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Record of PCB congeners, sorbents and potential toxicity in core samples in Indiana Harbor and Ship Canal

ANDRES MARTINEZ[†] and KERI C. HORNBUCKLE^{*,†}

[†]Department of Civil & Environmental Engineering, IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, IA, USA

Abstract

Indiana Harbor and Ship Canal (IHSC) is an active navigational system that serves a heavily industrial area of southern Lake Michigan. We have determined the amount of polychlorinated biphenyls (PCBs), congener distributions, sorbent types and potential for dioxin-like PCB toxicity from two IHSC sediment cores. Vertical distributions of $\sum$ PCBs (sum of 161 individual or coeluting congeners) ranged from 410 to 91000 and 1800 to 41000 ng g⁻¹ dry weight (d.w.) for cores 1 and 2, respectively. Core 1 showed its highest accumulation rate for the year ~1979 and exhibits a strong Aroclor 1248 signal in sediments accumulating over the last 60 years. It appears that from the late 1930s until the beginning of the 1980s there was a large and constant input of PCBs into this system. This pattern differs from lake cores from the Great Lakes region which commonly exhibit a rapid increase, a peak, followed by a sharp decrease in the PCB accumulation rates. Core 2 also has a strong Aroclor 1248 signal in the top layers, but deeper layers show evidence of mixtures of Aroclors and/or weathering processes. High levels of black carbon as a fraction of total organic carbon were found in both cores (median ~30%), which reflect the long history of local combustion sources. No strong relationship was found between $\sum$ PCB concentration and sorbents. Both cores contain dioxin-like PCBs that are highest in concentration below the surface. The high levels of PCBs in the deep sediments are of concern because of plans to dredge this system.

Keywords

PCBs; sediment; core; Aroclor 1248; TEQs

1. Introduction

Indiana Harbor and Ship Canal (IHSC) in East Chicago Indiana, is well known for its high levels of persistent, bioaccumulating and toxic compounds (PBTs) and is one of the largest tributary sources of these pollutants into Lake Michigan (International Joint Commission, 2003; USEPA, 2004, 2006). In 2006, we conducted a field study of polychlorinated biphenyls (PCBs) contamination in IHSC (Martinez et al., 2010a; Martinez et al., 2010b).

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*Corresponding contact information: 4105 SC, Iowa City, IA 52242; keri.hornbuckle@uiowa.edu; Phone: (319) 384-0789 FAX: (319) 335-5660.

Appendix A. Supplementary Material Thirteen figures, two tables and sorbents analysis are available as supplementary material, which can be found free of charge via the Internet at X.

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Our study focused on PCBs in the surficial sediment, water, and overlying air and the potential for PCB release. We found that this system is indeed highly contaminated and PCBs in the surficial sediment were as high as 35,000 ng g⁻¹ d.w. and resembled the commercial mixture Aroclor 1248 (Martinez et al., 2010a). However, we did not collect sediment cores and we know of no reports of PCBs in the deep sediments in IHSC. Here, we report the results of a second field study designed to address PCBs that may have accumulated in deeper sediment. We were motivated to understand the history of PCBs in the area and the potential impact of navigational dredging.

Sediment core records of PBTs provide one of the most effective datasets for examining the history of these contaminants in the environment (Eisenreich et al., 1989; Hermanson et al., 1991; Wong et al., 1995; Zhu and Hites, 2005; Li et al., 2009). Sediment core records have also been used to determine possible sources (Kim et al., 2008) and weathering processes of PBTs in sediment (Magar et al., 2005). We hypothesized that sediment cores collected in IHSC could elucidate the history of PCBs use in the surrounding area.

The United States Army Corps of Engineers (USACE) plans an important dredging project in IHSC (US Army Corps of Engineers, 2005). The purpose of the dredging project is to maintain congressionally authorized navigation depths for large barges to pass through the canals. The project will require the removal of PCB-contaminated sediments although contamination is not the main design criterion for this project. Even though dredging is one of the most common remediation technologies for large contaminated sediment sites, there is still uncertainty in the final outcomes with respect to reducing environmental and human health impacts (Committee on Sediment Dredging at Superfund Megsites, 2007). We hypothesize that dredging will expose high levels of PCBs that are currently buried and that the distribution of specific congeners present in newly exposed subsurface sediment could have an impact on the potential harm posed by release of PCBs to IHSC, Lake Michigan, and the surrounding communities. Therefore, the aim of this study was to investigate the amount and relative distribution of PCB congeners in deep sediment in IHSC, as well as the potential toxicity of the sediment. We also examined the potential role of total, organic and black carbons as predictors of PCB relative concentrations in the sediment.

2. Methods

2.1. Sampling Method

Two IHSC core samples were collected May 8th 2009 from aboard the U.S. EPA's *R/V Mudpuppy* (Figure 1). A submersible vibro-coring system was employed, with a PVC tube (length 4.6 m, internal diameter 0.095 m). Core 1 was segmented every 0.15 m, resulting in 29 slices and Core 2 every 0.31 m, resulting in 15 slices. Both cores had the same length. After the cores were sliced, the segments were homogenized on the ship deck and 3 precleaned amber jars were filled, around 200 g each. The samples were brought to The University of Iowa and kept refrigerated at 4 °C until extraction and analysis.

2.2. Analytical Method

Briefly, wet sediment (~3 g) was homogenized with combusted diatomaceous earth (7 – 15 g d. w.). A surrogate standard consisting of 500 ng of PCB14 (3,5-dichlorobiphenyl), PCB65-d5 (2,3,5,6-tetrachlorobiphenyl-2',3',4',5',6'-d5, deuterated) and PCB166 (2,3,4,4',5,6-hexachlorobiphenyl) was added to each sample. Pressurized fluid extraction (Accelerated Solvent Extractor, Dionex ASE-300) was employed to extract the samples, using a 1 to 1 acetone hexane solution. Details are presented elsewhere (Martinez et al., 2010a). The extract was concentrated, acid washed, and eluted through combusted silica gel (1g), KOH-silica (30% v/v) (3 g), combusted silica gel (2 g) and H₂SO₄-silica gel (2:1 w/w)

(6 g) with hexane, and HCl-activated granulate copper was used to remove sulfur in solution (Sundqvist et al., 2009). When necessary, the sediment extract was eluted through a fresh cleanup column one or two additional times. The solution was concentrated to 0.5 mL and set into GC vials and internal standard was added (100 ng PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl)). PCB quantification was carried out employing a modification of U.S. EPA method 1668B (USEPA, 2008). Tandem mass spectrometry GC/MS/MS (Quattro Micro GC, Micromass MS Technologies) in multiple reaction monitoring mode was utilized to quantify all 209 congeners in 161 individual or coeluting congener peaks (Figure S1). The GC operated at the following conditions: injector temperature 270 °C, interface temperature 290 °C, initial temperature 75 °C, initial time 2 min. The GC temperature program is 75 to 150 °C at 15 °C min⁻¹, 150 to 290 °C at 2.5 °C min⁻¹, and final time 1 min. Total organic carbon (TOC) was analyzed by high-temperature combustion followed by infrared detection (USEPA, 1988). Black carbon (BC) was analyzed by first removing the inorganic carbon through acidifying and drying, then pre-combusted at 375 °C to remove natural organic carbon. The remaining sample was analyzed as TOC for BC (Gustafsson et al., 1997; Grossman and Ghosh, 2009).

2.3. QA/QC

Mean and standard deviation percentage recoveries of PCB14, PCB65-d5 and PCB166 were $62 \pm 21\%$, $67 \pm 21\%$ and $59 \pm 11\%$ respectively. Percentage recoveries of surrogate standards were used to correct congener mass as follows: PCB14 recovery was used to correct PCB1 to PCB39, PCB65-d5 was used to correct PCB40 to PCB127 and PCB166 was used to correct PCB128 to PCB209 (sorted by IUPAC number). Laboratory blanks, which consisted of combusted diatomaceous earth, contained < 5% of total mass of PCBs detected in the samples, except for sample 3.9 - 4.1 m in Core 1 which had an unusually low PCB mass (= 8.7% of the total PCB concentration measured in samples). Standard Reference Material 1944, New York, New Jersey Waterway sediment was extracted and quantified to test to the accuracy of our methods. The mean percent difference between the measured and certified values (27 congeners) was $15 \pm 8.9\%$. The congener masses were corrected as explained above (Figure S2). Limit of quantification (LOQ) for each congener was defined as 6 times the standard deviation from 3 laboratory blanks. Congener masses were calculated using two substitution methods for values below the LOQ, i.e. substitution with zero and with original values. Results showed no variation between both methods, thus, the first method is reported here.

3. Results and Discussion

3.1. Vertical PCB Core Characterization

Qualitatively and quantitatively, the two cores present important differences, such as vertical Σ PCBs concentration and congener profile distributions. The difference in PCB concentrations and congener distributions between the cores could be due to the cores' location in IHSC (Figure 1). Core 1 was collected far from Lake Michigan and the main canal where there is less vessel traffic and less water flow interaction with Lake Michigan. Core 2 was collected from the harbor and the water is more turbulent. Although we do not know the spatial history of dredging in IHSC, it is possible that the area where Core 2 was collected was dredged the last time IHSC was dredged (1972), while Core 1 has never been dredged (Petrovski, 1995).

Core 1 Σ PCB concentrations ranged from 410 - 91000 ng g⁻¹ d.w. (n=29) (Figure 2). The lowest concentration was found in the 3.9 - 4.1 m section and the highest at 1.0 - 1.2 m section below the sediment-water interface. Although the concentrations are low before ~1930s (section 2.3 - 2.4 m and deeper), concentrations of many congeners in each of those

sections were above our LOQ. The top layer concentration ($1200 \text{ ng g}^{-1} \text{ d.w.}$) is consistent with our previous finding in IHSC at this location (also $1200 \text{ ng g}^{-1} \text{ d.w.}$) (Martinez et al., 2010a). Tri- and tetrachlorobiphenyls are the predominant homolog groups found in this core, following the same trend as ΣPCB concentration (Figure S3). Core 1 was dated using an mean mass sedimentation rate for IHSC of $2100 \text{ g m}^{-2} \text{ yr}^{-1}$ (Petrovski, 1995). This rate is 100 fold higher than rates reported for Lake Michigan, 10 fold higher than Green Bay (Hermanson et al., 1991), and very similar to Kinnickinnic River- an industrial tributary in Milwaukee (Karls and Christensen, 1998). The vertical profile reflects the intense and long period of PCB use in IHSC (~50 years). It appears that from the late 1930s until the beginning of the 1980s there was a large and constant input of PCBs into this system. This long constant time period in the vertical profile pattern differs from lake cores from the Great Lakes region (Eisenreich et al., 1989; Hermanson et al., 1991; Wong et al., 1995), where there is a rapid increase, a peak, followed by a rapid decrease in the PCB accumulation rates. However, cores collected in Green Bay show a similar trend, with a constant PCB accumulation rates for long time periods (Hermanson et al., 1991). This vertical profile pattern reflects direct and specific sources of PCBs (e.g. paper mills in the Fox River) into the system and not an indirect or integrated collection of sources. In the open lake cores, inputs from atmospheric transport and deposition, and inputs from integrated diverse sources dominate the observed PCB accumulations. The vertical profile from Core 1 strongly suggests that the PCB source is local. The highest accumulation rate ($1.9 \text{ g m}^{-2} \text{ yr}^{-1}$) was found in 1979 (midpoint section), similar to Green Bay cores. This peak is around 10 years after the maximum historical records of the sales/production volumes of PCBs in the United States (peaks in 1966 - 1969) (Eisenreich et al., 1989) (Figure 2). It is possible that industries nearby started using PCB in the mid-1930s in open and semi-closed applications and halted when such use was forbidden in the end of the mid-1980s, and now is legacy contamination impacting this water system.

Core 2 ΣPCB concentrations ranged from $1800 - 41000 \text{ ng g}^{-1} \text{ d.w.}$ ($n=15$) (Figure S4). The lowest concentration was found in the surficial sediment, which is also consistent with our previous findings at this location (Martinez et al., 2010a). The harbor system was dredged in the 1970s and although we do not have detailed records of that work, we hypothesize that the Core 2 site area was disturbed and we did not attempt to date this core.

3.2. Core Carbon Characterization

The total organic carbon fraction (f_{TOC}) median in Core 1 was 15% (Interquartile range (IQR) 14 - 16%), the black carbon fraction (f_{BC}) median was 4.3% (IQR 3.9 - 4.9%) and the organic carbon fraction ($f_{\text{OC}} = f_{\text{TOC}} - f_{\text{BC}}$) median was 11% (IQR 9.7 - 12%) for Core 1 ($n=29$). The ratio BC:TOC median was 28% (IQR 27 - 31%) (Figure 3). Total organic carbon fraction median in Core 2 was 17.4% (IQR 13 - 20%), f_{BC} median was 6.1% (IQR 5.5 - 8.2%) and f_{OC} median was 11% (IQR 7.2 - 12%) ($n=15$). The ratio BC:TOC median was 41% (IQR 36 - 43%) (Figure S5). Cores 1 and 2 values are in the top extreme of other sediments around the world (Cornelissen et al., 2005). Although BC values are high in both cores, Core 2 values were found to be significant higher than Core 1 ($p < 0.001$), but not for TOC nor OC. Core 2 is located closer to the steel mill stacks in IHSC than Core 1. Incomplete combustion of fossil fuels is one of the most import sources of BC into the environment (Koelmans et al., 2006). This may explain the higher levels of BC found in Core 2. Moreover, no BC trend was found in both cores, reflecting a steady input of BC into the system, contrary to what was found in other cores in the Great Lakes region (Karls and Christensen, 1998).

3.3. Homolog Group Distributions

Figure S6 depicts the vertical homolog group fraction distribution in Core 1. This core is enriched in tri- and tetrachlorobiphenyls ($75 \pm 4.2\%$ in mass), where generally tetra- is predominant. There is little variation in the homolog group fractions with depth, with a small increase in tri- and a small decrease in hepta-, both from the top to ~0.90 m (~1989). This suggests that a small amount of weathering processes, such as microbial degradation (Ishaq et al., 2009) or desorption from the sediment to the overlying water, have occurred in this core for the last ~60 years. Additionally, deeper sections (before 1930s) show a significant increase in high chlorinated congeners (PCBs 206, 207, 208 and 209), which seems unusual. We have not been able to identify any sampling or analytical artifact that could explain the presence of these congeners at these depths. However, this pattern has been identified in lake core samples, suggesting that non-Aroclor sources could be responsible of this input (Hu et al., 2011). Core 2 is also enriched in tri- and tetra- ($67 \pm 11\%$ in mass), where tetra- is predominant from top to 1 m and then tri- is predominant. From top to bottom, there is a slight increase in mono- and di-, a larger increase in tri-, an important decrease in penta- and hexa-, and the rest of the homolog groups generally maintain constant (Figure S7). Comparison between the congener profile distributions of the top and the bottom layers suggest that the less chlorinated congeners in the top layer are diffusing more rapidly into the overlying water than the more chlorinated compounds. This finding was also observed when fluxes from sediment to water were estimated (Martinez et al., 2010b). In addition, it is possible that aerobic and anaerobic microbial degradation might be occurring in this core (i.e. less low chlorinated congeners and more middle chlorinated congeners in the top layer, and more low chlorinated congeners and less middle chlorinated congeners in the bottom layer) (Borja et al., 2005) (Figure S8).

To compare the similarity between congener profiles in each section as well as with commercial mixtures Aroclors, the cosine theta metric ($\cos \theta$) was employed. The $\cos \theta$ allows us to examine similarities between congener profiles. This metric uses the cosine of the angle between two multivariable vectors (the profiles) where a value of 0.0 describes two completely different vectors and 1.0 describes two identical (Magar et al., 2005). Most congener profile sections in Core 1 are very similar, although as they are further separated in the core, the similarity decreases. For example, a $\cos \theta$ of 0.97 and 0.81 were obtained between the top section and section 0.46 – 0.61 m and section 3.8 – 3.9 m, respectively. In general, $\cos \theta$ between Core 1 sections and commercial mixtures yielded the highest similarity with Aroclor 1248 signature (Aroclor 1248 > 1242 > 1016 > 1254 > 1221) (Table S1). This similarity with Aroclor 1248 was particularly strong in the top 2 meters (~1940s to the present) (Figure 4). Core 2 congener profile distributions also showed a better similarity with Aroclor 1248, but not as good as Core 1. Aroclors 1242 and 1016 also showed a good agreement with most of the sections of Core 2 (Table S2).

The similar congener profiles do not prove that only Aroclor 1248 was used in IHSC, although the Aroclor 1248 signal is very strong. Biotic and abiotic processes occurring in environmental matrices can change the original Aroclor signal, as well as mixtures of Aroclors, which could lead to misinterpreting the original Aroclor mixtures entered the environment (Chiarenzelli et al., 1997).

3.4. TEQs

Although it is well known that bioavailability of PBTs and their toxic effects are directly related to the freely dissolved phase in the pore water in the sediment and not from the bulk concentration, here we look at the potential toxicity of the sediment. Notice that our analytical method allows us to individually separate 11 of the 12 dioxin-like PCBs, where PCBs156+157 coelute. Toxic equivalent quantities (TEQs) were calculated using the most

recently revised 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalent factors (TCDD TEFs) for the 12 dioxin-like PCBs (Van den Berg et al., 2006). Core 1 ranged from 0.68 to 120 pg TCDD TEQ g⁻¹ d.w., where the highest value was found in year 1967 (~1.4 m deep) (Figure 5). Core 2 ranged from 3.0 to 25 TCDD TEQ g⁻¹ d.w., where the highest value was found in section 3.1 – 3.4 m deep (Figure 5). A good agreement between Σ PCB concentration and TEQs was obtained for both cores (Core1: $R^2 = 0.99$, $p < 0.0001$, Core 2: $R^2 = 0.8$, $p < 0.0001$). The major contributor of the TEQs in Core1 is PCB118, followed by PCB77, and PCB105. PCB77 is the major contributor of TEQs in Core 2, followed by PCB118 and PCB105.

4. Conclusions

Results from this investigation have exposed the following issues: First, Core 1 appears to reflect the history of local use of PCBs in IHSC, with a constant and large use over an extensive period of time (~60 years). In addition, Core 1 presents PCB concentrations higher than 50000 ng g⁻¹ d.w. or 50 ppm (31% of Core 1 layers > 50 ppm), which is considered a hazardous waste (USEPA, 1998) and therefore, IHSC could be designed as a Superfund site by the Comprehensive Environmental Response, Compensation, and Liability Act. Second, very high values of organic sorbents (TOC, OC and BC) were found in these two cores. No strong relationship was found between Σ PCB concentration and TOC, OC and BC, suggesting that there are other types of sorbents not analyzed here, such as oil, that control the association of PCBs into the sediment (Ghosh et al., 2000), as well as sorbents acting in parallel (Accardi-Dey and Gschwend, 2002; Allen-King et al., 2002) (see analysis in supplementary material). Third, both cores show elevated values of TEQs in deeper sediments, as well as total PCBs. The release of dioxin-like and other PCBs from sub-surface sediment could become an even larger source of these compounds to the local environment than is currently the case. Therefore, PCB concentrations in the sediment should be included in the dredging strategy, so that the potential release of PCBs to the environment is reduced.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

- Accardi-Dey A, Gschwend PM. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environ. Sci. Technol.* 2002; 36:21–29. [PubMed: 11811485]
- Allen-King RM, Grathwohl P, Ball WP. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Adv. Water Resour.* 2002; 25:985–1016.
- Borja J, Taleon DM, Aurensenia J, Gallardo S. Polychlorinated biphenyls and their biodegradation. *Process Biochem.* 2005; 40:1999–2013.
- Chiarenzelli JR, Scrudato RJ, Wunderlich ML. Volatile loss of PCB Aroclors from subaqueous sand. *Environ. Sci. Technol.* 1997; 31:597–602.

- Committee on Sediment Dredging at Superfund Megsites. Assessing the Effectiveness. National Academy of Sciences; 2007. Sediment Dredging at Superfund Megsites.
- Cornelissen G, Gustafsson O, Bucheli TD, Jonker MTO, Koelmans AA, van Noort PCM. Extensive Sorption of Organic Compounds to Black Carbon, Coal, and Kerogen in Sediments and Soils: Mechanisms and Consequences for Distribution, Bioaccumulation, and Biodegradation. *Environ. Sci. Technol.* 2005; 39:6881–6895. [PubMed: 16201609]
- Eisenreich SJ, Capel PD, Robbins JA, Bourbonniere R. Accumulation and diagenesis of chlorinated hydrocarbons in lacustrine sediments. *Environ. Sci. Technol.* 1989; 23:1116–1126.
- Ghosh U, Gillette JS, Luthy RG, Zare RN. Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environ. Sci. Technol.* 2000; 34:1729–1736.
- Grossman A, Ghosh U. Measurement of activated carbon and other black carbons in sediments. *Chemosphere.* 2009; 75:469–475. [PubMed: 19200572]
- Gustafsson O, Haghseta F, Chan C, MacFarlane J, Gschwend PM. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* 1997; 31:203–209.
- Hermanson MH, Christensen ER, Buser DJ, Chen LM. Polychlorinated-biphenyls in dated sediment cores from Green Bay and Lake Michigan. *J. Great Lakes Res.* 1991; 17:94–108.
- Hu D, Martinez A, Hornbuckle KC. Sedimentary records of non-Aroclor and Aroclor PCB mixtures in the Great Lakes. *J. Great Lakes Res.* 2011; 37:359–364.
- International Joint Commission. Status of Restoration Activities in Great Lakes Areas of Concern: A Special Report. Final. 2003.
- Ishaq R, Persson NJ, Zebuhr Y, Broman D, Naes K. PCNs, PCDD/Fs, and Non-orthoPCBs, in Water and Bottom Sediments from the Industrialized Norwegian Grenlandsfjords. *Environ. Sci. Technol.* 2009; 43:3442–3447. [PubMed: 19544837]
- Karls JF, Christensen ER. Carbon particles in dated sediments from Lake Michigan, Green Bay, and tributaries. *Environ. Sci. Technol.* 1998; 32:225–231.
- Kim YS, Eun H, Cho HS, Kim KS, Watanabe E, Baba K, Katase T. The characterization of PCDDs, PCDFs and coplanar PCBs during the past 50 years in Gwangyang Bay, South Korea. *J. Hazard. Mater.* 2008; 154:756–765. [PubMed: 18063300]
- Koelmans AA, Jonker MTO, Cornelissen G, Bucheli TD, Van Noort PCM, Gustafsson O. Black carbon: The reverse of its dark side. *Chemosphere.* 2006; 63:365–377. [PubMed: 16226291]
- Li A, Rockne KJ, Sturchio N, Song W, Ford JC, Wei H. PCBs in sediments of the Great Lakes - Distribution and trends, homolog and chlorine patterns, and in situ degradation. *Environ. Pollut.* 2009; 157:141–147. [PubMed: 18771832]
- Magar VS, Johnson GW, Brenner RC, Quensen JF, Foote EA, Durell G, Ickes JA, Peven-McCarthy C. Long-term recovery of PCB-contaminated sediments at the Lake Hartwell superfund site: PCB dechlorination. 1. End-member characterization. *Environ. Sci. Technol.* 2005; 39:3538–3547. [PubMed: 15952356]
- Martinez A, Norström K, Wang K, Hornbuckle KC. Polychlorinated biphenyls in the surficial sediment of Indiana Harbor and Ship Canal, Lake Michigan. *Environ. Int.* 2010a; 36:849–854. [PubMed: 19268364]
- Martinez A, Wang K, Hornbuckle KC. Fate of PCB Congeners in an Industrial Harbor of Lake Michigan. *Environ. Sci. Technol.* 2010b; 44:2803–2808. [PubMed: 20131898]
- Petrovski, DM. Use of Bathymetry for sediment characterization at Indiana Harbor. In: Demars, KR.; Richardson, GN.; Yong, RN.; Chaney, RC., editors. *Dredging, Remediation, and Containment of Contaminated Sediments*. ASTM; Philadelphia: 1995. p. 40-49.
- Sundqvist KL, Tysklind M, Cato I, Bignert A, Wiberg K. Levels and homologue profiles of PCDD/Fs in sediments along the Swedish coast of the Baltic Sea. *Environ. Sci. Pollut. R.* 2009; 16:396–409.
- US Army Corps of Engineers. Justification of Estimates for Civil Function Activities Department of the Army, Fiscal Year 2006. In: Great Lakes and Ohio River Division. , editor. *Congressional submission fiscal year 2006*. 2005. p. 21-26.
- USEPA. Determination of total organic carbon in sediment (Lloyd Kahn Method). 1988.
- USEPA. Disposal of Polychlorinated Biphenyls (PCBs). *Fed. Regist.* 1998.

- USEPA. Results of the Lake Michigan Mass Balance Project; Polychlorinated Biphenyls and trans-Nonchlor Data Report. 2004.
- USEPA. Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyls Modeling Report. 2006.
- USEPA. Method 1668B: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. 2008.
- Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N, Peterson RE. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.* 2006; 93:223–241. [PubMed: 16829543]
- Wong CS, Sanders G, Engstrom DR, Long DT, Swackhamer DL, Eisenreich SJ. Accumulation, Inventory, and Diagenesis of Chlorinated Hydrocarbons in Lake Ontario Sediments. *Environ. Sci. Technol.* 1995; 29:2661–2672.
- Zhu LY, Hites RA. Identification of brominated carbazoles in sediment cores from Lake Michigan. *Environ. Sci. Technol.* 2005; 39:9446–9451. [PubMed: 16475320]

Highlights

- Sediment cores were collected from the largest direct tributary source of PCBs to Lake Michigan.
- PCBs (160 peaks including dioxin-like PCBs), black carbon, and TOC were measured.
- PCBs increase with depth with the highest correlating to years 1940 through 1990.
- The system exhibits an unusually strong Aroclor 1248 signal.
- The cores record the history of PCB use in a small but intensive industrial site.
- Dredging in 2012 will increase the release of PCBs even after dredging is completed.
- This site is a very large regional source of PCBs that will increase in the near future

Research Highlights

High levels of PCBs, TEQ toxicity, as well as black carbon as a fraction of total organic carbon were found in deep sediment in IHSC.

Figure 1. Indiana Harbor and Ship Canal, East Chicago, Indiana. Red circles show the core sample locations (Core 1: latitude $41^{\circ} 38.7425$ N and longitude $87^{\circ} 28.3277$ W, Core 2: latitude $41^{\circ} 39.9058$ N and longitude $87^{\circ} 26.2944$ W). The blue and yellow polygons represent the dredging area and the confined disposal facility (CDF), respectively (US Army Corps of Engineers, 2010).

Figure 2.

Vertical profiles of PCB accumulation (line), Σ PCB concentrations (black dots) and PCB sales production in the U.S. (dash line (Eisenreich et al., 1989)) in Core 1. Error bars represent one standard deviation (see 8th and 9th black dots from the top to the bottom, n=3 analytical quantification). A constant PCB accumulation is plotted for each section, which was calculated from the midpoint mass of each section. Deeper than the 1930 depth horizon, total PCB concentration is low and not dated. Notice that the use of PCBs was banned in January 1978, unless it was carried out in a “totally enclosed manner” (Erickson, 2001).

Figure 3. Bulk density, f_{BC} ($\square$), f_{OC} (Δ), f_{TOC} ($\circ$), and the percent of total organic carbon that is in the form of black carbon in Core 1.

Figure 4.

Congener profile distributions in surface sediment Core 1 (a), section 2.13 – 2.29 m deep (~1940) (b), and Aroclor 1248 (c) (analyzed by our analytical method). Each congener was normalized to the total concentration of PCBs in the sample.

Figure 5. Vertical profiles of pg TCDD TEQ g⁻¹ d.w. for cores 1 (a) and 2 (b). See the different x and y-axes scales for each plot.