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The Utility of AVS/EqP in Hazardous Waste Site Evaluations

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Silver Spring, Maryland

NOTICE

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Introduction

To aid in their understanding of contaminant behavior at Superfund sites, the Coastal Resource Coordination Branch (CRCB) of the National Oceanic and Atmospheric Administration (NOAA) organized and chaired a workshop entitled "The Utility of AVS/EqP in Hazardous Waste Site Evaluations." Twenty-four invited scientists, active in the field of sediment evaluation, along with the CRCB staff and representatives of the U.S. Environmental Protection Agency (EPA) and the U.S. Fish and Wildlife Service, attended the workshop held September 13-15, 1994, at the Marine Biological Laboratory in Woods Hole, Massachusetts. A complete listing of participants is provided in Appendix A.

The purpose of the workshop was threefold:

(1) Clarify the scientific theory on which the equilibrium partitioning (EqP) and acid volatile sulfides (AVS) methodologies for sediment evaluation are based.

(2) Determine what the EqP and AVS methodologies can and cannot tell us about sediment contamination and toxicity.

(3) Identify how these methodologies can be applied to the evaluation of hazardous waste sites.

Individual presentations and panel discussions were used as vehicles of information transfer. Overall, 15 presentations were given by leaders in the fields of EqP and AVS, and four panel discussions were convened with each panel addressing three specific questions, except for Panel III that addressed six questions (Panel III was formed by merging two of the original panels). Panels consisted of three to five participants, with each participant bringing a specific element of expertise to the panel. While a formal agenda (Appendix B) had been prepared for the workshop, to facilitate and maximize the free exchange of ideas, discussions generated by either the individual presentations or the panels were generally allowed to run their course. The unstructured atmosphere promoted uninhibited discussions and helped attain consensus on several issues.

The following proceedings are an attempt to capture the tone and level of enthusiasm generated by workshop participants. Summaries are provided of each presentation and panel discussion. In preparing these summaries, an attempt was made to not only summarize the facts presented by the speaker(s) but also, to provide a sense of the overall workshop atmosphere. Audience members were encouraged to express their interpretation of the data being presented and ask questions throughout the sessions. Therefore, when appropriate, the presentation summaries include summaries of these ensuing discussions, indicated by [ ] and italics. Brackets and italics are also used for editorial clarifications for the reader. When multiple authors are listed for a presentation an asterisk (*) is used to indicate the presenting author.

Since this document constitutes only a summary of the workshop presentations and does not include any of the data or graphics included in the presentations, it is strongly recommended that if the reader has any questions or if anything is unclear, he should refer to the literature, contact the presenter directly, or contact Don MacDonald, Workshop Coordinator and Chairman (E-mail: Don_MacDonald@hazmat.noaa.gov) for more information. To help the reader, a list of references, by author, is included as Appendix C. This list includes articles by the workshop participants, some of which contain the data on which the presentations were based; articles cited in the presentations; as well as, other articles dealing with EqP and AVS. This reference list is not meant to be all inclusive on these topics but a starting point for anyone interested in more detailed information on these subjects.

NOAA would like to extend a sincere thank you to all attendees for their participation in this workshop. The information generated though the presentations, panel discussions, and question and answer sessions is extremely valuable to the CRCB in our evaluation of Superfund sites. We encourage additional discussions and research in this area and would be willing to serve as a repository of data collected in an effort to better understand the chemical and biological processes that regulate toxicity at aquatic sites.

NOAA's Role in the Superfund Process

Alyce Fritz

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NOAA serves as a Federal trustee in the protection and management of natural resources. Trusteeship extends to natural resources that are found in or under waters navigable by deep draft vessels, in or under tidally influenced waters, waters of the contiguous zone, the exclusive economic zone, and the outer continental shelf, and in inland areas serving as habitat for marine mammals and other protected species. Examples of resources managed under trusteeship include marine fishery resources and their supporting ecosystems, anadromous fish, endangered species, and marine mammals. The Hazardous Materials Response and Assessment Division (HAZMAT) is charged with applying science and technology to problems resulting from releases of oil and hazardous substances to protect the public interest. The primary goal of HAZMAT is to work hand-in-hand with other trustees to reduce risks to coastal habitats and resources through preparedness and response activities. Technical support is provided to EPA regional offices for evaluating natural resource concerns at hazardous waste sites. The program works to improve coordination with Federal and state natural resource trustee agencies under its Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (i.e., Superfund) responsibilities.

NOAA's interests are pragmatic—NOAA must address resources and contaminant issues for nearly 500 sites, 30 of which are high priority sites. To provide technical support for environmental investigations to determine ecological risks, NOAA must continuously draw from the "environmental toolbox". While many of the new research results are based on sound science, their utility in correctly assessing hazardous waste sites is often unclear. The utility of AVS and EqP methods in hazardous waste site evaluations is of primary interest to NOAA because it is necessary to not only know what contaminants are present, but also what portion is bioavailable. NOAA has specific questions regarding the application of the AVS/EqP approach: How should it be used with mixtures of contaminants? In what phase of the evaluation process should AVS and/or EqP information be used? What is the recommended approach for ecological risk assessment at hazardous waste sites? NOAA's primary goal for this workshop is to reach consensus on technical issues associated with the AVS and EqP approaches and identify ways that this type of data can best be applied to risk assessment.

Opening Comments

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The purpose of the AVS/EqP Workshop is to review the tools available to NOAA to fulfill their mandate. Specifically, how can the AVS and EqP approaches be used by NOAA as they recommend and provide comment on sampling programs to evaluate conditions at hazardous waste sites. What type of information can the various methodologies provide? What are the most appropriate tools to use to evaluate hazardous waste sites? If the AVS and EqP approaches are appropriate tools, what caveats apply to their use? Many times the remedial activities are more destructive to habitats and trust resources than if the contaminants were left in place. To ensure optimum management of contaminated environments, NOAA must apply the appropriate tools during data evaluation. The task at hand is not an easy one, particularly when multiple contaminants are at issue.

Assessing the Assessment Tools

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Over the past 20 years, tremendous resources have been dedicated to identifying problems associated with toxic substance releases. In these efforts, cost per value has been a major consideration. In other words, studies that do not support management decision-making are not looked on favorably, regardless of cost. In contrast, since even the relatively most expensive assessment costs are only a small proportion of possible (or actual) clean-up costs, if the work will assist in the decision-making process, it will usually be approved even if it seems very expensive in comparison to what the scientific investigators are used to. Many of the assessment tools tend to be precise or accurate, but not both. For example, chemical analyses are quite precise, but the analytical results are not good estimates of contaminant bioavailability. On the other hand, biological measurements and bioassays are accurate predictors or assessors of effects to biological communities but because of the normal high level of variation in natural organisms and the difficulty of transferring laboratory information to the field, they are not precise.

The two techniques to be discussed over the next few days are intended to address some of those limitations. These procedures are of interest because they offer hope that the accuracy of assessments of the impacts of releases of toxic substances associated with sediments can be improved without large increases in the basic costs of the assessment and without the need to create and prove the utility of a wholly new technological approach.

Three major factors should be considered in this workshop on the utility of AVS and EqP approaches: good science, applicability to the real world, and the potential to support management decisions. AVS and EqP are based on fundamental chemical principals and good science; partitioning does occur and sulfides do affect the bioavailability of some metal contaminants. These principals support the contention that the availability of substances in the sediments is primarily a function of only a few, easily measured, parameters. However, it may not be possible to accurately translate these principals to situations in the field. Both approaches are based on thermodynamics and are expected to provide accurate estimates when steady-state conditions exist, but, in the real world, steady-state conditions are not always applicable. Secondly, the bioavailability of contaminants is dependent on characteristics that vary from time to time, and while we know what most of those characteristics are it is not clear that we have the capability to accurately measure all the factors influencing this bioavailability. For example, to what extent is a simple measurement of bulk total organic carbon (TOC) representative of the absorptive capacity of the sediments. The following key question should be asked when evaluating these assessment tools: When does it become more difficult and expensive to collect AVS and EqP data than to use alternative, direct measurement methods (e.g., toxicity tests)? The answer to the question of whether these approaches can be used in the real world is the primary focus of this workshop.

While focusing on the real-world applicability of these approaches, we can't lose sight of how they can be used in the context of a risk-management decision. Two difficulties exist with respect to AVS and EqP data supporting management decisions:

(1) To what extent are there technical difficulties with the application of AVS and EqP data?

(2) What is the mechanism for incorporating such information into the decision making process?

At the present time, the process for incorporating risk assessment, especially ecological risk assessment, is not well established, and this lack of an a priori method to incorporate this type of data frequently initiates additional debate rather than aiding in decision making. As an example, while developing a work plan for an ecological assessment at a site, the potential responsible party's (PRP) lead ecological scientist agreed to include toxicity testing but was positively opposed to including benthic community studies. The reason for his attitude being that at another site benthic community studies had been performed and the data demonstrated significant differences between the reference station and the site, but because no determination had been made in advance as to what type of effects would be considered important enough to warrant remediation, it just resulted in endless debate on the meaning of the data.

The ultimate bottom line is: In what way can AVS and EqP data be used to further the identification of seriously contaminated sediments? In this regard we have to keep in mind that our remediation options are presently very limited: the contaminated sediments need to be isolated from biota and that basically means either removal (i.e., dredging) or capping. Our criteria for taking these actions is essentially the toxicity of the sediments to biota. We currently have some direct measures of this toxicity (e.g., toxicity tests) as well as some direct chemical measurement guidelines (e.g., Puget Sound apparent effects thresholds [AETs], effects range low [ERLs], effects range medium [ERMs]). The question is: how will EqP and/or AVS approaches improve our capability for determining sediment toxicity?. Specifically, the following questions are still unanswered and should form the basis for assessing the usefulness of AVS and EqP:

Can AVS and EqP data:

- replace other more expensive or complex methods of measurement?
- estimate non-measurable effects, such as those to higher trophic level organisms caused by biomagnification?
- identify "problem" substance(s) under mixed waste exposure conditions so cleanup can be focused on the problem substance(s)?
- explain/support other biological and chemical measures?

In summary, the two general questions which should be addressed by this workshop are: Do these techniques tell us what they claim? and Where do these approaches fit into the EPA decision-making process?

[*Comments from the audience dealt with the importance of remembering the biota, since they are what we are concerned with. When asked "If we are concerned with bioavailability why not measure contaminants in the biota?" Dr. Dexter responded that organisms suitable for bioaccumulation studies are not always available at the study site.*]

An Introduction to Equilibrium Partitioning Applied to Nonionic Organic Chemicals and Metals

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One of the major principles associated with sediment quality criteria is that bulk chemical concentrations are useless for criteria development and clean-up levels; they are useless because they ignore bioavailability. Bioavailability is properly accounted for by accounting for the phase. Sediment contaminant concentrations are often reported in units of dry weight, whereas tissue contaminant concentrations are generally reported in wet weight. Why? By reporting sediment as dry weight, there is the implicit assumption that water is irrelevant in sediment; that water is irrelevant to chemical activity in sediment. Why not report sediment chemical concentrations as micrograms per liter of sediment plus water? The correlation should be made with respect to chemical activity, as is done in chemical thermodynamics—that is μgrams (μmoles) of chemical divided by the weight of the phase it is in: in water, μg chemical/liter water, in air μg chemical/liter atmosphere, in sediment μg chemical in the phase in which it occurs. Bioavailability is properly expressed by the concentration of the chemical in terms of the phase in which it occurs, so we can get what is called the chemical activity correct.

If dry weight is off by only a factor of two or so, which is within normal measurement error, then dry weight would be adequate and there would be no need for the EqP and AVS approaches. However, dry weight concentrations associated with toxicity (e.g. mortality) can vary over orders of magnitude. We have to know where the chemicals are residing. For nonionic hydrophobic organic compounds, organic carbon is the primary phase in sediments. Nonionic hydrophobic organics concentrations should be normalized to organic carbon. For metals, AVS and organic carbon are the major controlling parameters.

Biological tests are not necessarily the answer; they are not the be all and end all; they only measure the degree of toxicity, they cannot identify the toxic component. The name of the game we have chosen to play is "causation". What is causing the observed bioeffects? If you don't know the cause of the toxicity, then you may not know the source of the toxicity. Conducting a clean-up effort without knowing the source is dangerous because after the cleanup is complete the area may become recontaminated because you have failed to identify and control the source of the contamination.

I want to take you through the history of the development of EqP to provide clarification of our assumptions. It's important to understand how and why we came to where we are.

Studies done by Bill Adams (Adams et al. 1985) on the acute toxicity of kepone to choronimid larvae showed more than an order of magnitude difference between various dry weight sediment concentrations associated with the toxicity. When Adams plotted the toxicity against the corresponding pore water concentrations there was very close agreement. Based on this analysis one would assume that pore water was the sole route of exposure. Suppose he had plotted the organic carbon normalized sediment concentrations against toxicity instead of the pore water concentrations; he would have found fairly close agreement between level of toxicity and these carbon normalized concentrations. He might then have concluded that organic carbon was the route of exposure for kepone.

Both conclusions are incorrect. You cannot tell from an equilibrated experiment the source of the dose. EqP makes no assumptions as to the route of exposure (pore water versus organic carbon phase); the major assumption is simply that equilibrium exists. The equilibrium refers not to an equilibrium between the organism and the pore water or organic carbon, but an equilibrium between the organic carbon and the pore water, such that it doesn't matter how the organism actually receives its dose. That is the fundamental assumption on which EqP is built. Another basic assumption is that when the pore water concentration is the same as the water-only concentration, the organism is seeing the same chemical activity in the sediment/pore water exposure as it is in the water-only exposure. This assumption says nothing about which phase is exerting the activity.

In order to test the assumption that the water-only LC_{50} was equivalent to the pore-water LC_{50}, the LC_{50} in water only was determined for several organic chemicals (i.e., phenanthrene, fluoranthene, acenaphthene, kepone, dieldrin, endrin, DDT) and tests were run on three sediment samples by spiking them with the various compounds. The toxicity of the various samples was determined and the corresponding pore water concentrations measured. Then by using the concept of toxic units, it could be determined if toxicity was properly predicted. *[Pore-water toxic units (PTU) = pore-water concentration/pore-water* LC_{50}. *Predicted PTU (PPTU) = pore-water concentration/water-only* LC_{50}].

If 50 percent mortality occurs when the PPTU = 1, our assumption is correct. When the PPTUs for all the data points were plotted against percent mortality, a reasonably good dose response curve was obtained with the 50 percent mortality point falling between about 0.6 and 3 PPTU; except for DDT, the most hydrophobic of the compounds tested. This range is for all the data points for all chemicals. If the plot was based on calculated LC_{50}s rather than the individual data points, the range would be smaller. The tests supported the assumption that you can predict the toxicity of a single contaminant in sediment based on what you know about its toxicity in water only. We have to show that the theory works for single contaminants before we try it with mixtures of contaminants.

If pore-water concentrations were easy to determine there would be no point in proceeding; just use pore-water concentrations as criteria for sediments. Since that is not the case, we need to be able to estimate pore water concentrations based on solid phase chemistry, or in the case of establishing criteria, to estimate the solid-phase concentration that is liable to have an adverse biological effect from the pore-water concentration known to be toxic.

A relationship between solid phase and pore water phase concentrations has been determined for nonionic hydrophobic organic compounds: $C_s = f_{oc} K_{oc} C_d$. The organic carbon concentration (f_{oc}) is the only sediment specific property of concern, and the organic carbon partitioning coefficient (K_{oc}) is the only chemical specific property of concern. So the organic carbon normalized sediment concentration (solid phase sediment concentration (C_s) divided by (f_{oc}) is proportional to the pore-water concentration (C_d), with the proportionality constant being the K_{oc}: $C_s / f_{oc} = K_{oc} C_d$.

Therefore to establish an LC_{50} concentration for sediment (solid phase), you insert the water only LC_{50} concentration, which is assumed to be the same as the pore-water LC_{50}, and multiply by the K_{oc}. This gives you the carbon normalized LC_{50} for the sediment.

> *[A discussion ensued at this point on the variability of type of organic carbon in sediments and its effect on the* K_{oc} *value and thus on the overall calculation. The result appeared to be that in most sediments the organic carbon type variability is within experimental error and would probably have little effect on contaminant availability and* K_{oc}. *However, there are*

exceptions, such as sediments containing; coal, wood chips, or high levels of PAH contamination. These exceptions must be kept in mind when analyzing any sediment data. Also, there wasn't agreement on what constitutes experimental error. Dr. DiToro pointed out during the discussion that it was important to use the K_{oc} based on the K_{ow} determined by the EPA Athens Lab because literature values can vary by two orders of magnitude.]

Okay, so here's what we did to test the theory. We made a prediction of the organic carbon normalized LC_{50} from the water-only LC_{50} by multiplying it by K_{OC}. We then plotted our mortality data for the seven chemicals against the predicted LC_{50} data. The plot was not quite as tight as the pore-water plot. Our uncertainty analysis tells us that based on this experimental suite of data we can predict the sediment LC_{50} within a factor of two. Now, I want you to understand that this one plot tests essentially every assertion that we've made. Of course, it's only been used for lab exposures with spiked sediments, but it does test the assertion that the water-only LC_{50} can be used to predict the toxicity of sediment exposures.

[A discussion ensued around the wide range of scatter in the plot and the fact that within the factor of two range, the mortality ranged from zero to 100 percent It was pointed out that the large scatter was partially due to the plotting of individual test results. While within the factor of two range for the predicted sediment LC_{50}, there was essentially no predictability *below the range the vast majority of the results were less than 50 percent mortality and above the range close to 100 percent mortality was observed.]*

From a water-only test and a chemical property (K_{OC}), we were able to calculate a sediment LC_{50} value within a factor of two. I think that's a very powerful demonstration of the underlying theoretical soundness, at least within this range of experimental information. If you have to get it greater than a factor of two, you have a real problem. I don't think any assessment methods are good to a factor of two.

[At this point the workshop broke for lunch. After lunch Dr. DiToro continued his presentation addressing metals contamination and AVS.]

Early on we performed an experiment where we measured interstitial water cadmium (Cd) concentrations with electrodes in sediments that had been spiked with various concentrations of Cd. Plotting the interstitial water Cd concentration against sediment Cd on a dry-weight basis shows that we only get non-detects until we hit a very high Cd concentration. Then suddenly the interstitial water-Cd concentration jumps by two orders of magnitude: Cd sulfide was forming while Cd was being added to the sediments. It is not a big surprise that metals and sulfide interact in sediment; but what was remarkable was that it was 20 or 30 µmoles per gram, which is much higher than pore-water sulfide could possibly be.

Where was the sulfide coming from? We looked in the pore water and there wasn't a tenth to a hundredth of the sulfide that we needed to explain all the Cd sulfide forming. We finally came up with the following suggestion. Dissolved Cd is in equilibrium with solid Cd sulfide ($Cd^{+2} + S^{-2} \leftrightarrow CdS(s)$). Iron sulfide, which is the major form of sulfide in sediments, or at least a portion of it, namely the AVS, is also in equilibrium ($FeS(s) \leftrightarrow Fe^{+2} + S^{-2}$). When you add Cd to a system that is already in equilibrium, Cd and the sulfur combine, forming Cd sulfide ($Cd^{+2} + FeS(s) \leftrightarrow CdS(s) + Fe^{+2}$). So effectively, what we think happens in sediments is that when heavy metals are added to the sediment they basically titrate the AVS that is in the sediment in the form of iron sulfide. They form an insoluble metal sulfide, which is less soluble than the iron sulfide and not bioavailable. So the hypothesis is that there is a reservoir of sulfides in sediments. When the experiment to measure the release of iron was done, we found a stoichiometric iron release.

Chemistry modeling indicates that regardless of pH, iron concentration, ionic strength, or other conditions, the following is always true: The activity of the metal, the divalent activity in the pore water over the total metal added, is always less than the ratio of the metal solubility products ($\{Me^{+2}\}/[Me]_A < K_{MeS}/K_{FeS}$).

Repeating the experiment, this time keeping track of the AVS (the term AVS comes from the geochemists, who have been using it for years; it is an operational speciation of sulfide in sediments), we measured the dissolved metal concentration and we had nothing, nothing, nothing and then all of a sudden metal concentration jumps up. The jump occurred when the added metal exceeded the concentration of AVS associated with that sediment. In quite a number of cases, the concentration jumps up later than the AVS suggesting that there are some other binding phases in there as well. We think the next most important binding phase is organic carbon.

So the question was, did this really work in natural sediments? Here is the operational way to do this problem. You give us the sediment; we measure the following things: the total amount of AVS and the amount of Cd, copper (Cu), nickel (Ni), zinc (Zn), and lead (Pb). All of these metals are measured at the same time if they are in substantial quantities; this is what we call the "simultaneously extracted metal".

Now then, if the amount of metal that is extracted is less than the iron sulfide present, it means that in that sediment there is, besides the amorphous metal sulfides, an additional amount of AVS. Therefore, any metal that was released, in anyway, would immediately titrate the AVS and turn back into an amorphous metal sulfide. The chemistry tells us that an excess of AVS over the total extractable metals that can form insoluble sulfides should result in the activity of that whole laundry list of metals being very small. The other thing that you should realize is that you can't treat all these metals independently. The five metals Cd, Cu, Ni, Pb, and Zn have to be treated together. There is not a criterion or an action level for Cu. There is only an action level for the total molar concentration of all the metals that form sulfides, more insoluble than iron sulfide. That is the fundamental reason that I think the dry-weight metals' criteria can't possibly be correct in metal situations where there is more than one metal. They are not independently applicable.

If, on the other hand, you end up with a simultaneously extracted metal concentration greater than the AVS concentration, then you know that there is no iron sulfide in the system. Furthermore, you know that there must be metals in the other phases and they can then cause pore-water concentrations to increase and possibly cause toxicity. What counts is how strong and how much of the other binding phases are present.

So, if this sulfide mechanism is correct, it says

(1) You cannot do metals separately, you have to do them all at once.

(2) It is the AVS that controls the lack of toxicity.

Looking at a real data set, when the response data for the 17 sediments from Foundry Cove were plotted against dry-weight concentration, there was no relationship between organism response and dry-weight Cd and Ni. On the other hand, when the same data set is plotted against the molar ratio of simultaneously extracted metals to AVS, you get a relationship that tells you that if the ratio is <1 you see no mortality. However, if the ratio is >1, we don't really know if it will be toxic.

Question Is it more available via ingestion?

DiToro It appears not to be. I mean there are oligochaetes in that data set. The strongest bond that a metal ion can make is to a sulfur group. There is nothing that is chemically stronger than that. You use acid to dissolve it, basically. Quite a lot of it won't dissolve. It turns out that if you do a weak hydrochloric extraction, for example Cu sulfide hardly reacts at all. It's even stronger than the chloride extraction. In which case the organisms haven't a chance at getting a hold of it. They just don't have ligands that can complex that stuff more strongly than the sulfides. That's what the experiment suggests.

Question What happens in a periodically saturated environment, such as wetlands?

DiToro Wetlands. We have thought about this a lot and have misled ourselves and a lot of people on what went on. We used to think that because iron sulfide oxidized rapidly that was important. What really matters is how fast the metal sulfides themselves oxidize. As far as we know right now very few of them oxidize very quickly. My guess would be that they are very stable, with the exception of Cd sulfide that oxidizes rapidly.

Generic Screening versus Site-Specific Reality: What Works, What Doesn't, and Why?

Peter Chapman

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Sediments are a complex issue, with many processes (i.e., micro environments, redox gradients, AVS, physical/chemical interactions, and biology) affecting contaminant bioavailability. Biologists, who are primarily concerned with effects to the organisms, look to chemistry for explanations of observed results, and assistance in assessing what should be remediated. The primary question is "What are contaminated sediments?" Today, contaminated sediments can be defined numerically or by biological effects. Site-specific criteria are also used to define contaminated sediments. However, each approach has management implications. The basic message of my presentation is that AVS and EqP are "tools in the environmental assessment toolbox" that serve three useful purposes: (1) hypothesis testing, (2) prioritization, and (3) helping explain observed effects (or lack thereof). Case studies will be presented to demonstrate where the approach works, and where it doesn't.

AVS, with simultaneously extracted metals (SEM), provides a basis for predicting the lack of bioavailability for some inorganic contaminants (i.e., when the ratio of SEM/AVS is <1). AVS is not universally applicable; it does not work for all inorganic contaminants, and lack of bioavailability can also occur when the ratio is >1. Existing criteria for some organic compounds are based on EqP values. The primary concern with this approach is that EqP-derived values are based on single contaminants and we are often faced with a complex mixture of contaminants. There is no guarantee that other things in the sediment are not also causing effects. AVS and EqP should *not* be used alone, as inflexible guidance (i.e., as though set in stone) without consideration of site-specific conditions. Thought must be applied to the evaluation of contaminated sediments.

AVS and EqP should be used primarily during level 1 of a risk assessment—as a screening and prioritization tool to focus expertise and resources. A tiered approach is recommended with the primary goals to (1) identify polluted sediments, (2) prioritize problems, and (3) remediate effectively. Results from level 2 measurements should be assist in explaining observed bioassay results and/or field effects. There are many ways to interpret AVS and EqP data; suggested approaches include weight-of-evidence and pass/fail.

I would like to present two examples of how AVS and EqP have been used in evaluating contaminated sediment.

The first example involves a creek that is exposed to landfill leachate. Chemical analyses (including AVS, SEM, and TOC) were done first, followed by sediment toxicity tests. The SEM/AVS ratios were high, always >1 (which indicates there may or may not be bioavailability), and we really couldn't say from AVS what was happening. There was no clear pattern in the bioassays. Survival ranged from 18 to 92 percent. In this case, the AVS theory was not violated; but the lack of toxicity was not predicted. In the end, the AVS approach really didn't help us. We used the AVS tool, it didn't work in this case but the theory wasn't violated.

The second example involves polycyclic aromatic hydrocarbons (PAH)-contaminated sediments near an aluminum smelter. A wide spectrum of analyses was conducted for this site: water, sediment, and tissue analyses; laboratory sediment toxicity tests; exposure studies; bioaccumulation and histopathology with fish, crab, and other species; and benthic evaluations. The data indicate that PAHs are not bioavailable, even though the concentrations are very high. The source of PAHs was coal and coke material. TOC values ranged from 0.1 to over 25 percent. The question becomes, how do you normalize to TOC with "unrealistically" high TOC values. Can you trust the TOC data? EqP predicted toxicity, but none was observed in laboratory bioassays.

> *[A discussion occurred on whether or not EqP and sediment quality criteria (SQC) based on EqP are meant to be predictive of toxicity. The EPA proposed SQCs based on the EqP methodology are meant to indicate a concentration of contaminant below which effects are not expected to be observed according to the ambient water quality criteria (AWQC); in other words, a contaminant concentration that is protective of the majority of the benthos. The EqP methodology, if coupled with* LC_{50} *can be predictive of the same toxic effects for which the* LC_{50} *was derived.]*

As previously stated, AVS and EqP are tools, but sometimes these tools don't work. Tools and screening procedures all have advantages, disadvantages, and assumptions. There is no "single, perfect, universal tool."

[A general discussion occurred at this point supporting Dr. Chapman's statement: "There is no 'single, perfect, universal tool." No single tool will supply all the necessary data for making decisions at any site. Different tools supply different information, and the tools to be used at any particular site depend on the conditions at the site as well as the questions being asked. It was also pointed out that the screening process is not a simple yes or no process, it is a general evaluation of existing data, based on the questions needing to be answered, in order to focus future expertise and resources on where they will be most beneficial.]

There are many additional issues that must be explored before the AVS and EqP approaches can be utilized to their fullest extent. These issues include estuarine conditions—what are the salinity effects on metals; riverine conditions and freshets—what other variables must be evaluated; routes of exposure—food vs. pore water, and validation—what is it and what does it involve?

Certain Chemical Aspects of Heavy Metal-Sediment Interactions: The Role of Organic Carbon and the Kinetics of Metal Sulfide Oxidation

John Mahony

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The purpose of this presentation is to discuss the role of organic carbon in heavy metal binding in sediments relative to pore water concentration and bioavailability. Our work arose from the anomaly in sediments that had very high SEM/AVS ratios, with respect to Cu (i.e., much >1) and yet were not toxic. Without any experimentation, we concluded that something else was binding the Cu and based upon the available literature, we believed organic carbon was the binding material. We conducted a series of experiments, and based on the results of that work, we concluded that organic carbon is not terribly important for some metals (i.e., Cd), but it is for others (i.e., Cu and Pb). The organic carbon concentration in sediment invariably explains some of the anomalies in the results obtained to this point. However, there is no general correlation between AVS and TOC.

To study the role of organic carbon binding in sediments, we designed a system that keeps total anaerobic conditions throughout (i.e., the sequential batch titration procedure) and used Cd, Pb, and Cu as our test metals. It is essential to maintain anaerobic conditions because iron sulfide, which is essentially the AVS, will be converted to hydrous iron oxides, thereby destroying the ability to make measurements of binding or AVS. The system consists of a series of flasks containing sediment and de-aerated water. Nitrogen gas is continuously pumped into the flasks to maintain anaerobic conditions. Metals are added to each flask at known concentrations, with one flask being the control (i.e., no metal addition). This system is fairly uniform with equilibrium being reached. We believe we have a quasi-pore water condition, so that the metal concentration that we measure in the overlying water is actually what one would find in pore water under similar circumstances. We also measure AVS in the sediment at the same time that we perform the experiment. This system prevents sediments from converting any of their chemical properties during their exposure to metals.

The system was verified (i.e., determined that the metal is actually reacting with the "iron sulfide" in the sediment) by adding iron sulfide (or sediment) and the metal of concern to each of the vessels, and then measuring the concentration of both iron and metal in the water. When you reach a molar ratio of 1, the AVS is exhausted (i.e., no more binding sites for the metal) and the metal is released to the pore water. As metal is added to the system, iron is released until the point is reached where it levels off because there is no more AVS and no more iron can be released by adding more metal.

The organic carbon in sediments responsible for binding metals is primarily humic material. The quality of organic matter does make a difference, and in some cases possibly a very large difference. It is suggested that, for SQC, organic carbon does play a role in partitioning metals and, in some cases, can play a dominant role. Binding between the humic material and metals occurs as the humic material comes in contact with water, the carboxyl and phenolic groups become protonated, protons are released, and the metal is sorbed. However, these are not true chemical bonds because the process is absorption, not a true displacement reaction. The bonding energies here are less than those energies that would be found in true chemical bonds.

The sorption theory has a number of different aspects to it, and perhaps the simplest of these is the Langmuir Theory. We have used the Langmuir Theory to understand the relationship between AVS, organic carbon binding, and metal availability. At low aqueous concentrations and low sorbed concentrations, the Langmuir Theory can be used to estimate the partitioning coefficient. Instead of using the sorbed concentration in the usual context (i.e., mg/kg or moles/g-dry), we use mg/g-organic carbon.

For each of the metals used in the Anaerobic Sequential Batch Titration Procedure we developed three curves: the first shows a total sorbed metal, the second is non-AVS sorbed metal, and the third is organic carbon normalized sorbed metal. In addition to what was reacting with the AVS, you're plotting the metal that was sorbed divided by the organic carbon content of the sediment. For Cu, there is a very tight, well-defined trend concerning the absorption phenomenon, and the trend follows the Langmuir Theory very well. The trend was not so dramatic for Pb. From our data and use of the Langmuir Theory, we showed the maximum amount of metal that can be adsorbed on an organic carbon normalized basis. Organic carbon becomes important for Cu and Pb because there is a large amount of sorptive capacity based upon the carbon concentration. Metals first bind to sites associated with AVS and then to organic carbon sites. By knowing the sorptive capacity of sediments (i.e., the amount of organic carbon present) and the concentration of AVS, the ability of sediments to remove metals from solution (i.e., from the interstitial pore water) can be determined. This binding action then makes the metals unavailable for biological uptake.

"Does organic carbon have an affinity for other metals?" is a commonly asked question. Our next step in understanding metals' availability is an attempt to answer this question. Our work has focused on a particular suite of metals because of the electrodes available at the time to measure metal concentration. As analytical techniques improve our research into the significance of other metals will continue.

The Influence of Sediment Stability and Disturbance on Marine Amphipod Toxicity

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Bioassays are routinely used in the Superfund process to identify potential threats to resources associated with exposure to sediment-bound contamination. It is important that the potential causes of observed toxicity be identified so the appropriate remedial options can be considered. We must be able to distinguish between effects due to physical factors (i.e., grain size) and various types of contamination because different clean up actions will be applied based on the cause of toxicity (i.e., physical factors vs. non-persistent chemical compounds that are rapidly lost or changed vs. persistent chemical compounds that tend to remain associated with the sediment and do not change chemical structures rapidly). The results of laboratory toxicity tests are used to initiate clean up activities; remediation is often terminated when the laboratory tests indicate clean up goals have been attained and the residual contamination will not adversely affect the environment or human health. We, the scientific community, are good at identifying effects due to exposure to a single contaminant, as well as predicting what the concentration and effect will be, based upon equilibrium partitioning theory and AVS. However, we are less certain when it comes to complex contaminant mixtures.

A fundamental area of research in our Marine Sciences Laboratory (MSL) is the development of methods to better distinguish between potential causes of the observed effects. Our approach, a stability/disturbance testing scenario, can be used to implicate broad classes of potential factors that cause toxicity. I would like to use this platform to present the theory behind our approach as well as examples of its application.

The stability/disturbance testing scenario involves conducting multiple 10-day toxicity tests using the burrowing infaunal amphipod, *Rhepoxynius abronius*. Sediment treatments are tested following standard procedures (ASTM 1992). The amphipods are added to the test containers after varying time intervals following initial disturbances created during the preparation of the sediment treatments (up to 100 days). The final exposure occurs after redisturbing sediment that has undergone the entire period of stability. The change (or lack of change) in survival compared with the degree of disturbance and periods of stability provide indications of which sediment characteristics controlled the initial toxicity results.

Differences in test organism sensitivity among various test periods are evaluated by conducting reference toxicant exposures and assessing amphipod survival in native (control) sediment. These procedures allow comparisons to be made among tests conducted at different times.

The primary question examined under the stability and disturbance testing scenario was whether disturbance of sediment conditions influences toxicity. Tests conducted at MSL have revealed three basic patterns of response. In the first response pattern, there is no change to toxicity under any of the conditions of stability or disturbance. In the second and third response patterns, toxicity decreases during increasingly longer periods that the sediment is left undisturbed. The difference between the second and third case is that under the condition of sediment redisturbance toxicity will either increase or decrease relative to the stable conditions. In Response Pattern 2, the redisturbance toxicity is equal to the final toxicity observed after periods of stable conditions. In Response Pattern 3, the redisturbance toxicity increases beyond the toxicity observed during stability and approaches the toxicity observed during the initial disturbance tests conducted prior to allowing stable conditions to develop in the laboratory.

Response Pattern 1

When disturbed sediment conditions provide the same level of toxicity as stable sediment conditions, the contributing factors are proposed to be those sediment attributes that do not change as a result of disturbance. An example of this type of sediment characteristic is sediment grain size. The grain size of a sample is unaffected by disturbance, and the toxicity resulting from less than optimum grain size distributions is the same under both conditions of sediment disturbance and stability.

Response Pattern 2

When toxicity decreases during periods of stability and does not increase after redisturbance following long periods of stability, the cause of the observed toxicity is probably related to a change in the availability of toxicants through time. Examples of contaminants that appear to behave in this manner are: interstitial water ammonia, easily metabolized toxins, strongly bound contaminants, or volatile materials. The toxic forms of these materials are lost or sequestered during the sediment stability period, and do not become bioavailable after disturbance.

Response Pattern 3

When disturbance increases toxicity, the contributing factors are those sediment contaminants that again become available in toxic form after disturbance. Examples of contaminants that appear to become more bioavailable during disturbance include non-polar organic compounds. The disturbance appears to increase the availability of the toxic forms of these chemicals. One method that might explain this increase in toxicity is that disturbance increases the dissolved forms of the contaminants that are thought to be the most toxic. The same process may occur during disturbance of sediments with heavy metals that are bound to AVS.

> *[This topic initiated heavy discussion from the audience. It was suggested that the spiked-sediment tests on which EqP and AVS are based are realistic and not "worst case". There was general agreement that spiked sediments need to be aged before being tested. Furthermore it was stated that field data compared to laboratory data indicate that the best laboratory data come from sediments that are disturbed as little as possible, and that 10-d acute tests with R. abronius are reasonably robust at predicting whether or not non-acute effects will be manifest in the field.]*

The experimental procedure and observed response patterns outlined above were used to help explain experimental results obtained from different studies conducted at the MSL. Three examples of the use of this testing strategy were evaluated. In the first case, sediments with no measurable chemical contamination obtained from fine-grained sediments of Alaskan Glacier Flour origin; coarser but still fine-grained sediment from Oakland Harbor, California; and coarse-grained sediment from the test organisms native sediment at West Beach, Washington were evaluated over periods of more than 60 days. In each case, the survival of the test organisms was consistent throughout the period of exposure during varying periods of stability or under disturbance conditions. Survival in Glacial Flour sediment was approximately 68 percent; in the coarser, but still fine-grained sediment from Oakland Harbor, the survival was 75 percent; and in the coarse-grained native sediment from West Beach, the survival exceeded 90 percent.

In the second response pattern, sediment cores were obtained from hard-packed sediments that were buried more than 10 feet deep. One of these sediments (the older bay muds of Richmond Harbor, California) contained no measurable persistent chemical contaminants (pesticides, PAH, polychlorinated biphenyls (PCB), organotins, etc.); the other sediments from the deeper more compacted sediments in New York Harbor had a range of chemical contamination. The survival of test organisms after the initial disturbance and mixing of sediment was very low for each of these areas. As the time under stable conditions increased, survival also increased until it was more than 85 percent after periods of more than 40 days of stability. The final tests under redisturbed conditions showed the same high survival observed during the latter stable conditions.

Under these examples of Response Pattern 2, the mortality of the amphipods was attributed to the concentrations of ammonia in interstitial water that were high at the outset of the experiment, eventually reduced during stable conditions, and remained low under redisturbance. One explanation for elevated ammonia concentrations during the early parts of the testing period that were not encountered during the latter periods, is that the nitrogen cycle and subsequent ammonia concentrations are controlled by bacteria. The populations of these bacteria were not sufficiently large at the beginning of the experiment because of their rarity in deeply buried sediments. Once the sediments were under aerobic conditions the bacteria were able to increase in abundance to population sizes that were able to denitrify the available ammonia production from decay of organic matter to the less toxic nitrates and nitrites.

In the third response pattern, the initial disturbance and mixing of sediments resulted in high toxicity. Under increasingly longer periods of stable conditions the survival increased. However, under the redisturbance condition (after long periods of stability) survival decreased again to the level observed during the original disturbance period. Sediments that provided these types of responses were obtained by performing sediment spiking experiments using multiple sediment types and various concentrations of radio-labeled DDT and endrin as contaminants. We also used natural sediments that were contaminated with PAH obtained in Alaska and another sediment obtained from Oakland Harbor, California with elevated PAH and tributyltin (TBT). The increase in toxicity under disturbance situations and the decrease under stable conditions is hypothesized to be a result of the disturbance of equilibrium conditions between more bioavailable (dissolved) and less bioavailable phases of the contaminants. The disturbance increases the availability and exposes the test organisms to more toxic fractions of the contaminants.

The stability and disturbance testing procedure outlined above appears to allow investigators the ability to distinguish between groups of potential causative factors of toxicity. The changes in toxicity seem to be related to physical and chemical changes that occur during the periods of disturbance and stability. Our present testing protocol of disturbance and mixing of sediments just before testing appears to be a method that maximizes potential toxicity, and as a result, is protective of the environment and therefore more conservative.

The issue now becomes, what should be done with this type of information? If toxicity is observed that does not change under stable and disturbed sediment conditions then the effect is potentially due to factors that are not influenced by disturbance (e.g., sediment grain size or food quality or quantity). If toxicity is influenced by disturbance and stability, then the factors controlling the toxicity are probably related to the influence of disturbance on the bioavailability of the contaminant. This approach to analyzing sediment toxicity is different from our standard practices, but it may be a method that will allow us to identify and control for various toxicity effects. The thrust of this research is that the type of factor causing toxicity should be determined because sediments should be processed and remediated differently based on the type of contaminant causing the observed responses.

There are other issues that should be addressed when evaluating laboratory bioassay data, For example, are we underestimating the effects in the environment? A response observed under laboratory conditions will likely also be seen in the field, but we can not be sure there will be no effect in the field when no effect is observed in the lab. Also, the effect of sediment holding times should be reevaluated -- are six months too long? The use of sediment quality criteria with respect to sediment evaluations, and the ability to predict effects of contaminant mixtures are among the issues that need further study.

> *[An extensive discussion occurred at this point, first over other approaches for determining which sample component is responsible for observed toxicity (e.g., concurrent elutriate tests and TIE procedures), then over sample handling procedures. The questions of concern were: How do sample handling procedures affect toxicity test results? Are existing protocol handling procedures appropriate? and What are the proper handling procedures? It was agreed that sample handling is an important issue but nothing was resolved.]*

K_{OC} and K_{DOC} in Sediment Pore Water

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When I was asked to come to this workshop, I thought long and hard about what subjects to discuss. What topics would really meet the objectives of this workshop? This workshop deals with how to use EqP and AVS to evaluate the problems of hazardous waste sites. I have therefore tailored my talk to address this topic. My approach has been to examine the recent literature on partitioning of non-polar organic compounds to organic carbon and couple that with work we have been conducting at the Waterways Experiment Station.

Clay particles are coated with iron, manganese, and aluminum oxides; organic matter; and various other minerals. This system is not as simple as it appears when examining an idealized representation. Nature is altogether more complex. Rebhun et al. (1992) examined plating out humics onto clay particles. They found that they could attain approximately 60 percent coverage of the clay surface, while the other 40 percent remained uncovered. After that point, the organic matter began stacking on other organic carbon. This study demonstrates, in addition to our own experience with contaminant sediments from such places as New Bedford, Indiana, and Black Rock harbors, that the situation is rarely simple. I like, and use, the partitioning theory because I'm a chemist. I think sulfides are important and I think organic carbon is important in controlling the concentrations of metals and non-polar organics, respectively, in pore water. Things that are predictable make our job easier, but when it comes to actual, real-world sediments, we are often surprised. In other words, the data do not fit our preconceived notions.

Rebhun et al. (1992) investigated partitioning in a system consisting of 10 percent clay, 90 percent sand, and various concentrations of adsorbed humic acid. Until the concentration of humic acid reached approximately 0.5 percent, a linear relationship existed between the partitioning coefficient and the fraction of humic material. Below 0.5 percent humic acid, behavior became non-linear as other factors, such as partitioning to clay minerals, began to get more important. At higher organic carbon contents (> 0.5%), organic carbon is the dominant sorbent, but at lower levels, other sediment phases become increasingly important. A review of the literature shows that many factors affect K_{OC} and K_{DOC}. These include pH and/or ionic strength (Schlautman and Morgan 1993), surface reactions (McGinley et al. 1993), and competitive sorption behavior with mineral-bound humics (Murphy et al. 1994).

I attended the American Chemical Society (ACS) national meeting in San Diego in March and McGroddy reported on the work she and Farrington had done (McGroddy and Farrington 1994). They found that inputs of PAHs in the form of soot affected the availability of PAHs and lowered their partitioning into pore water.

Contamination in sediments can affect the partitioning behavior of PAHs. Chin and Gschwend (1992) found that sediment pore water colloidal material from a contaminated area are better sorbents for PAHs than colloidal material from cleaner areas by a factor of two. It may be a result of higher lipid content in pore water, higher oil content, or the non-polar nature of organic matter. Examining the nature of organic matter is a difficult problem. There are four to five different methods researchers are using to investigate the polarity of sediment and soil organic matter. Of course, oil contamination in sediments, something that occurs in just about all man-impacted sediments, will enhance the absorption of non-polar organic contaminants. From our own experience, anomalous sorption results occur when coal or slag is present in sediment. These man-generated components bind non-polar organic contaminants more tightly than do humic acids.

The hydrogen/oxygen (H/O) ratio is one measure of the aromaticity of carbon present in sediment. The higher the ratio (i.e., the more hydrogen with respect to oxygen) the higher the aromaticity of the organic carbon. The data of Grathwohl (1990) and Garbarini and Lion (1986) showed that as the log H/O ratio increases the log K_{OC} also increases. Gauthier et al. (1987) showed that as the fraction aromatic carbon in humic acids isolated from sediments increased, K_{OC} values obtained for pyrene increased. These results are what you would expect, because the higher the fraction of aromatic carbon, the more hydrophobic the organic carbon becomes, increasing the ability of the carbon to sorb non-polar organic contaminants. These results indicate that the quality of organic carbon in sediments, specifically its aromatic character and the kind and extent of human impacts, affect the K_{OC} of non-polar organic contaminants.

Davis (1993) measured K_{DOC} values for pyrene with humic substances isolated from soils and water. He did not see a linear relationship between K_{DOC} and the fraction aromatic carbon. This implies that partitioning of non-polar organic contaminants to sediment organic carbon may be even more complex. We don't completely understand the situation, which should lead to caution.

Pore water contains contaminants that are truly dissolved and bound to dissolved organic carbon (DOC). Contaminant concentration measurements in pore water often show high concentrations, occasionally even higher than solubility limits. This is because the bound contaminant concentration increases the apparent pore water concentration. To examine the constancy of K_{DOC}, we tested a wide range of sediments with different concentrations of TOC. Pore water TOC concentrations from these sediments ranged from 3.1 ppm up to 177 ppm. Pore water was separated from sediment by centrifugation and spiked with radioactive fluoranthene. The bound and truly dissolved fluoranthene fractions were separated using Peter Landrum's reverse phase partitioning method. We then plotted truly dissolved fluoranthene concentrations versus fluoranthene associated with organic carbon in pore water. Good linear correlations were obtained for each pore water. The lowest r^2 was approximately 0.85, but the different pore waters showed very different slopes, indicating very different K_{DOC}s.

Measured K_{DOC}s are from two to four times lower than predicted by partitioning theory. Therefore, using K_{OW} to predict K_{OC}, and then assuming that K_{OC} equals K_{DOC}, would introduce significant error into the situation. As we previously observed with K_{OC}, the source of organic carbon strongly affects partitioning of non-polar organic compounds.

Now, to the bottom line. What does this mean for use of AVS and EqP at hazardous waste sites. First of all, K_{OC} and K_{DOC} may not be predicted by K_{OW} and may need to be measured, especially in contaminated sediments. Hazardous waste sites are by definition contaminated and will pose real problems in predicting contaminant mobility and behavior. We really have to be careful. AVS and EqP may be used as a screen, but too many sediment processes that we don't fully understand are occurring to rely on AVS and EqP for criteria. It is very difficult to make good TOC measurements in some sediments, much less use TOC as a predictive tool. Factors other than TOC can affect partitioning, especially in sediments impacted by people.

Porewater Toxicity Testing: A Direct Measure of EqP

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Over the past seven years, I have been involved in developing, evaluating, and field validating porewater toxicity tests. Today I would like to describe these tests and summarize some of our recent field studies. Our work suggests that porewater toxicity testing provides a direct measure of EqP. A primary advantage of the porewater toxicity test approach is the ability to conduct tests with very sensitive life stages of sensitive species, which is not possible with the solid-phase tests that are now commonly used by regulatory agencies. Species that have been used successfully in porewater testing include polychaetes (*e.g., Dinophilus gyrociliatus*), fish larvae (e.g., red drum, *Sciaenops ocellatus*), benthic copepod nauplii (e.g., *Longipedia americana*), and sea urchins (e.g., *Arbacia punctulata*). The polychaete *Dinophilus* is quite small (approximately 1-mm long) and has a very short life cycle (7 days), which allows us to conduct full life-cycle toxicity tests using a minimum amount of pore water. The primary endpoint for the polychaete test is egg production. For the red drum, we use developmental abnormalities as the endpoint. Again, it is a very short test, with effects usually elicited within 24 hours of exposure. We have conducted several different tests with the sea urchins, including cytogenetic, fertilization, and embryological assays.

In the past, we have routinely used a pneumatic porewater extraction device that allows us to quickly process large numbers of samples to minimize the variability associated with storage effects. Normally, samples are processed within 24 hours of receipt by our laboratory. Some recent studies suggest that centrifugation may minimize the loss of some highly hydrophobic contaminants. With the sea urchin assays, we are able to test a large number of samples simultaneously, thus minimizing the between-test variability.

We have conducted field validation studies with sediments from Galveston and Tampa bays. In the Galveston studies, no toxicity was observed with the standard amphipod tests, but toxicity was observed with the sea urchin fertilization and embryological development assays. The Tampa Bay sediments also exhibited excellent concordance between the predicted and observed toxicity for the sea urchin fertilization test but not for the amphipod test. We believe that the amphipod tests underestimate toxicity because the sediments are manipulated and "flushed" with clean water, replacing the pore water that has become equilibrated with the sediment-associated contaminants. We believe that this use of pore water provides a more realistic representation of the contaminants that are potentially bioavailable to infaunal organisms.

The sediment triad approach was used in a large multidisciplinary study conducted in the Gulf of Mexico. Several stations were revisited over a period of two years; sediment chemistry, laboratory toxicity studies, and benthic community structure were measurement endpoints. The most interesting data were generated for an oil production platform situated close to the most northerly occurring tropical reef and marine sanctuary. Because of its proximity to the reef, drilling and production discharges from an oil platform were shunted to within about 10 meters of the bottom. Laboratory toxicity test results indicated the urchin embryological development assay was more sensitive than the urchin fertilization assay for the contaminants at this site. During this effort, we had the opportunity to collect sediments during the winter, and then again six months later in the summer. Our toxicity test results were very reproducible and the same spatial pattern in toxicity was observed. We also subjected selected porewater samples to a suite of toxicity tests. Toxicity tests conducted with polychaetes, sea urchins, and benthic copepods had a high correlation, indicating that the urchin assay is a good surrogate for the kinds of organisms that normally inhabit interstitial water.

Bulk sediment chemistry data for Zn, Cd, Pb, Cu and mercury (Hg) were compared with threshold effects levels (TELs) and probable effects levels (PELs) of MacDonald (1994) and the comparable values (i.e., effects range low [ERL] and effects rang medium [ERM]) of Long et al. (1995). In the Tampa Bay study, there was excellent agreement between the predicted and observed toxicity with the sea urchin porewater toxicity test, but little or no concordance with the amphipod solid-phase test. There was also a high degree of association between the presence of certain contaminants and the toxicity observed with the sea urchin fertilization assay. Similarly, there was a high degree of association between the sediment concentrations of several metals and the observed toxicity with the sea urchin embryological development assay at the highly contaminated oil production platform in the Gulf of Mexico, where excellent agreement between the predicted and observed toxicity was also seen. The sea urchin fertilization and embryo development tests with pore water provide measures of chronic sublethal impacts on sensitive life stages of sensitive organisms. The PELs, therefore appear to be more predictive of these chronic sublethal impacts than the more obvious acute lethal effects. Likewise the TELs appear to be protective for chronic sublethal impacts as well, as demonstrated by the high degree of concordance between the TEL predictions and the observed toxicity with the sea urchin porewater tests.

It is not particularly surprising that there is often little or no agreement between the predicted toxicity and toxicity observed with the amphipod test. The amphipod test uses an adult life stage (the least sensitive stage) and mortality as the endpoint. In addition, the standard amphipod test protocol underestimates the potential toxicity of contaminated sediments because the pore water, which has taken weeks or perhaps months for the hydrophobic contaminants to come to equilibrium, is flushed out and replaced with fresh overlying water before the start of the exposure. The combined insensitivity of the test species and endpoint and the artificial manipulations of the test sediment prior to exposure, result in a test that has limited ability to predict the potential chronic impacts of moderately contaminated sediments.

Predictions of Cadmium Accumulation in Benthic Organisms

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It is evident that the development of rational, efficient and economical strategies to manage the problem of metal contaminated sediments will depend on our ability to predict how these remedial actions would improve the water quality and affect aquatic organisms. The prediction of metal accumulation/toxicity in benthic organisms is complicated because these organisms can accumulate trace metals from various sources: sediment, water, and food. The bioaccumulation of metals from each of these sources is influenced by numerous factors: pH, ligand concentration and type, and various sediment components. To further complicate the picture, a relationship exists between dissolved and particulate metal. Therefore, predicting the bioaccumulation of metals by benthic organisms will require an understanding of the biogeochemical processes involved. I would like to illustrate this with Cd.

During the last few years, I have been involved in the measurement of Cd in several compartments of the sediment-water system. These compartments include: interstitial water of the upper (oxic) layer of the sediment, the adjacent several centimeters of the overlying water, the particulate component of the oxic sediment and the diagenetic iron (Fe) and manganese (Mn) deposits (Fe and Mn oxides). Cd concentrations were also measured in various benthic organisms including freshwater bivalves (*Anodonta grandis*) and herbivorous insect larvae (*Chaoborus punctipenis*).

Our study sites were from about 40 lakes exhibiting a wide range of pH and Cd concentrations. These lakes were distributed over an area of about 350,000 square kilometers in the provinces of Ontario and Quebec.

First, I would like to show you that the Cd concentrations found in field collected *A. grandis*, agree with the free ionic activity model, or to be more correct, do not disagree with it. This means that the concentration of Cd in the organism is equal to a constant, times the dissolved Cd^{+2} concentration in the overlying water. Second, we will look at the relationship of Cd in the sediment and the overlying water. This will be described by using sorption reactions with the aid of apparent surface complexation constants. Then we will combine these two types of concepts, the free ion activity model and the surface complexation model to predict Cd in *A. grandis* using sediment variables. Third, I will apply this model to another organism, *Chaoborus*.

To test the derived free ion activity model relating the Cd level in the organism to the Cd in the water overlying the sediments, we plotted field data, tissue concentrations from *Anodonta* versus free Cd ion concentrations in overlying water collected with peepers. The results are a linear regression with an r^2 of 0.81. While this result is interesting, the free Cd concentrations are very small, difficult to measure, and may be variable over time. Therefore we derived a formula relating the Cd level in the organism to the Cd in the sediment using sorption reactions.

Why do we use sorption reactions? We use them because if you do some thermodynamic calculations in the oxic zone of the sediment, you cannot find a solid phase that will precipitate and control the concentration of trace metals. You have to think of other types of reactions. The one that is probably most logical is the sorption reaction. An oxic sediment contains few phases that can sorb trace metals. You can think of iron oxide, manganese oxide, organic matter, and maybe aluminum oxide, but the latter has not been fully demonstrated.

The free Cd ion concentration ($[Cd^{+2}]$) can be related by sorption reactions to the sediment Cd, iron oxide and organic matter concentrations and the pH of the water, all of which can be readily measured. Using the field data we generated plots of the measured tissue concentration versus the calculated $[Cd^{+2}]$ from the field sediment characteristics. This gave us a linear regression with an r^2 of 0.82. When we plotted the same tissue data against the total Cd concentration in the sediment the points were scattered all over the place.

We then applied this approach to data on *Chaoborus punctipenis*, an insect larvae that spends the day in the sediment and then migrates into the water column at night to feed on zooplankton. The resulting plots of *Chaoborus* Cd to the calculated $[Cd^{+2}]$ showed a very low r^2, presumably due to the low values of *Chaoborus* Cd found in the acid lakes. The correlation is much improved if competition is assumed at the biological uptake sites between H^+ and $[Cd^{+2}]$. *Chaoborus* Cd then becomes a function of $[Cd^{+2}]/[H^+]+K$, where K can be considered as an 'acidity constant' of the binding sites. This was not a problem for the bivalve because no bivalves were found in the acid lakes.

Summing up, any model used to predict metal levels in organisms must be field calibrated, and to be useful, must be able to predict results at locations (lakes) other than those used for the calibration. To be useful the models also must be based on an understanding of the geochemical and biological processes involved in bioavailability and bioaccumulation of metals. Such a model would be a very useful tool for management of contaminated sediments. We have attempted to create such a model here. It is not perfect and more work needs to be done on it (e.g., the inclusion of the role of Mn oxide). Field and laboratory work need to be coordinated because what is taking place in the laboratory cannot necessarily be extrapolated to the field. But, we have made a start.

Predicting the Toxicity of Metals-contaminated Sediments using AVS and Interstitial Water Normalizations: Results from Spiked Sediment Laboratory 10-day Lethality and 4-month Colonization Tests

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The purpose of my presentation is to provide information, developed from sediment spiking experiments, that will help you see why we believe SEM/AVS ratios and interstitial water metal concentrations help explain the bioavailability of metals in sediments that can be used to predict which sediments may or may not be toxic due to metals. A number of people, other than myself, could be giving this presentation because this has been truly a collaborative effort. The presentation will be divided into two principle sections: the first deals with 10-day lethality tests in which interstitial water concentration and SEM/AVS ratios were measured; the second is a 118-day salt-water colonization experiment conducted with Cd-spiked sediments.

The lethality test discussions are divided into two parts: the first part deals with the amphipod toxicity tests that were conducted at the EPA Narragansett, Rhode Island Laboratory, because all of these tests had essentially the same experimental design. I'll then include all the other salt-water toxicity test results from experiments conducted at Narragansett Laboratory and the Battelle Laboratory in Sequim, Washington, as well as freshwater test results from the EPA Duluth, Minnesota Laboratory. This will include data already published by DiToro and others (DiToro et al. 1990, 1992) on Cd, Cd and Ni, and data produced by Walter Berry, others, and myself at Narragansett on Cu, Pb, Zn, and mixtures of metals. The mixture's data will be used to show why the AVS normalization requires the summation of the molar concentrations of metals.

The experimental design for all tests followed the same general procedure. Metals were added to vessels containing sediments, stirred and allowed to equilibrate for 4 to 10 days. A typical experiment contained a control and SEM/AVS ratios of 0.1, 0.3, 1, 3, 10, and sometimes 30 and 100. Sediments for each treatment were placed in four individual chambers; two chemistry and two biology replicates. On day zero of the 10-day tests, one chemistry replicate was sampled to determine AVS, SEM, and total metals. Also on day zero, between 5 and 20 organisms of the appropriate species were placed in the three remaining replicates. Peepers had been placed in the sediments of these three replicates the day before testing began. At the end of the tests, the AVS, SEM, total metal, and interstitial metal concentrations were measured in the chemistry replicate. The biology replicates had the interstitial water removed from the peepers and stored before chemical analysis. The sediments were sieved to check for survival of the test organisms.

Typically, there were two to three sediments tested with a range of AVS concentrations for each of these experiments. These were all flow-through experiments, so we are reasonably sure that the organisms were responding to the sediment-associated metal or the interstitial metal but not the metal in overlying water.

Test data were evaluated on the basis that sediments were classified as non-toxic, when there was less than 24 percent mortality, and toxic when mortality was greater than 24 percent. When percent mortality was plotted against the SEM/AVS ratio, essentially no toxicity was observed when the ratio was <1.0. When the SEM/AVS ratio was >1.0, again, these data are only for salt water amphipods test conducted at the Narragansett Laboratory, most, but not all, of the sediments proved to be toxic.

When the SEM/AVS ratios were plotted against interstitial water metal concentrations and the SEM/AVS ratio was <1.0 most of the metal in the interstitial water was below our detection limits. When it was >1.0, interstitial water concentrations generally were high. It is this release of metals into the interstitial water causing very, very large concentrations, 10s, 100s, or 1,000s of toxic units, that explains why the chemistry in the anaerobic portion of the sediment is causing toxicity to organisms that live in the aerobic zone.

Next we plotted toxicity against interstitial water toxic units (IWTU). The IWTU is the interstitial water concentration divided by the metal-specific water only LC_{50} for the specific test organism. The results were generally what was expected. Below one IWTU the sediments displayed less than 50 percent toxicity, and above one IWTU most of the sediments had greater than 50 percent mortality. Some exceptions, of course, did occur both above and below one IWTU. Non-toxicity in sediments with IWTUs >1.0 were probably the result of other factors that are controlling availability in interstitial water samples.

We also spiked sediments with equi-molar concentrations of Ni, Cu, Zn, and Cd and plotted the release of these metals into the interstitial water. Based on the metal sulfide solubility constants for these metals, the expected order of release would be Ni, Zn, Cd, and Cu. This is exactly what was observed using sediments from two different locations. These results emphasize the utility of a fundamental understanding of the chemistry of the metals in sediments to help interpret observations from sediment risk assessments.

Now we're going to look at, not only our amphipod data, but all the data for spiked sediment tests from published and unpublished sources, for freshwater as well as salt water sediments. The same patterns appear as before. When the SEM/AVS ratios were <1, essentially no mortality was observed; when ratios were >1.0, not all the sediments were toxic, but a large percentage of them were. There was little if any difference between the freshwater and salt water data.

The reason some of the sediments that had relatively high SEM/AVS ratios, but no observed toxicity, may be biological rather than chemical. In tests conducted with *Neanthes arenaceodentata*, a very complex matrix of worm burrows was observed in the sediments at low SEM/AVS ratios for sediments spiked with Ni. When the ratios exceeded about 5.7, the burrowing depth was diminished. At higher ratios the worms survived by essentially remaining on the surface, avoiding the contaminant.

Summing up this collection of data, when the SEM/AVS ratio was ≤ 1.0, the sediments were not toxic 96 percent of the time. When the ratios exceeded 1.0, the sediments were toxic 74 percent of the time. The same kind of numbers occur when IWTU are used for the prediction (94 percent, 80 percent). If SEM/AVS ratios and IWTUs are combined the prediction of non-toxic sediments doesn't improve much (97 percent); however, the prediction of sediments that are toxic improves markedly (88 percent). We believe it is important not only to look at the SEM/AVS ratios, but interstitial water concentrations as well. It really helps you to understand whether toxicity in field sediments is associated with metals.

The final portion of my presentation will examine the results from a chronic toxicity test that I developed a long time ago at the Gulf Breeze, Florida Laboratory; it happens to be my favorite toxicity test. It begins with sediment filled aquaria, that over time are colonized by larvae and other life stages of benthic organisms occurring naturally as plankton in the unfiltered sea water flowing through the aquaria. In the initial tests using this experimental design, chemicals were added to the incoming water, but in the last 4 or 5 years there have been a number of tests conducted with spiked sediments. Typically, there is a control and three contaminant treatments, with usually 6 to 10 replicates. In the experiments that have been conducted to date, an average of 7 phyla, 44 species, and about 3,000 individual animals were found per test. These chronic tests last from six weeks to four or five months. They test the most sensitive life stages of marine organisms because the settling larval stages are exposed. The test endpoints included: abundance of individual organisms, numbers of species of different phyla, and diversity. The water exposure experiments are very sensitive. The no-effect levels have always proved to be less than the water quality criteria; the observed effect level of these tests has always been above the water quality criteria water concentration.

In the experiments using Cd spiked sediments that I will describe, there were 12 replicates per treatment. Four of these replicates were chemistry replicates and eight were biology replicates. The treatments we used were control and nominal SEM/AVS ratios of 0.1, 0.8 and 3.0. The chemistry treatments were sacrificed on days 14, 28, 56, and 117 of the 118-day test. Cores were taken of the sediment, which were about 8 centimeters deep, to determine the time dependent profiles of SEM, AVS, and SEM/AVS ratios. Peepers were placed in each of the replicates for interstitial water measurements. In the eight biology replicates, the first sampling event examined the periphyton communities that developed by about day 80. On day 118, all the biology replicates were sieved to remove the macrobenthic organisms.

The chemical analyses of homogenized sediments indicated that SEM, AVS, and SEM/AVS ratios were essentially constant throughout the experiment. However, the pattern of AVS concentrations with depth reveals sediment AVS profiles similar to those that occur in natural systems. These AVS profiles developed during the first two to four weeks, after which they stabilized. Thus, the SEM/AVS ratio in the 0.8 nominal SEM/AVS treatment was about 1.5 because of AVS oxidation. The profile persisted throughout the experiment for all the treatments.

By week six we noticed periphyton communities in the three lowest treatments and the control, but none in the 3.0 treatment until about day 80. When the biological data on macrobenthic organism abundance were analyzed, there was no difference at all between the control and the lowest treatment. The 0.8 treatment had reduced numbers of polychaetes and an unknown species of nematode, but had no effect on overall species abundance. The 3.0 treatment displayed numerous effects, including reduced numbers of annelids and annelid species, harpacticoid copepods, and nematodes. The average size of the worm *Neries succinea* also was reduced, which we believe was not a growth effect but due to a delay in colonization of these aquaria.

When cluster analysis was performed on the species presence/absence data, three clusters were produced: the control and the 0.1 treatment, the 0.8 treatment, and the 3.0 treatment. We know, because the same number of species was present in the 0.8 treatment and the controls, that the presence/absence data demonstrates that the species composition of the community has shifted. In the highest treatment both kinds and numbers of species were affected. When we compared the interstitial water Cd concentrations to the criteria continuous and the criteria maximum concentrations for Cd in water, the control and the lowest treatment were always below the chronic criterion. In the nominal SEM/AVS 0.8 treatment the measured interstitial Cd concentrations were always above the chronic Cd criterion and occasionally exceeded the acute criterion. In the 3.0 treatment the interstitial water concentration exceeded all water quality criteria. Therefore, biological responses observed agree with those expected given measured SEM/AVS ratios and interstitial water concentrations.

So I would like to conclude by saying that sediment toxicity data from spiked-sediment tests indicate that SEM/AVS ratios and IWTU are particularly useful tools in causally linking organism response to metals concentrations in sediments and that it seems to apply not only in acute lethality experiments but also to chronic effects.

Question Could you comment on the relatively small fraction of sediments that were toxic between the SEM/AVS ratios of 1 and 10?

Hansen Exceeding an SEM/AVS ratio of 1.0 may not result in available metal toxicity because other binding phases exist in sediments that bind metals and some of the organisms can avoid toxic sediments. Therefore, the prediction of toxicity is uncertain. Therefore, SQC for metals, if they ultimately are developed, would be used to identify acceptable, not unacceptable, sediments. John Mahony has been conducting research to combine AVS measurements and partitioning coefficients for organic carbon to permit prediction of those sediments likely to be toxic. We are hoping ultimately to be able to develop sediment criteria predictive of unacceptable sediments.

[Dr. Hansen recommends that readers should consult the "Briefing Report to the EPA Science Advisory Board on an Equilibrium Partitioning Approach to Predicting Metal Bioavailability in Sediments and the Derivation of Sediment Quality Criteria for Metals" (EPA-822-D-94-002) for a complete summary of this approach. It is available from the U.S. EPA, Office of Water Resource Center, at (202) 260-7786.]

Marathon Battery: What Were the Questions?

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The Marathon Battery Site is situated in New York State directly across the Hudson River from West Point. During the Civil War, the area was a cannon production facility. Later, part of the property became a Cd-Ni battery production plant, which is the source of contamination in the marsh and wetland areas. The final remedy and cleanup levels were difficult to achieve. There were many arduous conversations associated with these decisions, and we never went back when the work was in progress to redefine what the questions and goals were. The purpose of today's discussion is to evaluate, "what were the questions being asked, and what tools are appropriate for those specific questions?"

There was physical evidence of Cd sulfide in sediments; although a large amount of waste was discharged directly into the Hudson River and never reached Foundry Cove, the sediments near the Kimble Ave. sewer outfall contain up to 12 percent dry weight Cd and Ni. A cleanup level of 100 ppm Cd was used for this area, although some hot spots with sediment Cd concentrations greater than 500 ppm were left unremediated because of the high degree of disturbance associated with the physical removal effort. No specific cleanup level was established for Ni because it was assumed that Cd and Ni co-occurred and that by remediating for Cd, Ni contaminated sediments would also be removed.

A study was developed to evaluate monitoring options for the effectiveness of remediation. This plan included x-ray fluorescence measurements, sediment and water sampling for chemical analyses, benthos enumeration, in situ and laboratory toxicity tests with *Hyalella* (however, the in situ tests were not very productive), and bioaccumulation studies. One of the problems we faced was that the area under investigation was a very dynamic system that responds to tidal variations. Temperature and dissolved oxygen changed significantly over the course of 24 hours. One of our concerns was to be sure that the final monitoring plan accounted for the natural variability. We are frequently faced with having to interpret a data set that does not truly represent the system; in this case, the data set is fixed. The system has dynamic aspects. We review the data and think about the system in terms of that particular data set, and we often forget to go back and think about the *system* and review the original questions.

We did observe a high variation in *Hyalella* survival during the in situ exposures. This was probably due to test chambers silting over and low dissolved oxygen conditions within the chambers themselves. In some cases all animals were dead in one chamber while there was no mortality in the next; the data were very inconsistent. We found that approximately 1,000 ppm was the mortality breakpoint for both Ni and Cd. Sediments in East Cove were not uniform with respect to grain size. The bioaccumulation data are very interesting, with a decreasing rate of accumulation during the initial time period, followed by an increasing rate of accumulation. We believe that these results are due to a storm event that caused sediments to become resuspended, and thus making the metals more bioavailable. The bioaccumulation data show that in the more contaminated areas, more metals are accumulated. These data are presented as background information and to get an idea of what types of analyses were done at this site.

The collected data were used to answer the three major questions asked relative to site management:

(1) Are the sediments toxic, and if so, at what concentrations?

(2) Are the contaminants biologically active, or, what is the magnitude of food chain accumulation?

(3) Does the East Foundry Cove pose a threat as a source of Cd and Ni to the Hudson River system—is there a potential for catastrophic release to the Hudson River system?

For these particular site management issues, it was not important to know what was going on with respect to AVS. The third question was an important issue, but unfortunately the issues of concern were never well stated.

One major question was not asked: Which of the two metals is causing the toxicity? It was assumed to be Cd. When AVS was used, the results suggested that Ni was responsible for the observed toxicity, and not Cd. However, for this particular site, it was not critical that the toxic element be identified, because the two metals co-occurred and would be remediated simultaneously. It wasn't important whether it was Ni or Cd that was actually causing the toxicity relative to the remediation decision that was made.

Based on the questions we asked, using AVS as a screen *could* have given the wrong or incomplete answer (i.e., that there isn't a problem in East Foundry Cove sediments). The conclusion would be misleading, because that wasn't the question. One needs to be site-specific when evaluating contaminated sediments, and site-specific considerations are too complex for generic statements. One must think through the issues and the process, use the best tools, and be conscientious that the users of the tools are asking the right questions and applying the most appropriate tools. Asking the correct questions is an extremely important aspect of the entire process.

[A discussion followed the presentation concerning the utility of AVS and EqP for identifying areas to be remediated and the difference between a purely scientific evaluation and a Superfund site evaluation that is constrained by management and regulatory policy.

John Mahony (he was involved in field and laboratory work at this site) felt that using AVS as a screen would have indicated "hot spots" for cleanup but would not have indicated that cleanup was needed in some areas where cleanup occurred (whether this latter cleanup was needed was not clarified). However, in this case it did not matter what was causing the toxicity (the Cd or the Ni).

Walter Berry argued that there are two questions which should be asked, which are similar to the ACOE's complaints regarding dredging: (1) Are the in-place, relatively undisturbed sediments toxic? This question is one where AVS and EqP can play a role. (2) Are these metals potentially available to the system? This is a bulk sediment issue, not appropriate for AVS and EqP (as it is simply a question of whether the metals will be mobile and flushed into the Hudson River). The answer provided was that Superfund operates within a risk management/legal decision process.]

Use of SEM/AVS Ratios and Pore Water Metal Concentrations to Predict Metal Bioavailability in Field Sediments

Gary Ankley

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Dr. Ankley was unable to attend; his talk was presented by David Hansen.

As with the presentation that I gave yesterday, Gary lists a multitude of contributors to the data contained in this presentation, including scientists from the EPA laboratories at Duluth and Narragansett, John Mahony from Manhattan College, scientists from their contractor located at the University of Wisconsin-Superior, and the co-research with Landis Hare of the Université du Québec (Hare et al. 1994).

This presentation will focus on the results of laboratory toxicity tests, conducted with field collected sediments, from both salt water and fresh water sites, and field experiments that were conducted by the Duluth Laboratory and by Landis Hare, with laboratory-spiked sediments placed outside in the field.

The first part of the presentation is on field samples, tested in laboratory toxicity tests. The salt water location samples were Belledune Harbor in Canada, which had high concentrations of Cd, Pb and Zn; an unnamed salt marsh in Massachusetts that has high Zn, Cu and a variety of other metal concentrations; and Foundry Cove, which had high Cd and Ni concentrations. The fresh water sites included: the Keweenaw Waterway and Steilacoom Lake in Washington, both Cu sites; Turkey Creek, Missouri, a Zn site, and Foundry Cove, a Cd and Ni site.

The biological methods included 10-day lethality tests with fresh and salt water amphipods, marine polychaetes (*Neanthes* sp.), or the freshwater oligochaete *Lumbriculus*. Typically these tests had two biological replicates with 10 to 20 organisms per replicate. All had periodic or flow-through conditions to maximize the exposure by the sediment and interstitial water rather than the overlying water. Again, there were multiple replicates so that we could have both day zero and day 10 chemical and biological replicates.

The analytical determinations were: porewater metals, AVS, SEM, and total metals concentrations in the sediment.

When we examine a figure showing salt-water toxicity data from these three field sites, we see similar plots to those for the spiked-sediment data I presented in my talk yesterday. In a plot of mortality against the SEM/AVS ratio we rarely see toxicity below a ratio of 1.0, and above 1.0 sometimes there is and sometimes there isn't any observed toxicity. This lack of toxicity above a molar ratio of 1.0 occurs because of the presence of other metal binding phases in sediments. Similarly, mortality is generally lacking in sediments having interstitial water toxic units less than 0.5. When IWTUs exceed 0.5, toxicity may or may not occur. This is due to other binding phases within the interstitial water, such as DOC, that can complex the metals.

> *[An extended discussion ensued at this point addressing mainly regulatory and management issues. The key issues were: how to decide what sediments warranted cleanup based on this data, and the difference between management decisions and good science. The bottom line was scientific evaluations and management evaluations are not the same thing. Good science requires that you use all your available tools to assess a site, don't just rely on one. If you have metals contamination you should use both SEM/AVS ratios and IWTUs along with your other tools. Management decisions must take into account costs and practicality and thus are based on something less than ideal science.]*

I very strongly advocate that you use both SEM/AVS ratios and IWTUs as endpoints to classify risks from metals in sediments. With the spiked-sediment data our ability to classify sediments is about the same for SEM/AVS and IWTUs. With the field-sediment data, use of IWTUs was a bit better for predicting toxicity. If you are going to evaluate a site having sediment contaminated with metal, you really shouldn't rely on SEM/AVS analyses alone; you should also be measuring interstitial water concentrations. Either endpoint is acceptable to identify those sediments that are not likely to have toxicity. But if you are trying to sort out causality or identify which sediments and metals are toxic, then you need both endpoints.

Keweenaw Waterway, as you recall, was a Cu site with huge SEM/AVS ratios and interstitial water toxic units up to about 20. When the SEM/AVS ratios were <1, the sediment was non-toxic; when >1 10 out of 10 sediments were toxic. When the IWTU were <1, one of two was not toxic; when >1, 9 of 9 were toxic. In contrast, Steilacoom Lake, another Cu site, displayed no toxicity both when the SEM/AVS ratio exceeded one

(8 of 8 nontoxic) or were <1. The IWTU never exceeded 0.5, even in sediments having SEM/AVS ratios greater than one.

> *[John Mahony pointed out that when they measured the carbon in Steilacoom Lake they found it was very high, between 6 and 10 percent carbon, while the Keweenaw Waterway had virtually no carbon to bind excess metal.]*

Turkey Creek, a Zn site, had patterns of toxicity similar to the Keweenaw results, no toxicity below an SEM/AVS ratio of one and some toxicity above one. When the IWTUs were less than 0.5, 3 of 4 were nontoxic, and 1 of 3 was toxic when the IWTU exceeded 0.5.

The Foundry Cove data had SEM/AVS ratios from 0.5 to 189; IWTUs ranged from 0.4 to 110. Overall, 12 of the 16 sediments were toxic to *Hyalella*; only two were toxic to *Lumbriculus*, a species much more tolerant to these metals. When the SEM/AVS ratios were less than one, 4 of 5 were not toxic; greater than one, 11 of 11 were toxic. Here's an instance where molar exceedances were a perfect match with observed toxicity. When the IWTU was less than 0.5, one of one was non-toxic; 12 of 15 were toxic when there was greater than 0.5 toxic units. These data again bring home the point of the need to quantify both interstitial metal and SEM/AVS ratios.

When we look at a figure of SEM/AVS ratios versus percent mortality for the pooled data from the four freshwater sites we see the expected pattern: at ratios <1 no mortality observed; >1 some of the sediments were toxic and some were not. This absence of toxicity can be explained by the presence of other sediment binding phases such as organic carbon. We saw with some of the data that I showed yesterday that avoidance behavior also can affect the exposure zone of the organism thus reducing observed toxicity.

When we look at a plot of all the data from published and unpublished studies dealing with both spiked- and field-sediment toxicity tests, we see the same pattern as with the individual data sets: no toxicity at molar ratios ≤ 1, and a concentration-dependent response as the ratio increases above one. What's important is there aren't any data in the upper left quadrant of the plot, that is in the portion of the figure below a molar ratio of one and above 24 percent mortality. If, in your field study, data occurs in this upper-left-hand region, metals are likely not the cause of the observed mortality. The IWTU plot of all the data shows the same thing. Thus, both IWTUs and SEM/AVS ratios may be important indicators of non-metals associated toxicity.

Now we're going to begin talking about two experiments with spiked sediments that were placed in the field. Landis Hare spiked sediments with Cd and returned them, in trays, to the lake from which they had been taken. The study, which lasted longer than a year, looked at Cd and AVS concentrations, Cd bioaccumulation, and insect abundance and size. Based on sediment chemistry the treatments remained separate for the duration of the test. The insect abundance and size data were less discriminatory, possibly because many of the organisms leave the sediment and feed in the water column and may not return to the same tray. The bioaccumulation data showed that, with the species that are not linked intimately with the sediments, there is no difference in tissue concentrations as treatment concentrations increase. But for those species that are more tightly coupled to the sediments when the SEM/AVS ratios were <1, there were no differences or small differences in the tissue accumulation; once the ratio exceeded 1 there was a concentration-dependent accumulation.

Gary has a similar study in progress with treatments spanning a range of Zn SEM/AVS ratios, with horizon-specific chemistry and benthic community structure analyses. Preliminary results found measured SEM/AVS ratios clumped around one. He hypothesized that because the trays were placed in the pond at a time of sulfide production the sulfide reacted with the free Zn in the trays; thereby, tying up the Zn and reducing the Zn sulfide molar ratios. In the winter, the molar ratios that were supposed to be >1 were, <1. In the winter when we would have thought there would be oxidation of AVS, that did not occur in the high nominal Zn concentration sediments. Zn sulfide, which has a very low oxidation rate, was the only sulfide present. Therefore, SEM/AVS ratios in those treatments were maintained at a molar ratio of ≤. That was reflected in the measured porewater concentrations, where at the beginning of the experiment Zn was detected in pore water, but as the experiment progressed, the Zn concentration decreased to below detection limits. As a result, there were no observed effects on benthic communities.

The concern with extrapolating any toxicity test or chemistry measurement data to the real world is have you captured the exposure properly. This is particularly true when the collected samples have been homogenized. The concern is the microscale associated with organisms that burrow into the sediment and the structure of the oxic/anoxic zone. By homogenizing the test sediments, your conclusions based on these results may not be relevant to the microscale. I think, if you were here yesterday, you would have seen that the depth profiles of AVS found in some of the toxicity tests that we conducted, did in fact have microscale structure and likely relevance to the field. There is a lot of structure that occurs even in a toxicity test as a result of worms or other species burrowing. I believe that the telling information is the huge interstitial metals concentrations that do occur when the binding capacity is exceeded. I think they are sufficient to allow a reasonable linkage between homogenized lab sediments and field sediments. The evidence that I think is the strongest is the similarity in the peeper measurements made in the field at the salt marsh in Massachusetts and what we observed in the same sediments homogenized in the laboratory studies. We have folks here arguing that you shouldn't be measuring AVS because of fine scale structure in the field. So how fine a scale do you want to do this chemistry folks? Do you want to get down to the millimeter level in some of your sites? I don't think you do. I think risk assessments are built on the assumption that we're going to miss some risks, and what we have to do is maximize the accuracy of assessments keeping costs practical. The little fine scale analyses that should be made in the laboratory and field research may not be appropriate in large-scale evaluations.

[Dr. Hansen recommends that readers should consult the "Briefing Report to the EPA Science Advisory Board on an Equilibrium Partitioning Approach to Predicting Metal Bioavailability in Sediments and the Derivation of Sediment Quality Criteria for Metals" (EPA-822-D-94-002) for a complete summary of this approach. It is available from the US EPA, Office of Water Resource Center, at (202) 260-7786.]

Sediment Contamination, Toxicity, and Macrobenthos: Comparability of Laboratory and Field Observations

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The focus of today's talk is the comparability of lab and field observations, concerning arguments of sediment contamination and sediment toxicity and biology. Specifically, the issue of field validation of 10-day laboratory toxicity tests conducted with amphipods. Amphipods have been used broadly in a variety of research and regulatory programs, including the development and verification of the various kinds of sediment quality guidelines (e.g., marine sediment criteria based on the EqP approach and the regional AETs). Because data from laboratory bioassays with amphipods are used so broadly, the verification of these tests is very important to all of us, particularly regarding the various strategies that might be employed.

The field verification of laboratory toxicity tests has to be done with two kinds of applications in mind: first, the field-collected sediment must be evaluated, and second, the sediment must be experimentally manipulated (i.e., spiked sediments) so that conclusions can be made.

Three different examples of field verification will be presented. The first, involving a site on the Palos Verdes Shelf, focuses on a specific contaminant, DDT and its metabolites. The second, also involving DDT, begins with spatial correlations and then addresses specific cause-and-effect relationships relative to spiked-sediment toxicity tests. The third deals with the use of a model to go from observations of toxicity to predictions of toxicity. To address the question of relevancy of laboratory tests in evaluating ecological impacts associated with contaminated sediments, both correlative and investigative analyses were applied to the results of 10-d acute toxicity amphipod tests (*Rhepoxynius abronius, Eohaustorius estuarius, Hyalella azteca, Leptocheirus plumulosus, Corophium spinicorne, Corophium volutator, Ampelisca abdita*) and field collected metrics. Field parameters measured included amphipod density, infaunal index, species diversity, and species richness.

Los Angeles County discharges hundreds of million of gallons of effluent into the Palos Verdes Shelf each day. There is a pronounced gradient within the area, particularly for organic enrichment and a variety of chemicals. We used sediments from this area to investigate the correlations among the three elements of the triad—benthic community structure, toxicity, and bulk chemistry. We conducted three levels of verification with the toxicity test. The simplest was conducting toxicity tests with amphipods and comparing results to the benthic community—are amphipods found at sites where the sediments are shown to be toxic in the laboratory? To aid in our evaluation, we used the index developed by Jack Word and associates from Battelle that ranges from 0 to 100, with values <10 representing highly toxic sites, values around 50 representing altered or disturbed sites, and values greater than 80 representing unimpacted sites. We found very few resident amphipods in sediments shown toxic in laboratory studies. We also found sediments that were clearly non-toxic, according to laboratory test results, which were associated with disturbed benthic communities (i.e., the index was around 50). These results corroborate yesterday's discussion about the relative sensitivity of laboratory tests, and that it is possible to have sediments test nontoxic in the laboratory but still have disturbed ecological conditions. This is why it is imperative to have chronic tests as well as sensitive toxicity tests. Overall, our results indicated that laboratory toxicity was correlated with degraded benthic communities, degraded amphipod assemblages, and elevated contaminant concentrations.

To move on to DDT, we examined sediments from three different study areas—the Lauritzen Channel (part of Richmond Harbor in San Francisco Bay), an open coastal marine system on the Palos Verdes Shelf, and a freshwater stream system in Huntsville, Alabama. The fundamental differences among the sites are in the ecology and species of the amphipods that were used in the sediment toxicity tests. Pooling results from laboratory toxicity tests for all three sites, we get a clear concentration response pattern — no toxicity hits at very low concentrations of DDT (normalized to organic carbon) then a concentration related response as DDT concentrations continue to increase. This is a remarkably good correlation, particularly since we're evaluating field-collected data from three different kinds of habitats. We have data on amphipod abundance for two of the sites (Lauritzen Channel and Palos Verdes Shelf). In areas were DDT concentrations are low, amphipod assemblages are abundant and diverse. There are also many areas were DDT concentrations are low and amphipods are not abundant. These data are not unexpected because there are many factors other than DDT that control the distribution of amphipods. As the concentration of DDT increases, the abundance of amphipods decreases until you get into a quadrant where amphipods are rare or totally absent.

I would like to now focus on the Lauritzen Channel study. Several contaminants of concern were identified, with DDTs, PAHs, and metals identified as the principal contaminants. We used a toxic unit (TU) approach to evaluate the toxic contribution made by each principal contaminant of concern. For metals, the TU was <<0.2 (based on the SEM/AVS ratio), indicating that metals are not a problem at this site. For PAHs, the TU was around 0.28, which is in the range that toxic effects could be observed, but it is not sufficient by itself to explain the 100 percent mortality observed in laboratory toxicity tests. The TU for DDT was >5.0. This assessment suggests that DDT is the primary contaminant causing observed mortality.

The Huntsville, Alabama, data were taken one step further. We calculated an LC_{10}, which we believe indicates a threshold level of toxicity of DDT based on spiked-sediment toxicity testing. The data from this study support our hypothesis that it is possible to obtain estimates of chemical concentrations that cause effects and/or degradation in the field using spiked-sediment toxicity tests, and the spiked sediment toxicity test is relevant to sediment toxicity in the real world. Sediment toxicity tests with sensitive amphipods applied to field-collected and experimentally spiked sediments provide ecologically relevant information. This information is particularly important since, with the exception of screening level concentrations (SLC), all other methods of deriving sediment quality chemical-specific numbers depend heavily on data from these amphipods.

And finally, a look at the PAH model developed to predict toxicity. There are papers written that address the sources of error and limitations associated with the model, and the model does need to be evaluated by the research community. Nevertheless, the model suggests the following:

- If mortality is < 13 percent, then sediments are not toxic.
- If mortality is > 24 percent, then sediments are toxic.
- If mortality is between 13 and 24 percent, the level of toxicity cannot be predicted.

The model begins with field chemistry and uses equilibrium conditions to convert the bulk chemical data to make predictions of interstitial water concentrations. The model then predicts the 10-day interstitial water LC_{50} for each of the 13 PAH compounds. The model then calculates toxicity units for each of the PAH compounds, and finally summarizes the individual toxicity units to derive a single toxicity unit for the sediment under evaluation. The response model is used to predict the probability of significant acute toxicity associated with those sediments. Sediment PAH concentrations and TOC values were used as input data for this model, and predicted and observed toxicity were used to verify the model. A close association between observed and predicted toxicity was obtained, with no significant difference between observed and predicted toxicity. The model accurately predicted the probability of toxicity at field sites where PAHs were the dominant contaminant. However, if PAHs are not the dominant contaminant, this particular model cannot predict the toxicity due to DDT or any other contaminant, but it can give an estimate of the relative contribution of PAHs to overall toxicity. If the relative contribution is very small, then you can believe that something else is the major cause of the observed effect.

With respect to amphipods, there are differences in sensitivity among species and it is difficult to make generalizations, but generally all the seven species listed above would be considered "sensitive species." One species in particular that is not considered sensitive is *Grandidierella japonica*. This species has been found to inhabit sediments determined highly toxic to other species in laboratory toxicity tests. Current research projects are being used to determine what makes this species less sensitive. Results of our work indicate: (1) adaptation and/or selection for resistant populations, or (2) in some cases, populations may be living in a thin, less contaminated layer. *G. japonica* is a shallow burying amphipod and could be portraying avoidance behavior similar to that mentioned by Dave Hansen for polychaetes and by other researchers investigating the effects of creosote-contaminated sediments on benthos in Puget Sound.

In the grand conclusion of all three examples, I would hope that we would have consensus on the fact that sediment toxicity tests with sensitive amphipods applied to field collected and experimentally spiked sediments provide toxicity estimates that are relevant to benthic ecosystem contamination and degradation in the field.

In response to the question of whether or not our triad evaluation approach to risk assessment precluded the need for using EqP, I think that EqP is an important part of the evaluation because we basically made the comparison with the organic carbon normalized concentrations. That's how we could find the exposure. I don't see it at all as an independent stand-alone toxicity type evaluation. I think that it is critically important and I would think that we might agree on that also, that we look at these other approaches concurrently to make the assessment.

Comparison Between the Results of Toxicity Testing with Marine Sediments and Predicted Effects Based on Chemistry

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Columbia Analytical Services (CAS) has developed a new sediment assay, the Cytochrome P450 Reporter Gene System (RGS), that is based on luminescent biochemistry. Firefly chromosome material has been incorporated into a line of genetically engineered human liver cancer cells, permitting application of luciferin/luciferase analyses. San Diego Bay sediments were simultaneously subjected to a series of chemical and biological analyses. The purpose of the study was to provide an overall assessment of San Diego Bay near the naval station. The 10-day amphipod (*Rhepoxynius abronius*) test was used with solid phase material, Microtox™ and the P450 RGS test were used with organic extracts of sediments, and oyster larvae and Microtox™ were tested with sediment elutriates. Elutriates would contain both soluble metals and organics, while the organic extracts contained primarily PAHs.

Reference station sediments were primarily sand; otherwise grain size was quite variable. There was some concern with the effect of grain size on amphipod survival, but the effects observed did not correlate with grain size. TOC ranged from 0.1 to 2.8 percent. In decreasing order of importance, the toxic metals identified were Zn, Cu, Pb, and chromium (Cr). SEM/AVS analyses were done on all sediment samples. The toxic metals added together resulted in high levels for the stations closest to the shore; the reference stations had very low levels. However, the ratio of SEM to AVS resulted in somewhat anomalous results. Stations away from shore (toward the center of the channel) exhibited the highest ratios of SEM to AVS; because the sulfide levels were low, 22 of 30 stations had ratios >1. The PAH data demonstrated a decreasing gradient with distance from shore for all transects, except the reference transect. The highest PAH concentration, approximately 20 ppm, was measured in sediments collected from the shore stations near the docking facilities.

The elutriate tests with oyster larvae were not very informative. Two of the larger hits occurred at the reference stations; stations where PAH and Zn concentrations were highest did not show significant effects. The oyster larvae data did not correlate with the ratios of SEM to AVS, nor with the concentrations of sediment PAH. None of the 30 elutriates significantly reduced the luminescence of the bacteria in the Microtox™ test. When the organic extracts of sediments were applied to the Microtox™ test, there were some significant effects, but these did not have a high correlation with sediment PAH concentration. In contrast, the new P450 RGS results from exposure to the same organic extracts were highly correlated with sediment PAH content. The solid-phase tests with amphipods were apparently not sensitive enough as no sediment produced 50 percent mortality. There were several sediments that produced between 30 and 40 percent mortality, but these responses did not correlate with sediment chemistry.

The best correlations were obtained for the sediment PAH and P450 data. The observed effects were associated with PAHs; the concentrations of pesticides and PCBs in sediments were below detection limits. The PAH and metals data were compared to the EPA sediment criteria for three PAHs, the Washington State Sediment Criteria and the most current ERM values. At only one station did all four indicators show an adverse effect. Two of the stations contained concentrations of three to four metals that were above the ERM and some individual PAHs above the ERM and the Washington State Sediment Criteria. Also, the total of high molecular weight PAHs was above the ERM. Therefore, the ERM values, the Washington State Criteria and the P450 RGS response predicted the effects observed at the most contaminated stations.

Twenty-two of the thirty stations had SEM/AVS ratios >1, and as per theory, the toxicity of these sediments was not predictable. Eight sediment samples caused toxicity with amphipods (i.e., mortality exceeded 30 percent), and for three of these samples, the SEM/AVS ratios were <1, which suggests no toxicity. The observed toxicity was attributed to PAHs. Because of the manipulations and oxygenation of the sediments, AVS should probably not be considered when doing elutriate tests. TOC normalization was not useful in this case, possibly because there was not a great deal of difference. However, it is an important measurement and should always be made. We expected the organisms to be more sensitive than they were. For this particular study, the chemical benchmarks were more predictive than the laboratory bioassays with oyster larvae or amphipods. The P450 assay is a tool that can be used as a biological test and a detection system. It is sensitive to dioxin, PCBs, and PAHs. This work was done with sediment extracts; future studies will include the evaluation of sediment pore waters.

Assessing Toxicity in Multi-Metal Contaminated Sediment: Application of Theoretical and Investigative Approaches

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We used a suite of tools during a sediment investigation for a site located in an urban industrial area, adjacent to a freshwater harbor. Sulfuric and hydrochloric acids were produced at the site, with the primary waste products being pyrite cinders. Although there are several contaminants associated with pyrite cinders, the contaminants of concern were Cd, Cu, Hg, and Zn. This site was a good candidate for application of the SEM/AVS technique because of the contaminants of concern, the presence of iron, and the dynamics of the system that relates them.

Prior to our involvement, bulk chemical measurements were the only data collected for this particular site. There is a noticeable absence of organic compounds in the sediments. Concentrations of Cd, Cu, Hg, and Zn were up to 15,000 mg/kg-dry weight, which exceeded nearly all screening and/or advisory criteria (e.g., ERLs, ERMs). Based on the chemical measurements the sediments adjacent to the site were characterized as highly toxic. As with the other approaches we've been discussing, bulk chemistry is a screening tool and should be used as such. It is a way to characterize the site during the initial investigation phase and serves a particular purpose—it provides a range, or at least an idea, of the contaminants that might be present. Bulk chemistry data can also be used to determine which tool to take from our environmental tool box. In addition, bulk chemistry data can also indicate whether you are dealing with extremely hazardous wastes or dangerous wastes that might lead to emergency removal. However, caution should be taken when making assumptions regarding toxicity based solely on bulk chemistry data. The bulk chemistry data do provide the rationale and information we need to set up the assessment approach to determine the degree of toxicity, but further interpretations of the potential effects of observed contamination should not be done until additional assessment data are available.

We were brought into this investigation because the initial analyses indicated the sediments to be extremely contaminated and, based on the sediment screening guidelines, the entire area would need remediation. This particular site is situated in a sector of the country where criteria are part of the decision process for cleanup, and by using the sediment criteria for these four metals, nearly all the sediments adjacent to the site required cleanup. Our assessment process incorporated a suite of tools, including physical and chemical analysis of sediments, derivatization of SEM/AVS ratios, laboratory toxicity testing, and modified toxicity identification evaluations (TIEs). The physical data allowed us to better understand the sediment matrix being tested, which was particularly important information when evaluating the toxicity test data. Grain size and other sediment characteristics can be significant factors in toxicity test results and we needed to separate the effect of physical factors from contaminant exposure.

> *[A question was brought up regarding the validity of using AVS to evaluate the potential hazards from sediment Hg contamination. Dr. Johns felt that because Hg forms a sulfide that is less soluble than iron sulfide, AVS is appropriate for evaluating the potential acute toxicity of Hg to benthic organisms, but a separate evaluation would have to be done to determine the risk of biomagnification and toxicity to higher trophic level organisms posed by Hg contamination.]*

The concentration of chemicals measured during our investigation were quite similar to those measured during the initial investigation; there had been no major contaminant concentration shifts at the site over the past few years. SEM/AVS ratios for five stations were <1 (i.e., no toxicity) and 16 had ratios >1 (i.e., potential toxicity). We could have stopped the investigation at this point with the conclusion that the majority of the sediment at the site was toxic. However, SEM/AVS ratios >1 are prone to false positives because of the other binding factors that may be present in the sediment that further reduce bioavailability. The highest ratio obtained was 125; the majority of ratios were between 2 and 10. These 16 sites that had ratios >1 were of particular interest to us with respect to laboratory toxicity testing. Based on the SEM/AVS theory, sediments from the stations with ratios >1 had more available metals, and hence the potential for toxicity. However, we didn't have a lot of confidence in our ability to predict which sediments are going to be toxic; therefore, it was necessary to conduct the laboratory toxicity tests.

No significant effects were found with the *Chironomus* growth test. However, results of the 10-d survival tests with both *Hyalella* and *Chironomus* led to a modified TIE (i.e., 48-h acute toxicity tests with *Ceriodaphnia*)—the *Hyalella* test had nine hits, the

Chironomus test four. The *Chironomus* tests agreed with no toxicity for the five stations where SEM/AVS ratios were <1. The *Hyalella* results agreed less with the SEM/AVS data—in two cases toxicity was encountered when the SEM/AVS ratio was <1. The *Hyalella* results suggest toxicity is not limited to metals contamination, even in a system where metals dominate the contaminants of concern. SEM/AVS >1 for 16 stations were not predictable with respect to toxicity, as per theory. Interestingly, the TIE for stations that were toxic in solid phase tests did not show a match—only one of the stations toxic in the solid phase was also toxic to *Ceriodaphnia* in porewater assessments. There doesn't appear to be a good explanation for this discrepancy (i.e., toxicity in the whole sediment tests but not in the porewater tests). If you accept that TIEs have the ability to determine and identify the source of toxicity observed in whole sediment, then you would conclude that the observed toxicity at only one station is due to metals—toxicity at the other 12 stations is due to some other contaminant or physical factor.

> *[A discussion occurred at this point concerning the potential for changes in sediment and pore water sample toxicity as a result of handling and storage. The bottom line appeared to be that handling and storage times should be minimized; and to better interpret the results of toxicity tests, the physico-chemical properties of the samples should be measured at the time of the toxicity tests.]*

A qualitative analysis of the benthic community suggests the area is fairly healthy. It is dominated by vegetative macrophytes, being quite lush up and down the entire system. Amphipods, as well as aquatic snails, and mussels, were present at all sites. It would have been very useful to have quantitative benthic data to aid in interpretation of the chemistry and laboratory toxicity data (i.e., sediment quality triad).

The summary data suggests that by using more techniques we are better able to evaluate the area of concern. On a site-wide basis, there is gross metals contamination; there are a certain number of stations for which the SEM/AVS ratios were <1, indicating there should be no toxicity because the metals were bound and not biologically active. Of the stations for which the SEM/AVS ratios were >1, only about half elicited toxic responses in laboratory bioassays. By stopping the investigation before conducting the TIEs, the overall conclusion would be that approximately half of the area requires remediation. However, the TIE data indicate that a much smaller area may contain toxic concentrations of metals. In addition, it is possible to have toxicity in a metals-dominated system even though the SEM/AVS ratio is <1. This situation is one where additional contaminants (i.e., organic compounds) are present and, either alone or in conjunction with the bioavailable metals, are causing toxicity.

The nature of this study and others involving complex aquatic systems, are the basis for the question "is there a suite of tools we should always use?" Because of this complexity, we need to use an array of assessment tools in the evaluation process.

Strengths and Weaknesses of the EqP Approach as Applied to Hazardous Waste Sites Risk Assessment

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The EqP approach is based on good science. There is sufficient and convincing evidence that the theory has been validated in the laboratory and the field. EqP is applicable to the benthic environment in terms of predicting risk. However, this approach is insufficient. EqP is not the weak link in exposure estimation; the weak link is sediment-water column mass balancing and bioaccumulation modeling.

How should risks be predicted for higher trophic level species? We should design models that look for specific parameters and processes that have the largest impact on the risk estimation. It is not sufficient to use just EqP or AVS in the decision process for site remediation. Other information, such as the receptors requiring protection, their mobility and behaviors, the spatial distribution of contaminants and resources within the system, and the end use of the site, must come into play. The available data should be used to determine what is accumulated in the prey tissue and what is being consumed by the predator. In some cases, it makes sense to measure biota tissue concentrations or doses directly, rather than depending on predictions. This is particularly true for the mid-trophic level species where it is easy to acquire specimens and analyze tissues. Empirical relationships have been developed that can be used to predict bioaccumulation. As indicated earlier, as one moves beyond benthic trophic levels, the influence of the porewater concentrations is not a big factor in estimating exposure and, therefore, risk.

[*An example of the bioaccumulation model developed for the Rocky Mountain Arsenal was presented.*] There are numerous factors (i.e., lake morphology, in- and out-flow rates, suspended solids, sediment loading) that had to be considered in estimating exposure at this site. The time required to identify these factors, as well as the associated uncertainty, justify the measurements of prey items and the use of a direct model instead of modeling exposure as a function of sediment contamination levels. The EqP approach is valid, but the way it's being used creates potential problems, particularly if you don't know how to define the important variables. Sensitivity and uncertainty analyses should be used to identify these parameters. This will give flexibility to the management decision regarding the end effect.

Sensitivity analysis allows the variables to be ranked in terms of their relative contribution to the overall uncertainty about risk. The results of this analysis can be used to identify which parameters are important enough to be modeled probabilistically, and to develop a cost effective modeling strategy that improves the data. By using all the analytical tools and considering all the options presented by the data available for a site-specific risk assessment, good customized procedures can be developed to predict contaminant bioaccumulation and risk in upper trophic level species.

To answer the questions being asked about hazardous waste sites, we must use all the available tools and rationalize the differences between tools to form a defensible approach. What is the best approach for predicting risk to upper trophic level biota? The first step is to design models and data collection efforts with the goal of maximizing expected value of information. Upper trophic level bioaccumulation should be modeled probabilistically (less information is required as compared to point estimates, allows for sensitivity and uncertainty analyses to identify driving parameters, provides more useful information for risk management decisions). The shortcomings (i.e., reliability of parameter distributions, correlation assessments) of Monte Carlo analysis must be recognized and site-specific data should be used to calibrate models. Finally, use decision analysis to balance risks, costs, and benefits of risk management options.

The applicability of parameter values from the scientific literature should be closely scrutinized. For example, biomagnification factors generally are not transferable to other sites because of differences in methods for estimating bulk concentrations in exposure media, differences in the many physico-chemical processes that govern the rate of uptake of exposure medium contaminants by biota, and differences in the biology and ecology of sites. Therefore site-specific biomagnification factors should be used. Site-specific data improve the reliability of parameter distributions by incorporating more data. Field data should be used to modify data to improve predictions.

One must consider all the options in designing models and data collection efforts, including mechanistic models (e.g., EqP), semi-empirical models (i.e., food webs), empirical models (e.g., statistical estimators of contaminant biomagnification factors), and the use of direct, site-specific data to improve reliability and investigate parameter correlations (e.g., sample prey tissue rather than predictions from sediment data). It is important to use empirical relationships. Because predictive bioaccumulation models inherently have a high degree of error, a direct approach is recommended to measure the concentration of contaminants in prey items.

In conclusion, EqP is a good approach for benthic ecology, but it must be used in combination with other tools to establish risk-based cleanup goals. Models should be built to answer specific questions. Sharpened, well-rounded analytical expertise and creativity are needed to take advantage of emerging [*and present*] tools.

Panel I Discussions

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Question 1: What can and cannot the SEM/AVS ratio *really* tell us?

The following consensus statement was drafted during this panel discussion and later refined as more information became available and agreement was reached.

For sediment in which the contaminant(s) of concern include one or more of the following: Cd, Cu, Ni, Pb, and Zn, an SEM/AVS molar ratio of <1 indicates the bulk of these metals are complexed with sulfides and are essentially not bioavailable and hence acute toxicity from these metals is highly unlikely. An SEM/AVS molar ratio >1 does not necessarily indicate that these metals are bioavailable and acutely toxic; other factors may be affecting their bioavailability and toxicity. Toxicity refers to laboratory tests only and does not necessarily apply to bioaccumulation of the metals or alterations in the benthos. {Noted Cautions:

(1) *The numerator and denominator must be considered when evaluating the ratio, almost no AVS compared to some SEM has a different meaning than a similar ratio wherein the AVS concentration is much higher; also, very low concentrations of both SEM and AVS should not be considered predictive.*

(2) *The consensus statement is only valid if AVS concentrations are above operational detection limits.}*

The panel indicated that SEM/AVS allows you to look at availability of metals for interaction with organisms, if the ratio is <1 then metals are not available, if >1 then metals *may be* available. Toxicity is not predicted if the ratio is >1. Situations where biology does not agree with chemistry will occur when you try to use chemical models to predict biological effects.

John Mahony noted that if the Cr source is chromate, AVS is applicable; if chromate is not the source, this approach should not be used.

Dominic DiToro indicated that Hg will not be amenable to SEM/AVS analysis; the issue is methylation, not ionic Hg, so the causative mechanism (of adverse effects) is different from other metals. SEM/AVS has not yet been subject to uncertainty analyses; this needs to be done but until it is, the absolute value of 1.0 is all that can be used. He further clarified that, for site investigations, it is generally not enough to just determine the SEM/AVS ratio; toxicity tests are often also necessary and a highly valuable tool. Certainly, remediation decisions require more than just chemical measurements.

Alyce Fritz felt that if the SEM/AVS information was available, then some decisions not to proceed will be based solely on the chemistry data. However, if there is a choice of whether to do SEM/AVS or toxicity testing, the preference will be for toxicity testing. In an ideal situation, you should get both pieces of information. The controversy over whether or not SEM/AVS can stand on its own as a decision-making tool for Superfund will most likely continue. How should this tool be used?

Jack Word reminded us that the SEM/AVS approach is indicative of *acute* toxicity and is not applicable for estimating chronic or sublethal toxicity. The value of this approach is that it allows one to identify that metals may be the issue, helps identify the contaminants of concern, and points you in a direction for further study. However, Dominic DiToro countered saying some chronic data is available. Chris Ingersoll indicated that it is necessary to look at bioaccumulation. The SEM/AVS ratio holds, for the most part, for bioaccumulation; however, there are exceptions to this approach also. Data were presented where midges accumulated Cu with an SEM/AVS ratio <1. Dominic DiToro further stated that at ratios <1, in a pure system there are virtually no metals available for interactions under any circumstances in biological organisms, which is the way the theory is presented. At ratios >1, depending upon whether you're addressing the real world or the ideal system, there are metals present that may or may not be able to interact with biological organism. The consequences of the interaction may be expressed in acute bioassays or in the benthic community structure. Metals are not available at ratios <1; metals may be available at ratios >1, the consequences of which are determined with bioassays. The area of bioaccumulation is one that requires additional investigation. It is uncertain if good data sets concerning SEM/AVS versus bioaccumulation exist. There are some definite trends for these two properties, but there are also inconsistencies. There is an additional need to look at bioaccumulation as one of the subtle responses.

It was suggested that tools other than SEM/AVS be considered (aside from toxicity tests and community structure analyses), including porewater toxicity units (e.g., which address free metals); TIE; other physical/chemical parameters (e.g., TOC, grain size, ammonia, other confounding compounds {multiple metals, organics}); sample collection, handling, and analytical techniques.

Also, the uncertainty boundaries must be established for the ratio, and there is a need to qualify whether bound metals will ever be available again. There was considerable discussion regarding the lack of toxicity when ratios are >1. The finding of no toxicity may be species dependent, with some species actively avoiding toxic sediments.

The issue of acceptable mortality loss was raised. As per recommended protocols, the sample must show a statistically significant difference from control. In general 20 to 25 percent mortality has been accepted for the cutoff for significant mortality. How does mortality close to cutoff reflect on the possibility of an organic toxin also? When mortality data approach the cutoff, it was suggested to consider using an additional tool.

Dominic DiToro closed this question with the comment that we are really asking two questions: what does the SEM/AVS ratio tell us with respect to the field and laboratory data, and how should we initiate a site assessment. These are two separate questions, with the second based more on practicality.

Question 2: How do temporal (e.g., seasonal) and spatial changes in physico-chemical parameters affect our assessment of hazardous waste site conditions?

Spatial and temporal effects are two very different issues. There are two spatial scales we must be concerned with: the macroscale (i.e., the area that is the object of the investigation) and the microscale (i.e., the area that the biota is exposed to). The macroscale is clearly objective(s) driven; it is a function of the objectives of the investigation, the site, the characteristics, etc. Everything that is done for the investigation (i.e., AVS/SEM, EqP, toxicity tests) applies on a macro-scale level. The microscale, the area immediately surrounding the organism, is affected by the presence of biota; in fact, they are able to oxidize metals right around their tubes or in the immediate vicinity. However, there is little evidence that the microscale effect has any impact on the development of the data (on a macroscale level). The present macroscale approach seems to be working. The microscale is probably not too important with respect to toxicity and bioaccumulation, although it may explain some of the anomalous bioaccumulation results. The effects of the microscale on toxicity or bioaccumulation remain an area for active research.

With regard to the temporal situation, seasonal changes may well occur, and certainly do in some systems (but perhaps not in others; it is probably too early in the research cycle to make any predictions as to why, when, and where this may occur). There is evidence that freshets in rivers, and the conditions associated with additional sediment deposition, have a major effect (e.g., possibly really reducing AVS concentrations). However, the point was made that the "noise" may be too great to see real differences ("noise" would include recognized sediment heterogeneity) and, very limited sampling occurs in the winter months, even after storm events. This represents an important data gap that should be addressed.

A specific question was asked regarding diurnal fluctuations of SEM/AVS in estuaries and creeks? The general feeling was there was probably not much fluctuation.

Another issue addressed was how to deal with isolated pockets of contaminants (e.g., creosote). When assayed in the lab, they show a much more consistent (and possibly lethal) distribution.

Overall, it may be very difficult to decide in the field if the measured differences are from spatial or temporal effects.

Question 3: Which parameters of the system should be measured and how can these data be applied to an entire ecosystem?

This question was not discussed due to lack of time. On a system level, we can't think much beyond bioaccumulation and potential biomagnification.

Panel II Discussions

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Jim Meador
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Philippe Ross
The Citadel

Question 1: Is equilibrium a good assumption in the environment?

The Panel broke this question into four parts:

(1) What is equilibrium?

(2) What factors/processes disrupt equilibrium?

(3) On what spatial and temporal scale do these processes occur?

(4) When non-equilibrium conditions occur, does it matter?

The Panel agreed that to answering Question 1, the first step was to define equilibrium and provided the following definition: the condition when a contaminant concentration in the various phases does not change over a significant period (months to years), assuming that the total contaminant mass remains constant.

It was pointed out by Peter Landrum that this is the definition of steady state, not of equilibrium. He defined equilibrium as the condition when the free energy in a system is a minimum. Dominic DiToro agreed in definitive terms, but countered that we're working on a smaller scale (i.e., equilibrium between sediments and interstitial water), and that the definition provided by the Panel is probably a good working definition.

Two problems arose regarding the equilibrium:

(1) Equilibrium is not really measurable in sediments.

(2) Equilibrium is only partly attained. What is meant by EqP is a metastable equilibrium (i.e., no change) between sediment and pore water.

On this basis, equilibrium can operationally be defined by the definition provided by the Panel, though technically speaking, this really defines steady state.

To address the second and third parts of the equilibrium question, what factors/processes disrupt equilibrium and on what spatial and temporal scales do these processes occur, the Panel developed a table (see next page) that addressed the various relevant processes that could violate the assumption of steady state in the sediment. They attempted to estimate the frequency that these processes occur in nature, over what areal scale, and what impact they would have on the bioavailable concentration of the metal. The table was offered as a strawman in hopes of stimulating discussion regarding the equilibrium processes. The audience requested a checklist that could be used by investigators to make decisions regarding the equilibrium models. It's the heart of the assumptions of equilibrium that cannot be readily accepted. It's the heart of the model that we have no information on for most of the sites. Something is needed so information can be collected to make a determination whether equilibrium exists, or does not exist. If these models are going to be pushed, the basic assumptions of the models must be checked as to whether they exist, they're not intuitive at the Superfund sites. Are the assumptions of equilibrium generally met, or generally not met, at a site? This is the basic question.

There was also a request for information as to when the assumptions will be violated. It is imperative that site managers understand the worst-case scenarios that could be missed with limited funding or sampling to avoid situations such as when sampling shows conditions are acceptable and no remedy is required, but later an acute toxicity event occurs that is unacceptable on a population/community level. The request included the appropriate way to design a study to predict, or hit, the catastrophic events that are unacceptable at hazardous waste sites.

Dominic DiToro stated that for the five SEM/AVS metals (i.e., Cd, Cu, Ni, Pb, and Zn), uptake reactions with iron sulfide (FeS) are so fast that kinetics are not an issue (as long as time scales are greater than about 1 hour). Not much is known about oxidation processes except that stability appears to vary by metal and tends to be generally slow. With regard to organic matter, there appears to be two phases: a rapidly sorbed component that goes into equilibrium within hours, and a more resistant component that requires weeks to months to reach equilibrium. Evidence that natural, undisturbed sediments are in equilibrium is primarily indirect; apparently there is no way to directly test this. Nothing is known about wetting and drying systems (i.e., tidal wetlands); all information to date is from fully submerged systems.

Suggested table of factors effecting sediment equilibrium and the scales over which they may operate.

	Temporal Scale			Areal Scale			Sediment Depth (cm)			Change in Bioavailable Concentration		
	day-wk	wk-mon.	mon-yr	cm^2	m^2	km^2	1-5	5-25	>25	<3x	10x	>10x
Input of contaminant mass												
Removal of contaminant mass												
Dilution of IW												
Input of particulate organic carbon												
Mineralization of organic carbon (δ in quality)												
Metabolism of organic carbon (δ in quantity)												
Input of co-solvents												
Anoxia in bottom water												
pH in IW												
Salinity in IW												
Alkalinity in IW												
Sediment stability												
Inundation												
Exceed solubility												

The preceding discussion lead to the following potential Consensus Statement:

> *"It appears that in most cases undisturbed sediments can be considered as being at equilibrium; however, there are situations and processes that may violate the equilibrium assumption and that one must be knowledgeable and wary of. Note that measurements cannot really be made better than about a factor of two; equilibrium should be considered within this*

reality". [While the concept behind the statement was generally agreed upon, consensus could not be reached on the precise wording of the statement to make it acceptable to everyone.]

Question 2: **Are the following assumptions valid: (1) pore water is the sole route of exposure to contaminants, (2) porewater exposure is equivalent to surface water exposure?**

The panel opened this discussion with the statement that pore water is not the only route of exposure to contaminants; ingestion is also an important route for some organisms. The route really does not matter because they both come to equilibrium. However, there are situations where it may be important, such as for suspension-feeding clams that may never be exposed to the sediment-bound contaminants. [*Note: there was no consensus as to whether sediment ingestion effected EqP theory.*] The second issue is does it matter whether pore water is the sole route of exposure.

Peter Landrum noted that *Diaporeia* ingests sediments and this is an important uptake route, such that much higher tissue concentrations occur than would be predicted from pore water alone. The issue becomes application of the sediment quality criteria. Do they apply just to the infaunal deposit feeders, or to all benthic organisms regardless of different feeding strategies (deposit feeders versus filter-feeders) or distributions within the sediment columns (epibenthic organisms versus deep-dwelling species)? During development of the sediment quality criteria for non-ionics, BASFs (the lipid-normalized tissue burden divided by the carbon-normalized sediment concentration) were generated for a variety of species and feeding strategies that clearly had different exposures. Results of the analyses indicated that the BASFs were no different; the same mean variability in BASF was obtained for filter-feeding sediment dwellers as for burrowing, sediment-feeding organisms. Although the issue may still be unresolved, it was suggested that there is no compelling reason why one should reject the idea that filter feeders are different. There was no consensus to this idea; many participants felt that the BASF data are so highly variable that you can't say.

The discussion turned to the "total" exposure that includes aqueous exposures and exposure through food sources. Dominic DiToro suggested that it doesn't matter whether the organism gets the dose from food or the water, because equilibrium becomes the major issue. He questioned whether the approach is applicable to organisms of different feeding modes and suggested the best way to answer the question is by analyzing animals of different feeding strategies. By looking at field data, we see a lot of variability, but get the same trends regardless of feeding strategy. Dominic DiToro stated that EqP does cover exposure through ingestion; it is not a philosophical argument, but it is based on data. Robert Dexter asked whether different organisms placed at the same site and allowed to come to equilibrium would have the same concentration of contaminants in their tissues. Dominic DiToro responded that they would, with a large degree of variation associated with the measurements.

The second part of the question of whether pore-water exposure is equivalent to surface-water exposure was interpreted in two ways:

(1) Is exposure of an organism in sediment equivalent to that in the overlying water?

(2) Is exposure of an organism in extracted porewater equivalent to exposure of the same organism in "spiked" dilution water.?

The workshop director clarified the question by stating that we were interested in what's happening in the environment, i.e., if the effects were the same for organisms that were exposed to pore water as for organisms that were inhabiting the overlying water. Possible differences (for both 1 and 2) pointed out by the Panel relative to the above were:

☐ More complex interactions in pore water,

☐ More ammonia (and possibly other confounding parameters) in pore water.

☐ More humic material (=OC) in pore water.

☐ More color (i.e., optical alteration) in pore water.

☐ More bacteria in pore water, less UV impact.

Possible differences relative only to (1) above are:

☐ Less diurnal DO variation in pore water.

☐ Less short-term salinity variation in pore water.

☐ Different phase partitioning processes.

☐ More refuge possibilities in pore water.

It is more probable for the organism to have refuge from a pore-water concentration that it doesn't like than from a surface-water concentration that it doesn't like. However, this may or may not be true for animals that go between the surface water and pore water.

The point was made that the wording "surface water" is incorrect; the comparison is actually with overlying water. Surface water could be mistakenly thought to be the water at the interface with the atmosphere, which may well be more similar to pore water (because both are interfaces).

The Panel argued that the answer to part 2 of the above question is yes if the comparison is made based on free contaminant concentrations; no if one fails to take into account the binding phases. There was a lot of discussion and no major disagreement, but no attempt was made to make this a consensus statement. It was acknowledged that measuring pore water is the weakest link in the process; it is a difficult procedure and not readily accomplished by all laboratories.

Question 3: **What effect does the presence of other organic compounds and partitioning phases have on the bioavailability and toxicity of individual nonionic organics?**

There was general discussion on this issue. The Panel summarized that DOC does effect bioavailability and porewater concentrations can be higher than the "free" concentrations, but the latter are what are of concern, which is covered by the EqP theory. There was no disagreement on the above.

Panels III and IV Discussions:

Walter Berry
SAIC

Peter Landrum
NOAA

John Mahony
Manhattan College

Burton Suedel
EA Engineering, Science & Technology

Jack Word
Battelle MSL

Question 1: **Both SEM/AVS and EqP are normalization processes and require the measurement of other components. Can these other components be reliably and/or accurately measured?**

Yes. The most difficult problems are in sample preparation as compared with actual methodology, for example, when you have wood chips or other large materials present. There are methods available for all necessary components, at least for sediments within a "normal" range of organic carbon for instance. Outside this range, there is less certainty simply because of lack of experience with these sediments.

A question arose regarding the ability of contract analytical laboratories to come close to the standards of research laboratories who have done most of the work to date. John Mahony believes that contract laboratories can reach and maintain the requisite standards as long as they follow standard procedures and regularly run a standard (e.g., for AVS the standard is a sodium sulfide solution). It is possible to make consistent and accurate AVS measurements as long as good analytical chemical procedures are followed. Concern was repeated regarding potential problems with contract laboratories and non-standard sediments found at Superfund sites (e.g., sediments that contain ground coke, etc.) and guidance was requested regarding specific QA/QC for AVS. The need for standards and standardization was repeated.

The influence of DOC in interstitial water on TOC measurements was also discussed. The method used for DOC measurements is important and can influence the results by a factor of two or three. Also, the handling and storage procedures for sediments can have a significant influence on the analytical results. While oxidation of sediments will have an affect on AVS measurements, Walter Berry's experience has been that most sediments within the "normal" range of AVS, can be homogenized, placed into a jar without oxygen, and held in the dark at 4°C, with little change in the AVS content. Jim Brannon however, emphasized that for small quantities of sediment the analytical work should be done under nitrogen. The appropriate procedures are very dependent on the quantity of sediment you are working with.

There was an apparent consensus that, under the extreme conditions often found at hazardous waste sites, work needs to be done on methodologies for sample collection and handling.

Question 2: Co-occurrence of high contaminant concentrations (as measured by chemistry) and naturally occurring toxicants (e.g., ammonia and hydrogen sulfide). How should they be handled with respect to sediment evaluation and remediation?

There was common agreement that when we evaluate sediments, we are not just addressing one factor. Sediments are a mixture and contain other contaminants and natural products. As far as naturally occurring toxicants, ammonia and hydrogen sulfide are potential confounding factors. Whole sediment TIEs can elucidate whether these are problems, and procedures are now available in manuals and other documents for dealing with ammonia (e.g., the Inland Testing Manual). Handling and storage procedures are also a factor in sediment toxicity. The longer sediments with a high organic carbon content are stored the more likely it is that ammonia will be produced. Collection, handling, storage, and sample preparation (i.e., method used to obtain pore water) affects everything, not only the chemistry but the biology as well.

There was discussion regarding the relationship between un-ionized and total ammonia. It was pointed out that there are fewer "rules" at hazardous waste sites than in "normal" sediments. However, toxicity is still pH dependent, with more consistency in freshwater than in salt water (based on studies to date; there is a lot of work going on in this area).

The severity of the ammonia problem was discussed at length. The Panel attempted to make a consensus statement that ammonia is frequently a problem in freshwater surface sediments, and less of a problem in marine sediments unless the samples are taken from deep sediments. There were major disagreements on this point, with some individuals arguing it is a major factor in freshwater in shallow sediments but less so than in marine sediments, and others stating that there is not a major problem in freshwater. The issue of sediment storage was again discussed. The 10-day, 6-week, and 8-week holding times, as recommended in the dredge sediment evaluation guidance manuals, were questioned. The development of a very dark, black surface layer on sediments stored at 4°C suggests something is happening to the sediments. Whether it's tied to ammonia or sulfides is uncertain. However, the general feeling was that less manipulation and shorter holding times were better.

Very little information appears to be available regarding hydrogen sulfide, which may well not be a problem in "normal" sediments with low to moderate contamination. However, hazardous waste sites may well be very different (though this needs to be determined).

Question 3: When multiple contaminants are present in toxic sediments can SEM/AVS and/or EqP identify the contaminant(s) responsible for the toxicity?

The basic answer to this question was "no". These methods can provide insights but, by themselves, do not provide the whole answer. The toxic components should be identified by other methods, such as a TIE. A caution was added that the proper way to use SEM/AVS with multiple metals, which is typical of most hazardous waste sites, is to add all five metals (i.e., Cu, Cd, Pb, Ni, and Zn) together and compare that value to the AVS. The individual metals should not be normalized to AVS. Iron, manganese, and Cr are not included in the comparison. Another caution was added: when solubility limits are approached, EqP will not be predictive.

Question 4: What are the components of a sampling plan to evaluate contaminant bioavailability based on SEM/AVS and EqP?

The sampling plan should reflect the questions being asked. Sampling plan development should consider the following.

(1) Exposure conditions (organisms, depths, sediment composition). The kind of exposures to be concerned with must be identified in order to sample the appropriate matrix, both for depth of the sediment to be collected and depth of the sediment to be concerned about. The biology and chemistry must be matched to the exposure conditions.

(2) Appropriate sampling equipment: the allowable degree of disturbance must be known when deciding which type of equipment to use. The sample integrity must reflect the initial questions being asked.

(3) Preliminary characterization (pH, Eh): what can be done at the site to obtain data that helps us understand the situation and provides some sort of baseline information for comparison with future test results.

(4) Sample protection: what precautions during manipulation and shipment should be taken to ensure sediment integrity? Temperature is a variable that should be closely watched as it directly affects sediment integrity. There was a consensus that the more the sediments are manipulated, the less it can be expected that they resemble what is in the field.

There was detailed discussion regarding the pros and cons of compositing, field replicates *versus* laboratory replicates, etc. The only conclusion was that resolution of these issues depends on the question(s) being asked.

Question 5: What are the logistical variables that need to be identified and standardized (e.g., sample storage, handling, acid concentration, sulfide evolution rate, analytical considerations)?

The following factors were identified as important in the field:

- Sample storage: for SEM/AVS it is recommended that sediments be stored at 4°C; sediments should not be frozen as this may effect other critical aspects of sediment; storage should be no more than 3 weeks; generally you should test as soon as possible.
- Sample handling: the appropriate container must be used, i.e., glass for AVS with Teflon top; the sample integrity should be maintained (i.e., little to no mixing or homogenization) with little head space in the jar; the samples should be immediately refrigerated; if available, a large glove box with a Nitrogen atmosphere is recommended.

Once in the laboratory, other factors become important, including:

- Acid type/concentration: 1M hydrochloric is recommended as the standard, although HCl can't always be used; some metals (i.e., silver [Ag]) precipitate in the presence of chloride ions; nitric acid can be used in this case; phosphoric acid (but not with Ag) is used by some. HCl is appropriate for the five AVS metals; HCl is also appropriate for Hg_2Cl but not HgCl.
- Sample size: 1 to 2 g is recommended for AVS/SEM analyses.
- Digestion time: 30 minutes is recommended for most sediments; however, if the material in the reaction vessel has not settled or there is no distribution of color, then additional time is required.
- Daily standards: the need for calibrated standards was again highly stressed; standards should be used for all analyses (sodium sulfide for AVS analyses).

The discussion did not attempt to address all the factors that should be standardized. John Mahony pointed out that many of these issues fall into the realm of "alchemy," that is, experienced investigators know what they are doing and do not follow the book. However, laboratory personnel must be effectively trained to do these analyses correctly. A lot of discussion followed regarding problems getting contractors to accomplish this. Also, it was agreed that there is a need for a well-defined standing operating procedure (SOP) that lists the qualifications for contractors and provides accurate and complete guidance for these contractors (including the use of standards). With this type of document, it could be determined if contractor's work was done properly.

The following variables should always be measured whenever SEM/AVS and EqP are being used: pH, salinity, TOC, grain size, and sulfide.

Question 6: How does sampling alter sediment toxicity?

This question was not directly addressed due to lack of time, but had been part of many of the previous discussions. With regard to AVS, it was pointed out that PRPs should be aware that lack of care will make matters "worse" for them, not better.

Panel V Discussions

Peter Chapman
EVS Environmental Consultants

Dominic DiToro
HydroQual, Inc.

Spyros Pavlou
Foster Wheeler Environmental Corporation

Question 1: **How much additional field validation of the approaches is required?**

Question 2: **What type(s) of validation should be pursued?**

Question 3: **What would a field validation program consist of to validate SEM/AVS and EqP?**

The Panel suggested that they use this session to make a few initial comments regarding these questions and then open the floor to general discussion and questions.

In response to question 1, the Panel proposed that the use of the word "field" is inappropriate. There are a whole variety of tools; validation can take many forms and we shouldn't restrict it just to field validation. We need to take a look at how the tools interact. When we look at AVS or EqP, have we done enough validation in terms of laboratory studies to make it possible to go out in the field and do "field" validation? What does field validation mean?

A brief presentation was made regarding the use of field transplant studies to validate results obtained in laboratory studies. The approach is based on complementary studies that include a combination of theory and predictions and laboratory bioassay and field exposures, which generate a preponderance of evidence to help answer the validation question. With this type of triad it is possible to validate, in some way at least, the predictions until you are able to make a better case for what you're trying to demonstrate.

There is a need for validation, but validation must be done a little bit craftily at this time. In the past, the approach has been to do field experiments and then try to relate some of the laboratory test results with the field. There are two primary issues: validation of the science and validation of the methodologies to prove that the science works. The implementation of the tools is an important issue and should be separated from the science of the tools.

There was general agreement that we should test and rationalize differences between methods, not simply take adversarial positions. To accept a validation methodology, we should do it in a way that we test and rationalize differences in methods, rather than focusing on a "preferred" method. The experimental design is extremely important; we should design the study to test the methods, because it is possible to configure an experiment that will give the desired answer. It was proposed that we perform the tests in a way that allows comparison of the results, with all conditions being equal. With this approach we can determine whether or not there is consistency in the data. The issue then becomes understanding why there is no consistency.

The issue of uncertainty was again discussed. What are the bounds? During the discussions presented over the past few days, factors of two, five, and ten have been proposed with respect for interpretation of data. Is an SEM/AVS ratio of 0.75 different from 1.2? How far can one push the boundaries of the methods (e.g., wood chips in sediments)? What works and what does not? The allowable mortality must also be defined. Effective management decisions can only be made by comparing the variability both within and between data sets and to do this we need to define what is allowable. A similar concern was expressed for organic carbon. When are we pushing the uncertainty levels? It was requested that we put some bounds on the uncertainty for the various parameters.

The issue of spatial variability was discussed again. From a probabilistic view, it was suggested that the number of samples collected for analysis be sufficient to justify a probability distribution. Therefore, the data (e.g., AVS data) will have some uncertainty based on the way the sample was collected. The probability approach must be used carefully; the goal is to collect enough samples that permit you to make some sense of the data.

The bioaccumulation issue should be discussed in greater detail (perhaps a following workshop). This should include the spatial averaging of exposure. Many cleanup and implementation decisions are based on the upper-level food consumption and risk, and we must accurately define the risk to exposed biota. To accomplish this, it was suggested that the screening tools (i.e., AVS and EqP) be linked to the risk assessment process and, ultimately, to risk management. Spyros Pavlou indicated that the Marine Board, of which he is a member, is in the process of incorporating contamination assessment with risk management decisions to implement an action and develop the most cost-effective actions. He further suggested that the members of the workshop link the risk assessment and the risk management processes with the assessment methods.

Dominic DiToro noted that it is extraordinarily difficult to actually do a field validation; in fact one can only do a field invalidation. We don't know why it worked, if it worked; we only have concurrence. Exactly how to validate is the major question. We haven't done a good job with validation because we don't know how to validate very much. The ultimate test is the arena of utility. We have utility if more and more investigators find that the methods are useful in interpretation of their data. If the methods fade because of conflicting or uninterpretable results, then the methods will be forgotten. However, there is one observation that can be made that will invalidate the AVS/EqP methodology, and that is if there is a co-occurrence of an organism and a concentration that is predicted to kill that organism. That becomes an invalidation. The absence of an organism might be for any reason, but the co-occurrence strongly indicates invalidation.

The problems and questions that we are faced with are both confusing and frustrating because nobody knows all the answers, and we don't know how to find the answers. How do we do an ecological risk assessment? If we look in the tool box, we find that it's embarrassingly bare. It is undeniably true that there is no one way to answer these questions "yes" or "no," "pass" or "fail". There is no single tool that will give all the answers (this includes AVS and EqP). Compared to other well-developed sciences, the science of environmental risk assessment is in its infancy. When something does work, it then becomes the topic of microscopic examination (i.e., SEM/AVS). However, the general feeling was that at least the community was interested in the approach, even though there may be some disagreement as to its utility.

There was an extensive discussion that mixed policy and science (e.g., sediment quality criteria based on AVS and EqP). Dominic DiToro described the uncertainty analysis conducted on the EPA criteria based on the EqP prediction methodology. The analysis was conducted on all the data sets used to develop the criteria. The analysis tested the ability to predict sediment toxicity tests from independent measurements (i.e., water only measurements and independent estimates of octanol water partition coefficients). The EPA criteria development process included field validation efforts. Rick Swartz pointed out that one should go to the field earlier rather than later, and that some field sites will be easier to work with than others (i.e., field validate at the simplest sites first).

One of the most powerful tools for field validation is colonization experiments (e.g., placing trays of sediment back in the environment). A suggestion was made for conducting work with undisturbed cores; dosing can be done in micro- or mesocosms. Peter Chapman pointed out that validation can be correlative (e.g., observations of the benthos related to other "tools") or investigative (e.g., undisturbed cores, trays of contaminated sediment put back in the field, etc.). He also recommended that, given that hazardous waste sites are only consistent in their inconsistency, there be an attempt to piggyback useful validation-type studies in hazardous waste site investigations. But these will only be useful if they are reported.

Dominic DiToro clarified the application of EqP. There is a misunderstanding about the range of its applicability, with some investigators applying the approach to large organisms like fish. They then make the assumption that the fish is in equilibrium with the sediment. The EqP theory only works for benthic organisms, and even for that specific group of organisms there is a lot of scatter in the data. However, it has general applicability.

Spyros Pavlou reiterated that the SEM/AVS process is a screening tool that may represent the worst-case scenario. There are many more things that go into evaluation of Superfund sites than AVS or EqP. They should be used to identify the areas that require further investigation. The uncertainty associated with either technique becomes less important as more tools are brought into the evaluation process. However, if the decision is based solely on one approach, then you must know the uncertainty associated with that approach. There was a request that both biology and chemistry be used to make the decisions; neither should be used alone. AVS and EqP should be used for screening, to help set priorities, and to assist in determining cause-and-effect.

NOAA's Overview and Summation

The Woods Hole Oceanographic Institute was a stimulating venue for the open exchange of information. The many theories and viewpoints presented over the course of the workshop lead to several open discussions that gave all participants an opportunity to express their concerns and opinions. The workshop was successful in achieving the goals as set forth by NOAA. Clarification was provided regarding:

(1) the scientific theory on which EqP and AVS methodologies are based,

(2) the utility of EqP and AVS in the evaluation of contaminated sediments, and

(3) the application of these approaches at hazardous waste sites.

There was overwhelming agreement that the EqP and AVS methodologies have a place in the risk assessor's tool box, but these tools must be <u>properly</u> used with the investigator understanding and implementing all associated caveats.

The presenters discussed both the strengths and weaknesses of the methodologies as well as our ability to accurately characterize aquatic systems. Overall, there was general agreement on many aspects of the methodologies, but there were many areas where disagreement prevailed suggesting the need for additional research. During the early stages of the workshop it was suggested that we attempt to reach consensus on as many AVS/EqP issues as possible. Candidate consensus items were recorded and edited as new information became available. Consensus was reached when the vast majority, if not all, of the 24 participating scientists agreed. The following six consensus items resulted from the AVS Workshop.

Consensus Item #1:

> *Bulk chemistry determinations alone are generally relatively poor predictors of contaminant bioavailability or toxicity.*

As with many other tools in the investigator's toolbox, the utility of bulk sediment analysis is limited when evaluating hazardous waste sites. Bulk sediment analysis data can be used to identify the presence and distribution of contaminants within an aquatic system and suggest which ones may be of major concern. Also, because of management and regulatory issues effecting hazardous waste sites, bulk sediment data still may ultimately be the measure by which areas requiring remediation are delineated. However, these measurements are not predictive of bioavailability, toxicity, or potential threat to aquatic biota. The realization that bulk chemistry determinations could not provide information regarding contaminant bioavailability or toxicity has prompted researchers to investigate other approaches. The EqP and AVS methodologies are two attempts to provide chemistry data that can either help predict or explain sediment toxicity. It must be remembered that these methodologies do not replace bulk sediment analysis at hazardous waste sites, but rather supplement it. This is because remediation decisions are not just based on whether the sediments are toxic in situ, but also on whether they may act as a source for downstream contamination.

Consensus Item #2:

> *Pore water is the primary route of exposure to many contaminants for benthic organisms; however, ingestion is also an important route for some organisms.*

The only methods by which benthic organism can uptake contaminants are active or passive absorption through the gills or skin (including the gut lining). For absorption to occur, the contaminant must be in a dissolved form either in the surrounding pore water or in the gut. Contaminants enter the gut via the ingestion of pore water or sediments; contaminants associated with sediments may become available for absorption as a result of pH conditions and metabolic processes. While no consensus was reached on whether sediment ingestion effects the ability of EqP and AVS theory to predict bioavailability and/or toxicity, Dr. DiToro expressed the view that the metal sulfide bonds are too strong to be broken by any activity in an organism's gut so sediment ingestion should have no effect on the application of AVS theory. It is still a question with regard to the EqP theory for non-ionic organic contaminants. However, the work of Meador et al. (in press) suggests that sediment ingestion can increase the bioavailability of at least some non-ionic organic contaminants. They compared the bioaccumulation of PAHs by two different benthic organisms: *Rhepoxynius abronius* (a non-deposit feeding amphipod) and *Armandia brevis* (a non-selective deposit feeding polychaete). Over a wide range of PAH exposure, no significant difference was found between species in the tissue concentrations of low molecular weight PAHs. There was a large differential observed between species for the bioaccumulation of high molecular weight PAHs, with the polychaete accumulating more than the amphipod.

Consensus Item #3:

> *The EqP and AVS approaches to sediment analysis are based on sound science and theory; partitioning does occur, and sulfides do complex with some metals (Cd, Cu, Pb, Ni, Zn), affecting their bioavailability.*

The third consensus item is based on the EqP theory, which states: there is a calculable relationship between sediment contaminant concentrations and contaminant toxicity. Therefore, if you know the water-only LC_{50} (or some other water-only toxic benchmark) you can calculate a sediment LC_{50} for the contaminant based on its K_{OC} and the organic carbon content of the sediment. Data were presented at the workshop supporting this for **single** non-ionic organic contaminants under laboratory conditions. (Work has yet to be done on mixtures of non-ionic organic contaminants, the more common case in the real world.) The theoretical basis for the AVS approach is that the sulfides of the five metals have lower solubility constants than either Fe or Mn sulfides, and if they are added to a system containing FeS and/or MnS, they will displace the Fe and/or Mn forming an insoluble metal sulfide and thus make the contaminant metal non-bioavailable. Like the first, Consensus Item #3 was readily agreed to, although there were many questions regarding how this could be applied to the real world.

Consensus Item #4:

> *For sediment in which the contaminant(s) of concern include one or more of the following: Cd, Cu, Ni, Pb, and Zn, an SEM/AVS molar ratio of <1 indicates the vast majority of these metals are complexed with sulfides and are essentially not bioavailable and hence acute toxicity from these metals is highly unlikely. An SEM/AVS molar ratio >1 does not necessarily indicate that these metals are bioavailable and acutely toxic; other factors may be affecting their bioavailability and toxicity. Toxicity refers to laboratory tests only and does not necessarily apply to bioaccumulation of the metals or alterations in the benthos. [Noted Caveats: (1) The uncertainty of the measurements must be taken into account when comparing the ratio to the absolute value of 1. (2) Both the numerator and denominator must be considered when evaluating the ratio: almost "no" AVS compared to "some" SEM has a different meaning than the same ratio wherein the AVS concentration is much higher. Very low concentrations of both SEM and AVS should not be considered predictive. (3) The consensus statement is only valid if AVS concentrations are above operational detection limits.]*

Consensus was reached on this item concerning what the AVS methodology can and cannot currently tell us, although it was necessary to include several caveats. This consensus item includes several important issues, each of which should be thoroughly discussed. The first major issue is that currently there are only five metals applicable to the AVS methodology: Cd, Cu, Ni, Pb, and Zn. Other metals are being investigated, but now there is insufficient evidence or data to suggest they behave in a similar manner. Second, the SEM portion of the SEM/AVS ratio is the *sum* of the molar concentrations for these five metals; the ratio is not meant to be calculated on an individual metal basis. The AVS methodology is not considered useful in evaluating Hg contamination because although inorganic Hg also forms an insoluble sulfide (HgS), the primary concern regarding Hg is the biomagnification of organic Hg. However, HgS is less soluble than any of the other five metal sulfides, and if significant quantities of <u>inorganic</u> Hg are present they could compromise the evaluation of the bioavailability of the other five metals by making the sulfide unavailable for binding.

The interpretation of the SEM/AVS ratio is a very important step in the sediment evaluation process. The purpose of the ratio is to determine how much of the metals present are bound and biologically unavailable. If the ratio is <1, theory indicates that virtually all five metals are bound up as sulfides and are unavailable to biological receptors. Hence, the unavailable metals are not toxic. This theory was supported by data from toxicity tests conducted with both spiked- and field-collected sediments. A ratio >1 <u>only</u> indicates that all metals are <u>not</u> bound up as sulfides. There are several reasons why acute toxicity may not be observed at ratios greater than one: the metals may be bound to other ligands and not be bioavailable; they may be in ionic form but at sufficiently low concentrations as to not be acutely toxic, or the test organisms may actively avoid the contaminants. The ratio by itself gives no indication as to the quantity of metals that are bioavailable, and this is where the second caveat is of concern. For example, if the SEM concentration is 0.6 µmoles and the AVS concentration is 0.3 µmoles, the SEM/AVS ratio is 2 with 0.3 µmoles of metals potentially bioavailable. However, if SEM=6 µmoles and AVS=3 µmoles you still have a ratio of 2 but now you have 3 µmoles of metals potentially bioavailable. So, the ratio is fine for indicating no toxicity, but can't tell when to expect toxicity. At this point, some other mechanism must be used to determine bioavailability and toxicity (i.e., field or laboratory toxicity tests).

It has been recommended that in the future the difference between SEM and AVS (SEM-AVS) be used instead of the ratio (SEM/AVS). The difference is more informative than the ratio. As in the above hypothetical example, the difference would provide information on the amount of bioavailable metals. Also, if the difference is calculated sequentially for the five metals, starting with the one with the least soluble sulfide, the metal(s) that is actually bioavailable could be determined. Dr. Hansen expressed the opinion that, based on his spiked- sediment colonization tests, in the future we will be able to predict chronic effects through the use of SEM-AVS in conjunction with our understanding of the role of organic carbon.

Consensus Item #5:

> *The quantity and type of organic carbon can affect the bioavailability of non-polar organic contaminants as well as some metals.*

It was readily agreed that the quality and quantity of organic carbon found in the sediments affects the bioavailability of non-polar organic contaminants. Dr. Mahony indicated that once the AVS are used up via complexation, the organic carbon can strongly affect the bioavailability of Cu, and to a lesser extent Pb. With regard to the importance of the type of organic carbon present, it was generally agreed that humic materials were common in most sediments and subtle variations in the quality would probably have little effect on contaminant availability and K_{OC}. However, contaminant availability could be influenced by the presence of large masses of organic carbon, such as coal, wood chips, creosote, or dense plant material. The presence of foreign material and large chunks of debris must be kept in mind when analyzing and interpreting chemical data for sediments. It was also noted that hazardous waste sites are special cases where the type of organic carbon may be an important factor in determining bioavailability of contaminants.

Consensus Item #6:

> *There is no single, 'perfect' tool that should be used in isolation for making decisions. This includes, for example, single-chemical criteria, toxicity tests, and faunal studies. The best decisions are based on the collection, use, and fundamental understanding of biological and chemical data.*

This last consensus item is possibly the most important from a risk assessor's or manager's viewpoint. It provides the limits and boundaries of these methodologies and enforces the concept of a multi-faceted approach. This consensus item puts a perspective on the overall risk assessment process and forces us to realize that EqP and AVS are not "magic bullets" that will provide the ultimate answer. However, they can be useful in the evaluation process for contaminated sediments at hazardous waste sites, if they are used properly with full knowledge of their limitations and in conjunction with the other available tools.

A seventh consensus item could be listed, although it was not formally presented as such at the workshop it was repeatedly emphasized:

> *"always be aware of the uncertainty inherent in your analyses."*

Agreement within a factor of two is considered very good for any replicate environmental measurements, whether it be chemical or biological. Some consider a factor of five or even an order of magnitude as not unreasonable depending on the parameter measured. This uncertainty is not only due to our limited ability to make certain types of measurements, but is also due to the natural variability found in the real world. When analyzing any data set or the output of any model, decision makers must be aware of the uncertainty associated with the values they are attempting to evaluate. Awareness of uncertainty can be especially important if sample data are being compared to any form of criteria. If the criterion is an SEM/AVS ratio of 1, is 0.9 <1 and is 1.9 truly >1? Only if the decision makers are aware of the uncertainty can they be expected to draw reasonably appropriate conclusions about conditions at a site.

Although the group was able to reach consensus on six issues, a number of disputed and unresolved issues still remain, including:

> *"Does equilibrium exist in natural sediments? How does EqP work with mixtures? How does sediment ingestion effect the EqP analysis? What are the proper procedures for collecting and preparing sediment samples for SEM and AVS analyses?"*

A consensus statement was almost reached regarding equilibrium in natural sediments. The predominant belief was that within our ability to measure, equilibrium (or at least steady-state conditions) exists in natural, undisturbed sediments. In this case, equilibrium is defined for the contaminant in the appropriate solid phase of the sediment and the pore water, not for the solid phase or pore water and the biota. However, due to lack of resolution on what constitutes undisturbed sediments, the recognition that hazardous waste site sediments are highly disturbed and may receive continuing inputs, the special situation of periodically inundated sediments, and several other questions and caveats, a consensus could not be reached.

No data were presented to address either the mixtures or ingestion questions. As for sediment sample handling, it was suggested that if done with reasonable care; samples could be homogenized with only a minimum loss of AVS because the contaminant metal sulfides are less easily oxidized than the Fe or Mn sulfides. It was also stated that if relatively small samples were being collected, then any handling should be done under a nitrogen atmosphere. There was general agreement on the need for specific protocols for sample collection, handling, and analysis.

Another question asked was:

> *"Since AVS is only present under anoxic conditions, how does it effect the oxic sediments where the biota live?"*

The basic theory was presented that the free metal ions in the pore water will migrate from the region of relatively high concentration (oxic sediment pore water) to the region of relatively low concentration (anoxic sediment pore water) where they will be removed through the formation of metal sulfides. This was supported by incremental porewater concentration curves for collected sediments in the laboratory and in situ sediments. Both sediments showed similar conditions. A possible way around this question is the work Dr. Tessier presented on determining a calculable relationship between metal (Cd) concentrations in oxic sediments and in biota. It would be interesting to see if there is a relationship between what he is doing in oxic sediments with what is being done with AVS in anoxic, i.e., are the oxides he is measuring a direct indicator of the sulfides that would be present in the anoxic layer.

In conclusion, we find that the EqP and AVS approaches to sediment analysis are among the tools that can be used to evaluate sediment contamination at hazardous waste sites. However, they only should be used with a full understanding of their advantages and limitations, and before they can be used to their fullest potential several questions need to be answered. Finally, as was reiterated throughout the workshop, there is no miracle tool or single number that gives all the answers; AVS and EqP, like any of the other available tools (e.g., bulk chemistry, toxicity tests, community studies), should not be used in isolation. Decisions at a hazardous waste site need to be based on an integrated approach using both site-specific biological and chemical data.

Appendix A

Workshop Participants

Participants

Name	Affiliation
Jack W. Anderson	Columbia Analytical Services Carlsbad, California
Walter J Berry	Science Applications International Corp. Narragansett, Rhode Island
James M. Brannon	USACOE Waterways Experimental Station Vicksburg, Mississippi
R. Scott Carr	National Biological Survey Corpus Christi, Texas
Peter M. Chapman	EVS Environmental Consultants North Vancouver, British Columbia
Theodore H. DeWitt	Battelle Marine Science Laboratory Sequim, Washington
Robert N. Dexter	EVS Environmental Consultants Seattle, Washington
Dominic M. DiToro	HydroQual, Inc. Mahwah, New Jersey
David J. Hansen	US EPA Environmental Research Lab Narragansett, Rhode Island
Christopher G. Ingersoll	National Biological Survey Columbus, Missouri
D. Michael Johns	EVS Environmental Consultants Seattle, Washington
James L. Lake	US EPA Environmental Research Lab Narragansett, Rhode Island
Peter F. Landrum	NOAA Great Lakes Environmental Research Laboratory Ann Arbor, Michigan

Name	Affiliation
Brenda K. Lasorsa	Battelle Marine Science Laboratory Sequim, Washington
John D Mahony	Manhattan College Riverdale, New York
James P. Meador	NOAA National Marine Fisheries Service Seattle, Washington
Spyros P. Pavlou	Foster Wheeler Environmental Corp. Stuart, Florida
Philippe Ross	The Citadel Charleston, South Carolina
K. John Scott	Science Applications International Corp. Narragansett, Rhode Island
Mark D. Sprenger	US EPA Environmental Response Team Edison, New Jersey
Burton Suedel	EA Engineering, Science & Technology Hunt Valley, Maryland
Richard C. Swartz	US EPA Environmental Research Lab Newport, Oregon
André Tessier	University of Quebec Sainte-Foy, Quebec
Jack Q. Word	Battelle Marine Science Laboratory Sequim, Washington

NOAA Coastal Resource Coordination Branch Staff

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John Lindsay
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Other Attendees

Name	Affiliation
Dave Charters	US EPA Environmental Response Team Edison, New Jersey
Chris Hall	Genwest Seattle, Washington
Jackie McGee	Genwest Seattle, Washington
Nancy Morse	US Fish and Wildlife Service Edison, New Jersey
Royal Nadeau	US EPA Environmental Response Team Edison, New Jersey
Mary Reiley	US EPA Office of Science & Technology Washington, D.C.
Sandra Salazar	EVS Environmental Consultants Seattle, Washington
Susan Svirsky	US EPA Region I Boston, Massachusetts
Dave Tomey	US EPA Region I Boston, Massachusetts

Appendix B

Agenda

Tuesday September 13

	Moderator: Donald MacDonald	
9:00 - 9:50	Greetings and opening comments	Alyce Fritz Donald MacDonald
9:50 - 10:20	Assessing the assessment tools	Robert Dexter EVS Environmental Consultants
10:20 - 10:35	Break	
10:35 - 11:10	An introduction to EqP applied to nonionic organic chemicals and metals	Dominic DiToro HydroQual, Inc.
11:10 - 11:45	Generic screening versus site-specific reality: What works, what doesn't and why	Peter Chapman EVS Environmental Consultants
11:45 - 1:00	Lunch	
	Moderator: Mary Matta	
1:00 - 1:30	Certain chemical aspects of heavy metal-sediment interactions: the role of organic carbon and the kinetics of metal sulfide oxidation	John Mahony Manhattan college
1:30 - 2:00	The influence of sediment stability/disturbance on toxicity of non-polar organic compounds to marine amphipods	Jack Word Battelle MSL
2:00 - 2:30	K_{OC} and K_{DOC} in sediment pore water	Jim Brannon US Army COE WES
2:30 - 3:00	Pore water toxicity testing the direct application of EqP	Scott Carr US NBS
3:00 - 3:15	Break	
	Moderator: Alyce Fritz	
3:15 - 3:45	Prediction of Cd accumulation in benthic organisms	André Tessier University of Quebec
3:45 - 4:15	Predicting the toxicity of metals-contaminated sediments using AVS and interstitial water normalizations: results from spiked sediment laboratory ten-day lethality and four-month colonization tests	David Hansen US EPA ERL
4:15 - 4:45	"Marathon Battery: What were the questions?"	Mark Sprenger US EPA ERT
4:45 - 5:15	Sediment contamination, toxicity and macrobenthos: comparability of laboratory and field observations	Rick Swartz US EPA ERL

Wednesday September 14

Moderator: Jay Field

8:00 - 8:30	Use of SEM/AVS ratios and pore water metal concentrations to predict metal bioavailability in field sediments	Gerald Ankley US EPA
8:30 - 9:00	Comparison between the results of toxicity testing with marine sediments and predicted effects based on chemistry	Jack Anderson Columbia Analytical Services
9:00 - 9:30	Assessing toxicity in multi-metal contaminated sediment: Application of theoretical and investigative approaches	Michael Johns EVS Environmental Consultants
9:30 - 10:00	Strengths and weaknesses of the EqP approach as applied to hazardous waste sites risk assessment	Spyros Pavlou Foster Wheeler Environmental Corp.
10:00 - 10:30	Break	
10:30 - 12:15	**Panel Discussion I** **Moderator: Mary Matta**	Panelists
	1. What can and cannot the SEM/AVS ratio *really* tell us?	Chris Ingersoll NBS
	2. How do the temporal (e.g., seasonal) and spatial changes in physico-chemical parameters affect the SEM/AVS ratio and how does this variability affect our assessment of hazardous waste site conditions?	Brenda Lasorsa Battelle MSL John Scott SAIC
	3. Which parameters of the system should be measured and how can this data be applied to an entire ecosystem?	
12:15 - 1:15	Lunch	
1:15 - 3:00	**Panel Discussion II** **Moderator: John Lindsay**	Panelists
	1. Is equilibrium a good assumption in the environment?	Theodore DeWitt
	2. Are the following assumptions valid?	Battelle MSL
	a. pore water is the sole route of exposure to contaminants;	Jim Meador NOAA, NMFS
	b. pore water exposure is equivalent to surface water exposure.	Philippe Ross The Citadel
	3. What effect does the presence of other organic compounds and partitioning phases have on the bioavailability and toxicity of individual nonionic organics?	
3:00 - 3:15	Break	

Wednesday September 14

3:15 - 5:00 **Panel Discussion III**
Moderator: Mike Buchman

1. Both SEM/AVS and EqP are normalization processes and require the measurement of other components. Can these other components be reliably and/or accurately measured?

2. Co-occurrence of high contaminant concentrations (as measured by chemistry) and naturally occurring toxicants (e.g., ammonia and hydrogen sulfide) – how should they be handled with respect to sediment evaluation/remediation?

3. When multiple contaminants are present in toxic sediments can SEM/AVS and/or EqP identify the contaminants responsible for the toxicity?

Panelists

Walter Berry
SAIC

John Mahony
Manhattan College

Jack Word
Battelle MSL

Thursday September 15

8:00 - 9:45 **Panel Discussion IV**
Moderator: Alyce Fritz

1. What are the components of a sampling plan to evaluate contaminant bioavailability based on SEM/AVS and EqP?

2. What are the logistical variables that need to be identified and standardized (e.g., sample storage, handling, acid concentration, sulfide evolution rate, analytical considerations)?

3. How does sampling alter sediment toxicity?

Panelists

Peter Landrum
NOAA Great Lakes ERL

Burton Suedel
EA Engineering, Science & Technology

9:45 - 10:00 Break

10:00 - 11:45 **Panel Discussion V**
Moderator: Don MacDonald

1. How much additional field validation of the approaches is required?

2. What type(s) of validation should be pursued?

3. What would a field monitoring program consist of to validate SEM/AVS and EqP?

Panelists

Peter Chapman
EVS Environmental Consultants

Dominic DiToro
HydroQual, Inc.

Spyros Pavlou
Foster Wheeler Environmental Corp.

11:45 - 12:15 Wrap-up

Appendix C

References

The following list contains references dealing with AVS and EqP as well as other topics related to the workshop. It includes all references cited by the various presenters. The list is not meant to be comprehensive; it is a starting point for anyone wishing to explore the subject in more detail than was covered by this summary of the proceedings.

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Appendix D

Acronyms and Abbreviations

ACS	American Chemical Society
AET	apparent effects threshold
AVS	acid volatile sufides
AWQC	ambient water quality criteria
BASF	bioaccumulation sediment factor
CAS	Columbia Aquatic Sciences
Cd	cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CRCB	Coastal Resource Coordination Branch
C_d	dissolved or pore water phase chemical concentration
C_s	solid phase chemical concentration
Cu	copper
DOC	dissolved organic carbon
EPA	Environmental Protection Agency
EqP	equilibrium partitioning
ERL	effect range low
ERM	effect range medium
Fe	iron
f_{oc}	organic carbon concentration
HAZMAT	Hazardous Materials Response and Assessment Division
Hg	mercury
IW	interstititial water
IWTU	interstititial water toxic units
K_{DOC}	dissolved organic carbon partitioning coefficient
K_{oc}	organic carbon partitioning coefficient
K_{ow}	octonol-water partitioning coefficient
LC	lethal concentration
Me	metal
Mn	manganese
MSL	Marine Sciences Laboratory

Ni	nickel
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
OC	organic carbon
PAH	polycyclic aromatic hydrocarbons
Pb	lead
PCB	polychlorinated biphenyl
PEL	probable effects level
PPTU	predicted pore water toxic units
PRP	potential responsible party
PTU	porewater toxic units
QA/QC	qualtity assurance/quality control
RGS	reporter gene system
S	sulfur
SEM	simultaneously extracted metals
SLC	screening level concentrations
SOP	standing operating procedure
SQC	sediment quality criteria
TBT	tributyltin
TIE	toxicity identification evaluation
TEL	threshold effects level
TOC	total organic carbon
TU	toxic unit
USACOE	U.S. Army Corps of Engineers
USFWS	U.S. Fish and Wildlife Service
WES	Waterways Experimental Station
Zn	zinc