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Mercury Concentrations in Water and Hybrid Striped Bass (*Morone saxatilis* × *M. chrysops*) Muscle Tissue Samples Collected from the Ohio River, USA

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Abstract We report on long-term aqueous mercury (Hg) measurements collected at fixed locations along the Ohio River, offer insights into patterns of water and fish tissue Hg levels, and calculate site-specific bioaccumulation factors (BAFs) along an extensive longitudinal basis. We examined the relationship between total recoverable Hg concentrations in water and fish samples collected from 12 locations on the mainstem Ohio River. Water samples were collected on a bimonthly basis from each location over a 6-year period preceding the collection of fish tissue samples. This abundance of data enabled us to calculate the long-term average aqueous Hg concentrations and approximate the lifetime aqueous Hg exposure experienced by fish, enabling the calculation of appropriate BAFs. Hybrid striped bass (HSB; *Morone saxatilis* × *M. chrysops*) were collected from the Ohio River, composited (three fish), and analyzed for Hg in muscle tissue from each location. Concentrations ranged from 0.2 to 0.4 mg/kg and 41.7% of all samples collected were higher than the US Environmental Protection Agency regulatory threshold of 0.3 mg Hg/kg wet weight. Hg levels generally increased with fish weight, length, and age. However, Hg concentration in the water was the strongest predictor of tissue concentrations. We found that both water and tissue concentrations increased with drainage area, albeit at different rates. This discrepancy in spatial patterns revealed that the bioaccumulation rate of methylmercury might not be consistent throughout the Ohio River mainstem. BAFs calculated at each location supported this finding, as values decreased with increasing drainage area. Our study serves to fill critical, previously identified data gaps and provides decision-makers with the information necessary to develop more appropriate BAF development and risk-management strategies.

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Mercury (Hg) contamination is an issue of global concern. Hg enters the environment from a number of sources, including natural and anthropogenic pathways, eventually making its way into the aquatic ecosystem. Understanding, quantifying, and separating the emissions from natural, anthropogenic, and reemitted sources is an extremely complicated process. Numerous anthropogenic sources have been identified, including common processes in the coal-fired electrical generating industry, manufacturing of temperature and pressure devices, and chlorine and caustic soda production by Hg cell chlor-alkali facilities (USEPA 1997). However, the US Environmental Protection Agency (USEPA 1997) reports that the primary anthropogenic source of Hg emitted to the atmosphere comes from coal combustion facilities. That US EPA report conveys that some of the highest deposition rates from anthropogenic and global contributions for Hg are predicted to occur in the Ohio River Valley.

Mercury is transported around the globe as a gas and is subsequently deposited on the Earth's surface through both wet and dry deposition mechanisms. It is then converted to methylmercury (MeHg) by natural processes, primarily by anaerobic sulfur-reducing bacteria (Morel et al. 1998; USEPA 1997). In the aquatic environment, methylation primarily occurs in the sediment, but it can also occur in the water column. The rate of methylation is not only influenced by the microbial activity (Morel et al. 1998; USEPA 1997) and depositional loadings (Hammerschmidt and Fitzgerald 2006) but also by a number of other factors, including suspended sediment load, dissolved organic carbon (DOC), nutrient content, pH, temperature, and other variables (Driscoll et al. 2007; Gabriel et al. 2009; Qian et al. 2001; Sellers et al. 1996; USEPA 1997; Wiener et al. 2006). Driscoll et al. (2007) reported thresholds for physiochemical parameters [pH <6, total phosphorus (TP) <30 μg/L, DOC > 4 mg/L, and acid-neutralizing capacity (ANC) <100] conducive to optimizing MeHg bioavailability and resulting Hg concentrations in fish tissue that exceed the USEPA fish tissue criterion (0.3 mg/kg). Walters et al. (2010) suggested that mid-continent great rivers are relatively inefficient producers of MeHg, as supported by their findings that MeHg concentrations in these great river fish were relatively low as compared to other aquatic systems and regions. Furthermore, Rypel et al. (2008) found that MeHg concentrations in fish from unregulated rivers were 1.75 times higher than in regulated (flows controlled by dams) rivers and suggested that this was due to unregulated rivers having more extensive interactions with floodplain features such as oxbows, wetlands, marshes, and other areas more suitable for the production of MeHg.

Methylmercury is highly toxic and is associated with a number of adverse human health effects, including developmental neurotoxicity, cardiovascular and immunological effects, and other deleterious health effects mostly associated with the nervous system (ATSDR 2009; Clarkson 1990; USEPA 1997; USEPA 2001). MeHg is efficiently accumulated and transferred to organisms at higher trophic levels (Cizdziel et al. 2003; Mason 2002; USEPA 1997). Most of the Hg found in the edible portions (muscle tissue) of trophic level 4 fish (TL_4: top carnivores) such as hybrid striped bass (HSB) is reported to be the methylated form (Bloom 1992; Grieb et al. 1990; Morel et al. 1998; USEPA 1997). The USEPA (2001) uses a conversion factor of 1.0 when estimating the methylated form of Hg from measures of total Hg in muscle or whole-body samples taken from trophic level 3 (TL_3) or TL_4 fish. Therefore, all values for Hg reported in this study as fish tissue concentrations are assumed to be MeHg and discussed as such, although this assumption has not been verified with data from the Ohio River.

Dietary uptake of fish is the primary pathway of human exposure (USEPA 2001) to MeHg and is the most often referenced contaminant prompting the issuance of fish consumption advisories in the United States (USEPA 2009a). A 2009 nationwide study investigating Hg concentrations in fish tissue revealed that 27% of the 291 sampled stream sites exceeded the USEPA human health criterion of 0.3 mg/kg wet weight (Scudder et al. 2009). In 2008, researchers using data generated by USEPA regional surveys conducted through the Environmental Monitoring and Assessment Program (EMAP) found that 48.8% of the lakes surveyed nationwide had tissue (fillet) concentrations greater than the USEPA fish tissue criterion for MeHg (Stahl et al. 2009). A more localized, probabilistic survey conducted on the mid-continent great rivers of the United States estimated that ~7% of the river kilometers (rkm) of the Ohio River were likely to produce results exceeding the same USEPA criterion (Walters et al. 2010).

The occurrence of Hg in the muscle tissues of longer lived TL_4 species in the Ohio River is not well documented, as existing data are limited. Fish tissue samples are collected by the Ohio River Valley Water Sanitation Commission (ORSANCO) to support states in making fish tissue consumption advisory decisions. However, tissue samples are taken from fish routinely captured as part of other ongoing studies with alternative objectives. Although the "bycatch" from other routine sampling programs has provided a wealth of data and has successfully supported or enhanced the advisory development process, extensive data gaps were identified.

The purpose of this study was to fill some of those data gaps and provide resource managers with the data and information necessary to thoroughly examine and document Hg levels in the fish tissue from a representative TL_4 species collected from the Ohio River. We examined spatial patterns and relationships between observed Hg concentrations relative to fish age and body size. Additional analyses examined the relationship between Hg concentrations in tissue and measured water column concentrations of total recoverable Hg such that more informed management decisions might be made. Currently, the USEPA recommends that the relationship between water concentrations and concentrations observed (or expected) in fish tissue must be understood and documented on a site-specific basis if improved and more appropriate Hg criteria are to be proposed (USEPA 2009b). This study closely follows the guidelines provided by the USEPA (2009b) and highlights remaining areas of uncertainty and concern that should not be overlooked if these procedures are to be followed for the purposes of calculating bioaccumulation factors (BAFs) and the subsequent development of ambient water quality criteria (AWQC).

This study is unique in that it represents one of the most comprehensive datasets relating fish tissue and water column concentrations of Hg for the Ohio River. We were able to relate fish data derived from a multi-age, three-fish composite sample to temporally aggregated water data sufficient to calculate the long-term average aqueous Hg concentrations and approximate the lifetime Hg exposure experienced by the oldest fish in each composite. This was done by analyzing Hg concentrations in the water from the same locations over an extended period of time (≥6 years) and then collecting fish samples (in 2009) from those same locations. We then determined the age of the fish collected and related its tissue value with the appropriate temporally aggregated water concentrations.

Methods

Study Area

The Ohio River begins at the confluence of the Monongahela and Allegheny rivers at Pittsburgh, Pennsylvania and flows 1579 km in a southwesterly direction to its confluence with the Mississippi River at Cairo, Illinois (Fig. 1; White et al. 2005). There are currently 18 high-lift lock and dam structures in place that serve to maintain a minimum channel depth suitable for commercial navigation. There are over 600 National Pollutant Discharge Elimination System (NPDES) permitted discharges to the Ohio River mainstem, including 49 coal-fired power generating facilities (ORSANCO 2006). The Ohio River Basin, which covers over 528,200 km^2, is predominately deciduous forest (46.1%), with only 2.5% evergreen forest and 0.7% wetlands, with the latter two land-use types more conducive of producing MeHg (e.g., Hurley et al. 1995; Scudder et al. 2009).

Target Species Selection

Hybrid striped bass was the targeted species for the study because it represents a TL_4 top-predator with ubiquitous distribution throughout the Ohio River and is long-lived, easily captured, and frequently targeted for human consumption. According to a 1992–1993 angler survey conducted by Schell et al. (1996), HSB were ranked as one of the top 10 species harvested by anglers, and in 1992, they ranked as the fourth most consumed species from the Ohio River. Furthermore, larger individuals of this species are easier to collect in tailwater areas near the locations of aqueous Hg collections. Our target species selection criteria (relatively long-lived adults of a representative TL_4 species) are consistent with the recent recommendations of the USEPA (2009b), which provides guidelines for developing and conducting field-based bioaccumulation studies. This is also consistent with suggestions by Lepak et al. (2009) that highlight the critical need to select fish of harvestable size that are frequently consumed and most likely to have the highest Hg concentrations at a given location. Lepak et al. (2009) further highlighted the need to examine larger specimens by pointing out that in an attempt to sustain fish populations, most angling regulations inadvertently encourage the harvesting of larger fish that pose an elevated risk of Hg exposure to consumers.

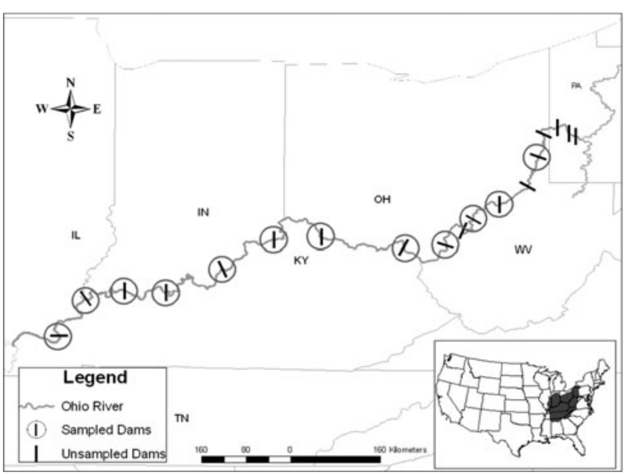

Fig. 1 The 12 locations on the Ohio River where HG concentrations in water samples and HSB fillets were analyzed

Sampling Design

The area included in this study encompasses portions of 91% of the mainstem Ohio River from Pike Island Dam (rkm 135.5) to its confluence with the Mississippi River. Water samples were collected from 12 of the 18 existing dam locations (Fig. 1) over a 6-year period and tissue samples were collected in 2009. ORSANCO maintains a routine sampling program to assess aquatic life and public water supply uses. This program entails the collection of water column grab samples from each of the locations once every other month. Hg (total recoverable) is included in the list of parameters measured as part of this monitoring program.

Water samples were collected as close to the centerline of the river as possible from lockchamber guidewalls or from raw water intake lines to get a sample from as close to the middle of the channel as possible from a fixed, shore-based sampling site. Typically, bridges would be used to provide shore-based access to the mid-channel area in ambient water quality studies, but because of the heights of the bridges across the Ohio River and the dangers associated with sampling on them, dams are the preferred sampling location. Collecting the water samples at the dams (or as close to them as possible) also enabled approximations of the long-term average Hg exposure experienced by fish that were collected from the tailwaters of each respective dam.

For the purposes of this study, we chose to compare aqueous Hg concentrations collected at dam locations with fish tissue concentrations obtained from the pool immediately downstream. Dams are significant barriers for fish movement and limit movement usually associated with spawning activities and species dispersal. A study conducted on the Ohio River by the Ohio Division of Wildlife (Vallazza et al. 1994) revealed that HSB did not move between pools, prefer the upper regions of each pool (nearer the tailwater areas), and selectively inhabit tailwater areas for a considerable portion of the year (March–November). Therefore, we assume that ranges of the target species are limited significantly as to produce “local” populations of adult fish residing between any pair of dams. Tailwater areas associated with dams are a preferred habitat of the target species (and one of the parental species) for a considerable portion of the year (Young and Isely 2007, and personal observation). On the Ohio River, tailwater areas have been identified as an important habitat type and a 1993 survey conducted by the Ohio Division of Wildlife states that 81% of the HSB caught were caught in tailwater areas (Schell et al. 1996).

At each sampling location, we collected a three-fish composite. If a three-fish composite sample could not be collected in the tailwater area (within 400 m of the base of the dam), crews extended the sampling area downstream until the required three fish were collected. All harvested fish were within 75% of the total length (TL) of the largest fish captured as part of this project. Using scales, we determined the age in years of the oldest individual in each composite. It was assumed that the oldest fish in each composite experienced the greatest exposure to ambient Hg concentrations and represented the highest potential for bioaccumulation. Using the age of the oldest fish in the composite, we were then able to relate fish tissue concentration data to water concentration data to characterize the exposure range.

Sample Collection

Water

Water samples for total recoverable Hg analysis were collected on a bimonthly basis between January 2003 and May 2009 following on-site procedures prescribed by USEPA Method 1638. This entailed using a 3.79-L high-density polyethylene (HDPE) bottle attached to a rope and nonmetal counterweight. The bottle was lowered to the water, allowed to sink to a depth of 0.6 m below the surface, and raised for processing. Processing involved using an ultraclean, gloved-hand, metal-free sampling protocol to transfer the sample from the sampling device to a 125-mL bottle that had been precleaned in a manner appropriate for the intended analysis. Sample bottles were placed in polyethylene bags, temporarily stored on ice, and held at 0–4°C until shipped to the lab for analysis.

Fish

Fish were collected using standardized boat electrofishing procedures (Emery et al. 2003). Each fish collected for fish tissue analysis was weighed (kg) and measured for TL (cm). Five to ten scales per fish were also taken just anterior to the dorsal fin, on the lateral body wall midway between the dorsal crest and the lateral line (Schmitt et al. 1999) for aging purposes. A scale press was used to press each scale onto a clear cellulose acetate plastic slide and then the annuli of multiple scales per fish were counted under a back-lit dissecting microscope (10–16×). Three to five scales were examined for each fish by two experienced biologists. The maximum age (based on multiple scales) determined the age for each individual. Fish were euthanized in the field by a swift cervical/cranial blow and descaled, and a single, left-side, skin-on fillet (with belly flap attached) was removed for fish tissue analyses. This filleting procedure reflects the methods used by the local consumers who would typically target this species as a food source. When in the field, a sufficient number of clean knives were possessed such that a new, clean knife could be used to fillet all fish unique to each composite. All knives were cleaned by washing with deionized water and detergent and rinsed/washed with ethanol. At each site, three fish fillets were composited in aluminum foil, stored in a polyethylene bag, and placed on wet ice until samples could be frozen. Samples were kept frozen until shipped to a contractual laboratory for analyses. All fish collected for this study were within 75% of the TL of the longest fish collected for the entirety of the study. This meets or exceeds composite TL consistencies cited in other recent literature (Stahl et al. 2009; USEPA 1993; USEPA 2009b). This was done to limit variability between samples due to the size of the fish contained in each composite, as numerous studies have shown a strong relationship between size and age of fish and Hg concentrations in muscle tissue (Burger et al. 2001; Cizdziel et al. 2003; Gilmour and Riedel 2000; Grieb et al. 1990; Gutenmann et al. 1992; Kehrig et al. 2009; Mason et al. 2006; Piraino and Taylor 2009; Qian et al. 2001; Sorensen et al. 1990; Walters et al. 2010). Length-normalized values would need to be generated before comparison between composites if the prescribed 75% of the TL was not maintained (Kehrig et al. 2009; Scudder et al. 2009). By maintaining such a high level of consistency among samples, we have reduced (not eliminated) sample bias based on length of fish contained in the composite.

Mercury Analysis

Water

Total recoverable Hg in water was analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) following USEPA Method 1631. This method specifies procedures for analysis, QA/QC requirements, and reporting limits, all of which were met throughout the entirety of this project. Field blanks were collected with each sample (100%). Field duplicate samples were collected for 10% of all samples collected annually. The median relative percent difference (RPD) of field duplicates was 23%. The rate of detections in field blanks was 3%, yielding a median blank result well below the 1.5-ng/L reporting limit. The median field blank concentration above the reporting limit was 5.9 ng/L. Furthermore, variability among sample results was minimized by using the same laboratory for all analyses. Hg concentration values below the reporting limit (1.5 ng/L) were eliminated from statistical analyses. We feel that this is a conservative approach in the calculation of BAFs, as including zeros or values reported as one-half the reporting limit would add uncertainty and could artificially inflate the BAF values.

Fish

Total recoverable Hg concentrations in fish tissue were determined using cold vapor atomic fluorescence (CVAF) per EPA Method 7471 with method detection limits of 0.0014 mg/kg wet weight. Instrumentation was routinely calibrated using standards containing 0.0, 0.2, 1.0, 2.5, 5.0, and 10.0 ppb Hg. All samples were run in batches that included a standard calibration curve, blanks, and spiked specimens. Accepted recoveries for spikes ranged from 70% to 110%; no batches were outside these limits (actual range: 82–93%). Analytical duplicates were performed for each batch of samples and the RPDs were all less than the maximum of 10% (actual range: 3–5%). The accepted recoveries for laboratory control duplicates were 75–110% and no batches were outside these limits (actual range: 81–99%).

Water/Fish Relationships

The USEPA uses BAFs to express the ratio of the concentration of a chemical in the tissue of an organism (ng/kg wet weight) to that chemical's concentration in water (ng/L; USEPA 2009b). The BAF (L/kg) is a ratio that represents the site-specific rate of bioaccumulation of a single parameter within a particular system. BAFs for total recoverable Hg were calculated for each location using the geometric mean of Hg water concentrations and Hg concentrations found in fish tissue.

Statistical Analysis

Data analysis followed standard statistical procedures and were performed with STATISTICA v9.0 (StatSoft, Inc. and 2009). Transformation of the data was not necessary, as we utilized Spearman rank correlations to examine basic relationships among Hg concentrations, fish variables, and spatial correlates. The level of significance was designated as <0.05, but values between 0.05 and 0.10 were reported and discussed as being important.

Results

Water

The total number of water column grab samples taken at any one of the sampling locations and used in this analysis ranged from 25 to 37 and was determined by the maximum age of the fish in the composite at any location (Table 1). Of the 399 water samples collected, 300 produced detections (Table 1). The percentage of detections recorded at any one site ranged from 62.2% to 86.1% of all sampling events. Values recorded ranged from nondetect (1.5 ng/L) to a maximum of 46.1 ng/L, with a geometric mean value of 5.06 ng/L for all values recorded above the detection limit (Table 1). Fifty-two samples exceeded the ORSANCO AWQC for human health protection (12 ng/L). This equates to 13.0% of the total samples taken or 17.3% of the total detections observed. Spatially, the geometric mean values of Hg concentrations in water were positively correlated with drainage area ($R = 0.839$, $p < 0.001$; Table 2 and Fig. 2a).

Fish

The TLs of individuals captured as part of the 12 composite samples collected were between 50.5 and 67.0 cm. The ages of all specimens collected ranged from 2 to 6 years. Hg was detected in 100% of the samples submitted for analysis and tissue concentrations ranged from 0.2 to 0.4 mg/kg wet weight with a geometric mean of 0.28 mg/kg (Table 1). Five of the 12 samples collected (41.6%) were higher than the USEPA criterion for human health protection value of 0.3 mg/kg in fish tissue. As expected, Hg concentrations in muscle tissue exhibited positive Spearman rank values with both TL ($R = 0.380$, $p < 0.22$; Table 2) and age ($R = 0.476$, $p < 0.12$; Table 2). Hg concentrations in muscle tissue were strongly correlated with average weight ($R = 0.650$, $p < 0.02$; Table 2 and Fig. 3) of the composited fish in the sample as well as the concentration of Hg found in the water ($R = 0.710$; $p < 0.01$; Table 2 and Fig. 4). Concentrations in fish tissue also significantly increased with increasing drainage area ($R = 0.692$, $p < 0.013$; Fig. 2b). This relationship was not confounded by fish ages, weights, and TLs, as these factors were not correlated with increasing drainage area (Table 2).

Table 1 Summarized data at each of the 12 locations from which Hg concentrations in water and fish tissue was gathered

	Aqueous mercury								Mercury in fish					BAF
Site name (Tailwaters)	# Hg samples used[a]	# Hg detections	Max Hg (ng/L)	Geomean Hg (ng/L)	Geometric std. dev.	AWQC violations[b]	% violations of samples	% violations of detections	2009 Collection date	Avg TL (cm)	Avg Wt (kg)	Ages of fish in composite (years)	Hg result (mg/kg)	BAF L/kg)
Pike Island	37	23	15.11	3.89	0.64	1	2.70	4.30	14-Apr	61.4	3.5	3,4,6	0.23	59,110
Willow Island	37	27	27.09	4.43	0.69	2	5.40	7.40	9-Jun	59.8	2.5	3,3,6	0.28	63,253
Belleville	26	20	10.82	3.33	0.53	0	0.00	0.00	11-Jun	60.3	2.7	3,4,4	0.28	84,005
RC Byrd	25	20	12.95	2.83	0.48	1	4.00	5.00	15-Apr	55.1	2.3	2,3,4	0.2	70,591
Greenup	30	23	34.3	3.99	0.93	3	10.00	13.00	16-Apr	57	2.8	4,4,5	0.26	65,191
Meldahl	35	24	21.5	4.1	0.75	2	5.70	8.30	2-Apr	61	3.5	4,4,6	0.29	70,693
Markland	31	23	46.1	4.71	0.82	3	9.70	13.00	17-Apr	56.8	2.5	4,4,5	0.2	42,465
McAlpine	37	28	28.5	5.32	0.73	4	10.80	14.30	23-Apr	61.9	3.8	5,5,6	0.4	75,192
Cannelton	37	27	29.7	7.08	0.9	9	24.30	33.30	22-Apr	56.5	2.6	4,5,6	0.33	46,609
Newburgh	36	31	39.6	7.82	0.93	11	30.60	35.50	23-Apr	58.6	3.2	3,4,6	0.33	42,194
JT Meyers	37	31	43.76	7.25	0.94	10	27.00	32.30	21-Apr	57.8	2.9	3,4,6	0.3	41,384
Smithland	31	23	33.87	6.78	0.89	6	19.40	26.10	20-Apr	59.9	3.9	3,4,5	0.34	50,127
Summary	399	300	46.1	5.06	0.84	52	13.00	17.30					0.28	57,590

[a] The number of aqueous Hg samples used was dependent on the maximum age of composited individuals at a location

[b] Exceedance of ORSANCO's AWQC of 12.0 ng/L

Table 2 *R*-values of Spearman rank correlations

	Max. age	Total length	Weight	Drainage area	Hg in water
Hg in water	0.572 (0.052)	−0.077 (0.812)	0.308 (0.331)	0.839 (0.001)	–
Hg in tissue	0.475 (0.118)	0.380 (0.224)	0.650 (0.022)	0.692 (0.013)	0.710 (0.010)
BAF	−0.335 (0.287)	0.441 (0.152)	0.049 (0.880)	−0.552 (0.063)	–
Drainage area	0.177 (0.581)	−0.175 (0.587)	0.357 (0.255)	–	0.839 (0.001)

Note: *p*-Values are in parentheses. Alpha <0.05 indicates a significant relationship; $p < 0.10$ is noted as a weak relationship

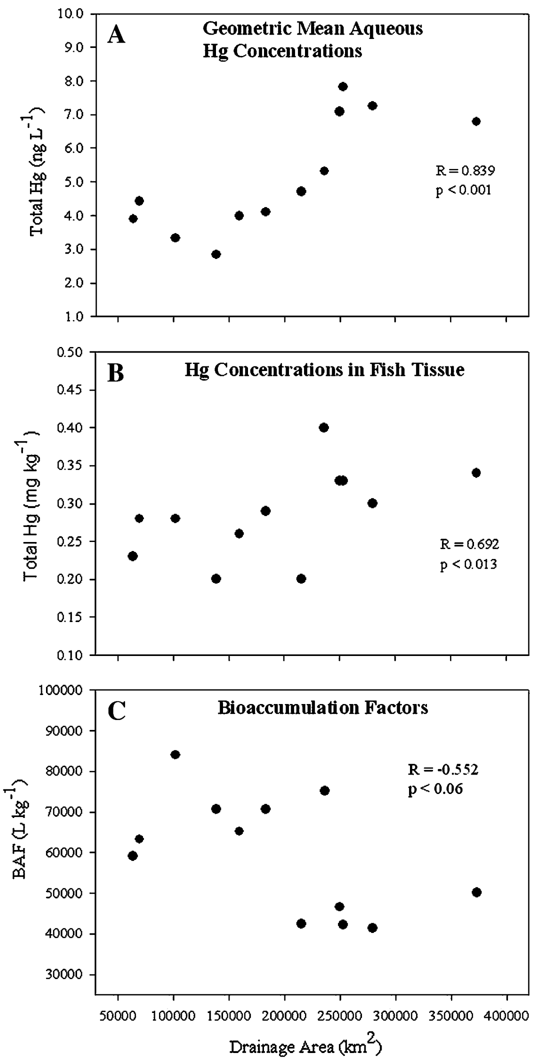

Fig. 2 Plot of the **a** geometric mean of Hg concentrations in water, **b** Hg in HSB fillet composites, and **c** bioaccumulation factors as a function of drainage area

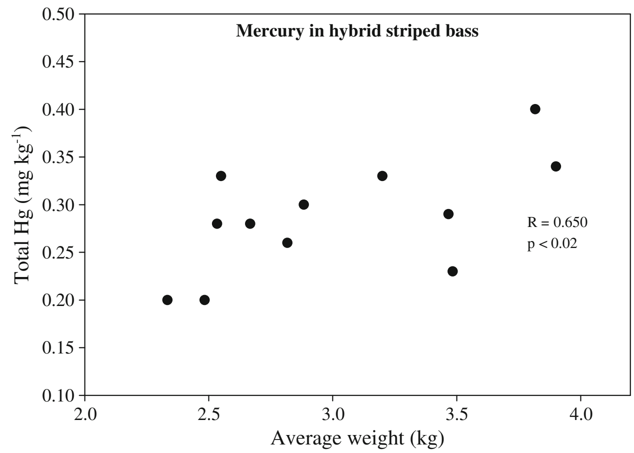

Fig. 3 Hg concentration in HSB fillets as a function of the average weight of the three fish in each composite sample

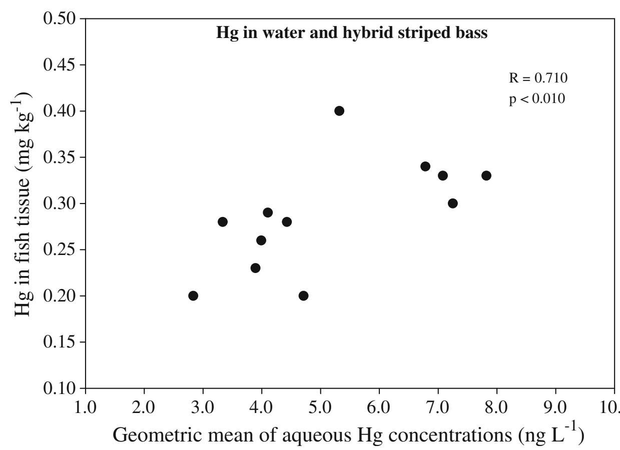

Fig. 4 Relationship between Hg concentrations in HSB fillet composites and the geometric mean of aqueous HG concentrations at each of the 12 locations

Water/Fish Relationships

Mercury concentrations in fish tissue are strongly correlated with concentrations found in the water where the fish were collected. BAF values ranged from 41,384 to 84,005 L/kg tissue, with a geometric mean of 57,590 L/kg tissue (Table 1). BAF values displayed a weak, negative correlation with increasing drainage area ($R = -0.552$, $p < 0.06$; Table 2 and Fig. 2c).

Discussion

Water

Surface freshwaters lacking known sources of Hg contamination generally contain less than 5 ng/L of total Hg (Gilmour and Henry 1991). In this study, a maximum value of 46.1 ng/L and a geometric mean of 5.06 ng/L are within the range of values reported from a nationwide study conducted by the USGS in 2009 (0.27–446 ng/L; median: 2.09 ng/L; Scudder et al. 2009) and a similar study by that same agency in 1997 (range 0.27–1106.7 ng/L; median: 2.28; Krabbenhoft et al. 1999). Although the observed values in this study fall within the ranges reported by two nationwide studies, the maximum does not approach or exceed the maximum values reported in either study. We also found that ORSANCO's AWQC (12 ng/L) for the Ohio River are frequently violated. The existing AWQC is intended to reflect EPA's national water quality criterion for MeHg, which is expressed as a fish tissue concentration of 0.3 mg/kg of wet-weight fish tissue. Thus, we surmised that if violations of the water quality criteria were observed, the fish criteria might also be violated.

Atmospheric deposition is the primary source of Hg in the Ohio River Valley and has been identified as one of the top three depositional areas in the United States (USEPA 1997). If atmospheric deposition of Hg were the only source of Hg to the Ohio River basin and occurred with geospatial uniformity, one might assume that water concentrations along the length of the river would remain constant or nearly so, as loadings would increase proportional to discharge volume. The positive relationship between Hg concentrations in water and increasing drainage area is evidence of (1) an uneven distribution of Hg deposition rates within the Ohio River basin, (2) the influence of point source contributions of Hg, (3) the influence of one of many factors not measured or considered as part of this study such as basin land-use characteristics, in-stream chemistry, and so forth, or (4) any combination of the above. Additional studies might be needed to better understand the spatial patterns observed in this study.

Fish

Our Hg detection frequency and range is consistent with other studies that have reported results for striped bass, a parent species (Cizdziel et al. 2003; Mason et al. 2006; Piraino and Taylor 2009) or other TL_4 species (Burger et al. 2001; Scudder et al. 2009; Stahl et al. 2009; Walters et al. 2010). However, direct and detailed comparisons to other studies are complicated by several factors. Hg concentrations in fish can vary among species of the same trophic status and are additionally influenced by the age, weight, and the length of the fish used for study (Burger et al. 2001; Cizdziel et al. 2003; Gilmour and Riedel 2000; Grieb et al. 1990; Gutenmann et al. 1992; Kehrig et al. 2009; Mason et al. 2006; Piraino and Taylor 2009; Qian et al. 2001; Sorensen et al. 1990; Walters et al. 2010). Hg concentrations in striped bass have been previously reported, whereas white bass and HSB concentrations are rare or absent altogether from the available literature. In order to place this study into context, it was necessary to proceed with comparing our results to a few other relevant findings. However, we were overly critical when attempting to compare the results of this study to those published by others and took steps to highlight any and all potential discrepancies between study designs, including differences in species, size, weight, and so forth. We would caution future studies to do the same, unless all these factors are measured, understood, and taken into consideration.

Many state agencies and published reports, including ORSANCO (2006) measure total Hg in fish tissue, make the assumption that all or most of the Hg measured is MeHg, compare observed total Hg values against the USEPA fish tissue criterion (0.3 mg/kg), and, subsequently, report frequent exceedances of that criterion in the Ohio River and other aquatic systems (Brumbaugh et al. 2001; Piraino and Taylor 2009; Rypel et al. 2008; Scudder et al. 2009; Stahl et al. 2009; Walters et al. 2010). Piraino and Taylor (2009) found that 75% of legally harvested size (>70.2 cm) and 12% of all striped bass sampled in Narragansett Bay (Delaware, USA) had Hg levels exceeding the USEPA regulatory threshold. However, it is again difficult to directly compare our findings (41.6% of samples higher than the USEPA criterion) to those of Piraino and Taylor's (2009), as none of our fish were greater than 67.0 cm in length and their study also included fish as small as 26.2 cm (which is almost one-half the TL of our smallest fish). The relatively high percentage of values observed in HSB that were greater than the criterion is contrary to recent reports from the Ohio River Basin of Hg concentrations in another TL_4 fish, the largemouth bass (*Micropterus salmoides*; Walters et al. 2010). Overall, the high percentage of our samples that were higher than the USEPA fish tissue criterion is not surprising given that the AWQC that were established to protect for this criterion are often violated as well (See Table 1).

This study reports a significant relationship between the average weight (in composite) and the Hg concentrations in tissue and positive Spearman rank values with age and TL. This was expected, as numerous other studies report length, weight, and/or age as significant predictors of Hg concentration in muscle tissue (Burger et al. 2001; Cizdziel et al. 2003; Gilmour and Riedel 2000; Grieb et al. 1990; Gutenmann et al. 1992; Kehrig et al. 2009; Mason et al.

2006; Piraino and Taylor 2009; Qian et al. 2001; Sorensen et al. 1990; Walters et al. 2010). Our results provide evidence that even when the EPA guidelines are followed, variability (and uncertainty) can be introduced due to demonstrated relationships between contaminant levels in composite tissue samples and the average fish age, weight, length, and so forth of the fish within each composite. We also observed a positive relationship between concentrations of Hg in fish tissue and increasing size of the drainage area at each location sampled. However, this spatial pattern was expected and is explained by the relationship between water and tissue concentrations.

Fish/Water Relationship

The concentration of Hg found in fish tissue is a function of (1) the concentration of Hg available in the surrounding water, (2) the rate at which the fish bioaccumulates Hg, and (3) the duration of exposure. An increase in either exposure period or concentration in the water will result in higher values in fish tissue. Length and weight of the fish are simply another way of expressing age or length of exposure. Therefore, it is no surprise that TL, weight, and age of the fish from our study are related (significantly or by trends) to the concentration of Hg found in muscle tissue.

The USEPA uses BAFs to express rates of bioaccumulation. Most previous studies focus on BAFs calculated for MeHg (Brumbaugh et al. 2001; Kuwabra et al. 2007; Scudder et al. 2009); however, they do so by measuring total Hg in tissue, assuming all or most to be MeHg and measuring MeHg in water to express ratios. We did not directly measure MeHg concentrations in the water column or fish tissue, and supporting literature is not available that would allow us to accurately estimate the fraction of Hg occurring as MeHg in the Ohio River. Therefore, it is not possible to make accurate comparisons between site-specific BAFs developed in this study and the USEPA's national BAFs, which are associated with MeHg (USEPA 2001) or to BAFs reported by others (Brumbaugh et al. 2001; Kuwabra et al. 2007; Scudder et al. 2009). Instead, we measured and developed BAFs for total recoverable Hg values. We felt that a total recoverable Hg BAF would provide an important point of reference given that, by regulation [40 CFR 122.45(c)], NPDES permit limits must be expressed as such.

Both concentrations of total Hg in the water column and concentrations of Hg in fish tissue show a positive relationship with increasing drainage area. However, they do not increase proportional to one another. This is reflected in the calculated BAFs, which decrease with increasing drainage area. This relationship was not expected and we further explored the relationship between BAFs and fish size and age; determining that none of these factors were correlated with the BAFs (Table 2). Based on the assumption that a significant portion (if not all) of the Hg found in fish tissue is MeHg, the fraction of total Hg occurring as MeHg in water might be greater in the upper Ohio River than in the lower and is responsible for the observed BAF spatial pattern. The fraction of total Hg occurring as MeHg in surface waters can vary widely and is dependent on a number of factors that affect the methylation efficiency of the ecosystem being examined.

Additional research is needed to better understand MeHg production dynamics in waters of the Ohio River basin and mainstem river. Suggestions for developing or improving future studies include the collection of MeHg data for both aqueous and tissue matrices, exploring bioaccumulation in other TL_4 species and species of lower trophic levels, expanding the spatial scope of such studies, and temporally reexamining these results in order to track long-term changes in Hg contamination. We are hopeful that this study will serve as a model for future field studies and generally will be a useful reference for those desiring to develop studies in support of site-specific BAF development as part of the AWQC process.

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References

ATSDR (Agency for Toxic Substances and Disease Registry) (2009) Toxicological profile for mercury. http://www.atsdr.cdc.gov/toxprofiles/tp46.html

Bloom NS (1992) On the chemical form of mercury in edible fish and marine invertebrate tissue. Can J Fish Aquat Sci 49:1010–1017

Brumbaugh WG, Krabbenhoft DP, Helsel DR, Wiener JG, Echols KR (2001) A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients: bioaccumulation in fish. US geological survey water resources investigations, USGS/BRD/BSR-2001-0009. US Geological Survey, Reston, VA

Burger J, Gaines KF, Boring CS, Stephens WL Jr, Snodgrass J, Gochfeld M (2001) Mercury and selenium in fish from the Savannah River: species, trophic level, and locational differences. Environ Res 87:108–118

Cizdziel J, Hinners T, Pollard J (2003) Distribution of mercury in the tissues of five species of freshwater fish from Lake Mead, USA. J Environ Monit 5:802–807

Clarkson TW (1990) Human health risks from methylmercury in fish. Environ Toxicol Chem 9:957–961

Driscoll CT, Han Y-J, Chen CY, Evers DC, Lambert KF, Holsen TM, Kamman NC, Munson RK (2007) Mercury contamination in forest and freshwater ecosystems in the Northeastern United States. Bioscience 57:17–28

Emery EB, Simon TP, McCormick FH, Angermeier PL, Deshon JE, Yoder CO, Sanders RE, Pearson WD, Hickman GD, Reash RJ, Thomas JA (2003) Development of a multimetric index for assessing the biological condition of the Ohio River. Trans Am Fish Soc 132:791–808

Gabriel MC, Kolka R, Wickman T, Nater E, Woodruff L (2009) Evaluating the spatial variation of total mercury in young-of-year yellow perch (*Perca flavescens*), surface water and upland soil for watershed-lake systems within the southern Boreal Shield. Sci Total Environ 407:4117–4126

Gilmour CC, Henry EA (1991) Mercury methylation in aquatic systems affected by acid deposition. Environ Pollut 71:131–169

Gilmour CC, Riedel GS (2000) A survey of size-specific mercury concentrations in game fish from Maryland fresh and estuarine waters. Arch Environ Contam Toxicol 39:53–59

Grieb TM, Driscoll CT, Gloss SP, Schofield CL, Bowie GL, Porcella DB (1990) Factors affecting mercury accumulation in fish in the upper Michigan peninsula. Environ Toxicol Chem 9:919–930

Gutenmann WH, Ebel JG Jr, Kuntz HT, Yourstone KS, Lisk DJ (1992) Residues of p, p′-DDE and mercury in lake trout as a function of age. Arch Environ Contam Toxicol 22:452–455

Hammerschmidt CR, Fitzgerald WF (2006) Methylmercury in freshwater fish linked to atmospheric mercury deposition. Environ Sci Technol 40:7764–7770

Hurley JP, Benoit JM, Babiarz CL, Shafer MM, Andren AW, Sullivan JR, Hammond R, Webb DA (1995) Influences of watershed characteristics on mercury levels in Wisconsin rivers. Environ Sci Technol 29:1867–1875

Kehrig HA, Palermo EFA, Seixas TG, Santos HSB, Malm O, Akagi H (2009) Methyl and total mercury found in two man-made Amazonian reservoirs. J Brazil Chem Soc 20:1142–1152

Krabbenhoft DP, Wiener JG, Brumbaugh WG, Olson ML, DeWild JF, Sabin TJ (1999) A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients. In: Morganwalp DW, Buxton HT (eds) U.S. geological survey toxic substances hydrology program, proceedings of the technical meeting, Charleston, SC, 8–12 March 1999. Contamination of hydrologic systems and related ecosystems, vol 2. Water resources investigations report 99-4018B. US Geological Survey, Reston, VA, pp 147–160

Kuwabra JS, Aria Y, Topping BR, Pickering IJ, George GN (2007) Mercury speciation in piscivorous fish from mining-impacted reservoirs. Environ Sci Technol 41:2745–2749

Lepak JM, Shayler HA, Kraft CE, Knuth BA (2009) Mercury contamination in sport fish in the Northeastern United States: considerations for future data collection. Bioscience 59:174–181

Mason RP (2002) The bioaccumulation of mercury, methylmercury and other toxic elements into pelagic and benthic organisms. In: Newman MC, Robert MH, Hale RC (eds) Coastal and estuarine risk assessment. CRC/Lewis Publishers, Boca Raton, FL, pp 127–149

Mason RP, Heyes D, Sveinsdottir A (2006) Mercury concentrations in fish from tidal waters of the Chesapeake Bay. Arch Environ Contam Toxicol 51:425–437

Morel FMM, Kraepiel AML, Amyot M (1998) The chemical cycle and bioaccumulation of mercury. Annu Rev Ecol Syst 29:543–566

ORSANCO (Ohio River Valley Water Sanitation Commission) (2006) Biennial assessment of Ohio River water quality conditions. Technical Report. ORSANCO, Cincinnati, OH

Piraino MN, Taylor DL (2009) Bioaccumulation and trophic transfer of mercury in striped bass (*Morone saxatilis*) and tautog (*Tautoga onitis*) from the Narragansett Bay (Rhode Island, USA). Marine Environ Res 67:117–128

Qian SS, Warren-Hicks W, Keating J, Moore DRJ, Teed RS (2001) A predictive model of mercury fish tissue concentrations for the southeastern United States. Environ Sci Technol 35:941–947

Rypel AL, Arrington DA, Findlay RH (2008) Mercury in southeastern U.S. riverine fish populations linked to water body type. Environ Sci Technol 42:5118–5124

Schell SA, Bright DJ, Marshall JA, Greenlee MA (1996) Ohio River recreation use survey 1992–1993. Ohio Department of Natural Resources, Division of Wildlife, Final Report State Project F4DR03. Ohio Department of Natural Resources, Athens, OH

Schmitt CJ, Blazer VS, Dethloff GM, Tillitt DE, Gross TS, Bryant WL Jr, DeWeese LR, Smith SB, Goede RW, Parish TM, Kubiak TJ (1999) Biomonitoring of environmental status and trends (BEST) program: field procedures for assessing the exposure of fish to environmental contaminants. US Geological Survey, Biological Resources Division, Columbia, MO

Scudder BC, Chasar LC, Wentz DA, Bauch NJ, Brigham ME, Moran PW, Krabbenhoft DP (2009) Mercury in fish, bed sediment, and water from streams across the United States, 1998–2005: US geological survey scientific investigations report 2009-5109

Sellers P, Kelly CA, Rudd JWM, Machutchon AR (1996) Photodegradation of methylmercury in lakes. Nature 380:694–697

Sorensen JA, Glass GE, Schmidt KW, Huber JK, Rapp GR Jr (1990) Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota Lakes. Environ Sci Technol 24:1716–1727

Stahl LL, Snyder BD, Olsen AR, Pitt JL (2009) Contaminants in fish tissue from US lakes and reservoirs: a national probabilistic study. Environ Monit Assess 150:3–19

StatSoft, Inc (2009) STATISTICA (data analysis software system), v.9.0. Available from www.statsoft.com

USEPA (1993) Guidance for assessing chemical contaminant data for use in fish advisories: fish sampling and analysis, vol 1. EPA 823-R-93-002. USEPA, Washington, DC

USEPA (1997) Mercury study report to congress. EPA-452/R-97-003. USEPA, Washington, DC

USEPA (2001) Water quality criterion for the protection of human health: methylmercury. EPA-823-R-01-001. USEPA, Washington, DC

USEPA (2009a) National listing of fish advisories. EPA-823-F-09-007. USEPA, Washington, DC

USEPA (2009b) Methodology for deriving ambient water quality criteria for the protection of human health (2000): technical support document. Development of site-specific bioaccumulation factors, vol 3. EPA-822-R-09-008. USEPA,Washington, DC

Vallazza JM, Deller JW, Lynch WE Jr, Johnson DL (1994) Seasonal behavior, movements, and habitat preferences of hybrid striped bass and sauger in the Ohio River. Ohio Department of Natural Resources, Division of Wildlife Final Report F-69-P. Ohio Department of Natural Resources, Columbus, OH

Walters DM, Blocksom KA, Lazorchak JM, Jicha T, Angradi TR, Bolgrien D (2010) Mercury contamination in fish in mid-continent great rivers of the United States: importance of species traits and environmental factors. Environ Sci Technol 44:2947–2953

White D, Johnston K, Miller M (2005) Ohio River Basin. In: Benke AC, Cushing CE (eds) Rivers of North America. Elsevier Academic, Burlington, MA, pp 375–424

Wiener JG, Knights BC, Sandheinrich MB, Jeremiason JD, Brigham ME, Engstrom DR, Woodruff LG, Cannon WF, Balogh SJ (2006) Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. Environ Sci Technol 40:6261–6268

Young SP, Isely IJ (2007) Diel behavior of adult striped bass using tailwater habitat as summer refuge. Trans Am Fish Soc 136:1104–1112