

Use of Sediment Core Profiling in Assessing Effectiveness of Monitored Natural Recovery

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Purpose

The National Risk Management Research Laboratory (NRMRL) of the U.S. Environmental Protection Agency (U.S. EPA) is developing effective, inexpensive remediation strategies for contaminated sediments. Monitored Natural Recovery (MNR) is included among such sediment management alternatives (1). Information summarized in this *Sediment Issue* pertains specifically to studies conducted by NRMRL (2, 3) that evaluated the recovery of surface sediments contaminated with polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). This information is intended to: a) be used as a reference for site managers and U.S. EPA decision makers who may be considering MNR as a contaminated sediments management strategy, and b) provide a better understanding of the mechanisms that



Sediment Core Sample Collection at Eagle Harbor

contribute to the natural recovery of contaminated sediments and the tools used to assess the natural recovery processes.

The results of two NRMRL studies (2, 3) undertaken to evaluate MNR processes and mechanisms are summarized below. These two studies were conducted at a marine site (the Wyckoff/Eagle Harbor Superfund Site off Bainbridge Island, WA) in cooperation with U.S. EPA Region 10 and the U.S. Army Corps of Engineers, and at a freshwater site (the Sangamo-Weston/Twelvemile Creek/Lake Hartwell Superfund Site in Pickens County, SC) in cooperation with U.S. EPA Region 4.

Introduction

MNR involves leaving contaminated sediments in place and allowing ongoing physical, chemical, and biological processes to contain, destroy, or otherwise reduce the bioavailability or toxicity of contaminants in sediment (1), while implementing a monitoring program to determine if attenuation of contaminants is occurring (4, 5). Reduction of a contaminant's bioavailability and toxicity occurs primarily at the sediment surface (typically defined as the sediment-water interface). In net depositional environments, natural capping with relatively clean sediments is often the dominant and more immediate recovery mechanism following source removal and/or control (2). Natural sediment deposition may reduce surface sediment contaminant concentrations over time, protecting the water column and biota from diffusion and advection of

contaminants from sediments (4). Additionally, deposition will reduce both the risk of resuspension of contaminated sediments during high-flow events and the potential for contaminant transport into the food chain (4).

Similar to natural attenuation of terrestrial contaminants, natural recovery of contaminated sediments relies on careful assessment and long-term monitoring of sediment recovery mechanisms, including sediment burial, contaminant weathering (e.g., dilution, volatilization, biodegradation, and sequestration), degradation, and potential transport.

Methods to Assess MNR Processes

For these two NRMRL studies (2, 3), assessment of MNR processes began with the collection of sediment core samples. Sediment cores can be used to establish vertical contaminant concentration profiles, age date sediments, and determine surface sedimentation and surface sediment recovery rates. These approaches are summarized below.

Contaminant Profiling and Fingerprinting. The sediment core profile may provide a historical record of the deposition on the bed surface; the sediment-water interface represents the date of sample collection and increasingly older sediments are found at increasing depths below the surface (2). In a typical core profile, the deepest portion of the core represents some time before contaminant-of-concern (COC) release and, at a given depth, the maximum COC concentration will reveal the time at which the sediments were impacted by the contaminant source. In net depositional environments, core sediments above this area of maximum concentration may show decreasing COC concentrations as the source is contained or removed and relatively clean sediments have been deposited.

Chemical fingerprinting relies on analytical methods to quantify unique chemical signatures or patterns in order to identify or distinguish different chemical sources. For example, PAHs often display unique compositions that can be used to identify sources (6). PAHs are commonly present in urban sedimentary environments due to long-term accumulation from naturally occurring background and urban run-off sources and as a result of releases from industrial facilities. Conventional hydrocarbon fingerprinting and PAH homolog distributions can be used to characterize contaminant sources and the extent of PAH weathering (6).

Sediment Age Dating and PSD Analysis. Lead-210 (^{210}Pb) or cesium-137 (^{137}Cs) isotope analysis can be used to enhance the core depositional profile by dating each core segment, providing an age profile along the length

of the core. These two isotopes are relatively common in sediments and can be used to determine the age of sediments over years or decades (7, 8). Age dating provides information on the temporal variations of contaminant release, sediment accumulation rates, and surface mixing depths (7, 9-13). ^{137}Cs is most useful in identifying strata deposited in the early 1960s, a period of atmospheric nuclear testing, while ^{210}Pb is deposited continuously from the atmosphere and can be used to estimate more recent dates (4). These two isotopes partition to particle surfaces, and their sorbed concentrations in sediment depend on the sediment particle size distribution (PSD) (e.g., fine-grained sediment generally contains higher activity than sandy sediment). Thus, the ability to accurately age date sediments is influenced by the uniformity of the PSD through the dated vertical profile and the historical consistency of the sedimentation rate over the dated period. When these two conditions are not met, the accuracy of the dating procedure is compromised. Age dating results may be combined with contaminant concentration profiles to estimate the time required to meet surface sediment remediation or recovery goals.

Surface Sedimentation and Surface Sediment Recovery Rates. Using surface sedimentation requirements (i.e., target cleanup goals) and age dating results, the time for surface sediment recovery can be predicted. Contaminant concentrations in sediment are plotted against depth below the sediment-water interface, and best-fit logarithmic regressions are defined for the surface sediment data. Best-fit logarithmic regressions are calculated to determine 95% prediction intervals for the dates when cleanup goals would be met, assuming site and source conditions remain constant.

Challenges Associated With Using Core Methods

Several challenges may be associated with the use of sediment core techniques to assess MNR:

- Natural background and/or urban run-off may be an ongoing source of contamination to the sediments.
- Making future predictions based on extrapolation of past data trends for sediment recovery rates may be difficult because there is no guarantee that the fate processes causing the exponential decay of surface sediment concentrations will continue at the same rate in the future. Therefore, long-term monitoring must remain an integral component of MNR so that the recovery of surface sediments can be determined.

Case Studies

Wyckoff/Eagle Harbor Superfund Site

Eagle Harbor, a shallow marine embayment off Bainbridge Island, WA, was formerly the site of the Wyckoff wood-treatment facility where large quantities of creosote were used from the early 1900s to 1988. Historical creosote seepage into the harbor resulted in substantial PAH contamination in the harbor sediments over time (14). Vertical contaminant profiling and age dating of sediment cores were used to assess and document the history of PAH accumulation, measure the extent of natural sediment capping, and document compositional changes and sources over time and space around the Wyckoff Site and within Eagle Harbor (2).

To control PAH migration into the water column and surrounding sediments, the area with maximum PAH concentrations was capped. Sediment cores were collected from 10 locations in uncapped areas in Eagle Harbor including six nearshore (near the Wyckoff facility) and four toward the middle of the harbor, as shown in Figure 1. These data (five segments per core) were used to determine PAH sources, sediment deposition rates, and PAH mass reduction due to weathering (e.g., dilution, volatilization, biodegradation, and sequestration).

The results of total petroleum hydrocarbons (TPHs) fingerprinting, analysis of 50 PAH compounds, and sediment age dating conducted on these core segment samples facilitated the classification of the Eagle Harbor sediments among three recognized primary PAH sources – namely, natural background, urban run-off, and creosote (from the former Wyckoff wood-processing facility).

The fingerprinting and source characterization process is discussed in detail in a previous publication (6), but a brief description of how sources are classified follows. Natural background fingerprints exhibit odd-carbon dominated n-alkanes (C_{25} – C_{31} compounds), which are indicative of plant epicuticular waxes from terrestrial plant debris. The urban run-off fingerprint is dominated by discrete peaks recognized as non-alkylated 3-, 4-, and 5-ring PAHs such as phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(j,k)fluoranthene, and indeno(1,2,3-cd)pyrene. Creosote fingerprints are dominated by discrete peaks identified as various 2-ring PAHs (C_0 – C_4 naphthalenes) and 3- and 4-ring compounds such as phenanthrene, anthracene, fluoranthene, and pyrene. Quantitative PAH data are used to confirm the peak identification.

As creosote weathers, it becomes dominated by 4- to 6-ring PAHs, increasingly resulting in PAH compounds resembling those found in urban run-off. Comparing PAH results, as in Figure 2, with depth and age provides information on the source. Total PAH (τ -PAH) histograms were constructed for each core, corresponding to the appropriate sediment segment. From sediment cores collected nearest the cap (near-shore) (Figure 2-b), it was determined that surface sediment contamination was dominated by urban run-off and weathered creosote, while deeper sediments were heavily contaminated with relatively unweathered creosote and some pure-phase creosote. Sediment characteristics for five of the six near-shore samples did not permit age dating; thus, estimated dates corresponding to depth segments are not provided in Figure 2-b. Cores located furthest from the cap in the center of the Harbor (Figure 2-c) were dominated by urban run-off with no signs of creosote contamination. Sedimentation rates were similar for the four cores located in the middle of the harbor and one near-shore core, ranging from 0.54 to 1.10 gm/cm²-yr.

Sediment accumulation rates (cm/yr) are plotted against core segment age in Figure 3, where sediment characteristics permitted age dating. Cores having nonuniform historical sediment deposition could not be dated using the ²¹⁰Pb data. Only one core adjacent to the former Wyckoff Facility (B01) and the mid-harbor cores (E01, E02, E03, E04) could be dated; therefore, only sediment accumulation rates for these cores are shown in Figure 3.

The results from this study (2) provided information on the ability of Eagle Harbor sediments to recover under natural conditions, identified the occurrence of creosote-

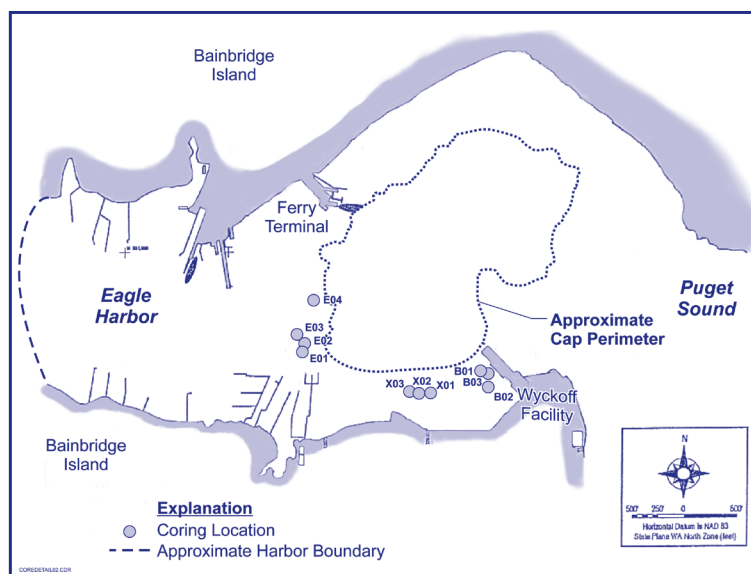


Figure 1. Eagle Harbor Site Map Showing Coring Locations. Reprinted with permission from (2). Copyright 2002, American Chemical Society.

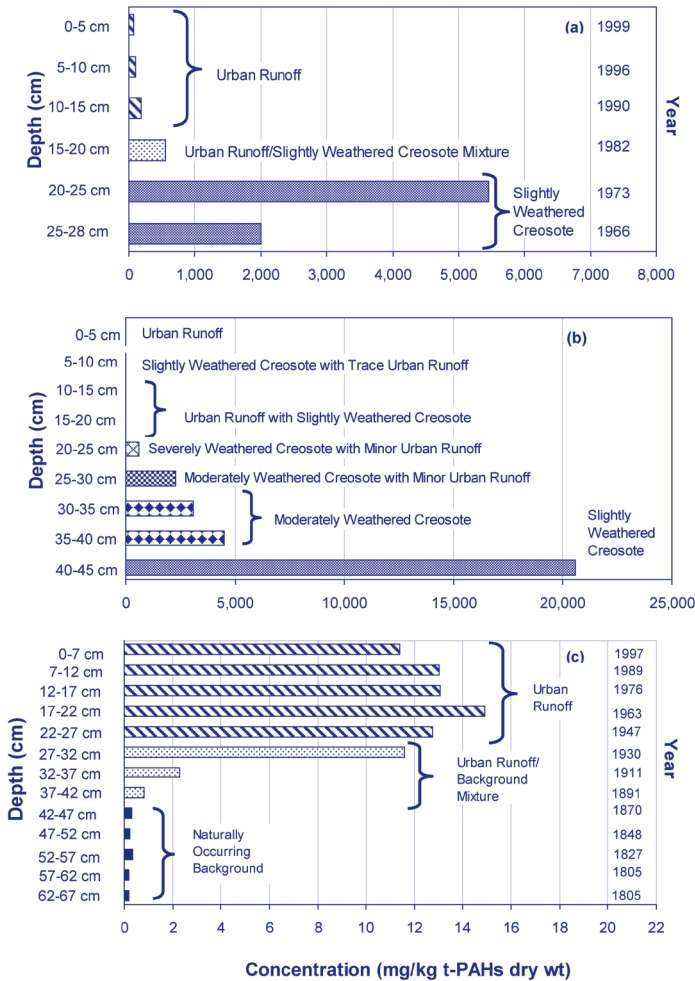


Figure 2. Eagle Harbor PAH Histograms Showing t-PAH Concentrations and Contaminant Source Characteristics. (a) B03 core located adjacent to the former Wyckoff Facility. (b) X03 core located near shore. (c) E02 core located mid harbor. Reprinted with permission from (2). Copyright 2002, American Chemical Society.

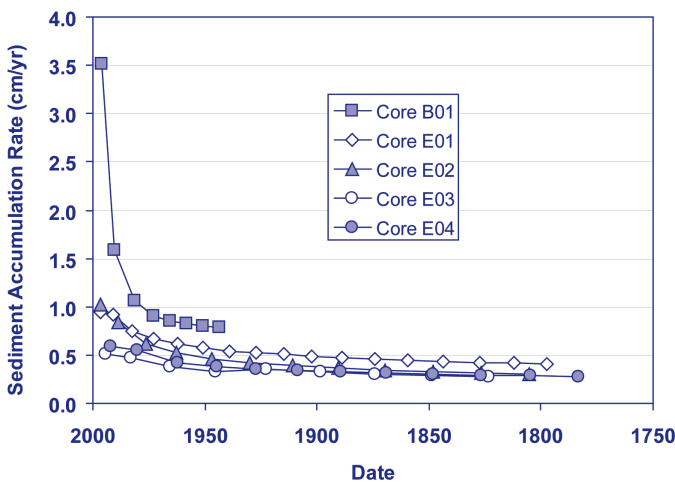


Figure 3. Eagle Harbor Sediment Accumulation Rates for Selected Harbor Cores (B01 core adjacent to the former Wyckoff Facility; EO cores located mid harbor). Reprinted with permission from (2). Copyright 2002, American Chemical Society.

derived PAH weathering in off-cap surface sediments, and distinguished between three distinct PAH sources in the harbor (creosote, urban run-off, and natural background). Recognition that urban run-off has contributed consistently to burial and served as an ongoing source of PAHs to the harbor's sediments, albeit in comparatively low concentrations, is a key piece of information. Such information may influence future sediment management decisions for this site with respect to long-term monitoring of surface sediments to assess cap performance.

Sangamo-Weston/Twelvemile Creek/Lake Hartwell Superfund Site

At the Sangamo-Weston/Twelvemile Creek/Lake Hartwell Superfund Site in South Carolina, the primary focus was the recovery of PCB-contaminated surface sediments resulting from natural sedimentation. As described in U.S. EPA (14), Lake Hartwell was contaminated by PCBs released from the Sangamo-Weston plant located upstream of the study area. Capacitors were manufactured at this plant from 1955 to 1978, and waste disposal practices included land burial of off-specification capacitors and wastewater treatment sludge on the plant site. An unspecified amount of PCBs were either buried or discharged with effluent directly into the water (14). NRMRL conducted a study in which core profiles were used to establish total PCB (t-PCB) concentration profiles, age date sediments, and determine surface sedimentation and surface sediment recovery rates in 18 cores collected along 10 transects in the lake, shown in Figure 4 (3).

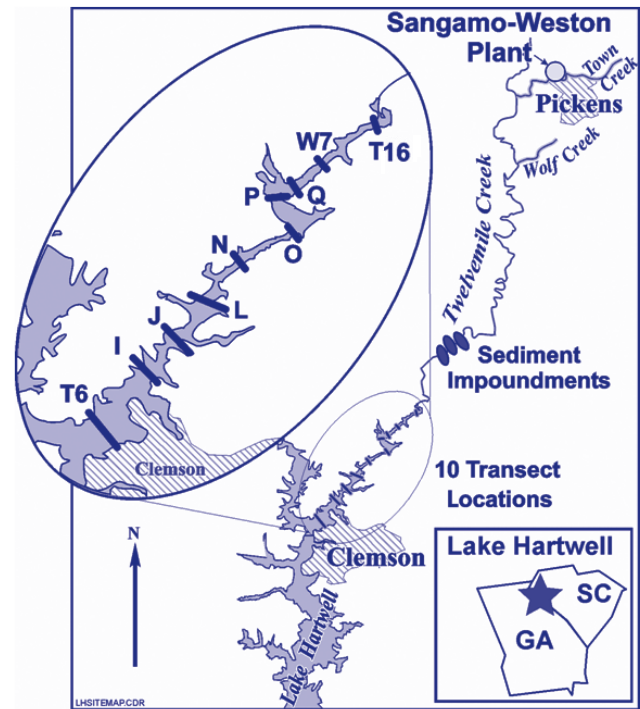


Figure 4. Lake Hartwell Transect Locations. Reprinted with permission from (3). Copyright 2002, American Chemical Society.

Vertical t-PCB concentration profiles were developed by plotting concentration against core depth for both the upgradient and downgradient transects. Figure 5 provides an example of t-PCB concentration plotted against core depth for two of the upgradient cores collected at Transects T16 and Q. In both cores, the highest PCB concentrations were associated with silt layers, which contained $57 \pm 6.9\%$ silt and clay and $2.6 \pm 0.86\%$ total organic carbon (TOC). The sand layers contained $96 \pm 2.9\%$ sand and $0.21 \pm 0.08\%$ TOC and had much lower PCB concentrations. These vertical concentration profiles showed that historical sediment releases resulted in substantial burial of PCB-contaminated sediment by sand with low t-PCB concentrations, so that each upgradient core contained less than 1 mg/kg t-PCBs in the surface sand layers. This concentration meets the cleanup goal of 1 mg/kg based on the 1994 Record of Decision for Lake Hartwell (14). Much higher PCB concentrations were present in buried sediment with maximum t-PCB concentrations measured at approximately 30 to 60 cm below the sediment-water interface. These higher concentrations are associated with the period of maximum PCB release into the watershed circa 1960-1980.

To estimate the rate of surface sediment recovery, best-fit logarithmic regressions were developed using surface sediment data by plotting sediment age against sediment concentration. As shown in Figure 6, sediment t-PCB concentrations are plotted against depth for six Lake Hartwell cores; each figure also shows the cleanup goal of 1.0 mg/kg t-PCBs. Of these six cores, only cores from Transects L (Figure 6-c) and T6 (Figure 6-f) fully penetrated the PCB-contaminated sediments to provide a complete vertical profile of PCB contamination. For the Transect L core, the vertical t-PCB concentration profile indicates

relatively low t-PCB concentrations at the sediment-water interface, increasing in concentration with depth until the maximum t-PCB concentration was measured at the 35 to 40 cm interval. The maximum t-PCB concentration was followed by progressively decreasing concentrations with depth until the t-PCB concentration approached the detection limit at ~85 cm below the sediment water interface, where sediments were likely deposited at the onset of PCB use at Sangamo-Weston. The sediments containing the maximum PCB concentrations are associated with the period of maximum PCB release into the watershed. For the Transect T6 core, the maximum t-PCB concentration occurred at the 15 to 20 cm depth interval; the shallower depth may be explained by the observation that Transect T6 had the lowest measured sedimentation rate. The behavior of the Transect J core profile (Figure 6-d) was inconsistent with the other cores collected in 2000 and cannot readily be explained; the Transect J core was represented by relatively low t-PCB concentrations (~1 to 1.5 mg/kg) over the entire 30-cm profile.

Best-fit logarithmic regressions were calculated to develop 95% prediction intervals for the dates at which cleanup goals would be met. Using these equations, sedimentation requirements to achieve each of the surface sediment cleanup goals were determined based on the present t-PCB value. Estimated time to achieve the 1.0-mg/kg surface sediment recovery goal stipulated in the Superfund Record of Decision (14) varied depending on the location of the sample. Estimated surface recovery to 1.0 mg/kg was predicted to occur between 2000 and 2012 for Transect I, 1988 to 2011 for Transect L, 1995 to 2010 for Transect N, and 1992 to 2016 for Transect O.

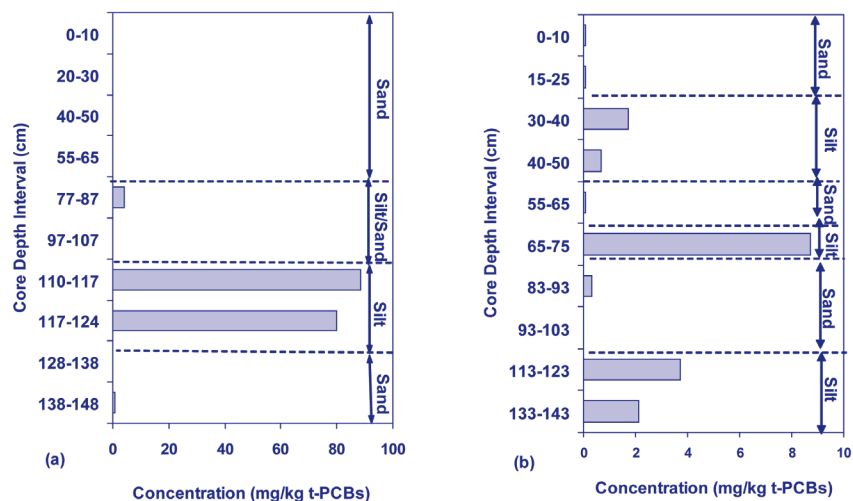
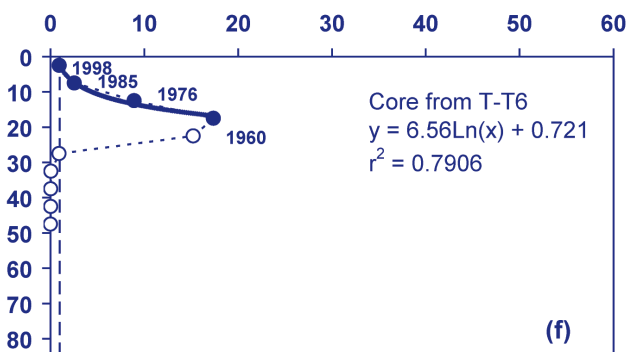
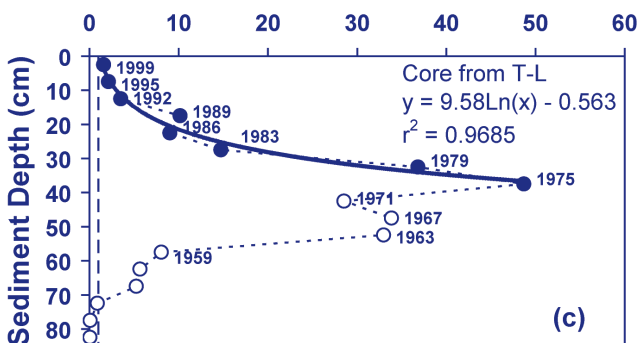
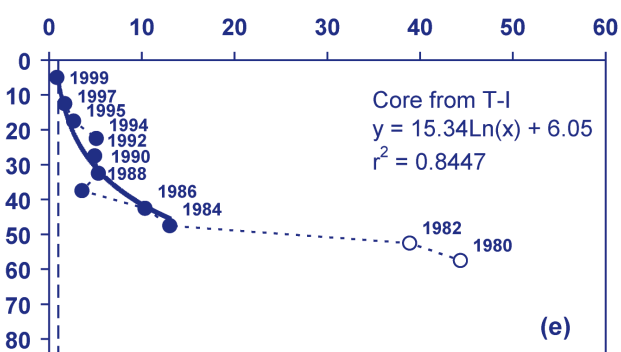
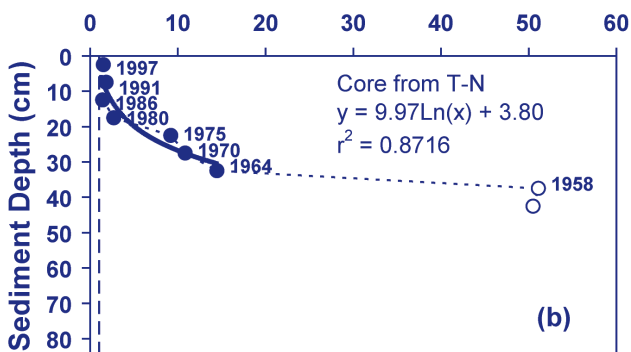
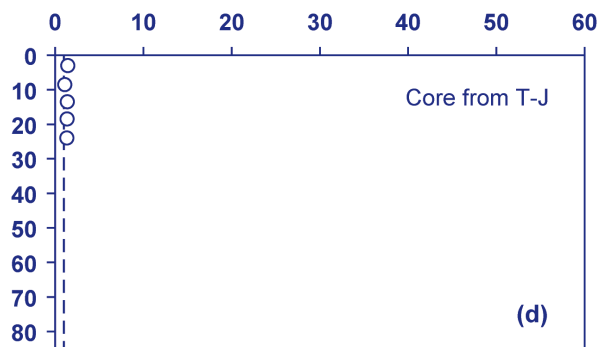
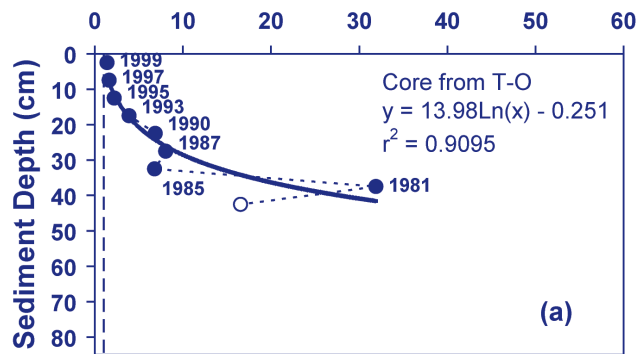


Figure 5. Vertical t-PCB Concentration Profiles for Cores Collected from Upgradient Transects T16(a) and Q(b). Silt/sand layers are shown on the right-hand side of each figure. Vertical axes are not to scale. Reprinted with permission from (3). Copyright 2004, American Chemical Society.



t-PCB Concentration (mg/kg)

t-PCB Concentration (mg/kg)

Figure 6. Lake Hartwell Sediment t-PCB Concentrations (mg/kg) Plotted Against Depth Below Sediment-Water Interface for Sediment Cores. Best-fit logarithmic curves are shown with corresponding equations and correlation coefficients to estimate surface sediment recovery. Solid symbols (●) represent data used to generate the curves. Open symbols (○) represent remaining data for depiction of vertical profile. Vertical dashed lines represent the 1-mg/kg t-PCB cleanup goal. Reprinted with permission from (3). Copyright 2002, American Chemical Society.

Conclusions

The success of MNR as a risk reduction approach typically is dependent on understanding the dynamics of the contaminated environment and the fate and mobility of the contaminant in that environment (1). The natural recovery process evaluated at both study sites summarized in this *Sediment Issue* relied on vertical contaminant profiling and age dating of sediment cores to assess the history of contaminant accumulation; measure the extent of natural sediment capping; and document contaminant accumulation, compositional changes, and sources over time and space. For the Eagle Harbor site, the investigation revealed that three distinct PAH sources (creosote, urban runoff, and natural background) contributed to the sediment contamination, with urban runoff continuing as an on-going source. In addition, no evidence was found to indicate that the study area was being covered by natural deposits of clean, uncontaminated sediments; thus, MNR was not employed as the final cleanup remedy.

Conversely, the cleanup plan for the Lake Hartwell site relies on natural recovery, which involves natural capping by the deposition of clean sediment entering the lake. The results of the investigation at this site were used to determine surface sedimentation, surface sedimentation rates, and predictions for the year cleanup goals would be achieved in the surface sediment. Given the inherent challenge of making future predictions based on extrapolation of historical data, long-term monitoring of the natural recovery remedy is needed at this site to determine whether recovery of surface sediments continues to occur.

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