

# Polychlorinated biphenyl contamination trends in Lake Hartwell, South Carolina (USA): Sediment recovery profiles spanning two decades

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## Abstract

To assess the ca. 20-year polychlorinated biphenyl (PCB) contamination trends in Lake Hartwell, SC, sediment cores from the Twelve Mile Creek arm were collected in July 2004 at two sites (G30 and G33) first sampled in the mid-1980s. Congener-specific PCB data as a function of depth from the sediment–water interface for the 2004 sediment samples were compared to data obtained from 1987 and 1998 samples taken from the same locations. Despite modest 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. Unlike G30, the more rapid recovery in the near-surface sediment of G33 suggests that the effectiveness of the U.S. EPA natural attenuation record of decision is site-specific and is unlikely to result in uniform surface sediment recovery throughout the most contaminated regions of Lake Hartwell.

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## 1. Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants with significant bioaccumulation potentials in environmental systems. Despite the cessation of domestic production in the late 1970s, sites contaminated with PCBs continue to pose a threat to human and ecosystem health. In aquatic systems, PCB partitioning and transformations are a function of molecular-level (i.e., congener-level) properties and structure (Erickson, 1986; Farley et al., 1994). The toxicological effects of PCBs also vary at the congener level (Safe, 1992). The variability observed in the physicochemical properties of PCBs suggests a differential partitioning (i.e., weathering) of congeners in multiphase environmental systems (Burkard et al., 1985; Dunnivant et al., 1988). Evidence of PCB physicochemical weathering in near-surface sediments in the Twelve Mile Creek arm

of Lake Hartwell (the current study site) was reported by Farley et al. (1994). At this site, the degree of PCB chlorination in shallow sediments was observed to increase with increasing distance downstream of the source. During sediment resuspension and transport events, the preferential sorption of higher chlorinated congeners and volatilization of lower chlorinated congeners were proposed as the dominant PCB weathering mechanisms (Dunnivant et al., 1988).

Aerobic and anaerobic PCB degradation processes have been reported in laboratory investigations (Abraham et al., 2002; Master et al., 2002). Typically, PCBs with up to four chlorine atoms are susceptible to aerobic biotransformations. In anaerobic environments, reductive dechlorination is the most commonly reported PCB biotransformation mechanism (Bedard and Quensen, 1995; Pakdeesusuk et al., 2003). Reductive dechlorination of PCBs is a two-electron transfer mechanism in which chlorine atoms on the biphenyl moiety are replaced with hydrogen atoms (Nies and Vogel, 1991). Reductive dechlorination typically

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operates on the higher chlorinated PCB congeners (i.e., PCBs with four or more chlorines). Consequently, in closed systems, reductive dechlorination can reduce the total PCB level on a mass but not on a molar basis.

In sediment systems, an accumulation of lower chlorinated PCB congeners with a concurrent decrease in higher chlorinated congeners serves as compelling, albeit indirect, evidence of reductive dechlorination (Pakdeesusuk et al., 2005). When sediment PCB data are compared to known source composition data for the evaluation of *in situ* reductive dechlorination, the assumption is often made that source PCB compositions are identical to those deposited at sediment sampling sites. This assumption is not necessary, however, when congener-specific data exist for two or more sampling times. In these instances, the data from any sampling time (most logically the earliest) can serve as a datum from which PCB historical trends can be assessed. In all cases, it must be recognized that reductive dechlorination may not be the only process responsible for historical changes in PCB metrics. Dissolution, volatilization, aerobic biotransformations and sediment transport may be significant mechanisms in addition to reductive dechlorination (Farley et al., 1994; Bedard and Quensen, 1995).

Microcosm studies involving Lake Hartwell sediments have confirmed the presence of indigenous microorganisms capable of reductively dechlorinating PCB congeners in Aroclor 1254 (Pakdeesusuk et al., 2003). Congener-specific PCB analysis confirmed an overall decrease in the weight percent of the higher molecular weight species and a concurrent increase in the lower molecular weight congeners. The average number of total chlorines per biphenyl (Cl/biphenyl) decreased from  $\approx 4.9$  to 3.0 after 260 days of incubation. Analysis of dechlorination products indicated the preferential removal of *meta* and *para* chlorines; a decrease in *ortho* chlorines was not observed. As such, increases in the fraction of chlorine atoms occupying *ortho* positions (% *ortho* Cl) with concurrent decreases in total chlorines per biphenyl serve as compelling (indirect) evidence of reductive dechlorination.

Lake Hartwell, in northwestern South Carolina, is heavily contaminated with PCBs from the manufacturing and waste disposal practices of a capacitor manufacturer operating near Pickens, SC, from 1955 to 1987 (US EPA, 2004). The production of PCB-containing capacitors ended at the site in 1976, concurrent with the passage of the Toxic Substances Control Act, which subsequently banned PCB production in the US (LaGrega et al., 2001). PCB loading into the Lake Hartwell system via direct surface discharge and groundwater infiltration of PCB-containing wastes is estimated at 200 metric tons,  $\approx 80\%$  as Aroclor 1016 and 20% as Aroclor 1254 (Wong et al., 2001). In the mid-1980s, Germann (1988) conducted a broad survey of Lake Hartwell sediments to determine the geographic extent of PCB contamination downstream of the source. Sediment analyses from this survey suggested that PCB levels were the highest in the Twelve Mile Creek arm of Lake Hartwell. The entire Sangamo–Weston/Twelve Mile Creek/Lake Hartwell site

was added to the EPA National Priority List in February 1990 (US EPA, 2004). The June 1994 record of decision (ROD) for this site called for natural capping of contaminated sediment with ongoing monitoring. A total-PCB cleanup requirement of 1.0  $\mu\text{g/g}$  was stipulated. The rationale for this monitored natural attenuation strategy is to cover contaminated sediment with a sufficient amount of increasingly clean sediment such that PCB residues are prevented from entering the aquatic food chain (Brenner et al., 2004). Natural capping also reduces the potential for resuspension and subsequent relocation of contaminated near-surface sediments. Given sufficient time, the EPA hypothesizes that natural attenuation processes (e.g., biodegradation, burial and volatilization) will reduce the mass load of PCBs in Lake Hartwell (US EPA, 2004; Magar et al., 2005a).

A large historical dataset spanning two decades has been compiled for the most contaminated regions of Lake Hartwell. The data represent sediment core samples collected in 1987 (Germann, 1988), 1998 (Pakdeesusuk et al., 2005) and 2004 (the current work). Bulk PCB metrics (e.g., total PCBs, average chlorines per biphenyl, homolog distributions) and congener-specific concentrations were determined for all three sampling dates, which allow an analysis of historical PCB contamination trends. Examination of PCB depth profiles affords an assessment of the natural attenuation ROD assigned to the Lake Hartwell Superfund site. Historical congener-specific PCB data also permit an evaluation of *in situ* reductive dechlorination processes. The primary goal of the current work is to elucidate PCB contamination trends at two sediment-sampling locations (G30 and G33) in the Twelve Mile Creek arm of Lake Hartwell, SC. Data addressing the influence of (bio)chemical PCB weathering on congener profiles are discussed. An evaluation of the efficacy of the natural attenuation ROD invoked by the EPA at this Superfund site is also provided.

## 2. Experimental section

### 2.1. Sediment sampling

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). A map of the sampling locations is shown by Pakdeesusuk et al. (2005). Sediment cores were collected using a Wildco gravity corer fitted with a Lexan<sup>TM</sup> tube (5 cm diameter, 76 cm length). The cores were transported to the L.G. Rich Environmental Research Laboratory (Clemson University, Anderson, SC) and extruded within 24 h of the sampling event. The cores were sectioned every 5 cm, homogenized by manual mixing for 3 min, and stored in solvent-rinsed glass jars (0.5 l) at 4 °C prior to analysis. Prior to homogenization, 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 Lexan<sup>TM</sup> tubes. Subsequent analyses were conducted for both the exterior and interior portions of the G30 and G33 (40–45 cm) fractions; sediment smearing was not observed.

## 2.2. PCB extraction

PCBs were extracted from sediment samples into acetone followed by solvent exchange into isooctane via a previously described sonication method (Dunnivant and Elzerman, 1987; Pakdeesusuk et al., 2005). Prior to sonication, all samples were spiked with octachloronaphthalene (3.4 µg in acetone) as a recovery standard. Extraction efficiencies averaged  $81 \pm 58\%$ . Results were not corrected for extraction efficiencies.

## 2.3. PCB analysis

Sediment extracts were analyzed for PCBs on a Hewlett-Packard 6890 gas chromatograph (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 <sup>63</sup>Ni electron capture detector (ECD). GC parameters are described by Pakdeesusuk et al. (2005). Blank GC runs (isooctane only) were conducted after approximately every five GC samples to check for analyte carry-over between injections. A 1:1 mixture of Aroclors 1016 and 1254 (AccuStandard; New Haven, CT) was used as a check standard after approximately every 12 field sample GC injections. Average GC–ECD response factors varied by less than 10% for all check standard analyses.

## 2.4. PCB quantification

Details of GC peak assignment, calibration and error propagation methods are described by Sivey (2005). Unless otherwise stated, all PCB error intervals reported below represent total analytical errors (Sivey, 2005). Total analytical error is a propagated uncertainty metric incorporating all significant error sources (e.g., sediment dry weight determinations, replicate GC–ECD analyses and calibrations). The current PCB quantification method, which quantifies 81 GC peaks, representing 128 PCB congeners, varies slightly from the method employed during the analyses of the 1987 and 1998 samples (Germann, 1988). Data from all sampling events were subjected to the current quantification method to facilitate congener-specific historical trend analyses.

## 3. Results and discussion

### 3.1. G30 PCB metrics and historical trends

Total PCB depth profiles for G30 samples collected in 1987 (Germann, 1988), 1998 (Pakdeesusuk et al., 2005)

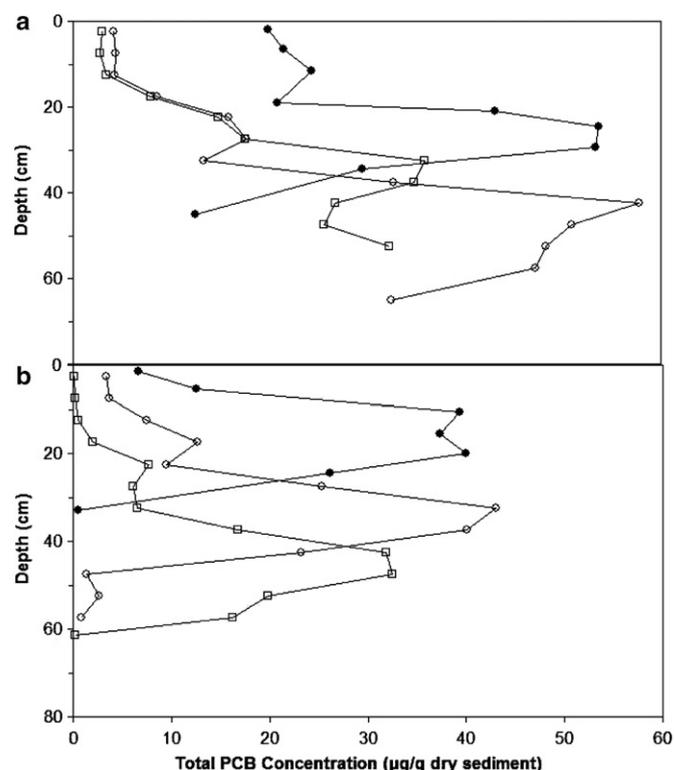


Fig. 1. Historical trends in (a) G30 and (b) G33 total PCB concentrations: (●) 1987; (○) 1998; (□) 2004.

and 2004 (the current work) are shown in Fig. 1a. The 2004 total PCB concentration at the sediment–water interface (0–5 cm) is  $3.0 \pm 0.2$  µg/g ( $9.5 \pm 0.6$  nmol/g). This value exceeds the EPA clean-up requirement of 1.0 µg/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. If recent near-surface recovery rates ( $0.19 \pm 0.01$  µg/g/yr; average annual decline in total PCB levels from 1998 to 2004) persist, G30 surface sediments will not be in compliance with the EPA clean-up requirement of 1.0 µg/g until 2015. Approximately uniform total PCB concentrations persist from 0 to 15 cm, indicating a well-mixed surface sediment layer. A sharp increase in total PCBs occurs at 15–30 cm. The maximum concentration captured by the 2004 core is  $36 \pm 1$  µg/g ( $141 \pm 8$  nmol/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.

Large decreases in total PCBs at the sediment–water interface are observed between 1987 and 1998 (Fig. 1a). Only 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 to 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 at this site. An average sedimentation rate of  $2.0 \pm 1.8$  g/cm<sup>2</sup>/yr was reported by Brenner et al. (2004) at a transect of Lake Hartwell near G30 based on 2000 and 2001 sediment core radioisotope dating. Assuming a sediment bulk density of 2.6 g/cm<sup>3</sup> (Farley et al., 1994), this sedimentation rate translates into  $0.8 \pm 0.7$  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 calculated by Brenner et al. (2004).

Historical chlorine distribution profiles can be useful in assessing trends in PCB composition over time. Fig. 2a outlines the G30 Cl/biphenyl profiles for all three sampling years under consideration. Fig. 3a depicts % *ortho* Cl historical profiles. The approximate source composition (4:1 mixture of Aroclors 1016 and 1254) is demarcated in both figures by a dashed line (Cl/biphenyl = 3.39; % *ortho* Cl = 46). Dissimilarities in Cl/biphenyl levels at the sediment–water interface suggest a variable PCB composition of deposited sediment at G30 over time. The average Cl/biphenyl of PCBs in deposited sediment increased over time. This change reflects increasing degrees of source PCB weathering, as indicated by the increasing distances

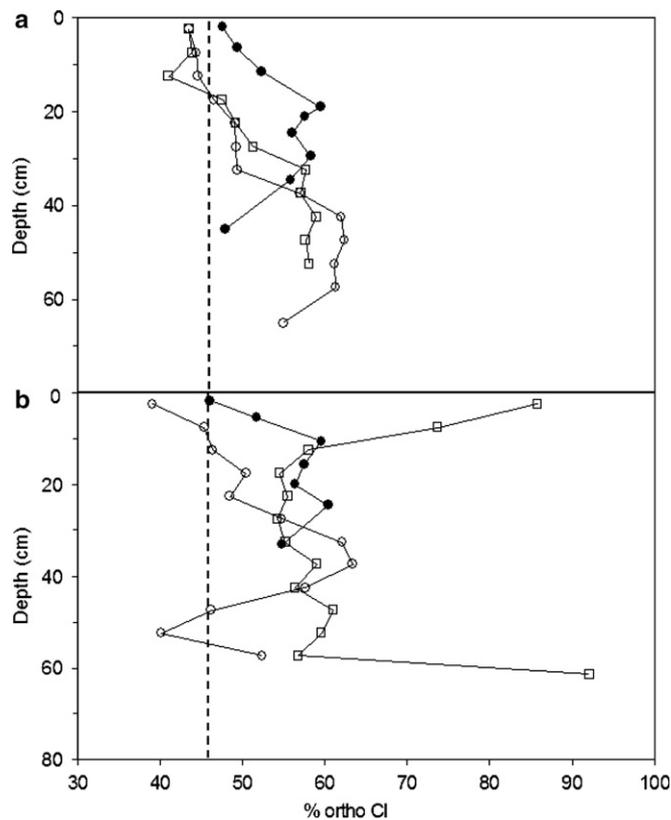


Fig. 3. Historical trends in (a) G30 and (b) G33 percent *ortho* chlorines: (●) 1987; (○) 1998; (□) 2004. The dashed line denotes the original PCB source composition (4:1 mixture of Aroclors 1016 and 1254).

from the dashed line in Fig. 2a 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). The influence of sediment impoundment releases upstream of G30 may also impact the PCB composition of shallow sediments at this site. Aerobic biotransformations of low molecular weight congeners may be significant as well. Evidence of a variable deposition composition is also indicated at the congener-level. Fig. 4 displays the mole percent distributions of selected congeners in near-surface sediments for all three sampling dates. Increases in higher chlorinated congeners (245–25 + 236–35; 235–245) with concurrent decreases in lower chlorinated congeners (2–2 + 26; 4–4 + 24–2) over time are observed. Overall, PCB toxicity (Safe, 1992) and bioaccumulation (Morrison et al., 1996) potentials increase with the degree of chlorination. The bioaccumulation and toxicity potentials of individual congeners can vary by more than two orders of magnitude. As such, despite the continued trend of decreasing total PCB concentrations in G30 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 chlorinated congeners over time. These trends, in conjunction with a total PCB concentration above the clean-up guideline, raise significant ecotoxicological concerns at G30.

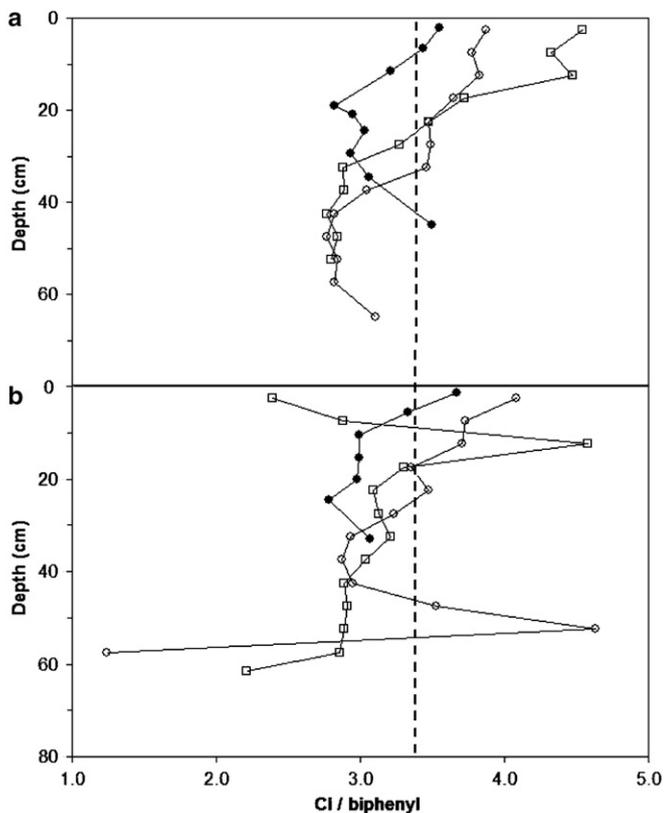


Fig. 2. Historical trends in (a) G30 and (b) G33 total chlorines per biphenyl: (●) 1987; (○) 1998; (□) 2004. The dashed line denotes the original PCB source composition (4:1 mixture of Aroclors 1016 and 1254).

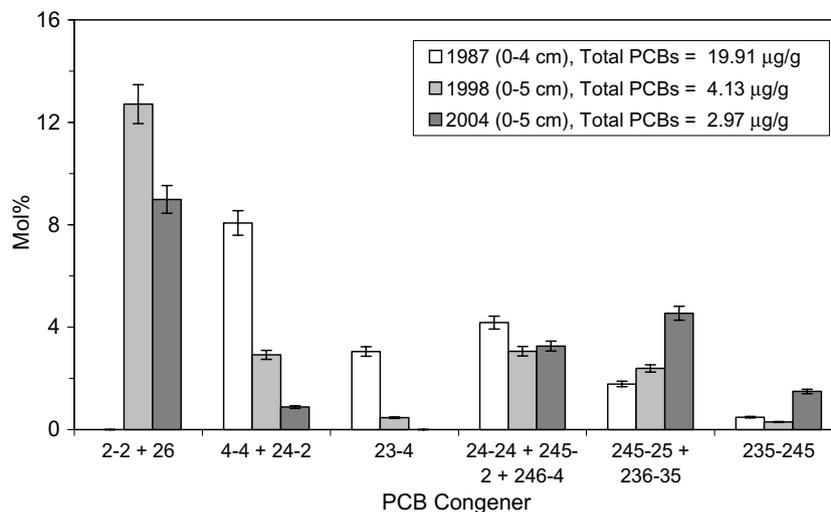


Fig. 4. Historical trends in the relative distributions of selected congeners at the G30 sediment–water interface. Error bars denote the error between the two analytical methods employed to obtain 2004 (Sivey, 2005) and pre-2004 (Pakdeesusuk et al., 2003) data.

As shown in Fig. 2a, the 1987 core depicts a rapid decline in Cl/biphenyl beginning near the sediment–water interface and continuing to a depth of 20 cm. For the 1998 and 2004 cores, a similar decrease in Cl/biphenyl levels occurs between 15 and 40 cm. Concomitant increases in % *ortho* Cl occur at the same depths (Fig. 3a). Taken together, these data are persuasive indicators of PCB biochemical weathering via reductive dechlorination (Pakdeesusuk et al., 2005) and that this process has likely been operating at this location for several decades. As sediment residence time increases with depth, Cl/biphenyl levels converge to  $\approx 2.9$  for all samples regardless of total PCB concentration (Fig. 2a). Similar convergence to approximately 60% *ortho* Cl with depth is also observed (Fig. 3a). At depths greater than 30 cm, changes in chlorine distributions are minimal (Figs. 2a and 3a), indicative of a plateau phase in reductive dechlorination at these depths (Pakdeesusuk et al., 2005). A plateau phase occurs when local reductive dechlorination rates approach zero. Historically, the plateau phase occurred at depths with total PCB levels exceeding those measured in the active reductive dechlorination zone (Fig. 1a). Therefore, a parameter other than (low) total PCB concentration must be responsible for the diminished reductive dechlorination rate. As observed by Pakdeesusuk et al. (2005), reductive dechlorination can be limited by a low availability of susceptible congeners (i.e., those with a spatial arrangement of chlorines favorable to biochemical reduction reactions) and by a population decrease in microbial communities capable of reductive dechlorination.

### 3.2. G30 Congener-specific analyses

Comprehensive congener distributions for the near-surface sediment (0–5 cm) and the fraction representing the highest captured total PCB level (30–35 cm) are depicted in Fig. 5. Of note is the predominance of higher chlorinated

congeners in the shallow sediments. The dramatic shift to lower chlorinated congeners with depth is evidence of PCB weathering via reductive dechlorination at this site.

### 3.3. G33 PCB metrics and historical trends

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 Fig. 1b. All three cores captured the entire PCB profile at this site. Consistent decreases in PCB levels at the sediment–water interface from 1987 to 2004 are observed. The 2004 total PCB concentration at the sediment–water interface is  $0.133 \pm 0.007 \mu\text{g/g}$  ( $0.56 \pm 0.03 \text{ nmol/g}$ ). If the decrease in PCB concentration in near-surface sediments is assumed to be linear between 1998 and 2004, this site became compliant with the EPA clean-up requirement of  $1.0 \mu\text{g/g}$  in 2002. The maximum concentration captured by this core is  $33 \pm 1 \mu\text{g/g}$  ( $128 \pm 5 \text{ nmol/g}$ ) at 45–50 cm.

The Cl/biphenyl and % *ortho* Cl profiles for G33 are shown in Figs. 2b and 3b, 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 at depths less than 15 cm and greater than 60 cm (Fig. 1b). In the 2004 core, a decrease in Cl/biphenyl from 3.21 to 2.86 is shown from 20–40 cm (Fig. 2b). The % *ortho* Cl values across these depths hover near 57% (Fig. 3b). In the sections of the cores with the highest PCB levels, Cl/biphenyl and % *ortho* Cl values converge near 2.9% and 60%, respectively.

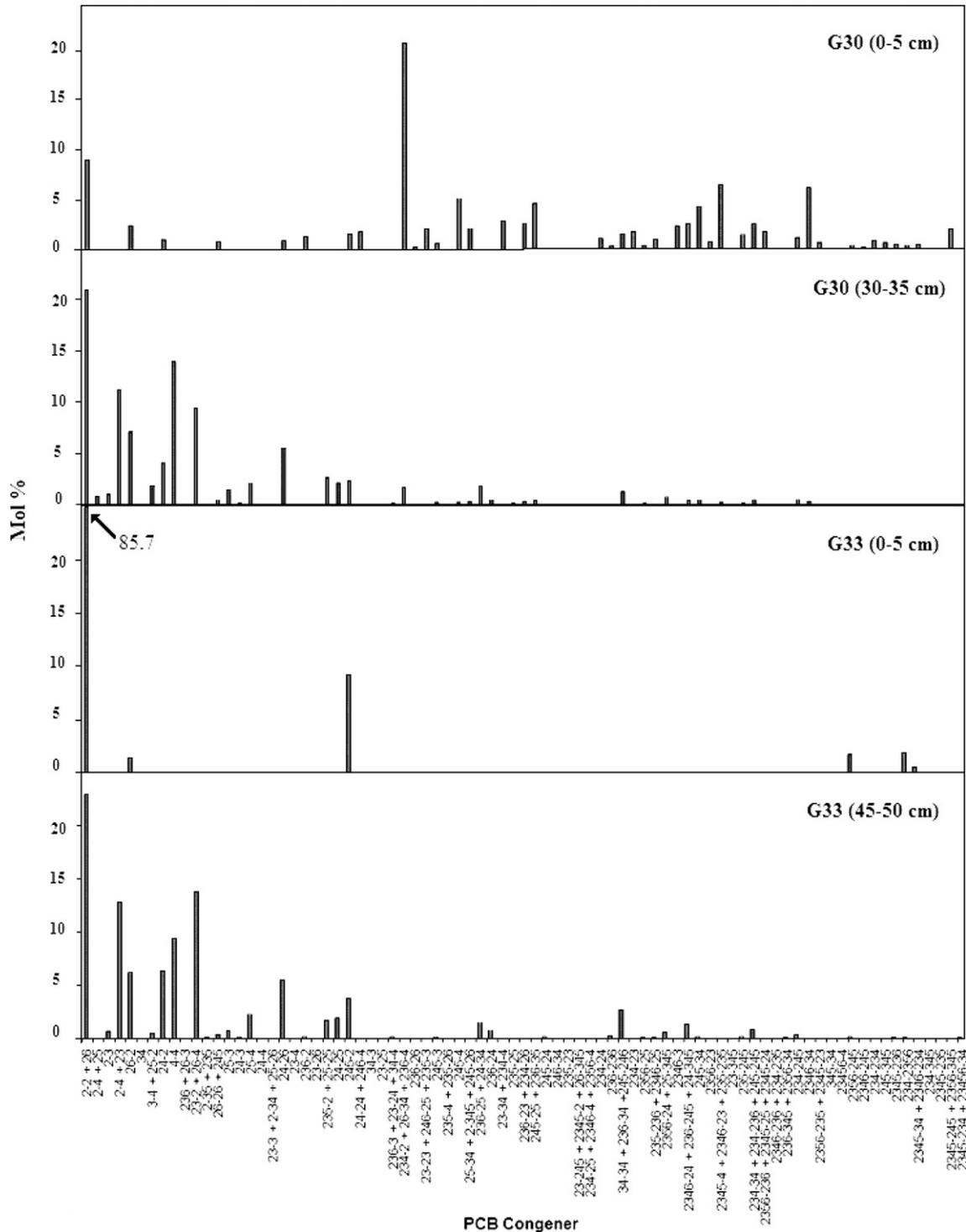


Fig. 5. Comprehensive congener profiles for the near-surface sediment and the highest recorded PCB contamination level at G30 and G33.

These data are considered modest evidence of reductive dechlorination at this site.

### 3.4. G33 congener-specific analysis

Comprehensive congener distributions for the near-surface sediment (0–5 cm) and the depth representing the highest captured total PCB level (45–50 cm) are shown in

Fig. 5. Of note near the sediment–water interface (0–5 cm) 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).

The PCB distribution from 45–50 cm is comprised largely of congeners with less than five chlorine atoms. Reductive dechlorination processes may be responsible for the

Table 1  
G30 and G33 site comparisons based on the results of the 2004 sampling event

		G30	G33
Sediment–water interface	Depth (cm)	0–5	0–5
	Total PCBs ( $\mu\text{g/g}$ )	$3.0 \pm 0.2$	$0.133 \pm 0.007$
	Cl/biphenyl	$4.6 \pm 0.3$	$2.4 \pm 0.1$
	% <i>ortho</i> Cl	$43 \pm 3$	$86 \pm 5$
	Sediment recovery rate ( $\mu\text{g/g/yr}$ ) <sup>a</sup>	$0.19 \pm 0.01$	$0.54 \pm 0.04$
Maximum PCB level	Depth (cm)	30–35	45–50
	Total PCBs ( $\mu\text{g/g}$ )	$36 \pm 2$	$33 \pm 1$
	Cl/biphenyl	$2.9 \pm 0.2$	$2.9 \pm 0.1$
	% <i>ortho</i> Cl	$58 \pm 3$	$61 \pm 2$

Uncertainty intervals denote total analytical errors (Sivey, 2005).

<sup>a</sup> Sediment recovery rates are based on the six-year average concentration differences between the 1998 and 2004 sampling events.

low levels of higher chlorinated congeners in this fraction. The congener-specific profile for 45–50 cm is representative of all samples from 35–63 cm (data not shown). 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 potentially less probable explanation is the deposition of PCB-contaminated sediment over a span of several years with extremely similar congener signatures resulting from *upstream* physical and/or biochemical weathering processes.

### 3.5. Site comparisons

Representative PCB results from sites G30 and G33 are juxtaposed in Table 1. Significant differences exist between the two sites at the sediment–water interface. Whereas G30 sediments are well above the clean-up standard of  $1.0 \mu\text{g/g}$ , G33 sediments are an order of magnitude below this level. The Cl/biphenyl level is also lower at G33. Taken together, these metrics implicate G30 as having a higher PCB toxicity and bioaccumulation potential relative to G33. Also of concern is the slower recovery rate at G30 ( $0.19 \pm 0.01 \mu\text{g/g/yr}$ ) relative to G33 ( $0.54 \pm 0.04 \mu\text{g/g/yr}$ ). 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.

Unlike at the sediment–water interface, the PCB signatures at maximum contamination depths of G30 and G33 are very similar. In both cores, Cl/biphenyl and % *ortho* Cl values approach 2.9% and 60%, respectively, as total PCB concentrations reach their local maximum values. Similarities at these depths are also evident in the congener distributions (Fig. 5). These results are consistent with the most biochemically weathered end-member (EM 3) from the polytopic vector analysis for Lake Hartwell sediments reported by Magar et al. (2005b). These results indicate that PCBs comprising the maximum concentration levels in both cores were likely subjected to comparable weathering processes, including reductive dechlorination. The data listed in Table 1 suggest that PCB weathering processes

occurred via similar mechanisms and to comparable extents at both sites.

In summary, the EPA remediation plan of natural sedimentation appears to be happening with a variable degree of success at sites G30 and G33. Local variations in sedimentation rates and PCB composition of deposited sediments appear to impact the efficacy of the natural attenuation ROD. The periodic release of contaminated sediment from impoundments upstream of the two sampling sites may also influence PCB profiles and recovery rates in a spatially heterogeneous fashion. These local disparities are responsible for the variable recovery rates calculated for the near-surface sediments at G30 and G33. 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.

Congener profiles at G30 and G33 provide evidence of *in situ* reductive dechlorination as a probable 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 is observed at both sites. Historical convergence to 2.9 average chlorines per biphenyl and 60% *ortho* chlorines with depth is also observed at both sites. Consistent with previous investigations (Pakdeesusuk et al., 2005), these trends are likely the result of *in situ* reductive dechlorination followed by a plateau phase with increasing distance from the sediment–water interface.

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