Persistent organic pollutants in fish tissue in the mid-continental great rivers of the United States

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Abstract

Great rivers of the central United States (Upper Mississippi, Missouri, and Ohio rivers) are valuable economic and cultural resources, yet until recently their ecological condition has not been well quantified. As part of the Environmental Monitoring and Assessment Program for Great River Ecosystems (EMAP-GRE), we measured legacy organochlorines (OCs) (e.g., pesticides and polychlorinated biphenyls, PCBs) and emerging (e.g., polybrominated diphenyl ethers, PBDEs) compounds in fish to estimate human and wildlife exposure risks from fish consumption. PCBs, PBDEs, chlordane, dieldren and dichlorodiphenyltrichloroethane (DDT) were detected in most samples across all rivers and hexachlorobenzene was detected in most Ohio River samples. Concentrations were highest in the Ohio River, followed by the Mississippi and Missouri Rivers, respectively. Dieldrin and PCBs posed the greatest risk to humans. Their concentrations exceeded human screening values for cancer risk in 27─54% and 16─98% of great river length, respectively. Chlordane exceeded wildlife risk values for kingfisher in 11–96% of river km. PBDE concentrations were highest in large fish in the Missouri and Ohio Rivers (mean >1000 $ng \bullet g^{-1}$ lipid), with congener 47 most prevalent. OC and PBDE concentrations were positively related to fish size, lipid content, trophic guild, and proximity to urban areas. Contamination of fishes by OCs is widespread among great rivers, although exposure risks appear to be more localized and limited in scope. As an indicator of ecological condition, fish tissue contamination contributes to the overall assessment of great river ecosystems in the U.S.

Keywords: persistent organic contaminants, contamination indicators, Upper Mississippi River basin, fish homogenates

1. Introduction

The mid-continent great rivers of the U.S., the Upper Mississippi, Missouri, and Ohio Rivers, provide drinking and industrial water sources, serve as commercial transportation corridors, and provide recreational opportunities for millions of people (Delong, 2005; Galat et al., 2005; White et al., 2005). Intense human use of these ecosystems creates high potential for contamination of aquatic biota including fish. For example, coke plants, steel mills, chemical plants, petroleum facilities, and other heavy industries have been a fixture of the Ohio River Valley for decades. In addition, agriculture comprises a large portion of the Ohio basin, and runoff of nutrients and pesticides are common sources of pollution from tributaries (White et al., 2005). Agricultural inputs are the greatest concern for the Upper Mississippi River, but some large urban areas with a legacy of industrial contamination are also located on this part of the river (Delong, 2005). Primary human impacts on the Missouri River include high dams in the upper reaches, and channelization, agriculture (Galat et al., 2005), and contamination by persistent chemicals in the Lower Missouri River, owing to urban and agricultural land uses along the river (Echols et al., 2008). As a result of these land use practices and inadequate protection of water quality, persistent toxic substances have accumulated in these rivers.

Fish tissue contamination is a reliable indicator of bioaccumulation of persistent toxic substances in the environment, and has been used to estimate contaminant exposure risk to higher trophic levels, including humans and piscivorous wildlife (Lazorchak et al., 2003; Hinck et al., 2006b; Ackerman et al., 2008; Stahl et al., 2009). Several recent studies have reported on fish tissue contaminants at large scales or in large river basins (Greenfield et al., 2005; Hinck et al., 2006a; Hinck et al., 2006b; Ackerman et al., 2008; Schwindt et al., 2008), but few of these

employed random site selection to allow extrapolation of results to unsampled locations (e.g., Peterson et al., 2007; Harvey et al., 2008; Stahl et al., 2009).

In spite of the cultural and economic significance of these three great rivers, large-scale synoptic surveys of fish tissue contamination are lacking for these systems, and none have used a probability-based design that allows for the extrapolation to the entire river. Past studies of fish tissue contamination in these rivers have been more limited in scale. Many have either included only a portion of the Upper Mississippi basin or sampling only a limited number of sites in each river (Schmitt, 2002; ORSANCO, 2004; Hinck et al., 2009). Others have focused on other endpoint organisms (Cope et al., 1999) or on the Lower Mississippi River (Watanabe et al., 2003).

The U.S. Environmental Protection Agency's (USEPA) Environmental Monitoring and Assessment Program for Great River Ecosystems (EMAP-GRE) was initiated to develop and demonstrate indicators to assess the condition of great rivers in the central United States (Angradi et al., 2009). This is the first large-scale study of these rivers employing a statistically-based sampling design. The probability design allows spatially unbiased estimates of condition. In 2004 to 2005, the EMAP-GRE program collected data on a wide range of ecosystem components including biotic assemblages (e.g., fish, macroinvertebrates, algae), water chemistry, aquatic and riparian habitat, and fish tissue from the Upper Mississippi, Missouri, and Ohio rivers. Each component provides information about the condition of the resource, and fish tissue contaminants, the focus of this paper, are indicators of exposure risk for wildlife and humans to legacy contaminants including polychlorinated biphenyls (PCBs), and organochlorine (OC) pesticides (e.g., including chlordane, dichlorodiphenyltrichloroethane (DDT), and dieldrin).

In this paper, we estimate the extent and magnitude of risk to humans and wildlife from exposure to these chemical contaminants in each river. Tissue contamination in small- and large-bodied fishes was determined to provide exposure assessments for both piscivorous wildlife and humans, respectively. Small species, such as minnows (Cyprinidae), have short life spans and are food for mammals and birds, such as American mink (*Mustela vison*) and Belted Kingfisher (*Ceryle alcyon*). Larger game species, such as catfish (Ictaluridae) and bass (Centrarchidae), are more likely to be consumed by humans. Therefore, our analysis provides both an ecological and a human health risk perspective. Flame retardants (polybrominated diphenyl ethers, PBDEs), an important class of emerging contaminants, were also measured to determine baseline tissue concentrations. Our final objective was to assess the influence of environmental factors (i.e., land uses) and fish autecology (e.g., body length and trophic guild) on tissue contaminant concentrations.

2. Methods

2.1. Sampling design

The EMAP design approach consists of the sample frame and the probability survey. The sample frame is a geographic information system (GIS) coverage of the resource to be assessed, in this case, the center line of each river derived from the National Hydrography Dataset (NHD, http://nhd.usgs.gov/index.html). The probability survey algorithm included an explicit random element in the site selection (Stevens, 1997), with spatial balance incorporated to disperse the sites and increase the representativeness of the sample (McDonald et al., 2004). Additional design details are available at www.epa.gov/nheerl/arm/designpages/design&analysis.htm (accessed August 11, 2009). A single sample design was created for all three rivers (Angradi et al., 2009). Briefly, a sufficient number of sites were allocated to each river (Figure 1) to insure

an adequate sample size from each state's portion of a great river to estimate condition (i.e., proportion of km in a given condition) with a desired level of precision.

The Missouri river was divided at river kilometer (rkm, from the mouth) 1211 (Ponca State Park, Nebraska) into an upper section consisting of a series of reservoirs and a lower section having a more natural hydrograph. The Upper Mississippi River (above the confluence with the Ohio River), was divided at rkm 327 into an upriver impounded reach, and a free-flowing unimpounded reach thence to the confluence. The Ohio River was treated as a single reach. The survey algorithm selected a single point on the river center line as defined by the NHD for each sample location. Field sampling was conducted relative to this point, and all site data accrued to this point for population estimates. As part of the probability design, each site received a weight indicating the number of rkm the site represented for population-scale estimates (Stoddard et al., 2005; see also http://www.epa.gov/nheerl/arm accessed August 11, 2009). Weights ranged from 12.8 to 57.6 rkm across all rivers, with an average weight of 31.1 rkm.

2.2. Sample collection

Fish were collected July through September 2004-2005 by day electrofishing of two separate 500 m reaches along a single main channel shoreline (Lazorchak et al., 2006). Composite samples for fish tissue were taken from the fish collected from one or both of these electrofishing reaches. Two samples, one of large-bodied species and one of small-bodied species, were collected for fish tissue analysis (Table S1). Large species typically represent fish targeted by recreational anglers and served as indicators of exposure of humans to contaminants in fish tissue. Smaller species represented potential prey for piscivorous wildlife and were an indicator of wildlife risk of exposure. The goal of sampling was to obtain a composite sample of similarly sized

individuals of a single species, according to a prioritized list of species for each size class of fish (Lazorchak et al., 2006; Table S1). However, in 23 cases it was necessary to retain a multi-species sample or a sample with larger than desired size variation among individuals. Fish were wrapped in aluminum foil, placed in a self-sealing plastic bag, and kept on ice or frozen until shipment to the laboratory. Fish were assigned into planktivore, omnivore, invertivore, generalized carnivore and piscivore trophic guilds based on preferred food of adults (Pflieger, 1975; Trautman, 1981). Omnivores consume multiple food types including detritus, algae, invertebrates and fish. Generalized carnivores are predators (e.g., freshwater drum) that feed on crayfish, other invertebrates, and fish and are distinct from piscivores (e.g., sauger) that feed almost exclusively on fish.

2.3. Analysis of organic compounds and lipids

Detailed methods for sample homogenization, extraction, analyses, as well as quality control procedures are provided in Supplementary Data. Whole fish homogenates were analyzed for 20 pesticides (chlordane components, DDT and metabolites, aldrin, dieldrin, endosulfan I and II, endrin, heptachlor epoxide, hexachlorobenzene (HCB), lindane, and mirex), 20 polychlorinated biphenyl (PCB) congeners, and six polybrominated diphenyl ether (PBDE) congeners (Table S2). Homogenates were mixed with anhydrous Na_2SO_4, and extracted in a Dionex ASE-200 accelerated solvent extractor using a combination of methylene chloride and hexane. A 5mL aliquot of extract was removed for lipid analysis, and total percent lipid was calculated using the gravimetric method. The remaining extract was cleaned by adding acentonitrile, freezing and centrifuging to remove lipids and then eluting through an alumina-N (level III) column with hexane. Analysis for organic compounds was by gas chromatography-electron capture detection (GC-ECD) following EPA method 508.1. Detection limits are shown in Table S2. Laboratory

fortified blanks (LFBs) were analyzed twice per batch to assess recovery and reproducibility (the relative percent difference [RPD] between two LFBs). Recovery averaged 93.5% (±17.6% SD) and RPD averaged 8.9% (±9.2% SD) among organic compounds (Table S2).

2.4. Statistical analysis

Data from all samples were combined into a single data set each for small and large fish, encompassing all specimens in that size group (Table S1). Statistical analyses were performed for total PCBs (sum of 20 congeners [Table S2]), total chlordane (sum of cis-chlordane, trans-chlordane, trans-nonachlor, cis-nonachlor, and oxychlordane), total DDT (sum of all forms of dichlorodiphenyldichloroethane (DDD), dichlorodiphenyldichloroethylene (DDE), and DDT), total PBDEs (sum of 6 congeners [Table S2]), aldrin, dieldrin, endrin, endosulfan (I and II), heptachlor epoxide, hexachlorobenzene (HCB), lindane, and mirex. Values below the detection limit were set to zero for summing across congeners or breakdown products.

Organic contaminant wildlife values (WVs) and human screening values (SVs) estimate environmental risks of fish consumption for sensitive wildlife and human populations (e.g., children and women of child bearing age). Wildlife risk values (WVs) for the consumption of small species were obtained for American mink and Belted Kingfisher (hereafter mink and kingfisher) from Lazorchak et al. (2003) and were based primarily on USEPA guidance (USEPA, 1995). Both mink and kingfisher are widely distributed throughout the sampling area and are realistic models of exposure. Both species are piscivorous and expected to experience the highest exposures to bioaccumulative contaminants through the aquatic food web, rather than through water ingestion (Lazorchak et al., 2003). Wildlife values were not available for many organochlorine pesticides, including aldrin, endosulfan, heptachlor epoxide, HCB, lindane, or mirex.

Human health screening values (SVs) for consumption of large species were calculated according to USEPA guidance (USEPA, 2000), and all contaminants were treated as carcinogens except endrin, endosulfan, and mirex. We assumed a human body weight of 70 kg, daily consumption rate of 0.0175 kg fish day^{-1}, and an acceptable lifetime risk of cancer of 10^{-5}. Oral reference dose (RfD) and oral cancer slope factor (CSF) values for non-carcinogenic and carcinogenic organics, respectively, were obtained from the U.S. EPA's Integrated Risk Information System (IRIS, http://www.epa.gov/iris/index.html, accessed June 11, 2008). Whole fish were analyzed rather than a typical human food portion (filets), so we followed Ackerman et al. (2008) and increased SVs for organics by 32%, to account for the lipophilic nature of these contaminants and the reduction in exposure expected from eating muscle tissue compared to whole fish (Amrhein et al., 1999; USEPA, 2000).

All WVs and adjusted SVs are provided in Table S3. However there are no criteria for PBDEs because they are emerging contaminants. For this contaminant, as well as all other contaminants, we determined the rate of detection among samples by river and river section. We did not assess the Upper Missouri River or Unimpounded Mississippi River separately due to small sample sizes for fish tissue (Table S4). For comparison with other studies, PBDE values were lipid-normalized for individual congeners before summing. Our use of a probability-based design allowed us to extrapolate our results to an entire river or reach and to estimate the variability around estimates of contamination extent (www.epa.gov/nheerl/arm/analysispages/monitanalysisinfo.htm, accessed August 11, 2009). We used sample site weights derived from the probability design to estimate the extent of each river or river section having fishes with contaminant concentrations (1) above the detection limit and (2) above WVs or SVs (based on wet weight concentrations).

We examined associations of contaminant concentrations with developed land cover. Longitudinal plots were constructed by river and fish size, and major tributaries and cities were noted along each river for context. Linear regression analysis was performed to identify associations between developed land use and organics while accounting for fish ecological traits. Only those organics that could be transformed to approximate normality were modeled on percent lipids, mean fish length, fish trophic guild (e.g., piscivore; treated as an indicator variable, Table S1), percentage developed land use (sum of National Land Cover Database (NLCD) categories 21-24) in catchments intersecting with the river within a 50 km network upstream of the site, and percentage developed land use within a 10 km upstream network (Angradi et al., 2009). Best subsets regression was performed in SAS v. 9.1 (SAS Institute, Cary, North Carolina), based on Mallow's C_p statistic (Myers, 1990; Neter et al., 1996), so that some models include predictors that were not significant but led to a lower C_p value relative to the number of variables in the model. Contaminants were modeled separately for each river and fish size. Residuals were examined using normal probability plots and plots against predicted values.

3. Results

3.1. Extent of contaminants

Several contaminants were rarely detected and/or were rarely above criteria values (Table S4). Aldrin, endrin, mirex, lindane, and endosulfan were detected in <10% of samples in any given river or section, and none occurred above the SV. Although heptachlor epoxide and HCB were detected more commonly across rivers, HCB only occurred once over the adjusted SV and heptachlor epoxide never did. Thus, all of these contaminants were excluded from further analyses. PCBs, PBDEs, and DDT were detected in nearly all samples of both large and small

fish (Table S4). Dieldrin and chlordane were more commonly detected in the Ohio River overall (>92% of rkm) than in other rivers in the study (~52 – 81% of rkm), although these contaminants were detected in all 16 samples from the Unimpounded Mississippi. Contaminants posing the greatest risk to human consumption were PCBs and dieldrin (Figure 2). Extent of rkm (among rivers) with fish tissue above human SV was 16-94% for PCBs and 27-54% for dieldrin. Chlordane posed the greatest risk to kingfisher, with 11-85% of the great rivers above the kingfisher WV. PCBs posed the greatest risk to mink (21% of rkm in the Ohio River), but the extent of risk was low compared to that for humans. In general, the Ohio River had the largest extent of rkm with contaminant concentrations greater than SVs and WVs followed by the Mississippi and then Missouri rivers, respectively (Figure 2). One exception to this general pattern was that the Missouri River had the largest percentage of river length above the human SV for dieldrin.

Fish tissue contaminant concentrations varied widely across rivers and sometimes between sections within rivers (Table 1). Many peaks in contaminant levels of large fish were associated with larger cities or confluences with larger tributaries (Figure 3). The patterns observed for large fish generally were followed by small fish (Figure 4), although small fish exhibited lower levels of all contaminants except dieldrin. Organic compounds were highest just downstream of Minneapolis-St. Paul (Twin Cities, MN) and St. Louis on the Mississippi River, Kansas City on the Missouri River, and near Pittsburgh, Louisville, and Evansville on the Ohio River. In some cases, there were no obvious sources of higher levels of contaminants, although information about some small tributaries was limited. The Missouri River had the second highest average concentration of chlordane and PBDEs, whereas the Mississippi River typically had higher PCBs than the Missouri.

Not all contaminants were modeled with regression, as chlordane and dieldrin were only common enough in the Ohio River. DDT and PBDEs were modeled in all rivers for both fish sizes, and PCBs were modeled in all combinations except small fish in the Missouri River. The regressions for the Ohio River explained the most variation, and those for large fish in the Missouri explained the least (Table 2). Overall, concentrations tended to be higher in larger, more lipid-rich fish from higher-level trophic guilds (i.e., piscivores and carnivores). This finding was consistent with biomagnification of these persistent compounds through food webs. Higher concentrations were also associated with a higher percent developed land use in the 50 km network with a few exceptions. This land use varied from 4-82% in the Mississippi River, 3-50% in the Missouri, and 3-58% in the Ohio. Only dieldrin and DDT concentrations in fish from the Ohio River were poorly associated with developed land cover.

The longitudinal pattern of total PBDE concentration was similar to that for PCBs in each river, regardless of fish size. For example, Spearman rank correlations between PCBs and PBDEs in large fish were 0.69, 0.82, and 0.84 in the Mississippi, Missouri, and Ohio rivers, respectively.

3.2. PBDE concentrations

The mean concentrations of PBDEs were much lower and less variable in the Mississippi than in other rivers, but in all rivers and sections, the mean lipid-normalized concentrations for large fish were two to three times those for small fish (Figure 5, Table S4). The maximum concentrations of total PBDEs in small fish were 704, 2914, and 2266 ng g^{-1} lipid in the Mississippi, Missouri, and Ohio rivers, respectively. Maximum values observed for large fish were 3030, 87121, and 16366 ng g^{-1} lipid, respectively. PBDE 47 predominated in both large and small fish, followed by PBDEs 100 and 99 in small and large fish, respectively (Figure 6).

4. Discussion

4.1. Extent of contamination

The Ohio River is known to have a PCB gradient, with higher levels upstream related to past industrial applications (Jeff Thomas, Ohio River Valley Water Sanitation Commission (ORSANCO), pers. comm.). Although levels of PCBs and organochlorines have been declining since the late 1980s (Jeff Thomas, ORSANCO, pers. comm.), the Ohio River still typically had higher concentrations for all contaminants except dieldrin, which was similar across systems. Given its legacy of industrial pollution in its upper reaches and heavy agricultural land use in the lower basin, we had expected the concentrations of PCBs and organochlorine pesticides to be highest in the Ohio River (Galat et al., 2005). The relatively high occurrences of dieldrin and PBDEs in the Missouri River were linked to metropolitan areas along the river and largely concentrated in the lower section.

The legacy contaminants posing the greatest exposure risk differ for wildlife and humans but are somewhat consistent across rivers. For humans, the greatest risk of exposure is posed by PCBs and dieldrin. Wildlife risk is highest for the kingfisher primarily due to chlordane. These risks occur throughout the Ohio River but were generally limited to the lower section of the Missouri River. The greatest risks for both humans and kingfishers in the Upper Mississippi River occur in the lower part of the impounded section.

Obviously, there is the potential for species differences in contaminant load, particularly when species are from different trophic guilds. We did not assess species difference in contaminant concentrations because few species had large enough sample sizes to allow for individual analyses. In addition, and more importantly, this study was not designed to assess differences in contaminant concentrations among species, and observed differences would be

confounded with site or river differences, and could never be strictly attributed to species. Finally, the goal of this study was to develop a composite picture of the contaminant exposure at the scale of an entire reach or river, so by using a prioritized target species list, we obtain a more representative sample across sites.

4.2. Comparisons with other studies

PCBs generally pose the greatest risk to human health in U.S. estuaries, exceeding SVs in approximately 30% of coastal waters (Harvey et al., 2008). Although area and length estimates are not directly comparable, in great rivers, the extent of risk was much greater for PCBs (up to 98% of river length) compared with coastal waters (~12-43% by area). Likewise, dieldrin poses widespread risk to human health in the Great Rivers of this study (26-54% of length among rivers), but was rarely detected above SVs in estuaries (Harvey et al., 2008). In terms of wildlife risk, comparable results for organic compounds were only available for Mid-Atlantic highland (MAH) streams of the eastern U.S. (Lazorchak et al., 2003). The extent above the WV for kingfisher was low and similar between MAH streams and Great Rivers for PCBs and dieldrin, but chlordane risk was more widespread in the Ohio River (85% of river length) compared with Appalachian streams (40% of stream length). The extent of DDT risk was nearly twice as great in the Ohio River than in Appalachian streams (~15%).

Directly comparing concentrations observed in these other probability studies is complicated because data are presented in varying formats. Only the maximum concentrations are provided for EMAP-National Coastal Assessment (NCA) (Harvey et al., 2008), and they were comparable for PCBs and considerably higher for DDT than maximum values observed here. When lipid-normalized, average organochlorine concentrations in great rivers (Table S5) were similar to those measured in MAH fish (Lazorchak et al., 2003). However, it is not clear

whether the magnitudes of normalized values are particularly high because screening values are not based on lipid-normalized values.

More general comparisons with other river studies lacking a probability-based design vary widely. In samples collected from large rivers across the U.S. (Hinck et al., 2008) median total PCB and dieldrin concentrations were much higher (64-110 ng g^{-1} ww and 5 ng g^{-1} ww across species, respectively) than the mean values found in this study. In the Yukon River, Alaska, the sums of PCBs, chlordane, and some forms of DDT were similar to mean values in this study (21-87, 0.7-10.3, and 13-14 ng g^{-1} ww, respectively), whereas dieldrin values were lower (0.2-0.6 ng g^{-1} ww) (Hinck et al., 2006b). Fish tissue concentrations of PCBs, chlordane, and dieldrin from the Columbia River were comparable to those found in the Ohio River, but DDE alone tended toward higher values than found in this study (Hinck et al., 2006a). Maximum observed concentrations of total DDT in the Willamette River in Oregon were nearly double those in the Ohio River, although PCBs and dieldrin were comparable between the two studies (Sethajintanin et al., 2004). In contrast, samples from the River Nestos in Greece had much lower concentrations for PCBs, DDT, and chlordanes on average than observed in this study, although the data from Greece were based only on fish muscle tissue (Christoforidis et al., 2008).

4.3. PBDE concentrations

PBDE 47 was the dominant congener followed by either PBDE 99 or 100, similar to findings reported for other U.S. systems (Anderson and MacRae, 2006; Brown et al., 2006; Xia et al., 2008). Mean ΣPBDEs concentrations in large great-river fish were much higher than those found in the Hudson River (Xia et al., 2008), the Detroit River (Rice et al., 2002), or the California coast (Brown et al., 2006), but were similar to those in fish from the Penobscot River

in Maine (Anderson and MacRae, 2006), or the Des Plaines River downstream of Joliet, IL (Rice et al., 2002).

5. Conclusions

Fish tissue contaminants in all three rivers were observed to a greater extent and in higher than expected levels, given that manufacture or use of these organochlorine pesticides and PCBs has been banned in the U.S. for at least two decades (http://www.epa.gov/pbt/pubs/cheminfo.htm, accessed 17 December 2008). Dieldrin, DDT, chlordane, and PCBs all bioaccumulate in the environment due to slow degradation rates and high lipid solubilities (Newman and Unger, 2003). The associations of these contaminants with developed land cover suggest that past uses of pesticides in residential areas and of PCBs in industrial applications remain detectible in fish today, and present ongoing exposure risks to both wildlife and humans. However, some of these contaminants are still in use in other parts of the world, and atmospheric deposition may also contribute to current exposure levels.

The widespread occurrence of PBDEs across all rivers and their bioaccumulative nature as indicated by higher concentrations in large fish confirms the importance of these compounds as emerging contaminants. PBDEs bioaccumulate, and they have been identified as potential endocrine disruptors in the environment (Rahman et al., 2001; Hale et al., 2003). Recent work has shown that a metabolite of BDE 47 in particular is toxic to both embryo and adult zebrafish (van Boxtel et al., 2008). The association between PBDE and PCB concentrations in fish indicates some relationship between the two in terms of sources of these contaminants, whether historical or current. Regardless of source, the PBDE values observed in this study provide a valuable baseline for future comparison and assessment.

The information provided by organic contaminant levels in fish tissue supports a large-scale multi-indicator perspective on ecosystem condition in the mid-continent great rivers of the U.S. On its own, fish tissue contamination as translated to wildlife and human health risk only provides a small snapshot of legacy and emerging contaminants in these systems. In combination with other indicators, however, it becomes an integral part of the larger picture of ecosystem health as a whole.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:XXXXXXXX.

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Table 1. Arithmetic mean (standard error) for contaminant concentrations in large and small fish at river and reach category scales. Values not provided for Upper Missouri and Unimpounded Upper Mississippi river sections due to inadequate sample sizes. Units for all contaminants are ng g^{-1} ww. Concentrations below the detection limit (DL) were set at one half the DL for all calculations.

Fish size	River/Section	Chlordane	Dieldrin	DDT	PBDEs	PCBs
Large	Upper MS	6.60 (0.63)	3.82 (0.33)	11.16 (0.60)	12.50 (1.07)	42.18 (2.64)
	Impounded MS	3.69 (0.41)	3.02 (0.30)	9.66 (0.59)	8.23 (0.68)	36.70 (2.38)
	MO	7.00 (0.84)	4.60 (0.47)	8.18 (1.15)	19.50 (1.70)	11.36 (1.38)
	Lower MO	7.91 (0.95)	5.17 (0.53)	9.04 (1.30)	21.81 (1.94)	12.71 (1.57)
	OH	23.77 (2.53)	4.12 (0.36)	18.32 (2.64)	45.66 (6.69)	123.12 (12.63)
Small	Upper MS	2.31 (0.23)	3.10 (0.18)	6.57 (0.37)	5.31 (0.39)	19.77 (0.93)
	Impounded MS	1.39 (0.14)	2.66 (0.11)	6.54 (0.37)	4.43 (0.28)	19.67 (0.84)
	MO	4.54 (0.40)	3.19 (0.25)	5.47 (0.38)	12.72 (2.08)	7.41 (0.74)
	Lower MO	5.14 (0.46)	3.59 (0.29)	6.14 (0.43)	14.18 (2.39)	8.43 (0.85)
	OH	19.41 (0.73)	4.75 (0.32)	15.60 (0.62)	28.10 (1.47)	90.31 (3.66)

Table 2. Selected models of fish contamination on developed land use from best subsets regressions by fish size and separately for the Mississippi (MS), Missouri (MO), and Ohio (OH) rivers. Variables coded as (--) were not included in the model based on best subsets regression, those as (*) were significant at 0.05, and those as (**) were significant at 0.01. Those variables left blank were selected for the model but not significant at 0.05.

Group (river, fish size)	Variable (transform indicated)	N	Guild	Mean length	% lipids	Log 50 km network	Log 10 km network	Adj. R^2	Mallow's C_p
MS Large	Log DDT	119	**	**	**	**		0.29	6.0
	Log PCB	119	**	**	--	*	--	0.23	3.6
	Log PBDE	119	--	**	--	**	--	0.22	1.3
MS Small	Log DDT	118		--	**	**	--	0.32	3.0
	Sqrt PCB	118	**	--	**	**	--	0.33	2.1
	Log PBDE	118	--	--	**	**	--	0.25	2.3
MO Large	Log DDT	112	--	--	--	**	--	0.14	0.8
	Log PCB	112	--	--	--	**	--	0.07	1.5
	Log PBDE	112	*	--		**	--	0.21	3.6
MO Small	Log DDT	92	--	*	--	**	--	0.21	1.7
	Log PBDE	92	**	--		**	--	0.28	2.8
OH Large	Log DDT	102	*	**	**			0.46	6.0
	Log PCB	102	*	**	**	**	--	0.44	4.4
	Log PBDE	102	*	**		**	--	0.51	4.4
	Log dieldrin	102	--	--	**	--	--	0.22	-0.2
	Log chlordane	102	*	**	**	**	--	0.52	4.0
OH Small	Sqrt DDT	110	**		**			0.58	6.0

	Log PCB	110	**	*	--	**	--	0.57	3.1
	Log PBDE	110	**			**	--	0.68	4.1
	Sqrt dieldrin	110	**	**	--	--	--	0.47	1.4
	Sqrt chlordane	111	**	--	**	**	--	0.61	2.6

Figure Legends

Figure 1. Locations of probability-based sampling sites across Mississippi, Missouri, and Ohio rivers.

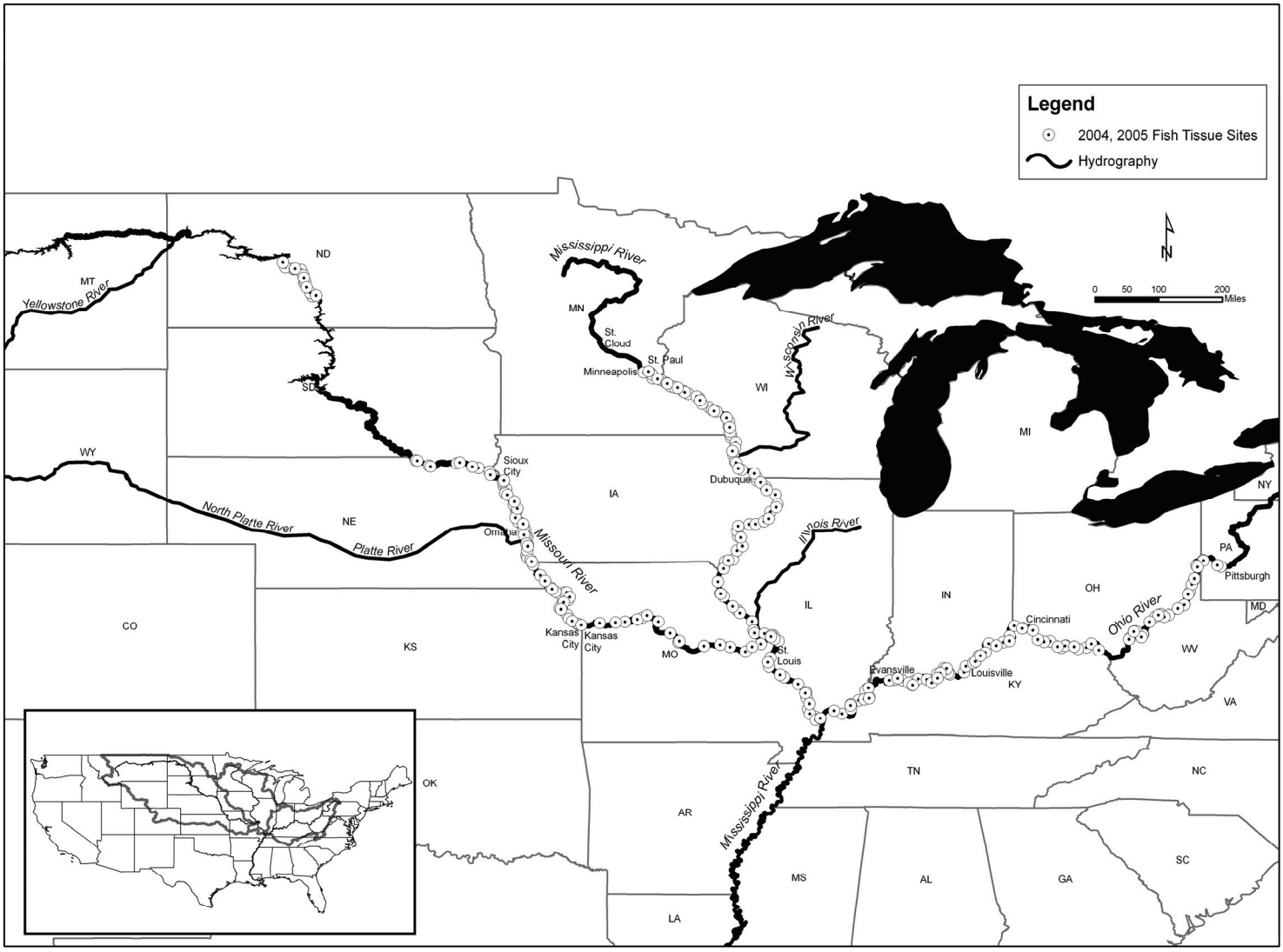
Figure 2. Extent of contaminants in levels above wildlife and human health screening values.

Figure 3. Longitudinal profiles of contaminants (ng g-1 wet weight) in large fish in the Upper Mississippi, Missouri, and Ohio Rivers. Note different scales on Y-axes for illustration purposes. Major cities and other points of interest are shown for spatial context. Reference lines represent human screening values. The term "Quad Cities" refers to the towns of Davenport and Bettendorf, IA, and Moline, Rock Island, and East Moline, IL. MNRR is the Missouri National Recreational River. The gap in the Missouri River plot represents 6 reservoirs that were excluded from the study. Non-detects were set at half the detection limit.

Figure 4. Longitudinal profiles of contaminants (ng g-1 wet weight) in small fish in the Upper Mississippi, Missouri, and Ohio Rivers. Major cities and other points of interest are shown for spatial context. Reference lines represent wildlife screening values for mink and kingfisher (KF). The term "Quad Cities" refers to the towns of Davenport and Bettendorf, IA, and Moline, Rock Island, and East Moline, IL. MNRR is the Missouri National Recreational River. The gap in the Missouri River plot represents 6 reservoirs that were excluded from the study. Non-detects were set at half the detection limit.

Figure 5. Mean (+/- 1SE) concentration of total PBDEs by fish size, river and section. Numbers next to symbols represent sample sizes.

Figure 6. Average distribution of PBDE congeners by river and section for large and small fish.


Legend
2004, 2005 Fish Tissue Sites
Hydrography
N
0 50 100 200
Miles
MT
Yellowstone River
ND
SD
WY
North Platte River
Platte River
NE
CO
KS
OK
Mississippi River
MN
St. Cloud
Minneapolis
St. Paul
WI
Wisconsin River
MI
Sioux City
IA
Dubuque
Omaha
Missouri River
Kansas City
Kansas City
MO
Illinois River
IL
St. Louis
IN
OH
Cincinnati
Ohio River
Evansville
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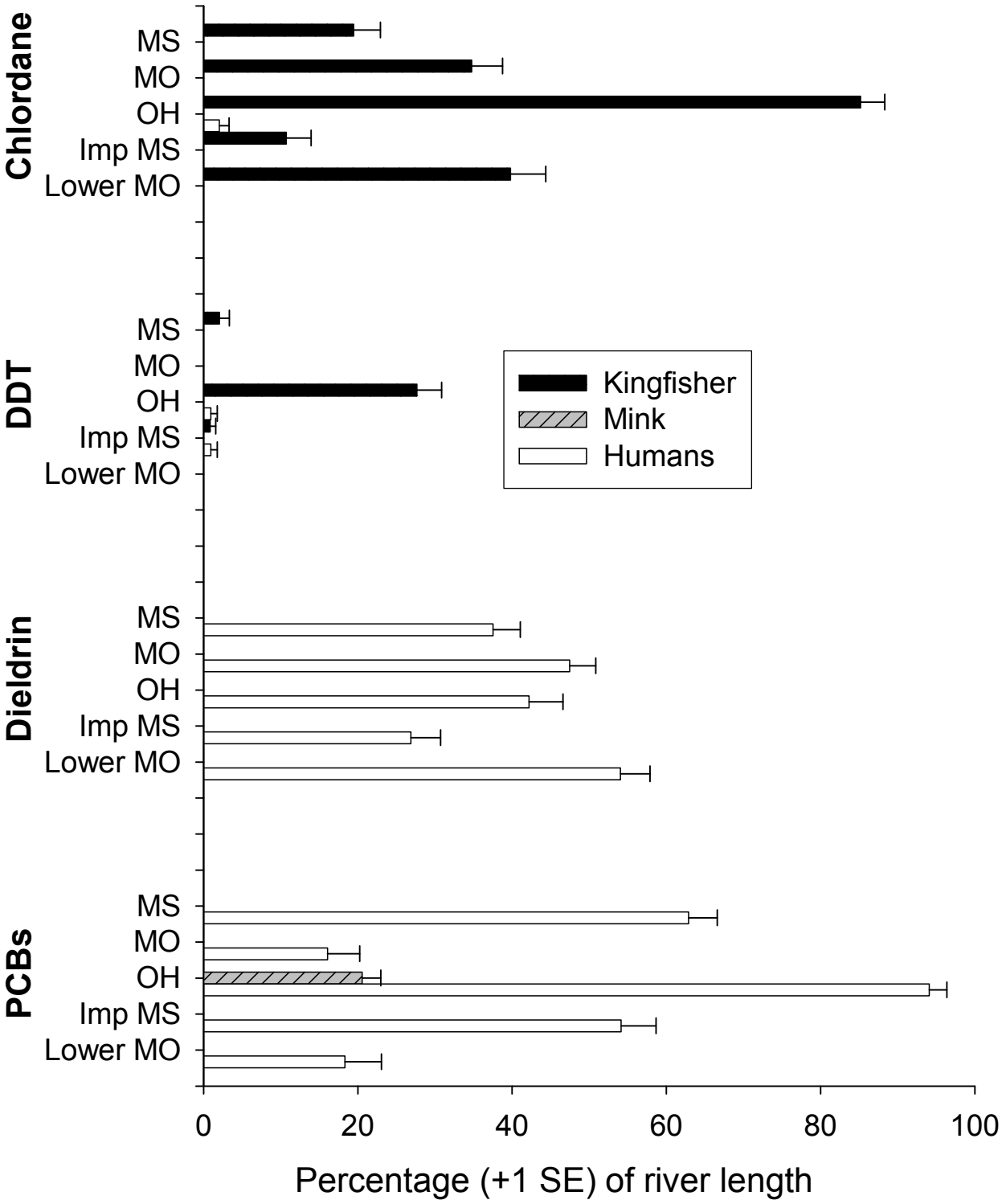
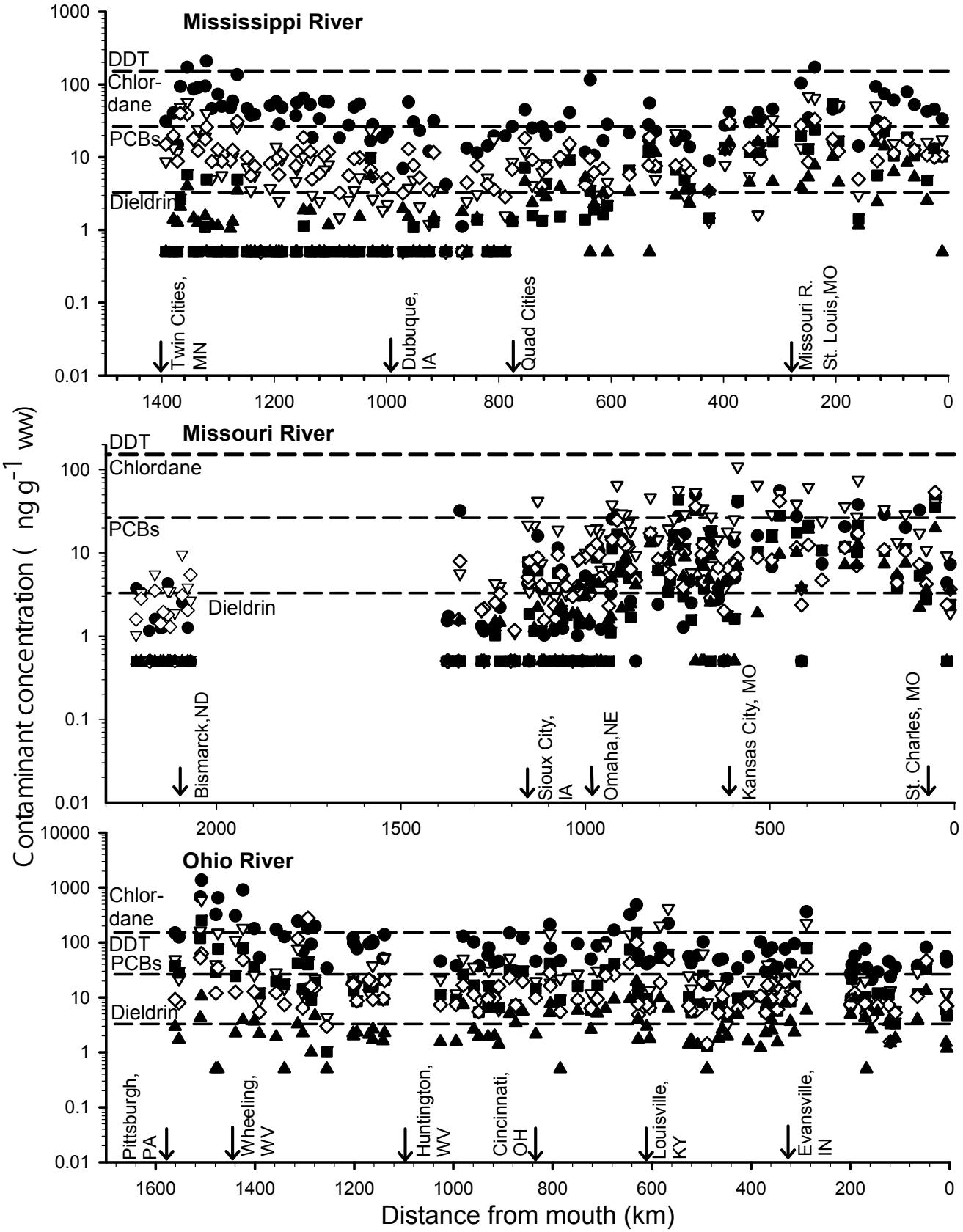
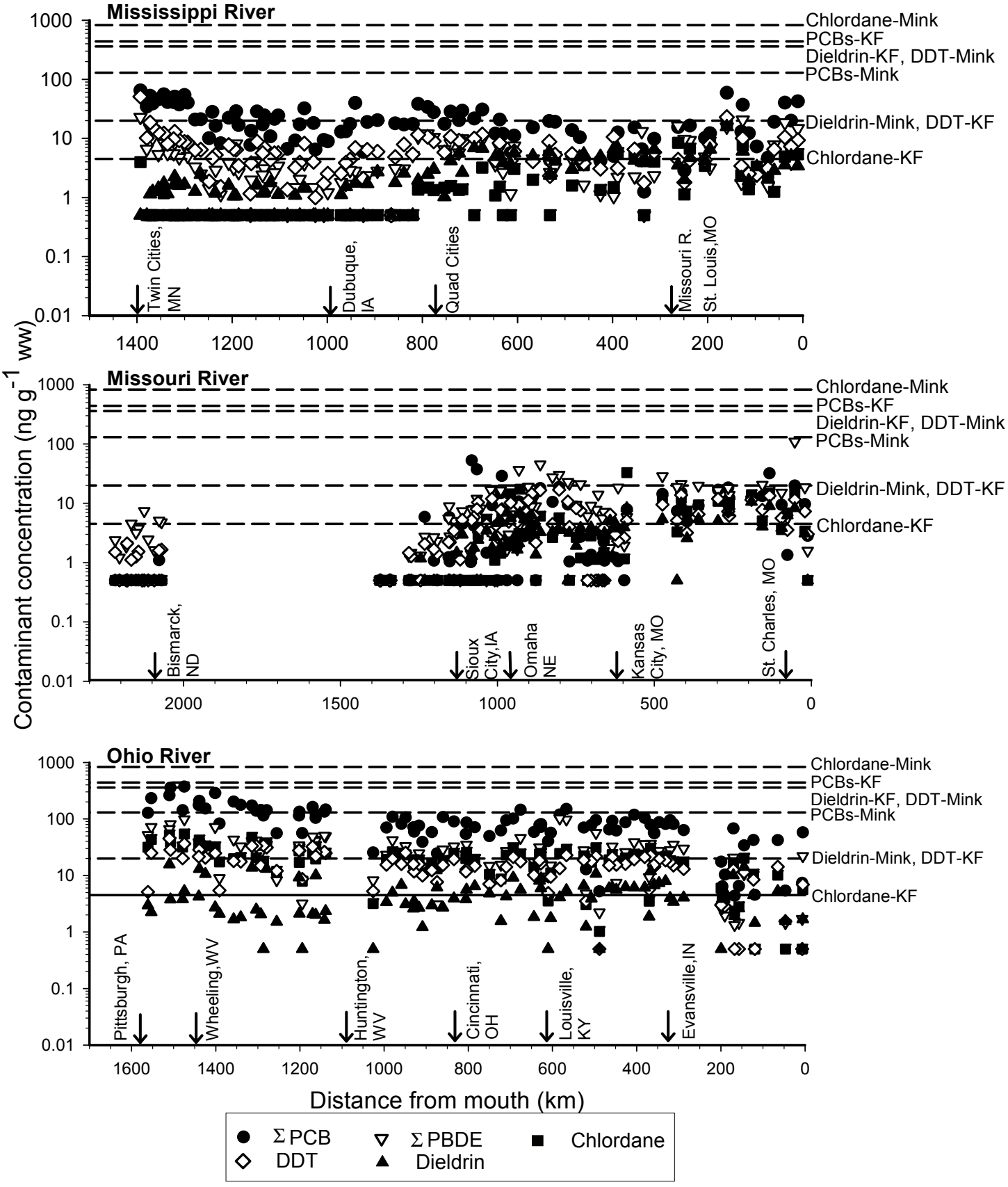
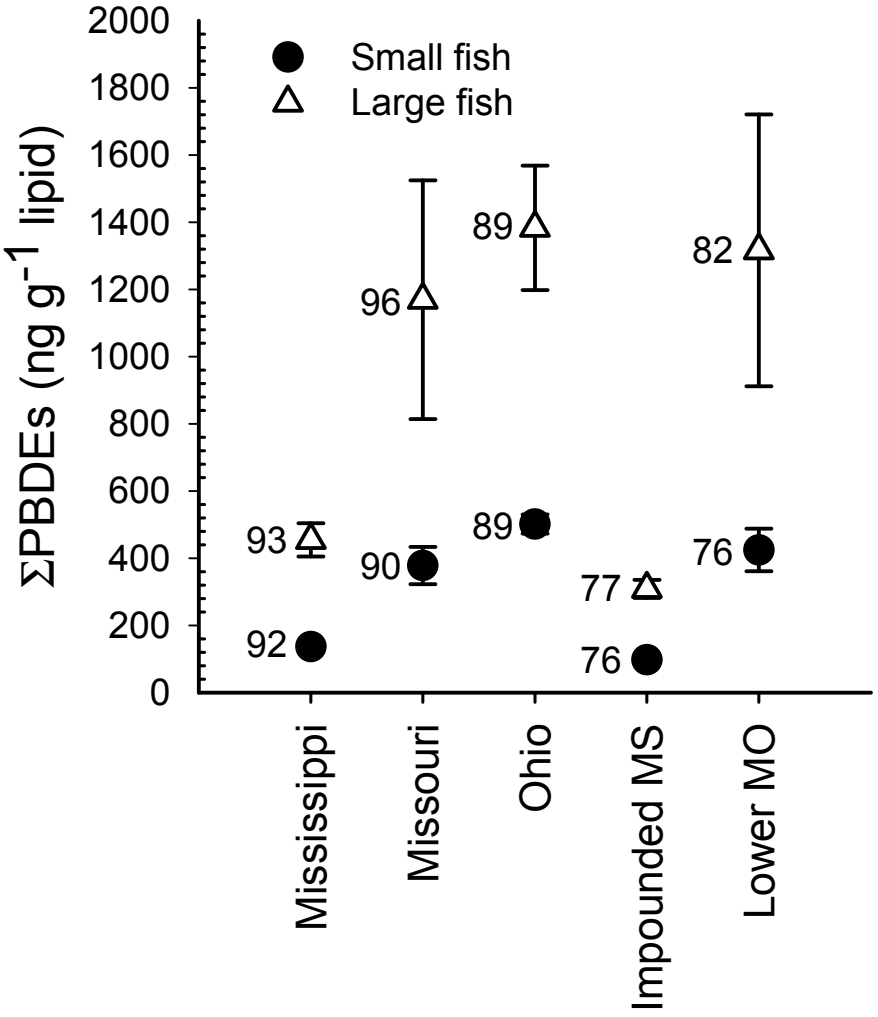
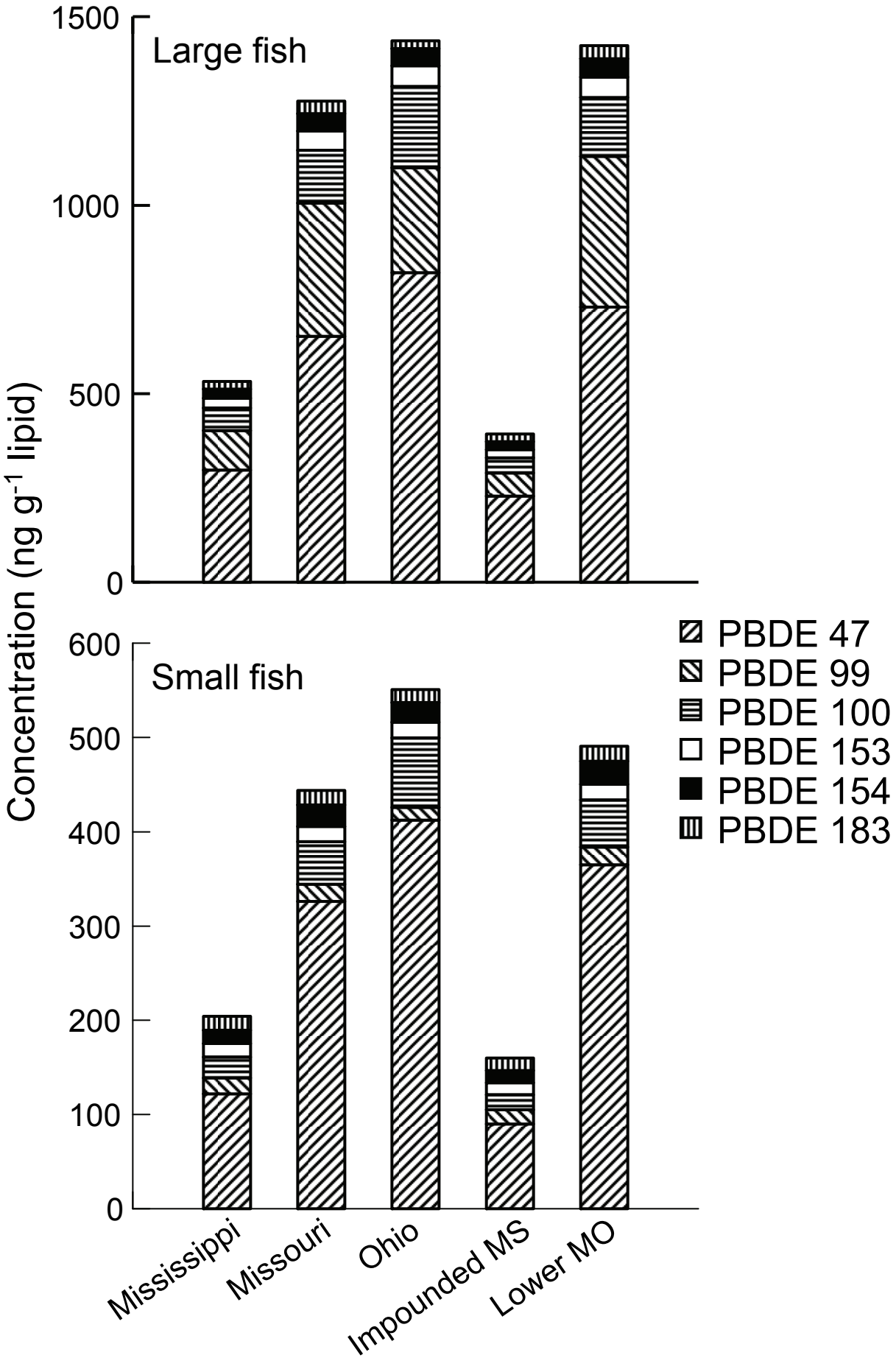
NY
MD
VA
TN
NC
AR
MS
AL
GA
SC
LA
Mississippi River


Chlordane
MS
MO
OH
Imp MS
Lower MO
DDT
MS
MO
OH
Imp MS
Lower MO
Dieldrin
MS
MO
OH
Imp MS
Lower MO
PCBs
MS
MO
OH
Imp MS
Lower MO
Kingfisher
Mink
Humans
0
20
40
60
80
100
Percentage (+1 SE) of river length


Mississippi River
DDT
Chlor-
dane
PCBs
Dieldrin
Twin Cities, MN
Dubuque, IA
Quad Cities
Missouri R. St. Louis,MO
Missouri River
DDT
Chlordane
PCBs
Dieldrin
Bismarck,ND
Sioux City, IA
Omaha,NE
Kansas City, MO
St. Charles, MO
Ohio River
Chlor-
dane
DDT
PCBs
Dieldrin
Pittsburgh, PA
Wheeling, WV
Huntington, WV
Cincinnati, OH
Louisville, KY
Evansville, IN
Contaminant concentration (ng g-1 ww)
Distance from mouth (km)
Σ PCB
Σ PBDE
Chlordane
DDT
Dieldrin


Mississippi River
Missouri River
Ohio River
Chlordane-Mink
PCBs-KF
Dieldrin-KF, DDT-Mink
PCBs-Mink
Dieldrin-Mink, DDT-KF
Chlordane-KF
Contaminant concentration (ng g-1 ww)
Twin Cities, MN
Dubuque, IA
Quad Cities
Missouri R.
St. Louis,MO
Bismarck, ND
Sioux City,IA
Omaha NE
Kansas City, MO
St. Charles, MO
Pittsburgh, PA
Wheeling,WV
Huntington, WV
Cincinnati, OH
Louisville, KY
Evansville,IN
Distance from mouth (km)
Σ PCB
Σ PBDE
Chlordane
DDT
Dieldrin


2000
1800
1600
1400
1200
1000
800
600
400
200
0
ΣPBDEs (ng g-1 lipid)
Small fish
Large fish
93
92
96
90
89
89
77
76
82
76
Mississippi
Missouri
Ohio
Impounded MS
Lower MO


Large fish
Small fish
Concentration (ng g-1 lipid)
1500
1000
500
0
600
500
400
300
200
100
0
PBDE 47
PBDE 99
PBDE 100
PBDE 153
PBDE 154
PBDE 183
Mississippi
Missouri
Ohio
Impounded MS
Lower MO

Appendix A: Supplementary data

Persistent organic pollutants in fish tissue in the mid-continental great rivers of the United States

Karen A. Blocksom, David M. Walters, Terri Jicha, James M. Lazorchak, Theodore Angradi, and David Bolgrien

S1. Analytical methods

S1.1. Sample homogenization

Whole fishes were homogenized using an electric blender (Waring 7011HS). Large fishes (>100g) were chopped into chunks and processed through either a meat chopper (Hobart A-120) or food cutter (Hobart 84145) prior to blending. Homogenates were transferred to polyethylene containers and frozen at -20°C until analysis.

S1.2. Sample extraction

Samples (~8g tissue) were mixed with 25g of baked sodium sulfate in a clean glass mortar. Samples were allowed to dry for at least one hour. Quality control samples (laboratory fortified blanks, LFBs, and matrixes, LFMs) were spiked with high-purity standards of all target organic analytes (pesticides, PCBs, and PBDEs) prior to extraction. Samples were transferred into Accelerated Solvent Extractor (ASE) cells (Dionex, Sunnyvale, CA) and extracted using methylene chloride and hexane (100° C, 1000 psi, 2 cycles of 5 minutes, 70% flush volume). Extracts were concentrated to ~ 3ml using an N-EVAP 111 nitrogen evaporator with a 50° C water bath. Extracts were dried using a 1inch diameter glass chromatography column packed with 20g sodium sulfate and glass wool and then eluted to 15ml using hexane. The extract was concentrated to 5ml using an N-EVAP 111 nitrogen evaporator with a 50° C water bath, and then brought to a final volume of 10ml using hexane. This volume was split, with 5ml of the extract transferred for lipid analysis. The remaining 5ml was solvent exchanged with acetonitrile, frozen, and centrifuged to remove lipids, and then solvent exchanged to hexane. The extract was eluted through an alumina-N (level III) column with methylene chloride/hexane mix as a final cleaning process.

S1.3. GC analysis of organic compounds

Analysis for organic compounds was by gas chromatography-electron capture detection (GC-ECD, Agilent 6890) following EPA method 508.1. For each run, 0.5 µL of extract was injected in pulsed splitless mode. Chromatic separation was achieved using a HP-5MS column (Agilent Technologies, 30m x 0.32mm id; 0.25µm film thickness). An initial oven temperature of 60°C was held for 2 minutes, followed by heating at 50°C/min to 120°C (8 min hold time), 20°C/min to 176°C (8 min hold time), 1.50°C/min until 210°C (no hold time), and then 10°C/min until 310°C (4 min hold time) for a total run time of 61.27 min. The presence of analytes was confirmed using an alternate column (DB-XLB, Agilent Technologies, 30m x 0.32mm id; 0.25µm film thickness). An initial oven temperature of 120°C was held for 1 minute, followed by heating at 7.5°C/min to 160°C (2 min hold time), 2.0°C/min to 240°C (no hold time), 5°C/min until 280°C (no hold time), and then 20°C/min until 325°C (5.5 min hold time) for a total run time of 64.08 min. Chromatographic data was analyzed using ChemStation software (Agilent Technologies). The analytes had to occur on both columns to be reported as present. The reported value was determined through the following protocol:

1) If values from the columns had <50% relative percent difference (RPD), then the mean of the two values was reported.
2) If RPD >50%, then:
    a. If one column had QC problems, then the data was reported from the other column.

b. If QC was similar between the columns, the lower value was reported

S2. QA/QC

S2.1. Organic compounds

Internal standard calibration curves were prepared from standard solutions ranging from 1-75 ng μL^{-1}. Seven points were included and each curve had to yield an r^2 > 0.95. Check standards were run twice per batch (n = 19 samples) with a QC standard of ±30% recovery for analytes. Laboratory blanks were also run twice per batch with a QC standard of <3X the minimum detection limit (MDL) of analytes. Two laboratory fortified blanks (LFBs) were analyzed in each batch to determine accuracy and precision (without matrix interferences) of the methods (Table S2). LFBs were spiked so that analyte concentrations were 9.375 ppb. Accuracy of the method was assessed as percent recovery of LFBs, which averaged 93.5% (±17% SD) among analytes (Table S2). Precision of the method was assessed at the relative percent difference (RPD) between the two LFBs from each batch. RPD was generally low (mean 8.9% (±9.2% SD) among analytes), indicating a high degree of precision. One laboratory fortified matrix (LFM) was run per batch to determine matrix interferences. One sample was chosen as the laboratory fortified matrix sample (LFM), split, and spiked with the target analytes. Similar to the LFBs, the LFM was spiked so that the analyte concentrations were 9.375 ppb. The background fish tissue matrix was subtracted from the LFM to determine the percent recovery. LFM recoveries averaged 67.6% (±19.3% SD) among analytes (Table S2). Reported values were not blank subtracted or recovery corrected.

S3. Analytical methods cited

EPA Method 508.1. Determination of chlorinated pesticides, herbicides, and organohalides by liquid solid extraction and electron capture gas chromatography. National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Cincinnati, OH 45268.

Table S1. Target species for fish tissue analysis. Species are listed in descending priority for both small and large target species. Criteria for prioritization were based on expectations of ubiquity and abundance within the Great Rivers based on analysis of historical collection data and discussions with regional fishery biologists. Fish length was measured as total length. N = total number of samples for each species. Twenty-three samples were multi-species composites (not shown). Trophic guilds: **C** – generalized carnivore; **I** – Insectivore; **O** – Omnivore; **P** – Piscivore; **PL** – Planktivore.

Priority	Species	Common name	Trophic guild	Size range (mm)	Length (mm)	% Lipid	N
Small Target[1]							
1	*Notropis atherinoides*	emerald shiner	I	<120	81.2	5.43	195
2	*N. blennius*	river shiner	I	<120	84.2	2.55	7
3	*Cyprinella spilopterus*	spotfin shiner	I	<120	70.9	4.65	6
4	*Pimephales vigilax*	bullhead minnow	O	<120	-	-	-
5	*Macrhybopsis storeriana*	silver chub	I	<120	108.8	4.49	4
6	*Cyprinidae* sp.[2]	other cyprinid sp.	PL	<120	75.1	3.47	27
7	*Dorsoma cepedianum*	gizzard shad	PL	<150	102.2	3.28	78
Large Target[3]							
1	*Sander canadensis*[4]	sauger	P	120-180	239.1	2.72	36
2	*S. canadensis*	sauger	P	180-240	-	-	-
3	*S. canadensis*	sauger	P	>240	-	-	-
4	*Micropterus salmoides*[4]	largemouth bass	P	180-240	235.5	2.34	48
5	*M. salmoides*	largemouth bass	P	240-300	-	-	-
6	*M. salmoides*	largemouth bass	P	>300	-	-	-
7	*Micropterus* sp.[5]	other black bass	P	>180	223.2	3.22	34
8	*Salmo trutta*	brown trout	P	>120	-	-	-
9	*Oncorhynchus mykiss*	rainbow trout	P	>120	-	-	-
10	*Ictalurus punctatus*[4]	channel catfish	O	120-180	382.4	4.36	30
11	*I. punctatus*	channel catfish	O	450-510	-	-	-
12	*I. punctatus*	channel catfish	O	180-450	-	-	-
13	*Aplodinotus grunniens*	freshwater drum	C	>120	270.4	4.28	56
14	*Moxostoma macrolepidotum*	shorthead redhorse	I	>120	311.4	6.30	22
15	*Moxostoma* sp.[6]	other redhorse sp.	I	>120	277.5	7.13	3

16	*Lepomis macrochirus*	bluegill	I	>120	151.9	3.17	4
17	*L. megalotis*	longear sunfish	I	>120	156.0	2.01	1
18	*Lepomis* sp.	other sunfish sp.	I	>120	-	-	-
19	*Cyprinus carpio*	common carp	O	>180	491.0	3.67	21
20	*Ictiobus bubalus*	smallmouth buffalo	I	>120	304.9	3.07	7
21	*Carpiodes carpio*	river carpsucker	O	>120	336.5	4.45	28
22	*Pylodictis olivaris*	flathead catfish	P	>120	269.2	2.30	22
23	*Morone chrysops*	white bass	C	>120	184.8	3.36	11
24	*Carpiodes cyprinus*	quillback	O	>120	187.7	2.86	6

[1] Other small species (n): threadfin shad (1)

[2] Other *Cyprindae* species (n): fathead minnow (2), golden shiner (5), red shiner (19), spottail shiner (1)

[3] Other large species (n): walleye (1)

[4] Mean length and n for species with multiple size classes (sauger, largemouth bass, and channel catfish) represent totals and are not calculated for individual size classes.

[5] Other black basses (n): smallmouth bass (29), spotted bass (5)

[6] Other redhorse suckers (n): golden redhorse (3)

Table S2. Estimated detection limits and summary quality control values. Abbreviations: LFB: laboratory fortified blank; RPD: relative percent difference; LFM: laboratory fortified matrix.

Compounds	Estimated detection limit (ng g^{-1} ww)	LFB recovery (%)		LFB RPD (%)		LFM recovery (%)	
		mean	SD	mean	SD	mean	SD
cis-Chlordane	0.22	92.2	12.5	7.7	6.6	71.3	13.9
cis-Nonachlor	0.19	94.3	13.6	7.2	6.2	63.0	13.5
trans-Chlordane	0.21	90.1	12.9	7.8	6.7	65.7	15.5
Oxychlordane	0.28	91.9	12.9	8.4	6.9	67.9	11.8
trans-Nonachlor	0.22	90.4	12.9	7.7	6.6	62.7	15.9
Aldrin	0.44	79.3	14.8	11.4	10.2	67.9	12.7
Dieldrin	0.20	92.9	13.1	7.6	6.0	79.3	18.8
Endrin	0.21	89.5	13.8	8.7	8.5	80.4	14.9
Endosulfan I	0.15	81.5	16.6	13.3	18.7	62.0	32.8
Endosulfan II	0.73	82.3	19.6	14.2	21.8	70.9	16.2
Hexachlorobenzene	0.32	69.6	15.6	16.4	15.2	70.8	14.5
Heptachlor epoxide	0.29	96.3	13.5	7.6	6.4	74.2	11.0
Lindane	0.27	92.4	12.5	9.4	6.7	82.5	10.7
Mirex	0.22	92.0	14.6	8.4	8.5	61.9	13.8
2,4'-DDD	0.20	97.8	13.8	7.2	6.2	77.3	13.4
2,4'-DDT	0.17	94.5	15.4	8.3	6.9	59.3	14.9
2,4'-DDE	0.23	92.1	14.4	8.7	7.0	62.5	20.7
4,4'-DDD	0.21	94.9	14.0	7.8	7.1	71.6	13.3
4,4'-DDE	0.19	91.8	14.9	8.4	7.1	67.5	26.9
4,4'-DDT	0.15	90.5	14.9	8.5	7.1	66.2	12.3
BDE #47	0.22	101.4	39.9	10.2	21	78.1	32.0
BDE #99	0.21	101.7	15.6	7.2	6.7	74.3	21.1
BDE #100	0.20	101.2	15.3	7.5	6.9	74.4	14.7
BDE #153	0.23	89.5	26.6	8.5	9.1	65.4	22.5
BDE #154	0.23	101.6	15.7	7.4	6.9	70.0	17.7
BDE #183	0.24	97.8	16.8	8.2	7.7	62.8	21.2
PCB #8	0.38	89.0	17.1	12.8	10.4	99.2	15.4
PCB #18	0.33	86.5	14.5	10.6	9.0	80.7	11.0
PCB #28	0.29	87.1	13.9	9.6	7.3	75.9	18.9
PCB #44	0.25	91.2	14.4	9.1	7.9	71.1	12.3
PCB #52	0.27	88.3	14.2	9.4	9.3	71.5	13.5
PCB #66	0.22	91.3	14.4	8.4	7.5	63.4	15.0
PCB #77	0.21	92.5	19.0	7.8	6.3	74.5	32.4
PCB #101	0.28	91.8	13.6	8.5	7.4	52.9	20.7
PCB #105	0.19	95.1	15.1	7.8	6.6	62.6	15.1
PCB #118	0.27	93.5	14.6	8.1	7.1	61.3	28.4
PCB #126	0.22	96.4	19.9	9.5	8.0	66.5	14.9
PCB #128	0.16	98.8	15.5	8.1	7.1	63.3	16.0
PCB #138	0.38	99.0	15.4	8.4	9.1	62.3	19.5
PCB #153	0.19	95.2	15.2	8.5	7.7	53.3	19.8
PCB #170	0.24	102.1	16.3	7.9	9.2	68.1	17.4
PCB #180	0.19	96.3	17.1	9.2	8.0	61.8	18.0

PCB #187	0.29	96.0	16.2	9.0	8.6	62.8	15.3
PCB #195	0.20	104.4	16.7	7.8	7.7	61.5	16.1
PCB #206	0.27	104.8	17.8	8.1	8.8	59.1	15.8
PCB #209	0.38	102.6	17.5	8.7	9.6	53.6	16.9
mean organic compounds	**0.25**	**93.5**	**17.6**	**8.9**	**9.2**	**67.6**	**19.3**

Table S3. Wildlife risk values (WVs) and adjusted screening values (SVs) for humans consuming fish for organochlorine pesticides and PCBs. All values are in ng g^{-1} wet weight. Total PCBs includes all congeners and total DDT includes all forms of DDD, DDE, and DDT listed in Table S2. Total chlordane represents the sum of cis-chlordane, cis-nonachlor, trans-chlordane, trans-nonachlor, and oxychlordane.

Contaminant	Mink WV	Kingfisher WV	Human SV
Total chlordane	830	4.5	151
Total DDT	360	20	155
Dieldrin	20	360	3.3
Endrin	40	220	1584
Total PCBs	130	440	26.4
Aldrin			3.1
HCB	--	--	33
Heptachlor epoxide	--	--	5.8
Endosulfan (I and II)	--	--	31680
Lindane	--	--	40.5
Mirex	--	--	1056

Table S4. Number of river kilometers (rkm) represented by sites sampled for fish tissue, percentage of rkm from which data were not obtained, and percentages (± SE) of those rkm where contaminants were detected.

Fish size	Contaminant	Mississippi (MS)	Missouri (MO)	Ohio (OH)	Impounded MS	Unimpounded MS	Lower MO	Upper MO
Small	Sampled rkm (N sites)	2784.4 (93)	2639.4 (92)	3128.4 (89)	2164.7 (77)	619.6 (16)	2306.2 (78)	333.2 (14)
	Unsampled rkm (%)	1.4	2.7	6.8	1.8	0.0	3.1	7.1
	PCBs	97.4 (1.6)	68.6 (2.9)	100 (0)	96.6 (2.1)	100 (0)	77.5 (3.3)	7.1 (6.0)
	PBDEs	91.3 (2.5)	87.0 (2.4)	98.7 (1.1)	88.9 (3.2)	100 (0)	87.2 (2.4)	85.7 (8.9)
	DDT	97.4 (1.6)	81.1 (2.7)	93.7 (2.2)	96.6 (2.1)	100 (0)	85.6 (2.6)	50 (11.9)
	Aldrin	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Chlordane	52.4 (2.9)	56.2 (3.0)	96.2 (1.6)	38.8 (3.7)	100 (0)	64.3 (3.4)	0.0 (0.0)
	Dieldrin	81.2 (3.0)	59.7 (3.5)	92.1 (2.6)	75.8 (3.9)	100 (0)	68.3 (4.1)	0.0 (0.0)
	Endrin	0.0 (0.0)	0.0 (0.0)	9.2 (2.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Endosulfan (I and II)	0.0 (0.0)	5.3 (2.6)	17.6 (3.5)	0.0 (0.0)	0.0 (0.0)	5.0 (2.8)	7.1 (6.2)
	Lindane	0.0 (0.0)	0.5 (0.4)	1.1 (1.0)	0.0 (0.0)	0.0 (0.0)	0.6 (0.5)	0.0 (0.0)
	Heptachlor Epoxide	17.1 (3.0)	16.2 (4.0)	40.6 (4.4)	18.4 (3.4)	0.0 (0.0)	18.6 (4.5)	0.0 (0.0)
	Hexachlorobenzene	0.0 (0.0)	1.7 (0.8)	86.3 (3.0)	0.0 (0.0)	0.0 (0.0)	1.9 (1.0)	0.0 (0.0)
	Mirex	0.0 (0.0)	0.0 (0.0)	4.8 (1.7)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Large	Sampled rkm (N sites)	2803.4 (94)	2735.5 (96)	3167.7 (90)	2183.8 (78)	619.6 (16)	2402.2 (82)	333.2 (14)
	Unsampled rkm (%)	1.4	0.0	0.9	1.8	0.0	0.0	0.0
	PCBs	97.9 (1.4)	85.5 (3.2)	99.1 (0.8)	97.4 (1.8)	100 (0)	88.4 (3.3)	64.3 (11.4)
	PBDEs	94.6 (2.0)	89.9 (2.2)	99.1 (0.8)	93.1 (2.6)	100 (0)	91.5 (2.3)	78.6 (7.8)
	DDT	95.5 (1.9)	92.5 (2.1)	99.1 (0.8)	94.2 (2.4)	100 (0)	95.4 (1.9)	71.4 (10.1)
	Aldrin	0.0 (0.0)	2.6 (1.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	2.9 (2.2)	0.0 (0.0)
	Chlordane	63.3 (2.7)	62.1 (3.3)	99.1 (0.8)	52.9 (3.5)	100 (0)	70.7 (3.8)	0.0 (0.0)
	Dieldrin	67.1 (3.7)	66.7 (3.1)	91.7 (2.4)	59.6 (4.5)	93.8 (5.2)	75.9 (3.5)	0.0 (0.0)
	Endrin	0.0 (0.0)	0.0 (0.0)	0.9 (0.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Endosulfan (I and II)	3.3 (1.7)	5.5 (2.4)	7.2 (2.5)	4.2 (2.2)	0.0 (0.0)	5.3 (2.6)	7.1 (6.0)
	Lindane	0.0 (0.0)	0.0 (0.0)	0.9 (0.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Heptachlor Epoxide	16.4 (3.2)	23.7 (4.2)	23.2 (3.8)	14.0 (3.2)	25 (9.3)	27.0 (4.7)	0.0 (0.0)
	Hexachlorobenzene	5.5 (2.0)	0.0 (0.0)	84.8 (3.0)	0.0 (0.0)	25 (9.0)	0.0 (0.0)	0.0 (0.0)
	Mirex	0.0 (0.0)	0.0 (0.0)	9.8 (2.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)

Table S5. Arithmetic mean (standard error) for lipid-normalized contaminant concentrations in large and small fish at river and reach category scales. Values not provided for Upper Missouri and Unimpounded Upper Mississippi river sections due to inadequate sample sizes. Units for all contaminants are ng g^{-1} lipid. Concentrations below the detection limit (DL) were set at one half the DL prior to lipid normalization.

Fish size	River/Section	% Lipid	Chlordane	Dieldrin	DDT	PBDEs	PCBs
Large	Upper MS	3.40 (0.18)	178.6 (13.7)	105.6 (7.0)	386.4 (23.3)	454.2 (49.3)	1516.8 (116.2)
	Impounded MS	3.21 (0.17)	101.1 (9.3)	84.0 (6.4)	349.7 (18.8)	308.1 (26.8)	1376.5 (90.1)
	MO	3.70 (0.18)	292.0 (45.8)	168.8 (18.8)	452.9 (130.4)	1169.0 (355.2)	625.9 (141.4)
	Lower MO	3.54 (0.18)	329.4 (52.1)	189.1 (21.5)	504.0 (148.5)	1316.4 (404.5)	702.1 (161.0)
	OH	3.76 (0.22)	668.6 (65.0)	116.8 (7.8)	485.2 (42.4)	1383.2 (185.3)	3762.4 (362.3)
Small	Upper MS	4.39 (0.16)	66.8 (5.8)	80.8 (3.4)	162.8 (8.2)	136.4 (10.8)	488.5 (21.0)
	Impounded MS	4.68 (0.17)	36.8 (4.2)	63.6 (3.2)	148.5 (9.4)	97.6 (6.5)	436.8 (19.8)
	MO	3.96 (0.15)	137.8 (13.1)	89.5 (5.7)	161.9 (9.3)	378.0 (55.2)	222.1 (18.8)
	Lower MO	3.92 (0.16)	156.5 (15.1)	100.9 (6.5)	182.4 (10.7)	424.4 (63.4)	253.1 (21.5)
	OH	5.80 (0.23)	338.6 (11.9)	85.8 (5.6)	275.1 (11.2)	501.4 (28.3)	1666.9 (73.8)