Recovery Co and BP Products North America Inc. The IHSC is an active canal system that continues to support large vessels. To remain viable for industrial shipping, the U. S. Army Corps of Engineers, Chicago District, is planning to begin a long-term dredging project in 2009 to restore adequate navigational depth. The sediment will be disposed in a Confined Disposal Facility (CDF), which is under construction, and will be located north of Lake George Branch, less than 100 meters from the canal (US Army Corps of Engineers, 2005b).

Due to years of heavy industrial operation, the area has been contaminated with heavy metals, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). As a result, the International Joint Commission designated the IHSC as an Area of Concern (International Joint Commission, 2003). The IHSC and Grand Calumet River has been shown to include regions that are toxic to invertebrates (Burton et al., 1996; Canfield et al., 1996; Ingersoll et al., 2002; Rathbun et al., 1996). Sediment collected from IHSC presents the highest toxicity in comparison to Buffalo and Saginaw rivers (Canfield et al., 1996; Rathbun et al., 1996), and are among the most contaminated and toxic Great Lakes sediments that have been evaluated (Ingersoll et al., 2002).

There is little published data of spatial extent and concentration magnitude of PCBs in the sediment in IHSC. The Army Corps report that PCBs were found in IHSC sediment since 1977 but has not published a full report (Pittman, personal communication). There is no data about methods of quantification of individual PCB congeners or quality control. Custer and coworkers report high levels of PCBs in tissue of lesser scaup (*Aythya affinis*), a diving duck dwelling in IHSC (Custer et al., 2000). Although not commonly used for food, the authors noted that the PCB concentration in 88% of the birds exceeded the PCB human consumption guidelines for edible poultry in USA (>3.0 μg g^{-1} lipid wt.) (FDA, 1979).

The U. S. Army Corps of Engineers have monitored airborne PCBs in the region since 2001 (US Army Corps of Engineers, 2005a). They have reported concentrations of PCB congeners that are comparable to concentrations measured in Chicago (a region of elevated airborne PCBs) and much higher than reported for remote and rural locations around Lake Michigan (Sun et al., 2007).

Due to the intense industrial activity in the area surrounding the IHSC during the time that PCBs were heavily used, we hypothesized that the IHSC surficial sediment would be heavily contaminated. We further hypothesized that the current congener distribution of PCBs in the surficial sediment continues to resemble the original commercial mixtures distributed by Monsanto Company in the middle part of the last century. Therefore, the central purpose of

mediment clayr th reseusped in o the iwatr conumenwhin eredging pperation,sbegin

2.2 Analytical Method

The analytical method employed for sample extraction is a modification of U.S. EPA Method 3545 (Bandh et al., 2000; Bjorklund et al., 1999; Josefsson et al., 2006; USEPA, 1995a). Briefly, samples were weighed (~3 g) and mixed with a known amount of combusted diatomaceous earth and spiked with 500 ng surrogate standard, PCB14 (3,5-dichlorobiphenyl), PCB65 (2,3,5,6-tetrachlorobiphenyl) and PCB166 (2,3,4,4′,5,6-hexachlorobiphenyl) (Cambridge Isotope Laboratories, Inc.). The sediments were extracted utilizing a pressurized fluid extraction (Accelerated Solvent Extractor, Dionex ASE-300), of equal parts acetone and hexane. The sediment water content was determined gravimetrically for each sample from a separate aliquot by drying for 12 hrs at 104° C.

Polar interferences and other compounds were removed by extraction with KOH and then with sulfuric acid. The final hexane extract was passed through a Pasteur pipette filled with 0.1 g of combusted silica gel and 1 g of acidified silica gel (2:1 silica gel:acid by weight) (USEPA, 1995b) and eluted with hexane. PCB204 (2,2′,3,4,4′,5,6,6′-octachlorobiphenyl) was added as internal standard (100 ng; Cambridge Isotope Laboratories, Inc.).

PCB quantification was carried out employing a modification of EPA Method 1668a (USEPA, 1999). Tandem Mass Spectrometry GC/MS/MS (Quattro Micro™ GC, Micromass MS Technologies) in multiple reaction monitoring (MRM) mode was utilized to quantify all 209 congeners in 163 individual or coeluting congener peaks (Table S2 in the supporting information), of which PCB14, PCB65 and PCB166 are surrogate standards and PCB204 is internal standard. The gas chromatogram (GC) was equipped with a Supelco SBP-Octyl capillary column (30 m × 0.25 mm ID, 0.25 μm film thickness) with helium as carrier gas at a constant flow rate of 0.8 ml min^{-1}. The GC operates at the following conditions: injector temperature 270° C, interface temperature 290° C, initial temperature 75° C, initial time 2 minutes. 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 minute. Figure S1 in the supporting information includes a calibration chromatogram, as well as a sample chromatogram. Linearity of the instrument response was confirmed and PCB congener mass calculation was performed applying relative response factor (RRF) obtained from the calibration curve for each congener. Total organic carbon (TOC) was

PCB151/135 and PCB138/163/129/160. However, the differences between the Aroclor and IHSC congeners are less than 2.5% by mass (Figure 5).

It appears that the IHSC was originally contaminated with Aroclor 1248, and that the small differences that now exist are the result of chemical, physical and biological transformations (weathering) in the sediments. The last time the IHSC was dredged was in 1972 - thirty-four years before our expedition; the surficial sediments may have been at the water-sediment surface for many years. Over time the lower chlorinated congeners (e.g. PCB 48) have been lost to volatilization, desorption and/or aerobic microbial degradation (Maltseva et al., 1999), and the high chlorinated ones due to anaerobic microbial dechlorination (Quensen et al., 1990). The relative enrichment of the lower-chlorinated and ortho-substituted congeners (PCBs 25 and 26/29) is probably a result of anaerobic microbial dechlorination (Quensen et al., 1990).

4. Conclusions

Employing tandem mass spectrometry we have conclusively determined that IHSC surficial sediments are contaminated with PCBs. The PCB levels found here are comparable to other PCBs contaminated sites in USA, most of them (although not IHSC) established by law as Superfund Sites. The analytical method used also allowed us to determine the PCB congener profile distribution in the sediment. The origin of the PCBs is not known but strongly resembles the original technical mixture Aroclor 1248. This mixture was used in hydraulic fluids, vacuum pumps, plasticizers and adhesives (US Department of Health and Human Services, 2000). Possible uses of this mixture in East Chicago included the equipment and auxiliary services for the adjacent steel mill and gas refinery and/or lubrication for the drawbridges spanning the canal. Finally, the PCBs in the sediments have undergone a small amount of weathering compared to the original 1248. The current congener profiles provide evidence of desorption, volatilization, and microbial dechlorination.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was funded as part of the Iowa Superfund Basic Research Program, NIEHS Grant ES013661. We gratefully acknowledge the Great Lakes National Program Office of the U.S. EPA for the donation of the *Mudpuppy* and crew. We thank Tom Ledolter for help in planning the Indiana Harbor and Ship Canal campaign, Christoffer von Schwerin for his useful work at the laboratory, and David Wethington (U.S. Army Corps of Engineers, Chicago Office) for assistance in sampling sediment from IHSC.

References

Bandh C, Bjorklund E, Mathiasson L, Naf C, Zebuhr Y. Comparison of Accelerated Solvent Extraction and Soxhlet Extraction for the Determination of PCBs in Baltic Sea Sediments. Environ Sci Technol 2000;34:4995–5000.

Bjorklund E, Bowadt S, Nilsson T, Mathiasson L. Pressurized fluid extraction of polychlorinated biphenyls in solid environmental samples. J Chromatogr A 1999;836:285–293.

Burton GA, Ingersoll CG, Burnett LC, Henry M, Hinman ML, Klaine SJ, et al. A comparison of sediment toxicity test methods at three Great Lake Areas of Concern. J Great Lakes Res 1996;22:495–511.

Canfield TJ, Dwyer FJ, Fairchild JF, Haverland PS, Ingersoll CG, Kemble NE, et al. Assessing Contamination in Great Lakes Sediments Using Benthic Invertebrate Communities and the Sediment Quality Triad Approach. J Great Lakes Res 1996;22:565–583.

Custer TW, Custer CM, Hines RK, Sparks DW. Trace elements, organochlorines, polycyclic aromatic hydrocarbons, dioxins, and furans in lesser scaup wintering on the Indiana Harbor Canal. Environ Pollut 2000;110:469–482. [PubMed: 15092826]

FDA. Polychlorinated biphenyls (PCBs); reduction of tolerances. Federal Register 1979;44:38330–38340.

Frame GM, Cochran JW, Bøwadt SS. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. J High Res Chromatogr 1996;19:657–668.

Gong Y, Depinto JV, Rhee GY, Xia L. Desorption rates of two PCB congeners from suspended sediments--I. experimental results. Water Res 1998;32:2507–2517.

Harkness MR, McDermott JB, Abramowicz DA, Salvo JJ, Flanagan WP, Stephens ML, et al. In Situ Stimulation of Aerobic PCB Biodegradation in Hudson River Sediments. Science 1993;259:503–507. [PubMed: 8424172]

Ingersoll CG, MacDonald DD, Brumbaugh WG, Johnson BT, Kemble NE, Kunz JL, et al. Toxicity Assessment of Sediments from the Grand Calumet River and Indiana Harbor Canal in Northwestern Indiana, USA. Arch Environ Contam Toxicol 2002;43:156–167. [PubMed: 12115041]

International Joint Commission. Status of Restoration Activities in Great Lakes Areas of Concern: A Special Report. 2003. Final

Josefsson S, Westbom R, Mathiasson L, Bjorklund E. Evaluation of PLE exhaustiveness for the extraction of PCBs from sediments and the influence of sediment characteristics. Anal Chim Acta 2006;560:94–102.

Maltseva OV, Tsoi TV, Quensen JF, Fukuda M, Tiedje JM. Degradation of anaerobic reductive

USEPA. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS. 1999.

USEPA. Superfund Record of Decision Sheboygan River and Harbor Sheboygan. Wisconsin: 2000.

USEPA. Results of the Lake Michigan Mass Balance Study: Polychlorinated Biphenyls and trans-Nonachlor Data Report. 2004.

USEPA. Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyls Modeling Report. 2006.

USEPA. US Army Corps of Engineers. Inferred PCB Levels — 0 to 12 inch depth. New England District; 2001. New Bedford Harbor.

Wisconsin Department of Natural Resources. Record of Decision Operable Units 3, 4, and 5 Lower Fox River and Green Bay, Wisconsin Record of Decision Responsiveness Summary. 2003.

Wisconsin Department of Natural Resources Madison. Feasibility Study for the Lower Fox River and Green Bay, Wisconsin, Proposed Remedial Action Plan for the Lower Fox River and Green Bay, and Record of Decision for Operable Unit 1 and Operable Unit 2. 2003. White Paper NO. 19 — Estimates of PCB Mass, Sediment Volume, and Surface Sediment Concentrations in Operable Unit 5, Green Bay Using an Alternative Approach. Response to Comments on the Remedial Investigation for the Lower Fox River and Green Bay, Wisconsin.

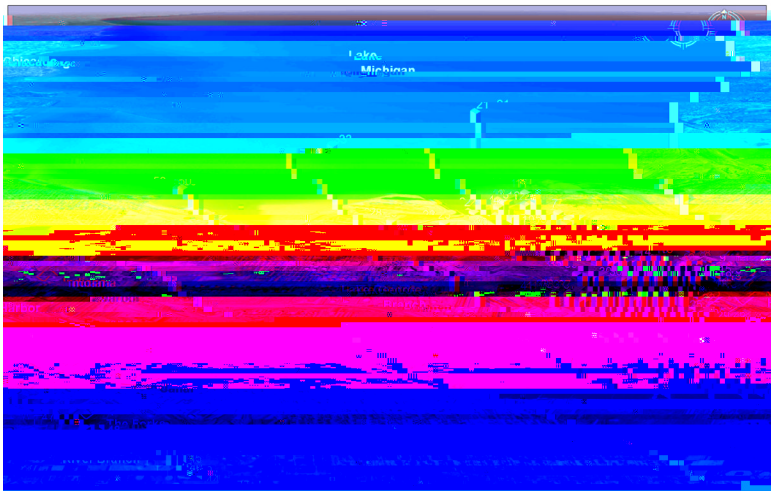
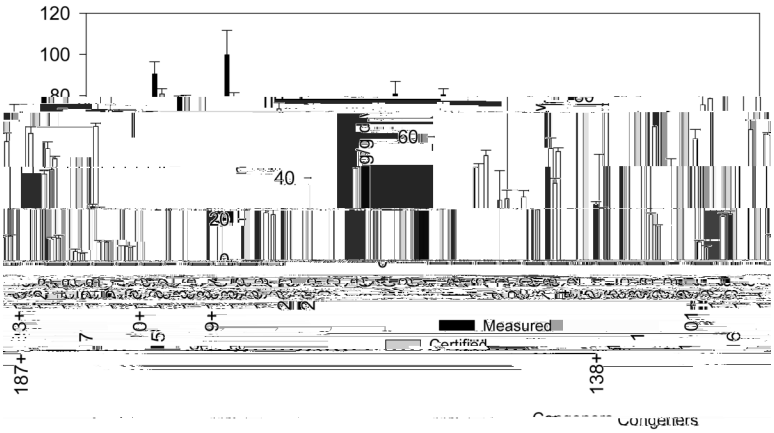


Figure 1.

Spatial location and measured ΣPCB concentration (ng g^{-1} d. w.) in surficial sediment of IHSC. The height of the bars represents the total PCB concentration and the number over or next to each bar is the sample ID (see also Table S1 in the supporting information). The canals regions are U.S Army Corps of Engineers designations.


120
100
60
40
Measured
Certified

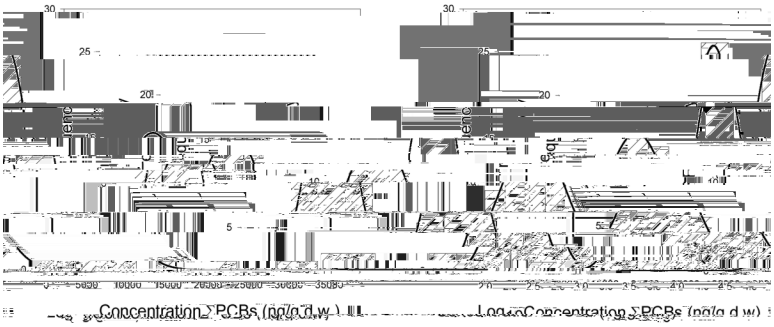


Figure 3.

Histograms of surficial sediment. Left plot in ng g^{-1} d.w., and right plot transformed to common logarithms. The curve in the left plot shows the lognormal distribution, while the curve in the right plot shows the fitted normal distribution.

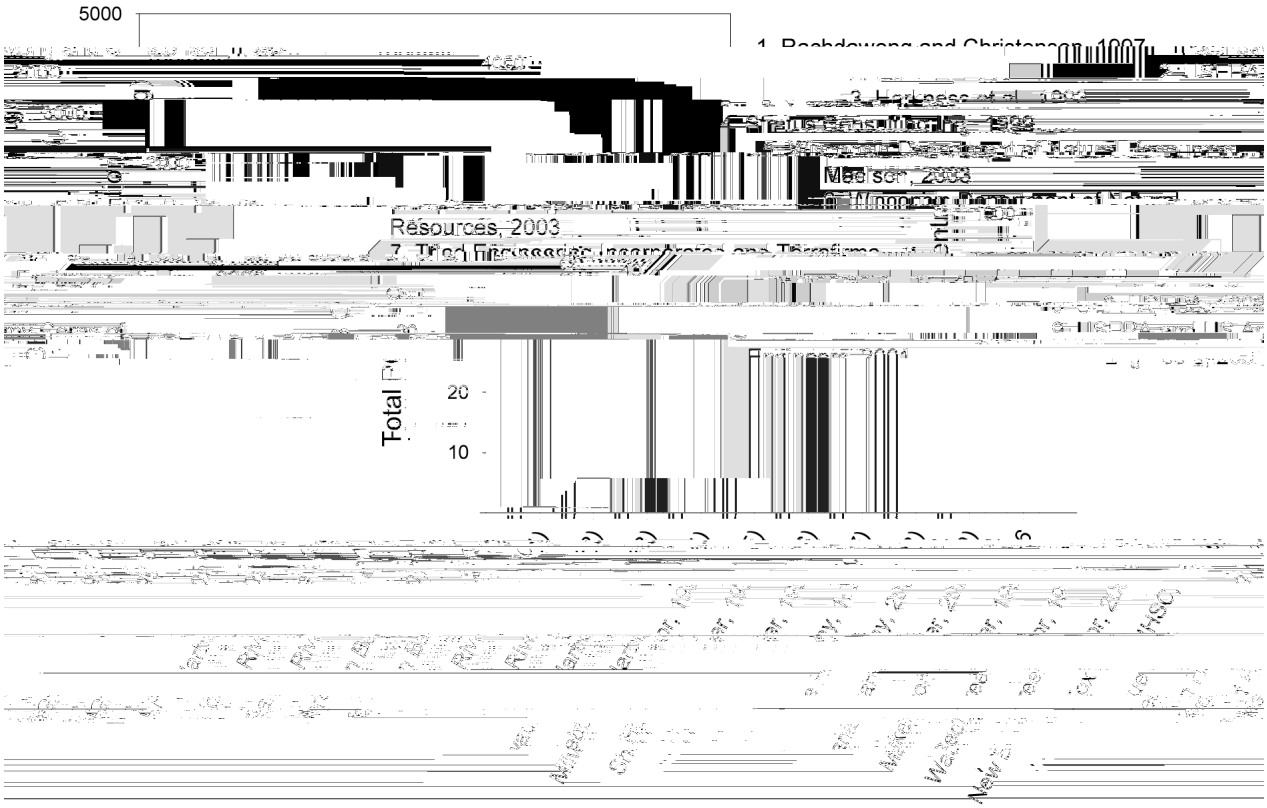


Figure 4.
Comparison of total concentration of PCB in surficial sediment with nine different sites across the United States, including IHSC (this study).

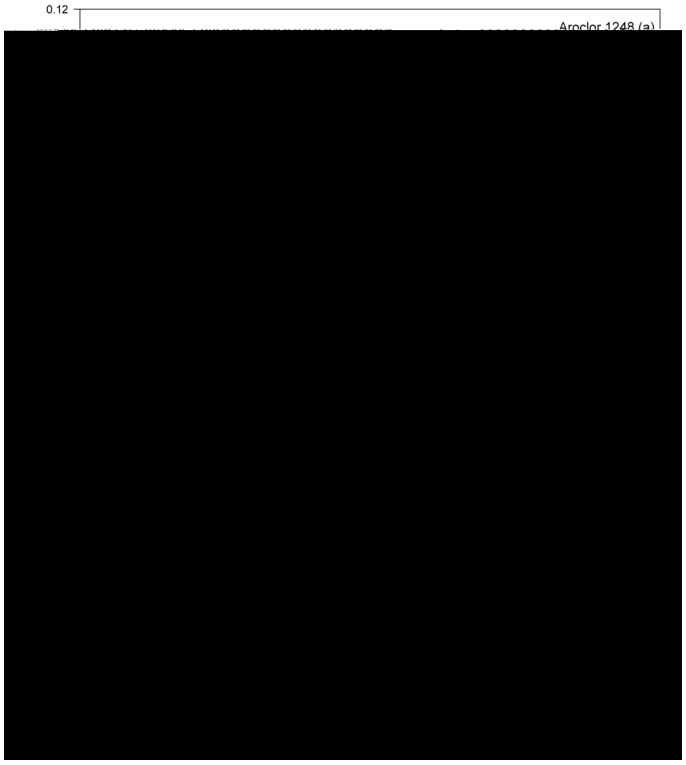


Figure 5.
Congener distributions in mass percentage for Aroclor 1248 (Lot B4020171) (a), mean congener distribution of the 60 sediment sites (b) and Aroclor 1248 minus mean samples (c). In the case of (b), each sample was normalized to its total concentration, and the error bars represents one standard deviation about mean. Congeners are ordered by IUPAC number and listed in full in Table S2 in the supporting information, including the values depicted in (b). The asterisk (*) indicates a difference at the 99% confidence level as described in the text.

Table 1