Methods and Tools for the Evaluation of Monitored Natural Recovery of Contaminated Sediments:

Lake Hartwell Case Study

Office of Research and Development
National Risk Management Research Laboratory

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Purpose

The National Risk Management Research Laboratory (NRMRL) of the U.S. Environmental Protection Agency's (U.S. EPA's) Office of Research and Development (ORD) has been conducting research to develop methods and tools for the evaluation of monitored natural recovery (MNR) of sediments contaminated with polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), mercury, and other legacy pollutants. This research is supporting a broad, national research program focused on contaminated sediments in U.S. waterways. This Research Summary provides a synopsis of a multi-year, interdisciplinary research project conducted by ORD, specifically NRMRL and the National Exposure Research Laboratory (NERL), at the Sangamo-Weston, Inc./Twelve-Mile Creek/Lake Hartwell PCB Contamination Superfund Site in Pickens County, South Carolina. The methods and tools described in this *Research Summary* are comprised of quantitative approaches for characterizing naturally-occurring mechanistic processes that are necessary to manage risk using MNR.

The information developed in this project is expected to be used as a reference for site managers and Federal, State, and local regulators who may be considering MNR as a site remedy or monitoring the progress of MNR at a contaminated sediment site(s). The methods and techniques evaluated and optimized in this study also provide the broader sediment community with an approach for characterizing environmental processes controlling the risk associated with contaminated sediments.

Introduction

Sediments are often the ultimate receptors of contaminants in aquatic systems. According to an estimate by U.S. EPA, approximately 10% (~1.2 billion cubic yards) of the sediment underlying the country's surface water is sufficiently contaminated to pose potential risks to humans and wildlife (USEPA, 1998). To manage the risk imposed by these sediments, it is critical to understand the fundamental mechanisms responsible for contaminant transport and fate. These mechanisms include chemical, biological, and physical processes responsible for the risk associated with the sediment. Metrics or approaches to characterize the effects of sediment remediation are needed to provide quantitative measures of success.

MNR is one approach for managing the risk associated with contaminated sediments. With MNR, the contaminants are left in place and existing physical, chemical, and biological processes that are expected to contain, destroy, and/or reduce their bioavailability or toxicity are monitored to assure effective management is progressing as predicted. These processes must be demonstrated to be viable, and occurring at an acceptable rate, to attenuate the risk of the contaminant remaining in place. Similarly, an effective and quantitative monitoring plan must be able to demonstrate definitively that these processes are progressing as predicted and that risk is being reduced over time at the anticipated rate.

MNR relies on a few primary mechanisms for mitigating contaminant risk to human and ecological receptors. First and foremost is a reduction in the contaminant's availability to receptors. This reduction can be accomplished either through a physical process of isolating the contaminated sediment itself or through a chemical process of contaminant sequestration or sorption. Physical isolation typically results from deposition of sediments not contaminated with the compound-of-concern (COC). Generally, exposure to contaminated sediment is expected to occur either in the water column during transport or, more commonly, at the water/sediment interface once deposited. Depending on the water body, contaminant exposure in the near surface sediment would be expected to occur in the biologically active zone of the sediment. This biologically active layer can vary from as little as a 1-3 cm to as much as 1-3 m in thickness depending on the habitat (Clarke, 2001.). The deposition of sediment, defined as accretion, is a natural on-going process in most water bodies. If the source of the COC has been effectively managed (a term often referred to as source control), the contaminated sediment will become physically isolated from the primary receptors in the aquatic system. However, sediment accretion rates vary spatially and temporally, are dependent on the hydrologic and physical conditions at the site, and are subject to change with alterations within the watershed or in the site conditions. MNR requires confirmation that a site continues to be a deposition-dominated site over time without significant mixing of the near-surface sediment.

Another important mechanism in MNR is often the chemical sequestration, or sorption, of the contaminant to the sediment matrix. With organic COCs, this sorption process is generally most favorable with hydrophobic, non-volatile contaminants binding to organic matter within the sediment. With inorganic COCs and less, commonly, organic COCs, the binding of the contaminant may occur with the inorganic clay and mineral structures of the sediment. In either instance, this sequestration or sorption of the contaminant has been shown, in some cases, to be effective in reducing the ability of a receptor (human or ecological) to take up the contaminant if exposed. This reduced exposure may reduce the risk of the COC. However, studies have shown the sequestration of contaminants, whether organic or inorganic, and any reduced availability are related to site-specific conditions (sediment type, organic matter content and structure, oxidation/reduction state, presence of sulfide, etc.). These conditions, therefore, should be evaluated on a site-specific basis during initial design for MNR and should be incorporated into the long-term monitoring plan to assure site conditions remain viable for continued reductions in contaminant availability (Magar, 2009).

The biological degradation, or biodegradation, of the COC should also be evaluated where considering MNR. If these processes are determined to be important mechanisms for either changing the availability or toxicity of the COC or reducing the inventory of the COC, biodegradation evaluations should be included as part of the long-term monitoring plan. Biodegradation is dependent on the physical/chemical characteristics of the contaminant itself and the viability of microfauna capable of biodegrading the COC. Biodegradation can reduce or increase the toxicity of COCs depending on the biological process and/or the specific COC. Finally, site conditions can inhibit or control the environment needed for optimal biodegradation rates.

Site Background

In 1994, U.S. EPA Region 4 issued a Record of Decision (ROD) (USEPA, 1994) establishing MNR as the remedy-of-choice to remediate Operable Unit #2 (OU2) of the Sangamo-Weston, Inc./Twelve-Mile Creek/Lake Hartwell PCB Contamination Superfund Site (Figure 1). OU2 consisted of the contaminated sediments in Lake Hartwell and Twelve-Mile Creek (TMC). OU2 was used as a field location by U.S. EPA-ORD to develop, test, and validate methods and tools to support the evaluation of MNR of PCB-contaminated sediments. A comprehensive set of measurements and analyses were conducted over a number of years to develop chemical, biological, and physical lines of evidence to document the progress of the MNR remedy in reducing PCB concentrations in surface sediments and the associated ecosystem.

Sangamo, Inc. owned and operated a capacitor manufacturing plant in Pickens, South Carolina, from 1955 to 1987. During operations, the facility used several varieties of fluids that contained PCBs. Waste was disposed of on the plant site and at six satellite disposal areas within a 3-mile radius of the plant. PCBs were also discharged with industrial wastewater effluent into Town Creek, a tributary of TMC. TMC is a major tributary of Lake Hartwell. Between 1955 and 1977, the average quantity of PCBs used by Sangamo-Weston ranged from 700,000 to 2,000,000 lb/yr. An estimated 3% of the quantities received and used by the plant were discharged into Town Creek, resulting in an estimated cumulative discharge of 400,000 lb of PCBs. PCB use was terminated in 1977, prior to a U.S. EPA ban on its use in January 1978 (USEPA 1994).

Lake Hartwell is a U.S. Army Corps of Engineers (USACE) reservoir located in the northwest corner of South Carolina along the Georgia state line (Figure 1). It is bordered by Anderson, Pickens, and Oconee Counties in South Carolina and Stephens, Franklin, and Hart counties in Georgia. It was created between 1955 and 1963 when the USACE constructed Hartwell Dam on the upper Savannah River, 7 miles from the confluence of the Seneca and Tugaloo Rivers. Lake Hartwell extends 49 and 45 miles up the Tugaloo and Seneca Rivers, respectively. At full pool elevation (660 ft MSL), it covers nearly 56,000 acres of water with a shoreline of 962 miles (USEPA, 1994).

Research Study Phases

U.S. EPA-ORD conducted research at the Lake Hartwell/TMC site between 2000 and 2008. This research evolved in phases as the study progressed and more information was required.

Phases I and II of the project were completed in 2000-2002 and consisted of chemical and age dating analyses of sediment core samples collected longitudinally and laterally on 10 transects previously established by U.S. EPA Region 4 for ongoing monitoring at Lake Hartwell (USEPA, 1994; USEPA, 2004). These studies focused on the use of chemical analyses of surface sediments and sediments at depth to characterize the decline of surface sediment concentrations over time (Brenner, Magar et al., 2004). Additionally, evidence of anaerobic dechlorination of higher-chlorinated PCBs was shown to be occurring at depth in the sediment, albeit, at very slow rates (Magar, Johnson et al., 2005).

Results from Phases I and II along with the required ROD annual monitoring data (USEPA, 2004) were evaluated in developing the subsequent studies at Lake Hartwell and TMC. Surface sediment PCB concentrations were declining at predicted rates; however, reductions in fish tissue did not appear to be declining similarly as projected. The result was an expansion of the project within ORD that encompassed Phases III-V over the next 6 years.

Phase III (2002-2003) served as a proof-of-concept effort in the development of innovative tools for monitoring the mechanisms responsible for the transport and fate of PCBs in this system. Measures during Phase III focused on the elements that comprise the Lake Hartwell and TMC ecosystem including environmental matrices (sediment, benthos, and water column) and food web components (fish, macroinvertebrates, plankton, and organic matter). Additional studies concentrated on the diffusion and advection of PCBs from contaminated sediment/pore water into the water column, as well as surrogate biological measures using passive samplers.

Phase IV (2004-2005) and V (2005-2008) of these studies focused on extending selected data sets for characterizing long-term trends and further validating selected methods and tools from prior studies at Lake Hartwell/TMC and other sites. Phase IV focused on characterizing seasonal variability of the mechanisms monitored. Phase V consisted of further food web and biotic studies along with studies of surface sediment stability and mixing.

Methods to Assess MNR Processes

MNR relies on several primary mechanisms to exist and progress at a predictable rate. These mechanisms generally involve naturally-occurring chemical, biological, and physical processes. Often, these processes are unrelated mechanistically with one another and may occur at different temporal and spatial scales. As such, multiple lines of evidence may be required to demonstrate success or progress of MNR toward the remedial objectives or goals. These site-specific lines of evidence are broadly categorized as chemical, biological, and physical lines of evidence. Through a

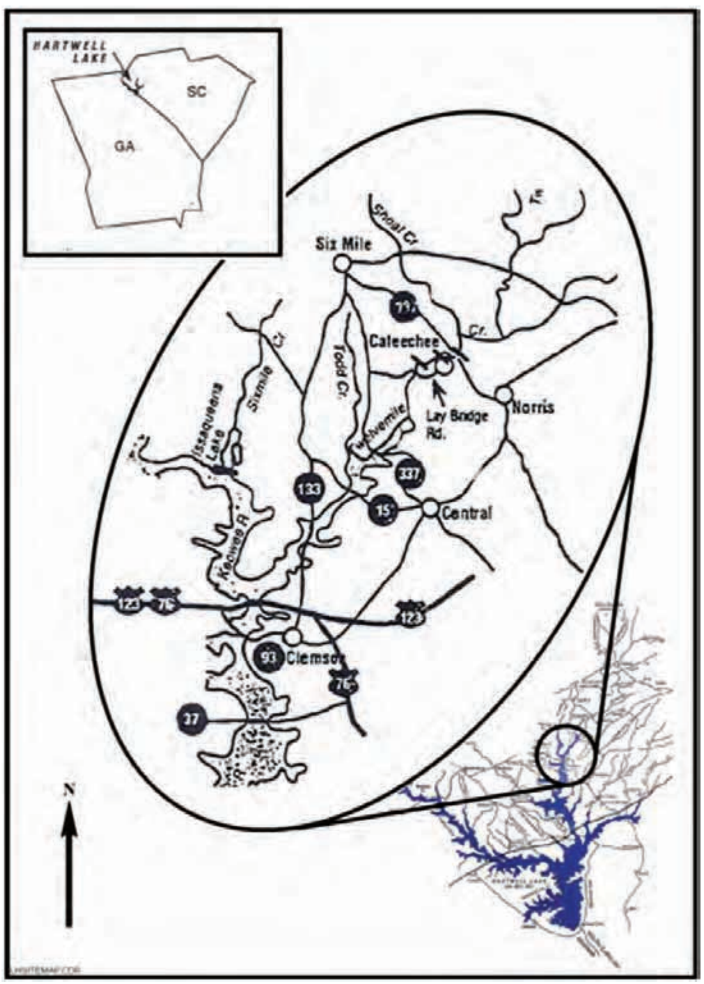

Figure 1. Location of Lake Hartwell and Twelvemile Creek Site.

weight-of-evidence approach, the progress of MNR can be evaluated.

Conceptual Site Model

Prior to evaluating a remedy for a contaminated sediment site, a conceptual site model (CSM) should be developed to identify the key processes affecting the transport and fate of the contaminant and receptors at risk. Once the designed remedy has been completed, verification of remediation effectiveness is required. MNR may require long-term monitoring to verify that the naturally-occurring processes necessary to manage the contaminant risk are proceeding as predicted. The CSM again should be used to assist in the choice of critical sample matrices and the periodicity required to demonstrate progress. Figure 2 shows the CSM generated for Lake Hartwell to aid in the development of monitoring tools for documenting the lines of evidence needed to characterize the progress of the remedy. This CSM was utilized by U.S. EPA researchers to guide the development of sampling tools and methods briefly described in this *Research Summary* document.

Chemical Lines of Evidence

In most cases, direct measurement of the COC in surface sediments is necessary to document its reduction over time. At Lake Hartwell, surface sediment was defined as the top 10 cm of the sediment. This depth was established in the Remedial Investigation /Feasibility (RI/FS) study and was followed throughout this research. Surface sediment samples were collected for all phases of the research in Lake Hartwell and, where available, in TMC. Direct measures of the COC are a primary line of evidence in MNR, and several approaches were evaluated at Lake Hartwell.

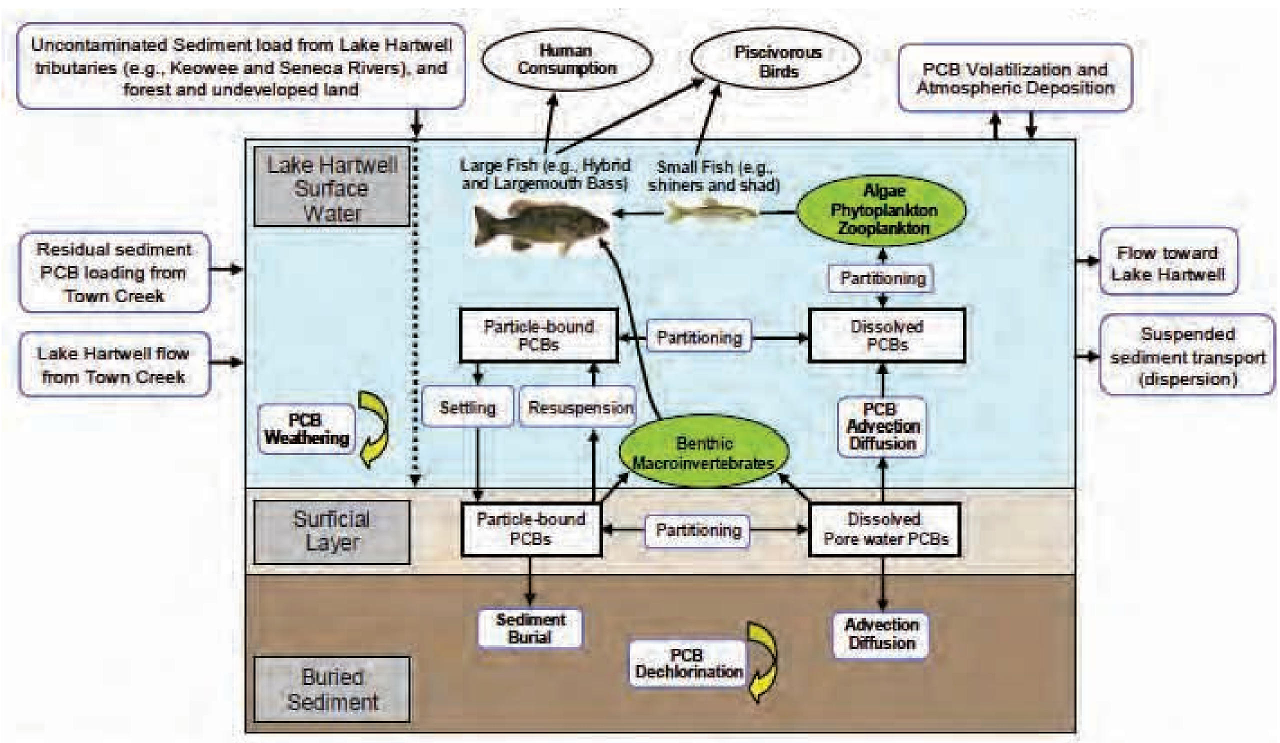

Figure 2. Conceptual Site Model for Monitored Natural Recovery as applied to Lake Hartwell (adapted from(Magar 2009).

When conducting a site investigation, it is important to ask: "What defines surface sediment?" The definition of surface sediment can be based on the depth of expected mixing due to hydrological events (high flow condition, propeller wash, etc.) and the biological active zone (BAZ) (MacDonald, Ingersoll et al., 2000; Eggleton and Thomas, 2004). The BAZ is inhabited by infaunal organisms including microbes, meiofauna, macroinvertebrates, and other organisms (i.e., early life stages of fish or amphibians) that spend all or part of their lives associated with sediments. The community of organisms present generally depends on the physical and chemical characteristics of the water body as determined by the watershed. The depth of the BAZ varies depending on sediment substrate characteristics (including particle size fractions, organic matter content, consolidation, and pore water geochemistry). These characteristics control the organisms present. In freshwater systems, the BAZ typically spans the top 20 to 40 cm of the surface sediment (Clarke, 2001; Nogaro, Mermillod-Blondin et al., 2009). The majority of benthic organisms will usually be associated with the upper 15 cm. However, certain invertebrate and/or amphibian species can extend the BAZ during a portion of their life history (e.g., up to 100 cm below the sediment surface) (Fleeger, Tita et al., 2006). Understanding the depth of the BAZ is critical in designing sediment and biological sampling plans for MNR sites.

Sediment Concentrations and Age Dating. Surface sediment concentrations were measured over the duration of the studies and combined with the data on sediment concentrations for samples collected under the ROD. In addition, core sampling was completed at selected transects to characterize the deeper sediments that reflect changes in historic surface sediment concentrations over time (Brenner, Magar et al., 2004). Results indicated that age dating sediments can provide a historic record of the surface sediment concentrations and, in this case, demonstrated a trend toward reduced concentrations of total PCBs (t-PCBs) over time (Figure 3). Researchers provided predictions of recovery time to reach human and ecologically significant surface sediment concentrations based on historic sediment deposition rates (Table 1). In addition, researchers also

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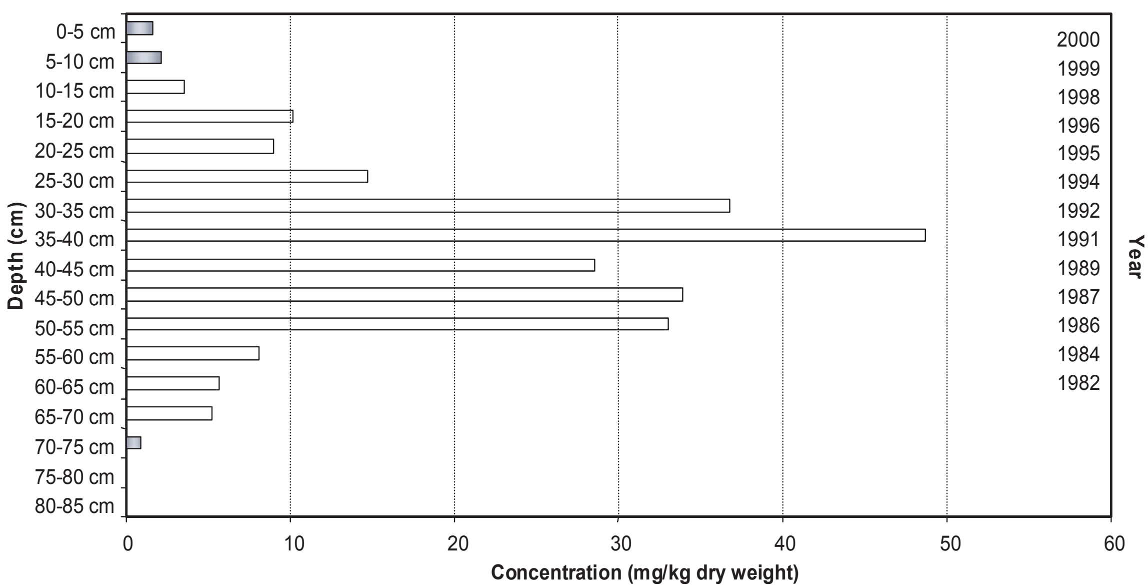

Figure 3. Total PCB (t-PCB) Vertical Concentration Profile in Core L with Age Dated Sediment.

Table 1. Required Sediment Deposition (in cm) to Achieve Selected t-PCB Surface Sediment Concentration Goals.

Core	Required Sedimentation to Achieve 1 mg/kg[(a)] t-PCBs (cm)	Required Sedimentation to Achieve 0.4 mg/kg[(b)] t-PCBs (cm)	Required Sedimentation to Achieve 0.05 mg/kg[(c)] t-PCBs (cm)
O	2.8	16	45
N	7.3	7.8	29
L	3.4	12	33
I	0	11	42
T6	0	3.5	13
Avg.	2.7 ± 3.0	10 ± 4.7	32 ± 13

(a) ROD Surface sediment cleanup goal (U.S. EPA, 1994).
(b) Mean value for site-specific sediment quality criteria calculated using the U.S. EPA's equilibrium partitioning approach (U.S. EPA, 1994).
(c) Effects range-low from NOAA, based on an evaluation of published criteria associated with biological effects on aquatic life (U.S. EPA, 1994).

evaluated reductive dechlorination of higher-molecular-weight PCB congeners occurring at Lake Hartwell (Magar, Johnson et al., 2005).

Passive Samplers. Researchers also developed and evaluated novel passive sampler designs utilizing semipermeable membrane devices (SPMDs) at three sites in Lake Hartwell, a background transect (BKG) with a low level of contamination and two contaminated transects (T-M/N and T-O) on Lake Hartwell. PCB availability was quantified using racks (RSPMDs) designed to hold SPMDs in contact with surface sediments, benthic domes (DSPMDs) designed to enclose and suspend SPMDs at the sediment-water interface, and commercially obtained SPMD cages suspended in the water column (WCSPMDs). The sampler designs and results from preliminary studies are described by Schubauer-Berigan et al. (Schubauer-Berigan, 2010 -submitted). For a detailed review of the underlying principals of SPMDs, see (Gale, 1998; Booij, Smedes et al., 2006; Huckins, 2006).

The above devices developed and tested at Lake Hartwell proved to be effective in providing reproducible quantitative estimates of the dissolved PCB fraction at the study areas and in the different spatial arrangements deployed (Table 2 and Figure 4). Measurable accumulation of PCBs was detected in all SPMD deployments above contaminated sediment levels in as little as 7 to 14 days. Time-weighted average total PCB concentrations were highly reproducible for field deployments, and variability was low within sampler type and study area (Table 2). A two-way analysis of variance showed significant effects by sampler type ($P < 0.0001$) and site ($P < 0.0001$) for mean time-weighted average (TWA) total PCBs (t-PCBs). Regardless of the SPMD sampler used, mean TWA t-PCBs were directly proportional to the level of contamination present (BKG < T-M/N < T-O). WCSPMDs and RSPMDs t-PCB uptake patterns were described by a significant exponential fit of the data ($r = 0.9768$, $p = 0.000006$ and $r = 0.9114$, $p = 0.0006$, respectively [Figure 4]). DSPMD and RSPMD samples had a higher percentage of higher-chlorinated PCBs compared to WSPMD samples. The SPMD samplers tested were particularly useful for quantifying spatial differences in the partitioning of PCB exposure within the water column and sediments.

The SPMD deployment approaches designed and tested in this study demonstrated promise as a rapid and robust method to aid in developing contaminated sediment risk management strategies and assessing the mechanisms influencing the effectiveness of these strategies. Some of the benefits of using passive samplers in addition to biological monitoring are that they can be deployed in sufficient numbers to help overcome issues of both spatial and temporal sampling variability and the data from one geographic area to another can be compared directly. Also, passive samplers can be used in harsh environmental conditions that would be lethal to caged organisms.

Biological Lines of Evidence

The biological metrics of exposure can consist of biota impacted by the COC or other indicators used to demonstrate exposure or effects. These metrics can use organisms that range from fish that have both ecological and human health risks to benthic infauna that can demonstrate both a direct impact of the COC or a link to higher trophic levels that are impacted.

In reviewing ROD-mandated monitoring data for Lake Hartwell, two issues became evident: 1) sampling longer-lived fish resulted in a bias based on gender, and 2) data appeared to indicate that persistent organic pollutants, like PCBs, may require as long as two generations of the targeted fish species (10-16 years) to show statistically significant changes in tissue concentrations. As a result of these observations, biological indicators of exposure were evaluated at Lake Hartwell that have shorter life spans and, therefore, were hypothesized to reflect shorter temporal responses to PCB exposure.

Macrobenthos Body Burden. One indicator that was adapted to evaluate the long-term recovery of contaminated sediments and the associated biota

Table 2. Mean Time-Weighted Average Concentrations of Total Dissolved PCBs as Measured Using Different SPMD Samplers (water column: WCSPMD; sediment surface rack: RSPMD; and submerged benthic dome: DSPMD) at Three Lake Hartwell Sites (Schubauer-Berigan 2010 - submitted).

	t-PCBs (ng/g SPMD/d)								
	WCSPMD			RSPMD			DSPMD		
Site	Mean	SE	n	Mean	SE	n	Mean	SE	n
BKG	3.0	0.01	3	2.2	0.19	3	5.9	4.60	3
T-M/N	127.4	5.16	3	93.8	4.74	3	59.7	6.92	3
T-O	196.0	7.77	3	154.2	9.18	3	139.0	13.56	3

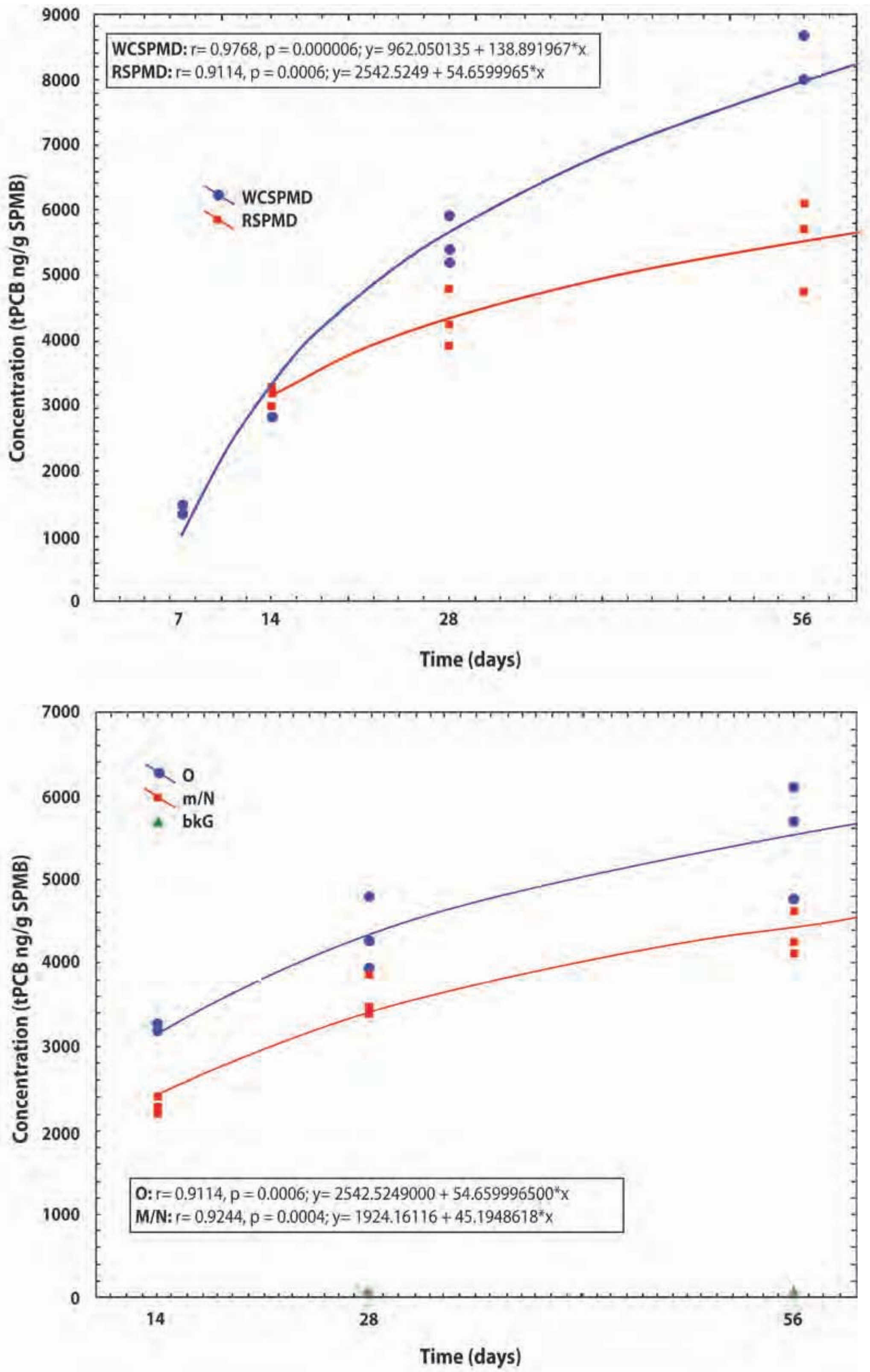

Figure 4. Regression Analyses (using an exponential fit) of the Time Course Experiments Comparing WCSPMDs and RSPMDs at Site T-O (top panel) and a Comparison of the RSPMDs Deployed at T-O, T-M/N, and BKG (bottom panel) (Schubauer-Berigan, 2010 - submitted).

following remediation was the measurement of COC body burden in aquatic macrobenthos. Researchers utilized artificial substrates (Hester-Dendy substrates) to collect macrobenthos for harvesting and quantifying the COC body burden.

Aquatic macrobenthic organisms were examined as an indicator of recent exposure to PCBs. A majority of the benthic invertebrates, such as midge larvae, annelids (aquatic worms), and other larvae, have life cycles that last 30-90 days (Pennak, 1978; Merritt, 2008). Contaminant tissue levels, referred to as body burden concentrations, in macroinvertebrates represent very recent contaminant exposure levels. At Lake Hartwell, the approach was first to determine if macroinvertebrates collected on artificial substrates, such as Hester Dendy's (HDs) (Klemm 1990) could discriminate between various contaminated sites and compare the body burden concentrations to sediment concentrations. In 2002, 20 nine-plate HDs were attached in four tiers of five to inverted wire cages. After 4 weeks of deployment in the water column, HDs were retrieved, dissembled, sorted, preserved (4ºC), and analyzed for total PCBs by summing PCB congeners as total PCBs (t-PCBs). Figure 5 compares t-PCB concentration in water, sediment, and macroinvertebrate tissue. Similar trends were noted in sediment t-PCB concentrations for macrobenthos body burden between sites, but some differences in the magnitude of PCBs were evident at site T-M/N.

These results indicate that macroinvertebrates can be used to assess sediment contamination among sites that have different contamination levels of PCBs, but additional validation over time is needed to demonstrate a more

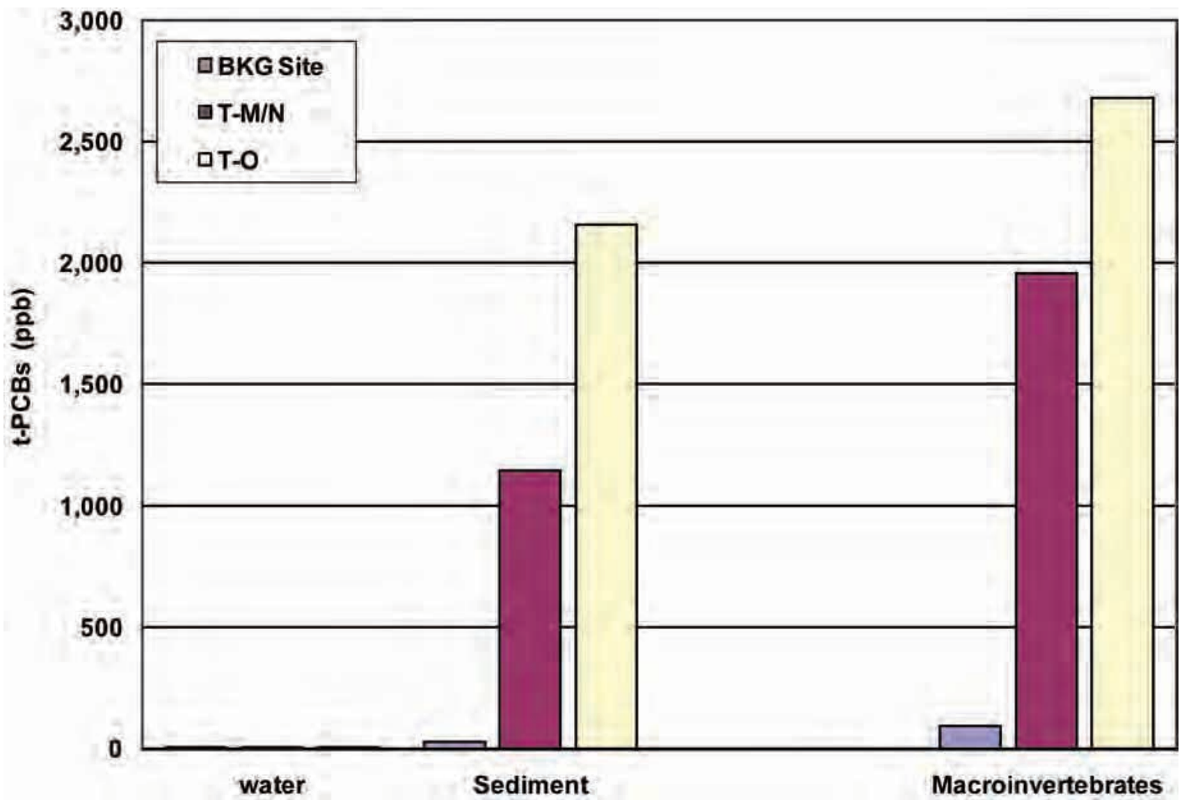

Figure 5. t-PCB Concentrations in Water (ug/L or ppb) and Sediment and Macroinvertebrate Tissue (ng/g wet weight or ppb).

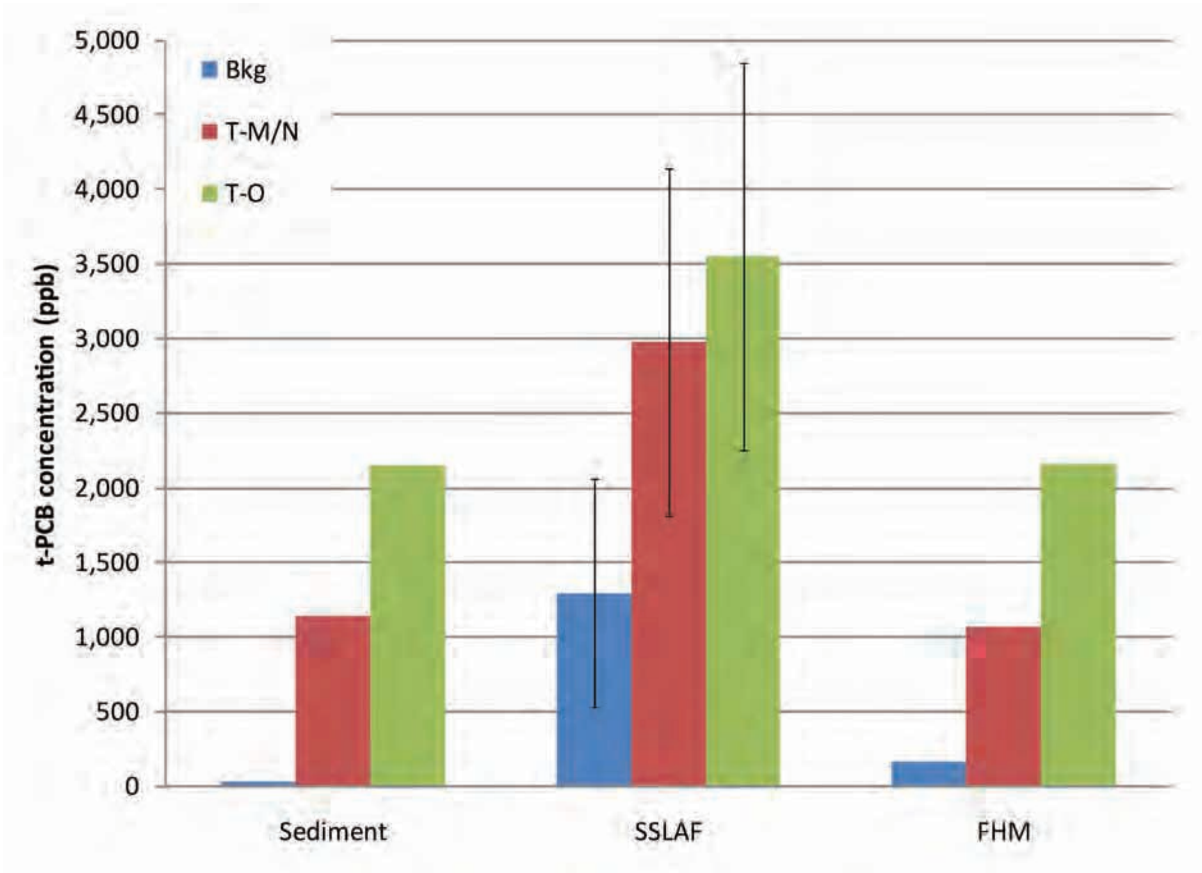

Figure 6. t-PCB Wet Weight Tissue (ng/g or ppb) for Two Indicators Used at Lake Hartwell: Collections of Indigenous SSLAF, Whitefin Shiners (*Cyprinella nivea*) and 14-day Deployed Adult (8-12 months old) Fathead Minnows (*Pimephales promelas*).

rapid response to changes in sediment concentrations than measured in higher trophic level fish.

Small Short-Lived Adult Fish (SSLAF). SSLAF were evaluated as an indicator of shorter-term responses within the indigenous fish populations as a short- and a long-term monitoring tool. As opposed to long-lived larger fish, SSLAF are expected to exhibit more rapid response to changes in the COC exposure in the system. The Cyprinidae (minnow family) is the largest of all fish families. Minnows are very important components within the food web because they are food to larger sport fish (e.g., largemouth bass, striped bass, etc.). There are several species of minnows and shiners across North America that are omnivores preying on insects, algae, detritus, and microcrustaceans. These fish reach maturity in 4-6 months and live 1-3 years. Many have good site fidelity (do not forage or migrate great distances) and may be excellent indicators of recent (1-3 years) contaminant exposures in sediment and water. Therefore, SSLAF should be a good biological indicator to track exposure changes in shorter periods of time and space than do longer-lived fish.

Figure 6 illustrates the wet weight tissue concentrations measured in two SSLAF indicators at Lake Hartwell: indigenous whitefin shiners, *Cyprinella nivea*, and 14-day deployed adult (8-12 months old) fathead minnows, *Pimephales promelas*. Whitefin shiners and 14-day deployed adult fathead minnows showed similar trends in tissue concentrations to the macroinvertebrates and related well to sediment t-PCB concentrations (i.e., higher tissue concentrations were measured at T-O than at T-M/N as reflected in the sediment concentrations).

Additional studies are being conducted to compare results of SSLAF to traditionally top carnivore, longer-lived adult fish, as are typically used for long-term monitoring. This shorter-term indicator may provide more rapid indications of improvements in sediment contaminant concentrations and ecological recovery and with less variance.

Food Web Studies to Identify Biological Indicators. In an effort to begin to integrate a number of biological indicators and measures and explore alternative indicators of ecological recovery, food web studies were also conducted at TMC and Lake Hartwell. Several studies were conducted to characterize the aquatic and riparian food webs associated with the TMC-impacted area. These studies combined a number of novel techniques used in contaminated small stream systems, including: stable isotope analyses to predict trophic position and contaminant levels (Walters, Fritz et al., 2008), congener and chiral PCB chemistry to indicate uptake and biological processing (Dang, Walters et al., 2010), and riparian export of PCBs to terrestrial predators (Walters, Fritz et al., 2008; Walters, Mills et al., 2009).

Food web studies in TMC and Lake Hartwell revealed that t-PCB body burden was largely explained by an organism's trophic position (i.e., the relative position in the food web as determined by stable isotopes of nitrogen, δ15N) and lipid content (Figure 7A, (Walters, Fritz et al., 2008; Walters-in review)). Ongoing high levels of PCBs were found in food web organisms throughout TMC suggesting that TMC could be an ongoing source of PCBs to the Lake Hartwell food web. This hypothesis was supported through ecosystem modeling for Lake Hartwell demonstrating that contaminated detritus loaded to the system was incorporated in the food web, thereby maintaining high levels of PCBs in fish even though concentrations in lake sediments were declining (Rashleigh, Barber et al., 2009).

Congener and chiral analyses were used in concert to identify patterns in transformation within TMC and Lake Hartwell. Biological and physical factors both strongly influenced congener composition. Higher-chlorinated congeners (HCCs) tend to be more hydrophobic and recalcitrant than lower-chlorinated congeners, and their proportional contribution to t-PCBs increased with trophic position in the food web (Walters, Fritz et al., 2008; Walters - in review). Likewise, the proportion of HCCs increased with downstream distance from the Sangamo - Weston site, indicating that lighter, less-chlorinated compounds were lost to the system via volatilization (Walters, Fritz et al., 2008). In contrast, patterns in chirality in TMC were unrelated to distance from the Sangamo-Weston plant. Rather, biological factors were important regulators in these types of transformations. Chirality of PCB signatures varied among organic matter types such as fine benthic organic matter (FBOM), coarse particulate organic matter (CPOM), and benthic algae, suggesting that distinctive microbial communities among these organic matter types have unique biotransformation processes (Dang, Walters et al., 2010).

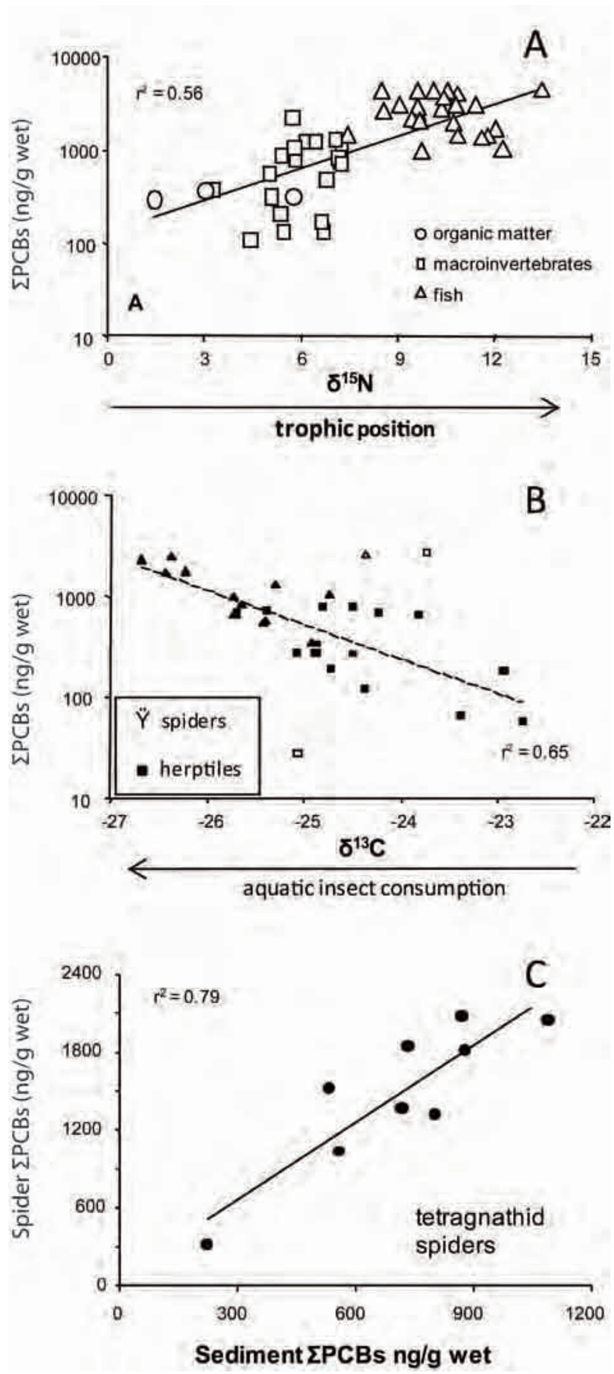

Figure 7. A) δ15N Predicts ΣPCBs in the Stream Food Web; B) δ13C Predicts ΣPCBs in the Riparian Food Web (open symbols are outliers excluded from model); C) Sediment PCB Concentrations Strongly Predict Spider PCB Concentrations Along a PCB Gradient in Lake Hartwell.

Riparian studies of aquatic-to-terrestrial flux of PCBs focused on three key questions: 1) Which species in diverse riparian predator communities are at highest risk of exposure?, 2) Are concentrations in predators linked to concentrations in sediments?, and 3) How far inland do these fluxes extend? PCB concentrations in riparian predators along TMC were largely driven by their dependence on adult aquatic insects (Fig. 7B) (Walters, Fritz et al., 2008). That is, predators that consume a high proportion of aquatic insects had much higher PCB concentrations than predators relying on uncontaminated, terrestrial prey. Ambient PCB sediment concentrations were highly correlated with riparian spider concentrations (Fig. 7C), suggesting that riparian spiders are effective indicators of ecosystem recovery as well as indicators of potential risks to other terrestrial species such as arachnivorous birds (Walters, Blocksom et al., 2010). Concentrations in spiders along the shoreline were high, in some cases >10-fold higher than calculated wildlife risk values for arachnivorous birds. However, the spatial extent of this contamination and risk was small and limited to less than 5 m of the lake edge. Aquatic insect prey were limited to this narrow band of terrestrial habitat close to the lake margin, and spiders beyond this zone demonstrated consistent and low levels of PCB exposure (Walters, Mills et al., 2009).

Physical Lines of Evidence

The accumulation of progressively cleaner sediment was documented early in the research conducted at Lake Hartwell (Brenner, Magar et al., 2004). Using age dating coring techniques in conjunction with PCB chemistry, researchers demonstrated that accumulation of cleaner sediment over time reduces surface sediment contaminant concentrations. The age dating approach was used to predict the time necessary for surface sediment concentrations to recover to a remediation target concentration. This approach and how this was further developed at Lake Hartwell (as well as other contaminated sediment sites) has been previously described (USEPA, 2008).

Sediment Stability. The stability of the deposited sediment is a key component for successful MNR remedies. It is critical that clean sediment accumulation over the contaminated sediment is stable and not subject to scour, thereby preventing exposure of the contaminated sediment in the future. One technique for measuring sediment stability consists of simulating erosion events using any number of commercially available sediment flumes devices. A diagram of a SedFlume used to evaluate Lake Hartwell sediment stability is shown in Figure 8. SedFlume is a straight flume with an open bottom test section through which intact sediment cores are inserted. The core has a rectangular cross-section (10 cm x 15 cm) and is less than 1 m in length.

The measures of erosion rates for sediments as a function of shear stress and depth below the sediment surface are briefly described here. The undisturbed sediment core was inserted into the flume until the sediment surface was even with the bottom of the SedFlume channel. The flume was run at a specific flow rate corresponding to a particular shear stress (McNeil, 1996). Erosion rates are estimated by measuring the core length at different time intervals as shown in Table 3.

The critical shear stress of a sediment bed, τcr, is defined as the shear stress at which a very small, but accurately measurable, rate of erosion occurs. For SedFlume studies, this rate of erosion has been practically defined as 10-4 cm/s. This rate represents 1 mm of erosion in approximately 15 minutes. Since it is difficult to measure τcr exactly at 10-4 cm/s, erosion rates were determined above and below 10-4 cm/s. The τcr was then determined by linear interpolation. The technique produces a τcr measurement with at least 20% accuracy (McNeil, 1996; Roberts, Jepsen et al., 1998).

In addition to erosion rate measurements, samples were collected to determine the water content, bulk density, and particle size distribution of the sediments. Bulk density was determined by water content analysis using methods outlined in (Hakanson, 2002). The water content, W, was determined (Table 3) and then used to calculate bulk density, ρb, (Table 3). Lastly, particle size distributions were determined using laser diffraction analysis. The method was valid for particle sizes between 0.04 and 2000 µm. Fractions over 2000 µm were weighed to determine the weight percentage greater than 2000 µm.

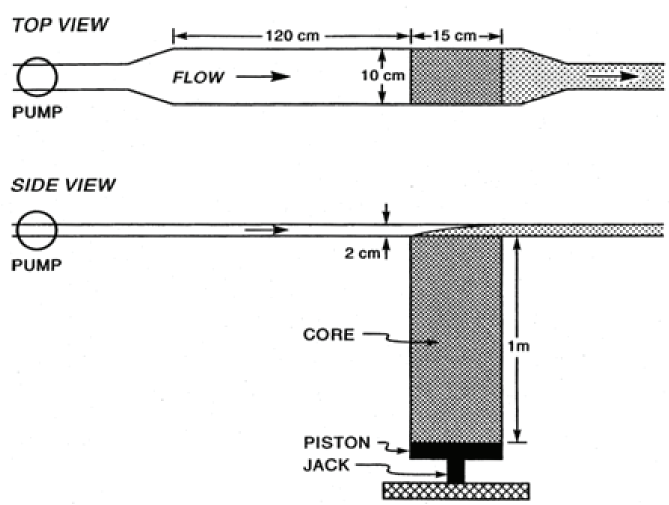

Figure 8. Schematic of the SedFlume Devise Used to Measure Sediment Stability.

Table 3. Sediment Stability Parameters Measured and Computed for Lake Hartwell.

Measurement	Definition	Units	Detection Limit
Bulk Density, ρ_b (wet/dry weight)	$\rho_b = \frac{\rho_w \rho_s}{\rho_w + (\rho_s - \rho_w)W}$	g/cm^3	Same as water content
Water Content	$W = \frac{M_w - M_d}{M_w}$	unit less	0.1 g in sample weight ranging from 10 to 50 g
Particle Size Distribution	Distribution of particle sizes by volume percentage using laser diffraction	μm	0.04 μm – 2000 μm
Erosion Rate	E = Δz/T	cm/s	Δz > 0.5 mm T > 15 s
Critical Shear Stress, τ_{cr}	Shear stress when erosion rate equals 10^{-4} cm/s	N/m^2	0 to 10.0 N/m^2 This value is interpolated as described in the text.

W = water content
M_d = dry weight of sample
T = time
ρs = density of sediment (2.65 g/cm3)
M_w = wet weight of sample
Δz = amount of sediment eroded
ρw = density of water (1 g/cm3)

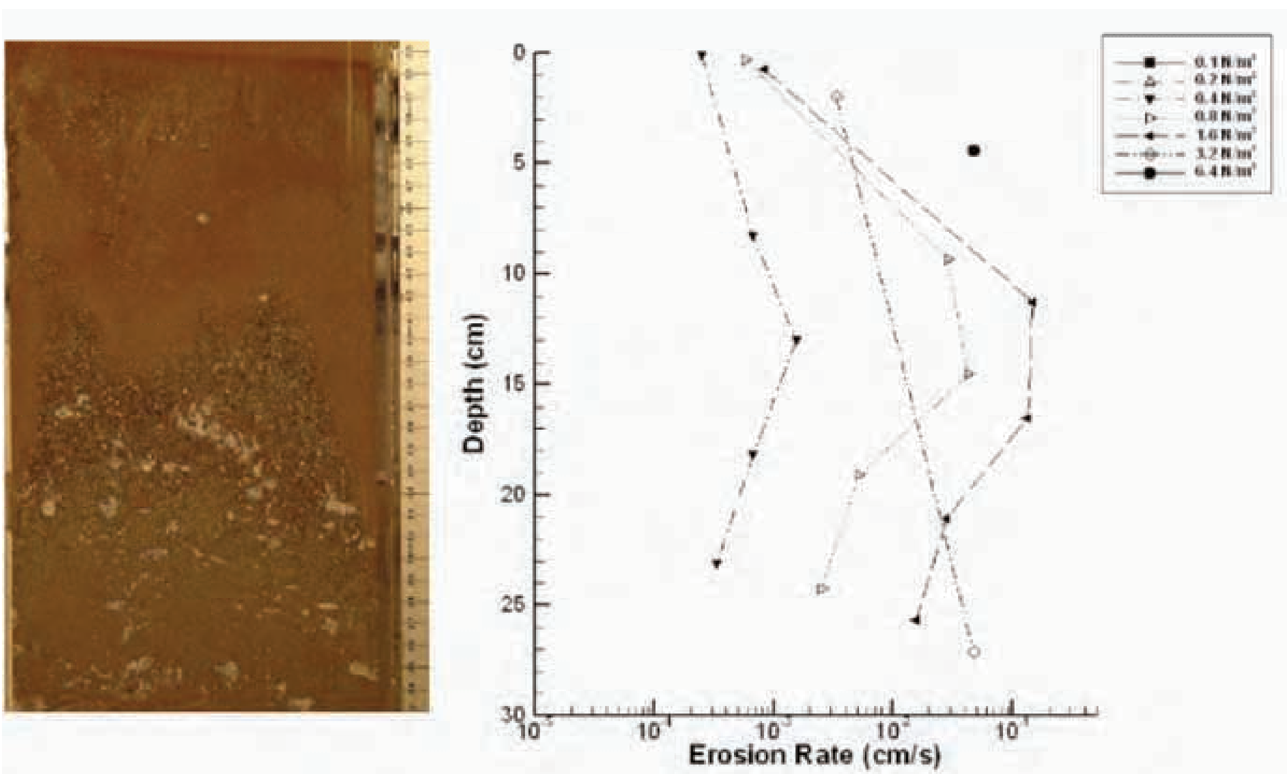

Figure 9. Picture of Core TN-SSE-01 Aligned with SedFlume Erosion Rate Data.

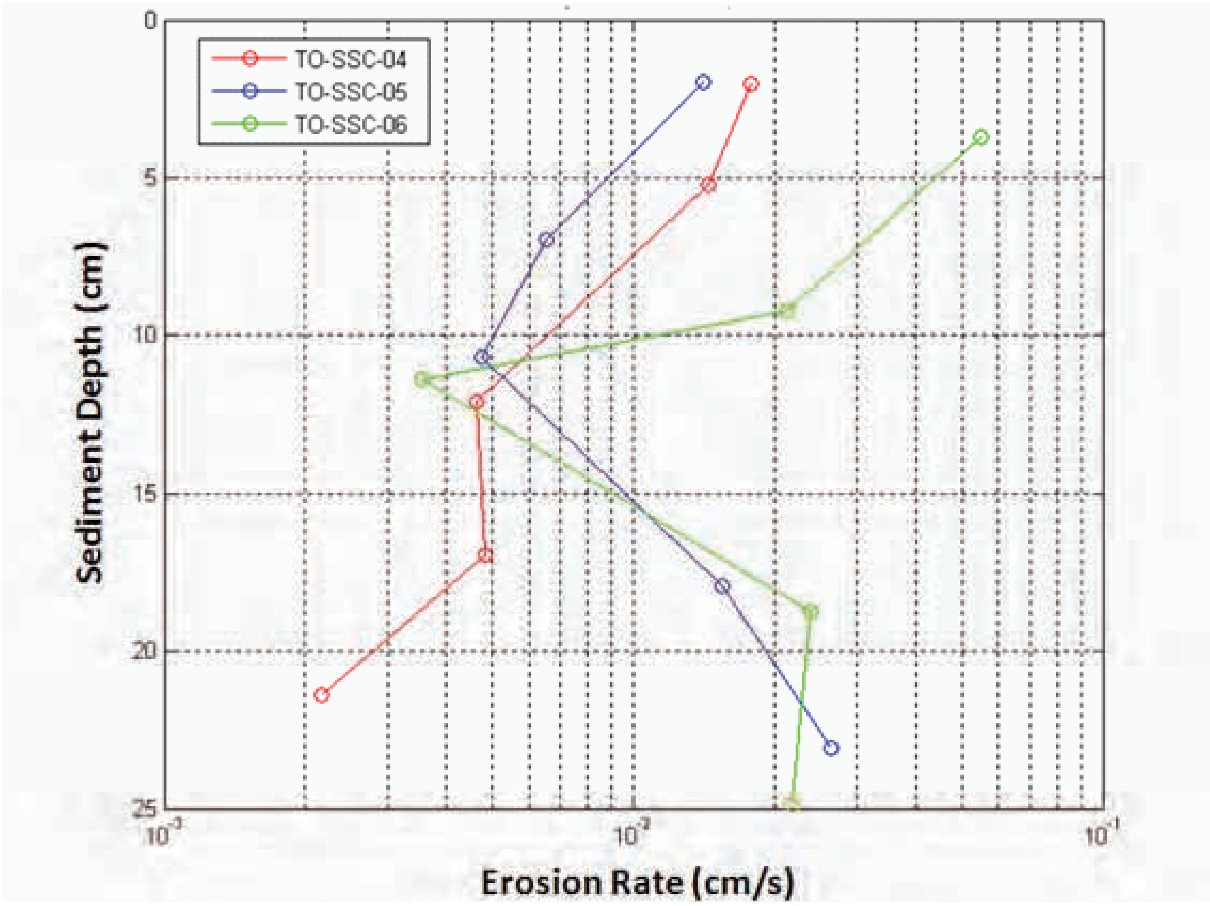

Figure 10. Erosion Rates (cm/s) as a Function of Depth (cm) for Three Cores on the O Transect at a Shear Stress of 1.6 N/m2.

As an example, Figure 9 depicts the results for the SedFlume erosion analysis of a core, TN-SSE-01. The sediment found in this core consisted of fine silt over a sand/silt mixture over a stiff, silty sand layer. Small worms were visible near the surface of the core, and no other organisms were observed in the sediments. Core TN-SSE-01 contained an easily eroded sandy layer from 6 to 18 cm depth. The bulk density measurements increased markedly here with a corresponding increase in particle size. Below this sand layer was a silty sand layer that became progressively more resistant to erosion (stiff) with depth. This trend was evident by the decrease in bulk density, particle size, and erosion rates at the deepest depths of the core.

To show the variable nature of sediments with respect to depositional characteristics and related stability within a small area (< 3-m radius), the average erosion rates (at the 1.6 N/m2 shear stress condition) for three replicate cores collected at Transect O are discussed below (Figure 10). The erosion rates demonstrate the same trend for all three replicate cores with a pronounced stiff (more erosion resistant) layer in the 10 to 15 cm interval. The magnitude of shear stress in the shallower and deeper regions of the cores show some variation, but this is likely due to heterogeneity in the sediments supported by corresponding particle size and bulk density differences and rapid sediment losses ("blowouts") in the core caused by gas pockets. Measurement of sediment stability is important to understand the permanence of the natural isolation that occurs during the accumulation of cleaner sediment over historically contaminated sediment surfaces.

Porewater Exchange through Groundwater/ Surface Water Interactions. The movement of water (sediment porewater) into and out of sediment can be controlled by the flux of water from the groundwater to the surface water. This groundwater/surface water interaction and various means of measuring porewater PCB concentrations were also investigated at Lake Hartwell. This displacement of the sediment porewater to the overlying water column and the associated receptors was considered a possible pathway to provide continued exposure to the aquatic system. To evaluate this mechanism, methods to characterize the groundwater/surface water interaction and porewater measurement methods were tested and analyzed. The

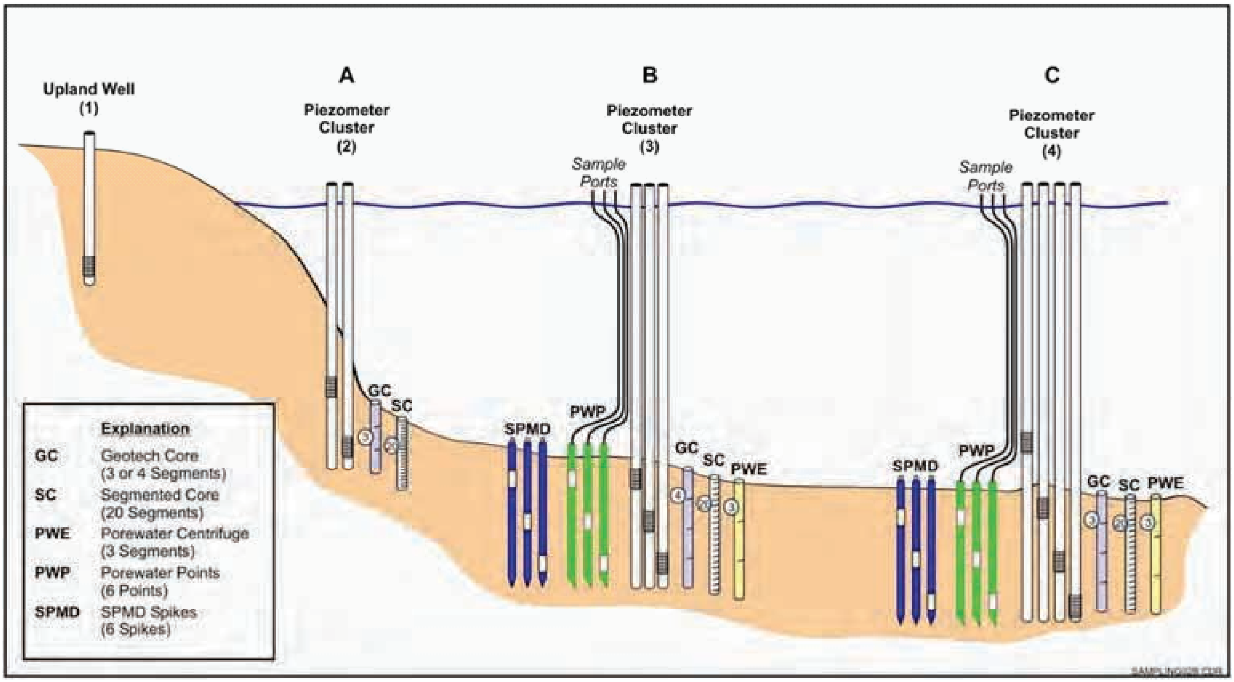

Figure 11: Piezometer and In Situ Sediment Deployments for Phase 4 and Phase 5

approach presented here uses a weight-of-evidence approach to characterize the sediment porewater to quantify the degree of mixing between groundwater and surface water, and with differential depth sampling, to quantify the magnitude and direction of the porewater movement. The approach relies on the collection of porewater, groundwater, and surface water samples and stable isotope data (oxygen and hydrogen) to define the proportion of groundwater and surface water in sediment porewater. Where available, traditional data (hydraulic head differential, conductivity, and temperature) were used as additional lines of evidence to corroborate the findings.

Three transects were monitored using vertically-stratified, clustered piezometer wells for quantifying the groundwater-surface water interaction. Two contaminated transects (T-O and T-N) and a background transect (BKG) were monitored continuously for 18 months. At each transect, a series of well clusters was installed to evaluate the vertical hydraulic gradient. Figure 11 shows the well clusters relative positions compared to the shoreline and transects. One well was screened in the water column to measure surface water elevations. A second well was screened just below the sediment/water interface (shallow). A third well was screened at mid-depth (mid-level), and the last well was screened at the deepest point (deep). Each well was instrumented with a pressure transducer/temperature/conductivity datasonde (600LS, YSI, Yellowsprings, Ohio). Additionally, the wells were sampled to characterize the porewater for PCBs and stable isotopes. Three additional porewater methods were co-located with these well clusters to allow comparison between the four porewater measurement approaches.

The wells were used to measure head potential (the potential for water to move from one point to another based on pressure or head differentials) at different sediment depths. The water level in the wells at each depth within the cluster was monitored to calculate the head difference between the three depth increments. The surface water level was an important parameter in determining the direction (gaining from the lake or losing from the aquifer) and magnitude of head potential. This reservoir along with the entire Savannah River basin suffered drought conditions during these studies, with surface water elevations varying as much as 25 ft. This monitoring method resulted in observed head potential trends that varied as much as ±2.0 ft. Typically, the head potential between the deepest well and the surface water was less than 12 in., indicating the local aquifer and surface water were connected and did not take long to equilibrate. Figure 12 illustrates an example of differential heads for Lake Hartwell sediment over time. The differential head measurements indicated that in the shallow sediment depths (10-25 cm) the sediment was hydraulically connected directly to the surface water. This observation indicates the sediment is unconsolidated and free to exchange with the water column. In the mid-depth wells (80-130 cm), the degree of connectivity depended on the sediment characteristics at the transect.

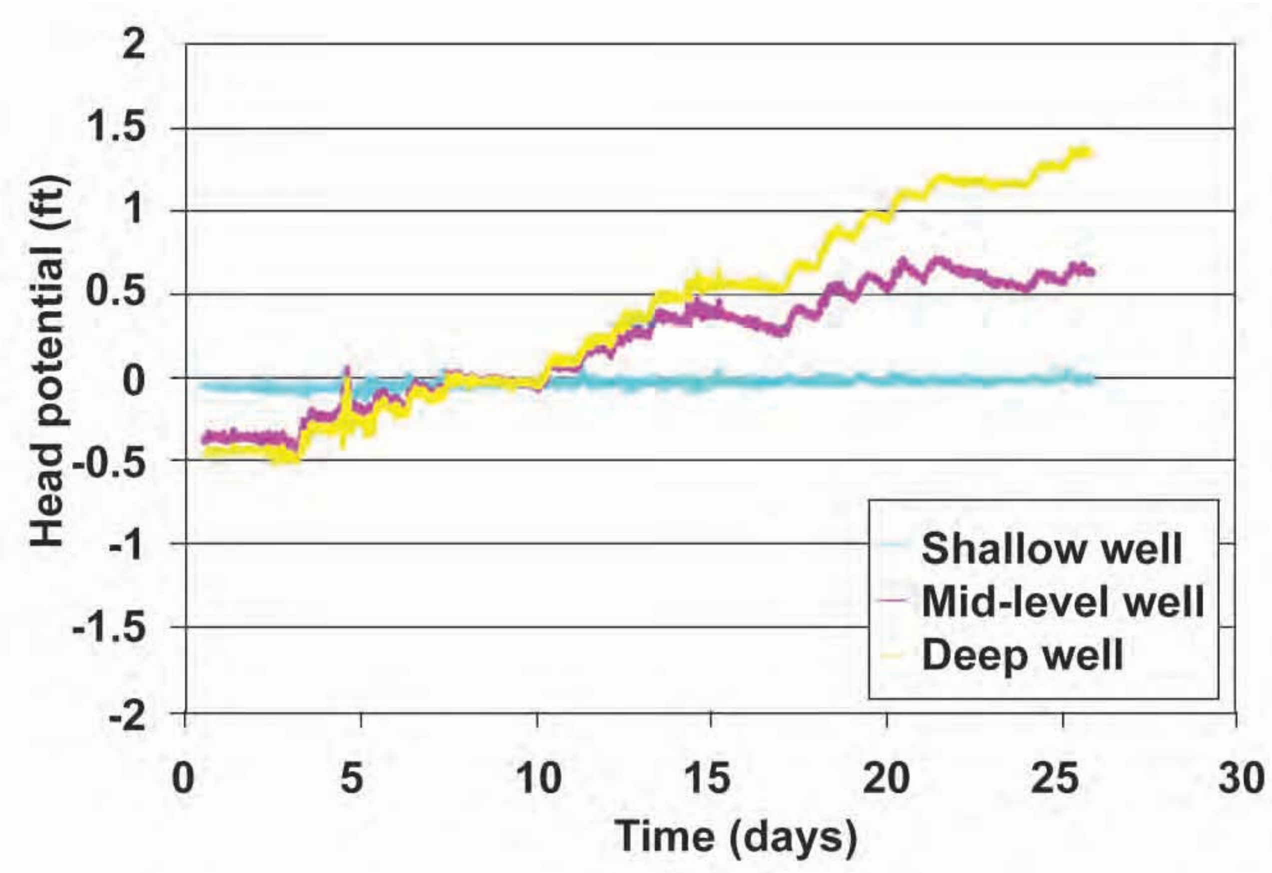

Figure 12. Head Potentials Shown for Vertically Stratified Wells in Lake Hartwell Sediment.

At T-O, the mid-depth was still connected with a slight dampening effect. At T-N, less connectivity was noted due to a more consolidated sediment. The deepest screened wells (180- 250 cm) indicated some connection to the water column, but the deepest screened wells did not exhibit day-to-day variations measured in the water column, but did exhibit the general declining trend of the surface water.

Sediment Porewater Exchange Using Stable Isotopes. Another approach to support the exchange of sediment porewater with the overlying surface waters was stable isotope measurements of porewater for oxygen and hydrogen. Variations in the stable isotope ratios in natural waters are widely studied to interpret hydrological processes. Isotopes of hydrogen and oxygen, being inherent in the water molecule, can be effective conservative tracers in understanding movement and mixing within the hydrologic compartments. An abundance of literature exists on the application of stable isotopes in hydrologic investigations (Clark I, 1997; Kendall, 1998; Machavaram, Whittemore et al., 2006) and is only briefly described here.

The ratios of most abundant stable isotope species of water molecules (HDO/HHO, HH18O/HH16O) in the water cycle are governed primarily by global precipitation/evaporation processes and are secondarily affected by local thermodynamic processes such as evaporation and mixing. Due to the differences in the vapor pressure and kinetic diffusivity of lighter and heavier isotopes, a preferential transfer of one isotope over the other occurs during phase changes. During evaporation, the lighter isotopes of H and 16O are preferentially transferred, thus causing the vapor to be isotopically 'lighter' (depleted) and the residual liquid to be 'heavier' (enriched). The reverse is true during condensation where D and ^{18}O are preferred. This 'isotope fractionation', which causes the ratios to change between the liquid and vapor phases, is governed by temperature, humidity, and the extent of transfer between the phases. Fractionation, in turn, results in distinct isotopic ratios for various hydrologic compartments that can be used as conservative tracers of water to investigate the interactions between compartments. Figure 13 illustrates the application of this approach to show the different isotope end-points for surface waters compared to aquifer-influenced porewater samples. Mixing models are applied to estimate the contribution of groundwater and surface waters to the sediment porewater (Mills 2010 - in preparation).

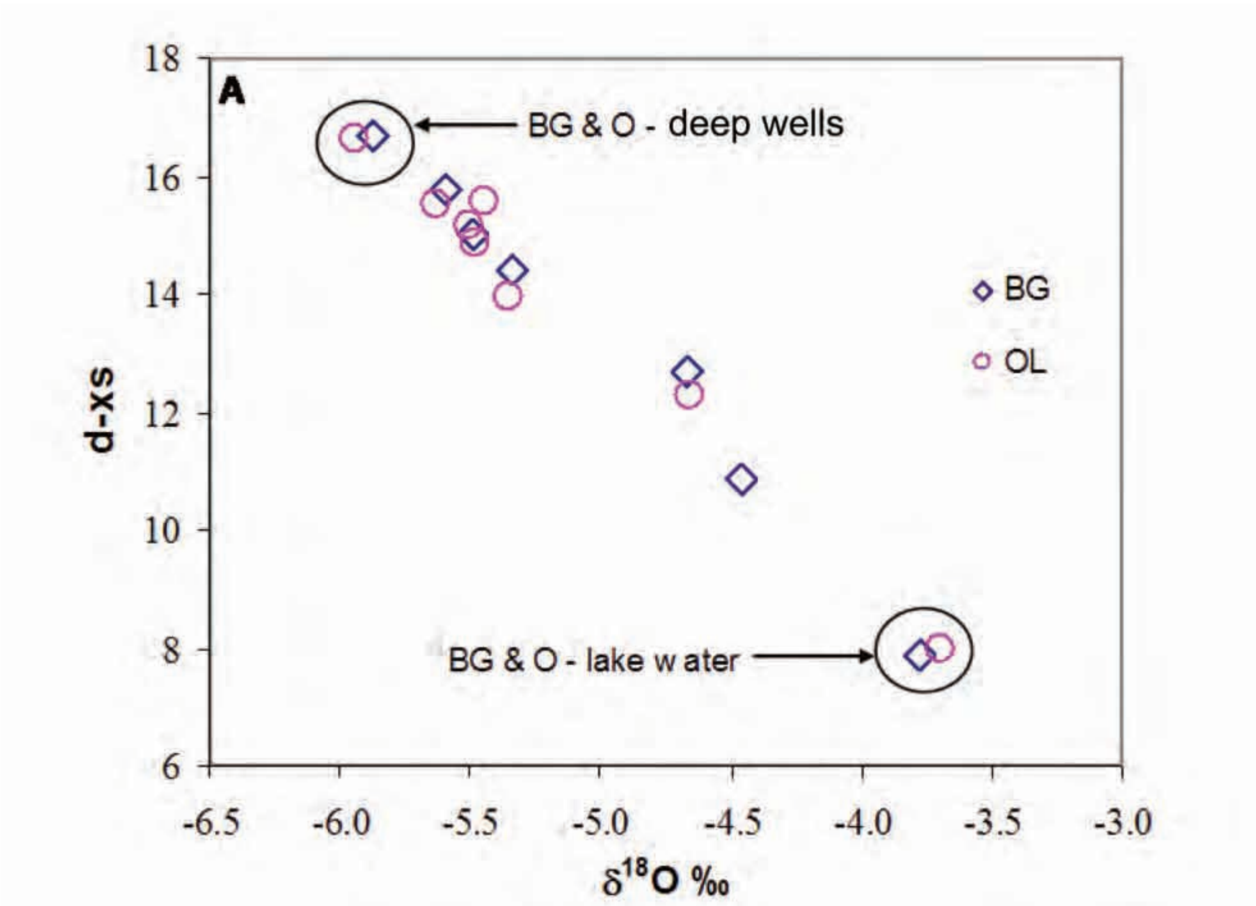

Figure 13. Mean d-excess values for Each Zone Measured and Plotted Against the Oxygen Isotope Data (BG = Background and O = Trasect O).

Porewater PCB Concentrations. Porewater in contaminated sediments is a concern from the standpoints of the direct exposure of sediment dwelling organisms and the release of contaminated porewater to the overlying water, resulting in subsequent exposure to both humans and wildlife. Research has shown that measuring porewater in contaminated sediments can be difficult and often is biased by the measurement technique (Ehlers, 2006; Tomaszewski and Luthy, 2008). One aspect of the research conducted at Lake Hartwell was to compare four methods of measuring porewater PCB concentrations. The first method was a traditional technique of elutriating the existing porewater from core samples collected at depth. The second, third, and fourth methods, respectively, consisted of direct sampling of the porewater using lysimeter-type samplers inserted at depth, lysimeter points with SPMDs deployed for 28 days, and SPMDs deployed in the subsurface wells used for head measurements. Further description and comparison of these methods are being developed for publication.

Advective Porewater Transport. Advective transport of the COC with porewater through contaminated sediments has the potential to be a significant long-term contaminant source to surface sediments and the overlying water column and, ultimately, the resulting human or ecological receptors. Once in the water column or surface sediments, the contaminants may enter the food chain or a direct pathway to human or ecosystem exposure. Continued research is needed to define the magnitude of advective transport mechanisms and determine under what conditions this mechanism may pose a threat to managing the risk of contaminated sediments.

Conclusions

Research conducted at Lake Hartwell and TMC was initiated to provide technical support to U.S. EPA Region 4 and to develop mechanistic-based tools and approaches to evaluate MNR and other contaminated sediment remediation strategies. The direct technical support provided to the Region 4 Project Manager resulted in modifications to the Lake Hartwell and TMC long-term monitoring plan to demonstrate MNR progress. Those changes included modifications to established fish tissue monitoring protocols (a balance of male and female fish), addition of congener specific analyses on a subset of samples, and incorporation of bivalve monitoring in Lake Hartwell (USEPA, 2004).

In addition, research initiated at Lake Hartwell has been further expanded to support additional contaminated sediment sites undergoing remediation by other management strategies such as capping and dredging. By basing the tools and approaches on sound science, conceptual site models, and mechanistic principles, combined with technical support as needed, these approaches and measures can generate reliable and useful data to support a wide variety of site conditions, COCs, and remediation strategies.

Point-of-Contact. Marc A. Mills, Ph.D.,

U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268

Tel. (513) 569-7322, mills.marc@epa.gov.

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