EFFECTIVE DECISION-MAKING MODELS FOR EVALUATING SEDIMENT MANAGEMENT OPTIONS

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EXECUTIVE SUMMARY

The USEPA, through its contaminated sediment management strategy (USEPA 1998), advocates a quantitative scientific approach to evaluating and remediating contaminated sediment sites. Although the strategy presents a sensible strategic approach, it does not provide the needed decision-making framework. The USEPA Great Lakes National Program Office proposed a framework as part of the Assessment and Remediation of Contaminated Sediments (ARCS) Program (USEPA 1993). This framework was implemented in several ARCS studies, but it has not been applied routinely, possibly because detailed guidance was not presented.

The typical approach to developing a contaminated sediment management plan has been to focus efforts initially on the feasibility of various remedial options. Typically, the efficacy of remediation is assumed or given cursory evaluation. Most notably, sediment removal is presumed to be an effective method to accelerate recovery at many sites and to be necessary to prevent the possibility that an increase in risk could occur following a catastrophic event. Evidence indicates that presumptions of efficacy are not always correct. The lack of efficacy of sediment removal in some cases likely was due to some combination of the following:

- The sediments may not have been the dominant source of the COC loadings to the ecosystem. For example, the contributing source may have been widespread low level concentrations of COCs, rather than definable “hot spots” or the COCs targeted by dredging were at depth and, consequently, were not contributing to the system or external continuing sources were still contributing COCs to the system.
- The removal action itself may have resulted in increased exposure. For example, surface sediment COC concentrations may have increased either because all of the higher concentrations in sediments at depth were not removed or because of resuspension or redistribution of higher concentration COCs (often found at depth) during the dredging operation.

The extent to which either or both of these circumstances are likely to occur can be determined if the assessments are guided by a decision framework grounded in sound science. This paper outlines a framework that provides the information needed to answer the following questions intended to guide the final remedial decision for the site:

- When will the site recover to acceptable conditions via natural processes (i.e., natural recovery)?
- Will sediment removal accelerate the recovery? If so, by how much?
- Are there other remedial options more effective at accelerating recovery?
- What risks exist from rare event phenomena if the COC-containing sediments are left in place?

The answers to these questions are derived from an understanding of the relationship between the COC concentration in the sediment and risks to human health and relevant ecological receptors. This exposure concentration-risk relationship is characterized on the basis of a conceptual model of the fate, transport, and bioaccumulation of the sediment-associated contaminants. The model characterizes the site-specific exposure concentration-risk relationship, the relevance of buried contaminants, and the manner in which risks will change in the future under natural attenuation or the various options for active remediation. It is developed and applied through baseline and prospective assessments of the site. The complexity and degree of such assessments are a function of the site-specific conditions and the quality/quantity of data needed to reach a risk-based decision.

The baseline assessment involves evaluations of the COC distribution, exposure pathways, the routes and rates of COC migration, the contemporary natural recovery rate, and baseline risk. The data needs for these analyses pertain to the bioavailable surface sediments, the vertical gradients within the sediment column, and the specification of concentration in units meaningful to fate and exposure.

The sediment data, along with measurements of COC in the water column and biota, form the basis for estimating COC exposure to aquatic biota, wildlife, and humans. These data must be spatially and temporally averaged to determine relevant exposure concentrations. The regions over which spatial averages are computed are defined by the habitat and movement of the organisms for which risk is being calculated. The time over which averages are computed is defined by the toxicokinetics of the COC within these same organisms. COC concentrations must be expressed in units relevant to risk. In general, the appropriate units are mass of COC per mass of sediment organic matter (typically quantified as organic carbon). For many metals, it is appropriate to contrast the metal concentrations to the concentration of sulfide available for metal complexation.

The rate of natural recovery is established based on historical measurements of COCs in water, sediment, and biota. In the absence of a sediment, water, or biota data record of sufficient length to establish the rate of natural recovery, the rate may be established from the vertical profile of the COC in sediment cores taken from areas of the site where continual deposition has occurred. By dating the various layers of such cores, the vertical concentration profile is converted to a temporal concentration profile.

An understanding of the degree to which natural recovery processes may ameliorate COCs in surface sediments requires an understanding of the potential role and overall significance of external sources of COCs. External COC sources may exert control over the rate and extent of natural recovery as well as affect the success of active remediation efforts. Therefore, external COC sources such as contaminated groundwater discharges, nonpoint surface water runoff, surface water discharges, nonaqueous phase seeps, or process discharges must be quantified.

Estimation of the efficacy of remedial actions involves reanalyzing the baseline risk assessment with predicted future concentrations of COC in water, surface sediment, and aquatic biota. This has been referred to in the text as a prospective risk assessment to distinguish it from the baseline risk assessment. Future conditions are predicted using the understanding of the site and the COC levels, trends derived in the baseline assessment, and knowledge of the scheduling and engineering details of the potential remedial action plans. The prospective assessment involves two types of predictions: (1) natural recovery and active remediation and (2) impact of a rare storm or high flow event.

Various approaches may be taken to predict future COC concentrations. Levels of complexity range from Tier 1 (qualitative/semiquantitative approach) to Tier 2 (quantitative approach). The appropriate approach depends on the complexity of the problem and the degree of accuracy desired. Complexity arises from the hydrodynamic and sediment transport characteristics of the site and from the existence of significant external or internal sources. In complex cases, the appropriate approach involves detailed data analyses and the development of quantitative mass balance models, particularly if the collateral impacts of the considered remedial options are significant. This Tier 2 approach has four modeling components: (1) hydrodynamics, (2) sediment transport, (3) COC fate, and (4) COC bioaccumulation. In simpler cases, correlation and extrapolation of site data and generic data may be adequate for decision making. Both types of approaches are outlined in the paper that follows as part of a proposed two-tiered approach to prospective assessment.

OVERVIEW

Sediments containing potential chemicals of concern (COCs; i.e., chemicals present at concentrations exceeding specified screening level criteria) are often viewed as candidates for remediation. Whether or not remediation is deemed necessary depends on the magnitude of direct or indirect health risks to humans or endangered species or to wildlife or aquatic organism populations. Which of the available remedial options is most appropriate depends on a myriad of site-specific factors, including the following:

- Size (area) and physical characteristics of the affected sediments
- COC levels in the surface sediments
- COC concentration profiles vertically within the sediment
- Whether or not "clean" soft (i.e., removable) sediments underlay sediment strata with COCs present above acceptable levels
- Hydraulic characteristics and nature of the water body
- Natural recovery potential
- Exposure pathways for humans, wildlife, and aquatic biota

The size and surface COC levels of the affected sediments have implications with regard to the sediments' function as a COC source for downstream locations and a direct source of exposure to humans, wildlife, and aquatic biota. The vertical concentration profiles within the sediment affect the potential risks associated with disturbance of the sediment and, together with the existence of "clean" soft sediment below the COC-containing sediments, the efficacy of removal actions. The hydraulic characteristics and nature of the water body affect the rate at which COCs are released from the sediments, overall sediment bed stability, and the efficacy of a remedial decision to leave the COC containing sediments in place. The natural recovery potential impacts the incremental risk reduction attainable by active remediation. The exposure pathways determine the response of critical receptors to changes in exposure concentrations.

Understanding and interpreting these factors so that effective remediation is achieved requires the application of a logical and systematic approach that incorporates sound science. The level of detail associated with this approach determines the accuracy of the subsequent assessments of remediation effectiveness. Greater detail is warranted where the negative impacts of active (i.e., intrusive) remediation on the ecosystem and the local community are substantial and where the costs of remediation are high.

The U.S. Environmental Protection Agency (USEPA), through its Contaminated Sediment Management Strategy (CSMS; USEPA 1998a), has advocated a quantitative scientific approach to site evaluation and remediation. Of particular note are the following two statements:

> "Assessment of sediment contamination and any subsequent steps taken by the Agency to reduce risks should be based on sound science, and, when available, site-specific information."

> "Selection of the appropriate remedial option at a contaminated sediment site will be undertaken on a case-by-case basis after careful consideration of the risks posed by the contaminants to human health and the environment, the benefits of remediation, the short- and long-term effects of implementing the remedial option, the implementability of the remedial option, and the costs of remediation."

Although the CSMS presents a sensible strategic approach, it does not provide the needed decision-making framework. The absence of such a framework has been viewed as an obstacle to effective contaminated sediment management (International Joint Commission 1997). The USEPA Great Lakes National Program Office has proposed a framework as part of the Assessment and Remediation of Contaminated Sediments (ARCS) Program (USEPA 1993a). A ten-step risk management framework was outlined in which the key step was developing quantitative mass balance models to be used in estimating the "… changes in risk, relative to baseline risk, that would result from implementation of the various remedial alternatives evaluated." The framework was implemented in several ARCS studies, but it has not been applied routinely, possibly because detailed guidance was not presented.

The approach most often applied to developing a remediation strategy for contaminated sediments has been to focus efforts on the feasibility of various remedial options. Typically, efficacy has been assumed or given cursory evaluation. In many cases, sediment removal was presumed to accelerate recovery and to be necessary to prevent the possibility that an increase in risk would occur following some catastrophic event. Evidence indicates that presumptions of efficacy are not always correct. Forty-five percent of the polychlorinated biphenyl (PCB) mass in New Bedford Harbor was removed in 1994 and 1995 through dredging, yet caged mussels have shown no reduction in PCB levels (USEPA 1997a). Twenty-seven percent of the PCB mass in the Grasse River was removed in 1995. Resident fish have shown no positive response, and may have shown a negative response (Alcoa 1999). The lack of efficacy in these cases likely was due to some combination of the following:

- The sediments may not have been the dominant source of the COC loadings to the ecosystem. For example, the contributing source may have been widespread low level concentrations of COCs, rather than definable "hot spots" or the COCs targeted by dredging were at depth and, consequently, were not contributing to the system or external continuing sources were still contributing COCs to the system.
- The removal action itself may have resulted in increased exposure. For example, surface sediment COC concentrations may have increased either because all of the higher concentrations in sediments at depth were not removed or because of resuspension or redistribution of higher concentration COCs (often found at depth) during the dredging operation.

The extent to which either or both of these circumstances are likely to occur can be foreseen if the factors cited earlier are evaluated using sound science. In fact, postremediation studies in the Grasse River have shown that both arguments are true. The dredged area was not the dominant source of PCBs to the river water and the fish (Alcoa 1999) and dredging reduced the average surface sediment PCB concentrations only by one half—from 150 to 75 parts per million (ppm; Alcoa 1999)—and only in a limited area.

Purpose and Approach

The purpose of this paper is to present a framework for evaluating contaminated sediment sites that reflects what has already been developed via the ARCS program and the approaches advocated in the CSMS. The goal is to provide guidance to those engaged in developing a sound, site-specific contaminated sediment management strategy founded on sufficient conceptual understanding of the system, as well as COC sources and potential impacts on receptors. The guidance includes a suggested approach for the prediction of future sediment, water, and biota contaminant levels for purposes of prospective risk assessment and assessment of risk reduction attainable by natural and active remediation. This approach is intended to provide objective information to the decision maker regarding the relative risk reduction attainable by the considered remedial actions and a means with which to make remedial decisions at the large number of sites where the optimal remedial action cannot be determined from a simple examination of data.

This paper provides information that can be used to answer the following questions that form the basis of the decision framework:

- When will the site recover to acceptable conditions via natural processes (i.e., natural recovery)?
- Will sediment removal accelerate the recovery? If so, by how much?
- Are there other remedial options more effective at accelerating recovery?
- What risks exist from rare event phenomena if the COC-containing sediments are left in place?

These questions are meant to guide the final remedial decision for the site.

Proposed Decision Framework

The optimal remedial strategy for a contaminated sediment site may be derived from an understanding of the relationship between the concentration of COCs in the sediment and risks to human health and relevant ecological receptors. This exposure concentration/risk (i.e., dose/response) relationship ultimately is based on a conceptual model of the fate, transport, and bioaccumulation of the sediment-associated contaminants. In past evaluations of remedial options, the typical practice has been to use a conceptual model incorporating the following assumptions:

- A direct proportionality exists between the concentration of COC in biota and the concentration in sediment.
- Processes exist to remobilize COCs associated with buried sediments (i.e., to make them bioavailable).

Use of these assumptions has led to the general conclusion that demonstrated or potential risks are best eliminated by removing the contaminated sediment. For example, USEPA Region II has stated "EPA has a statutory preference for technologies, such as dredging, that permanently remove the long-term risks from contaminated sediments (USEPA 1998b)." The *de facto* assumption that removal remedies are to be favored where remediation is suggested ignores the precept that strategy must be founded on an understanding of the site. It may be found to lack scientific foundation as shown by examples such as those cited earlier. The choice of an appropriate remedy requires understanding of the site-specific exposure concentration/risk relationship, the relevance of buried contaminants, and the manner in which risks will change in the future under natural attenuation or the various options for active remediation.

The decision framework presented here provides an approach for developing the requisite understanding. It is divided into baseline and prospective assessments.

- *Baseline Assessment*
  This component involves characterizing the COC distribution, evaluating baseline risk, estimating the historical natural recovery rate, and evaluating the importance of external (i.e., ongoing) sources. The complexity and degree of such assessment are a function of the site-specific conditions and the quality/quantity of data needed to reach a risk-based decision. It is consistent with the remedial investigation (RI) process conducted at Superfund sites and the Resource Conservation and Recovery Act (RCRA) facility investigation (RFI) conducted at RCRA sites. The primary differences from current routine practice relate to the specific approaches for each of the steps listed above.

  — <u>Characterization of the COC Distribution</u>
  In the approach typically used to assess contaminated sediments, the primary goal of sampling programs is to delineate the extent of contamination. Such sampling usually

involves the collection of sediment cores that are subsequently sectioned, homogenized and subsampled for analysis of the COCs. Samples are located on a regular grid, along transects or randomly within boundaries defined by sediment type or previous sampling. The resulting measurements of sediment COC concentrations are used to establish an areal view of site contamination. This picture is used to delineate regions of unacceptably high concentrations, sometimes referred to as “hot spots” and to provide a basis for calculating exposure for aquatic animals, wildlife, and humans. The vertical profiles within the cores are used to define the interface between COC-containing and “clean” sediments for the purposes of calculating the volume of contaminated sediment.

An additional and equally important use of data is to evaluate the effectiveness of possible remedial actions. This step is a critical part of the proposed framework. It involves analyses to determine potential and actual exposure pathways, the routes and rates of COC migration, and the ability of remediation to reduce exposure and long-term risk to both humans and environmental receptors. The data needs for these analyses pertain to the bioavailable surface sediments, the vertical gradients within the sediment column, and the specification of concentration in units meaningful to fate and exposure.

- COC Concentrations in Bioavailable Sediments
  COC transfer from sediments to the water column and the food web occurs from the sediments within an active surface layer [generally held to be within the upper 10 centimeters (cm) of sediment] in which particles are mixed by physical and biological action. Thus, an evaluation of current risk and source potential associated with sediments should be based on concentrations in this active layer.

- Vertical COC Concentration Profiles Within the Sediment
  At many sites, the COCs in the sediment originated from discharges to the water column (as opposed to the migration of contaminated groundwater through the sediments). The COCs are in the sediment because contaminated waterborne particles were deposited there. Present day discharges are lower, in most cases, than they were historically, and concentrations tend to be higher in buried sediment than at the surface. Examples of vertical concentration profiles for PCBs in Grasse River sediments, p,p’-dichlorodiphenyltrichloroethane (DDT) in Palos Verdes Shelf sediments, and mercury in Lavaca Bay (Texas Gulf Coast) sediments are shown in Figure 1. It is important to document such profiles because their structure bears on the issues of future risk and the efficacy of active remediation. Whether the more highly contaminated buried sediments will be eroded or brought to the surface as the result of a rare storm or high flow event depends on how deeply they are buried. The change in exposure concentrations likely to result from a sediment removal action depends on a number of characteristics of the vertical COC concentration profile. Principal among these are the following: (1) the relationship between COC concentrations in the bioavailable sediments and the buried sediments, (2) the COC concentrations in sediments near the bottom of the sediment column, and (3) the existence of a buffer of “clean” soft sediment between the sediments targeted for removal and hard pan.

- Interpretation of Spatial Patterns of COC Concentrations
  COC-containing sediments commonly exhibit substantial spatial variability in concentration, even at scales as small as a meter. For example, high density sediment coring in the Upper Hudson River revealed that samples within 2 feet of each other differed in concentration by about a factor of two on average and samples separated by 5 to 10 feet differed in concentration by about a factor of 20 on average (General Electric Company 1998). Because of this high degree of variation and the low

density of samples typical of most sites, interpolation of concentrations between sampling locations is difficult.

Generally, the results of an interpolation scheme are displayed with the use of contours or rasterized images. These contours and shaded images can impart a degree of spatial correlation that truly may not exist. For example, inverse distance weighting was employed on data in Lavaca Bay, Texas, to determine the spatial distribution of mercury contamination in the surface sediments. The interpolation was performed for both a historical data set and a sample set from the mid-1990s (see Figure 2). The uncertainty of the interpolation results in the historical data set is much greater than the uncertainty in results from the more recent sample set due to the small amount of data available in the 1970s as compared to the 1990s. The high values in the spatial distribution can be falsely interpreted as indicating a "hot spot," the areal extent of which is defined by the distances to neighboring sampling locations.

There are also cases in which spatial interpolation may not be representative of the system based on the sparse distribution of the sampling locations. In this case, it may be more accurate to analyze the data in terms of zonal averages to supply a general understanding of spatial patterns in the sediment. For example, in 1998, the Hudson River sediments were sampled for PCBs (see Figure 3). However, the sampling distribution was most dense in the near-shore, fine sediment areas. Because the near-shore areas are considered the more contaminated sediments, it would be inaccurate to spatially interpolate this data to represent the PCB patterns across the entire river. The interpolation results in the center channel would be skewed upward by the near-shore results and would be unrepresentative of the coarse-grained sediments located in this area where sampling points were less dense. In this case, the data set would be best represented by grouping the data into representative sample sets based on sediment type and location to obtain zonal averages throughout the river.

It is important that the statistical results of spatial interpolation be examined to provide an assessment of accuracy. Where the statistical information indicates poor spatial correlation, inferences from the spatial interpolation should be drawn with care and the benefits of additional sampling should be evaluated.

- Use of Relevant Concentration Units

  Sediment COC concentration is commonly reported in units of mass of COC per mass of dry sediment [e.g., milligram per kilogram (mg/kg)]. These units are useful for calculating the total mass of COC present at a site. However, they are of limited use in assessing COC migration and risk. Migration via groundwater advection or diffusion and the toxicity of nonbioaccumulative chemicals are mediated by pore water concentration, which is only weakly related to dry weight based sediment concentration. Further, the ingested dose of COC received by benthic organisms, which is important for bioaccumulatable chemicals, depends on COC mass per mass of sediment organic matter, because these organisms ingest a fixed mass of organic matter each day, not a fixed mass of dry sediment.

  Viewing concentrations on an organic matter basis can alter the interpretation of site conditions. For example, the PCB contamination in the sediments of the Upper Hudson River has been viewed historically as a "hot spot" problem because concentrations exceeding 50 ppm on a dry weight basis are generally found only in areas of fine sediment. However, the average concentration on an organic matter basis is similar in fine and coarse sediments (see Figure 4). Because coarse sediments account for about 80 percent of the sediment area, they contribute more PCBs to the water column than do the "hot spots." Further, both sediment types have equal strength as potential exposure sources to the food web. Their relative importance in this regard depends on their coincidence with habitat areas for relevant ecological receptors. The evaluation of exposure pathways and the efficacy of remediation are more complicated than would appear from examining the dry weight based concentrations.

— Evaluation of Baseline Risk
The sediment data, along with measurements of COC in the water column and biota, form the basis for estimating COC exposure to aquatic biota, wildlife, and humans. These data must be spatially and temporally averaged to determine relevant exposure concentrations. The regions over which spatial averages are computed are defined by the habitat and movement of the animals for which risk is being calculated. The time over which averages are computed is defined by the toxicokinetics of the COCs within these same animals. The details of such averaging and methodologies for quantifying risk are discussed in "Risk-Based Management Principles for Evaluating Sediment Management Options" in Appendix B.

— Estimation of the Historical Natural Recovery Rate
The rate of natural recovery of a contaminated sediment site is established based on historical measurements of COCs in water, sediment, and biota. In this context, natural recovery refers to the process by which natural biological, chemical, and physical forces reduce the concentration and toxicity and bioavailability of sediment COCs, thereby reducing associated human health and ecological risks. The principal mechanisms controlling the natural recovery of contaminated sediments include burial through the deposition of clean solids, sequestration and geochemical transformation, and biotransformation.

In the absence of a sediment, water, or biota data record of sufficient length to establish the rate of natural recovery, the recovery rate may be established from the vertical profile of the COC in sediment cores taken from areas of the site where continual deposition has occurred. By dating the various layers of such cores, the vertical concentration profile is converted to a temporal concentration profile.

— Evaluation of the Importance of External (i.e., Ongoing) Sources
The amelioration of sediment contamination through the natural recovery process can increase the relative importance of external sources of COCs. External COC sources may exert control over the rate and extent of natural recovery and affect the success of active remediation efforts. Therefore, external COC sources such as contaminated groundwater discharges, nonpoint surface water runoff, surface water discharges, nonaqueous phase seeps, or process discharges must be quantified.

- *Prospective Assessment*
This component involves estimating the efficacy of remedial actions to reduce risk and provide a comparative evaluation of implementation risk. The prospective assessment is roughly analogous to the assessment performed during the feasibility study or corrective measures study phase of site assessment under Superfund or RCRA. It consists of the reanalysis of the baseline assessment with predicted future concentrations of COC in water, surface sediment, and aquatic biota.

Future conditions are predicted using the understanding of both the site and the COCs defined in the baseline assessment, coupled with knowledge of the scheduling and engineering details of the potential remedial action plans. Various approaches can be taken to predict future concentrations. The appropriate approach depends on the complexity of the problem and the degree of accuracy desired. Complexity arises from the hydrodynamic and sediment transport characteristics of the site and the existence of significant external or internal sources.

External sources complicate historical data interpretation. They also impact the relative distribution of COCs between water and sediment and the temporal and spatial trends in water, sediment, and biota. As a result, it is difficult to use historical data to predict the long-term response of the system to source control. One approach is to implement source control and monitor the response of the system. Once sufficient trend data are available, a prospective risk assessment can be conducted to evaluate the benefits of additional remediation. An alternate approach is to conduct a quantitative analysis that attempts to define the impact of the source and the benefits achievable by source control and other remedial options. Such an approach has been conducted for PCBs in the Upper Hudson River [Quantitative Environmental Analysis, LLC (QEA) 1999]. Extensive data analysis and mass balance modeling were used to develop a quantitative tool capable of addressing directly the four key questions proposed previously. The model was extensively calibrated and validated against the extensive data available for this site. The model was then used to predict natural recovery and the effectiveness of source control and sediment removal. By contrasting these predictions, the information needed to develop a comprehensive remedial action plan that addresses both the sources and the sediments is available to the decision maker.

At sites where the baseline assessment indicates that external sources are not significant, the prospective risk assessment can be conducted at various levels of resolution. Two levels or tiers of analysis are presented in the remainder of this paper, which provides the details of the framework. The first tier uses data analysis as a basis for predicting future concentrations under natural recovery and active remediation. The second tier uses both data analysis and modeling in the manner used for PCBs in the Upper Hudson River. This second tier has significant precedent. It has been used by the USEPA at numerous sites including the James River (Kepone), Green Bay and the Fox River (PCBs), New Bedford Harbor (PCBs), and the Hudson River (PCBs).

BASELINE ASSESSMENT

The baseline assessment involves the four steps listed below. All of the steps are necessary for proper assessment. Various levels of effort are applicable to each of the steps, depending on the degree of accuracy desired in view of a necessary bias toward conservatism in the face of uncertainty.

1) Establish the spatial distribution of the COC on scales relevant to exposure and risk.
2) Quantify baseline risk.
3) Establish the historical rate of natural recovery.
4) Evaluate the importance of external (i.e., ongoing) sources.

Step 1. Establish Spatial Distribution of COC on Scales Relevant to Exposure and Risk

- *Step 1a. Conduct Sampling to Characterize Concentrations in Bioavailable Sediments*

  The activity of benthic macroinvertebrates is believed to be responsible for maintaining the active mixed layer in most surficial sediments. The depth of the layer is determined by biomass and the types of organisms present. Numerous studies have been conducted to examine sediment mixing. These studies have shown that the depth of significant mixing generally ranges between 1 and 10 cm, with most water bodies having mixing depths of a few cm. Because COC concentrations may vary significantly with depth in the sediment, it is important to section core samples such that the active layer is isolated. In most cases, this requires surface sections of 2 to 5 cm depth.

- *Step 1b. Define the Vertical Concentration Gradients with Resolution Sufficient to Evaluate the Efficacy of the Various Remedial Options*

  To evaluate whether a rare storm or high flow event will result in an increased risk, it is necessary to know COC levels at the maximum depths of erosion. In fine-grained (cohesive) sediments that typically contain buried contaminated sediments, these depths tend to be on the order of 1 to 15 cm. For example, modeling of hurricane-induced resuspension in Lavaca Bay (Texas Gulf Coast) indicated that most of the bay sediments experienced less than 5 cm of erosion and only a few percent experienced erosion greater than 10 cm (HydroQual, Inc. 1998).

  To evaluate the residual concentration likely to result from sediment removal, it is important to know the average concentration in the column of contaminated sediment, the concentration in the most deeply buried sediments, and whether contamination extends to hard pan. Where contamination extends to hard pan, dredges cannot get an "over bite" into clean material. Contaminated sediment will invariably be left behind. Depending on the depth of contaminated sediment and the dredging technology employed, the remaining sediment may have a COC concentration similar to the average of the whole column or of the sediment closest to the hard pan.

  On the basis of the need to determine concentrations in bioavailable sediment, erodible sediment and deeply buried sediment, samples should be sectioned in small increments near the surface and large increments to just beyond the presumed termination of contamination. As an example, an illustrative core sectioning protocol in 50 cm of contaminated sediment is shown in Figure 5.

- *Step 1c. Develop Interpretations of Spatial Patterns that Reflect the Degree of Spatial Continuity*

  Interpolation is used to delineate a contiguous area exceeding some threshold concentration and to assist in defining the average concentration in a region occupied by a receptor. Interpolation uses a distance weighting method. Some examples of the more common methods are inverse distance weighting, kriging, and spline. Further discussion on spatial interpolation and statistics can be found in Isaaks and Srivastava (1989) and Cressie (1993). The final method chosen is primarily dependent on the spatial distribution of the data set. For example, kriging is usually best employed when the data set is somewhat uniformly distributed over the area of interest, while inverse distance weighting may be a better choice when the data distribution is more random. The best way to determine the most appropriate interpolation method is to empirically compare the results of various methods to the original data set (Berry 1997). The result that most accurately represents the system while preserving the original data is the one that should be employed. In addition to examining the contours that result from interpolation, it is important to examine the statistical results of the analysis. These results allow an assessment of the accuracy and utility of the interpolation. To the extent that the degree of spatial correlation is low, care should be taken in drawing inferences from the interpolation. Where the cost and impacts of remediation are substantial, a finding of poor spatial correlation may warrant the collection of additional data to better define areas exceeding benchmark concentrations.

- *Step 1d. Express Concentration in Units Indicative of Source Potential and Biological Exposure*
  Organic matter, as measured by organic carbon, is the principal sorbant in sediment and concentration expressed as mg/kg organic carbon (OC) correlates with pore water concentration and toxicity of organic chemicals (USEPA 1993b). Thus, for organic COCs, sediment concentration in units of mass of COC per mass of organic carbon (e.g., mg/kg OC) provides the best metric for evaluating the spatial distribution of concentration.

  The toxicity of metals appears to be controlled principally by precipitation reactions with sulfides (DiToro, et al. 1991), and the molar ratio of the sum of divalent metals to acid volatile sulfide provides a useful metric for assessing spatial patterns. However, organic matter controls pore water concentrations where metal concentrations exceed the available sulfide (Mahoney, et al. 1996). Thus, metal concentration in units of mg/kg OC also provides a useful measure of bioavailability, particularly when the concentrations exceed sulfide concentrations.

Step 2. Quantify Baseline Risk

The detailed guidance for quantifying baseline risk is presented in Appendix B in “Risk-Based Management Principles for Evaluating Sediment Management Options.” Please refer to this aforementioned paper for an understanding of proposed approach to conducting this step in the assessment.

Step 3. Establish the Historical Rate of Natural Recovery

The rate of natural recovery can be approximated from an examination of historical surface sediment, surface water, and biota data for a site. Figure 6 illustrates the reduction observed in surface sediment, water column, and fish PCB levels within the upper Hudson River over a ten year period from the late 1970s to the late 1980s as a result of natural recovery processes. These data illustrate an approximately five-fold decline in surface sediment PCB concentrations with corresponding declines of ten-fold in surface waters and three-fold in resident large mouth bass. Two mechanisms were primarily responsible for this decline: (1) deposition of clean solids from upstream of the site and tributaries and (2) PCB dechlorination that reduced PCB bioaccumulation potential and, to a lesser extent, PCB mass.

In the absence of historical sediment, water column, and biota data, the natural recovery rate of a system may be assessed by examining finely segmented sediment cores. Sediment cores collected from depositional regions of a water body retain a historical record of the particulate-phase COC concentration. Using radionuclide markers (e.g., ^{137}Cs due to fallout from atmospheric nuclear weapons testing), an estimate of the depositional rate of the system can be established. This information can be used to associate COC levels within the sediment profile with specific time periods. From this time series, the natural recovery rate of surface sediment COC concentrations can be estimated. An example of this process is illustrated in Figures 7 and 8 for PCBs in an impoundment within the Housatonic River. The age of segments in finely segmented sediment cores was estimated using measurements of ^{137}Cs. A date of 1963 was assigned to the sediment segment containing the peak ^{137}Cs level. Based on the depth of this segment and the date of coring, an average net burial rate of 0.4 cm/year was calculated (see Figure 7). This rate was then used to establish dates for the remainder of the sediment segments. This process was repeated for five cores and the data were combined to yield and "average" profile (see Figure 8). These data indicate that surface sediment PCBs declined by over 500 mg PCB/kg organic carbon between 1960 and 1990.

Typically, natural recovery can be approximated as an exponential decline. Thus, the rate is estimated by fitting the data to an exponential equation. At sites with ongoing sources, the historical recovery may be more difficult to discern. In many cases, the effect is a reduction in recovery over time to a plateau as concentrations at the site become controlled by the ongoing source.

Step 4. Evaluate the Importance of External (i.e., Ongoing) Sources

The assessment of external discharges typically involves three steps. First, the mass loading rates of COCs from external sources are quantified by analyzing chemical monitoring data and associated volumetric discharge rates. Discharge rates may be measured (e.g., metered process discharges) or estimated (e.g., through groundwater modeling). Second, internal sources of COCs are quantified either through the application of mass balance principles to water column monitoring data or by estimating sediment-water exchange rates given the known distribution of COCs within surficial sediments. Differences in mass loading rates upstream and downstream of a contaminated sediment reach provide an estimate of the internal COC loading rate. Such internal COC source quantification is often performed during summer low flow periods when sediment-water exchange is dominated by diffusional processes and is relatively unencumbered by hydraulically induced interactions such as sediment resuspension. Finally, external and internal COC sources are compared. If external sources are small relative to internal sources, then they are not likely to exert a strong influence on the natural recovery rate or the system response to remediation. However, if external sources are significant, then additional source control measures must be implemented before considering active remediation of contaminated sediments, and the additional measures must be factored into natural recovery estimations.

Evaluations of sedimentation rate and natural recovery rate based on dated sediment cores and trends in fish suggested that external ongoing sources could be affecting mercury levels in Lavaca Bay, Texas. These analyses and application of mass balance principles to quantify the unknown external sources led to the discovery of a significant groundwater mercury source and altered the remedial approach taken to address the contaminated sediment problem in the bay. Portions of Lavaca Bay are routinely dredged to maintain shipping channels. These dredged sediments are chemically characterized for disposition purposes. Simple calculations of the mass of mercury removed from the bay via routine dredging operations revealed a mass imbalance, indicating the presence of a significant external source of mercury to the system. That is, the annual mass of mercury removed from the system via dredging exceeded that which could have been attributed to the redistribution of existing sediment contamination within the bay. Further investigations at the adjacent plant site led to the discovery of a significant groundwater source of mercury. It was this groundwater discharge and not the existing sediment contamination that was largely responsible for sediment contamination within the dredged channels. The discovery of the external source shifted the remedial focus from sediment dredging and subsequent placement within a confined disposal facility to on-site control of external mercury sources. This example illustrates the importance of quantitatively understanding external sources of COCs prior to developing remedial strategies for contaminated sediments.

In addition to direct quantification, the relative importance of external and internal sources of COCs can often be distinguished by notable changes in COC chemistry resulting from sediment diagenesis. Chemicals within sediments may be altered by numerous processes including biotransformation, chemical degradation, partitioning between solid and aqueous phases, and complexation. These processes may alter the chemical signature of the COC, thereby providing a means to distinguish between old COC deposits which have resided within the sediments for years or decades and new COCs derived from recent external sources to the system. For example, microbially mediated reductive dechlorination alters the congener distribution of source PCB Aroclors in predictable patterns, and these alterations can be used to distinguish between old PCB deposits that have undergone dechlorination and fresh PCB Aroclors derived from recent external loading.

The alterations of sediment PCBs via reductive dechlorination and chemical partitioning were used to differentiate between sediment and external plant site PCB sources to the water column of the Grasse River, New York. Figure 9 illustrates the close match between observed surface water PCB congener distributions and that expected within sediment pore waters (considering equilibrium partitioning and the congener distribution of PCBs within the sediment). In contrast, aqueous-phase PCBs found at low levels within plant site outfalls possess a distinctly different PCB congener distribution. Based on these observations, the external PCB loading from the outfalls was considered insignificant to the water column PCB loadings observed within the Grasse River as it did not significantly impact the chemical signature of the water column.

PROSPECTIVE ASSESSMENT

The prospective assessment involves two types of predictions: natural recovery and active remediation and impact of a rare storm or high flow event.

Natural Recovery and Active Remediation

A two-tiered approach is presented below. Tier 1 involves the analysis of data and extension of observed relationships to future conditions. Tier 2 involves the development of quantitative predictive models as tools for examining remedial scenarios.

- *Tier 1*
  Future concentrations of the COCs are predicted by extrapolating trends evident from historical data. This approach assumes that future conditions can be represented by conditions that existed during the period of historical record. Such an assumption is reasonable as long as external sources have not been, and will not be, significant. Where external sources have been important, the historical trend can be a poor predictor of future trends, particularly if the magnitude of the external sources changed significantly during the period of record.

  The basis for extrapolation may be the historical record in water, sediment, or biota. A static relationship among these media is assumed so that a historical record in one can be used for prediction of the other two. Relationships are location-specific, as illustrated in Figure 10. The top panel in this figure displays a static relationship at a location near the source. The bottom panel illustrates how this relationship might differ with distance from the source, as COCs flux from the sediment to the water column. For this reason, it is important to use data from the same location to establish relationships among media and to use multiple relationships to characterize the spatial dimension.

  The relationship is established by regression of the concentration data for biota (B), water (W) and sediment (S):

$$B = aW + bS \tag{1}$$

$$S = cW \tag{2}$$

  and, therefore,

$$B = eW = fS \tag{3}$$

  where:

$$e = a + bc$$

$$f = a/c + b$$

  and a, b, and c are the regression coefficients.

  This approach is used by the USEPA to predict bioaccumulation as part of the Great Lakes Water Quality Initiative (USEPA 1997b). It has also been used by the USEPA at contaminated sediment sites such as the Upper Hudson River (USEPA 1996). The intermedia ratio approach can be highly inaccurate because of the large difference in COC residence time in water and surface sediment and the impact of external sources on the relationship between water and sediment. If the system is not at steady state with external sources, the historical relationships are not indicative of the future relationships. In addition, any future change in the magnitude of external sources will cause a more rapid change in water column COC levels than in sediment COC levels. Thus, the approach should be used with caution at sites where external sources have been or are important.

Application of the intermedia ratio approach requires careful determination of the water column and sediment concentrations. The water column concentrations must be averaged temporally to provide an estimate of the seasonal or annual average concentration. The sediment and water column concentrations must be averaged spatially over the exposure region for the biota.

It is important also to note that the relationship between water column and sediment concentrations is site-specific, and the use of generic relationships or relationships from other sites is not recommended. This fact is illustrated in Figure11, which shows the ratio of surface sediment and water column PCB congener concentrations in relationship to the congener octanol-water partition coefficient for a number of water bodies. Similarly, the relationship of biota concentrations to water and sediment concentrations is species- and site-specific, depending on the structure of the food web and the water to sediment concentration ratio. This is illustrated by examining the spatial patterns of PCB contamination in sediment, water, and fish from the Upper Hudson River (see Figure 12). Throughout the 40 miles of river, sediment concentrations decline dramatically, while water column concentrations change very little. Concentrations in largemouth bass decline similarly to sediment, while the spatial pattern of PCB concentrations in caged fathead minnows is more consistent with that of the water column.

The intermedia ratios are used with the historical rate of recovery estimated in Step 3 of the baseline assessment to predict the trends in all three media. These trends provide the data necessary to calculate the prospective risk assessment under natural recovery.

Active remediation perturbs the system and alters the relationships among water, surface sediment, and biota such that the pseudo-steady-state presumed to persist under natural recovery is no longer valid. It alters the surface sediment COC concentrations in the area remediated and the flux of COCs to downstream locations. The first impact is accounted for by recalculating the average sediment concentration using the presumed postremediation concentration. The alteration of flux of COCs to downstream locations changes the intermedia relationships at downstream locations. Water column COC concentrations may decline in response to the reduced flux from upstream, resulting in an increase in the ratio of sediment to water COC concentrations. The original relationship may eventually be reestablished if it represented the pseudo-steady-state condition. In the Tier 1 analysis, the original relationship is presumed to be instantaneously reestablished and downstream sediment and biota levels are adjusted based on an altered water column concentration. The alteration of the water column concentration is calculated using the following assumptions:

- The flux of COCs from sediment to the water column is presumed to be proportional to the surface sediment COC concentration and the area of contamination.
- The increase in concentration as water passes over the contaminated sediment is directly proportional to the flux from the sediment.

With these assumptions, the change in concentration across a particular region of sediment is given by the following equation:

$$\Delta c = aS \qquad (4)$$

in which the coefficient α accounts for the area of contamination, flow, and COC mass transfer rate. Using the subscripts b and a to indicate conditions before and after sediment remediation and the subscripts u and d to designate upstream and downstream locations, the change in concentration due to remediation is given as follows:

$$\Delta c_a = \Delta c_b \frac{S_a}{S_b} \tag{5}$$

$$(c_d - c_u)_a = (c_d - c_u)_b \frac{S_a}{S_b} \tag{6}$$

The upstream concentration is presumed to be unchanged by remediation and Equation (6) simplifies as follows:

$$c_{da} = c_{db} \frac{S_a}{S_b} + c_u \left(1 - \frac{S_a}{S_b}\right) \tag{7}$$

The sediment concentrations are averaged over the entire sediment area between the upstream and downstream water column sampling locations. If the remediation occurs only in a portion of the area, this needs to be reflected by area-weighting the postremediation and nonremediation surface sediment concentrations.

Once the new water column concentration is calculated, the sediment and biota concentrations are calculated from the intermedia ratios. The trends are then applied to predict concentrations in the future. Note that this analysis overestimates the impacts of remediation because of the assumptions of instantaneous responses in the other media within the area of remediation and in all media downstream of the area of remediation.

The time required for remediation is accounted for by repeating the remediation calculation at a series of time points representing completion of phases of the remediation. The time interval depends on the total time for remediation, but should not be greater than one year.

- *Tier 2*

  A quantitative mass balance model is the tool used to predict future concentrations. This approach has been used at numerous sites, including the lower Fox River (Vellueux, et al. 1995), Green Bay (DePinto, et al. 1993), the Pawtuxet River (HydroQual 1995), the James River (O'Connor, et al. 1989) and the lower Hudson River (Thomann, et al. 1991) and the Upper Hudson River (QEA 1999). The processes affecting the COCs are mechanistically described, allowing for a realistic representation of the relationships among water, surface sediment, and biota and the ability to account for ongoing sources. Further, the cyclic or event-related phenomena such as temperature, light, flow, and solids loading that affect recovery rate are accounted for (Connolly 1997).

  The model has four components: hydrodynamics, sediment transport, COC fate, and bioaccumulation. These components are related through a sequential flow of information from one to the next. The hydrodynamic model provides water velocity and depth to the sediment transport and COC fate models. The sediment transport model provides flux rates of solids between the water and sediment and water column total suspended solids (TSS) to the COC fate model. The COC fate model provides water column and surface sediment COC concentrations to the bioaccumulation model.

  The models are equations developed from the basic principles of conservation of mass, energy and momentum, equations of state, and from laboratory and field studies of individual phenomena. The equations are general and can be applied to various surface water systems. The application of the equations to a specific system involves the determination of appropriate values for each of the parameters in the equations. Site-specific data are the basis for assigning values, either directly or by the process of model calibration. Each of the models must be calibrated and validated using the available data record. Calibration involves adjusting select model parameter values within the limits of technical judgement and the range of prior measurements to obtain improved agreement between calculated model results and observed data. Validation entails the independent comparison of calculated model results with observed data. Confidence in the model derives from confidence in the realism of the model equations, the accuracy and precision of the underlying data, previous successful experience using the model, the accuracy of the parameter estimates based on site-specific data as well as more general information, and the ability of the model to reproduce (or predict) observed data.

It is common that the primary mechanism of natural remediation in surface waters is burial of contaminated sediments by relatively clean sediments. Most of the solids loading responsible for burial typically enters the system in short-term events that occur only a few times each year (Ager 1981). Accurate estimation of the relationship between flow and solids loading and simulation of sediment transport during the event periods is necessary for accurately predicting burial rate and COC fate (Ziegler and Connolly 1995, Cardenas and Lick 1996, and Connolly 1997). A practical example of this postulate is found in a model of the natural remediation of Kepone in the James River estuary (O'Connor, et al. 1983 and 1989). The first version of this model assumed constant flow at the annual mean. This version significantly overpredicted the rate of decline of sediment Kepone concentrations. By modifying the model to account for flow variation and the variable solids loading, the predicted rate of decline agreed with the observed rate.

— <u>Hydrodynamics</u>

Hydrodynamics are described by two and three-dimensional models that account for the major forces affecting water motion. The accuracy of the hydrodynamic calculation typically depends on the scale of the numerical grid; the resolution and accuracy of bathymetric data and boundary forcing functions (e.g., stage height, salinity, wind speed and direction, tributary inflows); and the availability of sufficient current, temperature, salinity (if an estuary or coastal water) and water surface elevation data within the system to allow accurate estimation of bottom friction factors or equivalently bottom roughness heights.

The approach to calibration of a hydrodynamic model is dependent on the available data. Typically, the bottom friction factor is adjusted to maximize the fit between computed and observed values of water surface elevation and current velocity data. The approach is illustrated by two examples. QEA (1999) calibrated hydrodynamic models for each of eight dammed reaches of the Upper Hudson River by fixing the dam stage height at the downstream limit of the model at the measured value and then adjusting the bottom friction factors until good agreement was achieved between the predicted and measured stage heights at an upstream location. The models were validated by simulating a flood that occurred in May 1983 and comparing computed and observed stage height measurements (see Figure 13).

HydroQual (1998) calibrated a hydrodynamic model of Lavaca and Matagorda Bays on the Texas Gulf Coast. A fine scale numerical grid was employed with 5,280 horizontal elements and ten vertical layers used to describe the approximate 80 square kilometer bay system. A time series of water surface elevations at the connection to the Gulf of Mexico, wind velocities, and tributary inflows were used as forcing functions. The bottom roughness height was used as the calibration parameter. Calibration was assessed using a one month time series of water surface elevations at several locations within the bay system and current velocities measured at a single location in Lavaca Bay. The model predicted hourly water surface elevations at three locations with a mean error of 2 percent (see Figure 14). Predicted current velocities also agreed well with observations (see Figure 15).

— Sediment Transport

Sediment transport is simulated using a simplification of the distribution of particle sizes in a surface water. Typically, suspendable sediments are aggregated into two classes: one representing fine-grained (cohesive) particles with diameters less than 62 micrometers (μm) and the other representing fine sands with diameters between 62 and 250 μm (e.g., Ziegler and Nisbet 1994). Various empirical formulations exist to describe the deposition and resuspension of these particle classes. The parameters in these formulations are site-specific, particularly for resuspension, and require direct measurement (e.g., Tsai and Lick 1986 and Jepsen, et al. 1997). In addition to the obvious importance of accurately characterizing deposition and resuspension, the accuracy of the solids loading measurements (or the flow-solids loading correlation) and the accuracy of the particle size distribution of that loading are important determinants of model accuracy. In cases where the solids loading or the particle size distribution of the loading are poorly characterized, model calibration can result in incorrect estimates of the rates of resuspension and deposition. For example, if solids loading is underestimated, calibration may result in too much resuspension in order to achieve the measured suspended solids levels. Further, it is likely that the burial rate would be underestimated and, consequently, so would the rate of natural remediation. This difficulty occurred in a preliminary model for the Upper Hudson River (USEPA 1996). The solids loading for two tributaries were significantly underestimated, resulting in an overestimate of resuspension and the incorrect calculation of net erosion rather than net burial (Schweiger, et al. 1996).

The development of a sediment transport model begins by defining the characteristics of the sediment bed. A bed map is constructed in which the bed is divided into a minimum of three classifications: cohesive sediments, noncohesive sediments, and hard bottom. The noncohesive sediments may be further divided on the basis of median particle size. The erosive properties of the cohesive sediments are defined by measurement, and those of the noncohesive sediments are defined by specified values of an active layer depth and median particle diameter (Ziegler and Nisbet 1994). Tributary solids loading is defined by a data-based relationship between solids loading and tributary flow (e.g., Ferguson 1987; Walling and Webb 1988). Settling velocities of the cohesive sediment classes are defined by empirical correlation to particle size and concentration and water column turbulence (Ziegler and Nisbet 1995). The settling velocity of the noncohesive particles is a function of particle size (Cheng 1997). The model is calibrated by comparison to TSS data during flood conditions (e.g., Ziegler and Nisbet 1994) and also by comparison of predicted and observed rates of sedimentation (e.g., Ziegler and Nisbet 1995). Calibration parameters include the particle size composition of the solids loading and the median particle size and active layer depth of the noncohesive sediments.

The upper Hudson River hydrodynamic models discussed above were used with a sediment transport model to predict erosion and deposition of sediment and associated PCBs (QEA 1999). Suspended solids data from an April 1994 flood were used to calibrate the model. Comparisons of predicted and observed TSS at four locations are presented in Figure 16. The model closely approximates the observed data at the all locations. Of particular significance in the ability of the model to replicate both the temporal dynamics and the increase in TSS levels from upstream to downstream.

— COC Fate

COC fate models combine the water velocity and resuspension/deposition results of the previous two components with descriptions of the reaction and intermedia transfer processes that affect a COC. The transfer processes include sorption, exchange between the atmosphere and the dissolved phase in the water column, and exchange between the dissolved phase in the water column and the sediment bed pore water. The reaction processes include speciation, precipitation/dissolution, and chemical and biochemical degradation.

Sorption is described as a reversible equilibrium process, most commonly by a partition coefficient. Laboratory experiments indicating relatively slow desorption rates (e.g., Pignatello and Xing 1996) or reductions in the bioavailability of sorbed COCs with sediment aging (e.g., Loonen, et al. 1997) suggest that the assumptions of equilibrium and reversibility may be inaccurate. The significance of any inaccuracies has not been rigorously evaluated. Nonetheless, reversible equilibrium has been used with apparent success for over 20 years.

Speciation is described using chemical equilibrium models such as MINTEQA2 (Allison and Perdue 1994), MINEQL$^+$ (Schecher and McAvoy 1995) and WHAM (Tipping 1994). These models provide accurate estimates of speciation and precipitation/dissolution of inorganics as long as the major chemical species in the water are well known. These models are computationally intensive and their use in long-term natural remediation simulations involves compromises between the frequency at which the speciation is updated and the accuracy of the solution.

Chemical and biochemical reactions that create or destroy a COC are described in simple fashion. A second-order kinetic expression is used in which the reaction rate is proportional to the concentration of the COC and the concentration of another reactant such as the hydroxyl ion or bacteria. In the case of a biological reaction, the organism responsible for the reaction is not modeled. An organism concentration is input to the model either as a constant or as a time function. This also may be the case for a chemical reactant if a chemical equilibrium model is not incorporated within the modeling framework.

Because of the influence that site characteristics have on many chemical and biochemical reactions is not well understood (Boethling and Alexander 1979; Lartiges and Garrigues 1995), it is common to use simple first-order reaction rates that are defined from laboratory experiments or from model calibration (e.g., Dilks, et al. 1993 and Tell and Parkerton 1997). The accuracy of such descriptions is dependent on how well the model describes all other processes; the greater the number of parameters that must be adjusted during calibration, the more uncertain the model predictions.

A volatilization mass transfer rate constant is used to compute air-water exchange. It is calculated typically from empirical formulations dependent on the molecular diffusivity of the COC, water velocity, water column depth, and wind velocity (e.g., Mackay and Yeun 1983 and Rathbun 1990). The equations are fairly robust and yield accurate volatilization rates. The principal weakness of existing models is their inability to describe volatilization losses that occur at waterfalls. Such losses can be important for volatile chemicals (McLachlan, et al. 1990).

Transfer at the water-bed interface refers to the movement of COC between the water column and the sediment pore water. The models describe this process using a diffusion equation. A number of phenomena affect the transfer, including bioturbation, hydrodynamic pumping due to pressure gradients, and advection to or from groundwater.

As a result, the transfer rate is site-specific and varies temporally at a site (e.g., Riedel, et al. 1988 and Gill, et al. 1999). The diffusion model is an obvious simplification. In cases where water-bed transfer is an important mechanism, the accuracy of the model is dependent on the existence of data for calibration of this transfer rate constant.

A model of COCs in the Pawtuxet River, Rhode Island (HydroQual 1995) is used to illustrate model application. This model was developed using hydrodynamic and sediment transport models similar to those presented earlier for the Hudson River (Ziegler and Nisbet 1994). The time-variable flows and water-sediment solids transport predicted by these models was used as input to models of zinc, chlorobenzene, naphthalene, PCBs, and tinuvin 328. The models included volatilization; equilibrium sorption to organic matter; groundwater COC inputs; and, in the case of zinc, chemical equilibrium with sulfide in the sediment. The model was calibrated using measurements of the COCs in both the water column and sediment. The calibrated model was then used to predict natural recovery and the benefits of interdicting the flow to the river of COC-containing groundwater (i.e., groundwater capture) and sediment excavation and fill in the vicinity of a former coffer dam where wastewater from a former Ciba-Geigy facility was discharged.

Future river flows were simulated in the following manner. The statistics of the historical flow data were used to develop a 1,000-year synthetic hydrograph of annual flows. This record was examined to find a three-year pattern of flow that best matched the three-year period prior to the beginning of the projection (i.e., 1991 to 1993). The next 11 years in the record were used as the annual flows for the projection. These 11 annual flows were then matched with individual years in the 34-year record of daily flows that had the closest annual flow. These actual daily hydrographs were then strung together to form the hydrograph for model projections.

Solids loading was estimated using data-based relationships between river flow and TSS and the daily flows from the synthetic hydrograph.

The remedial actions were simulated in the following fashion. Groundwater modeling was used to estimate the change in groundwater flow due to the groundwater capture system. The modeling indicated that the flow direction through the sediments would be reversed by the capture system and this change was incorporated in the model to simulate the effect of groundwater capture. The excavation and fill were simulated by changing the sediment concentration at the location of excavation to zero.

Groundwater capture was shown to be an effective remedial strategy for chlorobenzene (see Figure 17) and also for naphthalene. Sediment excavation was found to be effective only in the vicinity of the excavation. Downstream sediment concentrations were not affected because the preremediation mass fluxes from the area designated for excavation were not significant contributors to the contamination at these locations. In the case of zinc, upstream sources resulted in recontamination in the coffer dam area after excavation and the benefits of the excavation declined through time (see Figure 18).

— <u>COC Bioaccumulation</u>

Bioaccumulation can be calculated at two levels of resolution within Tier 2. The simpler level uses the steady-state relationship between fish, water, and sediment COC concentrations given by Equation 1. This relationship can be easily be developed from data, however, it is subject to the limitations and inaccuracies discussed earlier.

The more complicated, but more accurate, approach uses a mechanistic model describing the processes of COC uptake and loss. Such models have been frequently applied. Examples include PCBs in lake trout from Lake Michigan (Thomann and Connolly 1984) and Lake Ontario (Connolly and Thomann 1991 and Gobas 1993), PCBs in lobster and winter flounder from New Bedford Harbor (Connolly 1991), PCBs in striped bass from the Hudson River (Thomann, et al. 1991), Kepone in striped bass from the James River (Connolly and Tonelli 1985), p,p'-dichlorodiphenyldichloroethylene (DDE) and PCBs in California sea lions and predatory birds (Glaser and Connolly 1999) from the California Channel Islands, and PCB and mercury in yellow perch from the Ottawa River (Norstrom, et al. 1976).

The mechanistic bioaccumulation model is based on the principals of conservation of mass and energy. COCs are taken up via respiration and ingestion and lost via diffusion across the respiratory surfaces and excretion. These models require information about the structure of the food web, field growth and respiration rates, and COC transfer efficiencies at the gill and gut. The primary advantages over the steady-state relationship (i.e., Equation 1) are that they account for the time variable nature of uptake and depuration and time variable physiological characteristics such as animal fat content. They are also capable of simulating the various life stages of the animal of interest.

Impact of a Rare Storm or High Flow Event

As with the evaluation of natural recovery and active remediation, a two-tiered approach is presented below. Both tiers involve the application of quantitative models. Tier 1 is limited to an assessment of erosion, whereas Tier 2 considers both erosion and subsequent redistribution of the COC.

- *Tier 1*

  The impact of a rare storm or high flow event on the temporal trends is simulated by adjusting the sediment concentration at the assumed time of the event. The postevent surface sediment concentration is assigned either the concentration in the sediment at the depth of erosion or the average concentration in eroded sediment, depending on which is higher. Both estimates are likely to be conservative because they do not consider the dilution with clean solids that is likely to occur. The temporal trends are then continued at the rates used in the absence of the event.

  The depth of erosion is estimated in a three-step approach that has been used by the USEPA in examining the erosion resulting from a 100-year flood on the Upper Hudson River (USEPA 1996). The first step is an estimation of the maximum velocities to be attained during the event. This estimation can be conducted using a hydraulic or hydrodynamic model. Numerous models exist, ranging in complexity from one- to three-dimensional. Alternately, a crude estimation of velocity can be obtained from the maximum flow for the event and an empirical relationship between flow and velocity. Such empirical relationships exist for river systems and generally have the form of flow equals velocity raised to a power (Leopold and Maddock 1953). The exponent is site-specific, although bounding estimates can be determined using the limit of generic ranges. Once velocity (u) has been estimated, the maximum bottom shear stress (ϑ) is calculated using the quadratic stress law:

$$t = C_f u^2 \tag{8}$$

  The bottom friction coefficient, C_f, is site-specific in that it depends on water depth and the roughness of the sediment. In cohesive or fine-grained sediment deposits, an approximate upper limit value is 0.006. Using this bounding value, the mass of sediment eroded per unit area, E, is calculated using the Lick resuspension potential equation (Gailani, et al. 1991):

$$E = \frac{a_o}{T_d^N}\left(\frac{t - t_{cr}}{t_{cr}}\right)^n \qquad (9)$$

Here a_o is the site-specific constant; T_d represents the days after deposition (limited by maximum of about 7 days); N,n are the exponents dependent on the deposition environment; and τ_{cr} is the effective critical shear stress for erosion.

The depth eroded is calculated by dividing E by the solids concentration or dry bulk density of the surface sediment. Site-specific parameters in the Lick equation are needed to accurately predict erosion depth. These may be determined by conducting erosion tests with site sediment (Lick, et al. 1995). Alternately, parameters from other sites can be used to provide a bounding estimate of erosion. Example data is presented in Figure 19.

- *Tier 2*

  The hydrodynamic, sediment transport, and COC fate models described in the Tier 2 approach for natural recovery and remediation are extended to the simulation of the rare event. The hydrograph for the event is specified by data from a historical event or is developed from historical data. Examples of methods to develop the hydrographic conditions are described for a 100-year flood in the Hudson River (QEA 1999) and for a hurricane in Lavaca Bay (HydroQual 1998). The principal uncertainty in the prediction comes from the extrapolation of the erosion function and the solids loading to conditions not experienced in the data set. The accuracy of such extrapolation was examined in the Lavaca Bay study (HydroQual 1998). The conclusion was that reasonable predictive capability was maintained.

  The advantage of the Tier 2 approach is that it yields estimates of COC transport during the event and it accounts for redeposition of solids that occurs at the tail of the event. This redeposition was found to be an important factor in the hurricane simulation for Lavaca Bay (HydroQual 1998). Uncontaminated watershed solids that entered the bay after the primary erosion event in the bay diluted the mercury concentration at the sediment surface and mitigated the impact of the event.

  A more detailed description of the approach to modeling the impacts of a rare storm or high flow event on contaminated sediments is provided in Appendix C in “Sediment Stability at Contaminated Sediment Sites.”

REFERENCES

Ager, D.V. 1981. *The Nature of the Stratigraphical Record*. John Wiley & Sons: New York, NY.

Alcoa. August 1999. *Comprehensive Characterization of the Lower Grasse River*. Report submitted to USEPA Region 2.

Allison, J.A and E.M. Perdue. 1994. "Modeling Metal-Humic Interactions with MINTEQA2." In *Humic Substances in the Global Environment and Implications on Human Health*, N. Senesi and T.M. Miano (eds). Elsevier: Amsterdam. p. 927-942.

Berry, J.K. February 1997. "Justifiable Interpolation." *GIS World*. 10(2):34.

Boething, R.S. and M. Alexander. 1979. "Effect of Concentration of Organic Chemicals on Their Degradation by Natural Microbial Communities." *Appl. Environ. Microbiol.* 37:1211-1216.

Cardenas, M. and W. Lick. 1996. "Modeling the Transport of Sediments and Hydrophobic Contaminants in the Lower Saginaw River." *J. Great Lakes Res.* 22:669-682.

Cheng, N-S. 1997. "Simplified Settling Velocity Formula for Sediment Particle." *J. Hydr. Eng.* 123:149-152.

Connolly, J.P. and D. Glaser. 1999. "DDE and PCB Bioaccumulation in Female Sea Lions of the California Channel Islands." Submitted to *Continental Shelf Res.*

Connolly, J.P. 1991. "Application of a Food Chain Model to Polychlorinated Biphenyl Contamination of the Lobster and Winter Flounder Food Chains in New Bedford Harbor." *Environ. Sci. Technol.* 25:760-770.

Connolly, J.P. 1997. *Modeling the Environmental Fate and Transport of Metals*. Society of Environmental Toxicology and Chemistry (SETAC) Pellston Workshop on Reassessment of Metals Criteria for Aquatic Life Protection. February 10-14, 1996, Pensacola, FL. SETAC Paper 114.

Connolly, J.P. and R.V. Thomann. 1991. "Modeling the Accumulation of Organic Chemicals in Aquatic Food Webs." In *Fate of Pesticides and Chemicals in the Environment*, J.L. Schnoor (ed.). John Wiley & Sons, Inc.: New York.

Connolly, J.P. and R. Tonelli. 1985. "A Model of Kepone in the Striped Bass Food Chain of the James River Estuary." *Est. Coastal Shelf Sci.* 20:349-366.

Cressie, N.A.C. 1993. *Statistics for Spatial Data*. Revised Edition. John Wiley & Sons, Inc.: New York, New York.

DePinto, J.V.; R. Raghunathan; P. Sierzenga; X. Zhang; V.J. Bierman, Jr.; P.J. Rogers; and T.C. Young. 1993. "Recalibration of GBTOX: An Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan." Final Report to USEPA Large Lakes Research Station, Grosse Ile, Michigan.

Dilks, D.W.; J.S. Helfand; V.J. Bierman, Jr.; and L. Burkhard. 1993. "Field Application of a Steady-State Mass Balance Model for Hydrophobic Organic Chemicals in an Estuarine System." *Wat. Sci. Tech.* 28:263-271.

Di Toro, D.M.; J.D. Mahoney; D.J. Hansen; K.J. Scott; A.R. Carlson; and G.T. Ankley. 1991. "Acid Volatile Sulfide Predicts the Acute Toxicity of Cadmium and Nickel in Sediments." *Environ. Sci. Technol.* 26:96-101.

Ferguson, R.I. 1987. "Accuracy and Precision of Methods for Estimating River Loads." *Earth Surf. Proc. and Land.* 12:95-104.

Gailani, J.; C.K. Ziegler; and W. Lick. 1991. "Transport of Suspended Solids in the Lower Fox River." *J. Great Lakes Res.* 17:479-494.

General Electric Company. August 1998. Comments of the General Electric Company on Phase 2 Report—Review Copy: Further Site Characterization and Analysis Volume 2C Low Resolution Sediment Coring Report Addendum to the Data Evaluation and Interpretation Report July 1998. Corporate Environmental Programs, Albany, NY.

Gill, G.A.; N.S. Bloom; S. Cappellino; C.T. Driscoll; C. Dobbs; L. McShea; R. Mason; and J.W.M. Rudd. 1999. "Sediment-Water Fluxes of Mercury in Lavaca Bay, Texas." Submitted to *Env. Sci. Technol.*

Glaser, D. and J.P. Connolly. 1999. "Use of a Bioaccumulation Model of p,p'-DDE and Total PCB in Birds as a Diagnostic Tool for Pathway Determination in Natural Resource Damage Assessments." Submitted to *Continental Shelf Res.*

Gobas FAPC. 1993. "A Model for Predicting the Bioaccumulation of Hydrophobic Organic Chemicals in Aquatic Food Webs: Application to Lake Ontario." *Ecol. Modeling.* 69:1-17.

HydroQual. 1998. *Development and Application of a Modeling Framework to Evaluate Hurricane Impacts on Surficial Mercury Concentrations in Lavaca Bay: Final Report to Aluminum Company of America.* Mahwah, New Jersey.

HydroQual. 1995. *Contaminant Transport and Fate Modeling of the Pawtuxet River, Rhode Island, Final Report to Ciba Corporation, Toms River, NJ.* Mahwah, New Jersey.

International Joint Commission. November 19, 1997. *Overcoming Obstacles to Sediment Remediation in the Great Lakes Basin.* White Paper by the Sediment Priority Action Committee, Great Lakes Water Quality Board.

Isaaks, E.H. and R.M. Srivatava. 1989. *An Introduction to Applied Geostatistics.* Oxford University Press: New York, New York.

Jepsen, R.; J. Roberts; and W. Lick. 1997. "Effects of Bulk Density on Sediment Erosion Rates." *Water, Air, Soil Poll.* 99:21-31.

Lartiges, S.B. and P.P. Garrigues. 1995. "Degradation Kinetics of Organophosphorus and Organonitrogen Pesticides in Different Waters under Various Environmental Conditions." *Envrion. Sci. Technol.* 29:1246-1254.

Leapold, L.B. and T. Maddock. 1953. *The Hydraulic Geometry of Stream Channels and Some Physiographic Implications.* Geologic Survey Professional Paper 252. Washington D.C.

Lick, W.; Y-J. Xu; and J. McNeil. 1995. "Resuspension Properties of Sediments from the Fox, Saginaw, and Buffalo Rivers." *J. Great Lakes Res.* 21:257-274.

Loonen, H.; D.C.G. Muir; J.R. Parsons; and H.A.J. Govers. 1997. "Bioaccumulation of Polychlorinated Dibenzo-*p*-dioxins in Sediments by Oligochaetes: Influence of Exposure Pathway and Contact Time." *Environ. Tox. Chem.* 16:1518-1525.

Mahoney, J.D.; D.M. Di Toro; A.M. Gonzalez; M. Curto; M. Dilg; L.D. De Rosa; and L.A. Sparrow. 1996. "Partitioning of Metals to Sediment Organic Carbon." *Environ. Tox. Chem.* 15:2187-2197.

McLachlan, M.; D. Mackay; and P.H. Jones. 1990. "A Conceptual Model of Organic Chemical Volatilization at Waterfalls." *Environ. Sci. Technol.* 24:252-257.

Makay, D. and A.T.K. Yeun. 1983. "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water." *Environ. Sci. Technol.* 17:211-217.

Norstorm, R.J.; A.E. McKinnon; and A.S.W. deFreitas. 1976. "A Bioenergetics-Based Model for Pollutant Accumulation by Fish: Simulation of PCB and Methylmercury Residue Levels in Ottawa River Yellow Perch (*Perca flavescens*)." *J. Fish. Res. Board Can.* 33:248-267.

O'Connor, D.J.; J.P. Connolly; and E.J. Garland. 1989. "Mathematical Models—Fate, Transport, and Food Chain." In *Ecotoxicology: Problems and Approaches*, S.A. Levin, M.A. Harwell, J.R. Kelly, and K.D. Kimball (eds.). Springer-Verlag: New York, New York. p. 221-243.

O'Connor, D.J.; J.A. Mueller; and K.J. Farley. 1983. "Distribution of Kepone in the James River Estuary." *J. Environ. Eng.* 109:396-413.

Pignatello, J.J. and B. Xing. 1996. "Mechanisms of Slow Sorption of Organic Chemicals to Natural Particles." *Environ. Sci. Technol.* 30:1-11.

QEA. May 1999. *PCBs in the Upper Hudson River*. Report to the General Electric Company. Montvale, New Jersey.

QEA. 1998. *Thompson Island Pool Sediment PCB Sources: Final Report to General Electric Company*. Montvale, New Jersey.

Rathbun, R.E. 1990. "Prediction of Stream Volatilization Coefficients." *J. Environ. Eng.* 116:615-631.

Riedel, G.F.; J.G. Sanders; and R.W. Osman. 1988. "The Effect of Biological and Physical Disturbances on the Transport of Arsenic from Contaminated Estuarine Sediments." *Est. Coastal Shelf Sci.* 23:693-706.

Schecher, W.D. and D.C. McAvoy. 1995. *MINEQL$^+$: A Chemical Equilibrium Program for Personal Computers*. Hallowell ME: Environmental Research Software. Version 3.01.

Schweiger, M.B.; J.G. Haggard; and J.P. Connolly. 1996. Comments of General Electric Company on Phase 2 report - review copy: Further site characterization and analysis volume 2B - Preliminary model calibration report Hudson River PCBs reassessment RI/FS. General Electric Company, Albany NY.

Tell, J.G. and T.F. Parkerton. 1997. "A Comparison of Multi-Medial Models Used in Regulatory Decision-Making." *SAR QSAR Env. Res.* 6:29-45.

Thomann, R.V. and J.P. Connolly. 1984. "A Model of PCB in the Lake Michigan Lake Trout Food Chain." *Environ. Sci. Technol.* 18:65-71.

Thomann, R.V.; J.A. Mueller; R.P. Winfield; and C-R. Huang. 1991. "Model of Fate and Accumulation of PCB Homologues in Hudson Estuary." *ASCE J. Environ. Engr.* 117:161-178.

Tipping, E. 1994. "WHAM—A Chemical Equilibrium Model and Computer Code for Waters, Sediments and Soils Incorporating a Discrete Site/Electrostatic Model of Ion-Binding by Humic Substances." *Computers & Geoscience* 6:973-1023.

Tsai, C.H. and W. Lick. 1986. "A Portable Device for Measuring Sediment Resuspension." *J. Great Lakes Res.* 12:314-321.

USEPA. 1993a. *Assessment and Remediation of Contaminated Sediments (ARCS) Program: Risk Assessment and Modeling Overview Document*. EPA-905-R-93-007.

USEPA. 1993b. *Technical Basis for Deriving Sediment Quality Criteria for Nonionic Organic Contaminants for the Protection of Benthic Organisms by Using Equilibrium Partitioning.* EPA-822-R-93-011.

USEPA. 1996. *Phase 2 Report—Review Copy: Further Site Characterization and Analysis Volume 2B—Preliminary Model Calibration Report Hudson River PCBs Reassessment RI/FS.* New York New York.

USEPA. October 1997a. *Report on the Effects of Hot Spot Dredging Operations New Bedford Harbor Superfund Site New Bedford, Massachusetts.* USEPA, Narragansett, Rhode Island.

USEPA. 1997b. *Water Quality Guidance for the Great Lakes System*. 40 CFR Part 132, fr06ju97.

USEPA. 1998a. *EPA's Contaminated Sediment Management Strategy*. EPA-823-R-98-001.

USPEA. September 1998b. *Responsiveness Summary Reynolds Metals Company Study Area Post-Decision Proposed Plan.*

Velleux, M.; D. Endicott; J. Steuer; S. Jaeger; and D. Patterson. 1995. "Long-Term Simulation of PCB Export from the Fox River to Green Bay." *J. Great Lakes Res.* 21:359-372.

Walling, D.E. and B.W. Webb. 1988. "The Reliability of Rating Curve Estimates of Suspended Sediment Yield: Some Further Considerations." In *Sediment Budgets*. IAHS Pub. No. 174. p. 337-350.

Ziegler, C.K. and J.P. Connolly. 1995. *The Impact of Sediment Transport Processes on the Fate of Hydrophobic Organic Chemicals in Surface Water Systems*. Water Environment Federation Specialty Conference, May 14-17, 1995, Cincinnati, Ohio.

Ziegler, C.K. and B. Nisbet. 1994. "Fine-Grained Sediment Transport in Pawtuxet River, Rhode Island." *ASCE J. Hyd. Engr.* 120:561-576.

Ziegler, C.K. and B. Nisbet. 1995. "Long-Term Simulation of Fine-Grained Sediment Transport in Large Reservoir." *ASCE J. Hydr. Engr.* 121:773-781.