

South Carolina Water Resources Research Institute

Annual Technical Report

FY 2005

Introduction

While continuing to be involved with numerous water issues across the state including membership on an ad hoc statewide committee identifying policy issues related to primary water concerns and analyzing population growth impacts on water resources, SCWRC has continued collaborating with multidisciplinary teams investigating natural system/social system interactions.

GIS, Spatial Analysis, Land Use and Urban Growth Modeling, Image Analysis

Several projects have supported this activity over the last two quarters. Foremost among these projects has been involvement with NOAA and South Carolina Sea Grant's LU-CES program which is studying the impacts of changing land use patterns on coastal watersheds. The Water Center has spearheaded work on urban growth modeling and prediction, which has stimulated smart growth policy discussions across the state. Urban growth projections are completed for all coastal counties and have been highlighted at a series of Sea Grant sponsored workshops on coastal communities. The Water Center has worked closely on human population growth management issues in the Saluda/Reedy watershed and has recently obtained funding to produce urban growth predictions for the entire upstate of South Carolina.

Work has recently finished on an urban forestry project, which has determined the extent of forested lands along the I85 corridor and linked that data to air and water quality models. Hyperspectral image analysis is being used to detect invasive wetland species in a collaborative project with SUNY Albany. These projects all incorporate the utilization of geographic information systems to better understand human interactions with our natural resources. The EPA office in New York has asked our team to submit a new proposal to expand our work geographically and to include several new wetland species of interest to them.

Water Quantity and Water Quality Assessments, Watershed Education

The Water Center is a collaborative partner in a comprehensive watershed assessment project. The project is currently centered on the Reedy River, part of the larger Saluda River watershed encompassing metropolitan Greenville in South Carolina. SCWRC continues work on a project funded from the South Carolina Department of Natural Resources to develop and implement a Reedy River Watershed education program. Information from the watershed assessment will be shared with stakeholders across the Reedy River Watershed through this new program. A proposal has been prepared to

SCWRC has recently funded studies to: 1) investigate the effects of endocrine disrupting compounds in a contaminated mill-pond; 2) study environmental predictors of mercury methylation potential and fish tissue concentrations; and 3) study contaminant transfer among sediments, the water column and the atmosphere in selected reservoirs of South Carolina. Recent meetings with key individuals from the South Carolina Department of Natural Resources, the South Carolina Department of Health and Environmental Control and South Carolina Sea Grant have produced a working group that will fund and undertake a

multi-disciplinary research program for the valuation of natural and cultural resources along the South Carolina coast.

The SC Water Resources Center has also recently teamed with the Georgia Water Resources Research Institute at Georgia Tech to sponsor workshops focused on water use in the Savannah River basin. This basin is shared by the two states, is in high demand for its abundant water, and is in great need of proper planning for cooperative management by the two states. Reports are being prepared from the first workshop in this series.

Research Program

Projects currently underway:

Toxicological Effects of Endocrine Disrupting Compounds in Lake Conestee and the Reedy River
Funding Agency: USGS/SC Water Resources Center PI: Dr. Peter van den Hurk - Clemson University

Environmental Predictors of Mercury Methylation Potential and Fish Tissue Concentrations in a Blackwater River Funding Agency: USGS/SC Water Resources Center PI: Dr. Alan Johnson - Clemson University
Contaminant Transfer among Sediments, Water Column, and Atmosphere in Reservoirs
Funding Agency: USGS/SC Water Resources Center PI: Dr. Peter van den Hurk - Clemson University
Reedy River Watershed Education Coordinator Funding Agency: South Carolina Department of Natural Resources
Partners: Clemson University Extension Service

"The Saluda and Reedy River Watershed Land Use and Water Quality Assessment" Funding Agency: V.Kann Rasmussen Foundation
Partners: Multidisciplinary effort at Clemson University, Lander University and Furman University

GIS-based Database Management and Spatial Modeling for Coastal Ecosystems Funding Agency: S.C. Sea Grant LU-CES Program/NOAA
Partners: University of South Carolina, NOAA NOS Southeast Fisheries Center

The NY State Wetland Monitoring System: A Remote Sensing Assessment Funding Agency: U.S. Environmental Protection Agency
Partners: SUNY-Albany

Forest Fuel Load Classification using Hyperspectral Image Analysis Funding Agency: USDA - U.S. Forest Service
Partners: SpectroTech, Inc.

Toxicological effects of endocrine disrupting compounds in Lake Conestee and the Reedy River

Basic Information

Title:	Toxicological effects of endocrine disrupting compounds in Lake Conestee and the Reedy River
Project Number:	2005SC11B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	3rd
Research Category:	Water Quality
Focus Category:	Water Quality, Toxic Substances, Surface Water
Descriptors:	None
Principal Investigators:	Peter Van Den Hurk, David Hargett, Stephen Klaine

Publication

1. Schreiber, E.S., Otter, R.R., Van den Hurk, P. (2006) A biomarker approach to measure biological effects of contaminant exposure in largemouth bass from Lake Conestee, SC, USA. Environ. Toxicol. Chem. In press.
2. Otter, RR, Schreiber, EA, van den Hurk, P, Klaine, SJ. Watershed-scale application of biomarkers to assess ecosystem health. Poster presentation at the 25th Annual Meeting of the Society of Environmental Toxicology and Chemistry. Portland, OR Nov 14-18, 2004
3. Schreiber, E.A., R.R. Otter, S.J. Klaine, and P. van den Hurk. The Use of Biomarkers to Evaluate Contaminant Effects on Largemouth Bass from Lake Conestee, SC, USA. Poster presentation at the 25th Annual Meeting of the Society of Environmental Toxicology and Chemistry. Portland, OR Nov 14-18, 2004
4. Schreiber, E.A, R.R. Otter, S.J. Klaine, P. van den Hurk. Effects of Legacy Contaminants on Largemouth Bass in the Saluda Watershed. Poster Presentation at the Annual Meeting of the Carolinas Chapter of SETAC. April 2005, Raleigh, NC.
5. Otter, R.R., E.A. Schreiber, P. van den Hurk, S.J. Klaine. Watershed-scale application of biomarkers to access contaminant exposure in largemouth bass. Oral platform presentation at the 26th Annual Meeting of the Society of Environmental Toxicology and Chemistry. Baltimore, MD. Nov 13-17, 2005

6. Schreiber, E.A. A biomarker approach to measure biological effects of contaminant exposure in largemouth bass from Lake Conestee and nearby reservoirs. Masters Thesis, August 2005.
7. Otter, R.R. Spatial Characterization Of Biomarkers In A Contaminated Watershed: Usefulness In Ecological Risk Assessments. Dissertation. May 2006.

Progress Report

August 2006

Toxicological effects of endocrine disrupting compounds in Lake Conestee and the Reedy River.

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Sponsored by:

SOUTH CAROLINA WATER RESOURCES CENTER

SOUTH CAROLINA COMPETITIVE GRANTS PROGRAM

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Executive summary

As urban development progresses wastewater treatment becomes vital as the human population in an area increases. However, wastewater treatment does not tend to include monitoring for pharmaceuticals and chemical metabolites that humans often excrete in urine or feces. Therefore, many hormone based pharmaceuticals consumed and later excreted remain in the effluent from wastewater facilities. Effluents in wastewater have previously been shown to contain elevated concentrations of hormone metabolites and pharmaceuticals that downstream wildlife is subsequently exposed to. Human hormone metabolites and pharmaceuticals have the potential to cause disruption in the normal hormone signaling mechanisms in endocrine systems of wildlife including fish, amphibians, and other animals exposed to the wastewater effluent either by direct contact and ingestion or indirect exposure such as consumption of contaminated fauna or flora.

In Greenville County the primary wastewater treatment facility is located just below the city of Greenville and the effluent is discharged into the Reedy River water basin above Lake Conestee. The Reedy River originates in the foothills of the Blue Ridge Mountains about 7 miles northwest of the city of Greenville, SC and flows south through the city of Greenville, the Piedmont, and into Laurens county. The river empties into an arm of Lake Greenwood that is formed by a dam on the Saluda River which also flows into Lake Greenwood.

The water quality in the Reedy River basin has been shown to be impacted from the diverse and highly urbanized land uses within the watershed. Recent water quality data has suggested that the wastewater treatment plant effluents comprise a significant portion of the flow in the Reedy River, especially during extended dry periods when the effluent discharge is

believed to account for greater than 60 percent of the flow of the Reedy River basin. Previous studies have demonstrated the presence of significant amounts of endocrine disrupting chemicals in the wastewater treatment plant effluents. The objective of this study was to examine the observed toxicological effects of the endocrine disrupting compounds (EDCs) that are released into the Reedy River from the Greenville wastewater treatment facility by using a suite of biomarkers that were measured in indigenous fish to characterize the exposure and biological effects of these contaminants.

Bluegills (*Lepomis macrochirus*) were collected during three different seasons (spring, summer, and fall) from several sites along the length of the Reedy River and from an unimpacted control site at Lake Robinson. The fish were analyzed for unnatural estrogenic effects such as: 1). Vitellogenin (VTG) egg yolk protein production in male fish, 2). Activity of estrogenic compounds in bile extractions, and 3). Inhibition or induction of steroid hormone metabolizing enzyme UDP-glucuronosyltransferase (UGT).

The hepatosomatic indices (HSI) measured for the bluegill showed seasonal variations between spring and summer sampling (Fig.1). No significant differences in H.S.I from along the sampling sites were apparent during the spring season. However, during the summer season the H.S.I for most of the sites was found to be higher than those measured during the spring season, with the fish at the SV5 site directly below the Greenville wastewater treatment facility having significantly elevated H.S.I compared to the fish collected at control sites.

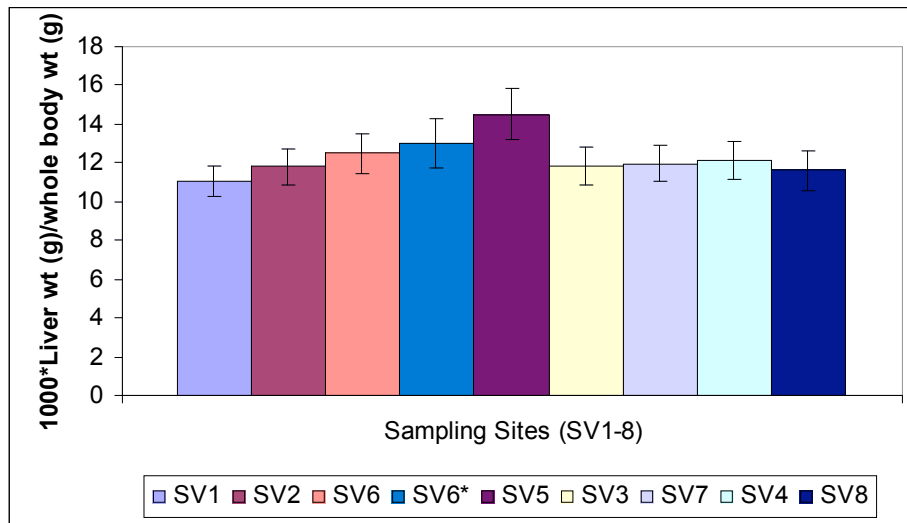
Bluegill that were collected in the sites downstream of the Greenville wastewater treatment facility were found to have significantly elevated levels of estrogenic activity in their bile conjugates relative to the specimens collected in reference sites during each season (Fig.2), providing evidence that the fish were exposed to elevated concentrations of xenoestrogenic

compounds downstream of the water treatment plant and that the xenoestrogens were also bioavailable to the bluegill.

Two biomarkers of effect were also examined: Vitellogenin concentrations in plasma of male and juvenile specimens and UDP-glucuronosyltransferase (UGT) activity in liver S9 fractions. The plasma VTG concentrations for fish collected in the spring season showed that several sites downstream of the Greenville wastewater treatment facility as far downstream as Boyd Mill Pond showed significantly elevated plasma VTG concentrations relative to the fish from control sites (Fig.3). The same general trend was seen during the summer season as well, however the SV5 site immediately downstream of the wastewater facility showed a two fold increase in plasma VTG concentration compared to the same site during the spring season. The measured UGT activity showed little variation between sites during either the spring or summer seasons, except immediately downstream of the wastewater treatment facility, where the measured UGT activity was significantly elevated during both seasons (Fig.4). The general trend in UGT activity that was seen during both seasons showed elevated UGT activity after the wastewater treatment plant, where UGT activity was highest, followed by a subsequent decline in activity the farther the sites were downstream from the facility.

The cumulative information provided by these biomarkers provided a more comprehensive understanding of the extent of EDCs contamination, its effects on biota, and may serve as a foundation for an ecological and human health risk assessments for the watershed.

A. Spring



B. Summer

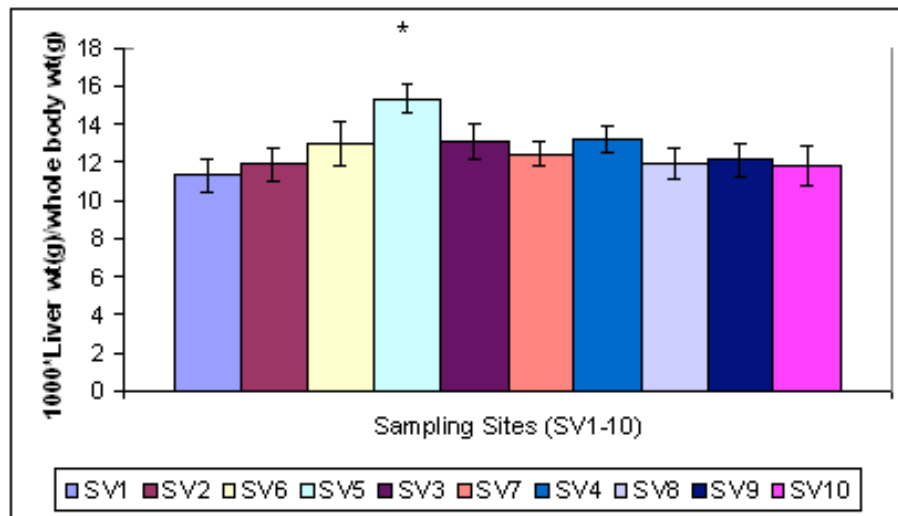
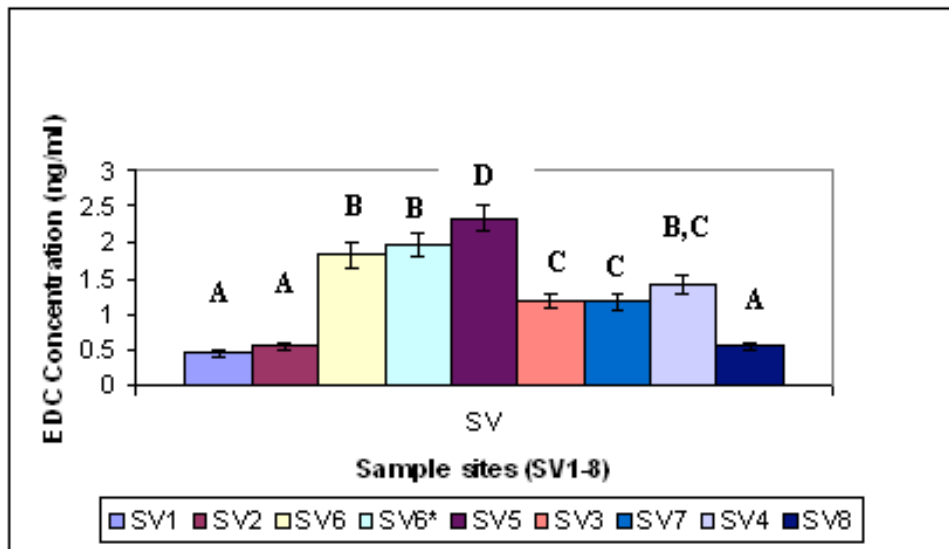


Figure 1. Hepatosomatic indices for *Lepomis macrochirus* collected in (a) spring, (b) summer, and (c) fall, from sites along the Reedy River watershed (SV1-10). SV1,SV2 = reference sites; SV6, SV6* = above WWTF1; SV5 = directly below WWT1; SV3 = above Conestee dam; SV7 = directly below Conestee dam; SV4 = below WWTF2; SV8 = 2 miles down of WWTF2; SV9 = Boyd Mill Pond; SV10 = Lake Greenwood. Significant difference from the reference site was determined (*; $p < 0.01$, ANOVA). Data presented are mean \pm SEM of $n=10$ from each site.

A. Spring



B. Summer

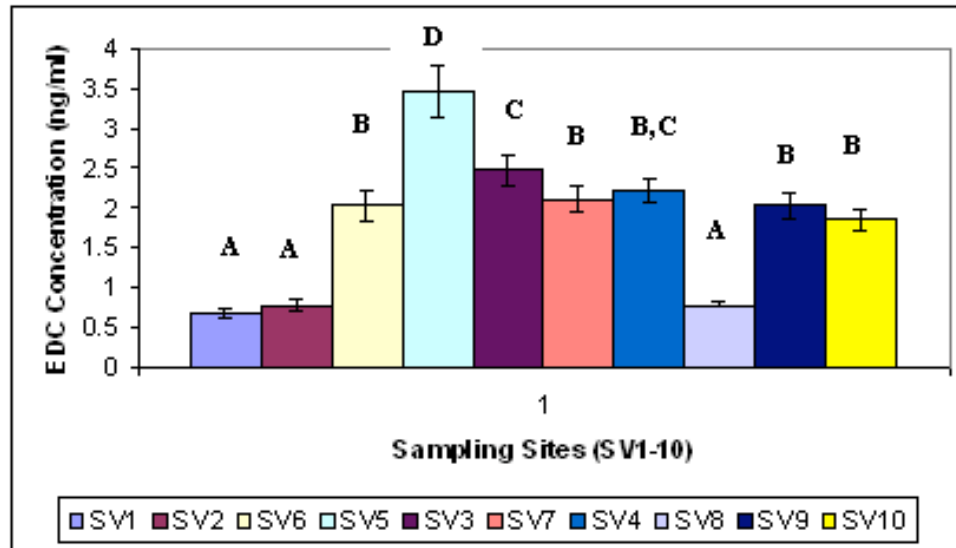
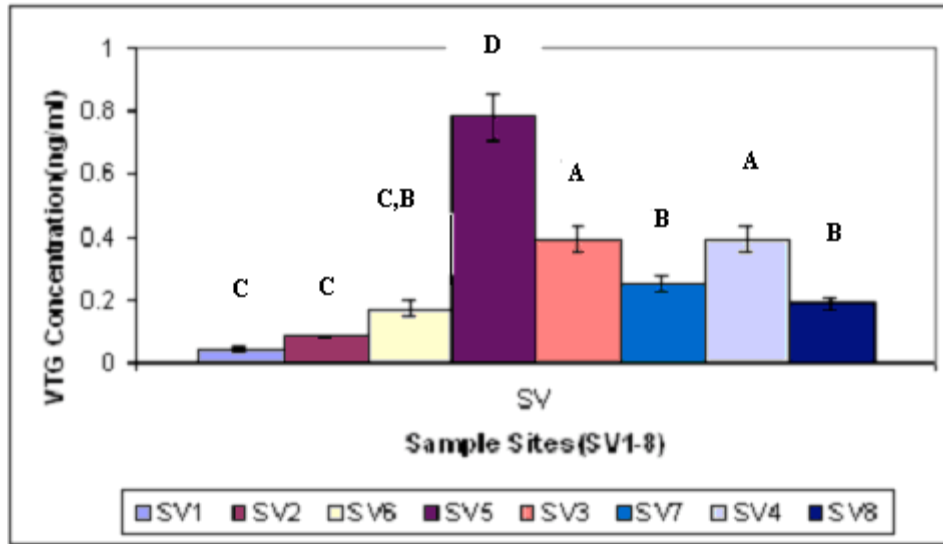


Figure 2: Estrogenic activity of bile conjugates of *Lepomis macrochirus* collected during (a) spring, (b) summer, and (c) fall along the Reedy River watershed (SV1-10). SV1,SV2 = reference sites; SV6, SV6* = above WWTF1; SV5 = directly below WWT1; SV3 = above Conestee dam; SV7 = directly below Conestee dam; SV4 = below WWTF2; SV8 = 2 miles down of WWTF2; SV9 = Boyd Mill Pond; SV10 = Lake Greenwood. Significant differences between sites during the same season were determined and are indicated by different letters (A-D) ($p < 0.05$, ANOVA). Data presented as mean \pm SEM of $n=10$ from each site.

A. Spring



B. Summer

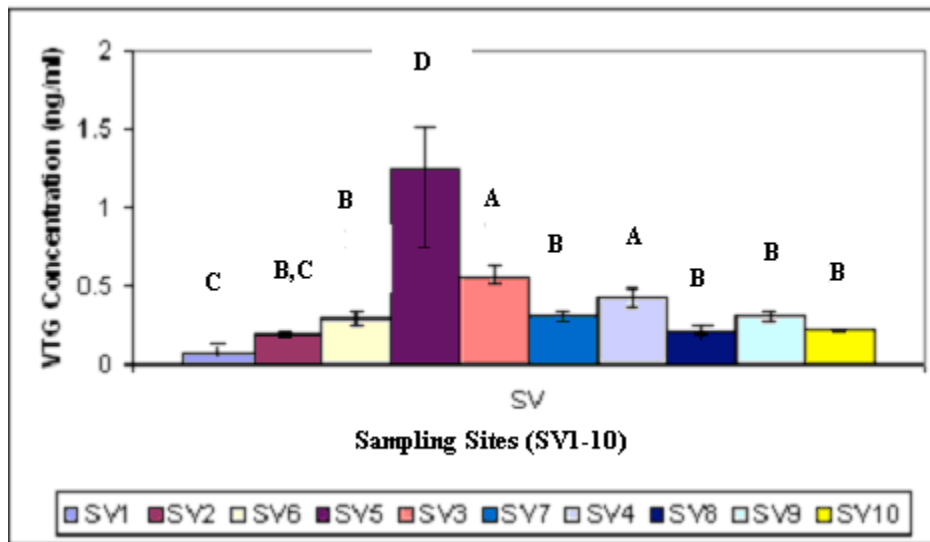
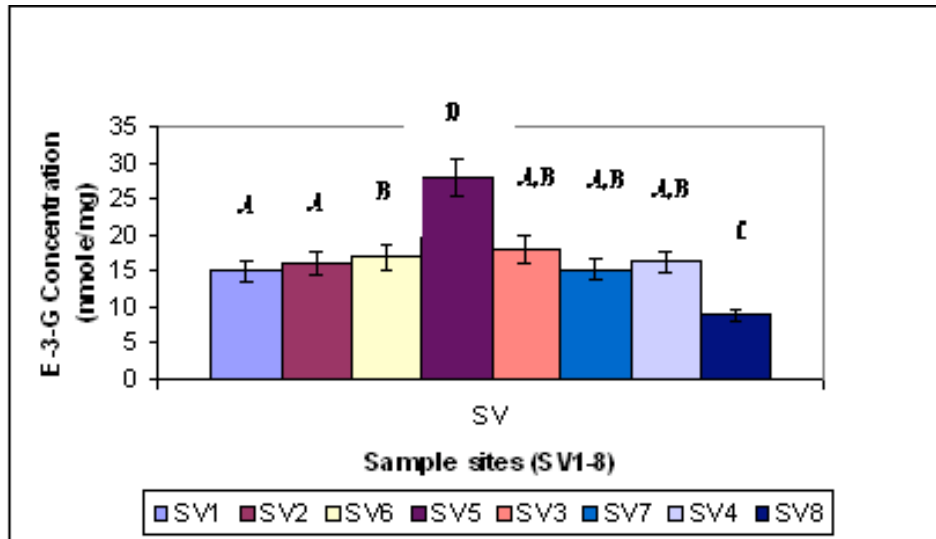


Figure 3: Plasma Vitellogenin concentration in *Lepomis macrochirus* collected during (a) spring, (b) summer, and (c) fall along the Reedy River watershed (SV1-10). SV1,SV2 = reference sites; SV6, SV6* = above WWTF1; SV5 = directly below WWT1; SV3 = above Conestee dam; SV7 = directly below Conestee dam; SV4 = below WWTF2; SV8 = 2 miles down of WWTF2; SV9 = Boyd Mill Pond; SV10 = Lake Greenwood. Significant differences between sites during the same season were determined and are indicated by different letters (A-D) ($p < 0.05$, ANOVA). Data presented as mean \pm SEM of $n=10$ from each site.

A. Spring



B. Summer

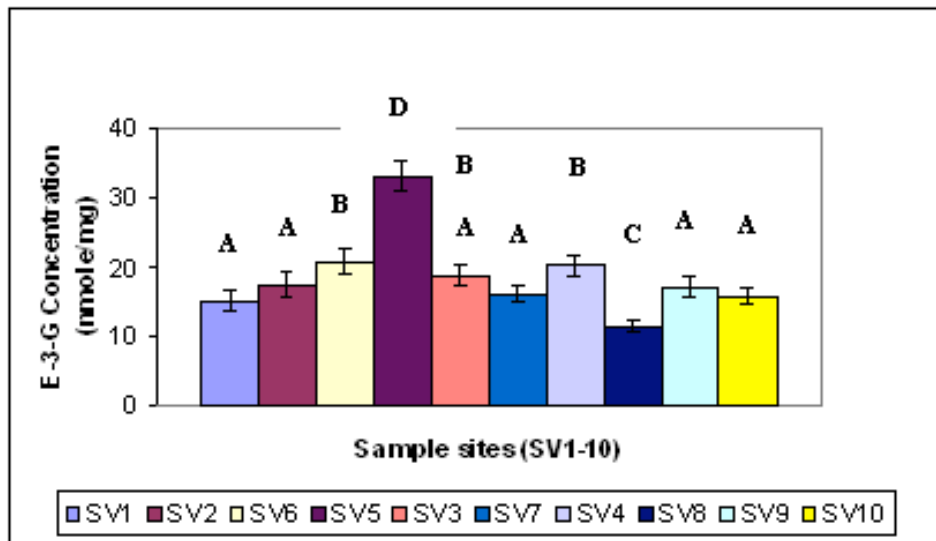


Figure 4: UGT activity in *Lepomis macrochirus* collected during (a) spring, (b) summer, and (c) fall along the Reedy River watershed (SV1-10). SV1,SV2 = reference sites; SV6, SV6* = above WWTF1; SV5 = directly below WWT1; SV3 = above Conestee dam; SV7 = directly below Conestee dam; SV4 = below WWTF2; SV8 = 2 miles down of WWTF2; SV9 = Boyd Mill Pond; SV10 = Lake Greenwood. Significant differences between sites during the same season were determined and are indicated by different letters (A-D) ($p < 0.05$, ANOVA). Data presented as mean \pm SEM of $n=10$ from each site.

Contaminant Transfer among Sediments, Water Column, and Atmosphere in Reservoirs

Basic Information

Title:	Contaminant Transfer among Sediments, Water Column, and Atmosphere in Reservoirs
Project Number:	2005SC13B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	3rd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Sediments, Hydrogeochemistry, Solute Transport
Descriptors:	None
Principal Investigators:	Cindy M. Lee

Publication

1. Sivey, John D. 2005. Comprehensive Congener-Specific Analysis as an Assessment Tool for Polychlorinated Biphenyl Contamination Trends in Lake Hartwell, SC. "MS Thesis," Department of Environmental Engineering and Science, School of the Environment, College of Engineering and Science, Clemson University, Clemson, SC, 137 pp.
2. Sivey, John D.; Brothersen, Tess, and Lee, Cindy M. 2005. Comprehensive congener-specific analysis as an assessment tool for polychlorinated biphenyl (PCB) contamination trends in Lake Hartwell, SC. In Proceedings of the 230th ACS National Meeting, Division of Environmental Chemistry, Washington, DC, August 28-September 1, 2005, Volume 45, Number 2, 83-88.

Evaluation of PCB Contaminant Trends over Two Decades by Achiral and Chiral
Analysis: Lake Hartwell, South Carolina

Submitted September 8, 2006

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Executive Summary

Polychlorinated biphenyl (PCB) contamination in Lake Hartwell has been a prominent regional issue for several decades. In 1994, the U.S. EPA issued a record of decision (ROD) for the Lake Hartwell Superfund site calling for natural capping with progressively cleaner sediment and ongoing monitoring. The EPA predicts that, given sufficient time, PCB contaminated sediments will be buried deep enough to prevent further exposure to aquatic organisms and thereby attenuate the potential for toxic effects at all levels of the food chain, including humans who consume Lake Hartwell fish.

To evaluate the efficacy of the EPA ROD and to better understand the PCB contamination trends in Lake Hartwell, sediment cores from the Twelve Mile Creek arm were collected in July 2004 at sites G30 and G33, first sampled by Germann (1988) in the mid-1980s. Sediment cores were sectioned every 5 cm prior to analysis. Sediment sonication extraction in acetone followed by solvent exchange into isooctane was used to prepare samples for gas chromatography (GC). An achiral GC method that quantified 128 congeners and a chiral GC method that measured five congeners were used.

Total PCB concentrations in 2004 near-surface sediments at sites G30 and G33 were 3.0 ± 0.2 $\mu\text{g/g}$ and 0.133 ± 0.007 $\mu\text{g/g}$, respectively. Total PCB concentrations in surface sediments exceed the EPA clean-up criterion of 1.0 $\mu\text{g/g}$ at G30, but not at G33. A higher degree of PCB chlorination was observed in the surface sediments of G30 (average Cl/biphenyl = 4.6 ± 0.3) relative to G33 (average Cl/biphenyl = 2.4 ± 0.1). Six-year average surface sediment recovery rates were greater at G33 (1.9 ± 0.1 nmol/yr) compared to G30 (0.80 ± 0.06 nmol/yr). The difference in recovery rates can be explained by the independent or simultaneous action of two processes: (1) a greater net sedimentation rate at G33 or (2) the deposition of less-contaminated sediment at G33.

Congener-specific PCB data as a function of depth from the sediment-water interface were compared to data obtained from 1987 and 1998 samples taken from the same locations (G30 and G33). Significant changes over time in the congener signatures of deposited sediments were observed at both sites, especially G30. Despite continued decreases in total PCB levels near the G30 sediment-water interface, historical increases in average degrees of chlorination may elevate the overall toxic risk at this site. At G30, total PCB trends give an incomplete and perhaps a misleading measure of sediment recovery. Unlike G30, the more rapid recovery in the near-surface sediment of G33 suggests that the effectiveness of the EPA ROD is site-specific and is unlikely to result in uniform surface sediment recovery throughout the most contaminated regions of Lake Hartwell.

Persuasive evidence of *in situ* reductive dechlorination was also found at both sampling sites. The shift toward lower degrees of chlorination with concurrent increases in % *ortho* chlorine levels with depth at both sites can best be explained by the mechanism of reductive dechlorination. Chiral analysis provided supporting evidence of *in situ* dechlorination. Corroborative results were also shown in the 1987 and 1998 datasets for sites G30 and G33. Despite the occurrence of biodegradation, historical reductions in total PCB loads within equivalent depths at site G33 were not observed. The entire PCB profile was not captured at G30, thus preventing an equivalent depth analysis at this site.

Introduction and Background

In the state of South Carolina and the southeastern region of the US numerous fish advisories exist, warning of the dangers of consuming fish contaminated with a variety of organic and metal contaminants. In 2004, South Carolina had the second largest number of water body specific guidelines at 72 following Georgia at 149 (EPA, 2004a, GA DNR, 2004). South Carolina has issued 61 advisories on lakes and reservoirs in SC for mercury and one for Lake Hartwell for polychlorinated biphenyls (PCBs) (SC DHEC, 2006a). North Carolina has 74% of its lake acreage under fish consumption advisories (EPA, 2004a), which include warnings due to mercury, PCBs, and dioxins (NC DHHS, 2004). Nationwide there are 884 advisories in 39 states for PCBs and 3,089 advisories for all contaminants (EPA, 2004a). Managers of these waters face uncertainty in their efforts to predict how long advisories must stay in place. Studies by the National Water Quality Assessment (NWQA) Program indicated that DDT levels in fish from the state of Mississippi remained at high levels far longer than predicted by environmental managers (USGS, 2003). The PCBs advisory for Lake Hartwell in SC and GA has been in place longer than EPA scientists anticipated given modeling predictions from the Remedial Investigation Report (Bechtel, 1993). Managers need better information about the fate and transport of contaminants in water bodies of recreational and commercial interest.

This work investigated the effects of one management strategy on the changes in contaminant levels in sediments of the Lake Hartwell reservoir at the headwaters of the Savannah River. The investigation was limited to two locations in the most heavily contaminated portion of the reservoir but spans three decades by comparing results from a 2004 sampling event with results from sampling in 1998 and 1987. Insight from the combination of two analytical methods provides important guidance for managers concerned with fish advisories due to sediment contamination. One method used comprehensive, congener-specific analysis of PCBs with depth and the other method used an innovative analysis of select congeners that sheds light on biotransformation due to their stereochemistry.

The history of the PCB contamination of Lake Hartwell has been extensively covered in a number of sources (Elzerman et al., 1991; Bechtel, 1993; Elzerman et al., 1994; Farley et al., 1994; Brenner et al., 2003; Pakdeesusuk et al., 2003a, 2005; Magar et al., 2005a, 2005b; Sivey and Lee, 2006). A brief summary of key events are provided here. A capacitor manufacturing plant located along a tributary, Town Creek, of Twelve Mile Creek was the source of the PCBs through its wastewater treatment plant. Twelve Mile Creek is a major tributary of Lake Hartwell, which was created by the US Army Corps of Engineers by damming the Savannah, Seneca, and Tugalo rivers between 1955 and 1963. The plant operated from 1955 to 1978 and disposed of an estimated 200 metric tons of PCBs before the ban on PCB use took effect in the mid-1970s (EPA, 1987). The plant used several commercial mixtures of PCBs over the years of operation, but the congeners that were released are well represented by 80% Aroclor 1016 and 20% Aroclor 1254 (Wong et al., 2001a).

The contamination of Lake Hartwell sediment and biota was discovered in the mid-1970s and the first fish advisory was issued in 1976 (EPA, 1987). At the time the US Food and Drug Administration (FDA) had set an action level at 5 mg/kg (EPA, 1987). The fish advisory was modified in 1984 when the FDA lowered the action level to 2 mg/kg (SC DHEC, 1987). In 2006, the public is warned not to eat any species taken from the Twelve Mile Creek arm or the Seneca River; hybrid bass and striped bass from the rest of the reservoir; and to eat only one meal a month of catfish and largemouth bass from the rest of the reservoir (SC DHEC, 2006b).

Lake Hartwell was placed on the National Priority List on February 21, 1990, and in June 1994 a Record of Decision (ROD) was issued for Operational Unit 2 (OU-2), which included the contaminated sediment, surface water, and biota (EPA, 1987; 1994). Figure 1 is a map of the heavily contaminated Twelve Mile Creek arm of Lake Hartwell. The ROD specified monitored natural attenuation through management of up-stream impoundments to ensure a supply of uncontaminated sediment to cap the contaminated portion of the reservoir. The ROD also called for institutional controls through continued fish advisories, public education, and on-going monitoring of the concentrations of PCBs in the sediment and aquatic biota.

The bioaccumulation model used by the EPA in the original assessment of the site predicted that the PCB concentrations in largemouth bass would be below the 2 mg/kg level between 2003 and 2005 (EPA, 2004b). However, tissue levels remain above the FDA action limit as of 2006 (SC DHEC, 2006b). In the first Five Year Review of the ROD for OU-2, the EPA predicted that the majority of surface sediment will have PCB concentrations that meet the 1 mg/kg clean up goal between 2007 and 2011 (EPA, 2004b). Brenner et al. (2004) considered the sedimentation rates for 18 cores obtained from the Twelve Mile Creek arm in light of age dating using lead-210 and cesium-137. Their results indicated that surface sediment would meet the 1 mg/kg goal between 1995 and 2003 and two locations met the goal in 1981 and 1987. However, Brenner et al. (2004) indicated that ten years of monitoring shows that the body burdens in largemouth bass and hybrid bass have not shown significant decreases despite large decreases in the surface sediment. They suggest that there are other mechanisms in addition to the surface sediment making PCBs available to these top trophic level fish.

Understanding the changes in the active sediment layer is crucial to making accurate predictions about the recovery of this system. Modeling results are generalized outcomes based on usually limited data; the EPA and other researchers acknowledge that long-term monitoring is necessary because conditions such as sedimentation rates may change (EPA, 2004b; Brenner et al., 2004). The results presented here consider the changes in the active sediment layer as well as with depth. Further understanding the interaction of biota with the active sediment layer must be enhanced to predict the true risk driver of contaminated fish, which is beyond the scope of this study.

Several of the studies of the PCB-contaminated sediment in Lake Hartwell and other locations have used congener-specific analysis to examine the processes. But no study has incorporated chiral analysis to consider sediment dynamics over time as this

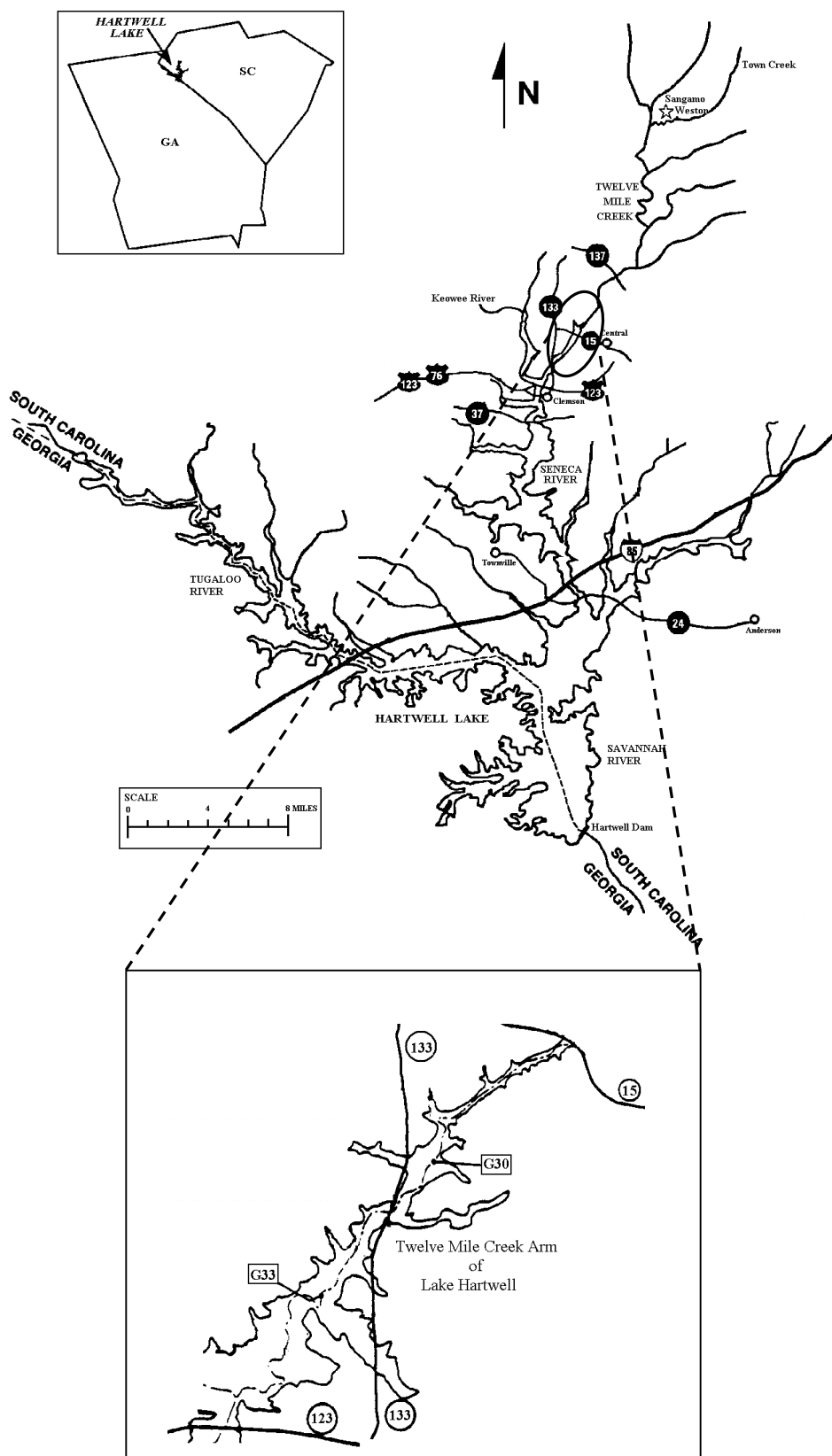


Figure 1. Location of sampling sites for 1987, 1998, and 2004 collection.

study does. Chiral analysis takes advantage of a few PCBs congeners that are asymmetric due to the biphenyl bond and the chlorination pattern. The

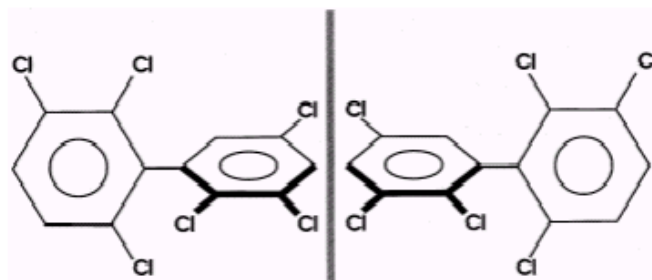


Figure 2. Enantiomers of PCB 136

asymmetry results in non-superimposable mirror images (Figure 2). These enantiomers share identical chemical and physical properties except for the direction of rotation of a plane of polarized light. They also can differ in their rates of reaction with other chiral molecules. Biological

molecules are often chiral; therefore, one enantiomer can react at a faster rate with an enzyme than the other one. The change can be measured by comparing the concentration of one enantiomer with the other. The enantiomeric fraction (EF) will equal 0.5 when both are present in equal amounts, which is known as racemic. The equations for calculating the EF are shown in the Methodology section below.

Chiral analysis thus provides a method for determining if biotransformation is occurring. Pakdeesusuk et al. (2003a) have used chiral analysis to investigate biotransformation of PCBs in Lake Hartwell with laboratory microcosms. Wong et al. (2001a, 2001b) measured the EF for selected PCB congeners in sediment and biota obtained from Lake Hartwell. Wong et al. (2001a) found nonracemic ratios for eight chiral congeners in sediment from four locations in the Twelve Mile Creek arm of Lake Hartwell collected in 1987. Their results provided clear evidence of bioprocessing of PCBs in the sediments. Measurements of four chiral congeners in aquatic and riparian organisms collected in 1994 from the Twelve Mile Creek arm showed different EF patterns than in sediment from the same general area (Wong et al., 2001b). The results are evidence that the organisms process the PCBs differently than the sediment microorganisms. The authors assumed that ratios measured in the sediments collected in 1987 did not differ significantly from sediment in 1994. There are no studies that consider the measurement of chiral PCBs in a single location over time.

PCBs have been used as conservative tracers by Pakdeesusuk et al. (2005) to evaluate dechlorination over a decade in Lake Hartwell. Congener-specific achiral analysis showed that although the distribution of lower and higher chlorinated congeners changed, the total moles of PCBs did not change from 1987 to 1998. Changes in the chiral signature with time have not been evaluated until this work. Chiral analysis provides another informative tool for managers of contaminated waterways in support of their decision-making.

Methodology

Samples from the water column and air collected by scientists from the EPA National Risk Management Research Laboratory and the National Exposure Research Laboratory in Cincinnati, OH, were not provided to this project as was originally planned due to logistical difficulties with the EPA contractors. Extracts from sediments and biota in Twelve Mile Creek, a major tributary of Lake Hartwell, were obtained from the EPA Laboratories, however, they were not obtained in time to analyze during the life of this project. Two sediment cores that were obtained in July 2004 were extracted and analyzed for achiral PCB congeners and chiral PCB congeners. The results were compared with data obtained from the same sampling locations in 1998 and 1987. The methods and results from these analyses are reported here.

Collection of Sediment Cores

Sediment cores were collected in July 2004 from sites G30 and G33 in the Twelve Mile Creek arm of Lake Hartwell (Figure 1). The G30 core was 55 cm long and the G33 core was 63 cm. The two sites were established in an extensive survey of PCB concentrations in Lake Hartwell sediment conducted by Germann (1988). Germann (1988) obtained cores that were 53 cm long from G30 and 39 cm from G33 using similar methods as reported here. In 1998, Pakdeesusuk (2002) obtained cores from G30 and G33 that were 70 cm and 60 cm, respectively.

All three projects used a Wildco gravity corer fitted with a LexanTM tube (5 cm diameter, 76 cm length) and an eggshell core catcher (5 cm). Before collecting the cores, the equipment was thoroughly rinsed with tap water and the LexanTM tubes were washed with warm, soapy water and rinsed several times with tap water followed by deionized/distilled water. The cores were transported to the L.G. Rich Environmental Research Laboratory (Clemson University, Anderson, SC) and extruded within 24 hours of the sampling event. During extrusion, the cores were sectioned into 5 cm lengths, homogenized by manual stirring (4 min) and stored in glass jars (0.5 L) at 4°C prior to analysis. Storage jars were rinsed with acetone and methanol before receiving the samples.

For the cores collected in 2004, the exterior portions (~1 cm) of the 40-45 cm sediment fractions from both cores (G30 and G33) were isolated and stored separately from the interior portions not in contact with the LexanTM tubes. Subsequent analyses were conducted for both the exterior (EXT) and interior (INT) portions of the G30 and G33 (40-45 cm) fractions to determine the extent of sediment smearing near the exterior of the cores during collection and extrusion.

Sample Preparation and Extraction

Sediment dry weight determinations were made for each 5 cm sediment fraction by taking triplicate samples (~3-4 g) from each homogenized fraction. The samples were

weighed into aluminum pans and dried overnight at 105°C. The ratio of the dry sediment weight to the wet weight, defined as the dry weight factor, was determined for each sample. Average dry weight factors and standard deviations were calculated for each 5 cm sediment fraction. Dry weight factors were used to convert wet weights of extracted sediment samples into dry weights to report PCB concentrations on a sediment dry weight basis.

PCBs were extracted using acetone and sonication by a method developed by Dunnivant and Elzerman (1987) and modified by Germann (1988) to minimize solvent. Sonication was accomplished with a Fisher 300 Sonic Dismembrator. The acetone was solvent exchanged with isooctane to produce the extract for analysis by gas chromatography (GC). Prior to sonication, all samples were spiked with 3.4 µg octochloronaphthalene (OCN) in acetone to determine recovery. The extraction efficiency averaged 81.2% (±57.9%). Results were not corrected for extraction efficiencies. Duplicate or triplicate extractions were conducted for each 5 cm sediment fraction.

For achiral GC analysis, about 350 µL of the isooctane extract and aldrin, which was used as an internal standard (8.0 µL at 591 ng/mL), were added to a 2-mL GC autosampler vial with insert. For chiral GC analysis, about 350 µL of the isooctane extract only were added to the 2-mL vial with insert. The GC vials had Teflon-lined septa and crimp tops.

Achiral GC Analysis

Calibration standards were prepared with a 1:1 ratio of Aroclor 1016 and 1254. Authentic standards were obtained from AccuStandard (location?). Details of the calibration method are provided below in the discussion of the data reduction methods.

For congener-specific analysis, sediment extracts were analyzed for PCBs on a Hewlett-Packard 6890 GC equipped with a 30 m fused silica capillary column (ZB-5, Phenomenex, Torrance, CA; 0.25 mm diameter, 0.25 µm film thickness) and a ⁶³Ni electron capture detector (ECD). All extracts were analyzed via duplicate or triplicate injection. GC parameters were analogous to those employed by Germann (1988) and Pakdeesusuk et al. (2005) for the 1987 and 1998 cores, respectively. An initial oven temperature of 100 °C was held for 2.5 min, followed by heating at 10 °C/min to 150 °C (0.5 min hold time), 1.1 °C/min to 225 °C (3.0 min hold time), and 10 °C/min to 260 °C (15 min hold time). Total run time per analysis was 97.7 min. The injector and detector temperatures were set at 250 °C and 325 °C, respectively. Helium was the carrier gas with a flow rate of 2.0 mL/min. Anode and makeup gas flow rates were set at 6.0 mL/min and 60.0 mL/min, respectively. Split vent flow was 57.5 mL/min initiated at 0.75 min. Autosampler injection volumes were 1 µL.

Blank GC runs (isooctane only) were conducted after approximately every five GC samples to check for analyte carry-over between injections. A PCB check standard (2000 ng/mL) was analyzed after approximately every 12 GC samples. Average GC-

ECD response factors varied by less than 10% for all check standard analyses; therefore, PCB recalibration was never required.

Chiral GC Analysis

Individual standards for each chiral congener to be evaluated were obtained from AccuStandard (New Haven, CT). Nine chiral congeners (84, 91, 95, 132, 135, 136, 149, 174, 176) can be separated with the Chirasil-Dex column (Wong and Garrison, 2000). Each racemic standard was injected (1 μ l) in triplicate to determine the retention time for each enantiomer. The percent relative standard deviation (%RSD) for the average EF of the triplicate analysis was less than 5%. A calibration check standard was composed of a mixture of all congeners that were measured.

Sediment extracts were analyzed with an Agilent 6850 which was equipped with a ^{63}Ni ECD and interfaced with a IBM-compatible PC loaded with HP ChemStation software (revision A.06.03 © Hewlett Packard 1990-1998). The capillary column was a Chirasil-Dex (25-m long, 0.25-mm i.d.) with a 0.25- μ m film thickness with an immobilized permethyl β -2,3,6-tri-*O*-methyl β -cyclodextrin on a polysiloxane backbone as the stationary phase. The column was purchased from Chrompack (Raritan, NJ).

The GC method was developed from work by Wong et al. (2001a) as modified by Hall (2004). The GC conditions for the chiral analysis had an initial temperature of 60°C that was held for 2.0 min followed by a temperature program of 10°C/min to 150°C and held for 0.5 min. A second temperature program of 1.0°C/min was taken to 200°C that was held for 20 min. An injection of 1.0 μ L was used in splitless mode with the injector temperature at 210°C. The detector temperature was 350°C. Helium was the carrier gas with a flow rate of 1.0 mL/min. Anode and makeup gas flow rates were set at 6.0 mL/min and 60.0 mL/min, respectively. Split vent flow was 57.5 mL/min initiated at 0.75 min.

Data Reduction Methods

For the achiral congener-specific analysis, peaks were identified by using relative retention times based on techniques developed by Frame (1997). Details of the method are available in Sivey (2005). For all field samples, coeluting congeners were assumed to be present in the same ratios as determined for a 4:1 mixture of Aroclors 1016 and 1254, respectively. The 4:1 Aroclor mixture closely approximates the source PCB composition discharged into Lake Hartwell (Germann, 1988).

The calibration consisted of five concentrations (100, 250, 500, 1000, 2000 ng/mL) of the 1:1 Aroclor 1016:1254 mixture that were injected three times each. Aldrin (36 ng/mL) was used as an internal standard.

Congener-specific PCB concentrations were computed via the following general equation:

$$[\text{PCB}] = \frac{k y V}{w} \quad [3.1]$$

where $[\text{PCB}]$ = sediment PCB concentration (\square g/g dry weight),
 k = dimensionless correction factor for concentration steps in the extraction procedure,
 y = PCB concentration in the concentrated sediment extract (ng/mL),
 V = GC vial volume (mL), and
 w = sediment dry weight (g).

Furthermore:

$$y = m x + b \quad [3.2]$$

where m and b are the slope and y-intercept of the PCB peak-specific calibration curve regression analysis.

$$x = \text{peak response factor} = \frac{A_x C_{IS}}{A_{IS}} \quad [3.3]$$

where A_x = integration area of the PCB GC peak,
 C_{IS} = concentration of the internal standard (IS), and
 A_{IS} = integration area of the internal standard GC peak.

For the chiral analysis, the enantiomeric fraction (EF) was determined by the following equation.

$$\text{EF} = (\text{peak area of E1}) / (\text{peak area of E1} + (\text{peak area of E2})) \quad (\#)$$

E1 is the first eluting enantiomer and E2 is the second eluting enantiomer. If the elution order has been established, then the following equation should be used.

$$\text{EF} = (\text{peak area of (+)}) / (\text{peak area of (+)} + (\text{peak area of (-)})) \quad (\#)$$

The elution order with the Chirasil-Dex column is known for PCB 132, PCB136, PCB149, PCB174. and PCB176 (Haglund and Wilberg, 1996; Wong et al., 2001a). It is not known for PCB 91 and PCB 95

The equivalent depths for the 1987, 1998 and 2004 cores were determined by matching the total PCB concentration depth profiles for the three time periods. Total moles of PCBs were calculated at each equivalent depth for the three sampling dates to determine the extent to which PCBs can serve as conservative tracers at the two sampling sites (G30 and G33). The total moles of PCBs captured in a cylindrical core fraction can be computed via Equation 3.6:

$$T_m = \square V C \quad [3.6]$$

where T_m = total PCBs (\square mols),
 \square = sediment bulk density (g/cm^3),
 V = core fraction volume (cm^3), and
 C = sediment PCB concentration (\square mol/g).

The volume of each core fraction can be calculated using Equation 3.7:

$$V = 0.25 \pi h d^2 \quad [3.7]$$

where h = height of the core fraction (cm) and
d = diameter of the core (4.8 cm).

Experimental Error

All of the 2004 PCB data reported above depend on the accurate determination of congener-specific PCB concentrations via GC-ECD analysis. These data are manipulated to obtain bulk GC parameters, including total PCB concentrations and chlorine distribution metrics. As such, the ability to identify and quantify error sources impacting PCB concentration determinations is essential when reporting experimental error limits.

Table 3.1 summarizes the major error sources affecting the congener-specific PCB quantification method outlined above in Equations 3.1 – 3.3. Propagation of the uncertainties listed in Table 3.1 provides an estimation of the total error in congener-specific PCB analyses. The following formula was used to perform PCB error propagations to yield an estimation of total analytical error:

$$\text{Total Error (as \%)} = \frac{1}{100} \sqrt{(E_{IS})^2 + (E_P)^2 + (3)^2 + (1)^2 + (E_W)^2} \quad [3.4]$$

For most PCB analyses, E_P is the largest error source; E_W is typically the smallest source of error.

Table 1. Identification and quantification of error sources impacting congener-specific PCB analyses.

Error Source	Error Parameter	Symbol/Absolute Value
Internal standard (IS) area quantification	Relative standard deviation of IS integration areas for multiple GC injections	E_{IS}
PCB peak area quantification	Relative standard deviation of peak integration areas for multiple GC injections	E_P
IS concentration determination	Propagation of experimental uncertainties in IS preparation ^a	~ 3%
Calibration curve regression error	ANOVA regression statistics	~ 1% ^b
Sediment dry weight determination	Relative standard deviation of triplicate measurements	E_W

^aExperimental uncertainties in internal standard preparation include precision limits of volumetric and gravimetric instruments as reported by the manufacturers. ^bCalibration curve regression error is an average value for all PCB peak calibrations.

Results and Conclusions

Sediment samples were obtained in July 2004 at sites G30 and G33 (one core per site) in the Twelve Mile Creek arm of Lake Hartwell. Sites G30 and G33 are ca. 36 and 38 km downstream of the original PCB discharge location (Farley et al., 1994) and represent heavily contaminated sites with historically similar sedimentation rates (Brenner et al., 2004). The sediment cores obtained in 2004 consisted largely of silt with some clay and little sand. Here the results from the achiral analysis are discussed first followed by the results from the chiral analysis. Detailed results for the chiral analysis can be found in Sivey (2005).

All sediment samples from sites G30 and G33 in Lake Hartwell underwent at least two PCB extractions with subsequent analysis by GC-ECD. Total PCB results for G30 and G33 cores are summarized in Figures 3 and 4, respectively. In both figures, error bars denote total analytical errors. An exhaustive list of total PCB concentrations for all samples and all extractions is compiled in Sivey (2005). The total PCB results for samples G30-40 INT and G30-40 EXT are consistent (see Figure 3), suggesting that smearing and radial sample heterogeneity are minimal in this core. The analogous results for core G33 are less consistent (see Figure 4), but still indicative of minimal sample smearing near the edges of the core.

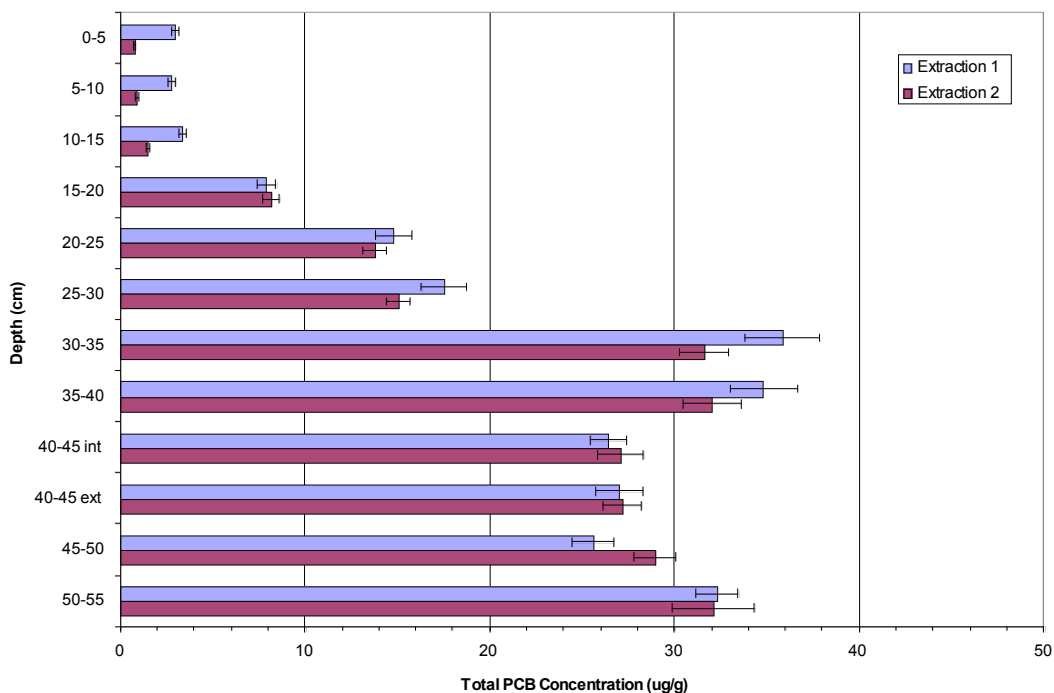


Figure 3. G30 total PCB concentration profile for all extractions. Error bars denote total analytical errors.

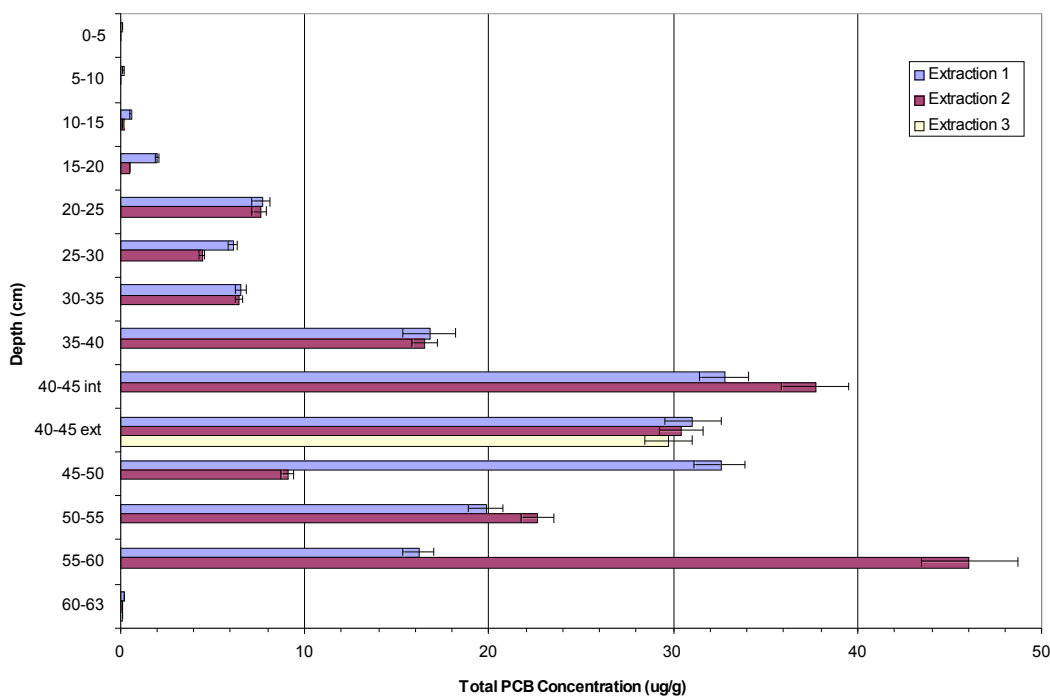


Figure 4. G33 total PCB concentration profile for all extractions. Error bars denote total analytical errors.

In general, good agreement was observed for extractions from the same sediment sample. When multiple extractions from the same sample were performed on the same date (e.g., G33-40 EXT and G33-60), minimal differences in total PCB concentrations were observed. For some samples in which extractions were conducted on different dates (e.g., G30-0, G30-5, G30-10 and G33-45), appreciable decreases in total PCB concentrations were observed from extraction 1 to extraction 2. However, this trend was not consistent across all samples; G30-45 and G33-55 are clear exceptions. Interestingly, extraction 2 efficiencies as measured by OCN recoveries were statistically equivalent to or greater than those of extraction 1 for all samples except G30-50 and G33-50 (see Sivey, 2005). Cl/biphenyl trends across multiple extractions were not consistent; comprehensive Cl/biphenyl results are shown in Sivey (2005).

Potential reasons for deviations in extraction results include sample heterogeneity, volatilization and sorption losses during handling and storage, the presence of interfering compounds, and GC-ECD analysis inconsistencies. To minimize the impact of these errors when evaluating PCB depth profiles, only extraction 1 data are used in the calculations and discussions that follow. Extraction 1 data are expected to be the most accurate due to their shorter handling times and subsequent minimization of analyte losses. For fractions in which separate internal and external analyses were conducted, the averages of these analyses are reported in the results below.

G30 Achiral Results

Total PCB concentrations as a function of depth from the sediment-water interface at site G30 are depicted in Figure 5. The total PCB concentration at the sediment-water interface is 9.5 ± 0.6 nmol/g (3.0 ± 0.2 $\mu\text{g/g}$). This value is above the EPA clean-up requirement of 1.0 $\mu\text{g/g}$ and is indicative of a high potential for biota exposure and bioaccumulation in organisms residing or feeding in near-surface sediment. Significant PCB mass transport via resuspension of sediment at this site is also of concern. Approximately uniform PCB concentrations persist from 0 to 15 cm, indicating that any recent sedimentation has not decreased total PCBs at the sediment-water interface. A sharp increase in total PCBs occurs at 15-30 cm. The maximum concentration captured by this core is 141 ± 8 nmol/g (36 ± 1 $\mu\text{g/g}$) at 30-35 cm. The entire vertical PCB profile was not captured in this core as evidenced by the concentrations failing to approach zero with depth.

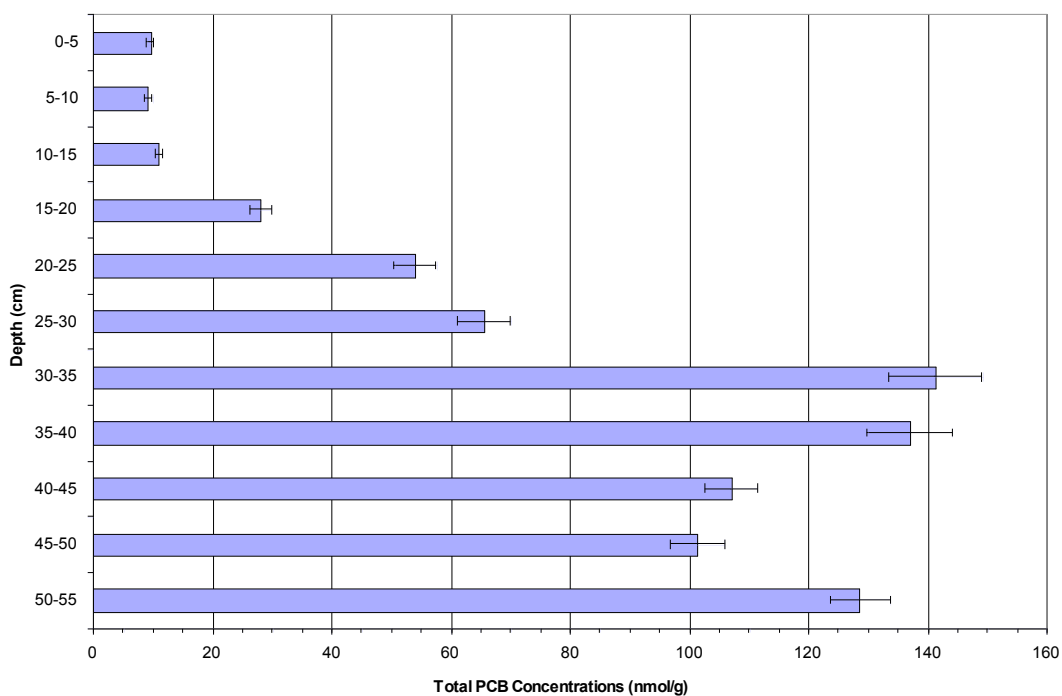


Figure 5. G30 PCB concentration depth profile. Error bars denote total analytical error for extraction 1 data.

The homolog mol% distributions for each G30 fraction are shown in Figure 6. For comparison purposes, the surrogate source composition of a 4:1 mixture of Aroclors 1016 and 1254 is included in Figure 6. The near-surface sediments (0-15 cm) are deficient in lower chlorinated homologs (di and tri) relative to the source composition. Volatilization and aerobic biodegradation of lower chlorinated species are the most probable mechanisms for the weathering of shallow PCBs. Uniform homolog distributions for the top three sediment fractions suggest that this weathering predominantly took place prior to deposition (i.e., upstream of G30). Beginning at 15 cm, a dramatic increase in lower chlorinated congeners is observed, concurrent with the aforementioned increase in total PCBs. For all fractions below 15 cm, an enrichment in dichlorinated species is observed relative to the source composition. Decreases in higher chlorinated congeners (tetra – hepta) below 15 cm are also evident.

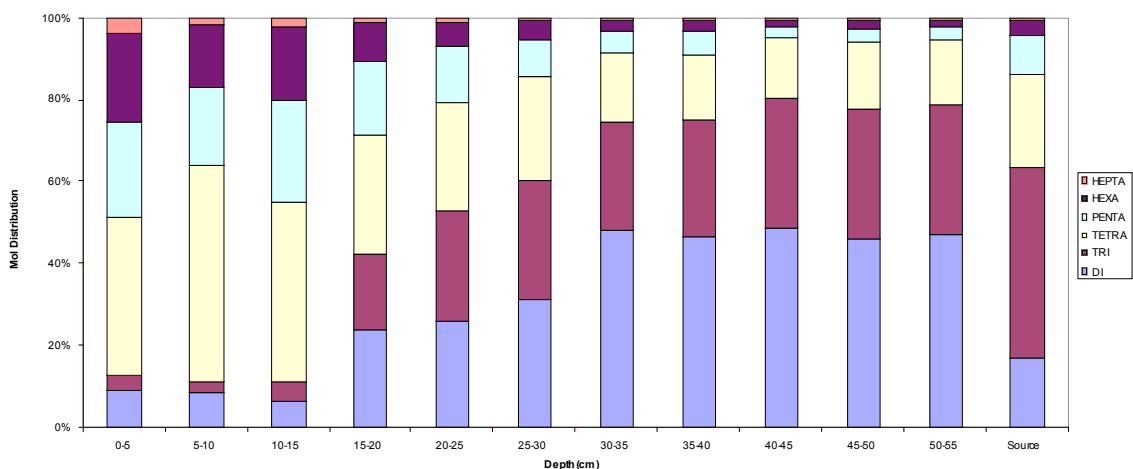


Figure 6. G30 homolog by mole percentage distribution. Source refers to a 4:1 mixture of Aroclor 1016 and 1254, respectively.

As shown in Figure 7, a rapid decline in average chlorines per biphenyl begins at 15 cm. A concomitant increase in % *ortho* chlorines begins at the same depth (Figure 8). Taken together, these data are persuasive indicators of PCB biochemical weathering via reductive dechlorination (Pakdeesusuk et al., 2005). Microbial reductive dechlorination removes chlorine atoms from higher chlorinated biphenyls and results in a lower chlorine per biphenyl average. Pakdeesusuk et al. (2003b) demonstrated that the microorganisms found in Lake Hartwell sediment do not remove chlorines at the *ortho* position, therefore, the percentage of *ortho* chlorines increases with dechlorination. Below 30 cm, changes in chlorine and homolog distributions are minimal, potentially due to a plateau phase in reductive dechlorination at these depths (Pakdeesusuk et al., 2005). A plateau phase occurs when local reductive dechlorination rates approach zero. Since total PCB concentrations increase with depth to 35 cm and then decrease only slightly, a parameter other than total PCB concentration must be responsible for the reductive dechlorination plateau. As pointed out by Pakdeesusuk et al. (2005), reductive dechlorination can be limited by the availability of susceptible congeners (i.e., those with a spatial arrangement

of chlorines favorable to enzymatic reduction reactions) and by the presence of microbial communities capable of reductive dechlorination.

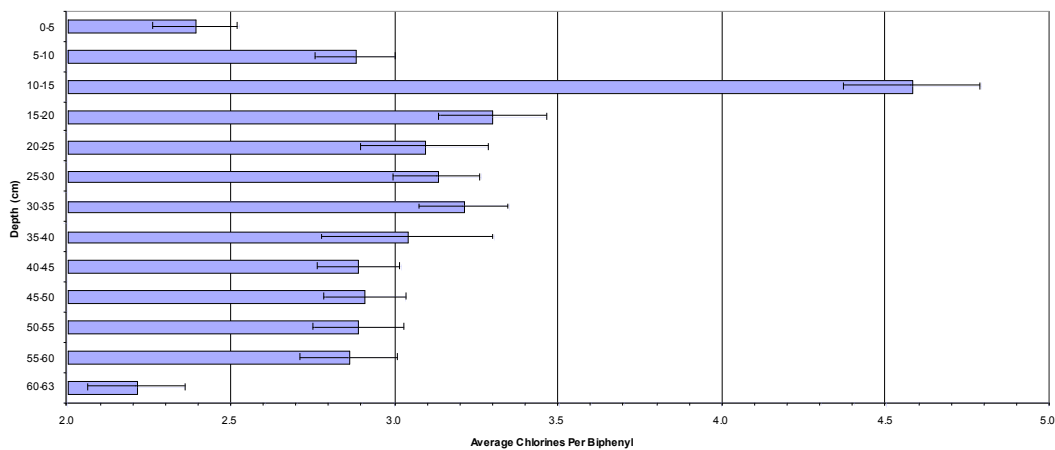


Figure 7. G30 chlorine per biphenyl with depth. Error bars denote total analytical error.

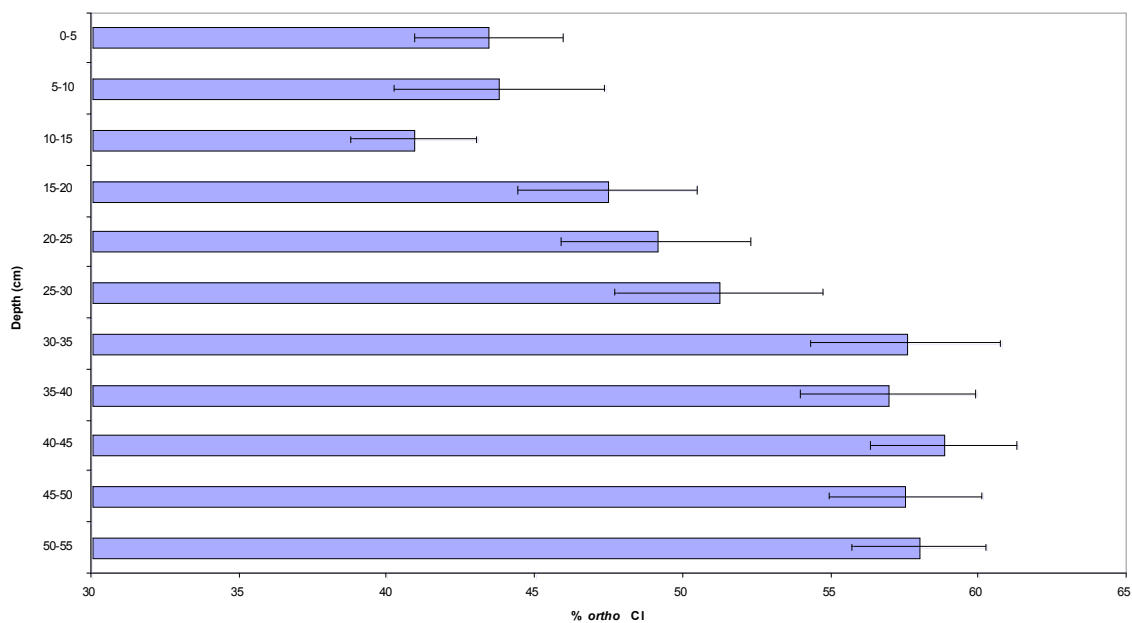


Figure 8. G30 percent *ortho* chlorine with depth. Error bars denote total analytical error.

The congener distribution for the near surface sediment at G30 is shown in Figure 9. Of note is the predominance of higher chlorinated congeners in this sample. Overall, PCB toxicity (Safe, 1992) and bioaccumulation potentials (Schwarzenbach et al., 2003) increase with molecular weight. These trends, in conjunction with a total PCB concentration above the clean-up guideline, raise significant ecotoxicological concerns at this site.

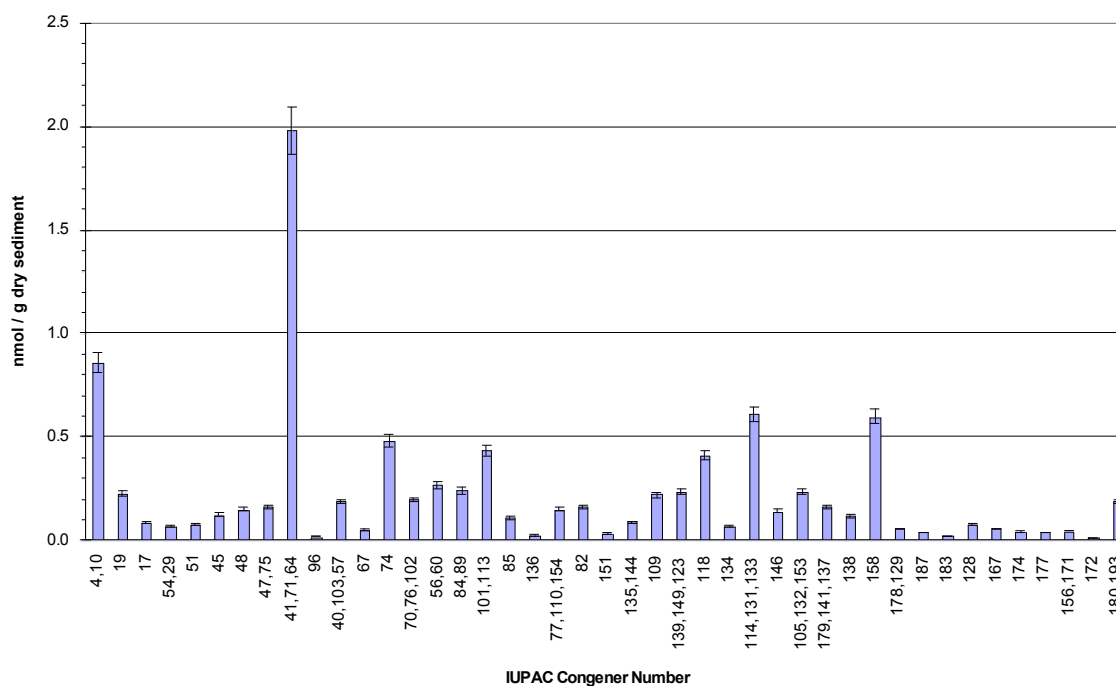


Figure 9. G30 (0-5 cm) congener distribution as mole percentage. Total PCB concentration equals 3.0 $\mu\text{g/g}$.

The congener distribution from 30-35 cm at G30, representing the highest captured total PCB levels, is shown in Figure 10. Evidence of PCB weathering via reductive dechlorination is obtained by comparing the congener-specific results from 30-35 cm (Figure 10) to those from 0-5 cm (Figure 9). These figures outline a dramatic shift to lower chlorinated congeners with depth. Congener-specific results for all G30 fractions are compiled in Sivey (2005).

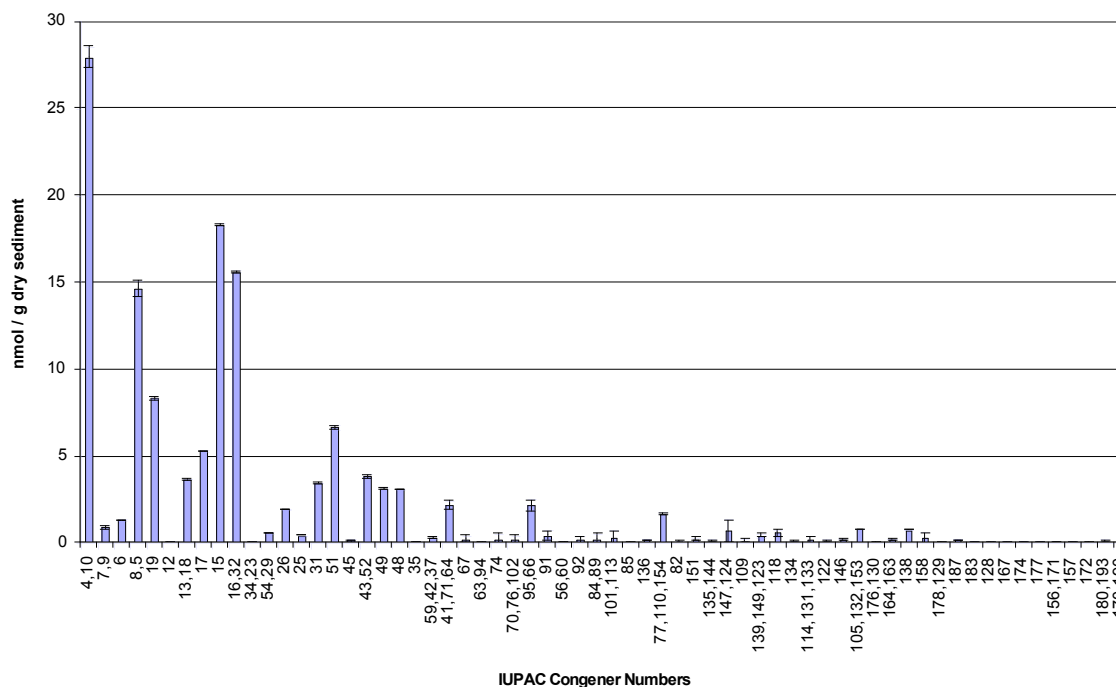


Figure 10. G30 (30-35 cm) congener distribution as mole percentage.
Total PCB concentration equals 35.9 μ g/g.

Total PCB depth profiles for G30 samples collected in 1987 (Germann, 1988), 1998 (Pakdeesusuk et al., 2005) and 2004 (the current work) are shown in Figure 11. Large decreases in total PCBs at the sediment-water interface are observed between 1987 and 1998. Comparably modest decreases are observed between the 1998 and 2004 data for near-surface sediments. The 1998 and 2004 PCB profiles are very similar from 0 – 30 cm, which implies minimal net sedimentation between these two sampling dates. However, the maximum PCB concentration at this site is most likely deeper than that captured by the 2004 sampling event. Therefore, a reliable calculation of recent sedimentation rates based solely on PCB profiles following the method described by Pakdeesusuk et al. (2005) is not possible. An examination of the historical data suggests that none of the cores captured the entire PCB profile, further complicating attempts to comprehensively assess PCB contamination trends. An average sedimentation rate of 2.0 ± 1.8 g/(cm² yr) was reported at a transect of Lake Hartwell near G30 based on 2000 and 2001 sediment core radioisotope dating (Brenner et al., 2004). Assuming a sediment bulk density of 2.6 g/cm³ (Farley et al., 1994), this sedimentation rate translates into 0.8 ± 0.7 cm/yr. The G30 near-surface results of the current work suggest a six-year average (1998-2004) sedimentation rate near the lower end of the range reported by Brenner et al. (2004).

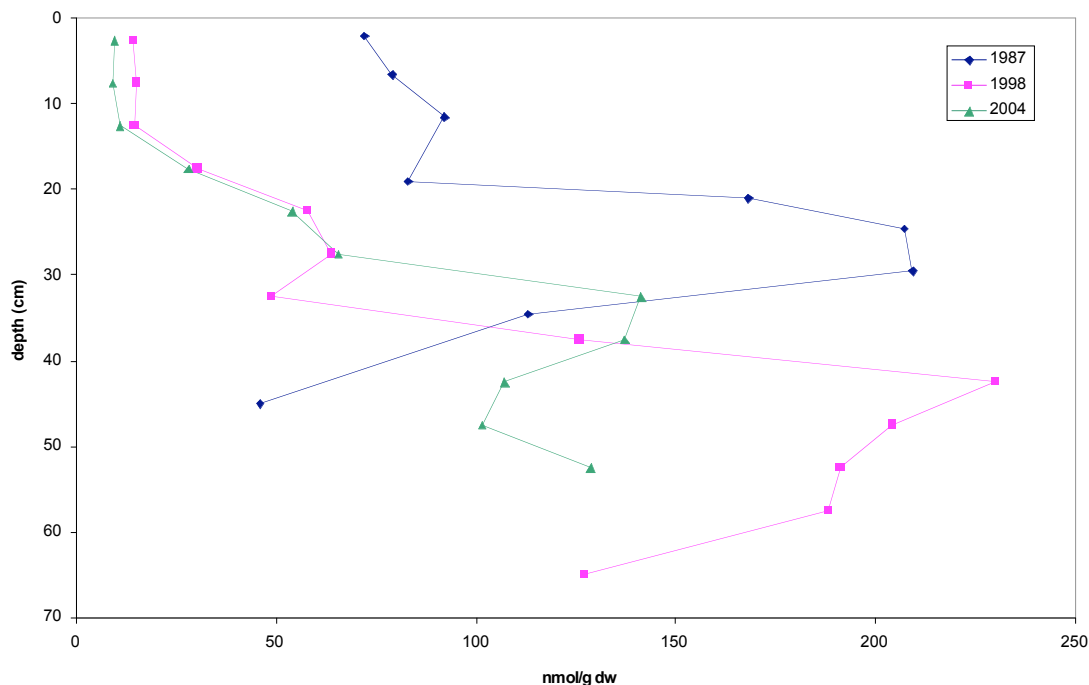


Figure 11. Historical trends in G30 total PCB concentrations.

Historical chlorine distribution profiles can be useful in assessing trends in PCB composition over time. Figure 12 outlines the average chlorines per biphenyl profiles for all three sampling years under consideration. Figure 13 depicts % *ortho* chlorine historical profiles. The approximate source composition (4:1 mixture of Aroclors 1016 and 1254) is demarcated in both figures by a dashed line. The overall trends for all sampling dates include a decrease in average chlorines per biphenyl and an increase in % *ortho* chlorines at depths below 15 cm. These data suggest that reductive dechlorination processes have been operating at this location for several decades. Further evidence of a reductive dechlorination plateau phase is found in Figures 12 and 13. As sediment residence time increases with depth, Cl/biphenyl levels converge to approximately 2.8 for all samples regardless of total PCB concentration. Similar convergence to approximately 60% *ortho* chlorine levels with depth is also observed. Dissimilarities in Cl/biphenyl levels at the sediment-water interface suggest a variable PCB composition of deposited sediment over time. The average Cl/biphenyl of PCBs in deposited sediment is increasing over time. This change reflects increasing degrees of source PCB weathering, as indicated by the respective distances from the dashed line in Figure 12 for near-surface sediment. The most probable mechanisms acting here include the preferential volatilization and sorption of low and high molecular weight PCBs, respectively (Farley et al., 1994). Aerobic bio-transformations of low molecular weight congeners may be significant as well. Evidence in support of a variable deposition composition is also indicated at the congener-level.

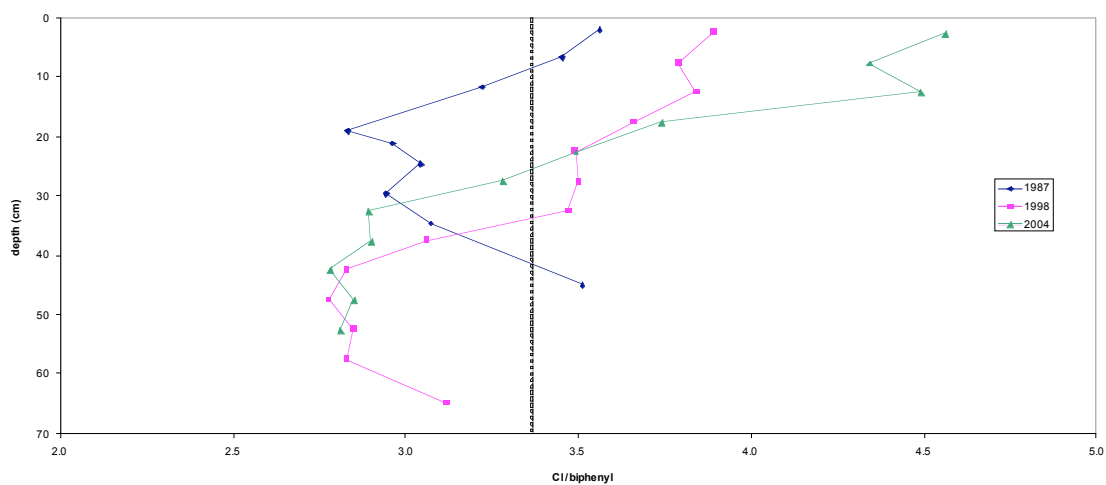


Figure 12. Historical trends in G30 chlorines per biphenyl. The dashed line denotes the original source composition (4:1 mixture of Aroclors 1016 and 1254).

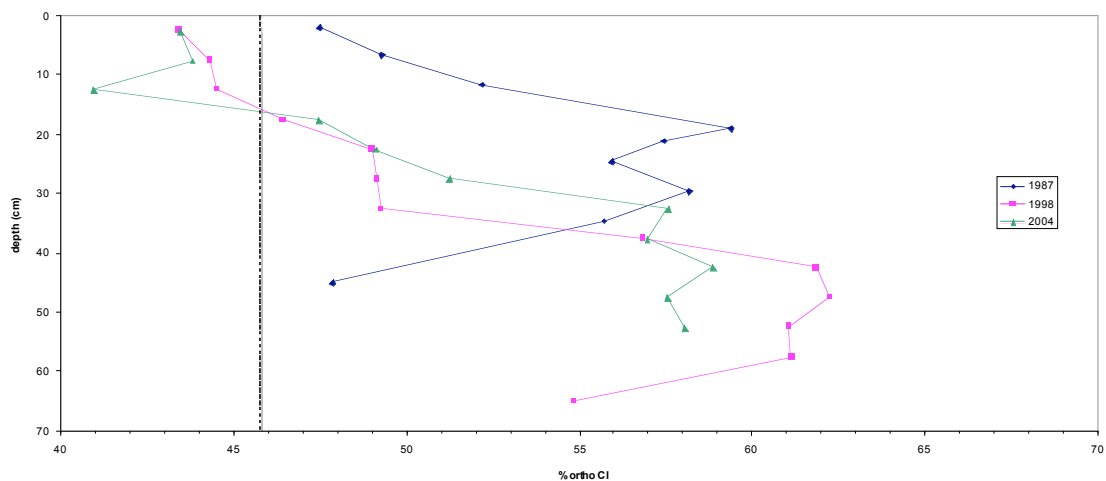


Figure 13. Historical trends G30 *ortho* percentages. The line denotes the original composition of the source (4:1 mixture of Aroclors 1016 and 1254).

Figure 14 displays the mol% distributions of selected congeners in near surface sediments for all three sampling dates. Details on how pre-2004 data was corrected for the change in analytical methods can be found in Sivey (2005). Increases in higher chlorinated congeners (PCBs 101, 113, 146) with concurrent decreases in lower chlorinated congeners (PCBs 4, 10, 15, 17) over time are observed. These data suggest that despite the continued trend of decreasing total PCB concentrations in near-surface sediments, a concurrent decrease in the bioaccumulation and toxicity potentials of these sediments may not be occurring due to the shift toward higher molecular weight congeners over time. The bioaccumulation (Schwarzenbach et al., 2003) and toxicity (Safe, 1992) potentials of individual congeners can vary by more than two orders of magnitude. As a result, it is possible for the overall risk posed by PCB-contaminated sediments to increase despite decreases in total PCB concentrations. Based on the results above, this observation may very well describe the current state of G30 sediments in Lake Hartwell.

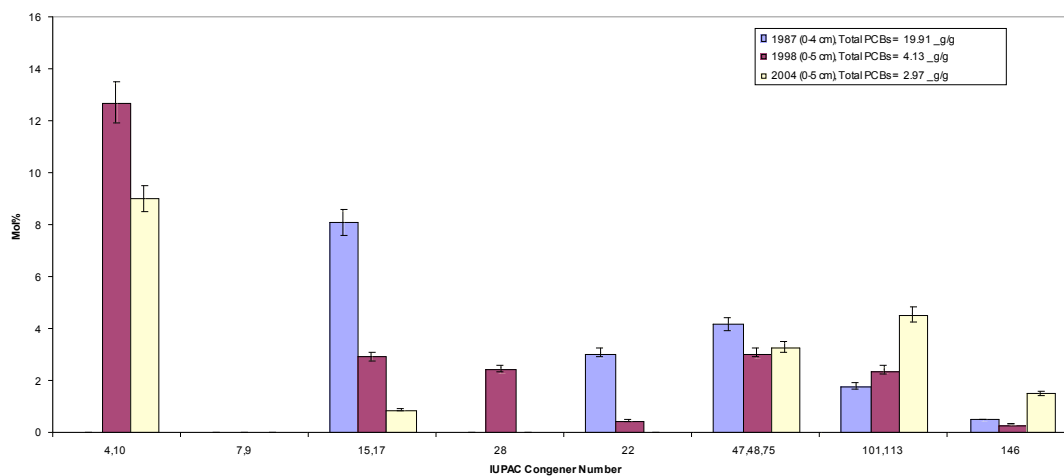


Figure 14. Historical trends in the relative distributions of selected congeners at the G30 sediment-water interface. Error bars denote the error between the two analytical methods used to obtain 2004 (Sivey and Brothersen, 2005) and pre-2004 (Germann, 1988) data.

G33 Achiral Results

Total PCB concentrations as a function of depth from the sediment-water interface at site G33 are depicted in Figure 15. The total PCB concentration at the sediment-water interface is 0.56 ± 0.03 nmol/g (0.133 ± 0.007 \square g/g). This value is well below the EPA clean-up requirement of 1.0 \square g/g. An overall increase in PCB concentration with depth is observed from 0-50 cm. The maximum concentration captured by this core is 128 ± 5 nmol/g (33 ± 1 \square g/g) at 45-50 cm. The total PCB concentration approaches zero in the final fraction of this core, implying that the entire PCB profile was captured.

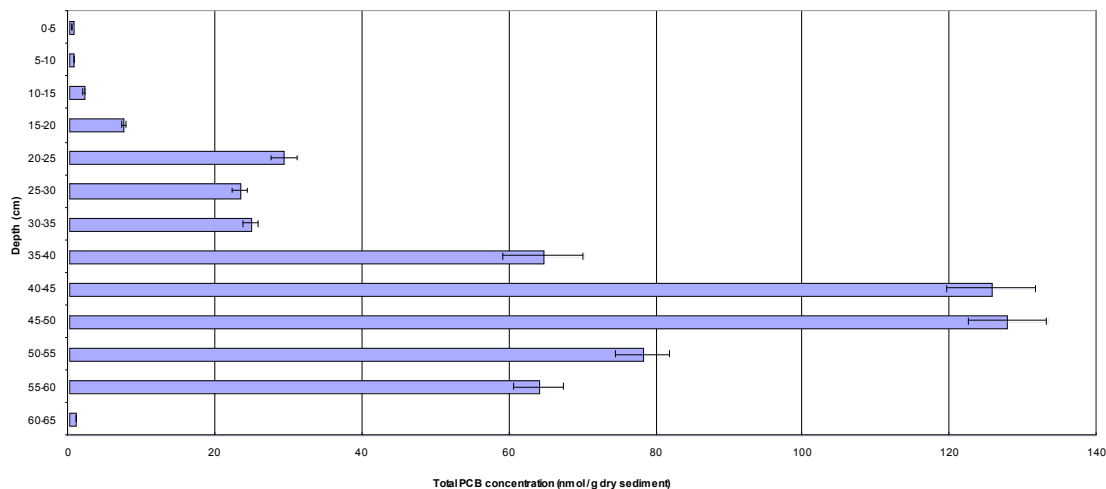


Figure 15. G33 PCB concentration depth profile. Error bars denote total analytical error for extraction 1 data.

The homolog mol% distributions for each G33 fraction are shown in Figure 16. The average chlorines per biphenyl and % *ortho* chlorine profiles for G33 are shown in Figures 17 and 18, respectively. It should be noted that all chlorine distribution metrics are susceptible to large errors at very low (i.e., $< 1 \mu\text{g/g}$) total PCB concentrations. As individual congener concentrations approach their quantification limits, the concentrations of those congeners that are quantified can dominate chlorine distribution parameters. This results from variations in congener GC-ECD responses, which are magnified as concentrations approach the quantification limits of the analytical method. Therefore, the reliability of all chlorine distribution metrics may be low for G33 fractions in the ranges of 0-15 cm and 60-63 cm.

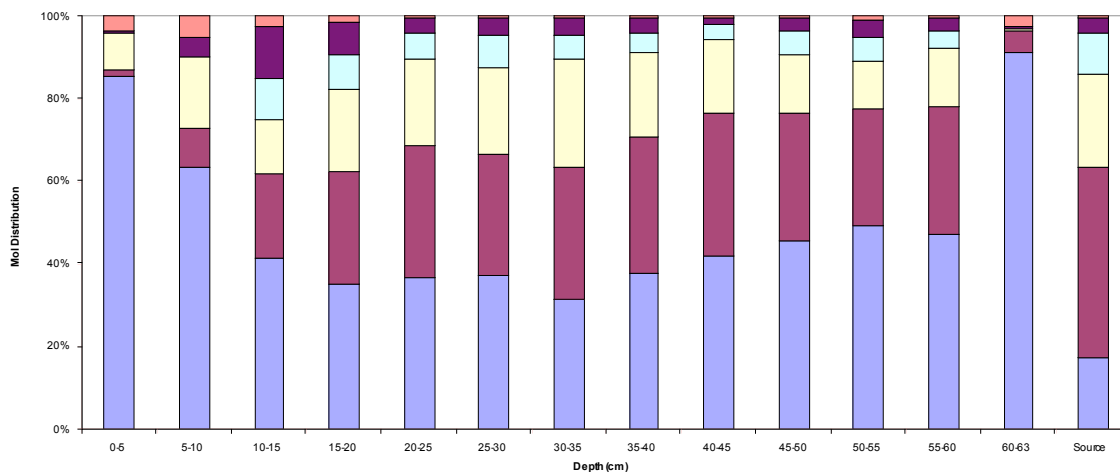


Figure 16. G33 homolog by mole percentage distribution. Source refers to a 4:1 mixture of Aroclor 1016 and 1254, respectively.

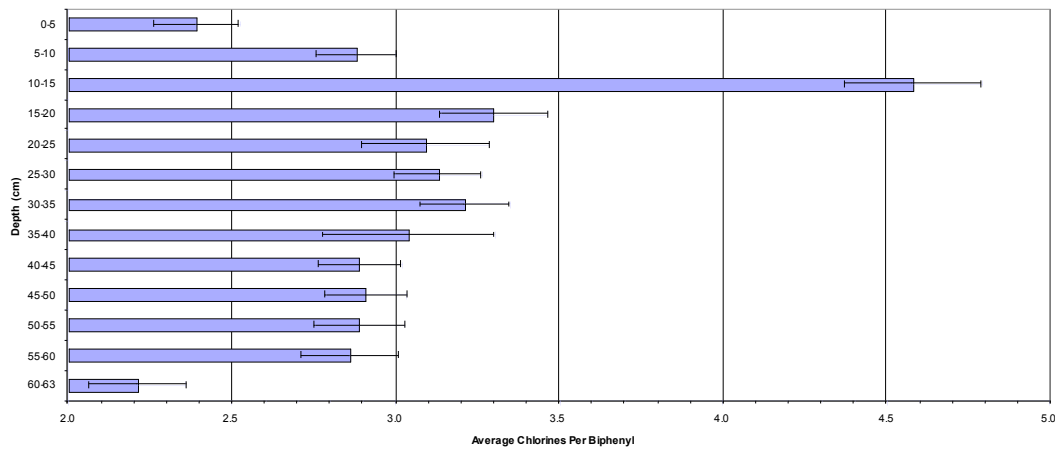


Figure 17. G33 chlorine per biphenyl with depth. Error bars denote total analytical error.

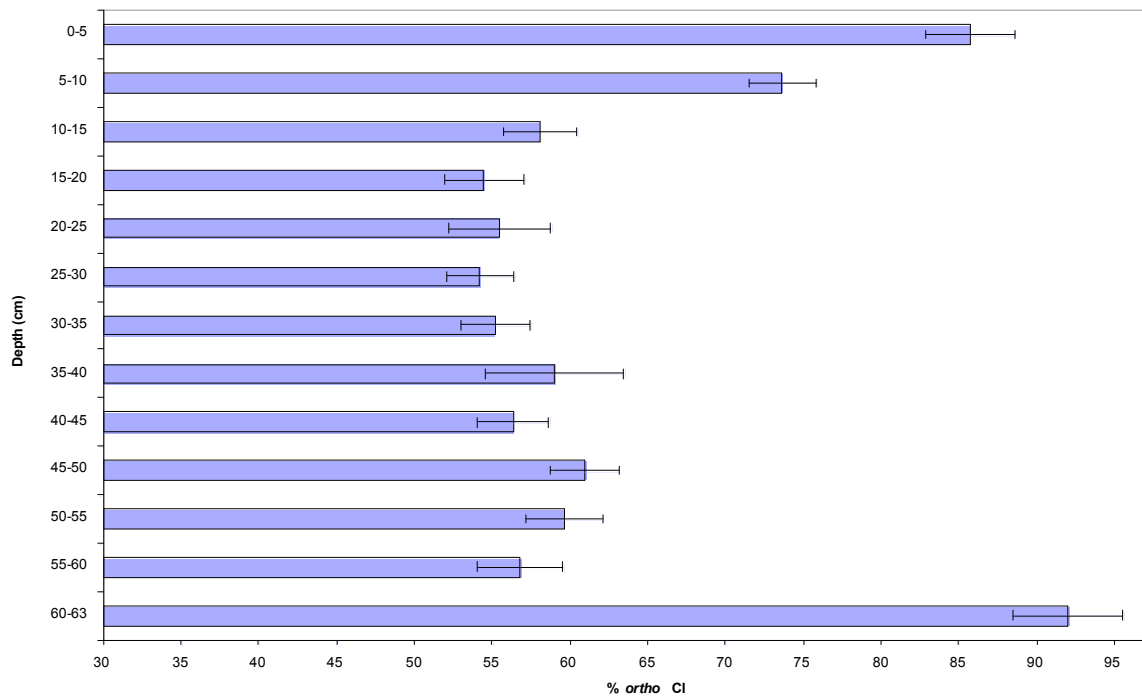


Figure 18. G33 percent *ortho* chlorine with depth. Error bars denote total analytical error.

It is evident from Figure 16 that all G33 fractions are enriched in dichlorinated congeners relative to the original source composition. A slight increase in the di-homolog group from 30-55 cm is observed. A minor decrease in Cl/biphenyl from 3.21 to 2.86 is shown over the same depths (Figure 17). The % *ortho* chlorine values across these depths hover near 57% (Figure 18); a statistically significant change in % *ortho* chlorines from 30-55 cm is not observed. These data are considered modest evidence in support of reductive dechlorination at this site.

The congener distribution for the near surface sediment at G33 is shown in Figure 19. Of note is the predominance of three congeners, PCB 4 (2-2), 10 (26) and 48 (245-2). Each of these congeners has two *ortho* chlorines and are of low relative toxicity among all PCBs (Safe, 1992).

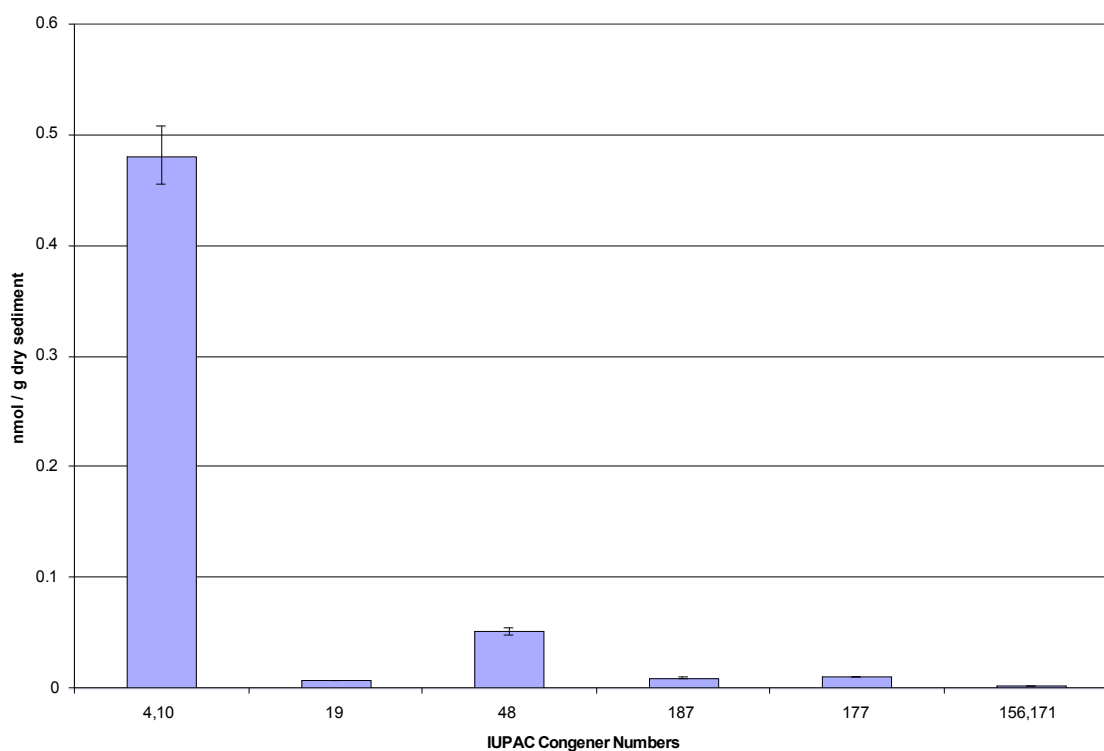


Figure 19. G33 (0-5 cm) congener distribution as mole percentage. Total PCB concentration equals 0.133 μ g/g.

The congener distribution from 40-45 cm, representing the highest PCB levels measured in the G33 core, is shown in Figure 20. Congeners with four or less chlorines comprise most of the PCB mass in this sample. Reductive dechlorination processes may be responsible for the low levels of higher chlorinated congeners in this fraction. The congener-specific profile for 40-45 cm (Figure 20) is representative of all samples from 35-63 cm. Congener-specific results for all G33 fractions are compiled in Sivey (2005). These results are evidence of a reductive dechlorination plateau phase, as proposed by

Pakdeesusuk et al. (2005). It may be argued that *in situ* biochemical weathering is not the only possible explanation for these congener-specific results. A less probable explanation is the deposition of PCB-contaminated sediment over a span of several years with extremely similar congener signatures resulting from *upstream* biochemical weathering processes. Further evidence in support of the *in situ* reductive dechlorination hypothesis is presented in the discussion of historical trends that follows.

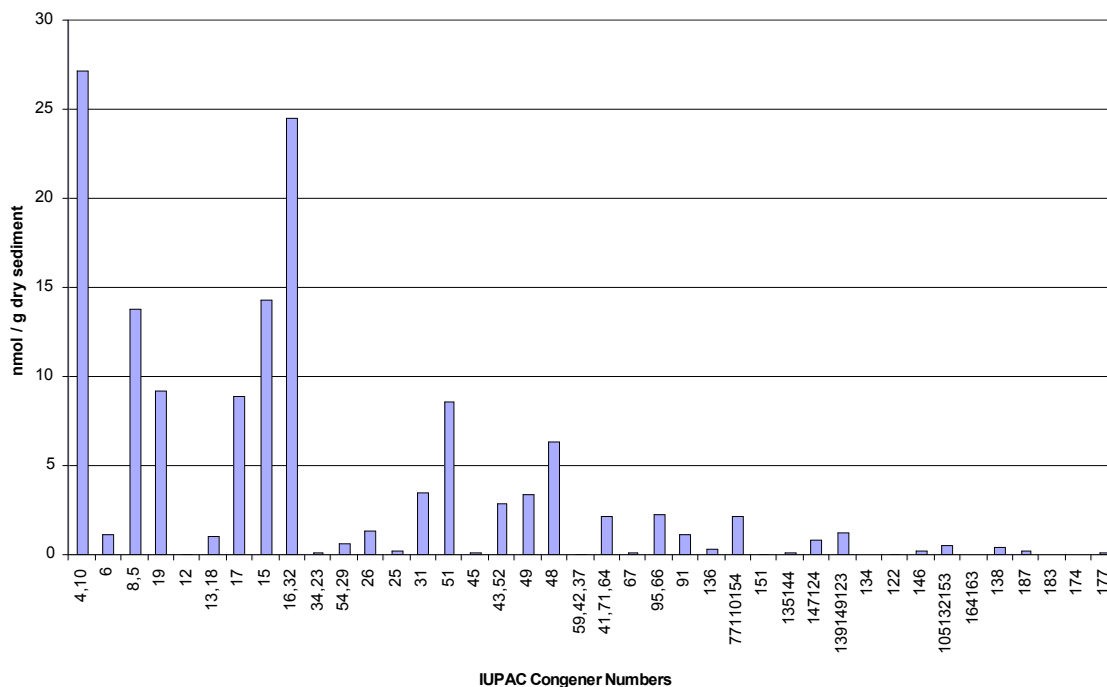


Figure 20. G33 (40-45 cm) congener distribution as mole percentage. Total PCB concentration equals 32.7 μ g/g.

Total PCB depth profiles for G33 samples collected in 1987 (Germann, 1988), 1998 (Pakdeesusuk et al., 2005) and 2004 (the current work) are shown in Figure 21. All three cores captured approximately the entire PCB profile at this site. Consistent decreases in PCB levels at the sediment-water interface from 1987 to 2004 are observed. If the decrease in PCB concentration in near-surface sediments is assumed to be uniform between 1998 and 2004, this site became compliant with the EPA clean-up requirement of 1 μ g/g in 2002.

An evaluation of the maximum PCB concentration depths of each profile can be used to estimate the average sedimentation rates between sampling dates (Pakdeesusuk et al., 2005). The results of these calculations are shown in Table 2.

Table 2. Average sedimentation rates for G33.

Time Period	Average Sedimentation Rate (g/cm ² /yr)
1987 – 1998	5.2 ± 0.6
1998 – 2004	6.5 ± 1.1
1987 – 2004	5.7 ± 0.4

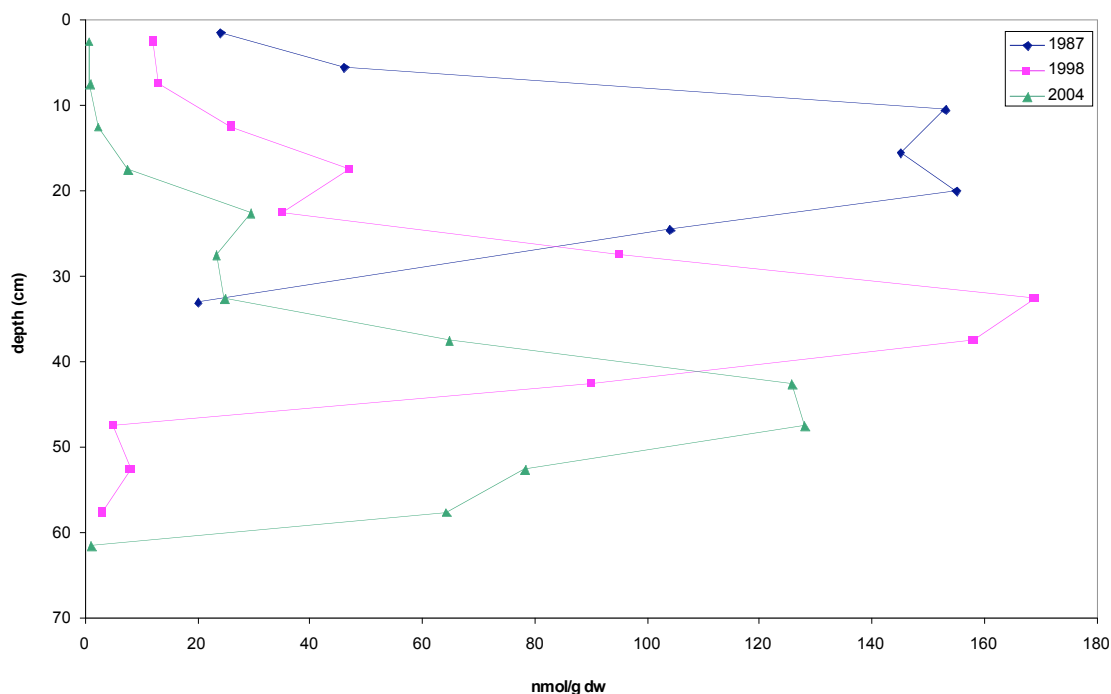


Figure 21. Historical trends in G33 total PCB concentrations.

Others have reported G33 average sedimentation rates at 1.8 ± 0.6 g/cm²/yr (Brenner et al., 2004) and 4.7 g/cm²/yr (Pakdeesusuk et al., 2005). The currently reported sedimentation rates agree with those reported by Pakdeesusuk et al. (2005), but are significantly higher than those reported by Brenner et al. (2004) for 2001 radioisotope data.

Knowledge of average sedimentation rates affords the assignment of equivalent depths for each sampling date. The results of this assignment are compiled in Table 3. Computing total moles of PCBs for the equivalent depths yields an estimation of

the total PCB load captured by each core segment common to all sampling dates. The results of these calculations are shown in Table 4.

Table 3. G33 equivalent depths. 1987 and 1998 data from Pakdeesusuk (2002) and 2004 data from the current work.

Equivalent Depth	1987 depth (cm)	1998 depth (cm)	2004 depth (cm)
1	0-3	20-25	30-35
2	3-8	25-30	35-40
3	8-13	30-35	40-45
4	13-18	35-40	45-50
5	18-22	40-45	50-55
6	22-27	45-50	55-60

Table 4. G33 historical mass balance. 1987 and 1998 data from Pakdeesusuk (2002) and 2004 data from the current work.

Sampling Date	Actual Depth (cm)	Total PCBs (μmol)
1987	0-27	119.4 \pm 6.7
1998	20-50	124.4 \pm 6.9
2004	30-60	109.4 \pm 6.1

Given that total PCB measurements for the employed methods have an average total error on the order of $\pm 6\%$, no significant change in total PCBs is observed from 1987 to 1998. A modest decrease in total PCBs is reported from 1998 to 2004, but this result may be a caveat of the fractionation length of sediment cores (5 cm). If, for instance, cores were segmented every 2 cm, this decrease may prove to be statistically insignificant. Overall, the *molar* concentrations of PCBs are not decreasing or are decreasing slightly as a function of time at this site. These results support the use of total PCBs as a conservative tracer in sediment systems like Lake Hartwell (Pakdeesusuk et al., 2005).

The average chlorines per biphenyl profiles for all three sampling years are shown in Figure 22. Chlorine distributions (as % *ortho* chlorine) for the three sampling dates are shown in Figure 23. As previously mentioned, all chlorine distribution metrics are susceptible to large errors at low total PCB concentrations, such as those found from 0-15 cm and 60-63 cm in the 2004 core. Unlike the 1987 and 1998 samples, the average degree of PCB chlorination at the sediment-water interface in 2004 is much lower than the original source composition. These results imply a high degree of PCB weathering prior to deposition at site G33. In the sections of the cores with the highest PCB levels, Cl/biphenyl and % *ortho* Cl values converge near 2.8 and 60%, respectively, with increasing depth.

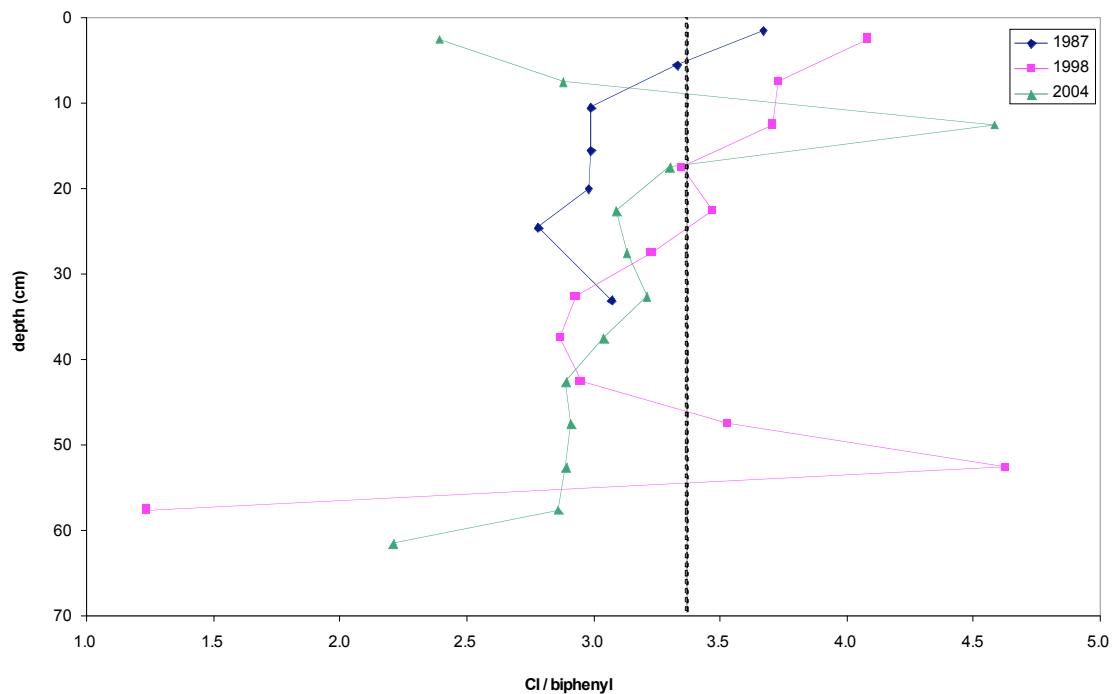


Figure 22. Historical trends in G33 chlorines per biphenyl. The dashed line denotes the original source composition (4:1 mixture of Aroclors 1016 and 1254).

An examination of chlorine distribution parameters on the basis of equivalent depths can be a useful tool for the determination of *in situ* transformation processes, including reductive dechlorination. Such an evaluation assumes that no mixing or PCB mass transport between equivalent depths has occurred. The equivalent depths are modeled as pseudo-closed systems with respect to PCBs. Historical trends in average chlorines per biphenyl and % *ortho* chlorines for the six equivalent depths in G33 (Table 3) are outlined in Figures 24 and 25, respectively. The general trends over time are for decreasing Cl/biphenyl and increasing % *ortho* chlorines. These results suggest that *in situ* reductive dechlorination has occurred at this site, in agreement with the microcosm studies performed by Pakdeesusuk et al. (2003b) using G33 sediment.

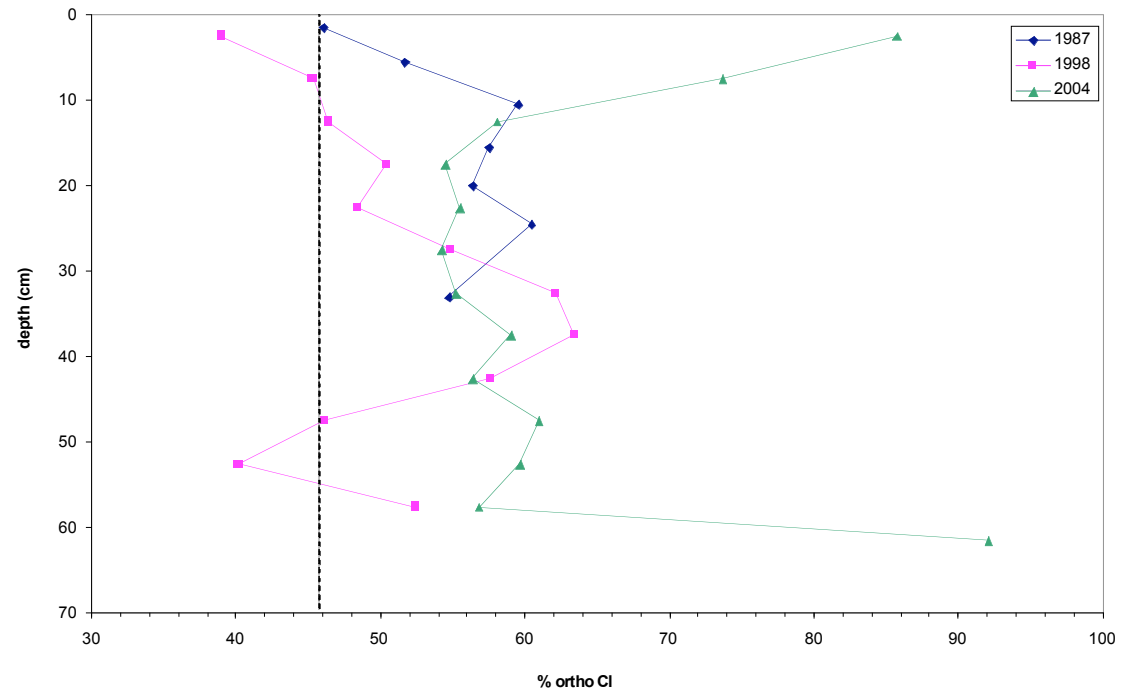


Figure 23. Historical trends G30 *ortho* percentages. The line denotes the original composition of the source (4:1 mixture of Aroclors 1016 and

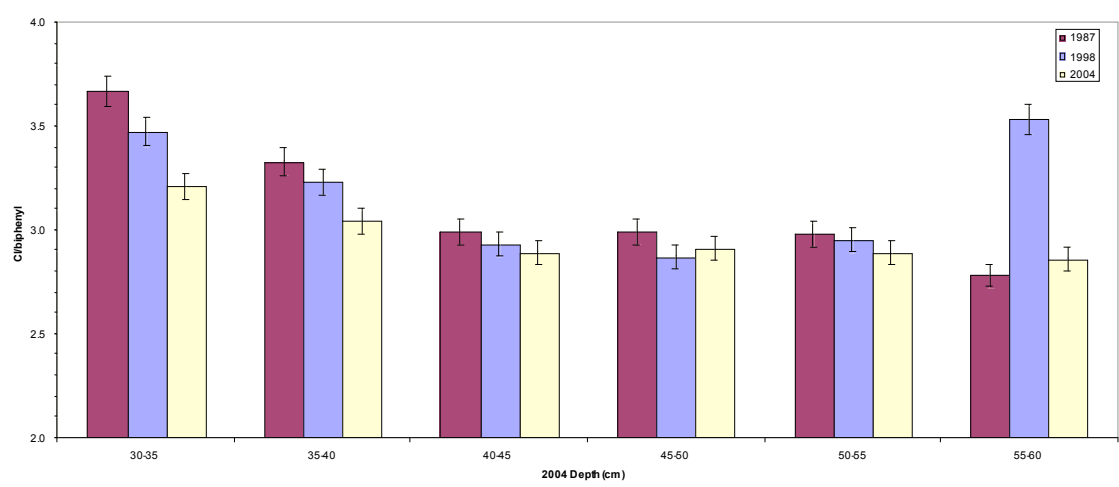


Figure 24. Historical trends in average chlorines per biphenyl for equivalent depths at G33. Error bars denote the error between the two analytical methods used to obtain 2004 (Sivey and Brothersen, 2005) and pre-2004 (Germann, 1988) data.

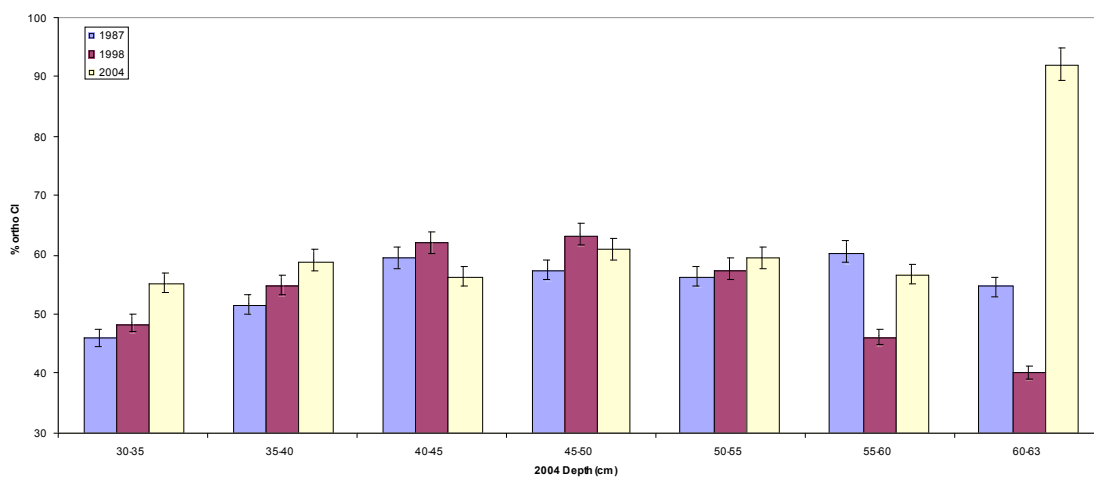


Figure 25. Historical trends in percent *ortho* chlorines at G33. Error bars denote the error between the two analytical methods used to obtain 2004 (Sivey and Brothersen, 2005) and pre-2004 (Germann, 1988) data.

Congener-specific historical trends for equivalent depth 4, which corresponds to the highest total PCB concentrations in each core, are shown in Figure 26. The only consistent trend over all sampling dates is the steady increase in mol% of PCB 47, 48 and 75. All three of these congeners are tetrachlorinated biphenyls. Without evidence of other consistent trends, these congener data are inconclusive regarding reductive dechlorination processes at this site. Analogous congener-specific graphs for all six equivalent depths at G33 are compiled in Sivey (2005).

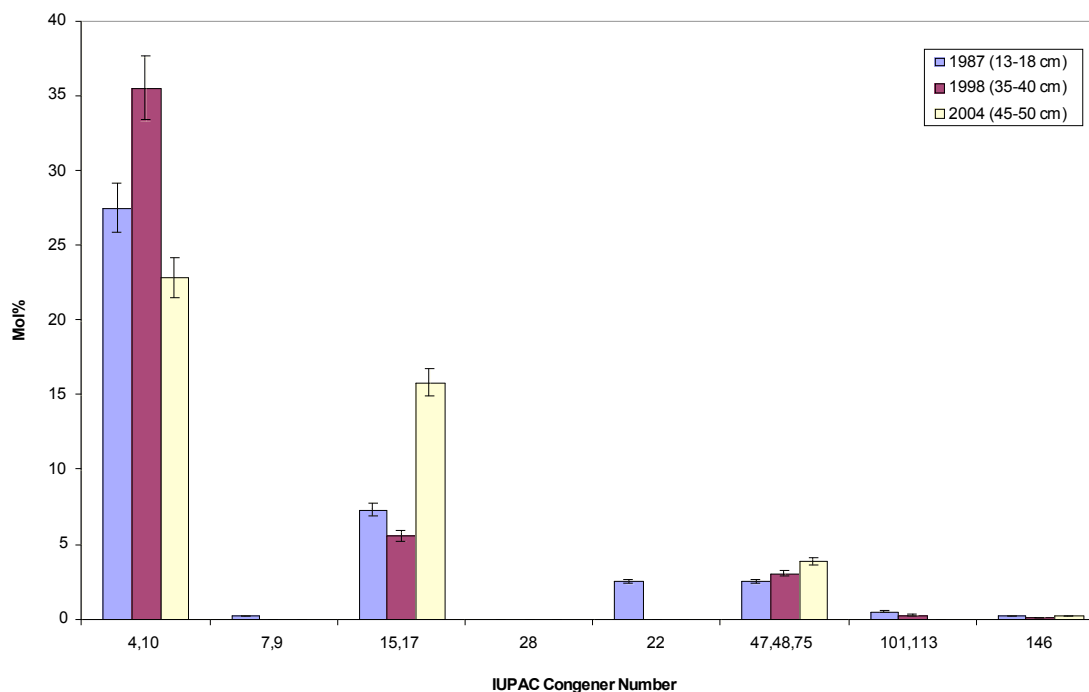


Figure 26. Historical trends for selected congeners in G33 equivalent depth 4. Error bars denote the error between the two analytical methods used to obtain 2004 (Sivey and Brothersen, 2005) and pre-2004 (Germann, 1988) data.

G30 Chiral Results

Three chiral congeners (PCB 91, PCB 95, and PCB 149) were detected in the G30 core that was collected in 2004 (Figure 27). At some depths, achiral analysis indicated measurable quantities that were not detected in the chiral analysis (Figure 28).

The EF for each of the three chiral congeners was less than 0.500 at all depths at which they were detected. This observation supports earlier studies that indicated that bioprocessing of the PCBs has occurred in the sediments since the time of introduction of the Arochlor mixtures to Twelve Mile Creek and Lake Hartwell (Farley et al., 1994; Pakdeesusuk et al., 2003a; Bzdusek et al., 2006). At the time of introduction (1955-1976) it is assumed that the chiral congeners were present as racemates with an EF of 0.5. The manufacturing process produces racemates and the handling of PCBs during the production of capacitors and other products would not change the EF.

The changes in EF with depth tended to decrease with an increase in depth for PCB 91 and PCB 95 (Figure 27). The EF of PCB 91 was at a maximum at 32.5 cm and decreased to a minimum at the deepest sample (52.5 cm). The EF of PCB 95 was at a

maximum at 17.5 cm and decreased to a minimum at 32.5 cm with a slight increase to 52.5 cm. The changes in EF for PCB 149 are slight but do reach a minimum at 52.5 cm.

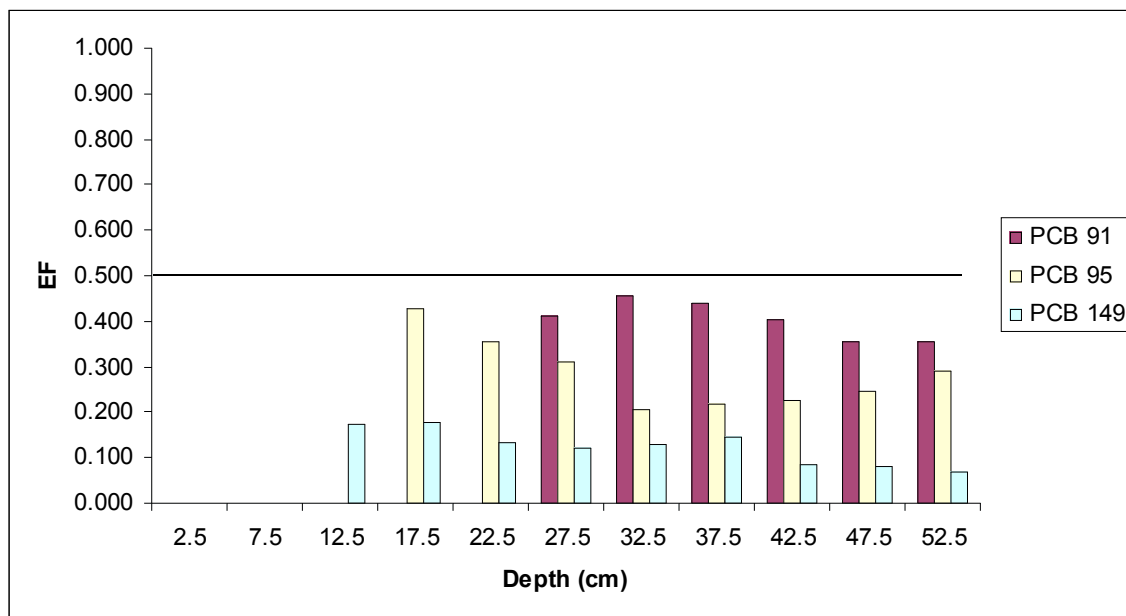


Figure 27. EF values with depth in G30. The line indicates the racemic value of 0.500.

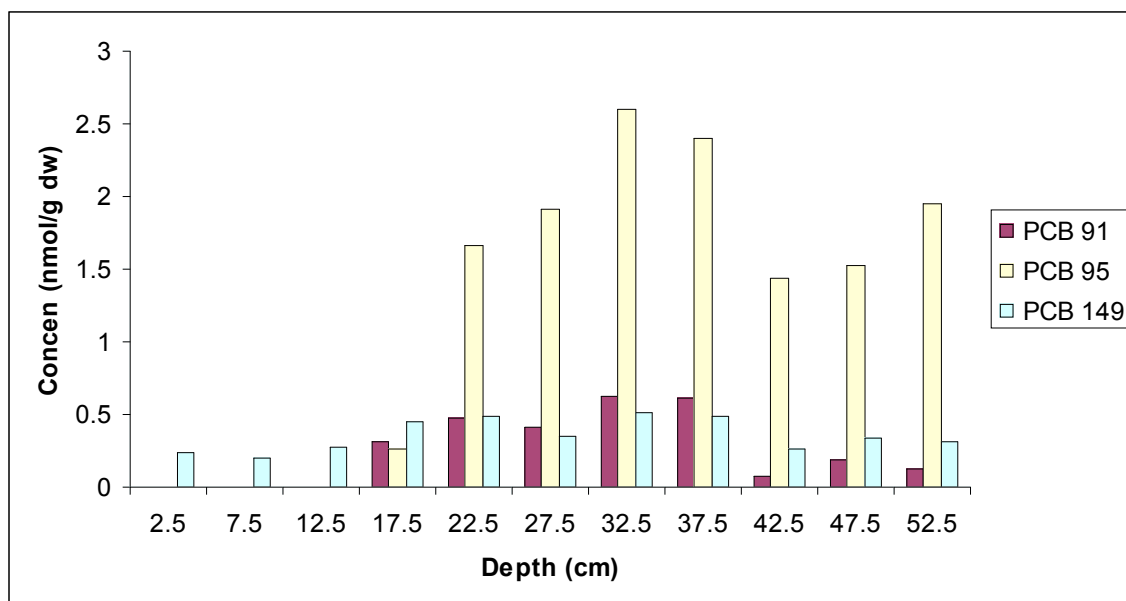


Figure 28. Concentrations of chiral congeners with depth for G30.

The EF values of less than 0.5 indicate that the enantiomer that elutes first on the Chirasil-Dex column is depleted relative to the second eluting enantiomer. For the Chirasil-Dex column, it is known that for PCB 149 the first enantiomer is the negative one (i.e., it rotates a plane of polarized light in a counterclockwise direction) (Wong et al., 2001a). The elution order for the enantiomers of PCB 91 and PCB 95 is unknown.

The changes in EF cannot be easily explained by changes in the concentrations of the congeners with depth. The maximum concentrations occur between 30 and 40 cm below the sediment-water interface, which is where the maximum total PCB concentrations are observed (Figure 5). It should be noted that PCB 95 coelutes with PCB 66 and PCB 149 coelutes with PCB 139 and PCB 123. PCB 91 does not coelute with any other congeners. Concentrations were not corrected because the trend is of interest not the absolute values.

Historical changes in EF at the G30 location are shown for one equivalent depth in Figure 29. In 1987, all congeners except PCB 95 had EF values close to racemic (Wong et al., 2001a). About a decade later in 1998, PCB 91 had a dramatic change in EF to a value greater than 0.5 and PCB 95 continued to decrease (Garrison et al., 1999). PCB 136 had an increase to greater than 0.6. The EF values greater than 0.5 for PCB 91 and PCB 136 indicated that the second eluting enantiomer was degraded at a faster rate than the first one. For PCB 136, the positive enantiomer has been identified as second in elution order for the Chirasil-Dex column (Haglund and Wiberg, 1996). The EF values for PCB 132 and PCB 149 remained near 0.5. In 2004, EF values for PCB 132 and PCB 136 were not quantified with the chiral GC analysis. Of the three chiral congeners that were quantified PCB 95 showed little change while both PCB 91 and PCB 149 showed dramatic changes. The EF value of PCB 91 changed from greater than 0.5 to less than 0.5. PCB 149 had an EF value markedly less than 0.5.

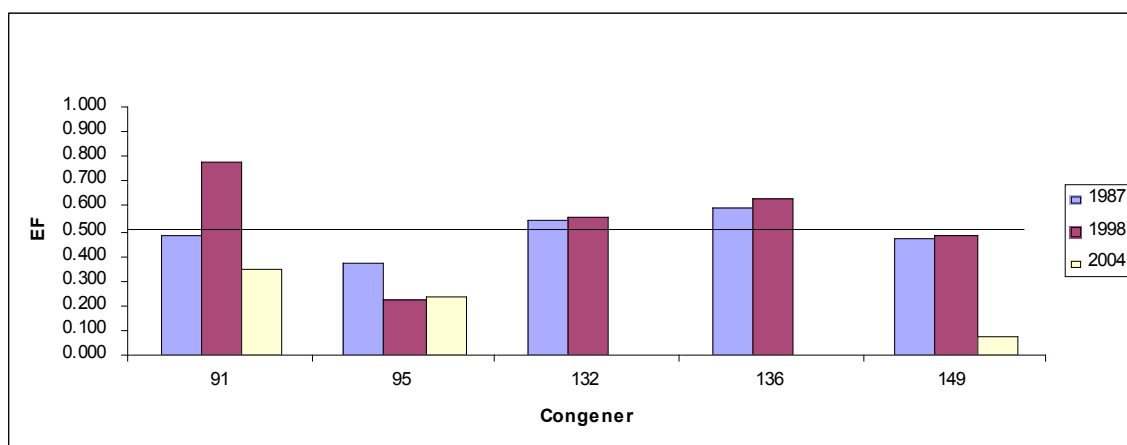


Figure 29. Historical changes in EF Values for G30. (1987, 22-27 cm; 1998, 45-50 cm; 2004, 45-50 cm). The line indicates the racemic value of 0.500.

Earlier microcosm studies may shed some light on the historical changes in EF values. Pakdeesusuk et al. (2003b) spiked PCB 132 and PCB 149 into microcosms inoculated with sediment from the G30 and G33 locations. Through the incubation period (254 to 350 d), the EF values for the spiked chiral congeners did not change. However, the product of the first dechlorination product for PCB 132 and PCB 149 did show changes in the EF with time. They both maintained an EF of about 0.5. The first appearance of PCB 91, which is the first dechlorination product of PCB 132, had an EF of less than 0.5 (0.42 in G30 and 0.26 in G33). It continued to decrease until it was less than 0.1 after 166 days of incubation. PCB 95, the first product of PCB 149, also showed an EF of less than 0.5 (0.37 in G30). The EF of PCB 95 continued to decrease to about 0.1 by 350 days of incubation. Therefore, the changes that were observed in EF values in the G30 field samples from 1987, 1998, and 2004 are not surprising except for the EF greater than 0.5 (0.78) for PCB 91 in 1998. Perhaps the microbial community changed at this depth in 1998 to favor the dechlorination of the second eluting enantiomer. Given the available data, that explanation is speculative.

It is important to note that PCB 91 is a likely product of dechlorination of other congeners including PCB 139 and PCB 149 (Wong et al., 2001a). PCB 95 is also a product of dechlorination of PCB 135 and PCB 144 (Wong et al., 2001a). Therefore, the concentrations of these are expected to increase as higher chlorinated congeners are dechlorinated. Also both occur at relatively high weight percentages in the estimated discharged Aroclor mixture of 1016 and 1254 (4:1) (Sivey, 2005). Therefore, these congeners are good markers to follow in future monitoring of Lake Hartwell sediment using chiral analysis. In turn, both are also dechlorinated to other products. In the microcosm studies, PCB 91 was rapidly dechlorinated to form PCB 51 and PCB 95 formed PCB 53 at a relatively slower rate (Pakdeesusuk et al., 2003b). Over the time period considered, concentrations of PCB 91 decreased and increased for PCB 95 at this depth (data not shown).

The change in the EF of PCB 149 in 2004 was surprising given the microcosm results of Pakdeesusuk et al. (2003b) and the lack of change observed from 1987 to 1998 (Wong et al., 2001a; Garrison et al., 1999). There are two possible explanations. One is that the lag time required for the microorganisms to induce the specific enzymes for dechlorination of PCB 149 is quite long and requires certain conditions. The other possibility is that the change in EF resulted from dechlorination of higher chlorinated congeners to form PCB 149. PCB 174 and PCB 183 are candidate congeners that would form PCB 149 upon dechlorination.

The data collected in 2004 and 1998 indicate that the changes observed in the EF for PCB 149 occurred throughout the length of the G30 core (Figure 30). (Data are not available for other depths for the core collected in 1987.) There was little sedimentation at this location, therefore, the depths in the 1998 core are the same as in the 2004 core. The change in magnitude is similar at all depths. The consistency with depth would tend to discount any explanation based on residence time because the PCBs were deposited at different times. Based on dating with lead-210 and cesium-137, Brenner et al. (2004)

reported dates of deposition for the 40 cm depth as around 1975 and for the 20 cm depth around 1989 for a core collected in 2000 in a location similar to G30.

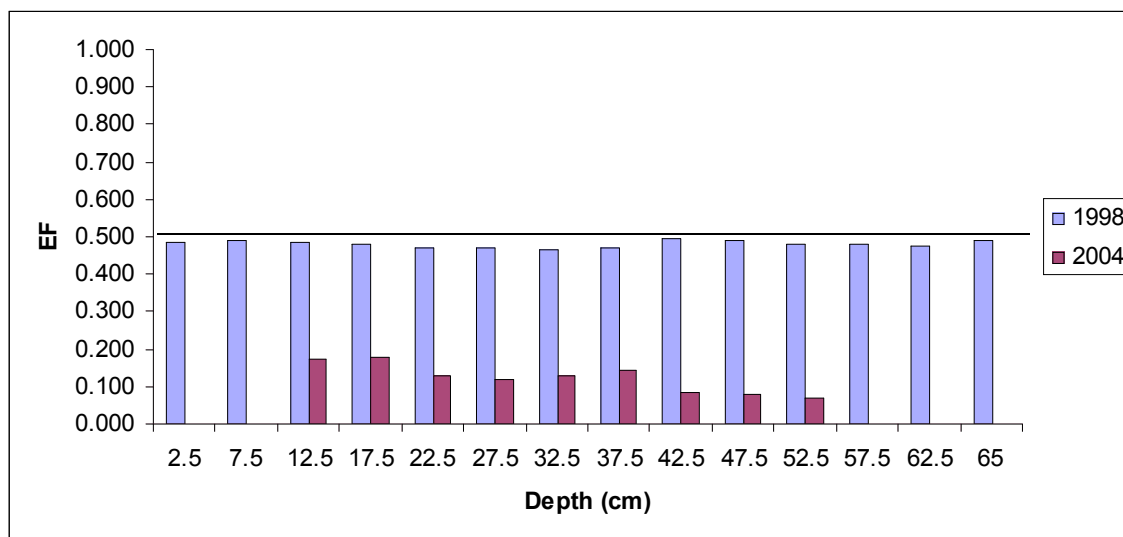


Figure 30. PCB 149 EF values with depth for G30 from 1998 to 2004. The line indicates the racemic value of 0.500.

The changes in EF with depth between the two time points for PCB 91 and PCB 95 are not as consistent (Figures 31 and 32). For PCB 91 (Figure 31), the EF values decreased in 2004. The 1998 EF values tended to increase with depth and were greater than 0.5. This trend appeared to coincide with increasing concentrations of total PCBs with depth. By 2004, the EF values were all less than 0.5, indicating a change in preference for dechlorination of the enantiomers. This reversal of apparent preference for enantiomers was observed in soil microcosms for PCB 84, PCB 95, and PCB 149 (Hall, 2005).

The EF for PCB 95 decreased with depth in 1998 (Figure 32) and also reflected increased concentrations of total PCBs with depth. By 2004, only a few of the depths showed a continued decrease in EF for PCB 95. Most of the samples had little to any change in EF. For both time periods, EF values were less than 0.5.

The achiral results for G30 showed evidence of slowing dechlorination or a plateau of inactivity. The chiral data supports a plateau after 1998 when considering the PCB 95 results. However, the changes in EF for PCB 91 and PCB 149 indicate that further dechlorination was occurring. The results are not necessarily contradictory because the chiral analysis considers only a few congeners while the achiral analysis considers about 100 congeners. The bulk indicators of total PCBs, chlorines per biphenyl, and percent *ortho*-chlorines may obscure activity with individual congeners.

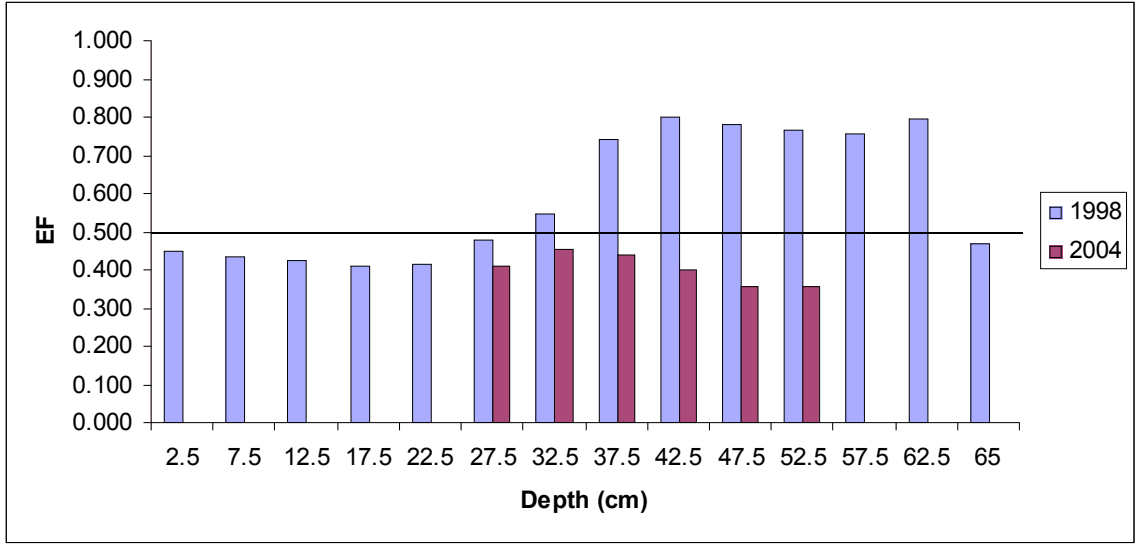


Figure 31. PCB 91 EF values with depth for G30 from 1998 to 2004. The line indicates the racemic value of 0.500.

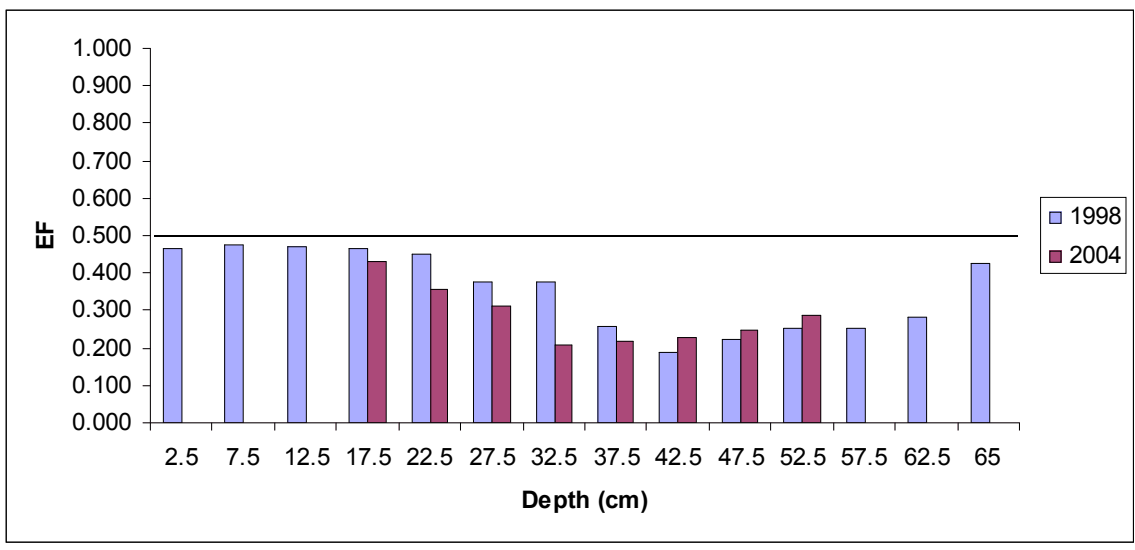


Figure 32. PCB 95 EF values with depth for G30 from 1998 to 2004. The line indicates the racemic value of 0.500.

G33 Chiral Results

The EF values for three chiral congeners (PCB 91, PCB 95, and PCB 149) were quantified for the G33 core collected in 2004 (Figure 33). The maximum in the concentrations of the congeners occurred between 40 and 50 cm (Figure 34). For most depths where achiral analysis measured concentrations of the three congeners, chiral analysis quantified EF values. In some cases, chiral analysis returned EF values where achiral analysis did not measure concentrations above the detection limits.

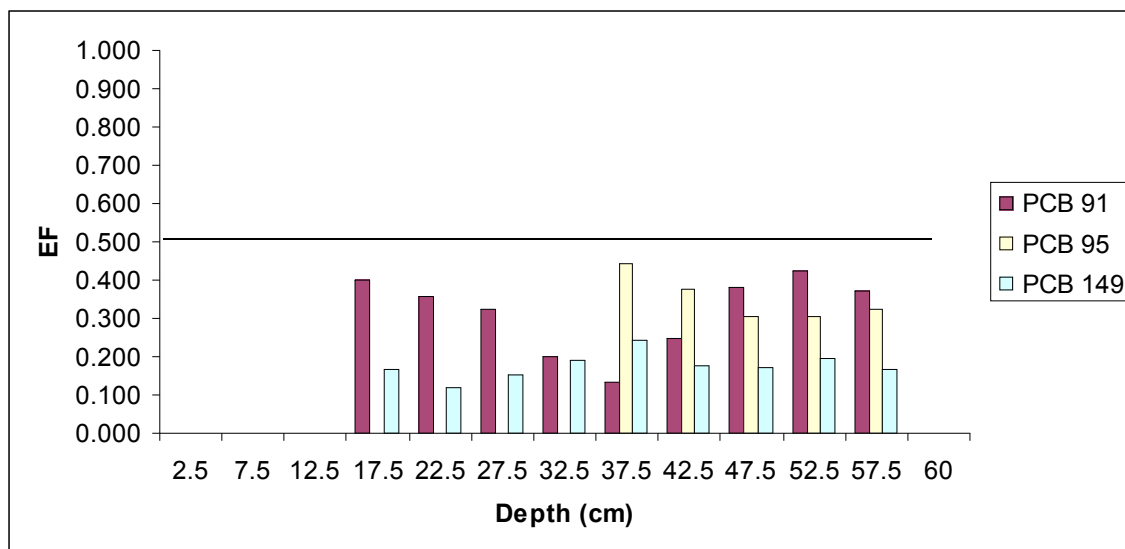


Figure 33. EF values with depth in G33. The line indicates the racemic value of 0.500.

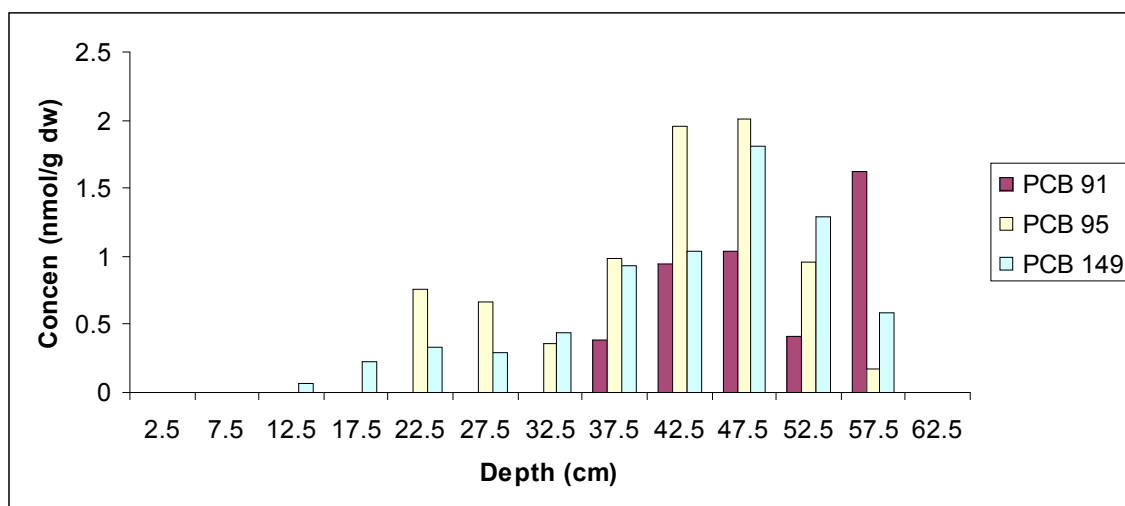


Figure 34. Concentrations of chiral congeners with depth for G33.

The EF values for all the chiral congeners (Figure 33) were less than 0.5 for all depths as was observed for G30 core. These values are indicative of bioprocessing occurring in the sediments to dechlorinate highly chlorinated PCBs and produce less chlorinated PCBs. These findings support earlier research (Farley et al., 1994; Pakdeesusuk et al., 2003a; Bzdusek et al., 2006). The concentrations of the three congeners follow the trends observed for total PCBs (Figure 5).

The EF of PCB 91 steadily decreased from its first appearance at 17.5 cm to its minimum (0.134) at 37.5 cm. It increased from the minimum to the deepest portion of the core. The changes in EF for PCB 91 in the G30 core were distinctly different with a maximum occurring in the middle of the core. The EF of PCB 95 was quantified first at 37.5 cm. It decreased to a minimum of 0.306 at 47.5 cm and maintained similar values through the remainder of the core. The changes observed in the G30 core differed with the minimum near the middle of the core and an increase towards the deeper part. The EF of PCB 149 did not exhibit any particular increasing or decreasing trend. It reached a minimum of 0.118 at 22.5 cm and a maximum of 0.245 at 37.5 cm. The changes in EF with depth for PCB 149 were similar to the changes observed in the G30 core.

Historical changes in EF from 1987 to 2004 for one equivalent depth at the G33 site are shown in Figure 35. The EF values measured in 1987 are close to the racemic value (Wong et al., 2001a). The 1998 values of EF are similar in all cases to the previous measurement (Garrison et al., 1999). In 2004 the EF decreased for PCB 95 and PCB 149, while it did not change greatly for PCB 91. The EF for PCB 136 was not quantified.

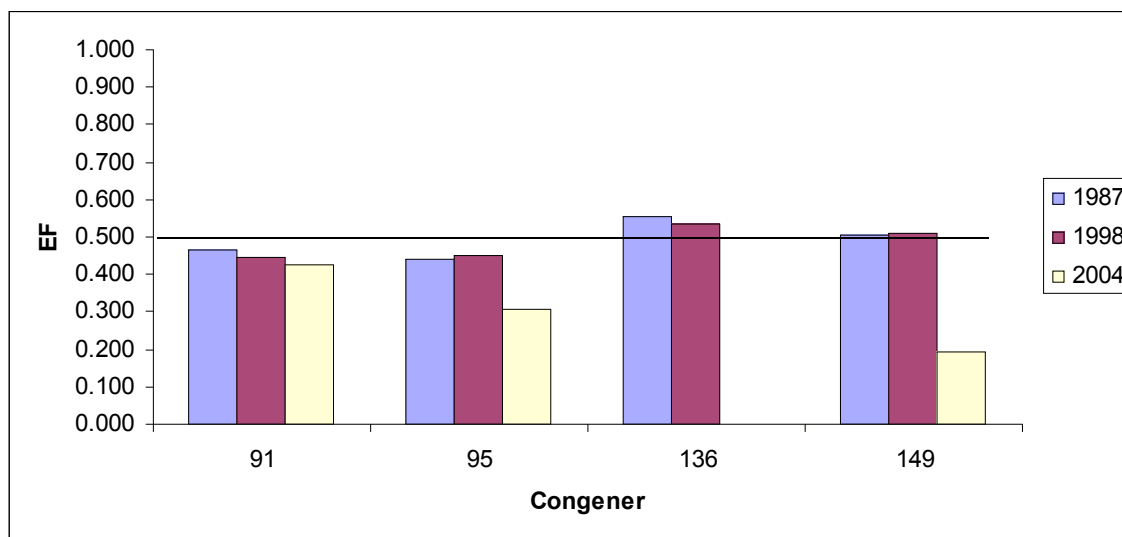


Figure 35. Historical changes in EF Values for G33. (1987, 18-22 cm; 1998, 40-45 cm; 2004, 50-55 cm). The line indicates the racemic value of 0.500.

The changes in EF with time are similar for PCB 149 and PCB 136 in both the G33 and G30 cores. However, the changes in EF for PCB 91 are strikingly different. In the G30 core, the 1998 measurement was greater than 0.5 and the 2004 EF was less than 0.5 (Figure 29). For the G33 core, the EF slightly decreases across the three time points and is always less than 0.5. The EF for PCB 95 decreased in 1998 and remained essentially the same in 2004 for the G30 core. In the G33 core, the first decrease was observed in 2004 with similar values in the 1987 and 1998.

Perhaps the differences in behavior can be attributed to differences in the microbial communities at the two different locations. The laboratory microcosm study by Pakdeesusuk et al. (2003a) found that in the microcosms inoculated with sediment from G33 and spiked with PCB 132, only one of three microcosms was active while all three microcosms with G30 sediment were active. The concentrations of the three congeners common to all three sampling years are similar in the two locations (data not shown). The maximum concentration of total PCBs are larger in the G30 cores (Figure 11) than in the G33 cores (Figure 21). It is likely that the higher concentration of total PCBs may induce the dechlorination enzymes more effectively at the G30 site (Sokol et al., 1998).

In comparing EF changes with depth between 1998 and 2004, the 2004 depth is shown as the equivalent 1998 depth. For example, the 1998 surface was at 12.5 cm in 2004 due to sedimentation. For PCB 149, an EF was not quantified in the section that was equivalent to the 1998 surface (Figure 36). As with the G30 core, the change in the EF for PCB 149 in the G33 core with depth from 1998 to 2004 was similar (Figure 36), indicating that the change was likely not affected by residence time. The magnitude of the change is similar at all depths.

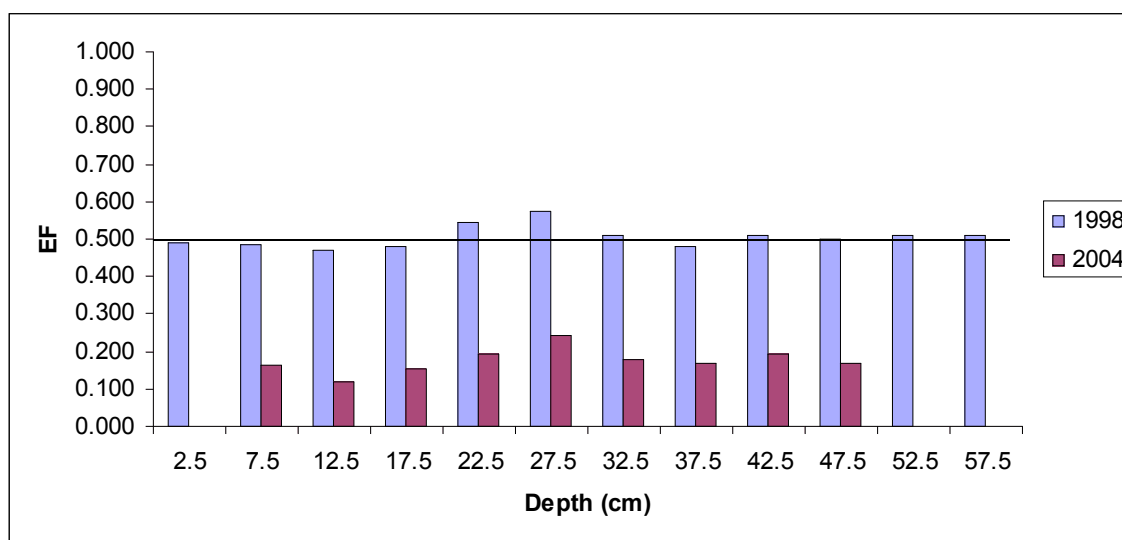


Figure 36. PCB 149 EF values with depth for G33 from 1998 to 2004. The line indicates the racemic value of 0.500.

For PCB 91, the general trend is for a decrease in EF between 1998 and 2004, but the magnitude of the change varies widely (Figure 37). The decrease in EF matches the maximum concentration of total PCBs observed for the two time points (Figure 21). The concentrations of PCB 91 decreased at every equivalent depth except 47.5 cm (data not shown). Microcosm studies indicated a rapid dechlorination of PCB 91 in a system spiked with PCB 132 which formed PCB 91 in its first dechlorination step (Pakdeesusuk et al., 2003a).

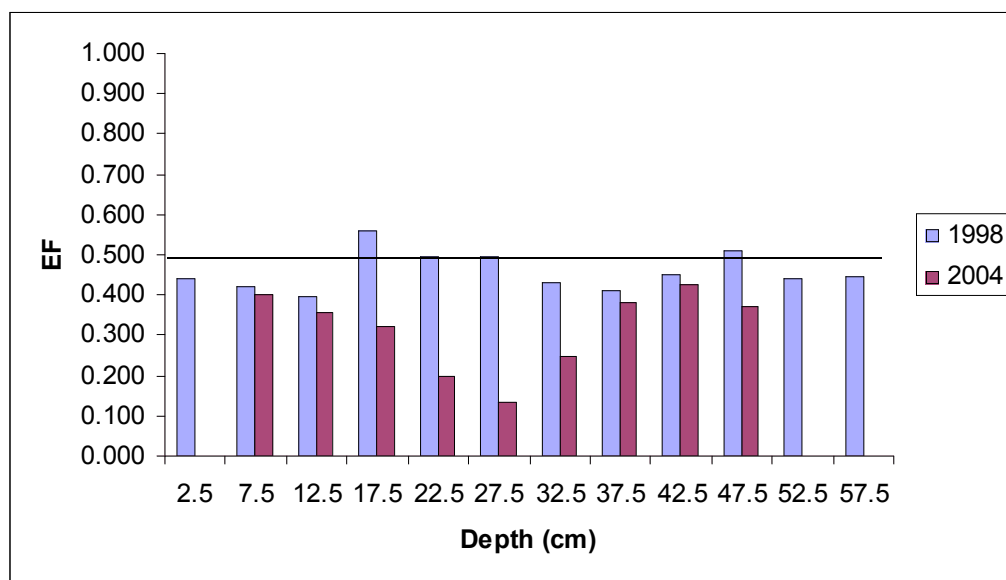


Figure 37. PCB 91 EF values with depth for G33 from 1998 to 2004. The line indicates the racemic value of 0.500.

The change for PCB 95 across the two sampling dates for the five equivalent depths is markedly different (Figure 38). The EF increases at 27.2 and 32.5 cm and clearly decreases from 37.5 to 47.5 cm. Apparently, the preference for dechlorination of the enantiomers changed at the 27.5 and 32.5 cm depths between the two collection times. The reversal in preference has been observed for PCB 95 in a soil environment (Hall, 2005). The concentrations of PCB 95 increased in 2004 at each 1998 equivalent depth (data not shown). If the changes in the EF for PCB 149 resulted in formation of PCB 95, which is a probable first dechlorination product of PCB 149, then the increase in concentration might be accounted for in the process.

From the changes in EF with depth and time, there is evidence of on-going dechlorination activity at the G33 location, which supports the observations made with achiral analysis. The bulk parameters such as total PCBs, chlorines per biphenyl, and percent *ortho*-chlorines indicated that biodegradation was continuing between 1987 and 2004.

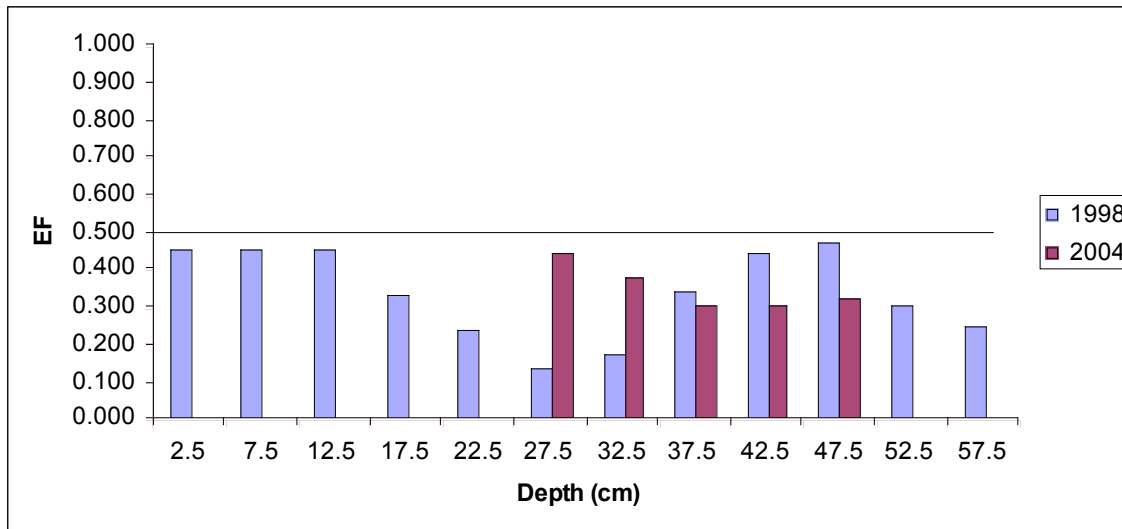


Figure 38. PCB 95 EF values with depth for G33 from 1998 to 2004. The line indicates the racemic value of 0.500.

Conclusions

Achiral congener-specific and chiral PCB analyses were conducted for sediment samples obtained in 2004 at sites G30 and G33 in Lake Hartwell, SC. Total PCB concentrations in near-surface sediments exceed the EPA clean-up criterion of 1 $\mu\text{g/g}$ at G30, but not G33. The average degree of chlorination is also greater at G30. Therefore, the PCB toxicity and bioaccumulation potentials are likely to be much higher at G30 relative to G33. A modest decrease in PCB levels at the sediment-water interface is observed at G30 relative to the previous sampling date (1998).

A six-year average recovery rate of 0.80 ± 0.06 nmol/yr is reported for G30 surface sediments. A more rapid decrease in total PCBs is observed at G33 (1.9 ± 0.1 nmol/yr). This difference in recovery rates can be explained by a greater net sedimentation rate at G33, the deposition of less-contaminated sediment at G33, or both. Since the entire PCB profile was not captured at G30, a rigorous quantitative evaluation of sedimentation rates at this site is not possible. However, the congener signatures in the near-surface sediments suggest that significant differences exist in the deposited PCB composition between the two sites. Specifically, lower total PCB concentrations with lower degrees of chlorination have recently been deposited on G33 relative to G30. Results from the sediment-water interface at G30 also demonstrate the importance of congener-specific analyses when evaluating the toxicological risks posed by PCBs. At this site, total PCB trends give an incomplete and perhaps a misleading measure of sediment recovery. With respect to toxicity potential at G30, a shift to higher chlorinated (i.e., more toxic) congeners may negate the historical decreases in total PCB levels.

In summary, the EPA remediation plan of natural sedimentation appears to be happening with a variable degree of success at these sites. Local variations in

sedimentation rates and PCB composition of deposited sediments appear to impact the efficacy of the natural attenuation ROD. To be sure, the uniform deposition of progressively less-contaminated sediments across the entire Twelve Mile Creek arm of Lake Hartwell is an unlikely phenomenon. These local disparities are responsible for the variable recovery rates calculated for the near-surface sediments at G30 and G33.

Congener profiles at G30 and G33 and chiral analysis provide evidence of *in situ* reductive dechlorination as a likely PCB weathering mechanism at these sites. A shift to lower degrees of chlorination with concurrent increases in % *ortho* chlorines with increasing depth from the sediment-water interface was observed at both sites. Historical convergence to 2.8 average chlorines per biphenyl and 60% *ortho* chlorines with depth was also observed at both sites. Consistent with previous investigations, these trends are likely the result of *in situ* reductive dechlorination followed by a plateau phase with increasing depth (Pakdeesusuk et al., 2005). Despite the occurrence of biodegradation, historical reductions in total moles of PCBs within equivalent depths at G33 were generally not observed. An equivalent depth analysis was not possible at G30 since the entire PCB profile was not captured.

Changes in the EF values over the time period considered (1987 to 2004) for one equivalent depth in both locations support the achiral observations that reductive dechlorination occurred. Of the three chiral congeners common to all three sampling times, decreases in the EF of PCB 149 clearly pointed to continuing dechlorination between 1998 and 2004. Changes in EF with depth suggested that changes in concentrations influence dechlorination in some cases. However, they were not consistent with the three congeners measured.

Implications for Management, Research, and Policy

Negotiations about the removal of three impoundments on Twelve Mile Creek were occurring in 2006 as part of the settlement of a Natural Resources Damage Assessment action (EPA, 2004b). The removal of the impoundments will facilitate transport of additional sediment into Lake Hartwell, which will increase the sedimentation rate in the most heavily contaminated portion of Lake Hartwell (EPA, 2004b). Long-term measurements of sediment such as accomplished by this work will provide crucial information necessary for evaluation of the Record of Decision for this Superfund site. The data serve as a baseline for comparison with measurements after removal of the dams. In conjunction with other efforts measuring PCB body burdens in wildlife, the data will provide insight into the key risk drivers for the site.

Management of reservoirs requires an understanding of influence on sedimentation on the lifetime of the impoundment. The data acquired from this study as well as others will give insight into how contaminated sediment will affect decisions about dam removal and close out of reservoir systems.

Natural attenuation is an attractive alternative to more costly remediation efforts. Lake Hartwell is one of the few sites with PCB contamination where natural attenuation

has been adopted. Therefore, results from the system will influence future decisions about clean-up at other PCB-contaminated reservoirs and also at reservoirs with other contaminants that have similar physical-chemical properties.

This work also has implications for microbial reductive dechlorination as a process to decrease risk due to PCB contamination. Congener-specific analysis allows decision-makers to consider the changes in particularly toxic congeners with time. The chiral analysis provides a mechanism to evaluate changes in microbial communities that perhaps can be influenced by additions of electron donors or other nutrients.

Future Research Directions

In order to gain a more complete understanding of recovery rates in the Twelve Mile Creek, it is recommended that further sediment analyses be conducted at other sites for which historical datasets are available. Congener-specific PCB analysis of water column and local air samples would also improve the current understanding of PCB mass transport phenomena at this Superfund site, including the importance of volatilization to the overall PCB burden in Lake Hartwell. Chiral PCB analysis in all three compartments (i.e., sediment, water and air) would also assist in elucidating the transport and transformation processes occurring in this system.

In a broader context, chiral analysis of PCBs should be coordinated with laboratory studies that take advantage of molecular techniques that characterize microbial communities to understand the specific enzymes involved in removal of *meta*- and *para*-chlorines. PCB-contaminated sediment from other locales should be evaluated to understand the influence of specific geochemical conditions.

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Environmental Predictors of Mercury Methylation Potential and Fish Tissue

Basic Information

Title:	Environmental Predictors of Mercury Methylation Potential and Fish Tissue
Project Number:	2005SC15B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	3rd
Research Category:	Water Quality
Focus Category:	Toxic Substances, Hydrogeochemistry, Models
Descriptors:	None
Principal Investigators:	Alan R. Johnson, Elizabeth R. Carraway, Mark A. Schlautman

Publication

1. Pac, C.R., A.J. Jones & E.R. Carraway. 2005. Metal Toxicity to *Ceriodaphnia dubia* as a Probe of the Kinetic Lability of Metal Complexes. Society of Environmental Toxicology and Chemistry (SETAC) North America 26 Annual Meeting, Baltimore, MD (November 13-17, 2005).
2. Jones, A.J., C.R. Pac & E.R. Carraway. 2005. Alkalinity Effects on Metal Speciation and Toxicity to *Ceriodaphnia dubia* in Waters of Varying Hardness. Society of Environmental Toxicology and Chemistry (SETAC) North America 26th Annual Meeting, Baltimore, MD (November 13-17, 2005).

Project title:

**Environmental Predictors of Mercury Methylation Potential
and Fish Tissue Concentrations in a Blackwater River**

Report date:

August 30, 2006

Investigators:

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Executive Summary:

Mercury (or Hg) contamination in freshwater fish has emerged as an important environmental issue at a national scale, with fish consumption advisories in 43 states by the end of 2004, an increase over 2001 and 2002 (US EPA). This project proposed to investigate biotic and abiotic factors affecting mercury contamination of fish in water characteristic of the “blackwater” rivers in South Carolina (generally low pH and dissolved oxygen levels and high concentrations of carbon, primarily humic and fulvic acids) through collection and analysis of existing data and through experimental studies.

Data on fish sampling and contamination levels obtained from the South Carolina Department of Health and Environmental Control (SC DHEC) was mapped and analyzed. Some of the additional characteristics to be included in the study (e.g., the National Atmospheric Deposition Program's (NADP) data for mercury and acid deposition, locations of coal-fired power plants and municipalities, toxic release inventories, prevailing wind and weather patterns, and drainage characteristics) were either unable to be obtained or were very limited (i.e., NADP data). The SC DHEC data was parsed for fish types sampled most commonly in order to analyze spatial trends within the Edisto River. Initial results indicate that within the fish data the sample sizes are too small to permit reliable analysis. Additional analyses will continue as PI and student time allow using a broader range of analysis tools such as quantile regression and classification and regression trees (CART). During the project period, Dr. Johnson was in Minnesota and unable to guide the student in more advanced analysis methods.

In the experimental phase of this project, sampling of the Edisto River according to the proposed timeline became problematic because of unusual weather patterns (high rainfall) and the resulting hydrologic conditions. Our plan to coordinate sampling with USGS personnel in Columbia was abandoned because of hydrologic requirements and their need to sample upon short notice depending on hydrologic conditions. Rather we began our study with samples obtained from another blackwater stream, the Ogeechee River in northeast Georgia. We focused on assessing Hg bioavailability via its toxicity to a zooplankton specie characteristic of freshwater food webs, *Ceriodaphnia dubia*, in the presence of Ogeechee River NOM-containing water. This organism has been used extensively in the study of other water contaminants such as copper and the effects of NOM complexation. Simultaneously, method development and verification proceeded for quantification of inorganic and organic Hg forms. Results from the mercury toxicity tests using Ogeechee River NOM show that toxicity is surprisingly independent of NOM concentration. One hypothesis that may explain this result is that at the low levels of Hg required to cause mortality to *C. dubia*, its predominant chemical form is a kinetically labile complex between the “soft” metal and the abundant “hard” oxygen-containing ligands on NOM. Such a labile complex would allow *C. dubia* (and other organisms) to displace NOM-bound Hg. While MINTEQ calculations and fluorescence quenching measurements indicate extensive binding of Hg to NOM, Hg toxicity is only reduced by a factor of three. The kinetic lability of Hg with model ligands and NOM is undergoing quantification (using a fluorescence quenching method) to test this hypothesis. Results show that a sulfur-containing ligand (cysteine) is significantly less kinetically labile than ligands containing oxygen and nitrogen (EDTA and NTA). Results with NOM are difficult to interpret and that is currently under further study. Corresponding studies using a Suwanee River NOM isolate have also been completed and are being analyzed. In Hg analyses, we have achieved sub-ppb levels of detection and quantification for inorganic or Hg²⁺. Relatively low recoveries initially hampered quantification of organic forms of Hg, but method modifications adopted recently have resulted in satisfactory results.

Information Transfer Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	0	0	0	0	0
Masters	3	0	0	0	3
Ph.D.	3	0	0	0	3
Post-Doc.	0	0	0	0	0
Total	6	0	0	0	6

Notable Awards and Achievements

A Discover Carolina program is being established at Lake Greenwood State Recreation Area's Drummond Center with the assistance of the SCWRC Watershed Education Coordinator. Two curriculum units were developed that focus on Lake Greenwood's aquatic ecology and watershed. Through a partnership with SC Life/Clemson University, a teacher training course was offered: Teaching Your Watershed at the park to test the curriculum. Six teachers took the course for credit, 1 audited the course. All were excited about the program and incorporating watershed education. Several teachers will definitely be bringing their class to the park to do the program and one is hoping to do a whole curriculum unit this year on Lake Greenwood.

A draft of the curriculum is near completion. The teachers will be officially reviewing the curriculum as part of their final project due in July and the SCWRC Watershed Education Coordinator will continue to edit and incorporate their revisions before posting to the Discover Carolina website in August. The Coordinator has begun to outfit the Drummond Center classroom and the park management has designated the classroom exclusively for the program.

In conjunction with a scientific assessment of the Saluda and Reedy River watershed, including projects that have been funded through the USGS WRRI program and the South Carolina Water Resources Center, the watershed education program was established to help school children and stakeholders understand processes shaping the Reedy River from its source to its end in Lake Greenwood.

Publications from Prior Projects

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