Published in final edited form as:

Chemosphere. 2016 February ; 144: 1943–1949. doi:10.1016/j.chemosphere.2015.10.090.

Polychlorinated biphenyl congeners in sediment cores from the Upper Mississippi River

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Abstract

We determined polychlorinated biphenyls (PCBs) and radionuclide ^{137}Cs in sediment cores from the Upper Mississippi River (UMR) and the Iowa River, Iowa, at their confluence. Vertical distribution of ^{137}Cs indicated negligible mixing in the UMR core, while the Iowa River core showed signs of mixing. A clear ^{137}Cs peak was found in the UMR core, which was correlated to 1963. The PCB vertical distribution in UMR core was similar to the historical trend in Aroclor production observed in Great Lakes cores, with a peak close to the ^{137}Cs peak, suggesting a date near 1960. In general, PCB congener profiles in both cores resembled the Iowa soil background signal. We concluded that despite evidence of mixing in the Iowa River core, both cores retain the PCB signature of historical and regional environmental exposure. Further, our results indicate that this iconic waterway has a long history of PCBs that reflects national production and use.

Keywords

Polychlorinated biphenyls; ^{137}Cs ; Upper Mississippi River; Iowa River

1. Introduction

The Upper Mississippi River (UMR) supports substantial and diverse biological resources that can be exposed to numerous contaminants that enter the UMR ecosystem directly or through tributary streams and groundwater (Wiener et al., 1984; USGS, 1995). Over its long history of settlement and development the UMR has received contaminants from a variety of industrial, agricultural, municipal, and residential sources including persistent organic pollutants (POPs). In particular, polychlorinated biphenyls (PCBs) and more recently emerging contaminants such as synthetic musk fragrances are examples of POPs that have been detected in the UMR (Steingraeber et al., 1994; Wiener and Sandheinrich, 2010). These chemicals tend to sorb and accumulate in the sediments, where they can be transported, deposited or redissolved into the water column. They can bioaccumulate in the food chain (Connell, 1990), and may reach levels that pose cancer and other health risks to

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.10.090>.

humans (Lauby-Secretan et al., 2013). The history of use of these chemicals in the UMR is not well known, and the POPs legacy in rivers itself has rarely been investigated.

There are few studies of POPs in the UMR sediments. Rostad et al. (1995) collected surficial sediments from pools 1 to 26 (ca. from Minneapolis to St. Louis) and found the highest PCB concentrations near metropolitan areas such as the Twin Cities (Minneapolis- St. Paul, MN), and the Quad Cities (Davenport–Bettendorf, IA, and Moline-Rock Island-East Moline, IL). Barber and Writer (1998) reported PCB values for UMR surficial sediment after the 1993 flood of 2–33 ng g⁻¹ dry weight (dw) where the highest values were found downstream of the Twin Cities.

The construction of the series of locks and dams along the UMR during the 1930s for enhancing commercial navigation has altered the hydrology of the river and subsequent sediment deposition. Following the 1930s construction projects, the lowland floodplains upstream of most locks and dams were inundated into large impoundments (pools). A pool is the reach of the UMR between two consecutive navigation dams. The slower current velocity characteristics of these pools and impounded backwater areas have made them efficient traps for sediments. We identified these locations for our investigation.

Given the lack of information regarding POPs associated with sediment in the UMR, the main aim of this investigation was to study chlordanes, PCBs and synthetic musk fragrances in a backwater area of a pool in the UMR and a backwater area of a major tributary (i.e. Iowa River). These three categories of POPs were chosen to better investigate their respective agricultural, industrial, and residential uses/sources. In addition, ¹³⁷Cs was measured in the sediment to determine possible initial nuclear and peak testing dates.

2. Methods

2.1. Sampling method

Two sediment cores per site were collected from a backwater area of the UMR in Pool 17 (Pool 17-UMR site) and an oxbow lake in the Horseshoe Bend wildlife refuge (Horseshoe Bend site), near the mouth of the Iowa River in May 2012 (Fig. 1). The rationale of the sampling locations was to observe differences in potential mixing and POPs occurrence and distribution. The Pool 17-UMR site was selected to evaluate the influence of POPs inputs from the UMR, particularly from possible upstream sources such as Muscatine and Davenport, IA and Moline, IL. The site was located ca. 20 km south of Muscatine and ca. 60 km downstream (southeast) from Davenport/ Moline. The Horseshoe Bend site was located ca. 20 km south from of the Pool 17 site, and was selected to capture the record of a major tributary to the UMR. Both locations present different hydrology characteristics that affect sediment deposition and sediment mixing. Thus the distribution of POPs in these cores would allow for an interesting comparison between two different riverine environments.

A submersible vibracoring system with a 0.076 m inner diameter tube was employed to collect the cores. The first core per site was sectioned every 0.02 m from 0 to 0.2 m and then, each 0.04 m until the end of the core. This core was used to measure the specific activities of ¹³⁷Cs. The second core was sectioned every 0.05 m and was used to determine

the bulk concentration of POPs. Total core length for all cores was the same and ca. 1 m in length. Cores from the same site were collected less than 1.5 m apart. Once the cores were collected in the field, they were transported upright that same day to the Lucille A. Carver Mississippi Riverside Environmental Station. Here, they were manually sectioned, weighed and stored in pre-cleaned plastic and glass containers. Plastic containers were used to store the sub-samples used for ^{137}Cs , and glass containers for POPs determination. The sub-samples were taken to The University of Iowa and refrigerated at 4 °C.

2.2. Analytical method

2.2.1. Bulk POP concentrations—The target POPs included three chlordanes (*trans*-chlordanes (CT), *cis*-chlordanes (CC), and *trans*-nonachlor (TN)); the complete list of 209 individual PCB congeners minus five surrogate and internal standards as 161 individual or coeluting congeners (see Table S1); six polycyclic musk fragrances: Galaxoline (HHCB), Tonalide (AHTN), Traseolide (ATII), Celestolide (ADBI), Phantolide (AHMI), and Cashmeran (DPMI); and two nitro musk fragrances: Musk Ketone (MK), and Musk Xylene (MX). Chlordane standards were purchased from Sigma–Aldrich Co. LLC (St. Louis, USA), PCB standards from AccuStandard (New Haven, USA), deuterated PCBs from CDN Isotopes (Quebec, Canada), and synthetic musk fragrance standards from LGC standards (Middlesex, UK).

Chlordanes, PCBs and synthetic musk fragrances were analyzed from three different sub-samples of the same sediment section. The sediment water content for these samples was determined gravimetrically from a separate aliquot by drying for 12 h at 104 °C. Analytical methods for chlordanes and PCBs are described elsewhere (Martinez et al., 2012). Briefly, two sediment sub-samples of each sections were manually homogenized, weighed (ca. 2 g) and mixed with ca. 10 g of combusted diatomaceous earth and spiked with 25 ng of surrogate standard, PCB14 (3,5-dichlorobiphenyl), PCB65-d5 (2,3,5,6-tetrachlorobiphenyl-d5, deuterated) and PCB166 (2,3,4,4',5,6-hexachlorobiphenyl). The sub-samples were extracted by pressurized liquid extraction (ASE, Dionex ASE-300) with equal parts acetone and hexane. The extracts were 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:sulfuric acid weight/weight) and eluted with hexane. The final solutions were concentrated to ca. 0.5 mL and 25 ng internal standard consisting of PCB30-d5 (2,4,6-trichlorobiphenyl-2',3',4',5',6'-d5, deuterated) and PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) were added to each sample. PCB30-d5 and PCB204 were used as internal standards to quantify PCBs, whereas only PCB204 was used to quantify chlordanes.

Synthetic musk fragrances were extracted through a modification of the method published by DiFrancesco et al. (2004). Approximately 2 g of sediment were mixed and ground with combusted diatomaceous earth (ca. 10 g), and spiked with surrogate standard of 50 ng of deuterated Tonalide (AHTN-d3) and deuterated Musk Xylene (MX-d15). Various extraction methods, solvent mixtures, and their proportions were tested in the ASE (Linebaugh, 2004). Best results were yielded using two extraction cycles per sample (10.3 MPa and 75 °C), with equal parts of hexane and acetone. Combusted sodium sulfate was used to remove the aqueous phase present in the extracted solution. Because sulfuric acid destroys the tested

synthetic musk fragrances, it was not possible to use acidified silica gel in Pasteur pipette for cleanup. Thus, ca. 7 g of combusted silica gel deactivated with water was set in larger columns and 60 mL of equal parts hexane and dichloromethane solution was used as an eluent solution. The extract was reduced and solvent-exchanged to hexane 3 times. The final extract was spiked with 50 ng of PCB30-d5 as internal standard.

Chlordanes and synthetic musk fragrances were analyzed using a Gas Chromatography/Mass Selective Detector Mode (GC/MSD, Hewlett–Packard 5973) in selected ion monitoring mode. The gas chromatograph (GC) was equipped with a Supelco SLB-5 ms capillary column (30 m × 0.25 mm ID, 0.25 mm film thicknesses) with helium as carrier gas. PCB analysis was carried out employing a modification of EPA method 1668C (USEPA, 2010; Martinez et al., 2012). Tandem Mass Spectrometry GC/MS/MS (Quattro Micro GC, Micromass MS Technologies) in multiple reaction monitoring (MRM) mode was used to quantify all 209 congeners in 161 individual or coeluting congener peaks. The GC was equipped with a Supelco SBP-Octyl capillary column (30 m × 0.25 mm ID, 0.25 mm film thicknesses) with helium as carrier gas.

2.2.2. ^{137}Cs activity—Radionuclide ^{137}Cs activity was measured through gamma counting of around 100 g of freeze-dried sediment (Robbins and Edgington, 1975). These measurements were performed by the National Water Research Institute, Environment Canada.

2.2.3. Quality Assurance and Control (QA/QC)—Laboratory blanks were included as 10% of samples and consisted of combusted diatomaceous earth handled the same as field samples. The limit of quantification (LOQ) for each compound was calculated as the upper limit of the 95% confidence interval from the mass from three laboratory blanks for each individual or coeluting compound. Any chemical mass value below the LOQ was substituted with zero. Precision in the quantification was assessed with surrogate standard recoveries for each sample and each chemical category. For chlordanes, percentage recoveries of surrogate standard PCB166 yielded $79 \pm 19\%$. For PCBs, percentage recoveries of surrogate standards PCB14, PCB65-d5 and PCB166 were $69 \pm 8.1\%$, $82 \pm 9.2\%$, and $92 \pm 9.4\%$, respectively. For synthetic musk fragrances, percentage recoveries of surrogate standards AHTN-d3 and MX-d15 were $81 \pm 32\%$, and $75 \pm 31\%$, respectively. Percentage recoveries of surrogate standards were used to correct POP mass as follows: PCB166 recovery was used to correct chlordanes; 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); and AHTN-d3 recovery was used to correct the polycyclic musk fragrances, and MXd15 recovery to correct the nitro musk fragrances. A published reference material for synthetic musk fragrances (NIST SRM 2585 Organic Contaminants in House Dust (Peck et al., 2007)) was analyzed using our method, yielding a mean percent difference between the measured and reported values of $17 \pm 15\%$. The percentage recovery of the measured values against the published values yielded a value of $114 \pm 20\%$ (Fig. S1).

3. Results and discussion

3.1. POP bulk concentrations

Total PCB concentrations (Σ PCB) ranged from 1.7 to 205 ng g⁻¹ dw for Pool 17-UMR core and 2.2–104 ng g⁻¹ dw for the Horseshoe Bend core. Interestingly, the top 0.1 m from both cores contains similar values of Σ PCB (ca. 20 ng g⁻¹ dw). This suggests that current inputs of PCBs are similar across the UMR watershed. Barber and Writer (1998) collected surficial sediment samples in 1994 after the 1993 flood in pools 16 and 18 (no data for Pool 17) and found very similar values to the top sections of our two cores. This suggests that there has been neither increase nor reduction in the input of PCBs during the past 20 years. Individual congener concentrations ranged from below LOQ to 18 ng g⁻¹ dw. Most of the highest concentrated congeners are present in Aroclor commercial mixtures, such as PCB44 (44 + 47 + 65), PCB52, PCB66, and PCB70 (61 + 70 + 74 + 76) (Frame et al., 1996).

The absence of chlordanes in the sediments was quite surprising. We have successfully measured chlordanes in soils from other sites (Martinez et al., 2012) and we are using similar methods to those used to measure chlordanes in Great Lakes sediments (Wong et al., 1995). Chlordanes spiked to sediment were not lost during the sulfuric acid cleanup step. Although there are no chlordanes measurements in soils reported for Muscatine, IA, or its surroundings, it is probable that this pesticide was widely used in this area in the past, at least in urban areas. However, no chlordanes were found in either Pool 17-UMR core, which is less than 20 km from Muscatine. This finding is consistent with Cope et al. (1999). They did not detect chlordanes in Zebra mussels in Pool 16, a few kilometers north of where we collected Pool 17-UMR core.

AHTN, HHCB and DPMI were detected above the LOQ more than 80% of the time; the rest of the synthetic musk fragrances were detected less than 24% of the time. Concentrations of AHTN, HHCB and DPMI ranged from LOQ to 63, 14 and 470 ng g⁻¹ dw, respectively. The values of AHTN obtained here were ca. 60 times higher than values reported in Lake Ontario, and in the case of HHCB, 3 times higher than Lake Erie and similar levels for Lake Ontario, respectively (Peck et al., 2006). In contrast to the PCBs, no trends in the vertical distributions were obtained for either site (Fig. S2 and S3).

3.2. Vertical distribution of ¹³⁷Cs

The vertical distribution of ¹³⁷Cs activity exhibited in Pool 17- UMR core is consistent with discrete inputs caused by the initial nuclear testing in 1954 and the peak testing in 1963 (Hermanson et al., 1991) (Fig. 2). The lack of a peak and a constant decrease in the ¹³⁷Cs indicate that the sediments collected at the Horseshoe Bend site were more mixed and do not reflect a steady deposition and accumulation of sediment over time. This core was collected in an oxbow lake near the mouth of the Iowa River where it discharges to the Mississippi River in Pool 18 (just downstream from Pool 17). The Iowa River has been able to move across the floodplain over time producing a more varied depositional environment than the Pool 17-UMR site. The Horseshoe Bend site shows a series of oxbow lakes, crevasse-splays, and wetland areas. Typically, the low gradient river channel in this area has migrated during

large flood events in order to seek the most efficient path for discharge to the Mississippi River.

3.3. Vertical distribution of PCBs

The vertical distribution of PCB is different in the two cores (Fig. 2). While the Pool 17-UMR core shows a clear peak ca. 0.5 m deep, similar to Great Lakes sediments (Eisenreich et al., 1989; Li et al., 2009; Hu et al., 2011), the PCB peak in the Horseshoe Bend site was not well defined (Fig. 2).

PCBs accumulation in Pool 17-UMR peaked between 1954 and 1963, which is ca. 7–10 years earlier than peak PCB production in the USA and data reported in Great Lakes sediments. It is interesting that the PCB historical signal is somewhat retained in the Horseshoe Bend core despite clear evidence of mixing from the ^{137}Cs results.

Most congeners follow the same vertical distribution found for total PCBs in both sites (e.g. PCB52, Fig. 3): more than 80% of all congeners in both cores showed a statistically significant correlation with total PCBs ($p < 0.05$). The 20% of the congeners that do not reflect the PCB signal include several that are not found in the most common commercial Aroclors (Frame et al., 1996). For example, PCB208 and PCB209 depict a completely different pattern (Fig. 3). Deeper sections show a concentration increase in these two compounds. PCB209 has been reported in sediments, including from contaminated harbor in Lake Michigan (Martinez and Hornbuckle, 2011), lacustrine sediments from Lakes Erie, Ontario (Hu et al., 2011) and Michigan (Li et al., 2009), surficial sediments in Texas (Howell et al., 2008) and Rhode Island (Hartmann et al., 2004), and suspended solids in the Delaware River (Rowe et al., 2007). We have previously shown that non-Aroclors sources to the environment include household paint pigments (Hu and Hornbuckle, 2010). Rowe et al. (2007) reported non-Aroclors released during the production of titanium dioxide. It is possible that these sources could be responsible for the occurrence of PCB208 and 209 in the UMR sediments. Aroclor 1270 contained 100% of PCB209, but the production was $<1\%$ of total Aroclors in USA (Brinkman and De Kok, 1980). Thus, it is unlikely that this Aroclor was the source of PCB209 in these sediments.

3.4. PCB congener distribution

The composition of PCB congeners in both sites is enriched in tetra- penta- and hexachlorobiphenyls, where pentachlorobiphenyls is predominant (Fig. S4). Most of the homolog group proportions maintain constant with depth for both cores, especially for hepta- and octachlorobiphenyls. This phenomenon suggests that little weathering of PCBs has occurred in these two cores. The average PCB congener profiles for both cores are shown in Fig. 4.

Statistical analysis of the congener distribution patterns in each sediment section indicates strong similarities between the cores and from top to bottom. $\cos \theta$ uses the cosine of the angle between two multivariable vectors (PCB congener profiles), where a value of 0.0 indicates that the two vectors are completely different and 1.0 describes two identical vectors (DeCaprio et al., 2005). In general, adjacent samples in the cores yielded high $\cos \theta$ (>0.85), whereas samples located far from each other in the same core yielded low $\cos \theta$

(<0.25). Comparison between all the samples from one core and also between both cores yielded similar results, with a $\cos \theta$ average from both cores of 0.6 ± 0.3 . This result suggests that the PCB patterns of most of the samples are similar, and both cores are impacted by the same PCB source(s), probably as result of industrial use of PCBs throughout the upper Midwest and subsequent integration of the signal from the large watershed of the UMR.

We compared the PCB signal with Aroclor mixtures (Aroclors 1016, 1221, 1242, 1248 and 1254), and only the three highest PCB concentration sections from Pool 17-UMR core yielded a high similarity with Aroclor 1248 ($\cos \theta > 0.9$). This finding may be an indication of widespread use of 1248 in the UMR watershed, or may simply be a result of environmental weathering of a mixture of Aroclors. Biotic and abiotic processes occurring in the environment can change the original Aroclor signal which could lead to misinterpretation of the original Aroclor mixtures that entered the environment. For example, spiked soils with Aroclor 1242 after volatilization yielded a very similar profile of Aroclor 1248 in the soil (Chiarenzelli et al., 1997), and a mixture of Aroclors 1254 and 1242 weathered in lacustrine sediments also yielded a similar Aroclor 1248 profile (Magar et al., 2005). Thus, there is not enough evidence to suggest that Aroclor 1248 is the only Aroclor that accumulated in these sediments.

In 2008, we conducted a study of PCBs in the surface soils of residential neighborhoods in Cedar Rapids, IA, one of the largest cities in the UMR watershed other than the Twin Cities. Cedar Rapids is located upstream from The Horseshoe Bend site (ca. 100 km) via the Cedar River, which flows into the Iowa River. We compared the core sections with the average congener profile from surficial soil collected from Cedar Rapids, Iowa, which resemble a surficial soil PCB background signal (USEPA, 2007; Martinez et al., 2012). Forty percent of all the samples from both cores yielded a $\cos \theta > 0.80$. Interestingly, the similarity between the core samples and the Iowa background signal was constant, except for the deepest sections (Fig. 4) due to the presence of the high chlorinated congeners in those sediment sections (PCBs 208 and 209). This outcome supports the hypothesis that both cores have been impacted by the same PCB source(s), which have also been impacting the soils of Iowa. These results also showed that the PCB patterns in most of the samples were independent of the locations and the upstream activities.

4. Conclusions

This is one of the few investigations of POPs in the UMR, and the only one that reports the presence PCBs and synthetic musk fragrances in sediment cores. The PCB vertical distribution shape in the Pool 17-UMR core resembles the USA Aroclor production and sediment cores collected in some of Great Lakes, with an estimated peak time in our core of ca. 10 years early, from the ^{137}Cs data. Generally, PCB congener profiles showed that both sites resembled the Iowa soil background PCB signal.

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 P42ES013661. At the University of Iowa, we thank our former laboratory director Jon Durst, Caroline Davis, Bailey Hadnott, Nicholas Herkert, Rachel Marek, Colin O'Sullivan, Brad Reuter, Zachary Rodenburg, and Rachel Yucuis for their help in the field campaign and in the laboratory. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS or the NIH.

References

- Barber LB, Writer JH. Impact of the 1993 flood on the distribution of organic contaminants in bed sediments of the Upper Mississippi River. *Environ. Sci. Technol.* 1998; 32:2077–2083.
- Brinkman, UAT.; De Kok, A. Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products. Elsevier/North-Holland Biomedical Press; 1980. Chapter 1. Production, Properties and Usage.
- Chiarenzelli JR, Scrudato RJ, Wunderlich ML. Volatile loss of PCB Aroclors from subaqueous sand. *Environ. Sci. Technol.* 1997; 31:597–602.
- Connell, DW. Bioaccumulation of Xenobiotic Compounds. Boca Raton: CRC; 1990.
- Cope WG, Bartsch MR, Rada RG, Balogh SJ, Rupprecht JE, Young RD, Johnson DK. Bioassessment of mercury, cadmium, polychlorinated biphenyls, and pesticides in the Upper Mississippi River with zebra mussels (*Dreissena polymorpha*). *Environ. Sci. Technol.* 1999; 33:4385–4390.
- DeCaprio AP, Johnson GW, Tarbell AM, Carpenter DO, Chiarenzelli JR, Morse GS, Santiago-Rivera AL, Schymura MJ. Polychlorinated biphenyl (PCB) exposure assessment by multivariate statistical analysis of serum congener profiles in an adult Native American population. *Environ. Res.* 2005; 98:284–302. [PubMed: 15910784]
- Difrancesco AM, Chiu PC, Standley LJ, Allen HE, Salvito DT. Dissipation of fragrance materials in sludge-amended soils. *Environ. Sci. Technol.* 2004; 38:194–201. [PubMed: 14740736]
- Eisenreich SJ, Capel PD, Robbins JA, Bourbonniere R. Accumulation and diagenesis of chlorinated hydrocarbons in lacustrine sediments. *Environ. Sci. Technol.* 1989; 23:1116–1126.
- 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. *HRC. J. High. Resolut. Chromatogr.* 1996; 19:657–668.
- Hartmann PC, Quinn JG, Cairns RW, King JW. Polychlorinated biphenyls in Narragansett Bay surface sediments. *Chemosphere.* 2004; 57:9–20. [PubMed: 15288194]
- 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.
- Howell NL, Suarez MP, Rifai HS, Koenig L. Concentrations of polychlorinated biphenyls (PCBs) in water, sediment, and aquatic biota in the Houston Ship Channel, Texas. *Chemosphere.* 2008; 70:593–606. [PubMed: 17850847]
- Hu DF, Hornbuckle KC. Inadvertent polychlorinated biphenyls in commercial paint pigments. *Environ. Sci. Technol.* 2010; 44:2822–2827. [PubMed: 19957996]
- Hu DF, Martinez A, Hornbuckle KC. Sedimentary records of non-Aroclor and Aroclor PCB mixtures in the Great Lakes. *J. Gt. Lakes Res.* 2011; 37:359–364.
- Lauby-Secretan B, Loomis D, Grosse Y, El Ghissassi F, Bouvard V, Benbrahim-Tallaa L, Guha N, Baan R, Mattock H, Straif K. Int Agcy Res Canc Monograph W. Carcinogenicity of polychlorinated biphenyls and polybrominated biphenyls. *Lancet Oncol.* 2013; 14:287–288. [PubMed: 23499544]
- Li A, Rockne KJ, Sturchio N, Song WL, 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]
- Linebaugh, EK. Civil & Environmental Engineering. The University of Iowa (MS Thesis); 2004. Accumulation of Synthetic Musk Fragrances in Great Lakes Sediment.
- 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, Erdman NR, Rodenburg ZL, Eastling PM, Hornbuckle KC. Spatial distribution of chlordanes and PCB congeners in soil in Cedar Rapids, Iowa, USA. *Environ. Pollut.* 2012; 161:222–228. [PubMed: 22230089]
- Martinez A, Hornbuckle KC. Record of PCB congeners, sorbents and potential toxicity in core samples in Indiana Harbor and Ship Canal. *Chemosphere.* 2011; 85:542–547. [PubMed: 21899876]
- Peck AM, Kucklick JR, Schantz MM. Synthetic musk fragrances in environmental standard reference materials. *Anal. Bioanal. Chem.* 2007; 387:2381–2388. [PubMed: 16906386]
- Peck AM, Linebaugh EK, Hornbuckle KC. Synthetic musk fragrances in Lake Erie and Lake Ontario sediment cores. *Environ. Sci. Technol.* 2006; 40:5629–5635. [PubMed: 17007119]
- Robbins JA, Edgington DN. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. *Geochim. Cosmochim. Acta.* 1975; 39:285–304.
- Rostad CE, Bishop LM, Ellis GS, Leiker TJ, Monsterleet SG, Pereira WE. Polychlorinated Biphenyls and Other Synthetic Organic Contaminants Associated with Sediments and Fish in the Mississippi River. Contaminants in the Mississippi River. U.S. Dept. of the Interior U.S. Geological Survey. 1995
- Rowe AA, Totten LA, Xie MG, Fikslin TJ, Eisenreich SJ. Air-water exchange of polychlorinated biphenyls in the Delaware river. *Environ. Sci. Technol.* 2007; 41:1152–1158. [PubMed: 17593713]
- Steingraeber MT, Schwartz TR, Wiener JG, Lebo JA. Polychlorinated biphenyl congeners in emergent Mayflies from the Upper Mississippi River. *Environ. Sci. Technol.* 1994; 28:707–714. [PubMed: 22196557]
- USEPA. Pilot Survey of Levels of Polychlorinated Dibenzo-P-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), Polychlorinated Biphenyls (PCB) and Mercury in Rural Soils of the U.S (Washington, DC). 2007
- USEPA. Method 1668C: Chlorinated biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS. 2010
- Meade, Robert H. USGS. Contaminants in the Mississippi River, 1987–92. U.S. Geological Survey Circular. 1995; 1133:140.
- Wiener, JG.; Anderson, R.; McConville, DR. Contaminants in the Upper Mississippi River. Proceedings of the 15th Annual Meeting of the Mississippi River Research Consortium; Butterworth, Boston. 1984.
- Wiener JG, Sandheinrich MB. Contaminants in the Upper Mississippi River: historic trends, responses to regulatory controls, and emerging concerns. *Hydrobiologia.* 2010; 640:49–70.
- 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. [PubMed: 22191970]

HIGHLIGHTS

- Sediment cores were collected from the Upper Mississippi River (UMR).
- PCB vertical distribution similar to Great Lakes, but peak time ca. 10 years earlier.
- PCB congener profiles resembled the Iowa soil background PCB signal.
- Chlordanes were not detected in the sediments.
- Synthetic musk fragrances were found, but no trend was observed.

Fig. 1. Sediment core locations, Pool 17 – UMR site ($41^{\circ} 16' 27.06''$ N, $91^{\circ} 6' 41.22''$ W) and the Horseshoe Bend site ($41^{\circ} 6' 31.56''$ N, $91^{\circ} 5' 23.94''$ W), collected in May 2012 (right panel). Red line in left panel represents the UMR. The location of both sites is approximately between locks and dams 16 and 18 of the UMR. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Vertical distribution of PCB (ng g⁻¹ dw) and ^{137}Cs activity (pCi g⁻¹) in Pool 17-UMR (left panel) and Horseshoe Bend (right panel) sites, respectively. Error bars for PCB concentration represent in Pool 17-UMR core one standard deviation (see 1st, 2nd and 5th circles from the top to the bottom, n = 3 analytical quantification). Long dash lines represent limit of quantification for PCBs (6.5 ng g⁻¹ dw). Dotted lines are approximately years 1954 and 1963 corresponding to first appearance and peak input of ^{137}Cs in the sediments. See the different x and y-axes scales for each plot.

Fig. 3.

Vertical distribution of PCB52, 208 and 209 ($\text{ng g}^{-1} \text{ dw}$) in Pool 17 (left panel) and Horseshoe Bend (right panel) sites, respectively. PCB52 follows the trend of ΣPCB while PCB208 and PCB209 do not. Error bars in Pool 17-UMR core represent one standard deviation (see 1st, 2nd and 5th circles from the top to the bottom, $n = 3$ analytical quantification). The long dash lines represent limit of quantification for individual congeners (PCB52 = 0.6; PCB208 = 0.01; PCB209 = 0.03 $\text{ng g}^{-1} \text{ dw}$). See the different x and y-axes scales for each plot.

Fig. 4. Mean individual profile distribution of Pool 17 UMR (top left) and Horseshoe Bend (bottom left) cores, respectively. Each congener was normalized to the total concentration of PCBs in the sample. The error bars represent one standard deviation above the mean. Right section shows the PCB congener profile similarly ($\cos \theta$) between Pool 17-UMR and Horseshoe Bend sites, and the PCB Iowa background surficial soil signal, respectively (USEPA, 2007; Martinez et al., 2012).