

MERCURY CONTAMINATION OF THE FISH COMMUNITY OF A SEMI-ARID AND ARID RIVER SYSTEM: SPATIAL VARIATION AND THE INFLUENCE OF ENVIRONMENTAL GRADIENTS

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Abstract—Mercury (Hg) contamination of aquatic ecosystems is a global environmental problem. Data are abundant on Hg contamination and factors that affect its bioaccumulation in lake communities, but comparatively little information on riverine ecosystems exists. The present study examines fish Hg concentrations of the Lower Rio Grande/Rio Bravo del Norte drainage, Texas, USA and several of its major tributaries in order to assess whether spatial variation occurs in fish Hg concentrations in the drainage and if patterns of Hg contamination of fish are related to gradients in environmental factors thought to affect Hg concentrations in fish communities. Fish, invertebrates, sediments, and water quality parameters were sampled at 12 sites along the lower Rio Grande/Rio Bravo del Norte drainage multiple times over a one-year period. Spatial variation was significant in fish Hg concentrations when fish were grouped by literature-defined trophic guilds or as stable isotope-defined trophic levels, with highest concentrations found in the Big Bend region of the drainage. Mercury in fish in most trophic guilds and trophic levels were positively related to environmental factors thought to affect Hg in fish, including water column dissolved organic carbon (DOC) and sediment Hg concentrations. It is likely that fish Hg concentrations in the Big Bend region are relatively high because this section of the river has abundant geologic Hg sources and environmental conditions which may make it sensitive to Hg inputs (i.e., high DOC, variable water levels). Results from the present study indicate that Hg contamination of the Rio Grande/Rio Bravo del Norte has substantial implications for management and protection of native small-bodied obligate riverine fish, many of which are imperiled. *Environ. Toxicol. Chem.* 2010;29:1762–1772. © 2010 SETAC

Keywords—Rio Grande/Rio Bravo del Norte Mercury Stable isotopes Mercury hotspot Environmental gradients

INTRODUCTION

Mercury (Hg) contamination of food webs is an environmental problem affecting aquatic ecosystems throughout the world [1,2]. Most aquatic ecosystems are contaminated with Hg emitted to the atmosphere by coal-burning power plants, waste incinerators, and other industrial processes, but natural sources of Hg such as the weathering of geologic deposits can contribute to Hg ecosystem inputs [2]. Mercury is released in several elemental and inorganic forms including Hg (II) [2]; Hg (II) is converted to methylmercury (MeHg) in aquatic environments by microorganisms such as sulfate reducing bacteria [3,4]. Methylmercury which bioconcentrates in algae is absorbed directly from the water column, whereas fish and other consumers are exposed to MeHg by ingesting contaminated food items [2]. Mercury is a biomagnifying contaminant and organisms at the top of food webs, such as large predatory fish, and piscivorous birds and mammals accumulate the highest concentrations of MeHg in tissues [1]. Methylmercury has negative effects on behavior, reproduction, growth, and survival in fish and wildlife at concentrations commonly found in the environment [5].

Traditionally, mercury contamination and cycling has been extensively studied in lake, reservoir, and wetland ecosystems [2], but the amount of research in stream and river ecosystems has increased recently [6–11]. In general, many of the factors which affect Hg accumulation in lentic ecosystems also affect Hg accumulation in lotic environments, including watershed

characteristics (i.e., percent wetlands), hydrology, atmospheric Hg deposition, and the concentration of chemical constituents that affect MeHg production, such as dissolved organic carbon (DOC) and sulfates (SO_4^{2-}) [9–12]. Riverine networks offer unique opportunities to examine the role of factors that affect Hg accumulation, because they often span physiographic gradients that have substantial effects on Hg methylation and Hg concentration in biota [6,7]. However, a recent assessment of Hg in lotic fish throughout the western United States found that fish Hg concentrations were not consistently related to environmental variables that affect Hg accumulation in lentic ecosystems [7]. Thus, the factors affecting Hg dynamics and bioaccumulation in riverine ecosystems require further evaluation.

The Rio Grande/Rio Bravo del Norte drainage in the southwestern United States is a large, complex river system that spans more than 3,000 km, from the San Juan Mountains of Colorado to the Gulf of Mexico in Texas, encompassing a drainage area of 290,000 km², and serving as a portion of the US–Mexico border. The lower portion of the Rio Grande drainage from the city of El Paso, Texas, USA to the Gulf of Mexico is an ecologically important area, containing 32 federal- and state-listed imperiled fish taxa [13], and serves as habitat for diverse bird communities. Information on the degree of Hg contamination of Rio Grande food webs is limited. In some portions of the drainage, Hg concentrations in river sediments are relatively high (>50 µg/kg) and are temporally increasing [14,15]. In addition, several wildlife species associated with the river are contaminated with Hg [16]. Several surveys of fish in the Lower Rio Grande drainage found that many piscivorous fish exceed U.S. Environmental Protection Agency (EPA) benchmarks designed to protect human and wildlife health [17–19].

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Table 1. Site name, coordinates, site type (mainstem or tributary), sampling dates, and mean values of environmental variables for each site^a

Site	Coordinates	Site type	Sampling dates	DOC (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (µg/L)	SRP (µg/L)	% OM	C:N (molar)	THg (µg/kg dw)	MeHg (µg/kg dw)
Contrabando (Co)	29°16'45.30" N, 103°50'31.01" W	Mainstem	Su 06	3.48	485	224.86	41.09	3.35	46.32	18.96	0.073
			Su 07								
Santa Elena Canyon (SE)	29°09'51.24" N, 103°36'35.34" W	Mainstem	Fa 07	3.34	494	261.36	46.50	2.11	83.39	120.00	0.106
			Su 07								
Hot Springs (HS)	29°10'38.90" N, 102°59'47.79" W	Mainstem	Fa 07	2.65	493	360.59	60.99	2.18	54.28	23.58	0.186
			Su 07								
Quemado (Que)	28°56'30.22" N, 100°38'38.81" W	Mainstem	Fa 07	1.08	57	231.00	32.36	1.64	133.85	19.30	0.047
			Su 07								
San Ygnacio (SYg)	27°09'56.57" N, 99°25'04.55" W	Mainstem	Fa 07	1.27	37	760.59	166.94	2.13	40.87	13.98	0.047
			Su 07								
Roma (Rom)	26°24'06.51" N, 99°00'08.94" W	Mainstem	Fa 07	0.38	16	79.15	4.91	2.62	29.65	8.67	0.047
			Wi 07								
Terlingua Creek (Terl)	29°19'37.70" N, 103°33'12.31" W	Tributary	Fa 06	2.98	360	368.32	18.95	3.43	77.32	56.11	0.440
			Sp 07								
Tornillo Creek (To)	29°10'37.33" N, 103°00'02.95" W	Tributary	Fa 07	0.49	386	378.04	4.49	1.18	30.12	8.48	0.019
			Su 07								
Independence Creek (Indy)	30°27'55.69" N, 101°49'33.06" W	Tributary	Fa 06	0.93	200	837.16	5.20	1.03	190.03	1.90	0.030
			Su 06								
Pecos River (Pec)	30°26'36.34" N, 101°43'04.39" W	Tributary	Fa 06	3.85	1340	836.09	2.52	1.74	160.70	1.68	0.059
			Sp 07								
Dolan Creek (Do)	29°53'05.16" N, 100°59'37.11" W	Tributary	Su 07	0.58	124	1406.88	36.04	2.61	110.53	6.43	0.166
			Fa 06								
Pinto Creek (Pin)	29°24'10.80" N, 100°28'21.89" W	Tributary	Sp 07	1.22	133	398.79	0.68	5.85	65.79	9.12	0.149
			Fa 06								
			Su 07								
			Fa 07								
			Wi 07								

^aDOC = dissolved organic carbon; SO₄²⁻ = sulfates; NO₃⁻ = nitrates; SRP = soluble reactive phosphorus; %OM = percent organic matter; C:N = sediment carbon to nitrogen ratio (molar); THg = sediment total Hg; MeHg = sediment methylmercury; Su = Summer; Fa = Fall; Sp = Spring; Wi = Winter; 06 = 2006; 07 = 2007.

The purpose of the present study was to examine Hg concentrations of trophically similar fish throughout the drainage and the spatial variation of Hg concentration of fish relative to environmental variables that can affect Hg methylation and bioaccumulation (i.e., Hg in sediments, DOC, SO_4^{2-}) [2–4]. Because Hg concentrations in fish are also highly dependent on food web position [10], trophic guild (TG) and trophic level (TL) of fish was determined using the literature and stable isotopes of nitrogen (N) to determine whether Hg concentration of trophically similar fish differs among sites along the Rio Grande drainage. We hypothesize that substantial differences will be observed among trophically similar fish throughout the Rio Grande drainage and that these differences will be related to spatial variation in environmental variables which affect Hg accumulation in riverine fish communities, such as sediment Hg, DOC, and SO_4^{2-} concentrations.

MATERIALS AND METHODS

Study design and site descriptions

Fish communities, sediments, and other environmental variables were sampled seasonally from 12 sites distributed throughout the lower Rio Grande drainage from June 2006 to October 2007, with each site sampled from two to five times over the study interval (Table 1, Fig. 1). These sites were selected because they are mostly perennially flowing sites and they encompass a range of environmental conditions [20]. The Big Bend area mainstem (Contrabando, Santa Elena Canyon, and Hot Springs) and tributary (Terlingua and Tornillo Creeks) sites are located within the arid Chihuahuan Desert ecoregion, which has some Hg-containing geological formations, and abandoned Hg mines are present throughout the region [21]. Although abandoned Hg mines are numerous throughout this area, it is thought that relatively little Hg is exported from these sites because of arid conditions and low runoff [21]. Independence and Dolan Creeks, tributaries to the Rio Grande/Rio Bravo, are spring-fed streams and are in protected areas with little direct human impact. The Pecos River is a major tributary to the Rio Grande/Rio Bravo, and Pinto Creek is a relatively small spring-influenced tributary to the Rio Grande/Rio Bravo which drains from the Edwards

Plateau. The lower Rio Grande mainstem sites are located in the semi-arid south Texas Plains and include Quemado (located below Amistad Reservoir), San Ygnacio (upstream from Falcon Reservoir), and Roma (immediately below Falcon Reservoir). In addition to geological sources, Hg is deposited from the atmosphere; most of the Hg deposited in this region likely originates from sources outside of North America [22], but sources of Hg emission also exist within the region, including coal-fired power plants in Texas and Mexico [23].

Fish and invertebrate collection

Fish collection efforts were focused on sampling smaller bodied non-piscivorous fish of the community. The present study focused on these taxa because they are important in the trophic transfer of contaminants to upper level consumers, are typically overlooked in many Hg studies, and many of these taxa are at risk of extirpation within the Lower Rio Grande drainage [13].

Fish were collected using seines, anesthetized with tricaine methanesulfonate (MS-222) and preserved in 70% ethanol (EtOH). Fish were kept on ice during transport to Texas State University—San Marcos (San Marcos, TX, USA). Once in the laboratory, fillet muscle (mostly epaxial muscle) was removed from individual fish, dried at 60°C for 48 h. If individuals were too small to yield adequate fillet muscle, guts were removed and the remainder dried whole. Dried fillets or whole fish were homogenized with a mortar and pestle, thoroughly cleaned with acetone prior to analysis for Hg and stable isotopes of nitrogen (to assess trophic position). Multiple studies have determined that preservation of fish tissues in EtOH has little to no effect on N stable isotope signatures [24], thus we assumed that EtOH preservation did not alter $\delta^{15}\text{N}$ values. In addition, preservation of fish tissues has minimal effect on Hg concentrations in fish tissues [25].

Stable isotope ratios of N in fish can be used to infer trophic relationships when interpreted relative to isotope ratios of other food items or organisms in the food web [26]. Therefore, macroinvertebrate samples were collected to estimate trophic position of study fish collected at all sites, seasonally. Macroinvertebrates were collected from fast- and slow-flowing habitats using a combination of Hess samples and dip- and

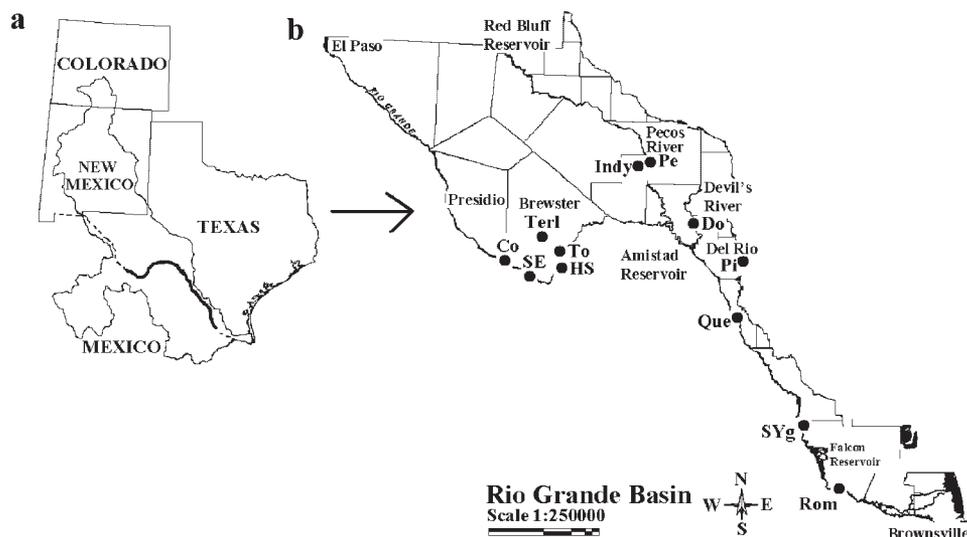


Fig. 1. Map of the Rio Grande/Rio Bravo del Norte drainage and sampling sites in Texas, USA, examined in the present study. Each dot represents a sampling site. Maps are modified from (a) Texas Natural Resource Conservation Commission [20] and (b) Van Metre et al. [15]. Site abbreviations are consistent with abbreviations in Table 1. Maps were used and modified with permission from the authors and publishers.

kick-nets. Collected invertebrates were placed in plastic bags with stream water, kept for approximately 2 h to allow gut content evacuation, and preserved in 70% EtOH until transported to the laboratory. In the laboratory, macroinvertebrate samples were sorted into taxonomic groups (typically to family) and rinsed with Milli-Q (Millipore) to remove attached organic matter. Prior to drying, foot muscle was removed from gastropods with a clean scalpel, and guts were removed from larger invertebrates (Odonata, large Hemiptera, and Megaloptera). Smaller invertebrate taxa (Diptera, Trichoptera) were kept as whole individuals and were prepared as composite samples of multiple individuals. All samples were dried at 60°C for 48 h.

Site-specific environmental variables

Environmental variables were assessed at each site, seasonally. Water temperature, dissolved oxygen (mg/L), specific conductance ($\mu\text{S}/\text{cm}$), and salinity (ppt) at each site were determined with a YSI model 85 or 650 MDS sonde (Yellow Springs Instruments). To analyze concentration of DOC and SO_4^{2-} , nitrate (NO_3^-), and phosphate (PO_4^{3-}), water was collected at each site as triplicate grab samples in clean opaque high-density polyethylene bottles, stored in a cooler on ice, and transported to Texas State University—San Marcos. Water for DOC, SO_4^{2-} , NO_3^- , and PO_4^{3-} analyses was filtered through ashed Whatman GF/Fs and analyzed within 2 d of collection (DOC and SO_4^{2-}) or acid-preserved for later analysis (NO_3^- and PO_4^{3-}). Dissolved organic carbon and SO_4^{2-} were determined on a Shimadzu TOC-V_{C_{SH}} Analyzer and a Lachat FIA Quickchem Autoanalyzer (Hach), respectively. Phosphate (PO_4^{3-}) was measured as soluble reactive phosphorus (SRP) using the molybdenum blue method [27] on a Varian Cary 50 UV-Vis spectrophotometer. Nitrate (NO_3^-) was determined with second derivative UV spectroscopy [28]. Blanks and check standards were performed with each analysis run for each water chemistry parameter (DOC, SO_4^{2-} , NO_3^- , and PO_4^{3-}).

In October 2007, duplicate sediment samples were collected at each site using a clean aluminum trowel. Each duplicate sample was composed of sediments randomly collected from three to four sediment accumulating areas within each site (i.e., pools, margin areas, at the end of runs). To collect sediments, the top 1 cm of sediment was removed and the next approximately 5 cm of underlying sediment was collected so that mostly anoxic, reduced sediments were collected. Sediments from each of the three to four locations in each replicate sample was combined in an acid-washed high-density polyethylene tub and thoroughly mixed. Sediment samples collected for total Hg (THg) and MeHg analyses were immediately placed into acid-washed glass bottles with Teflon-lined caps. Bottles were double bagged, stored on ice in coolers, and transported to the lab where they were stored at -80°C until they were freeze dried with a Labconco Freeze Dry System-Freezone 6. Remaining sediments were placed into 50 ml acid-washed high-density polyethylene screw cap test tubes, stored on ice in coolers, and transported to the lab. In the lab, we determined percent organic matter (%OM) and carbon (C) and nitrogen (N) content of duplicate sediment samples from each site. Percent OM of sediments was determined on duplicate samples for each site through loss at ignition. Sediment C and N content and C:N (molar) ratios were determined on a CE Elantech CN Soil Analyzer with blanks and check standards (*L*-aspartic acid) accompanying each analysis run.

Fish and sediment mercury analysis

Fish tissues and sediments were analyzed for THg with a direct mercury analyzer (DMA-80, Milestone) that uses thermal decomposition, gold amalgamation, and atomic absorption spectrometry [29]. We used THg as a proxy for MeHg in fish because more than 90% THg in fish muscle is MeHg [4]. Quality assurance included reference and duplicate samples. At approximately every 10th sample, reference samples of marine sediment (MESS-3, certified value 91 ± 9 ng Hg/g dry weight,) or dogfish *Squalus* spp. muscle (DORM-2, certified value = $4,640 \pm 260$ ng mercury/g dry weight) were analyzed and the mean percent recovery was $100 \pm 1\%$ (range = 92 to 107%, $n = 41$) and $100 \pm 2\%$ (range = 95 to 104%, $n = 11$), respectively. Duplicate samples were analyzed at approximately every 20th sample, and the mean relative percent difference was 7.85% (range = 0.3 to 11.4%, $n = 28$). Concentrations in fish are reported as μg THg/kg wet weight. To convert dry weight concentrations of THg to wet weight concentrations, we assumed fish tissues lost 79% of their weight upon drying [30]. Mercury concentrations in whole fish were corrected to make them equivalent to fillet Hg concentrations using the method of Peterson et al. [7]. Sediment THg concentrations are reported as μg THg /kg dry weight of sediment.

Methylmercury in sediments was determined with EPA method 1630 [31]. Briefly, samples were digested with KBr, CuSO_4 , and CH_2Cl_2 and the extractant was treated with sodium tetraethyl borate, purged with N_2 gas, and Hg was collected on a trap. Quality assurance included use of reference and duplicate samples. Estuarine sediment reference material (ERM-CC580, certified value 75.5 ± 3.7 ng mercury/g dry weight) and sample duplicates were run approximately every 10 samples. Mean percent recovery of reference material was $81 \pm 9\%$ (range = 74 to 88%, $n = 3$) and the mean relative percent difference among duplicates was $1.3 \pm 0.02\%$ (range = 1.02 to 1.40%, $n = 4$). Sediment MeHg concentrations are reported as μg MeHg /kg dry weight of sediment.

Determination of fish trophic guild and trophic position

Variation in Hg content among fish is often a reflection of trophic position [10], and one of the primary goals of the present study was to examine whether Hg concentrations of trophically similar fish differs among sites along the Rio Grande drainage. Thus, we determined trophic ecology of the various fish using two methods. First, fish were grouped into TGs based on literature-defined feeding ecologies [32]. Fish were categorized into three TGs: herbivore/benthivore/omnivore (H/B/O), invertivore (INV), and invertivore/piscivore (INV/P). Herbivorous, omnivorous, and benthivorous fish were grouped into a single trophic guild because these guilds often exhibit substantial dietary overlap and sample sizes at some sites for these individual guilds were occasionally small.

Trophic position of fish was determined using stable isotope analysis. Stable isotope analysis allowed for comparison of Hg concentration in fish (regardless of species) from different sites that are within the same trophic level. Stable isotopes ratios of nitrogen were determined for all fish and macroinvertebrates at the University of California—Davis Stable Isotope Laboratory (Davis, CA, USA). Stable isotope values are reported with δ notation, where $\delta^{15}\text{N}$ values are equivalent to

$$\left(\left[\frac{R_{\text{SAMPLE}}}{R_{\text{STANDARD}}} \right]^{-1} \right) \cdot 1,000$$

where R is the $^{15}\text{N}:^{14}\text{N}$ of the sample and standard (atmospheric N). Samples were analyzed for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and

duplicates were run approximately every 15 samples with a mean standard error of <0.15‰.

To estimate trophic position of invertebrates and fish, $\delta^{15}\text{N}$ values were utilized. Trophic transfers in food webs lead to gradual enrichment of consumer $\delta^{15}\text{N}$, thus $\delta^{15}\text{N}$ can be used to estimate trophic position of consumers [26]. In order to estimate the trophic position of an organism, an approach was used in which the consumer with the lowest $\delta^{15}\text{N}$ value in the community was designated as the baseline consumer with a trophic position of 2 [26]. The $\delta^{15}\text{N}$ of the baseline consumer was subsequently used to estimate trophic position for all other consumers in the food web using the equation

$$\text{Trophic position}_{\text{Consumer}} = \left(\frac{[\delta^{15}\text{N}_{\text{Consumer}} - \delta^{15}\text{N}_{\text{Baseline}}]}{f} \right) + 2$$

where $\delta^{15}\text{N}_{\text{Consumer}}$ is the $\delta^{15}\text{N}$ value for consumer for which trophic position is estimated, $\delta^{15}\text{N}_{\text{Baseline}}$ is the $\delta^{15}\text{N}$ value of baseline organism, 2 is the expected trophic position of the organism used to estimate baseline $\delta^{15}\text{N}$, and f is the $\delta^{15}\text{N}$ fractionation factor expected between a predator and its prey (3.4‰, [26]). Trophic position of each consumer was determined by standardizing each site on each sampling date with a site-specific $\delta^{15}\text{N}$ baseline taxonomic group [26], which was established by determining the consumer that exhibits the lowest $\delta^{15}\text{N}$ values at that site on a specific date. In the present study, baseline organisms at each site were found to be invertebrates primarily consisting of the following invertebrate groups: Gastropoda, Naucoridae, Psephenidae, Leptophlebiidae, and Baetidae. Designation of these taxonomic groups as isotopic base lines is generally consistent with the findings of other studies of river ecosystems [26]. Using $\delta^{15}\text{N}$ -inferred trophic positions for each fish, fish from each site were then designated into the following TL groupings: trophic level 2.0–2.9 (TL2), trophic level 3.0–3.9 (TL3), and trophic level 4.0 and up (TL4+).

Data analysis

In order to determine if Hg content of fish within the same TG and TL differed among sites in the Rio Grande drainage, Hg in fish was compared across the 12 study sites from each TG and each TL among sites using one-way analysis of variance (ANOVA). Site was used as the independent variable (factor) and the Hg concentration of fish in each TG and each TL were the dependent variables. All data were \log_{10} transformed prior to analyses in an attempt to meet assumptions of normality and homoscedasticity. Significance (α) was set at $p \leq 0.05$, but because multiple comparisons were made, a sequential Bonferroni procedure was used to adjust α in which we ranked response variable p -values from least to greatest and compared the lowest p -value to α/k , where k is the number of comparisons ($\alpha = 0.05/6 = 0.008$). Significance was inferred if the p value of a response variable was lower than the adjusted α . Progressively greater p values were sequentially compared to $k-1$, $k-2$, etc., until the p -value of a response variable exceeded the adjusted α . If a significant overall site effect was detected, homogeneous subsets were determined with Tukey honestly significant difference (HSD) tests with significance inferred at $p \leq 0.05$.

In order to determine whether differences in Hg in fish were related to environmental factors that can affect Hg bioaccumulation, principal components analysis (PCA) was used to summarize variation in environmental factors among the 12 sites in the Rio Grande/Rio Bravo drainage. In the analysis, sites were

represented by dummy variables and environmental variables (DOC, sediment THg, sediment MeHg, C:N, NO_3^- , %OM, SRP, and SO_4^{2-}) were z -score transformed. Specific conductance, pH, temperature, and dissolved oxygen (DO) were not included in the PCA. Dissolved oxygen was always >5 mg/L, and pH was always circumneutral across all sites, and their inclusion would have led to an inverted matrix. Specific conductance was not consistently recorded at all sites, and temperature was not utilized because examination of seasonality was not a goal of the present study. To examine if Hg in fish of the various TGs and TLs were related to the variation among sites in environmental parameters, mean THg of each group of fish at each site was regressed as a function of the PCA axis scores for each site using ordinary least squares (OLS) linear regression. Principal components analysis axis scores (PCA I, II, and III) represent a linear combination of environmental variables for each site; thus, this analysis allows for examination of the cumulative influence of environmental factors expressed along each PCA axis on Hg in fish.

Use of PCA scores in the above type of regression analysis allows for assessment of the cumulative influence of environmental variables on each principal component on fish Hg concentrations; however, this type of analysis provides little information on the relative strengths of individual variables in predicting Hg concentration in groups of fish and the nature of these univariate relationships. Thus, the relationship among THg of fish in the various TGs and TLs and the individual variables included in the principal components was further explored. To explore the relative strengths of these individual variables as predictors of mean Hg in the various TGs and TLs (the proportion of variation in Hg in fish of the various trophic

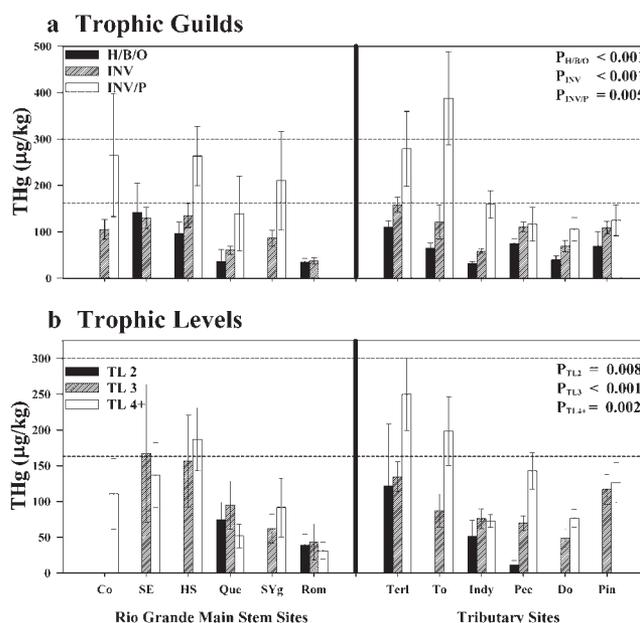


Fig. 2. Mean Hg concentrations ($\mu\text{g}/\text{kg}$ wet weight) in fish at each site grouped as (a) literature-defined trophic guilds and (b) stable-isotope-defined trophic levels. Error bars are ± 1 SE. Dashed lines that run parallel to the x-axis denote the U.S. EPA Wildlife Critical Value ($163 \mu\text{g}/\text{kg}$) and the U.S. EPA screening value for human health ($300 \mu\text{g}/\text{kg}$). Note the difference in y axis scales for panels (a) and (b). Site abbreviations along the x axis are consistent with abbreviations in Table 1. Literature-defined trophic guild designations in (a) are herbivore/benthivore/omnivore (H/B/O), invertivore (INV), and invertivore/piscivore (INV/P). Stable isotope-defined trophic levels in (b) are trophic level 2.0–2.9 (TL2), trophic level 3.0–3.9 (TL3), and trophic level 4.0 and up (TL4+).

Table 2. Results of one-way analysis of variance (ANOVA) examining the effect of sampling site on the Hg concentration of fish in the various trophic designations^a

Trophic group	df	F	p
H/B/O	9, 278	23.2	<0.001*
INV	11, 660	29.5	<0.001*
INV/P	9, 123	2.7	0.007*
TL3	10, 210	5.6	<0.001*
TL4+	11, 247	11.4	<0.001*

^a H/B/O = herbivore/benthivore/omnivore; INV = invertivore; INV/P = invertivore/piscivore; TL = trophic level.

* Significant at sequential Bonferroni adjusted α .

groups explained by the relationship), and the nature of the relationship among THg in the various TGs and TLs and these variables (a linear, quadratic, or exponential relationship), regression analyses were performed to examine if the mean THg of each fish trophic group was a function of individual environmental variables that had large loadings on the principal components. Again, a sequential Bonferroni procedure was used to adjust α . All analyses were performed using SPSS version 15.0.

RESULTS

Spatial variation in Hg concentration of Rio Grande fish

Total Hg in fish across TGs differed significantly among sites (Fig. 2a, Table 2); we analyzed, on average 89 (range, 28–250) fish samples for THg per site. Across all TGs, mean THg concentration of fish ($\mu\text{g}/\text{kg}$ wet weight) generally was highest at Big Bend area main stem sites (Contrabando, Santa Elena, and Hot Springs). herbivore/benthivore/omnivore THg concentrations were significantly different among sites; Santa Elena Canyon (142 ± 63) was highest, while Independence Creek (32 ± 4), Quemado (36 ± 26), and Roma (33 ± 8) were lowest. Invertivore THg concentrations differed significantly among sites: Terlingua Creek, Hot Springs, and Santa Elena Canyon were highest (159 ± 17 , 135 ± 26 , and 130 ± 23 , respectively), while Roma (33 ± 8), Independence Creek (58 ± 5), Quemado (60 ± 9), and Dolan Creek (69 ± 12) were lowest. Invertivore/piscivore THg concentration also differed significantly among sites, but post hoc pair-wise comparisons did not differ significantly with the Bonferroni adjusted α (Table 3). In general, INV/P THg concentrations were greater than other TGs at each site, with Tornillo Creek (387 ± 100) in the Big Bend area being the highest, and Dolan Creek (106 ± 26) the lowest.

Table 3. Results of post hoc paired comparisons of fish Hg concentration in each trophic group across all sites^{a,b}

Site	H/B/O	INV	INV/P	TL2	TL3	TL4+
Contrabando		A, B, C	A			A, B, C
Santa Elena Canyon	A	A, B	A		A	A, B
Hot Springs	A, B	A, B	A		A, B	A, B
Quemado	C	D, E, F	A	A	A, B	C, D
San Ygnacio		C, D, E	A		A, B	A, B, C
Roma	C	F	A	A, B	B	D
Terlingua Creek	A, B	A	A	A	A, B	A
Tornillo Creek	B, C	A, B, C	A		A, B	A, B, C
Independence Creek	C	E, F	A	A	A, B	C, D
Pecos River	A, B, C	B, C, D	A	B	A, B	A, B, C
Dolan Creek	C	D, E, F	A		B	B, C, D
Pinto Creek	B, C	A, B, C, D	A		A, B	A, B, C

^a H/B/O = herbivore/benthivore/omnivore; INV = invertivore; INV/P = invertivore/piscivore; TL = trophic level.

^b Homogeneous subsets determined through Tukey HSD (honestly significant difference) tests are designated with the same letter (A–F). Trophic groups defined in Figure 2.

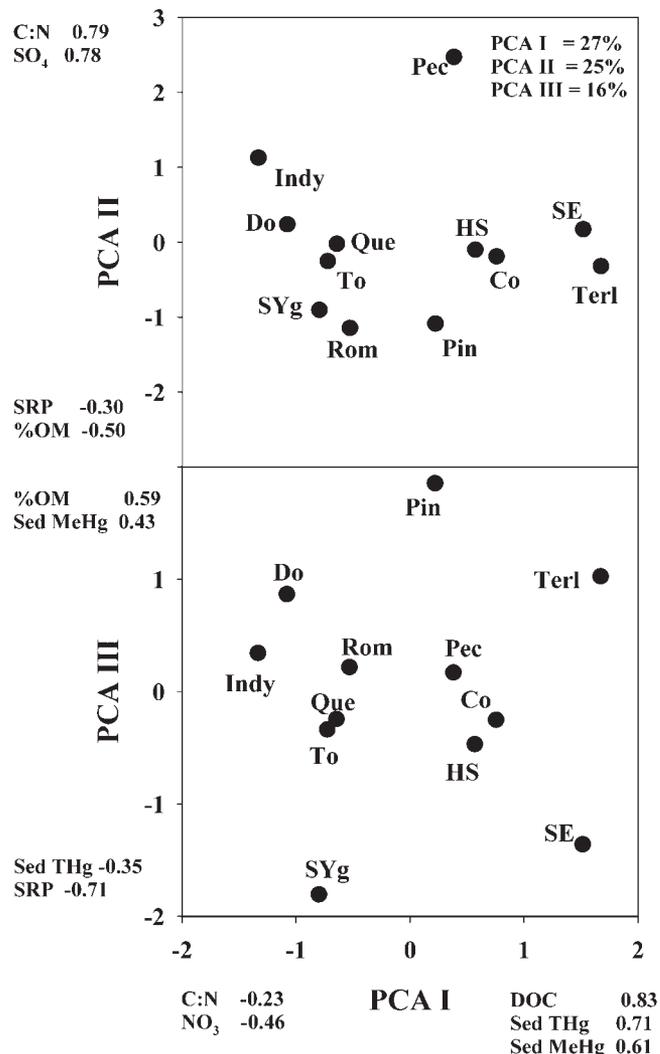


Fig. 3. Results of principal components analysis (PCA) showing axes I, II, and III with each site denoted in multivariate space. The percent of variation among sites explained by each axis is provided, as are the loadings for individual environmental variables associated with the each axis. Site abbreviations are consistent with abbreviations in Table 1. C:N = sediment C:N (molar); NO_3 = water column nitrate concentration; DOC = water column DOC concentration; Sed THg = sediment THg concentration; Sed MeHg = sediment MeHg concentration; % OM = sediment % OM; SRP = water column soluble reactive phosphorus (PO_4^{3-}) concentration; SO_4 = water column sulfate concentration.

On average, 40 fish samples (range, 5–100) were analyzed for both THg and $\delta^{15}\text{N}$ -derived TLs at each site. Total Hg in fish across TLs differed significantly among sites (Fig. 2b, Table 2). As observed in the results for THg concentration for TGs, the sites with the highest THg in fish tissues ($\mu\text{g}/\text{kg}$ wet weight) were located within the Big Bend reach. Trophic level 2 THg concentrations were significantly different among the five sites where fish from this group were collected, with Terlingua Creek (122 ± 86) being the highest, and the Pecos River (11 ± 7) the lowest. Trophic level 3 THg concentrations differed among sites; Santa Elena Canyon (167 ± 97), Hot Springs (157 ± 64), and Terlingua Creek (135 ± 21) sites were highest, whereas Dolan Creek (49 ± 13), and the lower Rio Grande mainstem sites (Roma: 44 ± 25 ; San Ygnacio: 62 ± 21) were lowest. Trophic level 4+ THg concentrations differed significantly among sites, but pair-wise post hoc contrasts were not significant with the Bonferroni adjusted α (Table 3). However, in general, TL4+ THg concentrations were relatively elevated at Santa Elena, Hot Springs, Terlingua, Tornillo, and the Pecos sites.

Spatial variation in environmental gradients

The first three principal component axes explained 68% of the total variation in measured environmental variables known to influence Hg concentrations in food webs (Fig. 3). Axis I explained 27% of the variation among sites and exhibited relatively large positive loadings for THg and MeHg concentration in sediments (0.71 and 0.61, respectively) and water DOC concentration (0.83), whereas sediment C:N ratio and NO_3^- concentration had relatively large negative loadings

(-0.23 and -0.46 , respectively). Ordination of the 12 sites along PCA I revealed that Contrabando, Santa Elena, Hot Springs, and Terlingua Creek were grouped together, indicating these sites had similarly high sediment THg, sediment MeHg, and DOC. In contrast, the relatively undisturbed spring-fed tributaries (Independence Creek, Dolan Creek) were associated with lower sediment Hg and DOC and higher NO_3^- and sediment C:N ratios. Tornillo Creek, located in the Big Bend region grouped with the downstream main stem sites (Quemado, San Ygnacio, and Roma) and Pinto Creek. Principal components axis II explained 25% of the variation among sites, with relatively high positive loadings for sediment C:N ratio and aqueous concentrations of SO_4^{2-} (0.79 and 0.78, respectively), and negative loadings for SRP and sediment % OM (-0.30 and -0.50 , respectively). Almost all sites were distributed in the middle of PCA II, indicating smaller variation among sites in the variables associated with this axis. The exception was the Pecos River, which had relatively high SO_4^{2-} and DOC concentrations. Principal components axis III explained 16% of the variation among sites, with positive loadings for sediment %OM and sediment MeHg (0.59 and 0.43, respectively), and negative loadings for sediment THg and water column SRP (-0.35 and -0.71 , respectively). As with PCA II, most sites fall in the middle of the axis.

Influence of environmental gradients on fish Hg concentrations

Mercury concentrations of fish in most of the TGs and TLs were a function of the environmental gradient differences expressed along PCA I (Fig. 4a–f). Across all sites, mean

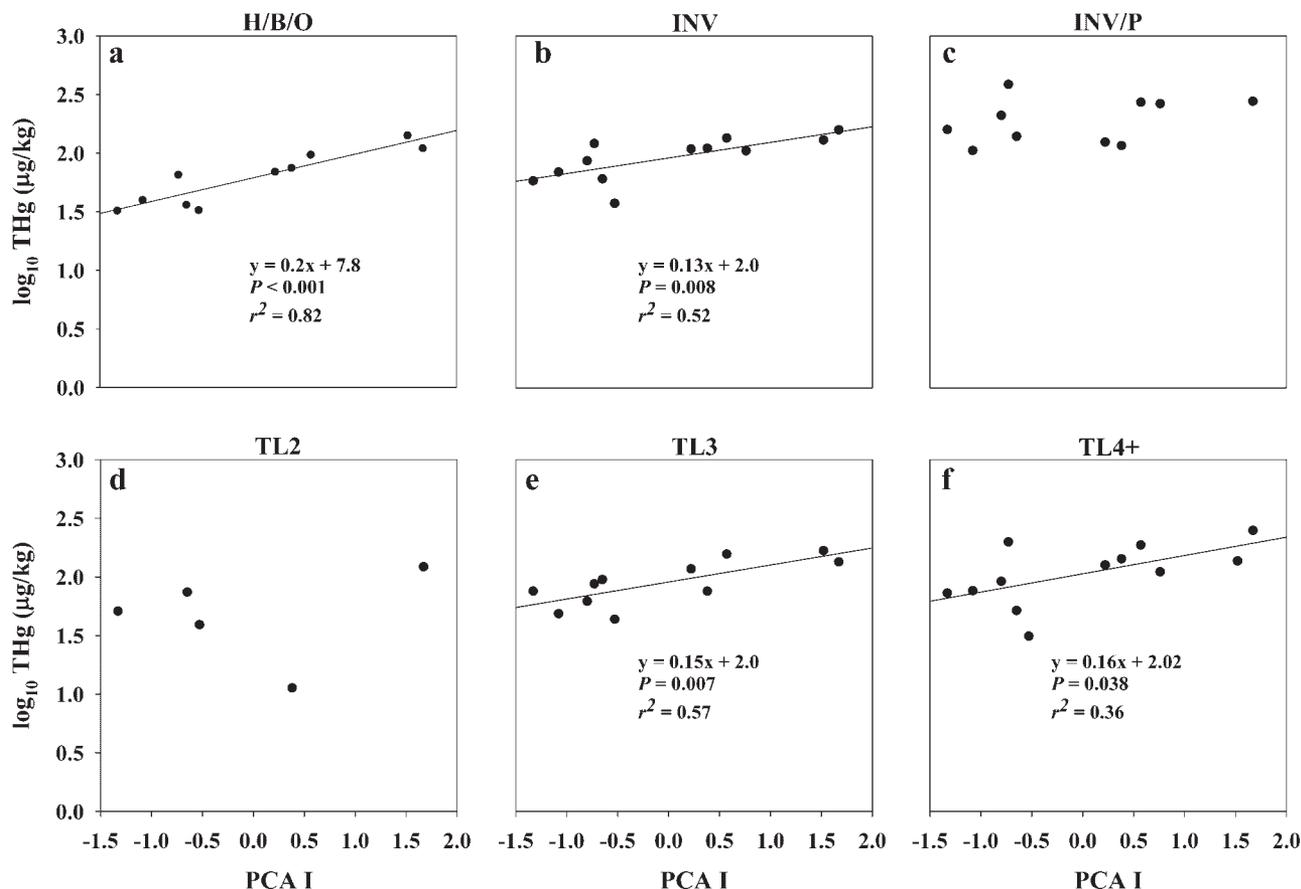


Fig. 4. Mercury concentration (\log_{10} [$\mu\text{g}/\text{kg}$ wet weight]) of fish in the various trophic groups (H/B/O, INV, INV/P, TL2, TL3, and TL4+) as a function of PCA I scores of the respective study sites. If no line, equation, p -value, and r^2 value are presented on a panel, then the relationship was found to be nonsignificant. Trophic guild and trophic level designations (H/B/O, INV, INV/P, TL2, TL3, and TL4+) are the same as Figure 2.

Table 4. Result of OLS (ordinary least squares) regression analysis examining the relationships log₁₀-transformed Hg concentration of fish in different trophic groups (defined in Fig. 2) and site-specific PCA (Principal Components Analysis) I scores (defined in Fig. 3)^{a,b}

Trophic groups		Environmental variables				
		DOC	THg	MeHg	%OM	
H/B/O	<i>r</i> ²	0.66	0.46	0.41	0.00	
	<i>p</i>	0.023	0.116	0.863	0.991	
	Equation	$y = -7.8x^2 + 53.8x + 11.7$	—	—	—	
INV	<i>r</i> ²	0.51	0.16	0.96	0.01	
	<i>p</i>	0.041	0.456	0.326	0.938	
	Equation	$y = -10.9x^2 + 63.3x + 35.3$	—	—	—	
INV/P	<i>r</i> ²	0.02	0.64	0.51	0.18	
	<i>p</i>	0.715	0.028	0.082	0.500	
	Equation	—	$y = -0.014x^2 + 5.4x + 126.1$	—	—	
TL2	<i>r</i> ²	0.75	0.40	0.71	0.23	
	<i>p</i>	0.251	0.605	0.072	0.417	
	Equation	—	—	—	—	
TL3	<i>r</i> ²	0.64	0.33	0.09	0.06	
	<i>p</i>	0.016	0.201	0.679	0.779	
	Equation	$y = -21.2x^2 + 108.1x + 4.4$	—	—	—	
TL4+	<i>r</i> ²	0.30	0.12	0.46	0.01	
	<i>p</i>	0.063	0.559	0.160	0.938	
	Equation	—	—	—	—	

^aThe *r*², *p*-value, and the regression equation are reported if the relationship is significant. Homogeneous subsets determined through Tukey HSD (honestly significant difference) tests are designated with the same letter (A–F). Trophic groups defined in Figure 2.

^bDOC = dissolved organic carbon; THg = total Hg; MeHg = methylmercury; %OM = percent organic matter; H/B/O = herbivore/benthivore/omnivore; INV = invertivore; INV/P = invertivore/piscivore; TL = trophic level.

THg concentration of H/B/O, INV, TL3, and TL4+ fish were a positive function of PCA I scores ($p \leq 0.038$, Fig. 4a, b, e, and f), indicating that THg concentration of these groups of fish in the Rio Grande drainage increased with sediment THg, sediment MeHg, and DOC (Fig. 4a, b, e, and f). However, mean THg concentration of INV/P and TL2 fish were not a significant function of PCA I scores (Fig. 4c and d). Mean THg concentration of fish trophic groups were not a significant function of PCA II and III scores ($p = 0.058$ to 0.989).

The relationships between THg of fish in the various TGs and TLs, and four variables in PCA I (DOC, sediment THg, sediment MeHg, and sediment %OM), were examined. Dissolved organic carbon was a strong predictor of THg in H/B/O, INV, and TL3 fish, and sediment THg was a strong predictor of Hg in INV/P fish (Table 4). Mercury in fish across all trophic groups did not exhibit a significant relationship with sediment MeHg or %OM (Table 4). In all cases where a significant relationship was detected, a unimodal (quadratic) function was the best descriptor of the relationship among fish THg and the environmental variable (DOC or sediment THg).

DISCUSSION

Spatial variation in Hg in fish and sensitivity to Hg loading

In the present study, Hg was at detectable concentrations in fish throughout the Lower Rio Grande drainage, demonstrating that Hg contamination is fairly widespread across the basin. In addition, Hg concentrations in fish at individual sites generally increased with trophic guild and trophic level; however, fish populations in the Rio Grande drainage exhibited significant spatial variation in Hg concentrations. Although fish in the Big Bend region (Contrabando, Santa Elena, Hot Springs, Terlingua Creek, Tornillo Creek) appear to contain elevated Hg concentrations when compared to other sites within the basin, Big Bend fish Hg concentrations are not substantially different from mean Hg concentrations of fish from throughout the western United States [7]. In a large scale study of Hg in fish from 626

western U.S. streams across 12 states, Peterson et al. [7] reported a mean invertivore Hg concentration of 167.4 $\mu\text{g}/\text{kg}$ (wet fillet weight) and a mean INV/P Hg concentration of 257 $\mu\text{g}/\text{kg}$ (wet fillet weight). These values are comparable to mean INV and INV/P values across all sites within the Big Bend area of the Rio Grande (INV = $125 \pm 14 \mu\text{g}/\text{kg}$, INV/P = $264 \pm 58 \mu\text{g}/\text{kg}$). Additionally, when fish Hg concentrations in the Big Bend area and those for the western United States [7] are compared to the lower Rio Grande/Rio Bravo mainstem sites (Quemado, San Ygnacio, Roma) and the spring-fed tributary sites (Dolan and Independence Creeks), fish communities in the lower Rio Grande/Rio Bravo and spring-fed tributaries have much lower Hg concentrations. Thus, Hg concentrations in fish of the Big Bend reach are elevated when compared to downstream sections of the drainage, but are close to the mean Hg concentrations reported across the western United States. These findings also suggest that Hg contamination of lotic fish communities is widespread in the western United States and can affect sites thought to be isolated from Hg sources [7].

In the present study, different patterns of Hg bioaccumulation in fish communities were observed when fish were either grouped by literature-defined TGs or by TLs determined through stable isotope analysis. In general, when fish were grouped according to literature-defined TGs, Hg concentration increased with TG (H/B/O < INV < INV/P) at most of the study sites. In contrast, when fish were grouped into TLs via $\delta^{15}\text{N}$ values, Hg concentration in fish increased with trophic level (TL2 < TL3 < TL4+) in approximately half of the study sites. Several possible reasons exist for the observed differences in Hg bioaccumulation in fish communities when TGs or TLs are used to group fish. Every fish that was analyzed for Hg was also a priori assigned into a TG, but approximately half of all fish were analyzed for both Hg and $\delta^{15}\text{N}$. Subsequently, the mean number of fish analyzed for Hg in each TG at each site (H/B/O = 28, INV = 55, INV/P = 12) was generally greater than the mean number of fish in each TL at each site (TL2 = 5,

TL3 = 19, TL4+ = 19). Thus, the smaller sample size of fish grouped by TL may have obscured the patterns observed when fish were grouped by TG. In addition, previous studies have noted incongruence in trophic classification of riverine fish using literature-defined trophic guilds versus isotopically defined trophic levels; these differences are thought to be due to high levels of omnivory in stream fish [33] and differences in the relative importance of algal- versus terrestrial-derived OM as food sources [34]. Indeed, riverine fish can rely greatly upon terrestrial OM sources, and complex ^{15}N fractionation processes and variability in $\delta^{15}\text{N}$ of terrestrial OM [35] might substantially alter $\delta^{15}\text{N}$ values of fish that utilize terrestrially derived OM. Therefore, given our results, it is recommended that future studies using stable isotopes to trophically classify riverine fish should make sure to obtain adequate sample sizes and have a detailed understanding of the relationships between food resources and the fish community.

In the present study, spatial variation of Hg in several trophic groups of fish throughout the lower Rio Grande drainage was related to local environmental variables, specifically concentrations of sediment THg and water column DOC. Previous studies have also found that these environmental variables can influence bioaccumulation and biomagnification of Hg in fish communities [10]. Sediment THg and DOC predicted fish Hg with similar strengths (e.g., r^2 values were approximately equal for predicting Hg in most fish groups). In addition, unimodal functions best described both DOC and sediment THg relationships with fish Hg concentrations. This is because both sediment THg and DOC co-varied across sites; sites with higher sediment THg also had higher DOC. Relatively high Hg loading to an ecosystem alone does not necessarily lead to Hg bioaccumulation [36]; conditions within the ecosystem must be conducive to the methylation and bioaccumulation of Hg in biota (sensitivity; [1]). Limited information on sensitivity criteria of riverine ecosystems to Hg loading is available, but sensitivity of lakes to Hg loading is generally thought to be described by five characteristics: DOC concentration, pH, acid neutralizing capacity (ANC), total phosphorus (TP) concentration, and the severity/degree of water level fluctuations [1,36]. Although sensitivity criteria for river systems likely differ somewhat from lake systems, it is predicted that lakes will be sensitive to Hg loadings when DOC >4 mg/L, pH <6, ANC <100 ($\mu\text{ eq/L}$), and water level fluctuations are pronounced [1,36]. Mean (± 1 SE) DOC in the Big Bend region is 2.70 ± 0.39 mg/L, pH across all sites within the drainage was circumneutral, and ANC was not measured in the present study. However, like other arid river systems, sites within the Big Bend reach experience substantial seasonal water level fluctuations due to highly variable flows [37].

Mercury in fish were highest in the Big Bend reach of the drainage, which exhibits relatively higher concentrations of sediment THg and water column DOC; however, the sources of Hg and DOC to the Big Bend reach remain poorly understood. The Big Bend sites exhibited relatively high THg sediment concentrations ($\bar{x} \pm 1$ SE = 49 ± 15 $\mu\text{g/kg}$ dry weight) and areas of this region have geologic formations with Hg and numerous abandoned Hg mine sites [21]. Although mine wastes at some sites in the Big Bend area exhibit high sediment MeHg concentrations (up to 79 $\mu\text{g/kg}$) and rapid Hg methylation rates, little indicates that much Hg from mine wastes is exported to local streams [38]. However, the relative importance of the different Hg sources (i.e., geological sources, mine wastes, atmospheric deposition) to the Big Bend region of the Rio Grande drainage remains unknown. In addition, DOC can have

a major influence on Hg concentrations in biota, but the relationship among DOC, MeHg production, and Hg bioaccumulation is complex [39]. The Big Bend sites generally exhibited higher DOC concentrations than the other study sites, but DOC sources to Big Bend sites are difficult to identify. These sites are all located within the Chihuahuan Desert ecoregion, and inputs of particulate and dissolved OM to these aquatic ecosystems from the surrounding arid landscape is likely low. It is possible that the relatively high DOC in these sites is autochthonously generated via riverine production or from upstream sources such as waste water discharges, but the relative roles of these sources remain unknown.

Identifying sites of elevated Hg in biota across a riverine network is critical because of the widespread distribution of Hg in the environment and its ability to contaminate areas far removed from humans [7]. However, identification of locations within an individual site that contribute to bioaccumulation of Hg in biota at may also be important for the management and restoration of Hg-contaminated ecosystems. Several studies have found that wetland areas within river drainages serve as MeHg production areas because conditions are more favorable for methylation [6,10,11]. These studies examined riverine systems in regions which are much wetter climatically (e.g., South Carolina, Georgia, Florida, Oregon, and Wisconsin) and their respective drainages generally contain much higher wetland cover than the sites in the present study. Much of the lower Rio Grande drainage contains little wetland area, especially the arid Big Bend reach. The only sites with substantial wetland and macrophyte development are the headwater sections of the two spring-fed sites (Dolan and Independence Creeks), which also have some of the lowest fish Hg concentrations. We hypothesize that Hg dynamics in the Rio Grande differ from conceptual models describing other North American rivers; in the Rio Grande and its tributaries, a majority of Hg methylation may occur within the main stream or river channel in periphyton mats or sediment-accumulating areas. Tsui et al. [12] found that *Cladophora* mats were important in-stream MeHg production sites in a river network with little or no wetland area. In addition, the Rio Grande and many of its tributaries have experienced substantial reductions in flow due to surface water damming and groundwater exploitation, which leads to lower mean flows and increased sedimentation [40]. These conditions may have led to an increase of in situ Hg methylation in the main stream channels and subsequent bioaccumulation in fish. Furthermore, flows have been greatly reduced across much of the western United States [40], which could lead to increased sedimentation and increased potential for Hg methylation and bioaccumulation.

Implications for human and wildlife health

Environmental toxicologists have recently called for increased examination of the spatial distribution of Hg concentrations in biota within landscapes [7] and the identification of so-called biological Hg hotspots [36]. Evers et al. [36] defines a biological Hg hotspot as a location in a landscape that is characterized by elevated Hg in biota that exceed established human or wildlife health criteria as determined by a statistically adequate sample size. By comparing Hg concentrations in yellow perch (*Perca flavescens*) from approximately 4,000 water bodies to U.S. EPA screening value for human health (300 $\mu\text{g/kg}$), Evers et al. [36] identified hotspots in northeastern United States and southeastern Canada. The present study did not contain an adequate number of sampling sites and the required spatial resolution to detect biological Hg hotspots in

the lower Rio Grande. However, we compared mean INV and INV/P Hg concentrations at sites across the drainage to U.S. EPA screening value for human health to identify sites that would qualify as areas of elevated Hg concentrations. Using U.S. EPA screening value for human health, the Big Bend region is a zone of elevated fish Hg concentrations (mean INV/P = 310 $\mu\text{g}/\text{kg}$). However, if we identify areas of elevated Hg within the lower Rio Grande utilizing established U.S. EPA wildlife critical value ($\geq 163 \mu\text{g}/\text{kg}$), five sites have at least one trophic group which exceed this value (Fig. 2a and b). Furthermore, if the data set of Peterson et al. [7] was compared to U.S. EPA wildlife critical value, much of the western United States would be identified as an area of elevated Hg levels that presents concerns for wildlife. Thus, identification of areas of relatively elevated Hg where piscivorous wildlife are most at risk among and within drainages using U.S. EPA wildlife critical value may present difficulties when substantial amounts of Hg are present in landscapes.

We compared Hg concentrations in fish tissues to U.S. EPA benchmarks which are used to protect human and wildlife health. Among the 1,064 fish samples analyzed for THg across all sites, 14.5% of fish exceeded U.S. EPA wildlife critical value for protecting piscivorous birds and mammals ($\geq 163 \mu\text{g}/\text{kg}$ wet weight; [36]) and 3.1% exceeded U.S. EPA screening value for fish muscle concentrations affecting human health (300 $\mu\text{g}/\text{kg}$ wet weight; [41]). Although the relatively large percentage of fish that exceed the U.S. EPA piscivorous wildlife benchmark is a concern for wildlife in the basin, the low incidence of fish exceeding U.S. EPA human health benchmarks is not surprising given that we did not sample large-bodied piscivorous fish which humans tend to consume. Previous studies have examined Hg concentrations in the lower Rio Grande aquatic communities [14,15,17,18] and, in general, the fish THg concentrations we report are similar to these other studies. Schmitt et al. [19] performed a survey of contaminant concentrations in the Rio Grande and found that Hg concentrations in common carp (*Cyprinus carpio*), basses (*Micropterus* spp.), and catfish (*Ictalurus* spp.) frequently exceeded the U.S. EPA wildlife critical value. Mercury concentrations in large predatory fish (flathead catfish, *Pylodictis olivaris*) and shiners (*Cyprinella* spp.) were relatively high (i.e., flathead catfish Hg $\approx 600 \mu\text{g}/\text{kg}$) in the Big Bend reach [17,18]. In the present study, we focused on smaller-bodied fish, most of which are not utilized by humans as a food source; however, we also captured two piscivorous longnose gar (*Lepisosteus osseus*) at Santa Elena Canyon (506 mm and 540 mm total length) and fillet Hg concentrations of these two fish were much greater than the U.S. EPA screening value for human health (1038.7 and 1109.7 $\mu\text{g}/\text{kg}$ wet weight, respectively). Previous studies have also collected a small number of large-bodied piscivores (longnose gar and flathead catfish) from the Big Bend region that exceed U.S. EPA screening value for human health [18]. Thus, it is likely that piscivorous fish in the Big Bend reach have Hg concentrations above the U.S. EPA screening value for human health; however, a focused effort to collect fish of this trophic group is required before any conclusion can be drawn about this prediction.

The present study additionally focused sampling efforts on small-bodied riverine fish because a large percentage of these taxa are at risk in the Rio Grande drainage; of the species that were collected, 16% are designated as endangered, imperiled, or at risk [13]. Although fish Hg concentrations were below known tissue burden concentrations that cause acute effects on growth and reproduction (6,000 to 20,000 $\mu\text{g}/\text{kg}$ fillet wet weight) [5],

muscle tissue Hg burdens of fish from multiple sites are high enough to be associated with the effects of chronic, nonlethal Hg exposure. For example, decreased spawning success in several species of freshwater fish has been observed at relatively low concentrations of Hg; mercury burdens of approximately 600 $\mu\text{g}/\text{kg}$ wet weight and tissue concentrations of as low as 90 $\mu\text{g}/\text{kg}$ wet weight can lead to suppression of sex hormone production [5]. The results of the present study are consistent with other studies of the Rio Grande and show that fish frequently exceed U.S. EPA wildlife critical value. Of the sites sampled for this study, <1% of fish had fillet Hg burdens greater than 600 $\mu\text{g}/\text{kg}$, and 44% had burdens greater than 90 $\mu\text{g}/\text{kg}$ wet weight. In particular, the Big Bend area had the highest incidence of fish Hg concentrations that exceeded these concentrations (<1% and 73%, respectively). Despite the high probability that a portion of the fish community at some sites experience some level of chronic Hg exposure effects, the population- and community-level implications of Hg burdens of these magnitudes remains unknown. These concentrations are particularly troubling given recent river restoration efforts in the Big Bend region, which include the reintroduction of the extirpated Rio Grande silvery minnow (*Hybognathus amarus*).

CONCLUSION

The present study shows spatial variation in fish Hg across the lower Rio Grande drainage, and that fish Hg concentrations are related to specific environmental variables. Understanding how environmental gradients affect Hg bioaccumulation in food webs is critical for predicting and managing wildlife populations and protecting human health [7], and the present study represents one of the first efforts to relate Hg concentrations in riverine fish communities to regional variation in environmental factors that affect Hg bioaccumulation. To date, studies of spatial patterns of Hg concentrations in riverine fish have had limited success using environmental variables to predict fish Hg, because the scale of observation was too coarse to detect the influence of factors that may play a role in fish Hg concentrations in a given system [7]. We confined the scale of the present study to a single relatively large drainage and detected strong influences of environmental variables which are known to affect bioaccumulation of Hg in fish. Future studies of Hg dynamics in the Rio Grande/Rio Bravo Del Norte drainage should focus efforts on sampling larger piscivorous fish, assessment of temporal patterns of Hg concentrations in sediments and the biota, and the identification of locations within sites where MeHg production occurs.

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