a good result from a model that is less explicitly process based.

I, too, have a couple of other models for consideration, but I did want to say that latter point.

And another prefatory comment from the start is, no, Dr. Thibodeaux, these models do not have bioturbation, either, but they are representatives of that process in the same deficient way. We should be better on that in the future.

I should also...I'm sorry. I have to go back. I won't go back, but just to say that Dr. Earl Hater is the co-author of mine. He's the real expert in sediment transport processes.

I'm going to be talking to some degree about sediment transport processes and their applications in models, and yet, most of these processes are flowing through some stream systems, and the focus here is really on ponds, so I'm going to talk about ponds as well. I'll go through the process part of it maybe too fast in order to get through on time.

This is the conceptual diagram, and the main point I want to make here is that the chemical concentration is what we're after in this fate model. It's informed by, its course by the sediment processes, so I'm going to focus on the sediment processes, but you have to keep in mind that they're not an end in themselves here, at least, but a means to get better chemical concentration.

Soils dynamics, I do believe, is important, and that's been well covered in previous talks, so this lists different ways in which I believe soils dynamics are important, and we end up in the bottom and buried below the bioturbation depth. I want to say it potentially sequesters chemical from biota. I think it's an important loss process, but still a comment, I think, that originally came from Larry Burns, it might be unwise to assume that buried chemicals stay buried forever, and that's a regulatory type of decision. In any case I, myself, do like to include burial and other processes explicitly.

Now, given that they are important, there are some technical issue that we have to address when we're applying sediment transport models. To some degree, there are similar technical issues with any kind of modeling.

Spatial heterogeneity has to be recognized, and these real environments which we represent as a simple two-layer pond, are really a combination, or a simple stream. They're never really simple when you get down to the details. When you focus in, they're infinitely complex.

There's always spatial heterogeneity that we do not take into account in the models. Can't get away from it.

There's temporal variability as well, and at some point, the process-based model that you have will not represent branding in motion, for instance. There's no need to, of course, but at some point, the models break down temporally as well as spatially.

We also have to recognize in the sediment realm, there's a virtual continuum in the sediment out there. It's not just one type or two or three. The models will inevitably have two or three or maybe ten, but they don't have everything, and it goes all the way from gravel down to dissolved organic matter or colloids, et cetera.

Finally, we have to recognize the availability of input data. We're always limited by that. No matter how good a job you do calibrating the model, getting test data sets, when you apply it somewhere else, you won't have all the force in functions. Even something like rainfall, you might have good daily rainfall that might be 20 miles away, and it's not going to be the same rainfall as your site.

So, you have to recognize these, so given these issues which will always be there, and given that we want to do a better job representing reality, what, Dr. Einstein, should we do? What is the goal of building the models?

And I...this has been sort of a...a guiding philosophy. I think a lot of people do share it, make things as simple as possible, but not any simpler. Which of course, begs the question of what is simple as possible.

So, how complex should the model be that we're trying to build up? I have several points to make here, and I'll try to make them reasonably fast. We can discuss it later.

First of all, it's obvious that some

environmental systems are more complex than others. An estuary is a lot more complex than a farm pond. Small streams can be quite complex, so it's not just the size of the water body that makes it complex.

Some pollutants are much more complex than others. Salinity or a monoamine dye tracer is not the same thing as, say, mercury.

Finally, management questions. Some management questions that are asked are relatively simple to answer and can be answered with conservative assumptions, the screening kind of models. What is a safe screening model, say. But other management questions are very difficult. Some management questions evolve. Well, how long is it going to take to clear out that estuary? What is a safe level to clean up this site to, given the possible flooding that might happen.

Keep in mind that when you design the model, you might be asked one question and design a perfectly good model for that question, but there's always mission creep. Managers will then say well, okay, that's good, what if...and so, it might be good to have a model a little bit more complex and capable than the question right at hand and anticipate the next one, like what was asked earlier about, in a sense, buffer strips, what happens if runoff from the field goes over another portion of land, what happens there. So, you do have to recognize that.

Now, if your model is too simple, there are some consequences, and I think we all recognize them. If you miss key processes...and let's just take burial as a...as a potentially key process for some chemicals...you might not be...you might not extrapolate correctly to the future. You might...your model might be wrong.

You might not actually be able to address even relevant management questions. If you have a steady state model, you cannot use that directly to answer questions about how long will it take to clean up.

It might be a perfectly good model, but it might not be defensible in an adversarial review, and we've all seen adversarial reviews where models are attacked unfairly. Sometimes, it's fair, sometimes unfair, but just sometimes it's better just to go ahead and say okay, I don't think it's important, but we'll put it in anyway.

Now, there are some consequences to overly complex models, however. It can add unnecessary data collection, computational burdens, and you'll see a little bit of that later in my talk.

Some people say it adds to uncertainty. I don't necessarily buy that. I'm not sure, philosophically, how more knowledge can lead to less knowledge, but some people that have studied this that are smarter than me in statistics assert that.

But I think the other thing is it shifts the focus away from the problem at hand into something that might be endless analysis. Coming from the Office of Research and Development, endless analysis sounds fine to me, but the regulatory agency, you need to keep your eyes on what is the question at hand. So, I have seen cases where too complex a model gets you sidetracked.

Okay, let's launch into some of the transport processes. This is a cartoon slide, and we have...it has...does not have a picture on here of internal biotic production of organic matter. I will say right at the start that one of the models I'll be talking about, the ERB model, was...does do internal biotic production and keeps track of the organic matter as a separate state variable.

And we generally divide the world into cohesive and non-cohesive solids. We have the settling and deposition processes for both erosion, scour or entrainment, bed load, and down in the sediment bed, we'll have consolidation and burial.

So, I'm going to go through some process equations that will cover some of the...most of these processes, and first of all, just to recognize in a flowing system, we have velocity profiles and the sheer stress profile, and the sheer stress at the bottom tends to be a property of that system that drives the...the exchange of the solids and the chemicals associated with the solids between the bed and the water column. So, the tail's a B.

So, calculating the different kinds of stress, the sheer stress that you can calculate the grain-related bottom sheer stress or skin friction factor is, I am told, from my esteemed co-author, is the proper one, and this is the formula given, the key here is that bottom sheer stress is a function of velocity squared, and it's an inverse function of the log of the...of the depth. That's another parameterization in there.

Now, settling. Non-cohesive settling is a function of the particle diameter and the density of the particle along with viscosity of the water. There are different expressions. Stokes is...is something that's been around for a long time. Notice that it's a...a function of the particle diameter squared and the density of the particle minus the density of the water.

A more complex expression than Ryn...and I'm not sure if I'm pronouncing his name right, so somebody could correct me right here...Ryan...Ryn, okay, thank you. I wasn't sure about that. I had three different pronunciations.

The...this breaks down the settling velocity into three regimes. The top regime is the same thing as the Stokes comes out, and once you do the math here, it's the same thing as the Stokes velocity.

And the bottom regime...and the Stokes is again a function of diameter squared and...and rows of this. The bottom is a function of diameter to the...the square of the...the square root of the diameter and the...and the density, and there's a transition zone.

So, you can see you can get it more complex and probably more realistic.

Now, that's settling. What's deposition? If you have spill water, they should be the same, but there's a probability of a particle sticking, and if you...if the water moves, that probability goes down, and if the water moves fast enough, the particle won't stay on the bottom.

So, there's a parameterization of this alpha term, probability of deposition, which is more...goes from 1 to 0 as sheer stress goes from 0 to a critical value. That critical value can vary quite a bit.

By the way, when you have a pond that...that has no outlet, it doesn't matter what the resuspension velocity is. The burial rate is equal to the mass coming in. Resuspension just makes the water column concentration of solids higher, but burial rate still stays the same at equilibrium.

Going into non-cohesive entrainment, there's velocity, WT bar. There's entrainment which is mass flux based, and these are based on particle diameter and density along with the bottom sheer stress and the critical sheer stress.

There are different formulas, many different ones out there. Van Ryn's expression here is, I believe, used in the model that Oldhager is working with, and you can see that it's a function of the particle diameter and the sheer stress over the critical sheer stress or critical sheer stress minus...the sheer stress minus the critical over the critical to the 1.5 power. Again, times a shields number. So, this will vary with particle size.

There are more complex formulations. There's one from C.N. Parker. I don't follow that literature well. I just know that they do collect data. They do spend their lives on this. It represents the processes but still needs to be parameterized, and I'm going to get back to that at the end.

But for cohesive sediment resuspension, this is a Lick formulation here. Functionally, looks same as the Van Ryn. It's a multiplier times...times sheer stress minus the critical value to a power. It's just the multiplier and the power will be different, and you'll notice that this is not by particle size, but it's for the cohesive hit.

There's a wide range of values that represent the different cohesiveness of the different types of soils or sediments, and they have to be determined experimentally and/or with model calibration. I understand that there are experimental apparatus, the set plumes that can be used to get these model parameters and constrain the model or constrain this part of the model, this equation, better.

There's bed load transport, and I'm not...well, some models have it. The good models, good sediment transport models so.

And, finally, I want to mention burial. Generally, our models will do this by mass balance, so the excess mass goes into a settling velocity or settling mass flux.

Given those sediment transport processes...and those aren't all, but that's...I'm trying to...trying to stay somewhat within my time...there are other things that are not covered usually in our models, because of their complexity. Stream bank erosion is one, though people are working on it.

Watershed erosion and delivery by particle size has been mentioned before. Generally, the watershed models give us total erosion and would parameterize that total erosion with particle size fractions from the parent soil, perhaps modified by some enrichment ratio. Nevertheless, they don't treat this erosion and delivery explicitly by particle size.

Flocculation in fine-grain sediments, there are ways to do that implicitly. I understand that explicit formulations are somewhat lacking.

Bed load armory, I understand they're implemented in...I'm not sure if it's just like Van Ryn's or, Willie, whether I can pronounce your...SEDS? SEDSLESAY...just go ahead and...okay...which has several particle sizes which are needed to do the armory.

And, finally, no model will handle fine-scale heterogeneity and temporal dynamics if you get fine enough.

Now, I want to move toward the models and example output. EXAMS is on the simple end. The EFDC model was a SEDS CLJ process based algorithms on the other end of the spectrum, and then WASP, the one I know personally the best and work with end up with...at the intermediate algorithms.

Now, EXAMS scientific modules, it does do flow continuity, although in the farm pond example here, it...it, you know, that was bypassed as just water dumped into the pond, but it..it will do flow continuity and do variable flow as well. Constant geometry, however, so it won't do small streams very well, but I think it will do ponds just fine.

Solids balance is not simulated explicitly. You input the total suspended solids in the water column and the benthic solids, and that's used descriptively. It does do organic chemical fate in a detailed way.

You've seen this before, this picture before, and there are a couple notes I wanted to make on it. I've been taking notes during the earlier talks.

The lumped mass transfer coefficient which takes into account the poor water diffusion settling and resuspension...don't worry about that...it's not just poor water diffusion of dissolved chemical. Larry did this in such a way that it actually turns over the solids as well and takes into account the water column solids, the benthic solids, and their partition coefficient in the water and the sediment.

So, if you have a high partitioning chemical, it's not going to overlook the mixing process for it. You know, this poor water diffusion won't do much for high partitioning chemicals, EXAMS will. So, it does cover sort of a solid turnover implicitly.

What it doesn't do here is this is a symmetrical process. The solids going down is equal to the solids going up which is okay. That, I think, handles bioturbation turnover reasonably well, but what it doesn't handle is you can have excess solids that leads to burial. This is just turning it over, and if you add a decay term on the bottom, that will kind of vary it, but you didn't have the excess solids feeding it, so it's not quite the right thing. So, it doesn't have an asymmetrical exchange there of the solids.

But you can put a constant first order rate in, and it will do something. Again, the way you use the model, how you parameterize it, is more important than the model. You can probably parameterize this to handle solids if you take a more complex model and sort of match these models up. Okay, enough of that.

Environmental fluids dynamic code, EFDC is on the high end of complexity for hydrodynamics. It's typically applied to estuaries, three dimensional. It's got various versions out there. It's got a little bit of a version control problem.

Our hydrodynamics link was lost, and we use that down in Region IV a lot for the estuaries. It's a very personal, very complex, and capable model. Does the salinity, temperature, hydrodynamics, and Earl Hater's been working with it to add the solids balances.

So, it's got directly coupled sediment and contaminant transport, wetting and drying of flood plains and mud flats, tidal marshes, near-field mixing in it, hydraulic control structures, et cetera.

A model like this desperate needs good software to help you run it. It's very difficult to run. It takes a lot.

The work on grid generating...grid generation code, there's one almost available. It's almost impossible to do it right by hand.

A sediment transport process is in it, are virtually the ones that I covered earlier. It does not, as far as I know, include internal production.

It's applied here to a Superfund site, Pucitonic River. There are two different modeling regimes, the upper and the lower. It's gotten in as a Superfund site with PCBs. A couple notes here I want to make sure I cover. Earl Hater is doing the bottom portion of it, about 30 to 35 km at a stretch. 4800 computational cells that includes the flood plain, water sediment in flood plain, 5-year simulation. I show one year from it. Takes three days to run on the computer.

So, we're talking about very high end. You're not going to keep running this over and over with different scenarios. You know, you turn it on and take a long weekend or something.

It's embedded in, like a lot of models, in...in...it's like the other models, HSPF feeds the sediment to EFDC here, and there is a, I think, QEA. I can't even read it. It says...there's a bio-cumulation model as well.

HSPF modeling domain, you can see the sub-watershed, and this would be typical of setup for SWAT and HSPF, but I won't go into how you set those up.

And, finally, some example output. There are five years of example output with PCB data below this Superfund site. These are log scaled, so you can see the extreme variability in the stream system covering flood plains as well as the seventh.

So, that's a very high end of what you might do in a flowing system.

I want to spend the rest of the time on the intermediate end. WASP seven is a very general set of water quality modules. It will do internal stream transport using kinematic wave routing, so it will have variable flow velocity, depth, width. It also will have outflow arrear equations, so if you have ponded reaches, it can do outflow over sills and weirs.

Or it can be linked with external hydro models so you can apply it at estuaries such as the FDC. It does solid balance silt, sand, and particulate organic matter in the water column and sediments, and it's got some different water quality modules that are independent but now, as of this year in a project I've done, linked together if you want them to be, or you can run them independently.

The Heat Mounts module is taken from C4OW2, and so, James Martin put that together in MOS. It takes solar radiation, MET data, wind speed, et cetera. Predicts water temperature along with pathogens and other things.

The water quality module, we have an advanced mutual module that's similar to many other advanced mutual modules around nutrient cycling, three species of phytoplankton, benthic algae, the organic matter fraction, dissolved oxygen and carbon.

This can be run independently, or you can run the...or it can take the output temperature, et cetera, from the heat model. Likewise, it produces an intermediate file that includes temperature and then the biotic substances, the production rates, et cetera, that feed forward to the mercury and organic chemical models.

So, you can run organic chemical models as a simple model, a simple pine models with input, or you can run them linked with very detailed variable biotic.

Okay, the same geometry with a kinematic wave routing is based on hydraulic coefficient, so you can, depending on what coefficients you set, you can have U-shaped stream reaches or V-shaped stream reaches.

The sediment transport processes, you know, the same general ones but they're not as detailed process based at this point. In the past, ROSS would allow the user to specify deposition and resuspension velocities. We now have internally in a test version in our own internal projects, both based on stream velocity to power, and we're not even going to publish that, because we're going to go ahead and put in the standard shift stress formulations. The results you see here are based on velocity to power...velocity minus critical velocity to a power.

The solids kinetics in ROSS, we have biotic solids and inorganic fines linked together in sands, and you can input the production rates, have them vary in time, and with temperature and dissolution rates.

Okay, gonna show a few pond simulations. First one is chemical only. It's EXAMS like, it's not exactly the same as EXAMS, because the sediment-water exchange is a little bit different. The sediment chemical version is the standard ROSS type of simulation. We're going to do this with steady loads and then unsteady loads.

So, basically, I'm trying to isolate the effect of burial on the pond on this.

It's a standard pond that I set up hopefully close to the EFED pond, 2 meter, 1 hector, and for the steady case here, just steady silt and...and PON and sand input as well as water input. You have to make an evaporation rate to match the input in order so there wouldn't be outflow, because ROSS will predict a variable water column and outflow.

Internal production, I just did a, at least at first for this a constant. Our production rate constant and dissolution rate in the upper sediment layer. We have two sediment layers defined here, 2 cm and 3 cm so the total is a...is a 5 cm layer. Deposition and resuspension in this...at this point are constant, but they vary in the next simulation. And then, the three chemicals I just picked.

I tried to get a span of partition coefficients from low to high and biodegradation rates in the upper sediment from low to high, because the active burial will be different for the high partitioning chemicals. It will be more important for those than it will be for the lower partitioning, higher decay chemicals. And the note, those chemicals are not the same as the OPP chemical 1,2, 3. These are just chosen here for purposes of this talk.

And there are some results. Water column...since I have steady input, no outflow, the concentration of chemical in this 20-year sim...solid in the 20-year simulation is constant. The sediment bed on the bottom left...and once we have constant density, it does a mass balance, and if there's more mass than...more mass coming in, the upper sediment layer will rise or fall, and then, at a sediment time step, we'll bury chemical out.

So, you can...you can see that...that the comp...the composition, sand, silt, organic matter in the sediment bed will change over time if you have done it in simulation, and burial velocity on the right-hand side is...is calculated here, 0.4 cm/year. In the steady input, that will match the solids coming in, solids plus the internal production rate.

Now, on the left is a chemical only simulation. On the right is the sediment chemical simulation. There's not a...you know, with something this small, mainly the thing that I want to call your attention to, chemical 1 is the...the low partitioning chemical. The difference between the left and the right which is due to burial is about 6 percent for chemical 1, and 26 percent for chemical 2.

Chemical 3, the higher partitioning chemical, it's greater than 33 percent. Likely to be 50 to 100 percent, but 20 years is not a long enough simulation to get any kind of steady state when there is no burial. When there is burial on the right-hand side, you see that it got to steady state.

I think these kind of match the simulations, in a sense, you saw earlier with the other models, and it would be good to check these models against each other. Usually, you learn something.

Finally, an unsteady simulation, I took run-off and erosion from the Suratt model which is applied to Middle Swamp in North Carolina, and I just adjusted that and put it into this farm pond simulation. 6-year meteorological record, and on that simulation with ROSS, I also had simulated variable production, and I put that into this as well, so it's internally biotic production.

The chemical concentrations were just set to 1  g/L in the runoff water, and as you can see, like you've seen in many earlier simulations, you get spikes for the runoff events. Here, you'll see on the bottom right spikes in the burial rate now as well.

And on the bottom left, you can see the composition of the upper sediment layer varying slightly, buffered.

And this is the chemical concentration. Water column on the upper right. So, again, you can see variability there.

How important is that variability? I think it's probably good to simulate it and then take the average rather than do a steady state simulation. And, in fact, OPP does that in simulation. They just don't do it with the solids, but they do it with the chemicals. Perhaps we'll find a way to do it with the solids.

I've got some Middle Swamp applications for stream system that shows the 12 digit HUC, and it's got 12 reaches in it. This is output, typical kind of output you'll get at the mouth. This is the lake modeling system with temperature, biotic production, and solids. Temperature on the bottom right. You can see the seasonal variations.

The...the depth and width and velocity are varying dramatically. And the bottom right shows some burial rates coming from this excess. I think it's not calibrated properly yet, so it's not a final result, but we have a lot of excess solids coming in this agricultural area. I don't really believe those production rates, but those are the burial rates, so this is the type of output you'll get in a stream system as opposed to a pond system.

And rushing on to the conclusions, 'cause we either have a late break or miss the break, one of the two.

Process based equations are available to represent sediment transport in diverse water bodies, and I think that they capture the trends that you want to capture. And I think simulations, particularly in streams, can be improved by incorporating those, and we're going to be...we are doing that in ROSS now.

But they also rely on site-specific parameterization. We have to pay attention to how we're going to do that if we use them.

The simulations will always be limited by...by the data that we have to drive them, and I do think that case study tests are going to be important between the models and with real data to properly parameterize and properly use whichever suite of models is chosen here.

So, I think that's the main...most of the points I wanted to make, and it's faster than I usually talk, so I'm going to take a breath here and turn it back to the moderator.

**DR. BUCHER:** Thank you very much, Dr. Ambrose.

I think what we'd like to do is give everybody a chance to take...catch their breath, and we'll take about a 15-minute break now and come back and address questions to you, if you wouldn't mind coming back at that time. And we'll see where we are in the afternoon then and adjust accordingly.

So, come back at about, oh, five after.

**(WHEREUPON**, a brief recess was taken.)

**DR. BUCHER:** Okay, I think we can begin. Take your seats, please.

**DR. AMBROSE:** Before the questions, I did want to mention that in ROSS, we do...in the heat model, we do ice cover, and that does affect, it feeds forward and it does affect gradation and volatization. There was a question earlier about that in another model.

**DR. BUCHER:** Okay. I've been asked again to remind folks to get close to the microphones and speak loudly.

We can now take questions on the last presentation. Yes, Dr. Mehta?

**DR. MEHTA:** You know, the last two presentations, both of those emphasized resuspension and deposition. You know, many lakes in Florida, they are like 2 meters deep, and the waves are one second or less because of the short phase, and so the waves don't reach 2 meters depth...okay...typically, unless you have a storm, and then you have the sub-micron size particles. What happens is that you get this, you get two layers, basically. You get a lower layer of sub-micron particles with high density, and then you got an upper layer which is basically a water.

Basically, what happens is that due to wave action and the boundary layer that it creates, even though you have no exchange within the bed and the water column, you do have mixing of the two waters, the lower particle-concentrated water and the upper one. And so, it...it's like a classical mixing process between two fluids.

And so, in...in...in...in fact, in many of those lakes, that's the primary process and not classical erosion and deposition except when you have strong winds and hurricanes and so on. So, it looks like that mechanism could be simulated as well to determine how the nutrients or contaminants exchange between the top of the water column and the bottom of the water column.

The other comment I had was regarding

the effect of temperature. You know, the effect of temperature on erosion is substantial, and, in fact, what happens is that when you bring the temperature down, the erosion rate decreases quite a bit. A lot of these models actually are not applicable to the situation that you describe, because without the temperature effect, you will be grossly over-predicting the rates of erosion and also the second thing is because of viscosity of the fluid exchanges, especially the viscosity's high use of these sub-micron particles.

So, there are a lot of these processes that...you know, you made a statement that process based equations are really, like to say that they are available, but they do not capture a lot of the phenomena that you see both due to effect of temperature and due to sub-micron particles and the effects of waves.

**DR. AMBROSE:** I was looking real quick, the effect of temperature on viscosity is certainly in some of these equations, but there might be other temperature effects that are not captured.

As to the...the other point you made, I think that goes into a general point about how you set up a model is more important. You know, certainly WASP and I'm sure EXAMS, and I'm sure that the...these other models could be set up with a bottom boundary layer but settling down to, at some exchange between the two fluid layers.

If...if...if that can be characterized well enough, I'm sure the models are robust enough to capture that in some way, and it may be that we ought to set up a pond with two water column layers. That might be a recommendation.

**DR. BUCHER:** Are there other questions?

(No response.)

**DR. BUCHER:** Thank you very much, then, Dr. Ambrose.

Next we'll move on and hear from Dr. Parker again concerning Conclusions On Simulating Sediment Dynamics for Pesticide Aquatic Ecological Exposure Assessments.

**DR. PARKER:** Well, thank you again, and hello again. I'm going to provide a few very brief summary comments, and...and then add a few considerations which I hope may just assist in...in your deliberations and questions over the next few days.

Dr. Ambrose has showed us that in modeling sediment dynamics, we can be about as complex as we wish and still not approach the ultimate complexity of nature which is...is far, far beyond what we will ever be able to...to model. Dr. Einstein in...in Bob Ambrose's slides reminds us to make things as simple as possible but not any simpler, and we, in EFED, ask ourselves what does that admonition mean for us, and...and I'm sure you'll be asking yourselves that question.

In the EFED modeling presentations, we've seen a summary of...of current EFED methods and...of aquatic exposure modeling and at least a brief rationale for...for their use and why they're useful for us. And Dr. Mackay and Dr. Gobas' presentations, we have seen how other scientists have looked at these same issues and...and come up with some similarities and...and some differences.

I thought it was very interesting in looking at the quotes, Dr. Ambrose's quote from Dr. Einstein, that young Hans Einstein would take up, based on that quote, would take up such a...a complex issue to...on which to base his career, and I'm sure there are other people in this room who have marveled on the complexity of the issues that they work with every day.

EFED faces a unique set of considerations that are, I think, different from all of the other EPA programs. I guess we all think we're unique, but we really are unique. EFED performs exposure assessments for national risk assessments and, occasionally, for more limited areas.

And each of our simulated sites represents exposure not only for that single modeled location but also for hundreds or thousands of additional sites. So, we're looking for our...our representations are...are much wider than just looking at a specific...looking at a specific site.

Our current risk assessment methods require a single concentration duration value for each exposure assessment endpoint, as we were pointing out this morning, for each crop on the pesticide label. Many times, we have 400 crops on a pesticide label, so that becomes a...a major consideration, and each of those crops has a unique growing area that is a function not only of soil and climate but also of the...of the market for the product or processing facilities which may or may not be...may or may not be available.

EFED's single farm pond is static by design in order to provide an appropriate conservative surrogate for other surface water, and in looking at that other surface water, certainly much of that is...is flowing surface water in which case the sediment dynamics are entirely different, and burial may happen on a temporary basis but very rarely on a permanent basis. It may be buried by one medium-sized storm that comes by, and it may...it may be buried for a while, but the next time a bigger storm comes by, it's...it's very much unburied and moving on downstream.

And even though looking at burying DDT, for example, for...for a period of time, it doesn't necessarily stay buried, and we don't want farmers that have to dredge their farm ponds in case that it does fill up in 30 years. If they're dredging their farm ponds, we don't want them to have a...a hazardous material that they're having to...that they're having to deal with.

EFED has explored using a flowing stream for higher tier exposure assessment as a response to a...a previous SAP. That SAP recommended that we evaluate some of the basin scale models, and we've made some effort and some progress toward...toward doing...toward doing that. Certainly, for higher tiers, that is...is an option for us.

We do use that single EXAMS parameter, the mass transfer coefficient, to represent mixing caused by a variety of...of...of causes that would certainly stir up the bottom portion of...of even a static...a static pond that causes mixing, and there again, looking at how appropriate is this single value for is it...is it complex enough to represent what we need to represent in terms of mixing between the water column and the...and the benthic layer.

And, again, looking at the...the admonition for...for EXAMS that synthetic chemicals may not...the assumption that they may remain buried may not always be the appropriate.

In light of the new hydrophobic pesticides that we've been looking at more recently, EFED is debating the appropriate level of conserva...conservatism and the factors which impact soil erosion. We...we realize that in a couple of these farm ponds, they were actually filling up in...in 30 years which was certainly not our intention. Our intention in...in modeling 30 years of...of rainfall is to look at the temporal variability from year-to-year based on wet years and dry years and not having a...not having a pond fill up, so that we have had a number of internal discussions in looking at whether those are actually appropriately parameterized.

So, that's basically the end of my summary. If anyone has clarifications or additional questions on modeling, I'd certainly be happy to try to answer them.

**DR. BUCHER:** Questions for Dr. Parker? Yes, Dr. Maddalena?

**DR. MADDALENA:** Yes, the last comment you made was in reference to wet years, dry years. If you focus on the PRZM which is the source model for the pond model, what happens in PRZM on wet year, dry years? Do your applications accumulate on a dry year, for example, or is there...I don't know what the chemistry is in PRZM, if there's actually...if that has a fate model contained within it as well.

**DR. PARKER:** Yes, yes, PRZM has, basically, the same inputs as...as EXAMS, so the pesticide stays in the field until it...until it degrades or...or sorbs or...or a few small rainstorms without runoff will slowly move that...that pesticide down into the ground water. So, between movement, beaching into the ground water or the vadose zone and...and runoff, there is less and less chemical in the field for runoff each time a new storm comes by.

So, typically, in looking at the...the output values from PRZM, the two or three major runoff events will happen within a week or so of...especially for a chemical that has somewhat...somewhat of a short half-life. The three major events of...for runoff and high concentrations will happen within a week or so after the...after the pesticide has been...has been applied.

So, you do, yes, you do definitely have degradation and binding in the field the same as you do in the...in the water body.

**DR. BUCHER:** Dr. Simonich?

**DR. SIMONICH:** I guess a more specific question about PRZM. Does it include a piling term, a term where...a scenario in which you can have a persistent pesticide that maybe could be depleted in the top layers of the...the soil and, in annual piling, be moved back up to the...the air/soil interface?

**DR. PARKER:** Yes, in short. It's more a case, typically, of moving it downward in that the...by the time you plow a second year, there's very little left from applications of the...of the previous year.

But you'll...you do sometimes pull a disk after you apply on the same swath across the field, and so, that is mixing it to a deeper and deeper level.

PRZM model allows us to put it in as a band on the surface, as a T band partially on the surface and partially incorporated, incorporated to most any depth that...that we wish, depending on the...the recommendations on the pesticide label, decreasing concentration with depth, increasing concentration with depth so we can really put the chemical wherever the label wants us to put the chemical, wherever the label wants the farmer to put the chemical to make it most effective for the crop that...and seed treatments. We've modeled seed treatments in which the seeds are pre-treated with the chemical, and the seeds go in at a specific depth. And so, we put the chemical at that depth as well.

The extraction teams in pulling the chemical out of the surface soil and before it runs off is...is decreasing with depth down to 4 cm, I believe, so if most of your chemical is in the surface, you get a lot more chemical in runoff than if most of it is...is...is deeper.

So, those are all factors as well that impact the amount of chemical in...in the runoff water.

**DR. SIMONICH:** And I'm just wondering if in the scenario of a more persistent and more hydrophobic pesticide, if you could have a scenario where piling might increase concentrations towards the surface at the air/soil interface compared to a less persistent, more water soluble chemical. I'm not sure of the answer to that, but I'm thinking probably it could be an important role in that. It may be different for different types of chemicals.

**DR. PARKER:** I haven't really thought about that as an issue, but I know in some of the pyrethroids that 99 percent of all of the chemical will come off in the sorbed phase with eroded soil. So, maybe 1 percent actually comes out dissolved in those...in the...in the water and then stays dissolved immediately anyway in the...in the EXAMS pond, and 99 percent will come off with the...with the eroding soil, and that tends to be the case with a couple of these examp...example chemicals.

**DR. BUCHER:** Are there any other questions?

(No response.)

**DR. BUCHER:** Thank you very much. Oh, yes, Dr. Maddalena.

**DR. MADDALENA:** One more...

**DR. BUCHER:** One more question. Sorry.

**DR. MADDALENA:** ...question. Sorry. To follow back and forth with Dr. Simonich over there, the accumula...we have to think differently now with these particular class of chemicals. I think the answer you gave is perfectly logical for the very classic chemicals that do degrade rather fast, but even your test case had some that will last in soil for thousands of days in which case if you don't have rain and you don't have even those particles removed, you could conceivably have some accumulation right at the surface...

**DR. PARKER:** That's true.

**DR. MADDALENA:** ... where over the course of 20 years, you could plow that in, in which case you probably would bring it back up.

But thinking of just the surface now and just that bound phase, is there an off site dust movement loss pathway from the PRZM model? Because I've seen California on a windy day, and I'm wondering if that is captured somehow for the very persistent pollutants.

**DR. PARKER:** You know, I've heard of...of that happening in nature in which dust particles will carry an amount of pesticide sometimes a great distance, but PRZM doesn't...PRZM doesn't simulate...doesn't simulate that. I would think that could happen and probably does, but we don't simulate it.

**DR. MADDALENA:** Okay, thank you.

**DR. BUCHER:** The final speaker today, Dr. Sappington of the Environmental Fate and Effects Division, Office of Pesticide Programs, Assessing Pesticide Bio-cumulation in Aquatic Food Webs.

**MR. SAPPINGTON:** Thank you. I looked at the agenda, and I'm the last talk for today, and I'm the last talk before lunch tomorrow. Teaches me I need to look at the agenda when it's being made a little more closely.

Okay, what I'm going to go over, keeping in mind the time, is a little bit of background on bio-cumulation, some terminology, as well as the types of data we typically receive. I'm going to walk through some of the key challenges that we face and review some of the available methods. And in doing this, I'm not talking about specific models per se like Dr. Ambrose went through with the sediment dynamics and water quality modeling, but more of the types of approaches, laboratory measured, field measured values, as well as food web models.

And then I'm going to provide a summary of...of where we've applied these types of methods for two example pesticides.

A couple terms should be familiar, but just to make sure we're starting off in, in the same nomenclature, bioconcentration represents uptake of a chemical through water only, in the case of aquatic organisms through routes of respiration or dermal, and it's typically characterized as the bioconcentration factor or BCF.

Bioaccumulation, on the other hand, includes bioconcentration, but it also addresses other routes of exposure should they be available in that situation, and that's characterized as the bioaccumulation factor. And those are just ratios, or you can derive them in different ways.

Usually, you're interested in the ratio that corresponds to a steady state accumulation where uptake and elimination are...are canceling each other out and the concentration has leveled off over time.

And for what we've heard several times today, for the types of chemicals that we're talking about, non-aqueous exposure routes can be important, and in that case, some of the metrics that we look to are trophic transfer factors or biomagnification factors which are ratios of chemical concentrations in one trophic level to the next. And for these compounds, it's usually best to do them on, compounds that partition preferentially into the lipid phase, to do this on a lipid normalized basis.

This is the conceptual model I explained earlier, and the bioconcentration processes come into play here. Bio-cumulation includes, again, the trophic transfer. And the types of receptors we're interested in, even though it's aquatic bioaccumulation, we're concerned about not only the aquatic organisms but what organisms that depend on them for their food. So, piscivorous wildlife, for example.

Types of data we commonly see are fish bioconcentration studies as well as the octanal water partition coefficients, and less commonly, we might have bioconcentration measured in lower organisms such as the oyster, we might have food chain transfer studies, as well as field mesocosm studies.

But these...these studies are only conditionally required, depending on the lower tier assessments. They're not required. And even the BCF study for fish is required only when the KOW, log KOW exceeds 3.

I want to take a...this one slide and walk through bioaccumulation assessment, just provide a thumbnail in another Agency program, the Office of Water. I used to work in the Water office and was involved in developing this methodology with other people at the Office of Research and Development, and I guess it shows you that you can leave an office, but the issue tends to follow you around wherever you go.

And what...what the problem was in...in the Water office was how to derive water quality criteria that incorporated bioaccumulation and that incorporated these other routes of exposure. This was in the context of estimating concentrations in biota that would be consumed by humans.

That particular method recognizes the different types of data that are available, ACS and field bioaccumulation factors as well as a factor that's indexed to the sediment concentrations, the biota sediment accumulation factor. It also employed a food web model, an earlier version that was developed by Dr. Gobas.

Bioavailability is handled by examining the freely dissolved concentrations, and I'm talking here about the mutual organic compounds, as well as lipid normalization. And so, there's a three-phase system in which you had freely dissolved chemical, chemical sorbed to DOC, and chemical sorbed to POC.

And this underwent peer review, and as part of that, we looked at some data sets...and this topic has come up today...to try to evaluate the performance of these different methods as well as the bioavailability corrections that we were making, and despite a lot of data being out there, what we found is that the type of data sets we needed were ones in which you had samples that were co-located in space as well as time and all the ancillary measurements as well, particularly for things like DOC and...and lipid fraction.

And so, the data sets that...that came out of the screen were largely those from the Great Lakes Green Bay Mass Balance Study, the Hudson River PCB data base, Lake Ontario which included PCBs as well as chlorinated pesticides, and a location in Louisiana, and the results from this evaluation were published by Dr. Burkhart who's in the back of the room in ES&T in 2003.

We also had peer reviewed these sets of approaches for application in the Great Lakes as well as for national application, so some of which you see in the white paper are, or actually, a lot of which reflects the thinking that had evolved in other Agency programs.

Current challenges, obviously, addressing accumulation via the diet, addressing concerns regarding persistence and potential accumulation over long time periods, and Dr. Gobas mentioned the importance of metabolism, and that is...that is extremely important when applying either a dynamic or a steady state through a bioaccumulation model. And it's not so much the math as it is getting the correct data for in vivo metabolism rates.

And I know our Office of Research and Development and other...other groups are working very hard at trying to evaluate ways in which we can infer in vivo metabolism, either from in vitro data or from...even from field data.

Understanding environmental degradates and how they may impact bioaccumulation of internal residue, and addressing bioavailability for how they handle further chemicals.

Now, I'm going to provide just a cursory overview of the strengths and limitations of different methods, and this was partially addressed in an earlier question about using measured or estimated data, do we have kind of a...a strict preference in that case, and...and the answer was no. It really varies depending on the quality of information from, from each of the studies and the nature of the problem.

But in general, for the laboratory bioconcentration studies, they do not...well, they're good at, obviously, measuring uptake from the water, but they exclude other routes. The characterization of exposure is one of their strengths, because, typically, that's measured fairly rigorously over time, and they also address the notion of...of biotransformation but only in the accumulating organism, not in the food...not what may occur in the food chain.

And so, the extent to which different organisms have different biotransformation rates will not be addressed here.

Environmental realism and multi-season exposure are a limitation of these tests for...for fairly obvious reasons, and I would just loosely classify them as a...sort of a moderate level of effort. They do take a couple of months to run, depending on the length of the depuration phase In comparing that to the food web models, the advantage here is you can address uptake through other exposure routes.

Characterization of exposure is sort of equivocal, because it really depends on the confidence you have in the inputs to the model, and many times, these are estimated concentrations. They don't have to be; they can be measured, but in the context of...of a new chemical, we're often left with...with using predicted concentrations.

Metabolism, I mentioned earlier about the issue of having proper data, and environmental realism is an issue, because all models are simplifications of reality, and we're having to make assumptions regarding food web structure and...and assumptions regarding environmental parameters such as temperature and...and so forth.

One nice advantage is that to the extent that we're concerned about multi-season exposure and accumulation, we can run these models for long periods of time and get an assessment of that, and they are convenient in terms of level of effort.

Now, the field mesocosm studies, experiments conducted in the field on...on small outdoor aquatic systems, again, have a number of advantages similar to the food web model with respect to uptake pathways, and the ability to characterize exposure really depends on the study.

Sometimes, it's done well; other times, it's...it's not done well. But they do incorporate any metabolism that might occur within the organisms or the food chain that's used in that particular study, and I think they do address environmental realism relatively...relatively well, although again, it depends on the study design.

Difficulty here is they're often conducted for just a few months, and so, the issue of multi-season exposure isn't addressed, and, frankly, the...the amount of effort that goes into these studies can be quite high.

And lastly, field monitoring data which was...is available but, obviously, only for those chemicals that...that are either out...out in the environment or if there's an experimental permit to conduct such studies for new chemicals have...can address multiple exposure routes as well as multiple seasons and have, obviously, a high degree of environmental realism.

Oftentimes, however, the biggest limitation with these studies, with monitoring studies, is getting an adequate characterization of exposure in the relevant environmental compartments, both spatially as well as temporally.

So, I'm going to walk through some of the assessment questions with respect to bioaccumulation or aquatic bioaccumulation that would come up during the problem formulation phase.

And, basically, we...we have to evaluate where the chemical is going to be found in the environmental compartment, issues related to persistence that we talked about this morning, the...how likely an exposure, dietary exposure, may be important, how degradates may affect both bioaccumulation as well as toxicity, and what about...what are our primary ecological receptors of concern. This defines, really, the scope of...of the bioaccumulation assessment, including the food web structure and...and so forth.

Metabolism we talked about, and how long does it take for the compound to reach steady state in, in organisms, and I'll go into this in a little more detail in subsequent slides. The other thing from a toxicity perspective is asking the question, well, what duration of exposure is...is toxicologically relevant to the assessment endpoint that...that I'm using? Is it a short term or is it long term exposure that's really driving the...the chronic risk?

In most cases for these compounds, we're worried about chronic effects.

The next question is having an understanding of how bioavailability might affect pesticide bioaccumulation. As Dr. Mackay indicated, although there are no real bright lines here, once you get above a log KOW of 5, you start really impact...bioavailability and absorption to dissolved and particular organic carbon becomes increasingly important.

And that's...that's important in interpreting the results of different studies, because the bioavailability conditions may be very different.

And then, understanding how the different approaches predict bioaccumulation and can we explain differences where they do occur. Is there a rational explanation for them?

So I'm going to walk through now the two example pesticides, and this is the profile that sort of relates to some of the early...previous questions I just outlined. This is pesticide 3, and the KOW range, depending on the isomer, the dominant isomer is 5.1, KOC of...of roughly 30,000, so we expected a partition to sediment, and aquatic photolysis, as measured, is relatively short, but in the system's deeper and more turbid systems, it's not considered to be a...a dominant loss process.

Exposure routes, based on models such as the ones Dr. Gobas has developed, we expect dietary exposure not to be a dominant contributor but also not to be completely negligible. So, it is a factor at this KOW but just not necessarily a dominant one, and that's, again, assuming no metabolism.

Environmental degradates were not a major issue with this...this assessment, and the ecological receptors I'm going to present were piscivorous birds and mammals...I'm just going to present the results for...for birds, because they were the more sensitive of the two taxa.

Regarding metabolism, while we didn't have in vivo metabolic rates, we, in our bioconcentration study and I believe the mesocosm study, degradates were measured in biota, and they were relatively minor, so that gives us some confidence that perhaps the biotransformation is...is not going to be a driver.

In steady state based on the BCF study, the depuration rate constant was 90 percent steady state, was achieved in approximately 50 days. So, there will be a time lag between, even if it's just a single organism, a time lag between the exposure concentration in water and the accumulation in the organism.

Critical exposure period, it was 80, and reproduction related endpoints, we assumed that to be roughly 30 to 60 days, to correspond with durations of accumulation in the parent and deposition in the eggs from that study. And BCF values on a wet weight basis are shown here, and we also had information from our mesocosm study.

So, what were the objectives here? First was to evaluate potential exposure to piscivorous birds, incorporating trophic transfer and any pesticide carryover. The second objective was to compare bioaccumulation models that were run in a steady state as well as the dynamic mode.

And the third objective was to evaluate the sensitivity in model predictions to assumptions regarding sediment dynamics, and some of this...well, and in doing this, we...we used the AGRO model, and we used an earlier version, the version 2, which had constant parameters for the deposition, resuspension, and the burial rates.

General approach, the first one was to use PRZM/EXAMS to give us our predicted exposure concentrations and the model published by Arno and Gobas for the food web in the steady state mode. We also ran this model in a dynamic mode, and Dr. Lawrence Burkhart was one who...who developed a code for the model in order to run it in the dynamic mode.

And we also ran, as I mentioned earlier, simulations with AGRO which, of course, is in the dynamic mode and includes sediment dynamics.

This is a schematic of basically what I went through, but it shows approaches 1 and 2 where not only was the objective to estimate concentrations in biota but also to see how the...the different types of models compare in terms of the predictions, and in this case, it's the dynamic and the steady state mode.

And so, what we did was on the steady state application, we used as input to the steady state model, 60-day average concentrations. The maximum 60-day average concentration with a return frequency of 1 in 10 years, and that's the same process that Dr. Parker explained earlier this morning. That was for water and sediment concentrations.

And, again, that reflects the time to reach steady state, roughly, as well as the critical exposure period, we think, is appropriate based on the toxicological endpoint. And then we simply put those values in...into the model and produced an estimate of bioaccumulation into...I mean, in the food web.

For the dynamic approach, we...we imported the daily values, not...not a single value, for water, sediments, temperature, and in this case, temperature did vary. We used a month-to-month variability function here, and you'll see the impact of that shortly. And, again, in the same...same model but just running the dynamic mode.

Okay, there's a question about appropriateness of steady state model predictions, and I just wanted to illustrate that here and in terms of how they might be used, even in highly dynamic situations. To illustrate this, we...we did a run of, with PRZM/EXAMS with short water and sediment half-lives, and this was done to maximize the variability in concentrations in the a...a biotic compartment, that is, in the water and sediments.

This is a plot just from one...one year from that simulation. This is with pesticide 3. The black lines, the spiky black lines here represent the dissolved water concentration, and the top line represents predicted concentration in piscivorous fish, and so, you see the time lag that...that we would expect based on the measured time to reach steady state.

Now, if, as Dr. Gobas pointed out, if we were to take a daily value, a daily maximum value, from the exposure time series and import that into the steady state model, we would have very high predictions, and...but what is...what is happening here is that the organism is essentially integrating exposure from the water column as well as the food, but, again, for this chemical, water column is...is a dominant uptake pathway over time.

And so, what we did was to take an average, a 60-day average concentration, of the water and sediment concentration. The other lines here represent other components of the food web as well as the sediment.

Another interesting point here, just to illustrate, is that the other components of the food web display faster accumulation kinetics. So, that's also important to keep in mind, depending on the organism that's driving the risk assessment.

So, what we did in order to try to compare apples and apples is we took a 30-year time series PRZM/EXAMS run...runs, and we took the maximum value that correspond to a given average. Okay? So, a 1-day average, a 60-day average, 188...180-day average, and...and an annual average. We took those maximum values across the entire time series for water and sediments and imported those into the steady state food web model.

Then what we did with the dynamic model is to actually not distill the data down into a single value but import all the daily values but choose the same averaging period, in this case, for the tissue concentrations. So, we would compare the 1-day average tissue concentration predicted by the steady state model with the 1-day...I mean, predicted by the dynamic model with the imported 1-day average of water and sediments to the steady state model. And we did that for each of the averaging periods.

And the plot on the lower right here shows a comparison of those results. This is for North Carolina cotton scenario. The top line represents the predictions from the steady state accumulation model, and these are at different application rates, so they don't really pertain to the...the assessment in the white paper, but the point here is that yes, absolutely, if you were to put a 1-day value into the steady state model as input, you're going to predict a very high concentration relative to the dashed line, the purple dashed line here is the results from the 1-day max from the dynamic model.

However, when you start to increase your averaging period, you start to see a convergence between the steady state and dynamic modeling results. And we think that reflects, basically, the degree of temporal dampening in the system but also the degree of variability in the system. So, you can get similar results even in highly dynamic situations.

Now, the third approach was to run the AGRO model which has been explained earlier and to compare that to the PRZM/EXAMS modeling results. As we had a number of input parameters, I'm just summarizing the major ones here, and KOW, we used the higher value for the dominant isomer. Application rates. In terms of half-lives, we have 268 days in the water and...and stable in the sediments based on the fate information.

Lipid fraction are shown here, and these are all kept the same between the two models. These values represent median values for the different trophic levels, and as one...one aspect, we can pick deterministic values, but lipid fraction varies quite widely across species as well as within the same species in the function of reproductive status and so forth, and this was a very sort of middle road value.

We zeroed out the flow, essentially, in the AGRO model to be consistent with EXAMS, and then the two models looked at addressed solubility like we've already discussed earlier, EXAMS just having the concentrations capped at solubility and in AGRO having them capped but then having the excess in the reserved pool which is dissolved back when concentrations in the water dip below solubility.

Two factors we...that were different,

major factors that were different. One was the organic carbon content and total suspended solids. The value used in AGRO was...was about 50 percent higher than...than that used in the PRZM model.

These values, when you look at USGS data for concentrations of particulate organic carbon, if you were to convert this to POC based on the assumed TSS at 30 mg/l, these values correspond to the upper 90th to 95th percentile in lakes and reservoirs across the country, and...but keep in mind that...that those lakes and reservoirs are likely to be much less turbid than our typical farm pond.

So, where we are in sort of the distribution of values of farm ponds is still somewhat unclear, but that's where these values shake out in terms of their represent...representativeness.

And the sensitivity analysis indicated that this was a sensitive parameter, basically a 50 percent increase here resulted. When we did the sensitivity analysis with AGRO, resulted in a 50 percent drop in concentrations in tissue as a result of the impact on bioavailability and water column concentrations.

None with regards to sediment dynamics. None were explicitly assimilated with...simulated with

EXAMS, and the constant values here were used in AGRO.

Here are the results in terms of the 60-day, maximum 60-day average, EECs, for in the water column as well as in sediment, and, again, you see with the asterisks here we had high-end scenarios.

I should have mentioned that each of these scenarios represents the low and high end for that particular crop group. We actually modeled quite a number of scenarios. I just distilled it down to...to these, but we were rubbing up against the solubility limit.

Results here predicted for concentrations in tissue, again, with the steady state approach, are shown in this plot for the six different scenarios, and the different bars represent different components of the food web, the higher red bar being the piscivorous fish, and these are on a...a wet weight basis.

And the band here shows the relationship of these predicted steady state concentrations to our toxicological value in diet for birds, the NOAC and the LOAC. So, we have exceedances here of our NOAC in all six cases but also our LOAC in five out of six.

Now, I'm going to go into the dynamic modeling approaches. The left-hand panel at the top shows the dissolved water concentrations predicted using PRZM/EXAMS, and I'm just showing the cotton scenario here. The blue lines represent California cotton, and the red represents Mississippi cotton which we discussed earlier, is a...a high-end scenario in terms of sediment loads to...to the system.

And what's obvious in the water column concentration with Mississippi cotton is that the pesticide loads are great enough that the solubility limit is reached in about 6000 days, and we forced, basically, truncated the values at that limit. And for the Mississippi cotton scenario, we do not reach that limit, although there is gradual increase over time, and this is partially reflected in the sediment profile where we see the increases over time.

With the AGRO model, again, the same scenario with the parameters that I mentioned earlier. You see a much different profile from the water column concentrations. We do not have a gradual increase over time, and we see a much more variable concentrations.

We were bumping up against the solubility limit on certain peak periods, but we weren't staying at those limits like we were with the PRZM/EXAMS model. And the sediment concentrations, it took about ten years to finally level out at...at a steady state concentration in both of these scenarios.

Okay, how does that translate to predictions in piscivorous fish? This is the same power scheme used for the abiotic concentrations. Again, this is PRZM/EXAMS with the dynamic versions of Arno & Gobas being run. What we see is a gradual buildup over time to about 6000 days and then this oscillation at a...basically an oscillating steady state.

What we think is occurring here and what's interesting is...is a previous...you remember from the previous plot, we essentially had a flat line with regards to the...the water concentration. We had variable temperature. Seasonal variation in temperature, and that affects the uptake rate constants as well as the growth rate, and we think that that's what this is representing here, is the variation in...and due to temperature changes.

And the sediment concentrations follow a...a similar pattern...I mean, at forage fish. The avian LOAC is...is shown here as well.

Again, we have the different predictions using the AGRO model. I've put for reference avian LOAC here, and we only have one spike of piscivorous fish that reaches up to that level. So, again, a very different picture. We do not see this long-term accumulation. We think that's due to the sediment burial being included in that model.

This is the statistics for the same plot for the dynamic results showing in terms of the EECs are the 1 in 10 year return frequency. And, again, a large difference between the EECs in tissue predicted with the EX...PRZM/EXAMS as input to the same model versus the AGRO.

This table just summarizes the results, and I...I threw in sort of what might be an empirical approach as well where we would use a BCF times the average water column concentrations, and we see relatively good agreement between the steady state and dynamic approach, although I will say that this is not a rigorous test, because if you think back to the profile of tissue concentrations, basically, these EECs are returning something close to year 27, because we have a...this...this buildup over time. And so, both models...the EEC is approaching that sort of steady state value at the end of the assessment.

Okay, so general conclusions, the first of which, it does appear that pesticide 3 appears well behaved in terms of the assumptions of no metabolism, and that's based on the biotransformation information that we have from the BCF study as well as if you take and look at normalized bioconcentration factor from that study and compare it to the KOW, they're in the same ball park, although, admittedly, there's a wide range in lipids there. But you're...you're in the same ball park, and even if you used the...the low and high end, we're within a factor of 2. So, we think that that supports the notion that metabolism is not a driver.

And the rate constants are relatively similar between the ones predicted using the model and that derived from...from the Booneville study.

Again, the steady state and dynamic modeling results produced similar tissue-based EECs, but what's critical here is the choice of the averaging period. It is, as Dr. Gobas has showed, clearly not appropriate to just take a daily value and put it into a steady state model.

And depending on the critical exposure period, there may be situations where you simply can't use the steady state model, because if the dynamics are such that you're worried about very short-term concentrations in fish tissue and you have a...a highly temporally dampened system, a steady state model will not give you that short-term variation or something that you could use to estimate that. But in this case, the results were similar.

And in that regard, I'm going to show a plot that was included in the technical support document to support the bioaccumulation methods within Office of Water and also published by Dr. Burkhart in 2003 in ET&T, and this is a plot that illustrates the effect of hydrophobicity on predicted accumulation kinetics in...in fish.

The top line shows predicted concentrations or simulated concentrations in the water column for a reach in the Mississippi River, so highly variable situation. The panel B shows the scaled concentration that's predicted in piscivorous fish for different KOWs, assuming that this water profile applies to different KOWs, and sediments were included in this as well.

And what you see here, the lower KOW values go from 2, and the highest goes up to 9, and what you see is at the lower KOW values, concentrations basically mirror those in...in the water column, concentrations in fish, but as you move up the KOW scale, the predicted concentrations start to dampen temporally to while...to...to where they basically are very poorly responsive to changes in...in exposure concentration. And this is over a year time period change here.

And this information was used in this publication to actually inform how you would go out and do a bioaccumulation study in the field, and the questions there are much like the questions in the context of the steady state model, and that is well, how often do I need to sample? How...how...what is the interval between sampling periods that most...is most appropriate? Do I need to keep the samples co-located in time, or do I need to, basically, sample fish tissue at one point but sample water column over a, say, a 30- or 60-day period leading up to the sampling of fish tissue?

And based on this and other information, recommendations were made on, basically, how to design field studies for estimating bioaccumulation factors.

Moving on with the conclusions, obviously, it's very clear that the bioaccumulation predictions are extremely sensitive to assumptions regarding...to the inclusion of sediment dynamics as well as the...I didn't show the results, but if you put different values for burial and deposition, they are sensitive to those values.

They're also sensitive to what we assume regarding KOW, and...and here, we're assuming that it's a...a known quantity with no variation, and that's obviously not the case. Lipid fraction is highly variable. Organic carbon fraction is variable.

There is an example in the white paper where these parameters were...were varied according to assumptions regarding their distribution and used in a probabilistic fashion. So, that's certainly an option to consider to the extent that the risk assessment is sensitive to these parameters.

Key uncertainties include application and parameterization of the sediment dynamic routines, what values are appropriate for farm ponds. Bioavailability above solubility, what do we really assume here, and is the laboratory-measured solubility, how accurate is that for field situations, or how representative is that, I should say. And variability in key input parameters.

I'm going to move on to pesticide 4. This is the profile. Dr. Gobas introduced this as well. High/low KOW. High organic carbon partition coefficient. Degradation in term...is...is not a major concern. We suspected that there was something going on possibly related to metabolism, although it appears that it could be related more to the growth dilution.

We had large differences between the measured bioconcentration factor in Booneville and what we would estimate using the model. And that's also reflected in the steady state value.

We also had concerns at this high log KOW about bioavailability in terms of uptake through the gut, and a trophic transfer study was conducted as part of this with rainbow trout being fed oligochaetes and you see that biomagnification factor there on a lipid basis.

We also had information with respect to accumulation through the sediment route of exposure with oligochaetes in two different studies, and we also had a...a mesocosm study that simulated realistic concentrations for spray drift. And this study was done with the formulated product, and it's suggested that maybe the bioavailability of the compound was greater in...in the formulation versus the active ingredient.

So, general approach here, again, was to say okay, we have different methods, so let's...let's give them a...a shot and see what they predict but keep in mind some of the limitations of the methods. So, empirical data, we have the BCF, the biomagnification factor, and the biosediment accumulation factor.

We have the Arno & Gobas model. We ran that with no adjustments to the rate constants. And we also ran it...and I'm calling this the hybrid approach where we used information from the empirical studies to inform the rate constants in the model, including the trophic transfer values.

We...because the different empirical studies capture different exposure routes, we used...we apply them differently for each exposure route and then sum them up. So, accumulation in water, we selected an EEC in the water column of 0.15 parts per billion...that was converted to parts per billion...and that is the solubility limit measured in the laboratory for this compound, and that also corresponds to the...the highest...we reached this limit based on the highest exposure scenario for...for the crops that we studied, and we applied the steady state bioaccumulation factor derived here and came up with a predicted steady state concentration.

We also applied the biomagnification factor to estimated concentrations in food, and the range here represents values in food predicted from a range of sediment, predicted sediment concentrations. We came up with those values as representing uptake from food, and we summed them to come up with a range of total accumulation, again, just a...a rough steady state estimate.

We also ran the model in default mode with no change in the uptake and elimination rates and other parameters. We used the same screening inputs for water and pore water, so these are...are very high values, and we obviously came up with very high values predicted in tissue.

The next...the third approach was to use some of the information that we gleaned from the measured studies, uptake and elimination rates from water and food for fish. We used the same screening level inputs, and we looked at predicted outputs in forage and piscivorous fish, and they ranged from 32 to 5.8 respectively in this case, because the piscivorous fish, the food uptake parameter, the BMF, biomagnification factor, was low, and so, they are consuming forage fish but not getting the trophic transfer that you would expect.

And when we...actually, the bottom plot used is the trophic transfer factor, and the top plot uses the elimination rate and the uptake rate from the BCF study.

And this just compares those results in reference to the chronic dietary effect levels for birds and for mammals, and we have ranges of two orders of magnitude. So, we weren't comfortable, in this case, with the default assumptions, although this issue of growth dilution will have to be evaluated, and it's certainly possible that the empirical approach, if...the juvenile bluegill which were actively growing...and I believe that's part of the...the study...study recommendations, and so, with a compound that's so hydrophobic and has such...is predicted to have such slow elimination, growth dilution becomes extremely important.

So, this is...this is important to consider in designing these studies and requesting studies from the...from the registrants.

Conclusions, pesticide 4, we...we...doesn't appear to adhere to all our assumptions, at least with respect to the oral uptake with...with...what's being predicted by a food web bioaccumulation model. We did attempt to use the empirical data for directly estimating bioaccumulation, adjusting for kinetic parameters, but there's some uncertainties here.

There's another aspect to these studies that is relevant, and that's the use of co-solvents. And, again, these are used, in part, to achieve concentrations in stock solutions that are appropriate in a diluter series, and they introduce uncertainties in terms...in terms of the bioavailability of these compounds in these studies.

And it's also important to consider the assumptions in the models that are being used as well as in the empirical data, careful evaluation of those information for applying them in pesticide risk assessments.

And for this compound, we had a wide range in variability in KOW, and I just...we just picked the middle value, but obviously, we go two orders magnitude of KOW, we're going to get a...a wide difference, and it just points out that we need to keep these factors in mind when...when...and not be overly precise in our estimates.

And that's it. Thank you very much.

**DR. BUCHER:** Okay, thank you very much. Are there questions? Yes, Dr. Mehta?

**DR. MEHTA:** Okay. You know, you showed that the Kine dependent model is...works much better than the previous model which is not surprising, I mean, the dynamic effects are very much part of nature, but do you anticipate additional changes, additional improvements in the model that the Arno & Gobas model that you...you think might help you, 'cause now you're talking...if you had used that model, that model, if it becomes a standard, it would be used for several more years. So, would you be interested in seeing more things in that model?

**MR. SAPPINGTON:** It's a good question. I think what comes to mind more right now...I mean, that model is a considerable refinement of the earlier model, in '93, and it addresses kinetically based accumulation in...in lower parts of the food web. It has a major advantage there.

I think I would pay attention, in particular, to our assumptions regarding the input parameters. We saw the effect of what we think are temperature differences and...and we often will just, you know, assume a constant temperature for our PRZM/EXAMS scenarios, and I think that keeping in mind the representativeness of our input parameters for the different regions that we're modeling, I think I would certainly evaluate that very carefully.

In terms of modeling itself, I mean, I...I think we have to pay attention to different types of food webs. This is a very simplistic food web, and keep in mind that...that different food webs may return different results, particularly benthic versus pelagic-driven food webs, especially since these compounds are going to be found on a mass basis preferentially, in the sediments.

But in terms of the under...underlying architecture, I don't have, you know, major recommendations other than to try to get a better handle on this, this metabolic transformation.

We did talk about earlier the idea of incorporating different year classes and addressing different life stages, if you will, of organisms, and that certainly could be added in here, although I hesitate. I mean, all of these sort of additions and layers of complexity, I think, should first start with a question of do we really need to do this, and so, what's particularly useful is that we have something that will point us in the direction and lead us down a logical path for conducting any of these types of refinements.

And so, if we got into, for example, modeling different life stages which have different lipid contents and different growth rates and so forth, I'd first want to know if the results were even sensitive, you know, likely to be sensitive to that. So, I'd want to apply it in a very careful tiered fashion, because we're doing a lot of these assessments in a...in a given year, and, you know, oftentimes, we'll have a pretty short time frame in which to work with.

**DR. BUCHER:** Dr. Norstrom?

**DR. NORSTROM:** Can you tell me whether...I couldn't quite get it, and I've forgotten from my previous reading of the Arno & Gobas paper...whether temperature depends if respiration rates is included? I know temperature depends on what oxygen content is.

**MR. SAPPINGTON:** I believe the uptake rate constant is temperature dependent, the K1 value.

**DR. NORSTROM:** I know it's back there, so the answer is yes, I gather?

**MR. SAPPINGTON:** Yes.

**DR. NORSTROM:** Okay.

**DR. BUCHER:** Yes, Dr. Hickie?

**DR. HICKIE:** You have a very elegant dynamic, I would say, lower food web model, and if you go beyond fish and we...we're using a very simple approach to deal with birds and mammals that are eating fish or aquatic invertebrates. And I'm just wondering, when do we need to have dynamic models for some of those animals?

I know it's a tremendous amount of work, but it...but I can see in some of your scenarios where fish concentrations are just bouncing around LOACs or NOACs. There comes a point where we need to do that.

**MR. SAPPINGTON:** Yes, and that gets back to that critical exposure period, and if it's relatively short, 30 to 60 days, and you're modeling with the IAC with the terrestrial organisms just bouncing around, then that will lead to questions about temporal differences in the diet of...of...of the terrestrial organisms, how that might affect your actual exposure rather just...I mean, essentially, by drawing that line, you're assuming that...that their entire diet is...is...is comprised of, in this case, pisciv...piscivorous fish.

We do have quite a bit of information about the dietary preferences, and...and so, this is a...a simplification of that. We can start to fractionate the diet, estimate trophic position, but in terms of doing that on a...a temporal scale, looking at how that might change over time, I can certainly see where it...where it would...could be important but, also, could be fairly challenging as well, I think.

**DR. HICKIE:** It...it's just classically a lot of PDT chemicals where you look for effects is on those higher animals, because biomagnification factors are often considerably higher.

**DR. BUCHER:** Anybody else?

**DR. NORSTROM:** Just a supplementary to that, I think in point of fact, it's more likely that piscivorous fish are going to be eating the forage fish than they are piscivorous fish in most cases, from my experience, anyway, in dealing with Great Lakes ecosystems.

**MR. SAPPINGTON:** Or the piscivorous birds eating the...

**DR. NORSTROM:** They're eating air life as well, the same as lake fowl. They're not eating lake fowls. In point of fact, it's...it's quite conservative.

**DR. BUCHER:** Yes, that was Dr. Norstrom. Last chance? Yes, Dr. DeLorme?

**DR. DELORME:** More out of curiosity than anything else for compound, for pesticide 3, why didn't you consider fish as an endpoint of concern, given that they're bioaccumulative?

**MR. SAPPINGTON:** The studies we had for fish indicated that pesticide 3 was not toxic up to the solubility limit in...in the fish, and so, we did not do the bioaccumulation modeling on the lower trophic levels. We could have, but we had no real toxicity endpoint that corresponded...you know, they were not toxic at the limit of solubility.

**DR. DELORME:** So, you didn't have any like full life cycle?

**MR. SAPPINGTON:** We...we had one full life cycle test that was modified to look at pulse exposures, but, again, the endpoints were above the measured solubility in the system, and a co-solvent was used, so you ended up with a tox endpoint above solubility.

**DR. BUCHER:** Yes, Dr. Thibodeaux?

**DR. THIBODEAUX:** Thibodeaux, Louisiana State University. Why fish? Are they easier to corral and catch and measure concentration? On farmland, why not deer, bobwhite? Or earthworms? Why fish?

It's a...remember, it's a chemical engineer asking these questions.

**MR. SAPPINGTON:** In terms of the bioaccumulation you mean?

**DR. THIBODEAUX:** Yeah. Fish is a food source where these others aren't?

**MR. SAPPINGTON:** Well, the entire aquatic food web would be, you can predict the concentrations in that entire food web. I didn't present the results, but we had information on concen...bioconcentration by earthworms, in these studies, and Kris Garber will be talking about the whole aspect of terrestrial bioaccumulation tomorrow, and that's just an area that's not as well developed as the aquatic system. The...the methods, largely, came out of the...the aquatic tox arena, and we know it's important, and, frankly, part of the reason why we're having this SAP is to start asking questions about bioaccumulation not only in aquatic but in terrestrial food webs as well.

**DR. BUCHER:** Yes, Dr. Meador?

**DR. MEADOR:** Keith, are you actually measuring basic metabolism, or are you just talking about total elimination rates?

**MR. SAPPINGTON:** In terms of the metabolism estimate, that's based on measurements of the concentration of the metabolites in tissue. So, it's not a rate as much as it is looking at the total residue and...and radioactive residue and then actually measuring the components of that, and I would...

**DR. MEADOR:** And they have different rates over time if you measured over time and you looked at the formation of metabolites.

**MR. SAPPINGTON:** Right.

**DR. MEADOR:** Which could be useful for some assessments.

**MR. SAPPINGTON:** Yeah, I agree. I mean, we have the...the advantage here of...of having the opportunity to be proactive in the design of some of these studies, particularly if they're follow-up. If we have major uncertainties related to metabolism, we can go back and request some additional studies.

And that's, in fact, what happened here in pesticide 4. Some of that was...reflects...I presented it sort of as one point in time, but part of that information reflected going back and...and getting additional information to address uncertainties.

**DR. MEADOR:** Yeah, for the long term, you'd like to know what the toxicity is of these metabolites.

**MR. SAPPINGTON:** Right.

**DR. MEADOR:** And you had said that today.

**MR. SAPPINGTON:** Right, absolutely.

**DR. BUCHER:** Okay, looks like we've reached the end of the first day of the meeting of the EPA FIFRA for Selected Issues associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative and Toxic Characteristics.

Tomorrow, we will convene at 8:30, and

we will continue with presentations from the Agency. There will be time after that for public comment, and then we will go into the section of the meeting where the discussants answer the charge questions.

Is there anything that you'd like to say before we break up?

**MS. CHRISTIAN:** Just a reminder. I mentioned this morning there is a big meeting tomorrow morning at 8...at 8:30 with DOD. They expect the line for breakfast to be longer than normal, so please plan accordingly.

And I look forward to seeing everyone tomorrow, and thank you to everyone.

**DR. BUCHER:** And I'd like to ask the committee to convene just for a few minutes in the room where we had the meeting this morning.

Yes, Dr. Lick?

**DR. LICK:** Is it okay to leave things here?

**DR. BUCHER:** You can leave papers here, yes.

**DR. LICK:** What about changes in the...

**DR. BUCHER:** We're going to cover that just briefly in...in this meeting right now in the other room here.

**(WHEREUPON,** the meeting was recessed at 5:30 p.m.)

CAPTION

The foregoing matter was taken on the date, and at the time and place set out on the Title page hereof.

It was requested that the matter be taken by the reporter and that the same be reduced to typewritten form.

Further, as relates to depositions, it was agreed by and between counsel and the parties that the reading and signing of the transcript, be and the same is hereby waived.

CERTIFICATE OF REPORTER

COMMONWEALTH OF VIRGINIA

AT LARGE:

I do hereby certify that the witness in the foregoing transcript was taken on the date, and at the time and place set out on the Title page hereof by me after first being duly sworn to testify the truth, the whole truth, and nothing but the truth; and that the said matter was recorded stenographically and mechanically by me and then reduced to typewritten form under my direction, and constitutes a true record of the transcript as taken, all to the best of my skill and ability.

I further certify that the inspection, reading and signing of said deposition were waived by counsel for the respective parties and by the witness.

I certify that I am not a relative or employee of either counsel, and that I am in no way interested financially, directly or indirectly, in this action.

MARK REIF, COURT REPORTER / NOTARY

SUBMITTED ON OCTOBER 28, 2008

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