



Characterization and fate of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in soils and sediments at the Portsmouth Gaseous Diffusion Plant, Ohio



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HIGHLIGHTS

- PCB, PCDD and PCDF may migrate from industrial sites and bind to sediments.
- We investigate the occurrence of PCB, PCDD and PCDF in sediments.
- PCB occurrence is related to organic carbon and stream dynamics.
- A consistent signature set of PCB congeners may be useful for future investigation.
- PCB concentration in receiving water bodies have decreased over time.

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ABSTRACT

The U.S. Department of Energy Portsmouth Gaseous Diffusion Plant is in the early stages of decommissioning and decontamination. During operations, the site drew a large amount of electric power and had multiple large switchyards on site. These are a source of polychlorinated biphenyls (PCB) contamination to both on-site and off-site streams. Some soil remediation has been completed in the main switchyard. During 2011 and 2012, fifteen sites were sampled at the surface (<10 cm) and subsurface (20–30 cm) to characterize the extent of PCB contamination, to identify weathering and migration of PCB contamination and to explore potential polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) contamination due to transformer fires and explosions in the 1950s and 1960s. Stagnant sites tended to exhibit more migration of contamination to deeper sediments than sites with fast-moving waters, and the highest concentrations were found at the bottom of a settling pond. A signature set of five dioxin-like PCBs were consistently found across the site with higher concentrations in carbon rich surface sediments. PCB concentrations had a significant inverse correlation with clay content, suggesting that PCBs did not bind to clays at this site. Remediation has reduced PCB concentrations throughout the site compared to levels found in previous studies and long-term upkeep of sediment lagoons is necessary to retain PCB and dioxin-rich sediments. The flow regimen, organic carbon and clay content play a very important role in the fate of PCBs in the environment at the surface as well as downward migration.

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1. Introduction

This study examines the distribution and fate of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the soils

and sediments at a U.S. Department of Energy gaseous diffusion plant and the environmental conditions that influence their fate in receiving water bodies.

Manufacturing of PCBs stopped in 1977 and use was banned in the United States in 1979, (USEPA, 2012); electrical equipment is a significant source (Kakareka and Kukharchyk, 2005). PCBs have various degrees of substitution of chlorine atoms for the ten hydrogen atoms on the biphenyl rings, leading to 209 permutations of structures, or congeners, with differing properties and toxicity

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(USEPA, 2011), twelve have been identified as “dioxin-like” with toxicities 100–1000 times higher than other PCB congeners (Kakareka and Kukharchyk, 2005). PCB mixtures, each made of a unique blend of congeners, are termed Aroclors, (USDHHS, 1995). They are identified by a 4-digit numeric code; denoting the number of carbon atoms in the biphenyl ring and the percentage of chlorine in the mixture (e.g. Frame et al., 1996). Aroclors 1254 and 1260 used before 1950 (Kodavanti et al., 2001; Rushneck et al., 2004); in the 1950s and 1960s, Aroclor 1242 was used, then, in 1971 Aroclor 1016 was phased in (Hutzinger et al., 1974).

In surface waters, PCBs can remain buried in sediments and be slowly released over time (Harner et al., 1995; Kannan et al., 1997; Faroon et al., 2003). Sediments act as a reservoir for PCBs (ATSDR, 2000) which may remain in sediments for years (Sinkkonen and Paasivirta, 2000). Biodegradation half-lives of PCBs in sediments and soils vary from several years to decades (Shelton and Tiedje, 1984; Brown and Wagner, 1990; Lake et al., 1992; Beurskens et al., 1995). Heavy congeners are more persistent in soil due to lower volatility; light congeners degrade more rapidly and migrate faster (Notarianni et al., 1998); dominance of light congeners may be a sign of degradation of heavy congeners (Sivey and Lee, 2007). PCBs may persist at toxic levels in sediments, despite dredging, particularly in downstream reaches of a contaminated river system (Cieniawski and Collier, 2003) and dredging may, increase

exposure to PCBs (Martinez et al., 2010). PCBs in soil and sediment may be broken down by biodegradation (Faroon et al., 2003; D'Angelo and Nunez, 2010). In river sediments, PCBs have been measured at different depths, showing the highest PCB concentrations in sediment layers buried during the time of PCB manufacture (Pollack and Butterfield, 2005), while other studies (Cousins et al., 1999; Armitage et al., 2006) found that PCB concentrations decreased with depth; this varies with the source of the contaminant and the stability of the particular congener in the sediment (Krauss et al., 2000; Sahu et al., 2009; Zhang et al., 2011).

PCDDs and PCDFs are significantly more toxic than PCBs (USDON, 1990; CADHS, 1998), varying with structural conformation (USEPA, 2010). PCDDs and PCDFs may be formed through combustion of PCBs (CADHS, 1998; USDON, 1990).

1.1. Study site

The U.S. Department of Energy Portsmouth Gaseous Diffusion Plant (PORTS) is located in Pike County, near Piketon, Ohio (Fig. 1); operations began in 1954. PORTS was one of three uranium enrichment facilities in the United States. Most activities at PORTS ceased 2001 and went into cold shutdown (DOE, 2011b). The PORTS facility covers 15.3 km² and it is crossed by Little Beaver Creek (Fig. 1). Facilities in the area are illustrated in Fig. 1.

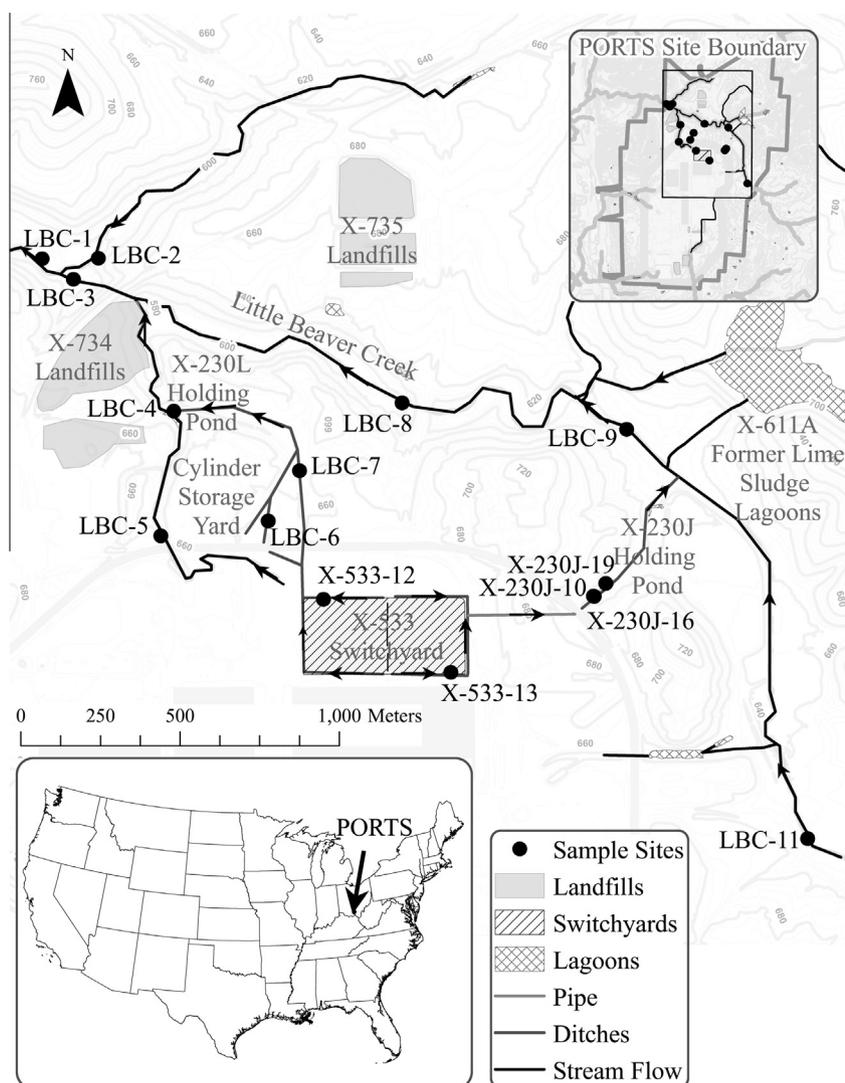


Fig. 1. Map of the PORTS PCB study area. Arrows designate direction of water flow.

Previous studies indicate a reduction over time of PCB Aroclor concentrations. Ohio EPA (OEPA) (OEPA, 1993) conducted biological and sediment sampling in Little Beaver Creek (LBC); levels were below the detection limit in all samples. In 1997, a biological and water quality study of LBC found PCBs in sediment samples, including multiple Aroclors (OEPA, 1998); Aroclor 1260 concentrations were a potential health hazard (OEPA, 1998). In 2005, a water assessment of streams around PORTS found elevated PCBs in LBC; all levels were too low to pose a human health hazard (OEPA, 2005). Total PCB levels were as high as $1400 \mu\text{g kg}^{-1}$ in fish tissue samples from LBC, twice the standard (OEPA, 2005). In 2007, DOE studied the source of contamination to LBC; soil samples from the switchyard (Fig. 1) contained PCBs in five of fourteen locations (2007). Sediment samples contained Aroclor 1260 in three of eight samples from LBC. A Resource Conservation and Recovery Act study and soil removal was conducted in 2010 (DOE, 2011a). Following the findings of PCB contamination in the X-533A Switchyard in 2007, decontamination and decommissioning (D&D) of the switchyard was conducted in 2010. After D&D, 228 soil samples were collected from the shallow soil in the X-533 Switchyard Complex (Fig. 1). Contaminated soil was excavated and removed from sites with concentrations above the PORTS remediation goal of 25 mg kg^{-1} .

The purpose of this study was to detect residual PCB contamination downstream of known PCB contamination at PORTS and to examine how environmental conditions affect the distribution of PCBs, PCDDs and PCDFs in the receiving water bodies. The sampling program focused on the water bodies downstream of the X-533 switchyard.

2. Methods

2.1. Field sites

A 5.0 km-long section of LBC was investigated in this study. Fifteen sample sites were identified along LBC, its tributaries, X-533 Switchyard's drainage ditches, and associated holding ponds (Fig. 1). A description of each site is presented in Table 1; sites are shown in Fig. 1.

The following sites were sampled on December 13, 2011: X-533-12, X-533-13, X-230J-10, X-230J-16, and LBC-9. The following creek sites were sampled on April 23, 2012: LBC-1, LBC-2, LBC-3 and LBC-4. On April 24, 2012 sites LBC-5, LBC-6, LBC-7, LBC-8, LBC-11 and X-230J-19 (surface only) were sampled.

2.2. Field methods

Two samples were collected at each field site: surface sediment (<10 cm) and subsurface sediment (20–30 cm) (OEPA, 2001; USEPA, 1994; Schumacher, 2002), targeting finer sediments. The surface and subsurface samples at a single location are labelled with A (surface) or B (subsurface) throughout this manuscript (e.g. LBC-1A and LBC-1B). Samples were homogenized before storage in amber glass jars with Teflon lids at 4°C (DOE, 2007). Samples obtained for the PCB analysis were also analyzed for total organic carbon (TOC), pH and iron concentrations. For grain-size analysis, a two-kilogram grab sample was sealed in plastic bags. Samples were shipped to GEL Laboratories in for analysis.

2.3. Laboratory analysis

All 209 PCB congeners were analyzed at the surface and subsurface at site LBC-3. Aroclors and the twelve dioxin-like PCBs were measured at the surface and subsurface of all sampling locations, where possible. Samples for analysis of PCDDs and PCDFs were collected during the two April sampling events. The five sites sampled in December 2011 were excluded from PCDD and PCDF analysis. Samples for analysis of TOC, soil pH and iron were collected at all sites at the surface and subsurface. GEL laboratories in Charleston, South Carolina conducted the analyses following standard methods (Method USEPA 1668, USEPA 1613B, GEL, 2011).

The average grain size for each sediment sample was calculated using Eqs. (1) and (2):

$$X_i = (\text{Grain size sieve A} + \text{Grain size sieve B})/2 \quad (1)$$

$$X = \sum_{i=1}^n X_i \cdot f_i \quad (2)$$

Table 1

Description of sample site locations, average grain size for the surface and subsurface samples for the whole sample and the fine (<2 mm) fraction.

Sample site	Description	River km on Little Beaver Creek (LBC)	Avg. grain size surface (mm)	Avg. grain size surface (<2 mm) (mm)	Avg. grain size subsurface (mm)	Avg. grain size subsurface (<2 mm) (mm)
LBC-1	Stream, pool	2.1	0.57	0.09	8.75	0.18
LBC-2	Stream, oxbow (downstream of the X-735 landfills)	Enters LBC @ 2.3	3.14	0.25	8.06	0.34
LBC-3	Stream; cut bank, not depositional	2.3	0.05	0.04	0.18	0.04
LBC-4	Inlet to holding pond (near the X-734 landfills)	Enters LBC @ 2.5	2.58	0.43	9.53	0.47
LBC-5	Tributary		2.57	0.17	1.89	0.23
LBC-6	Tributary		0.66	0.08	0.36	0.06
LBC-7	Tributary		2.65	0.10	0.68	0.10
LBC-8	Stream	3.2	0.32	0.06	0.61	0.07
LBC-9	Stream	3.9	4.79	0.49	5.21	0.60
LBC-11	Stream	5.0	0.11	0.10	2.12	0.18
X-230J-10	Inlet to holding pond		2.52	0.11	1.31	0.09
X-230J-16	Inlet to holding pond		2.28	0.11	1.43	0.09
X-230J-19	Holding pond, bottom sludge		0.06	0.06	–	–
X-533-12	Ditch, wet		0.27	0.06	0.10	0.05
X-533-13	Ditch		0.62	0.12	01.87	0.15

Table 2
Laboratory analysis results for sediment samples. Blank cells signify that the analyte was not tested. Descriptive statistics for sediment analysis are included. Note that Total Aroclor values are presented in different units.

	OCDD ng kg ⁻¹	1,2,3,4,6,7,8- HpCDD ng kg ⁻¹	PCB 189 ng kg ⁻¹	PCB 167 ng kg ⁻¹	PCB 156 ng kg ⁻¹	PCB 118 ng kg ⁻¹	PCB 114 ng kg ⁻¹	PCB 105 ng kg ⁻¹	Total Aroclor µg kg ⁻¹	Total HpCDD ng kg ⁻¹	% TOC
LBC-1A	261	17	110	368	1010	4420	72.7	1810	55.4	38.6	6.6
LBC-1B	161	<5	7.1	19.2	51.8	224	3.3	84.8	8.3	6.2	0.8
LBC-2A	149	<5	7.6	30.2	74.8	474	8.7	202	26.6	<5	2.7
LBC-2B	253	5.7	147	545	1270	5850	61.3	2420	15.1	11.7	0.8
LBC-3A	19.6	<5	<1	<2	3.8	4.49	<2	<2	<1.5	<5	0.7
LBC-3B	15.6	<5	<2	<2	4.3	<4	<2	<2	<1.5	<5	0.9
LBC-4A	123	<55	<2	47.2	112	487	<20	224	23.5	<50	1.0
LBC-4B	203	<45	<2	75.4	218	1180	26.4	495	16.7	<45	0.9
LBC-5A	278	<5	<2	<2	38	206	<20	92.1	21.9	<5	0.3
LBC-5B	983	15	<2	<2	42.1	113	<20	54.3	73.8	30.2	0.3
LBC-6A	98	6.8	24.6	82	283	902	<20	451	19.8	13.8	0.2
LBC-6B	107	<5	<20	24	64.9	250	<20	111	17.1	<45	0.1
LBC-7A	1020	<45	26.1	39.4	60.3	111	<20	40.6	48.9	<55	1.7
LBC-7B	751	<55	54.2	76.4	120	240	<20	83.9	59.7	<45	1.5
LBC-8A	4200	36.8	<20	<20	41.9	<40	<20	<20	<1.5	83.8	0.4
LBC-8B	2700	19.6	<20	<20	38.7	<40	<20	<20	<1.5	47.5	0.1
LBC-11A	19.6	<5	<20	<20	37.5	<40	<20	<20	<1.5	<5	1.1
LBC-11B	51.5	<5	<20	<20	36.9	<40	<20	<20	1.48	<5	0.5
LBC-9A			46.6	151	429	2400	35.5	821	48.7		2.0
LBC-9B			85.6	193	530	2830	50.3	993	79		1.9
X-230J-10A			27.9	39.9	85.2	188	<2	49.2	16.1		0.8
X-230J-10B			15.9	28.9	50.6	392	<2	67.4	3.4		0.9
X-230J-16A			17.9	35.4	67.2	158	<2	39	24.1		1.1
X-230J-16B			9.9	21.6	45.4	79.8	<2	18.8	<1.5		0.7
X-230J-19A	21 700	2290	392	729	1630	4810	<48	1140	224	4590	7.1
X-533-12A			18.9	27.1	27.2	27.3	<2	6.0	11.1		0.6
X-533-12B			23.8	27.7	19.6	22.7	<10	9.8	15.3		0.3
X-533-13A			176	475	1260	3220	18	1300	99.2		1.9
X-533-13B			28.4	79	164	408	<2	117	5.8		0.6
All sampling sites											
Average	1742	132	44.0	109	270	1003	14.6	368	31.7	261	1.3
Max	21 700	2290	392	729	1630	5850	72.7	2420	224	4590	7.1
Min	15.6	<5	<1	<2	3.8	<4	<2	<2	<1.5	<5	0.1
SD	4950	523	80.1	183	442	1638	18.4	611	45.6	1049	1.6
Surface only											
Average	2787	241	58.0	136	344	1163	14.9	413	41.4	479	1.9
Max	21 700	2290	392	729	1630	4810	72.7	1810	224	4590	7.1
Min	19.6	<5	<1	<2	3.8	4.5	<2	<2	<1.5	<5	0.2
SD	6767	720	104	216	520	1688	18.5	579	56.8	1445	2.1
Subsurface only											
Average	581	11.1	28.9	79.4	190	831	14.3	320	21.3	18.7	0.7
Max	2700	27.5	147	545	1270	5850	61.3	2420	79.0	47.5	1.9
Min	15.6	<5	<2	<2	4.3	<4	<2	<2	<1.5	<5	0.1
SD	861	10.1	41.4	143	339	1628	18.9	662	27.8	14.7	0.5
Average surface/ average 30 cm	4.8	21.6	2.0	1.7	1.8	1.4	1.0	1.3	1.9	25.6	2.6

Note: Total Aroclor is presented in different units than the remaining values.

Table 3
Laboratory analysis results of sediment samples normalized by total organic carbon. Blank cells signify values below detection limits or that the analyte was not tested (see Table 2).

	OCDD µg kg ⁻¹ of OC	1,2,3,4,6,7,8-HpCDD µg kg ⁻¹ of OC	PCB 189 µg kg ⁻¹ of OC	PCB 167 µg kg ⁻¹ of OC	PCB 156 µg kg ⁻¹ of OC	PCB 118 µg kg ⁻¹ of OC	PCB 114 µg kg ⁻¹ of OC	PCB 105 µg kg ⁻¹ of OC	Total Aroclor µg kg ⁻¹ of OC	Total HpCDD µg kg ⁻¹ of OC
LBC-1A	4.0	0.3	1.7	5.6	15.4	67.5	1.1	27.6	846	0.6
LBC-1B	19.4		0.9	2.3	6.2	27.0	0.4	10.2	995	0.7
LBC-2A	5.5		0.3	1.1	2.8	17.4	0.3	7.4	978	
LBC-2B	29.8	0.7	17.3	64.3	150	690	7.2	285	1781	1.4
LBC-3A	2.7				0.5	0.6				
LBC-3B	1.8				0.5					
LBC-4A	12.8			4.9	11.7	50.7		23.3	2448	
LBC-4B	22.6			8.4	24.3	132	2.9	55.2	1862	
LBC-5A	84.2				11.5	62.4		27.9	6636	
LBC-5B	343	5.2			14.7	39.4		18.9	25714	10.5
LBC-6A	47.8	3.3	12.0	40.0	138	440		220	9659	6.7
LBC-6B	167			37.4	101	390		173	26677	
LBC-7A	59.0		1.5	2.3	3.5	6.4		2.3	2827	
LBC-7B	51.8		3.7	5.3	8.3	16.6		5.8	4117	

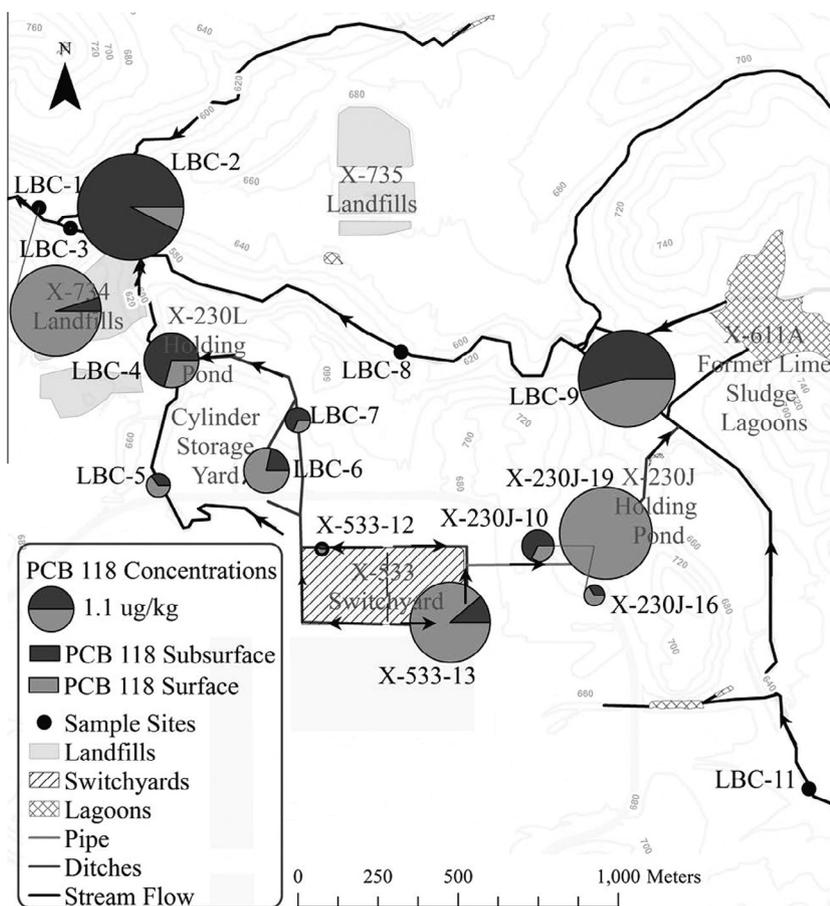


Fig. 3. Distribution of PCB 118 in the surface and subsurface. The size of each pie chart is proportional to the sum of the surface and subsurface concentrations.

and early 1960s there were some fires at both the X-533 and X-530 switchyards due to transformer explosions" (Sokol, 2012, personal communication). Site X-230J-19, sludge from the bottom of the holding pond draining the east side of the X-533 switchyard, showed the highest concentration of PCDDs and PCDFs tested. These compounds could be the result of fires.

Organic matter, iron and manganese oxides and hydroxides and clay minerals affect sorption of PCBs to soils or sediments (Manahan, 2009); organic matter is usually the most important phase to sorb them (Appelo and Postma, 2005). Results presented in Table 2 indeed show a strong correlation between TOC and PCBs and suggest that TOC in the surficial soils could be sorbing PCBs. Concentrations were normalized by dividing the PCB or PCDD concentration TOC in the sediments; selected corrected data is presented in Table 3. Total Aroclor and OCDD occur in the highest concentrations per kilogram of TOC. The average OCDD concentration per kilogram of TOC is higher for subsurface sediments than for surficial sediments (387 and 165 $\mu\text{g kg}^{-1}$ of TOC, respectively). The ratios of TOC normalized concentration in surface sediments to subsurface sediments are less than 1.0 for all the analyzed contaminants, except for 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD) and total Heptachlorodibenzo-p-dioxin (total HpCDD) (ratio equal to 1.3 and 1.5, respectively); however, 1,2,3,4,6,7,8-HpCDD was only found in both horizons at one site and total HpCDD was only found in both horizons at two sites, thereby making the comparison inconclusive. At 30 cm depth, the average concentrations of contaminants per kilogram of TOC are higher than at the surface suggesting that some of the contaminants have migrated downward from the surface and have sorbed onto a smaller fraction of TOC. Another possibility is that

the more persistent, heavier PCBs have sorbed strongly to older sediment during burial through deposition of new sediment. Of the PCDDs detected, OCDD behaves similarly to PCBs, while 1,2,3,4,6,7,8-HpCDD and total HpCDD are strongly correlated with TOC at the surface and do not show evidence of downward migration. The concentration at 30 cm depth versus the surficial concentration for OCDD, PCB 156 and total Aroclor have a higher concentration per kilogram of organic matter at 30 cm depth than at the surface (Fig. 2). Similar behavior is observed for the other congeners.

Higher concentrations of PCB 118 are typically found at the surface (0–10 cm) at sites that have a lower residence time (e.g. LBC-1 and LBC-6, Fig. 3), while sites that have long residence times (e.g. holding ponds, stagnant backwaters such as sites LBC-2 and LBC-4, Fig. 3), have higher concentrations of PCB118 in the subsurface horizon. Movement and storage of congener PCB118 as a function of residence time along drainage ditches, streams, and holding ponds can be explained by the data collected in this study. Given the appropriate residence time, PCBs are more likely to accumulate in the deeper soil horizon providing long-term storage and/or a source of slow continual release (Garvey et al., 2002). Site LBC-2, a stagnant backwater area, displays higher concentrations in the subsurface horizon, while site LBC-1, a site with continual movement of water has higher concentrations at the surface. This may support the theory that persistent PCBs are being buried with older sediments.

Sites X-533-12, LBC-8 and LBC-3 contain the smallest grain size with average fine grain size (<2 mm) of 0.06/0.05 mm, 0.06/0.07 mm, and 0.04/0.04 mm, respectively (surface/subsurface) (see Table 1). These sites also exhibited very low PCB concentrations,

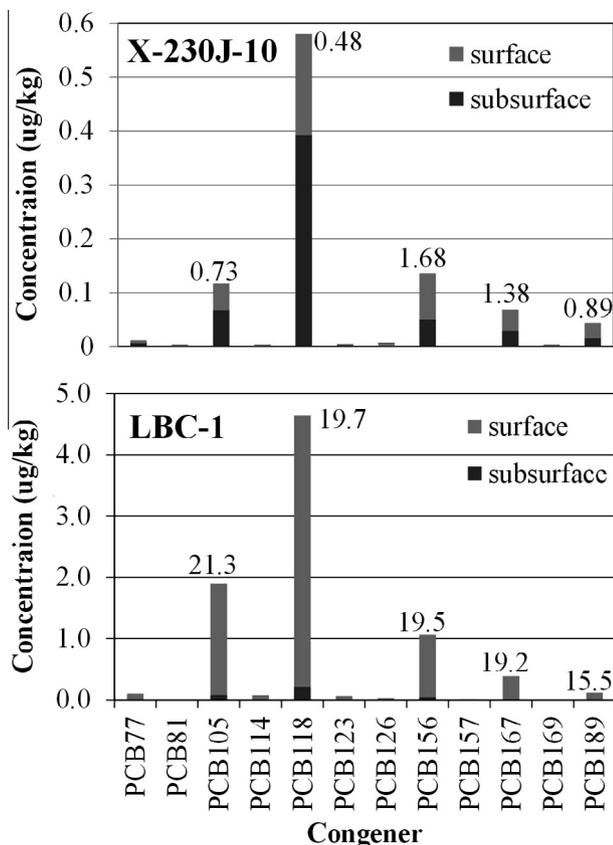


Fig. 4. Site X-230J-010 concentrations of dioxin-like PCBs at the surface and subsurface, signature set of congeners PCB105, 118, 156, 167, 189, varying from 0 to $0.392 \mu\text{g kg}^{-1}$. Site LBC-001 concentrations of dioxin-like PCBs at the surface and subsurface, signature set of congeners PCB105, 118, 156, 167, 189, varying from 0 to $4.42 \mu\text{g kg}^{-1}$. The ratio of surface to subsurface concentration is shown next to each bar.

near non-detection level, for many of the congeners measured. Conversely, sample sites containing higher average grain size also have higher concentrations of congeners. For example, stream substrate at site LBC-9 contains a large percentage of sand and shows a concentration of 0.82 and $0.99 \mu\text{g kg}^{-1}$ of PCB105 at the surface and subsurface, respectively, and 48.7 and $79.0 \mu\text{g kg}^{-1}$ of total Aroclor at the surface and subsurface, respectively. However, just downstream, site LBC-8, where clay and silt composition dominate the substrate, has PCB118 and total Aroclor levels below the limits of detection. There is a significant inverse relationship between clay content and concentration of congeners PCB118 ($p = 0.012$), 105 ($p = 0.029$), 156 ($p = 0.058$) and of TOC ($p = 0.032$). This result is unexpected because both clays and organic carbon have been found to sorb organic contaminants (Thibodeaux, 1996) such as PCBs, PCDDs and PCDFs strongly. This data suggests that where PCB concentrations are low, it is because OC is low in the clay-rich sediments and, at PORTS, adsorption of PCBs increases as OC increases rather than clay (USEPA, 1980; Erickson, 1997).

Of the dioxin-like PCBs analyzed, a set of signature congeners were consistently found at varying concentrations across the study area: PCB105, 118, 156, 167, and 189. For example, as shown in Fig. 4, site X-230J-10 (ratio of surface concentrations with respect to PCB189: 1.8:6.7:3.1:1.4:1; ratio of subsurface concentrations with respect to PCB189: 4.2:24.7:3.2:1.8:1), shows the same set of congeners present at LBC-1 (ratio of surface concentrations with respect to PCB189: 16.5:40.1:9.2:3.3:1; ratio of subsurface concentrations with respect to PCB189: 11.9:31.5:7.3:2.7:1), but at an order of magnitude lower concentrations. The ratio of surface to

subsurface concentration is shown in Fig. 4. This signature set could be used in the future as a screening tool for future remediation at industrial sites with PCB use history similar to that of PORTS.

4. Conclusions

PCB, PCDD and PCDF concentrations were related to organic content, stream dynamics and grain size. Concentrations were generally higher at the surface than at depth, while the compounds bound to organic matter with greater quantities per kg of TOC at depth than at the surface. The results suggests that in areas where the water is slow or static, either migration of contaminants to depth occurs or that deeper soil horizons represent the period of time in history when PCBs were still in use. An inverse correlation of the most abundant congeners (PCB 118, 156, 105) with clay content suggests that PCBs are not binding to the clay rich soils and sediments. A consistent 'signature' set of dioxin-like PCB congeners were found across the study area that could be used for further investigation. The results of this investigation suggest that the flow regimen, transport of sediments and clay content play a role in the fate of PCBs in the environment along the surface as well as the movement toward deeper sediments. These factors should be given appropriate weight for future studies of contamination of PCBs, PCDDs, and PCDFs at other sites.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.03.092>.

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