THE ROLE OF NATURAL ATTENUATION/RECOVERY PROCESSES IN MANAGING CONTAMINATED SEDIMENTS

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EXECUTIVE SUMMARY

When considering how to reduce human health and ecological risks posed by contaminated sediments within an aquatic ecosystem, it is important to recognize the considerable capacity of natural processes continuously at work within the system to reduce those risks. Technically referred to as natural attenuation, this approach to sediment remediation relies on the powerful natural processes that are inherent within all aquatic systems to reduce COC bioavailability and potential transport. The natural attenuation of aquatic systems is driven most often by quantifiable physical mechanisms such as the mixing and in-place burial of contaminated sediments with progressively cleaner solids delivered by the watershed. This natural sedimentation process can effectively reduce the physical availability of COCs for potential transport downstream and similarly reduce the biological availability of COCs for potential exposure to human and ecological receptors. Other potentially significant mechanisms include chemical processes such as adsorption and redox reactions and the complex biological processes involved in biodegradation.

Despite today's apparent emphasis on applying active remedial technologies in managing contaminated sediment, there is ample evidence that natural attenuation can be applied as an effective remedial alternative or to enhance the protectiveness of other alternatives selected for aquatic sites. While the regulatory community and public tend to view the natural recovery of sediments as a no action alternative, this paper discusses the capacity for natural attenuation processes combined with performance monitoring to be a protective, feasible, and cost-effective alternative that should be considered and fully evaluated against other potential remedies.

Unique to natural attenuation as a remedial alternative is its ability to reduce the mobility, toxicity, and potential exposure of COCs through inherent physical, chemical, and biological processes without the need for intervention typified by technologies such as sediment capping or dredging. Although natural processes are known to be active in all aquatic ecosystems, full recognition of the power of these natural forces in healing those systems and reducing human and ecological exposure is lacking. In recognizing that natural attenuation is increasingly relied on for addressing environmentally persistent COCs in soil and groundwater, the use of monitored natural attenuation can and must play a wider role in contaminated sediment management. To that end, this paper concludes by offering several recommendations, which are summarized below.

- *The natural attenuation alternative can be a protective remedy; it is not a no action alternative.* Currently, natural attenuation is reducing risks posed by contaminated sediments to some degree at virtually all contaminated sediment sites. The natural attenuation alternative which, as a risk management tool necessarily includes monitoring and appropriate institutional controls, can be a protective and preferred approach to managing contaminated sediment site risks.

  The policy-level recognition of the natural attenuation alternative as an effective remedy needs to be communicated to regulatory personnel in the field. In doing so, the key applicable principles of the USEPA guidance on using monitored natural attenuation for soils and groundwater can and should be adopted and promoted. The USEPA and other federal and state agencies have recognized the applicability of natural attenuation at the policy level, but actual selection and application of the alternative is lacking.

  The role of natural attenuation in addressing environmentally-persistent COCs in soil and groundwater is well documented and is increasingly relied on as one component of a site's overall remedial package. In addition, the USEPA has formally selected natural attenuation as a whole or partial remedy at several sediment sites. Fundamentally, it must be recognized that

natural attenuation is an intrinsic set of processes that operate continuously within all aquatic ecosystems. Given that premise, natural attenuation is necessarily already relied on before, during, and after other more intrusive remedies. However, additional effort is needed in the site assessment phases of remedial planning to discern what portion of overall recovery gains (or reversals) are attributable to natural processes versus source control, intrusive remedial action, and other actions.

- *Empirical evidence and model projections should be used to evaluate the effectiveness of natural attenuation in reducing risks.* Site data that identify the mechanisms and rates of ongoing natural attenuation are critical to establishing the feasibility of the natural attenuation alternative. These data are needed not only to establish the basic proof that attenuation is occurring but to calibrate and optimally to verify fate and transport models that predict future bioavailable COC concentrations. Empirical information such as sediment deposition rates, sediment mixing layer thickness, and time series data documenting changes in COC bioavailability or toxicity over time are important. Multiple lines of such empirical evidence should be sought. Organizing site data into a mathematical model that can predict how the system will change over time is an important extension of the basic understanding of the processes that are reducing risk at a site. Deterministic modeling may be the only practical way to address such issues as assessing the reliability of natural attenuation processes to continue to reduce risks under conditions other than those which have been observed (e.g., rare extreme hydrologic events) or to address the combined effectiveness of source controls and natural attenuation.

- *The natural attenuation alternative should be evaluated in comparison to other action alternatives for sediments on the basis of effectiveness, implementability, and costs.* Defining a reasonable time frame for natural attenuation to meet remediation objectives is a site-specific process that weighs among other factors the extent of current risks and impacts to resources, availability, and reliability of institutional controls to manage risks; uncertainties associated with predicted time frame; and the implementability, effectiveness, and costs of other alternatives. For example, levels of risk reduction produced by intrusive technologies may not be achieved significantly sooner than allowing ongoing natural recovery processes to proceed uninterrupted. This is especially true when many years are required to fully design, permit, and construct large-scale capping or removal remedies, including the potential need to design and permit a proper disposal facility. Again, even after such remediation is complete, natural recovery processes would be relied on to attenuate remaining risks posed by the residual materials left behind by intrusive technologies.

  Comparative evaluation of remedial alternatives is necessary. Simple pass/fail decision criteria for natural attenuation that have been suggested (e.g., surface sediment COC levels within a factor of two of remedial objectives as suggested by Templeton et al. 1993) that implicitly assume capping or dredging alternatives to be more effective should be avoided.

- *Where irreconcilable differences of opinion exist regarding the time frame or reliability of natural recovery, performance-based natural attenuation should be selected along with a contingent remedy.* A contingent remedy would be an alternative such as containment or dredging that would be implemented at a specified future date (e.g., the five-year review of a Record of Decision) if a natural attenuation remedy fails to meet appropriate performance standards. Considering the potential consequences of being wrong in making a determination that natural attenuation is not performing (i.e., the high financial cost as well as social and environmental costs associated with implementation of active sediment remediation), the decision maker should be highly confident that natural attenuation is not working and that other remedial options will significantly reduce risk before deciding to abandon the natural recovery option. Consequently, some lower confidence limit on performance measurements such as fish contaminant trend monitoring data would be appropriate for use for triggering decisions to implement the contingent remedy. Performance standards should include at a minimum those that relate directly or indirectly to the expected rate of risk reduction needed to achieve risk-based remedial objectives for the site. Development of the performance standards should minimally address the lines of empirical evidence that supported the original decision. In general, promoting contingent remedies might help bring to closure to the different opinions regarding sediment remedies that are rooted in different expectations regarding the effectiveness, implementability, and costs of sediment remediation technologies.

- *The social and environmental benefits of the natural attenuation alternative may outweigh those perceived to flow from intrusive technologies.* The final word on natural attenuation in sediments is the need for risk managers to come to realize that natural systems have a substantial capacity to attenuate and recover from the presence of contaminants. Conversely, experience with remedial dredging highlights the fact that technology, while powerful, is not necessarily as effective as the nonintrusive natural processes. In making a final determination on this pivotal question, the overall social and environmental benefits and costs must be evaluated. If empirical and predictive lines of evidence indicate that natural attenuation can achieve risk reduction goals within a time frame similar to technological approaches, the benefits of avoiding habitat destruction, avoiding the technical and administrative limitations of construction and landfilling, and avoiding the sometimes extremely high social cost of paying for technological intervention may indeed clearly signal that natural attenuation is the most appropriate remedy for many of the nation’s contaminated sediment sites.

INTRODUCTION AND PURPOSE

When considering how to reduce human health and ecological risks posed by contaminated sediments within an aquatic ecosystem, it is important to recognize the capacity of natural processes continuously at work within the system to reduce those risks. Technically referred to as natural attenuation, this approach to sediment remediation relies on the powerful natural processes that are inherent within all aquatic systems to reduce the bioavailability and potential for transport of chemicals of potential concern (COCs) [National Research Council (NRC) 1997 and U.S. Environmental Protection Agency (USEPA) 1998]. Unique to natural attenuation as a remedial alternative is its ability to reduce the mobility, toxicity, and potential exposure of COCs through these inherent physical, chemical, and biological processes without the need for intervention typified by technologies such as sediment capping or dredging. Among these processes, the natural recovery of aquatic systems is most often driven by quantifiable physical mechanisms (e.g., the mixing and in-place burial of contaminated sediments with progressively cleaner solids delivered by the watershed). This natural sedimentation process can effectively reduce the physical availability of COCs for potential transport downstream, and similarly reduce the biological availability of COCs for potential exposure to human and ecological receptors. Other potentially significant mechanisms include chemical processes such as adsorption and redox reactions, and the complex biological processes involved in biodegradation.

Despite the promise of natural attenuation as a protective and cost-effective sediment remedy, serious evaluation of its application has been lacking at many contaminated sites. The USEPA guidance on natural attenuation at contaminated sediment sites, first identified as a task in the USEPA's 1994 draft *Contaminated Sediment Management Strategy*, is apparently under development. Meanwhile, there exists within the regulatory community and the public a tendency to view natural recovery of sediments as a no action or walk away alternative, one that is inherently less effective and protective of human health and the environment than alternatives involving dredging, capping, or other intrusive technological approaches. In any case, natural attenuation is necessarily relied on to remedy contaminated sediments and restore aquatic systems if for no other reason than the inability of alternatives such as dredging to effectively remediate all contamination. As this paper will explain, there are several other reasons for evaluating the presence and effectiveness of natural attenuation and giving full consideration to the natural recovery alternative as a protective and verifiably permanent remedial approach to managing contaminated sediments.

Thus, the purpose of this paper is to summarize the primary physical, chemical, and biological processes involved in the natural attenuation of contaminated sediments and to illustrate how they can be measured and assessed for their potential significance in reducing the potential risks associated with contaminated sediment. This paper demonstrates that natural attenuation is much more than a no action alternative and can indeed be a protective, feasible, and cost-effective alternative that should be considered and fully evaluated against other potential remedies. This is especially true when the time frame for natural attenuation in meeting remedial objectives can be shown to compete favorably with the time and effort needed to implement containment or dredging alternatives.

OVERVIEW OF NATURAL ATTENUATION PROCESSES

Aquatic ecosystems have considerable inherent capacity to recover from either natural or human disturbances. An extreme but illustrative example of recovery from a natural disturbance is Spirit Lake, which was the largest and most prominent of lakes within the blast zone of Mount St. Helens when it erupted in 1980. Although permanently altered in terms of physical environment as a result of the eruption, Spirit Lake recovered from being essentially a biological desert after the blast to a revitalized system of diverse phytoplankton species and dissolved oxygen levels comparable to preblast conditions within just six years (Larson 1993).

Aquatic ecosystems also have considerable capacity to recover from the effects of human disturbances such as past chemical releases or the presence of postremediation residual contamination (which is common following dredging projects). For example, populations of fish and fish-eating birds within the Great Lakes Basin and elsewhere have experienced a remarkable recovery as natural processes attenuate residual contaminants over time. Notable indicators include cormorant, peregrine falcon, and bald eagle populations that have experienced strong gains in watersheds where natural attenuation processes are active even though active remediation of sediments containing organochlorine pesticides [e.g., dichlorodiphenyltrichloroethane (DDT)], polychlorinated biphenyls (PCBs), or other environmentally persistent compounds have been limited or not taken place.

Other well noted examples are the levels of PCBs and DDT in lake trout from the Great Lakes (1977 to 1992 data), which have been reduced by half every four to eight years (DeVault, et al. 1996). Similarly, striped bass and other fish in the Hudson River have experienced a substantial recovery from the high PCB concentrations once found in surface water, sediments, and fish, whereby New York State officials have announced that “PCB concentrations in striped bass have reached the point where continued limitations in the commercial fishery due solely to PCBs are not justified” (*New York Times*, February 23, 1999). Niemi, et al. (1990) have documented another 150 case studies showing similar examples of how physical, chemical, and biological processes work to naturally restore disturbed freshwater ecosystems. Several of the most prominent of these processes are identified and briefly summarized in the subsections below.

Physical Processes

The major physical processes of natural attenuation are the burial of COCs within depositional areas by progressively cleaner sediment and the dispersion of COCs from erosional areas. The in-place covering and mixing of contaminated sediments with progressively cleaner sediments delivered by erosion within the watershed is the predominant fate mechanism for persistent COCs in sediment. Through this burial process, COCs deposited are gradually sequestered deeper in the sediment bed and, therefore, farther away from the comparatively dynamic sediment surface, where they otherwise could be available for uptake by the food web or downstream transport in the water column. Such depositional areas are only infrequently, if ever, subjected to forces sufficient to erode sediment, whereas the erosional areas are subjected more frequently to forces sufficient to erode sediment. Not surprisingly, the potential for sediment erosion from depositional areas, especially as a result of rare and extreme hydrologic events, typically represents a significant data need at sediment sites even though the probability of sediment displacement from known depositional areas is low.

The rate of sediment deposition and the vertical extent of sediment mixing are key parameters determining the rate of change of COC levels in surface sediments. The greater the deposition rate and the thinner the mixed layer, the faster the levels of contaminants in surface sediment are attenuated.

Dispersion, recognized as a mechanism of natural attenuation for groundwater (USEPA 1999), is also a mechanism of natural attenuation for contaminated sediments. For coarse sediment substrates with low rates of net sediment accumulation and low bulk sediment COC concentrations, dispersion may be the predominant long-term process reducing the availability of sediment COCs. Sediment-borne COCs can thereby be transported to lower energy areas, where they can be mixed with and covered by progressively cleaner sediments. As evident in the results of modeling of PCB fate, this appears to have been explicitly recognized by the USEPA (1994) in the selection of natural attenuation for remediating Twelvemile Creek and the upper sections of Lake Hartwell, South Carolina. The model predicted dispersion of PCB from upstream erosional sections followed by deposition and burial farther downstream in Lake Hartwell.

Biological and Chemical Processes

Biological and chemical mechanisms of natural attenuation are to a large extent COC-specific. However, several widely recognized mechanisms are summarized in this subsection. Although the potential universe of COCs released to surface waters is relatively large, concerns at most of the major contaminated sediment sites and nationwide are associated with a smaller subset of COCs. According to the USEPA (1997), PCB, mercury, organochlorine pesticides (particularly DDT), and polynuclear aromatic hydrocarbons (PAHs) are “the most frequent indicators of sediment contamination.” In addition to mercury, the most common metals associated with contaminated sediment problems are copper, cadmium, lead, arsenic, and chromium (USEPA 1997).

Through various biochemical mechanisms, aerobic microorganisms residing in near-surface sediments and the anaerobic microorganisms in the subsurface zone of sediments can degrade organic chemicals and thereby reduce their concentrations and/or toxicity. For example, PAH compounds can biodegrade to a limited extent in sediments. Four- and five-ring PAHs are generally recalcitrant, while the two-ring naphthalene may have relatively short biological half-lives in aerobic sediment (Cerniglia 1992). Regarding PCBs, both aerobic and anaerobic biodegradation processes can degrade PCB compounds in sediments (Abramowicz 1990). In aerobic sediments, PCBs can be degraded through a co-metabolic process, although the process is generally limited to PCB congeners having four or fewer chlorines (Untermann, et al. 1987). Anaerobic dechlorination of PCBs occurs in marine sediment (Brown and Wagner 1990) and freshwater sediment (Quensen et al. 1988; Brown, et al. 1987a and 1987b) through the removal of meta- and para-chlorine on the PCB molecule, which detoxifies PCBs in anaerobic sediment (Tiedje, et al. 1993). Empirical estimates of half lives for chlorine in these positions were as short as three years for certain Hudson River sediment deposits (Brown, et al. 1987a). Biological processes can also mediate the reduced bioavailability of COCs in sediment through the production of sulfides by sulfate-reducing bacteria.

In anaerobic sediments, the cationic metals cadmium, copper, nickel, lead, and zinc form stable complexes with sulfides produced by sulfate-reducing bacteria (Ankley, et al. 1996). These complexes essentially eliminate the toxicity of these metals when excess sulfides (specifically acid-volatile sulfides) are present relative to the concentration of these metals (Berry, et al. 1996). There is also evidence of substantially reduced availability of these metals for bioaccumulation in benthic invertebrates when such conditions exist (Ankley, et al. 1996).

The chemical processes of sorption and oxidation-reduction (redox) can reduce the bioavailability of COCs in sediment. Adsorption of nonpolar organic chemicals to the organic carbon fraction of sediments or for certain metals to the surface inorganic particles reduces their bioavailability. Redox reactions can reduce the solubility and, hence, bioavailability of certain metals by changing their valence. In addition, sulfides can complex certain metals as well as inhibit the methylation of mercury by precipitating mercuric ions (Choi and Bartha 1994).

ASSESSMENT OF NATURAL ATTENUATION PROCESSES

The data needed to assess natural attenuation processes are collected during investigations to characterize the nature and extent of contamination at sediment sites. Multiple lines of evidence documenting the ongoing reduction in exposure or toxicity, the primary mechanism(s) of the reduction, and the associated rates of reduction can be and are appropriately sought by such investigations. In addition, data that would accommodate the projection of natural attenuation processes into the future also are appropriately targeted by such investigations so that the effectiveness of those processes as a component of a natural attenuation remedial alternative might later be considered.

A number of methods have been used to empirically estimate rates of natural attenuation. Two of the more common methods are regressions of time series data using the exponential decay function and using dated sediment cores to construct chronologies of COC transport. A summary of natural attenuation rates at various sites in terms of half-times assessed using these methods is presented in Table C-1.

Table C-1
Examples of Natural Attenuation Half-Times (Years)

Water Body	COC	Biota(1, 2)	Sediment(1)	Water(1)	Source
Fox River, WI	PCB			4.4	WDNR 1995
	PCB		5.4 (4.8-6.0)		BBL 1999
Fox River, WI (DePere to Green Bay)	PCB	10.4 (7.0-15)			BBL 1999
Fox River, WI (Green Bay)	PCB	7.9 (5.1-13)			BBL 1999
Fox River, WI (Little Lake Butte des Morts)	PCB	9.4 (7.0-17)			BBL 1999
Hudson River, NY	PCB	2.5		1.7	Brown, et al. 1985
	PCB		10.4 (4.4-23)		QEA 1999
James River, VA	Kepone	5.4 (4.9-5.8)			Virginia Department of Health (1990 to 1996; Sheretz 1998)
	Kepone	3 (Blue Crab)			Huggett 1989
Kalamazoo River, MI	PCB	6.2 (3.1-12)	6.7 (3.5-14)	4.3 (3.4-5.2)	BBL(6)
Southern Reservoirs(3)	Chlordane		9.4 (7.7-11)		Van Metre, et al. 1998
	DDT		12 (6.1-19)		Van Metre, et al, 1998
	Lead		9.8 (8.9-11)		Van Metre, et al. 1998
	PCB		9.4 (7-13.4)		Van Metre, et al. 1998
Lake Hartwell, SC(4)	PCB	4.2			USEPA 1994
Lavaca Bay, TX(5)	Mercury		3.2 (1.2-9.3)		Santschi 1999
Nassau Lake, NY(5)	PCB		12 (8.4-17)		BBL 1999

Notes:
1. Numbers in parentheses represent the range of values used to calculate the mean.
2. Biota are fish except as noted.
3. Reservoirs include Lake Anne (VA), Lake Blackshear (GA), Lake Harding (GA), Lake Walter F. George (GA), Lake Seminole (FL/GA), White Rock Lake (TX), Coralville Reservoir (Iowa), Elephant Butte Reservoir (NM), and Lowrence Creek (TX).
4. Based on Food and Gill Exchange of Toxic Substances (FGETS) model results.
5. Intrinsic rates are presented based on sediment mixing layer thickness and sediment deposition rates.
6. Data were collected as part of the remedial investigation conducted by BBL, as well as the Michigan Department of Environmental Quality (MDEQ).

The processes of natural attenuation are typically manifested by trends of bioavailable COC concentrations in sediment approximated by exponential decay curves. The reason for this is directly related to physical processes of sediment deposition, mixing, and burial expected to dominate natural attenuation processes at many sites, and the first-order-kinetics nature of the chemical and biological processes. A steady supply of sediment from upstream areas and its deposition and mixing with the bioavailable zone (near-surface) sediment predicts mathematically that the rate of change in bioavailable zone COC concentration changes exponentially over time toward the concentration of COC on incoming sediment. Estimating rates using half times is described in detail in Box C-1.

Box C-1
Rate Estimation Using Half Times

The basis for the use of half-times to represent rates of natural attenuation is found in the mass balance of COCs in the mixed layer of sediments, which controls exposure of the aquatic ecosystem to sediment COCs. For the simple example for a sediment COC that has had upstream sources eliminated (contaminant concentration on depositing sediment is zero), for a constant average thickness of the mixed sediment layer (Z_m) and a constant sedimentation rate (s), the rate of change in chemical concentration (c) in the mixed layer is given by the mass balance equation:

$$\frac{dc}{dt} = -\frac{s}{Z_m}c \qquad (1)$$

Incorporating first-order kinetic loss as might be approximated for certain biodegradation processes or chemical transformation processes in this simple chemical mass balance for the mixed layer is:

$$\frac{dc}{dt} = -\left(\frac{s}{Z_m} + k\right)c \qquad (2)$$

Here k is the first-order reactive loss rate. Solutions for Equations 1 and 2 for conditions of the initial concentration equal to C_o are exponential functions associated with the concept of half-time. For example, a solution for Equation 2 is:

$$C = C_o \quad e \quad -\left(\frac{s}{Z_m} + k\right)t \qquad (3)$$

The time required for the concentration in the mixed layer to be reduced by 50 percent , in other words, the half-time (i.e., $c/c_o = 0.5$), can be solved for using Equation 3 or regressions of data to the linear transformation of Equation 3.

Rates of natural attenuation may be empirically deduced from measurements made over time or through the analyses of sediment cores, which have preserved in their strata a chronology of the deposition and transport of COCs within a system. An example of measurements supporting the former approach are those from monitoring bioaccumulative sediment contaminants in fish, which are available for many sites. Linear regression of the logarithms of these observations against time can reveal the rates of natural attenuation. A specific example is provided in Figure C-1 for Kepone in James River striped bass. Striped bass data made available by the Virginia Department of Health from 1983 through 1996 and for two locations and plotted in Figure C-1 yielded half-times of 4.9 and 5.8 years. In the Upper Hudson River, PCB levels in total suspended solids determined from water-column monitoring have been declining since the 1970s at rates with an associated half-time of 5.8 years (QEA 1999). From monitoring PCB levels in the Upper Hudson water column and in yearling pumpkinseed during the period 1979 through 1983 (Schroeder and Barnes 1983 and Brown, et al. 1985) mean summer water-column and fall-caught yearling pumpkinseed PCB concentrations were shown to be rapidly declining with associated half-times of 1.7 and 2.5 years, respectively. However, such analysis may be of limited value in projecting rates of natural attenuation if some or all of the time series data were collected during a period when sources of chemical other than sediments contributed significantly to the measurements.

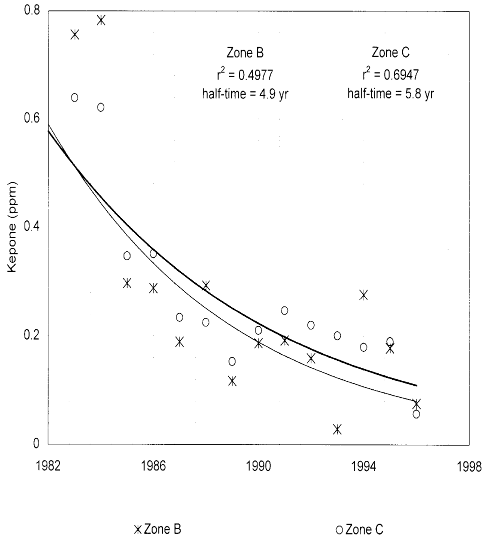

Figure C-1. Record of natural attenuation of Kepone in James River sediments, 1983 to 1996.

Use of Dated Cores

A common technique for developing COC transport chronologies entails chemical analyzing finely sectioned sediment cores. Analysis of certain radionuclides, in particular ^{137}Cs, provides a method of estimating the age of relatively recent sediment strata (Voskov, et al. 1991; Milan, et al. 1995; Bopp, et al. 1993; Kada, et al. 1994; and Valette-Silver 1993). Other radionuclides, such as ^{210}Pb (Bricker, 1993), radionuclides from reactor releases (Olsen, et al. 1978), and other methods (e.g., diatom speciation) have been used to determine the age of sediment strata. Analyses of the sediment contaminant concentrations in these strata can reveal the history of COC transport, including recent trends in transport. In addition to revealing the age of strata and, hence, sediment deposition rates, ^{137}Cs patterns also can reveal information about the thickness of mixed layer (Miller and Heit 1986).

Van Metre, et al. (1998) applied this technique to analyze sediment cores from 11 reservoirs in the eastern and central United States. Simple semilog linear regression models were used to estimate half-times for ^{137}Cs, PCBs, and total DDT in surface sediments that averaged, respectively, 10 ± 2.5 (standard deviation), 9.5 ± 2.2, and 13 ± 5.8 years. These rates reflect the continued transport and deposition of these chemicals as well as the sediment deposition, mixing, and burial processes. So, in the presence of continued deposition of COCs from active sources associated with use, air deposition, and release from waste discharges, these rates do not reflect the intrinsic rate of natural attenuation—the rate that would be experienced if the depositing sediment had no concentration of these chemicals. These intrinsic rates of natural attenuation are those associated with the underlying mechanisms of natural attenuation.

In the case of the physical processes of clean sediment deposition, mixing, and burial, the ratio of sediment deposition rate to mixing-depth thickness determines the intrinsic rate of natural attenuation. A recent example of estimating intrinsic rates of natural attenuation is provided by Santschi, et al. (1999) who determined ^{137}Cs profiles in 17 sediment cores from Lavaca Bay, Texas. Mixing layer thicknesses ranged from 2 to 10 cm. Intrinsic half-times ranged from 1.2 to 9.3 years with a median of 3.1 years. A series of eight cores collected from Nassau Lake (a 273 acre and shallow impoundment in New York) yield intrinsic half-times ranging from 8.3 to 17 years with an average of 12 years based on ^{137}Cs analyses. A mass balance model which accounted for a declining trend in tributary PCB loading to the lake indicates an overall half time for PCB in the mixed layer sediment of nine years (BBL 1999).

In general, understanding sediment deposition rates is very important to assessing natural attenuation and other methods and to dating using radionuclides, are available for estimation. For the inner harbor of the Sheboygan River and Harbor Superfund Site in Wisconsin, bathymetric surveys provided solid estimates of sediment deposition rates supporting the feasibility of natural attenuation. In this one-mile section of the Sheboygan River, the U.S. Army Corps of Engineers (USACE) conducted 14 bathymetric surveys at regular intervals over a 18-year period. Results showed continuous sediment deposition at high rates (up to 5 feet of deposition over the 18 years). In addition to independently explaining the presence of peak sediment PCB concentration well below the sediment surface, these observations were instrumental in calibrating a sediment transport model that was used to examine the potential effects of extreme-high-flow events. Sediment traps also can be useful in assessing sediment deposition rates and levels of COCs in depositing sediment; however, care must be taken in the design and placement of sediment traps to preclude either substantial underestimating or overestimating biases of sedimentation rates (Blomqvist and Håkanson 1981 and Kozerski 1994).

Chemical and Biological Processes

Various methods have been used to investigate the chemical and biological processes of natural attenuation. There is a large amount of experimental microbiological literature documenting various laboratory methods of assessing mechanisms and rates of COC biodegradation and biotransformation. Some of these methods have been brought to the field to provide proof of principle (Harkness, et al. 1993). In situ rates of biodegradation also have been empirically assessed using tools such as ^{137}Cs analyses of sediment cores and analysis of products and substrates in dated sediment strata (Brown, et al. 1987a).

FEASIBILITY ASSESSMENT

Despite today's apparent emphasis on applying active remedial technologies in managing contaminated sediment, there is ample evidence that natural attenuation can be applied as an effective remedial alternative or to enhance the protectiveness of other alternatives selected for aquatic sites. For instance, the USEPA has selected natural attenuation as the preferred remedial alternative or a component of the preferred alternative at several aquatic sites, including the Sangamo Weston, Inc./Twelvemile Creek/Lake Hartwell Superfund Site in South Carolina (for PCBs), the James River in Virginia (for the pesticide Kepone), the Commencement Bay/Nearshore Tidal Flats Superfund Site in Washington (for PCBs), and the Wyckoff/Eagle Harbor Superfund Site in Washington (for PAHs).

There is an important distinction between the processes of natural attenuation previously described and the natural attenuation alternative for sediment remediation. While natural attenuation refers to those processes that reduce the bioavailability of sediment contaminants over time, the natural attenuation alternative for a sediment site includes natural attenuation processes and performance monitoring. Institutional controls as may be necessary to manage risks while natural attenuation processes may be a necessary component to assure effectiveness and overall protectiveness. Such a definition of the natural attenuation alternative is analogous to the "monitored natural attenuation" remedy for soils and groundwater (USEPA 1999).

To select natural attenuation as a preferred remedy or component of another alternative, the regulatory frameworks most often applied to the management of contaminated sediment sites require a comparative analysis of feasibility among alternatives on the basis of effectiveness, implementability, and cost. The types of site-specific assessment data and empirical or modeling analyses discussed in the preceding section is necessary to support this comparative analysis. Absent an adequate data base of information on the magnitude and nature of recovery trends operating within a system (and the potential impacts and effectiveness of intrusive technologies should they be selected), the comparative analysis has difficulty rising above the subjective judgements that might intuitively lead one to conclude that the natural attenuation alternative is essentially the "no action" alternative. In avoiding this type of subjectivity and prejudgement of overall protectiveness of natural attenuation processes, there is no substitute for site-specific data that confirms the presence of natural recovery mechanisms and quantifies their rates, trends, and expected permanence relative to competing technological alternatives.

The comparison of natural attenuation to other alternatives on the basis of effectiveness, implementability, and cost is required by the National Oil and Hazardous Substance Contingency Plan (NCP), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), or similar risk-based cleanup statutes at the federal or state level. Using the CERCLA-type comparative analysis as a model, issues pertinent to evaluating the effectiveness, implementability, and cost of the natural attenuation alternative are summarized here.

Evaluating Effectiveness

Effectiveness comes in the form of sustained decreases in COC bioavailability and transport at the sediment surface, which, in turn, reduces exposure of aquatic organisms and, ultimately, the risks posed by contaminated sediment.

It is assumed that any necessary source control would be completed or would be undertaken as part of or in conjunction with a natural attenuation alternative and that the effects of source control can be predicted. To the extent that ongoing uncontrolled external sources would sustain COCs in bioavailable sediment (within the surface mixed layer) at levels that present significant risk, source control would be needed. The reduction in bioavailable COC concentration that would result from source control must be understood to explicitly assess the effectiveness of the natural attenuation alternative. For systems where both current source loading and natural recovery processes are at work in regulating bioavailable sediment COC levels, deterministic mathematical modeling may be the only practical way of quantitatively estimating future trends in COC levels in response to source control.

Much of the effort in evaluating the natural attenuation alternative typically is focused on gauging the effectiveness of recovery processes (primarily physical processes) in permanently containing COCs in place over the long-term, even under the influence of potentially erosive forces during high-flow storm events. The potential for the reversal of natural attenuation trends in response to rare events is a reasonable concern. However, events such as extremely high flows will not necessarily undo the benefits and long-term protectiveness of natural attenuation. A study by Barber and Writer (1998) may be the most comprehensive field investigation of the effects of extreme high flow on sediment COC distributions. The study assessed the effects of the 1993 flooding of the Upper Mississippi River through extensive sampling of surface sediments in 24 pools of the lock and dam network of the Upper Mississippi following the very rare greater-than-100-year-recurrence-interval flood. The investigators found that the high flows did not scour or expose the higher COC concentration sediments of the deeper sediment bed. In fact, levels of PCB in surface sediment declined due to the deposition of comparatively clean sediment—a clear example of physical natural attenuation processes at work in a large, complex system.

In addition to the issue of long-term protectiveness and consistent with detailed evaluation of effectiveness under the NCP, the effectiveness criterion also encompasses the degree of risk reduction and corresponding residual risk; the short-term risk to workers, the public, and the environment during implementation of the remedy; and the estimated reductions in mobility, toxicity, or volume of COCs through treatment. Because natural attenuation processes can reduce the toxicity concentration and mobility of sediment contaminants, they can accomplish treatment. Natural attenuation has virtually none of the short-term risks (i.e., risks to workers, public, and the environment due to remedy construction activities) associated with implementation of more active remedies involving sometimes arrays of sediment handling, excavation, dredging, sediment processing equipment, and transporting equipment.

Modeling Approaches

The level of risk reduction and the associated time frame as well as degree of toxicity or mobility reduction achievable through the natural attenuation alternative can be assessed through various modeling approaches. At one end of the spectrum of complexity are simple calculations such as Equation 3 that are analytical solutions for bioavailable sediment chemicals. These calculations may be suited to the task, but their inherent assumptions of constant sedimentation rate and mixing and spatial representativeness may be too limiting. More complex models can be used that explicitly represent sediment COC distributions, hydraulics, hydrology, sediment erosion, deposition, and transport in long-term mass balances for sediments and COCs. These models can make such representations with a high degree of spatial resolution to examine not only the expected long-term response of the system to continued natural attenuation and other remedial alternatives, but also to examine the potential responses to extreme conditions, such as flood flows. Many of these large models are applications of or derivatives of the Water Quality Analysis Simulation Program (WASP) and are often linked with separate hydraulic and sediment transport models. WASP4 was developed by and is supported by the USEPA to analyze water quality in rivers, lakes, and estuaries. A more detailed description of this approach to analysis of contaminated sediment sites is provided in “Effective Decision Making Models for Evaluating Sediment Management Options” (see Appendix B).

In addition to the complex models used to analyze the potential responses of contaminated sediment sites to various remediation approaches, several other models of intermediate complexity have been used to assess the effectiveness of natural attenuation. These models are described in Box C-2 below.

Box C-2
Model Descriptions

The following three models are all similar in that each represents the response of the system, once source terms are eliminated or controlled, as a function of two dominant parameters: (1) the sedimentation rate in burying contaminated sediments and (2) the bioturbation (or mixing) in reconstituting contaminated sediments back to the surface water-sediment interface.

RECOVERY Model

RECOVERY is a personal computer (PC)-based screening model developed by the USACE to assess the fate of in-place contaminated sediments in aquatic environments (Boyer, et al. 1994 and Sturgis, et al. 1993). The program allows the user to rapidly generate and evaluate recovery scenarios for contaminated sediments by predicting the concentration of the COC in water, in the upper mixed sediment layer, and in deep sediments over time. The physical representation is a well mixed water column underlain by a well mixed surface (active) sediment layer, and a deeper sediment layer potentially segmented into contaminated and clean regions. The COC is assumed to follow linear reversible equilibrium sorption and first-order decay kinetics. Modeled pathways include volatilization, burial, resuspension, settling, advection, and pore-water diffusion.

Officer and Lynch Model

The Officer and Lynch model (1989) is based on a series of theoretical relations that describe the distribution of sediment contaminants over time, incorporating site-specific conditions for mixing (specifically bioturbation) and sedimentation. The model also incorporates nonadvective sediment-water exchange over time. The model was first used to evaluate the observed natural recovery that had occurred after mercury discharges ceased from a chloralkali plant in Bellingham Bay, Washington. It has also been used to evaluate natural recovery within the Sitcum Waterway Remediation Project within the Commencement Bay Superfund Site, Puget Sound, Washington (Templeton, et al. 1993). Sediment dynamics parameters that need to be determined or estimated include gross sedimentation, net sedimentation, resuspension, mixed layer thickness, mixing rates, and source inputs.

Mackay Three-Compartment Model

As the result of a 1991 report expressing the collective opinion of a group of researchers that it would be beneficial to assemble a useful, simple, and easily applied mass balance model that could guide regulatory activities regarding persistent chemicals present in the Great Lakes ecosystem, Mackay developed a simple yet comprehensive rate-constant model. The model was developed to describe the relative importance of various COC fate processes and to estimate time response to loading reductions or elimination. The model tests three general compartments: the atmosphere, a single well-mixed water column, and a well-mixed surficial sediment layer. Loading terms can be land-based, tributaries, or atmospheric. Fate processes, including chemical degradation, outflow, sediment-water exchange, and sediment burial, are quantified to facilitate interpretation expressed as rate constants. The model has been applied to PCBs in Lake Ontario (Mackay, et al. 1994) and to 17 organic and inorganic chemicals in the Bay of Quinte (Lake Ontario).

EVALUATING IMPLEMENTABILITY AND COSTS

Implementability is a measure of the technical and administrative feasibility of implementing an alternative, including constructability issues, the need to obtain required permits and approvals, and the time required to complete the work and achieve remedial objectives for a site. Lacking active remedial components comparable to the intrusive nature of capping or dredging technologies, the natural attenuation remedial alternative necessarily includes performance monitoring to identify trends and quantify attenuation rates in bioavailability and exposure over time. Likely additional components can include institutional controls such as fish consumption advisories to mitigate human exposure until recovery reduces fish exposure to acceptable levels. These activities are inherently implementable as evident by the widespread occurrence of such programs across the nation. Present worth costs for monitoring programs and certain institutional controls can be readily estimated.

Regarding determination of an acceptable time frame for natural attenuation to achieve risk reduction goals, hypothetical examples illustrate that there is no simple answer other than through a comparative analysis of remedial alternatives. In cases where effective alternatives can be implemented quickly, cost effectively and with little or no collateral impact to public health and the environment and where risks are high and unmanageable by other means, the acceptable amount of time for a natural attenuation alternative would be relatively short. That time might be only slightly longer than the time it would take to implement an active remediation project. In a case where the alternatives have high monetary, social, and/or environmental costs and risks are low and manageable by other means, the acceptable amount of time would be considerably longer than the time it would take to implement active remediation. In developing guidance for the use of natural attenuation for soil and groundwater cleanup, the USEPA (1999) recognized that the reasonableness of a time frame for natural attenuation to achieve site remediation objectives needs to be assessed in relation to the time necessary for other alternatives to meet those same objectives.

To illustrate very simply one facet of this comparative evaluation, consider the 10+ year time frames for designing and implementing dredging remedies for large sites where local sediment disposal would be necessary. In such a case, the preference for natural attenuation proceeding with a half-time of 10 years can be immediately appreciated if dredging was not predicted to effect greater than a 50 percent reduction in exposure. If natural attenuation were proceeding with a half-time of five years, to compete strictly on the basis of effectiveness, an active remedy with a 10-year design and construction framework would need to achieve better than a 75 percent reduction in risk to be preferable.

RECOGNIZING NATURAL ATTENUATION AS AN EFFECTIVE APPROACH

In recognizing the capacity of aquatic systems to naturally recover in the presence of contaminated sediments, the USEPA has identified a potential role for natural recovery as a sediment management tool. This was set forth as a guiding principle in *EPA's Contaminated Sediment Management Strategy*:

> "Where short-term and long-term risks and effects are determined to be acceptable, and where statutes or international agreements do not require remediation or establish other preferences (e.g., preference for treatment under the Superfund Amendments and Reauthorization Act of 1986), the appropriate treatment of a contaminated sediment site may be to implement pollution prevention measures and source controls, and to allow natural processes such as biodegradation, chemical degradation, and the deposition of clean sediments to diminish risks associated with the site to within acceptable levels" (USEPA 1998).

The USEPA has applied this principle and selected natural attenuation as a remedial alternative at several contaminated sediment sites. Natural recovery also has been identified as a key remedial alternative for the restoration of river and lake bottoms from the effects of oil. In its *Primary Restoration* guidance, the National Oceanic and Atmospheric Administration [(NOAA); NOAA 1996] identifies natural recovery, dredging, and sediment agitation (i.e., the designed release of oil from sediments through agitation) as feasible alternatives for riverine cobble-gravel, sand, and silt-mud bottoms. For lakes and subtidal marine and estuarine habitats, natural recovery, dredging, and sediment capping are deemed feasible alternatives. The same guidance also concludes that "monitoring of natural recovery is the only feasible action for river and stream rock bottom habitats" (NOAA 1996).

In 1997, the NRC's Committee on Contaminated Marine Sediments published results of a three-year study on sediment management strategies, which recognized that natural attenuation can play an important role in effective management of contaminated sediments: "Natural recovery is a viable alternative under some circumstances and offers the advantages of low cost and, in certain situations, the lowest risk of human and ecosystem exposure to sediment contamination" (NRC 1997).

The principles established in formal regulatory guidance for the use of natural attenuation to clean up contaminated soils and groundwater are to a large extent appropriate for defining the role of natural attenuation at contaminated sediment sites. There has been considerably more experience in addressing soil and groundwater contamination at inactive hazardous waste sites than in the remediating contaminated sediments. However, some of the important issues of managing contaminated sediment sites are very similar to those which led to a formalized role for natural attenuation in addressing soils and groundwater cleanup nationwide.

Specifically, the USEPA's final guidance titled *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (USEPA 1999) sets forth a philosophy and several principles that are clearly applicable to natural attenuation as a sediment remedy as well.

> "EPA does not view monitored natural attenuation to be a 'no action' or 'walk-away' approach but rather considers it to be an alternative means of achieving remediation objectives that may be appropriate for a limited set of site circumstances where its use meets the applicable statutory and regulatory requirements. As there is often a variety of methods available for achieving a given site's remediation objectives, monitored natural attenuation may be evaluated and compared to other viable remediation methods (including innovative technologies) during the study phases leading to the selection of a remedy. As with any other remedial alternative, monitored natural attenuation should be selected only where it meets all relevant remedy selection criteria, where it will be fully protective of human health

> and the environment, and where it will meet site remediation objectives within a time frame that is reasonable compared to that offered by other methods” (USEPA 1999).

Natural attenuation is reducing the risks posed by contaminated sediments to some degree at virtually all contaminated sediment sites. The natural attenuation remedy which, as a risk management tool necessarily includes monitoring and appropriate institutional controls, can be a protective and preferred approach to managing contaminated sediment site risks, just as the use of monitored natural attenuation can be an effective tool for managing contaminated soils and groundwater.

RECOMMENDATIONS FOR POLICY DEVELOPMENT

While natural attenuation has received recognition at a policy level as a potentially appropriate and effective remedy for sediment sites, much work remains in terms of operationalizing the more effective assessment, evaluation, and use of natural attenuation to reduce risks posed by contaminated sediments. Much like natural attenuation has been increasingly relied on for addressing contaminants in soil and groundwater, the use of monitored natural attenuation can and must play a wider role in managing sediment sites. To this end, the following considerations and action items are recommended:

- *The natural attenuation alternative can be a protective remedy. It is not a no action alternative.* Natural attenuation is reducing the risks posed by contaminated sediments to some degree at virtually all contaminated sediment sites. The natural attenuation alternative which, as a risk management tool necessarily includes monitoring and appropriate institutional controls, can be a protective and preferred approach to managing contaminated sediment site risks. The recognition of the natural attenuation alternative as an effective remedy in USEPA policy needs to be communicated to regulatory personnel in the field. In doing so, the key applicable principles of the USEPA guidance on the use of monitored natural attenuation for soils and groundwater can and should be adopted and promoted. The USEPA and other federal and state agencies have recognized the applicability of natural attenuation at the policy level, but actual selection and application of the alternative is lagging. The role of natural attenuation in addressing environmentally-persistent COCs in soil and groundwater is well documented and is increasingly relied upon as one component of a site's overall remedial package. In addition, the USEPA has formally selected natural attenuation as a whole or partial remedy at several sediment sites. Fundamentally, it must be recognized that natural attenuation is an intrinsic set of processes that operates continuously within all aquatic ecosystems. Given that premise, natural attenuation is necessarily already relied upon before, during, and after other more intrusive remedies. However, additional effort is needed in the site assessment phases of remedial planning to discern what portion of overall recovery gains (or reversals) are attributable to natural processes versus source control, intrusive remedial action, and other actions.

- *Empirical evidence and model projections should be used to evaluate the effectiveness of natural attenuation in reducing risks.* Site data that identify the mechanisms and rates of ongoing natural attenuation are critical to establishing the feasibility of the natural attenuation alternative. These data are needed not only to establish the basic proof that attenuation is occurring but to calibrate and, optimally, verify fate and transport models that would predict future bioavailable COC concentrations. Empirical information such as sediment deposition rates, sediment mixing layer thickness, and time series data documenting changes in COC bioavailability or toxicity over time are important. Multiple lines of such empirical evidence should be sought. Organizing site data into a mathematical model that can predict how the system will change over time is an important extension of the basic understanding of the processes that are reducing risk at a site. Deterministic modeling may be the only practical way to address such issues as assessing the reliability of natural attenuation processes to continue to reduce risks under conditions other than those which have been observed (e.g., rare extreme hydrologic events) or to address the combined effectiveness of source controls and natural attenuation.

- *The natural attenuation alternative should be evaluated in comparison to other action alternatives for sediments on the basis of effectiveness, implementability, and costs.* Defining a reasonable time frame for natural attenuation to meet remediation objectives is a site-specific process that weighs (among other factors) the extent of current risks and impacts to resources; availability and reliability of institutional controls to manage risks; and the uncertainties associated with predicted time frame and the implementability, effectiveness, and costs of other alternatives. For example, levels of risk reduction produced by intrusive technologies may not be achieved significantly sooner than allowing ongoing natural recovery processes to proceed uninterrupted. This is especially true when many, many years are required to fully design, permit, and construct large-scale capping or removal remedies, including the potential need to design and permit a proper disposal facility. Again, even after such remediation is complete, natural recovery processes would be relied upon to attenuate remaining risks posed by the residual materials left behind by intrusive technologies. Therefore, comparatively evaluating remedial alternatives is necessary. Simple pass/fail decision criteria for natural attenuation (e.g., surface sediment contaminant levels within a factor of two of remedial objectives as suggested by Templeton, et al. 1993) that implicitly assume capping or dredging alternatives to be more effective should be avoided.

- *Where irreconcilable differences of opinion exist regarding the time frame or reliability of natural recovery, performance-based natural attenuation should be selected along with a contingent remedy.* A contingent remedy is an alternative such as containment or dredging that could be implemented at a specified future date (e.g., the five-year review of a Record of Decision) if a natural attenuation remedy fails to meet appropriate performance standards. Considering the potential consequences of being wrong in making a determination that natural attenuation is not performing (i.e., the high financial cost and social and environmental costs associated with implementation of active sediment remediation), the decision maker should be highly confident that natural attenuation is not working and that other remedial options will significantly reduce risk before deciding to abandon the natural recovery option. Consequently, some lower confidence limit on performance measurements such as fish contaminant trend monitoring data is appropriate for triggering decisions to implement the contingent remedy. Performance standards, at a minimum, should include those that relate directly or indirectly to the expected rate of risk reduction needed to achieve risk-based remedial objectives for the site. Development of those performance standards should minimally address the lines of empirical evidence that supported the original decision. In general, promoting contingent remedies might help bring to closure to the different opinions regarding sediment remedies that are rooted in different expectations regarding the effectiveness, implementability, and costs of sediment remediation technologies.

- *The social and environmental benefits of the natural attenuation alternative may outweigh those perceived to flow from intrusive technologies.* The final word on natural attenuation in sediments is the need for risk managers to come to realize that natural systems have a substantial capacity to attenuate and recover from the presence of contaminants. Conversely, experience with remedial dredging highlights the fact that technology, while powerful, is not necessarily as effective as the nonintrusive natural processes. In making a final determination on this pivotal question, the overall social and environmental benefits and costs must be evaluated. If empirical and predictive lines of evidence indicate that natural attenuation can achieve risk reduction goals within a time frame similar to technological approaches, the benefits of avoiding habitat destruction, the technical and administrative limitations of construction and landfilling, and the sometimes extremely high social cost of paying for technological intervention may clearly signal that natural attenuation is the most appropriate remedy for many of our nation's contaminated sediment sites.

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