Mercury Contamination Across a Riverine Foodweb

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Abstract

Lakes and reservoirs are frequently monitored by researchers for elevated mercury concentrations in sportfish. Rivers and streams, especially those of smaller orders, are less frequently monitored for mercury contamination. Mercury contamination in the environment comes predominantly from anthropogenic sources like artisanal gold mining and the burning of coal. We address this gap by surveying mercury levels in a stream community in the Kiamichi River in southeastern Oklahoma sampling fish, aquatic insects, and freshwater mussels at ten sites in the river. We found elevated levels of mercury across taxa within the river including large individuals of sportfish populations having concentrations (2986 ±1053 ng/g) above the Environmental Protection Agency (EPA) limit. Furthermore, we observed high concentrations in darters and logperch (1133 ±464 ng/g), non-sportfish species found predominantly in rivers and streams. Our results indicate that mercury contamination can reach elevated concentrations in rivers and streams posing risks to both humans and wildlife.

Introduction

Mercury is an environmental contaminant negatively affecting the health of both humans and wildlife (Scheulhammer, Meyer, Sandheinrich, & Murray, 2007). Mercury released into the atmosphere from human activities, predominantly coal fired power plants and artisanal gold mining, makes its way into aquatic environments where it can be converted into toxic methyl mercury (MeHg) by anaerobic bacteria and subsequently biomagnify in aquatic food webs (Selin, 2009). Because of these non-point, atmospheric sources of mercury, we now face a global mercury crisis. The southeastern US, including parts of east Texas and southeastern Oklahoma, contains numerous mercury contamination hotspots (Ray W. Drenner et al., 2013; R. W. Drenner, Chumchal, Wente, McGuire, & Drenner, 2011).

Many mercury monitoring programs focus on sportfish, such as bass or catfish, in lakes and reservoirs. Thus, consumption advisories are issued more often for these waterbodies compared to rivers and streams, which can also have levels of mercury above human health risk thresholds (Balogh, Huang, Offerman, Meyer, & Johnson, 2002; Bergeron, Husak, Unrine, Romanek, & Hopkins, 2007; Tsui, Finlay, & Nater, 2009). For example in the southeastern US, all 36 mercury advisories in the state of Oklahoma are for lakes and reservoirs (OK DEQ, 2016) and only two out of 14 advisories in the state of Texas are for rivers or streams (TX Parks and Wildlife, 2017). Given the prevalence of elevated mercury in fish in southeastern US reservoirs (Drenner et al., 2013) it is likely that a significant number of streams and rivers in this region also have elevated concentrations.

Rivers and streams are also home to many endemic non-sport fish, such as darters and minnows. These fish are an important part of many stream and riparian food webs, serving as food sources for both aquatic and terrestrial predators (Schlosser, 1987; Thomas & Taylor, 2013). Because these fish are rarely consumed by humans they are infrequently included in mercury surveys (but see Riva-Murray et al., 2011). However, because these fish are an important part of the food web, elevated body-burden of mercury in these populations will be transferred to higher trophic levels, including sportfish that may be consumed by humans.

To investigate the patterns and extent of mercury contamination in small river ecosystems, we sampled food web compartments in a southeastern Oklahoma river located in a predicted mercury contamination hotspot. Our sampling focused on macroinvertebrates, non-sport fish and sport fish. We asked 1) Does the sportfish body burden of MeHg exceed toxic thresholds for human health? and 2) Do macroinvertebrates and other non-sportfish species have elevated and/or dangerous concentrations of mercury?

Methods

Our study site was a 5^{th}-order tributary of the Red River, the Kiamichi River in southeastern Oklahoma. The Kiamichi River drains a largely forested watershed of 4,500 km^2, and is influenced by both a mainstem impoundment (Hugo Lake) and a tributary impoundment (Sardis Lake). Both lakes have mercury consumption advisories issued by the Oklahoma Department of Environmental Quality for multiple fish species (although it should be noted that the minimum Oklahoma advisory limit of 500 ng/g is higher than the U.S. federal advisory (Environmental Protection Agency) limit of 300 ng/g) OK DEQ, 2016). We sampled ten sites along the Kiamichi River in summer of 2013. Each site was a 100-m long river reach, and sites were separated by at least 500 m, although most sites were separated by a kilometer or more. Five of the sites contained dense assemblages of freshwater mussels (Bivalvia: Unionidae), a keystone group of consumers known to influence ecosystem function in the river (Allen, Vaughn, Kelly, Cooper, & Engel, 2012; Atkinson & Vaughn, 2015; Vaughn & Hakenkamp, 2001). Additionally, four of the sites were upstream of the outflow of Sardis Lake, which provides roughly 25% of the downstream flows where the remaining six sites were located (Figure 1) (Vaughn, Atkinson, & Julian, 2015). We sampled fish communities, macroinvertebrate communities, and a suite of abiotic parameters at each site.

2.1 Abiotic Sampling

We divided each site into five evenly-spaced transects (Figure 2). To ensure that sites represented similar habitat, a number of abiotic parameters were sampled. Current velocity (Hach FH950.0, Loveland, CO, USA) and substrate heterogeneity were measured at all five transects. Dissolved oxygen, temperature, pH, and conductivity were measured at the downstream, mid-point, and upstream transects at the left bank, river center, and right bank positions. Dissolved oxygen and temperature were measured using a Hach meter (Hach, HQ36d, Loveland, CO, USA) and pH and conductivity were measured using a PCSTestr Multi-Parameter (Oakton Instruments, PCSTestr 35 model WD-35425-10, Vernon Hills, IL, USA). We conducted pebble counts at every transect and measured length and height of 20 pebbles per transect for a total of 100 at each site (Kondolf, Lisle, & W.G.M., 2003).

2.2 Macroinvertebrate Sampling

Macroinvertebrates were collected with a Surber sampler at five randomly selected locations at each site. Water depth and sampling time (effort) were recorded for each sample and all substrate within the sampling area was thoroughly scoured to a sediment depth of 5 cm. The contents of each sample were preserved in 80% ethanol and macroinvertebrates were sorted and identified to family in the laboratory.

At sites with mussel beds, mussels were sampled with 10 haphazardly placed 0.25 m^2 quadrats following Vaughn et al. 1997 (Vaughn, Taylor, & Eberhard, 1997). Quadrats were excavated to a depth of 15 cm. Mussels were removed to shore, identified to species, and measured for length, height, and width of shell. Ten randomly selected individuals of the 2-3 most dominant species at each site were sacrificed and preserved in 80% ethanol for subsequent mercury analyses and all other individuals were returned to the river alive.

2.3 Fish Sampling

Fish were collected by electrofishing. We used a backpack electroshocker and moved from downstream to upstream going from bank-to-bank in a zig-zag pattern (Smith-Root, Inc. Model 12-B, Vancouver, WA, USA) using a pulsed direct current. Captured fish were kept in 20 liter buckets until the entire site had been sampled. Immediately after electroshocking, all fish were euthanized in MS222 and preserved in 80% ethanol for later identification to family and subsequent mercury analyses.

2.4 Mercury Analyses

Mercury analyses were conducted on a direct mercury analyzer (Milestone DMA-80, Sorisole (BG), Italy). Macroinvertebrates were run as whole body, composite samples by taxa. Mussel whole bodies were homogenized into a fine powder using a mortar and pestle and a Wig-L-Bug (Fisher Scientific, Waltham, MA, USA). A fillet was removed from fish larger than 8 cm, while for smaller fish the head and digestive tract were removed and the remainder of the body was dried and homogenized into a fine powder for analyses.

2.5 Statistical Analyses

All statistical tests were conducted using IBM SPSS Statistics Version 19. Mean total mercury concentrations for all taxa and invertebrate families were compared using a one-way ANOVA with a Tukey post-hoc test. Differences in mean mercury concentration above and below Sardis Lake were examined with a t-test. All tests used a significance threshold of $p \leq 0.05$.

Results And Discussion

Physicochemical and geomorphological parameters were similar among sites (Table S1). No pairwise comparison of the sites (mussel/non-mussel or above/below Sardis) had significantly different mean values of these parameters, except for depth which was slightly greater at mussel than non-mussel sites (Table S2). However, the 0.07 m mean difference in depth observed between sites is unlikely to be biologically meaningful.

Elevated mercury was found in macroinvertebrate consumers that comprise the base of the food web (Table 1). Elmidae (riffle beetle) and Plecoptera (stonefly, genus *Eccoptura)* larvae had low mercury concentrations relative to other groups sampled while Ephemeroptera (mayfly) and Trichoptera (caddisfly) larvae had relatively higher mercury concentrations (Figure 2). There were differences within the latter two groups as well. Ryacophilidae, a caddisfly family of mainly predators, had the highest overall mercury concentration. *Tortopus* (Polymitarcyidae), a genus of burrowing mayflies and *Stenoema* (Heptageniidae), a genus of grazing mayflies, also had higher concentrations than other groups sampled. While Polymytarcidae's close association with aquatic sediments, where mercury is methylated, might explain the higher concentrations in these larvae, it is less clear why Heptageniidae were also elevated (Table S3).

In addition to serving as a food source for aquatic predators, larval forms of aquatic insects complete their lifecycle by emerging from aquatic ecosystems into terrestrial adult forms. When these emergent insects leave their aquatic homes they transport the mercury in their bodies from aquatic (Gerrard & St Louis, 2001; Menzie, 1980; Raikow, Walters, Fritz, & Mills, 2011; Tweedy, Drenner, Chumchal, & Kennedy, 2013; Walters, Fritz, & Otter, 2008) to terrestrial food webs (Speir et al., 2014). Larval insects with a terrestrial adult form in the Kiamichi River ranged from approximately 30-300 ng/g total mercury. The same concentrations in spiders were found to pose a health risk to young songbirds in another study (Gann, Powell, Chumchal, & Drenner, 2015).

We found elevated mercury concentrations in all fish species sampled. At the base of the food web, stoneroller minnows (*Campostoma spadiceum*) had the lowest mercury concentrations of the fishes but were still higher than mussels. Though largely herbivorous, stoneroller minnows also consume invertebrates and detritus (Evans-White, Dodds, Gray, & Fritz, 2001), which could account for their elevated mercury concentration relative to mussels, another primary consumer (Figure 4).

We also observed surprisingly high mercury concentrations (Table 2) in darters (*Percina maculata, Percina copelandi, Percina caprodes, Etheostoma maculatum, Percina phoxocephala, Lepomis humilis, Etheostoma radiosum, Etheostoma nigrum, Etheostoma spectabile, Percina sciera,* and *Crystallaria asprella*), consistent with the only other study to have examined this group (Riva-Murray et al., 2011). The mercury concentrations of some darter individuals were as high as that of much larger piscivorous fish such as gar and bass, and they were comparable to or higher than centrarchids (Centrarchidae) and catfish (Ictaluridae) of a similar or larger size (Figure 4). The diet of darters (Percidae) is a possible explanation. A past study of the stomach contents of darters and sunfish stomach found benthic invertebrates, including mayflies, made up a high proportion of darters' diets while sunfish consumed far fewer mayflies and consumed more terrestrial insects (W.J. Matthews, personal communication). In the Kiamichi River mayfly larvae had some of the highest mercury concentrations in our system (Figure 3). Preferential consumption of mercury-rich mayflies may contribute to elevated mercury concentrations in darters. Age may also play a role in this relationship. Many darters live up to 5 years (Paine, 1990), while sunfish in the 5 cm length range are young of year (Cargnelli & Gross, 1996). Many of the darters we sampled likely had several years to accumulate mercury in their bodies. While darters are not consumed by humans, they are an important prey item for aquatic predators such as bass (Schlosser, 1987). Additionally terrestrial predators, such as birds, are important top level predators in many aquatic systems (Steinmetz, Kohler, & Soluk, 2003) and are likely consuming darters as well. If darters are accumulating more mercury than other prey items and are preferred prey for top level predators, they may be disproportionately responsible for mercury body burden in top level predators. Because darters tend to only occur in rivers and streams (Miller & Robinson, 2004), this may be a unique factor that contributes to mercury contamination in rivers and not lakes.

At higher trophic levels, we found several fish taxa with individuals at or above the EPA mercury consumption advisory limit (Table 2). The majority of smallmouth bass over 10 cm in total length were over the EPA consumption advisory limit as were some sunfish and catfish. These results likely represent a conservative estimate of the extent of mercury contamination in the river. We were only able to electroshock wadeable portions of the river. This likely biased our samples to smaller fish. For instance, the catfish sampled were all under 20 cm standard length and the largest bass was only 22.6 cm. There are certainly larger fish in deeper habitats in the river. These larger fish likely have mercury concentrations higher than smaller fish. Thus, our results represent a conservative estimate of the upper limit of mercury concentrations in fish in the river. Our findings strongly suggest that the Kiamichi River, and others like it, represent a risk to human health with regards to the consumption of fish from the river (Table S4).

No significant difference in mercury concentrations was detected for fishes between sites with and without dense mussel assemblages. We were unable to test for differences in invertebrate taxa due to several sites where the biomass of invertebrates was too low for mercury analyses.

Our data show that a mid-size river in Oklahoma has mercury concentrations comparable to those found in large lakes and reservoirs. However, while these are monitored for human health threats, smaller order streams such as the Kiamichi River, and rivers rarely receive the same attention with regards to monitoring. The mercury concentrations found in fauna in the Kiamichi River is high enough to pose a health risk to both humans and wildlife, like the two impoundments on the river. While monitoring all smaller order streams seems unfeasible, further research exploring the relationship between reservoir mercury (which is monitored) and stream mercury could help in the issuing of more comprehensive and effective mercury advisories.

Declarations

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Conflicts of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Data Availability

The datasets generated and analyzed for this study can be found in the Open Science Framework project associated with this publication OSF.IO/39M25 (DOI 10.17605/OSF.IO/39M25).

Animal Ethics Approval

All applicable international, national, and/or institutional guidelines for the care and use of animals were followed under University of Oklahoma IACUC Institutional Tracking Number R13-002. This article does not contain any studies with human participants performed by any of the authors.

Consent to Participate

N/A

Consent to Publish

N/A

Plant Reproducibility

N/A

Clinical Trials Registration

N/A

Author Contribution

BT and BS conducted the field research in this study with CV advising. BT conducted the mercury analyses and statistics with CV advising. BT contributed the majority of the writing with BS and CV providing edits and revisions.

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Tables

Table 1 – Average Abundance, Biomass, and Mercury Concentrations for Kiamichi River Aquatic Insects

Taxa	Average Abundance	Average Relative Abundance	Average Biomass (g)	Average Relative Biomass	[Hg] (ng/g)
Coleoptera-Elmidae	51.1 (±66.5)	27.5% (±24.6)	0.0196 (±0.0247)	16.4% (±19.0)	68 (±19)
larvae	28.2 (±45.0)	13.6% (±14.3)	0.0053 (±0.0056)	11.6% (±16.4)	71 (±24)
adults	27.9 (±31.1)	13.7% (±17.1)	0.0143 (±0.0207)	4.8% (±4.2)	65 (±15)
Ephemeroptera	71.3 (±104.9)	32.0% (±22.8)	0.0552 (±0.0683)	38.9% (±21.4)	127 (±53)
Heptageniidae	29.7 (±32.5)	22.3% (±15.9)	0.0089 (±0.0062)	16.6% (±15.9)	146 (±89)
Polymytarcidae	4.7 (±7.3)	2.2% (±4.4)	0.0167 (±0.0287)	11.9% (±24.0)	136 (±59)
Isonychidae	36.9 (±73.9)	7.5% (±14.3)	0.0296 (±0.0595)	10.4% (±20.0)	77 (±37)
Trichoptera	83.5 (±143.4)	31.2% (±22.8)	0.0302 (±0.0488)	20.9% (±21.5)	119 (±72)
Hydropsychidae	67.0 (±111.6)	25.6% (±16.8)	0.0199 (±0.0294)	14.9% (±13.0)	109 (±60)
Ryacophilidae	16.5 (±32.9)	5.6% (±7.4)	0.0102 (±0.0199)	6.0% (±9.7)	148 (±41)
Plecoptera	21.0 (±43.7)	9.3% (±5.9)	0.0216 (±0.0308)	23.8% (±20.9)	74 (±39)

Table 2 – Average Abundance and Mercury Concentration for Kiamichi Fishes

Taxa	Average Abundance	Average Relative Abundance	[Hg] (ng/g)
Stoneroller	9.6 (±12.2)	12.6% (±14.4)	578 (±227)
Darter	24.4 (±14.1)	32.2% (±15.1)	-
Small (2-8cm)	20.5 (±15)	26.3% (±16.7)	884 (±184)
Large (>8cm)	3.9 (±2.2)	5.9% (±3.9)	1133 (±464)
Sunfish	37.4 (±14.5)	50.8% (±13.9)	-
Small (5-7cm)	18.3 (±7.3)	24.4% (±7.7)	526 (±88.4)
Medium (7-10cm)	15.1 (±7.7)	20.6% (±9.1)	779 (±270)
Large (>10cm)	4 (±2.8)	5.8% (±4.3)	959 (±354)
Catfish	0.5 (±1.3)	0.6% (±1.4)	985 (±439)
Gar	0.3 (±0.5)	0.4% (±0.7)	2669 (±1403)
Smallmouth Bass	2.2 (±1.7)	3.4% (±2.9)	-
Small (4-5cm)	0.5 (±0.7)	0.8% (±1.3)	810 (±158)
Large (>10cm)	1.3 (±1.3)	2% (±1.9)	2986 (±1053)

Figures

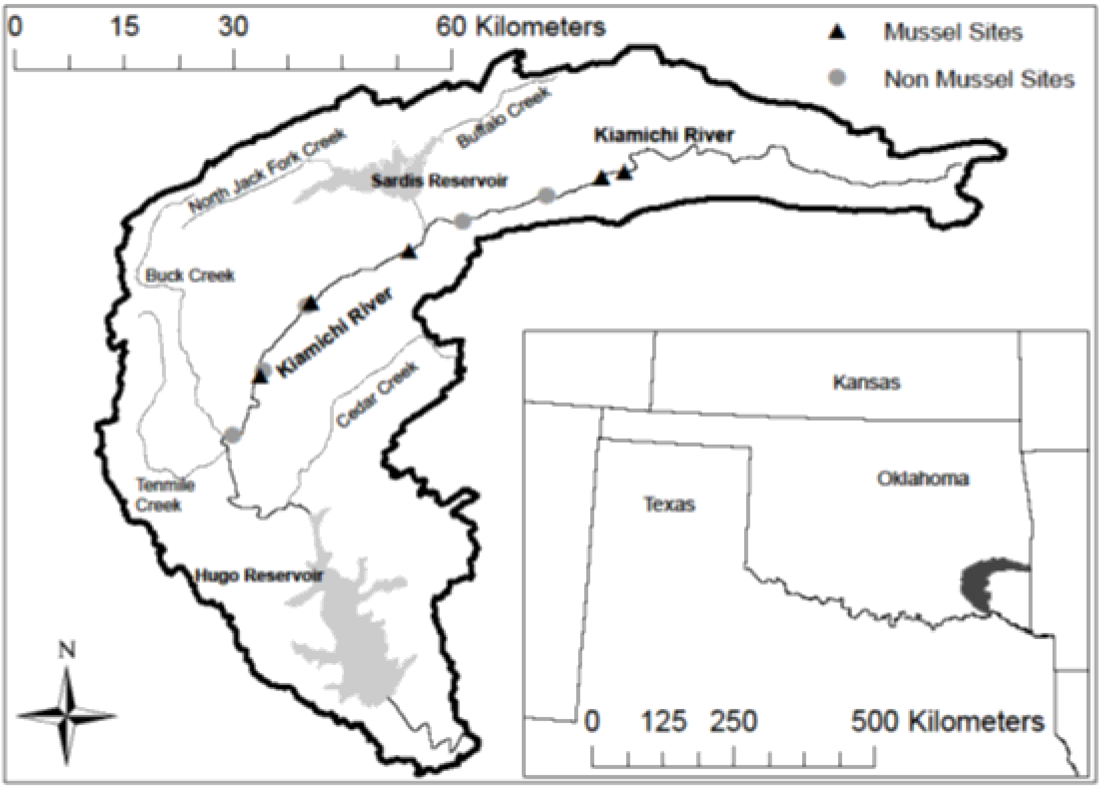

Figure 1

A map of the study site, the Kiamichi River in southeastern Oklahoma Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

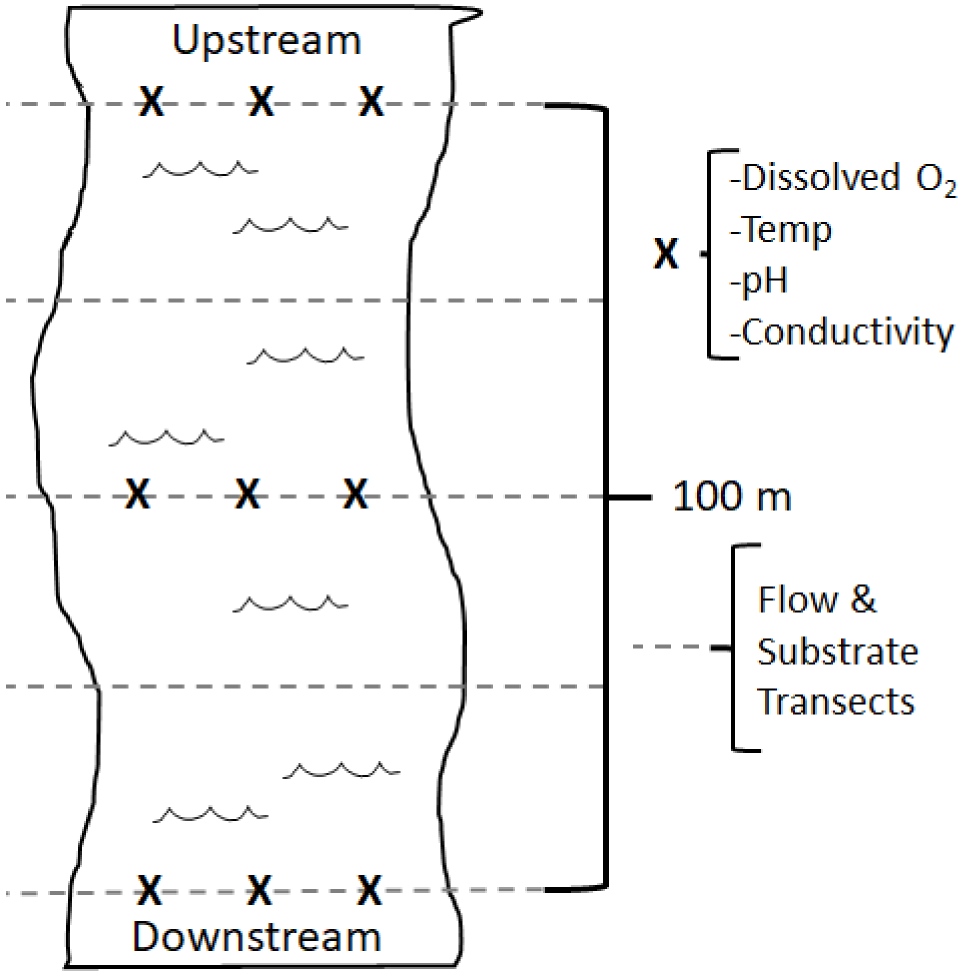

Figure 2

A schematic of the sampling transects in the study.

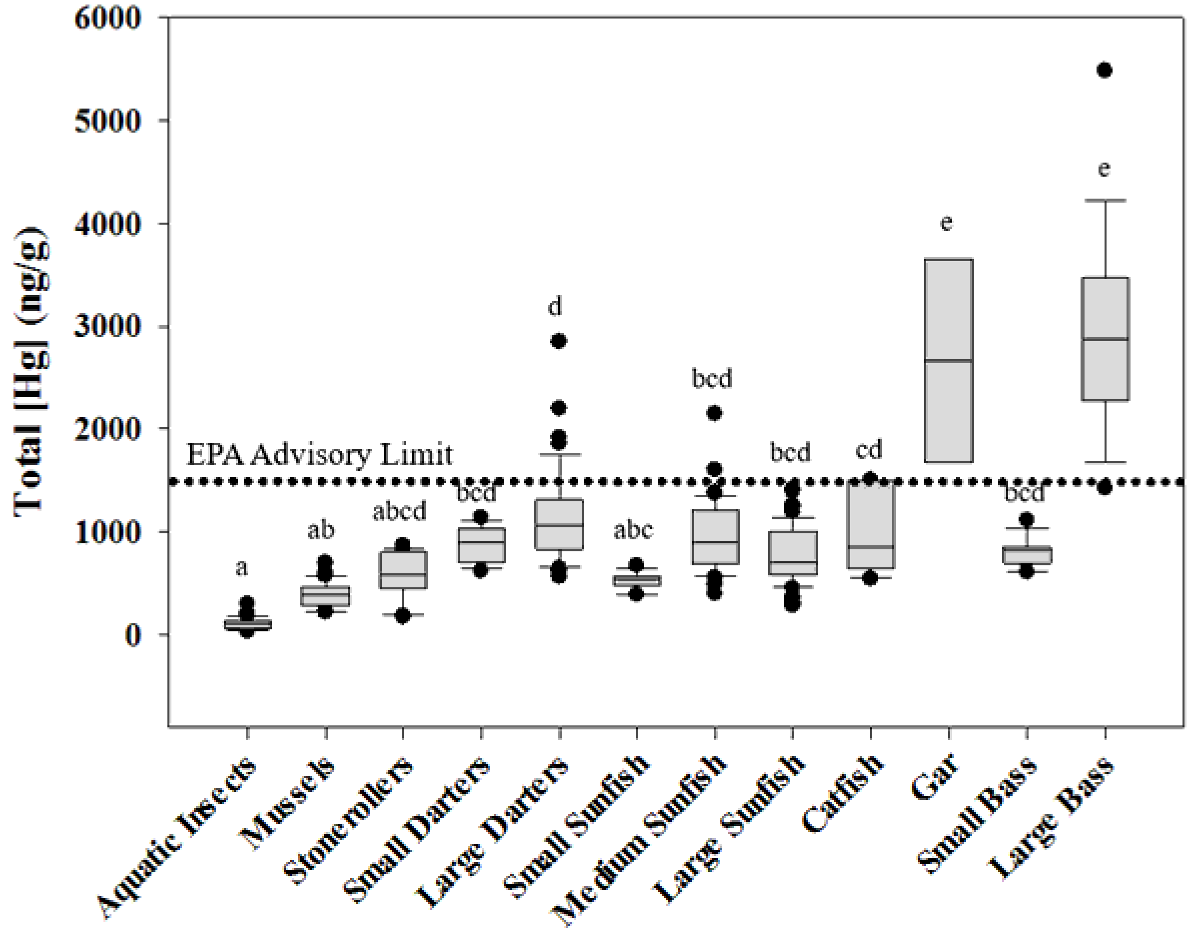

Figure 3

Average total mercury concentration in ng\g for families of aquatic insects. Letters denote homogenous groupings from a one-way ANOVA with a Tukey's post hoc test ($p < 0.05$)

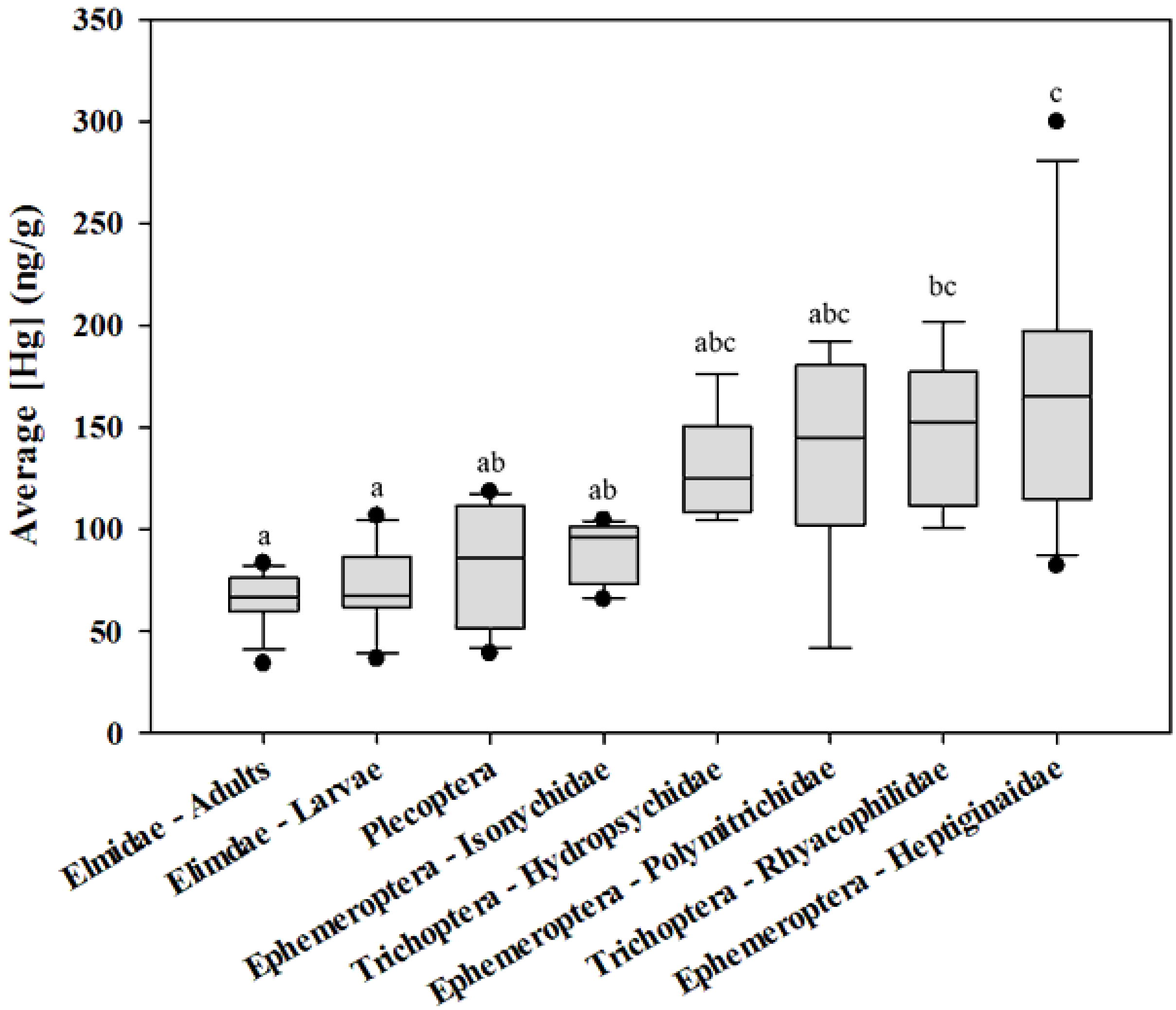

Figure 4

Total mercury concentration (ng/g dry weight) for major taxa in the Kiamichi River. Some fish taxa were split according to size groups based on total length: Small Darters (2-8 cm), Large Darters (>8 cm), Small Sunfish (5-7 cm), Medium Sunfish (7-10 cm), Large Sunfish (>10 cm), Small Bass (4-5 cm), and Large Bass (>10 cm). Letters denote homogenous groups from a one-way ANOVA with a Tukey's post-hoc test at p <= 0.05

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementaryMaterial.docx