MERCURY CONTAMINATION OF THE RIO GRANDE FISH COMMUNITY: SPATIAL VARIATION AND INFLUENCE OF ENVIRONMENTAL GRADIENTS

THESIS

Presented to the Graduate Council
of Texas State University-San Marcos
in Partial Fulfillment
of the Requirements

for the Degree

Master of SCIENCE

by

Alexandra Smith, B.S.

San Marcos, Texas
May 2009

ACKNOWLEDGEMENTS

I would like to thank my major advisor, Dr. Weston Nowlin, and committee members, Dr. Matthew Chumchal, Dr. Timothy Bonner and Dr. Chris Nice, for all of the hard work put into making this project successful and fulfilling. I never could have done this without them. I would also like to thank my lab mates and friends who helped me with field work: Alisa Abuzeineh, Brad Caston, Corey Pray, Pete Diaz, Jesse Becker, and Susanna Scott. I would like to thank Tom Heard and Josh Perkin for their help with identifying fish. Funding for this project was provided by the U.S. Department of Agriculture through the Sustainable Agricultural Water Conservation (SAWC) research programs established by Congress in 2004.

This manuscript was submitted on January 6, 2009.

TABLE OF CONTENTS

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

ABSTRACT

MERCURY CONTAMINATION OF THE RIO GRANDE FISH COMMUNITY: SPATIAL VARIATION AND INFLUENCE OF ENVIRONMENTAL GRADIENTS

by

Alexandra Smith, B.S.

Texas State University-San Marcos

May 2009

SUPERVISING PROFESSOR: DR. WESTON H. NOWLIN

Mercury (Hg) contamination of aquatic ecosystems is a global environmental problem and high levels of Hg can cause adverse health effects in humans and wildlife. Organisms at the base of the food web absorb methylmercury (MeHg) and this highly toxic and bioaccumulative form is passed onto fish and humans through their diets. While there is abundant data on Hg contamination and factors that affect Hg bioaccumulation in lake food webs, there is comparatively little data on large river systems. This thesis examines Hg concentrations of fish from the Lower Rio Grande drainage, Texas and several of its major tributaries in order to assess: (1) the overall level Hg contamination and potential risk to piscivorous organisms, (2) whether there is spatial variation in Hg

concentrations in fishes of the lower Rio Grande drainage, and (3) if patterns of Hg contamination of Rio Grande fishes are related to abiotic and/or biotic factors that vary among sites (i.e., dissolved organic carbon (DOC), organic matter in sediments (%OM), and sulfates). We sampled fish at 15 sites from the Big Bend reach to the lower Rio Grande Valley and found that 52% of small-bodied trophic level 3+ fish had Hg concentrations exceeded EPA Wildlife Criteria ($\geq$77 ppb). However, there was significant spatial variation in fish Hg concentrations with the highest concentrations found in the Big Bend reach. Principal Components Analysis revealed that fish Hg were positively related to river DOC, sediment total Hg, and sediment MeHg. Previous studies indicate that these factors are known to facilitate bacterial production of MeHg and its bioaccumulation. I hypothesize that high levels of inorganic Hg inputs to the Big Bend reach, such as runoff from abandoned cinnabar mines, Hg-rich rock formations, and atmospheric deposition from coal burning power plants in Mexico exacerbate Hg contamination of the fish community.

1. INTRODUCTION

Mercury (Hg) contamination of aquatic ecosystems is a widespread environmental problem in North America and the world (Driscoll et al. 2007, Harris et al. 2007). As of 2007, more than 2000 U.S. lakes and rivers have had advisories issued for Hg contamination and 48 states have issued fish consumption advisories due to elevated concentrations of Hg in fish (USEPA 2007). Mercury contamination of aquatic ecosystems can result from natural sources, such as volcanoes (Schierow 2004), and from anthropogenic sources, such as industrial discharge, atmospheric emissions, and mining activities; the most common anthropogenic source of Hg is coal burning power plant emissions (Eisler 1987, Gray 2003). High levels of Hg, especially its organic form (methylmercury, MeHg) can cause adverse health effects (Fitzgerald and Clarkson 1991, Gray 2003) and even death (Eisler 1987, USEPA 1997).

Mercury released from anthropogenic and natural sources is predominantly in inorganic form [Hg (II)] (Driscoll et al. 2007, Evers et al. 2007). Once deposited in aquatic environments, microorganisms such as sulfate reducing bacteria (SRB) convert inorganic Hg (II) into methylmercury (MeHg, Gilmour et al. 1992). Ingestion of MeHg contaminated food items is often the main pathway for MeHg uptake (Hall et al. 1997) and it is typically consumed at a faster rate than it can be removed from tissues, leading to MeHg tissue bioaccumulation (Morel et al. 1998, Watras et al. 1998, Schierow et al. 2004, Klinck et al. 2005). Therefore, large predatory fish, and piscivorous birds and

mammals (including humans) at the top of aquatic and aquatic-linked terrestrial food webs can accumulate high MeHg concentrations in tissues (Driscoll et al. 2007). In wildlife, high MeHg burdens are associated with acute effects on growth and survival (Scheuhammer et al. 2007); however, moderate and commonly observed Hg body burdens have substantial sub-lethal effects, leading to reduced fecundity and altered behavior (Scheuhammer et al. 2007).

Hg contamination and cycling in lake and wetland ecosystems has been a major focus of Hg ecotoxicology for many years (Hall et al. 1998, Bodaly et al. 1999, Cizdziel et al. 2003, Chen et al. 2005), but Hg contamination of river and stream ecosystems has received comparatively less attention (Paller and Littrell 2007, Peterson et al. 2007, Rypel et al. 2008). It is generally thought that factors similar to those considered to affect Hg accumulation in lakes also influence Hg in riverine biota, including watershed characteristics (i.e., percent wetlands, soil type), local and regional hydrology, precipitation and atmospheric Hg deposition patterns, and the concentration of chemicals constituents that affect MeHg production such as dissolved organic carbon (DOC) and sulfates (Shanley et al. 2005, Peterson et al. 2007, Rypel et al. 2008). Riverine networks offer unique opportunities to examine the role of factors that affect Hg accumulation because they can span climatic and physiographic gradients that can have substantial effects on Hg methylation and Hg levels in biota (Schmitt 2005, Franssen 2006). However, a recent assessment of Hg in lotic fishes throughout the western US found that fish Hg levels were not consistently related to environmental variables thought to affect

Hg accumulation (Peterson et al. 2007). Thus, our understanding of factors affecting Hg dynamics and bioaccumulation in riverine ecosystems requires further evaluation and understanding.

The Rio Grande/Rio Bravo del Norte drainage in southwestern USA is a large, complex river system that spans more than 3000 km, from the San Juan Mountains of Colorado to the Gulf of Mexico in Texas, encompassing ~290,000 km^2 (USGS 1998) and serving as the US – Mexico border along the states of Texas in the US and Chihuahua, Coahuila, Nuevo Leon, and Tamaulipas of Mexico (Fig. 1). The lower portion of the Rio Grande drainage from the city of El Paso, Texas to the Gulf of Mexico is an ecologically important area, containing 32 federally- and state-listed imperiled fish taxa (Bender 2005, Hubbs 2008) and serves as habitat for many aquatic and semi-aquatic birds (National Geographic Society 1987, Post 1998). Whereas the Rio Grande drainage has high ecological value, it is highly perturbed by anthropogenic activities; contaminants represent a substantial threat to the river and its biota (Lee and Wilson 1997, Van Metre et al. 1997, Mora et al. 2002, Mora et al. 2006, Mora et al. 2007).

Hg contamination represents a mounting concern for the Rio Grande and its biota; however, information on the degree of Hg contamination of the Rio Grande aquatic food web is limited. Hg concentrations in river sediments in some portions of the drainage are relatively high (>50 ppb) and sediment Hg in many areas is increasing (Lee and Wilson 1997, Van Metre et al. 1997). In concurrence with indication of elevated sediment Hg, multiple wildlife taxa associated with the river are contaminated (Mora et al. 2002,

Schmitt et al. 2005, Mora et al. 2007). Several surveys of fishes in the Lower Rio Grande drainage found that many piscivorous fishes exceed EPA wildlife criteria thresholds (≥77 ppb wet tissue mass) and multiple physiological biomarkers were consistent with chronic contaminant exposure (Eisler 1987, Schmitt et al. 2005).

The purpose of this study was to examine spatial variation in Hg concentration of fishes of the lower Rio Grande and several of its US tributaries and assess the role of local environmental conditions that can affect Hg methylation and bioaccumulation of Hg in fishes (i.e., Hg in sediments, DOC, sulfate (SO_4^{2-}), and sediment percent organic matter (% OM) (Gilmour et al. 1992, Wiener et al. 2003, Harris et al. 2007). I also examine relationship between Hg levels in fishes within the Lower Rio Grande drainage and their trophic guild (TG) and trophic level (TL). The following questions were addressed: (1) Do Hg concentrations exist in fishes of the Lower Rio Grande high enough to pose a threat to fish, wildlife, and human health? (2) Are there spatial differences in Hg levels in fishes from sites throughout the drainage when fishes of the same trophic guild (TG) or the same trophic level (TL) are compared? (3) Are spatial patterns of Hg levels in fishes related to abiotic and/or biotic factors known to affect Hg accumulation in aquatic food webs? Here, I also focused my fish collection efforts on sampling smaller bodied non-piscivorous fishes of the community. I 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 (Bloom 1992, Schmitt et al. 2005, Hubbs et al.

2008, Marrugo-Negrete et al. 2008). Understanding relationships between fish Hg concentrations, trophic relationships of fishes, and environmental gradients thought to affect Hg methylation and biomagnification will provide insight to the effective conservation and management of fish and piscivorous wildlife taxa, as well as the protection of human health in this complex, important, and relatively understudied drainage.

2. MATERIALS AND METHODS

2.1 Overall plan

Fish communities, sediments, and other environmental variables were sampled seasonally from sites distributed throughout the lower Rio Grande drainage from Summer 2006 – Winter 2007, with each site sampled from two to five times over the study interval (Table 1). Six sites along the mainstem of Rio Grande River were sampled: (1) at the Contrabando Creek confluence near the city of Lajitas [~6 km west of Big Bend National Park (BBNP)], (2) at Santa Elena Canyon within BBNP, (3) at Hot Springs in BBNP, (4) at Quemado below Amistad Reservoir, (5) at San Ygnacio above Falcon Reservoir, and (6) at the city of Roma below Falcon Reservoir (~290 river km from the confluence with the Gulf of Mexico). In addition, several the lower Rio Grande tributaries were sampled: (1) one site on the mainstem of the Pecos River near Sheffield, (2) two sites along Independence Creek near the town of Sheffield, (3) one site at Tornillo Creek in BBNP, (4) three sites along Terlingua Creek in BBNP, and (5) one location on Dolan Creek at the Devil's River near Dolan Falls (Fig. 1, Table 1). These sites were selected because they are mostly perennially-flowing sites in this arid and semi-arid landscape and they encompass a range in environmental conditions. Sites in the Big Bend region in the mainstem of the Rio Grande and Terlingua and Tornillo Creeks were selected because areas of the Big Bend region are geologically rich in Hg and several abandoned mercury mines are present in and around the city of Terlingua

(Sharp 1980, Avery et al. 1996, Gray et al. 2006). Independence and Dolan Creeks were selected because they are predominantly spring fed streams and are in protected areas with little direct human impact.

2.2 Determination of Fish Mercury Concentrations

Fish were collected at each site using hand nets and seines. These sampling techniques were selected for multiple reasons: my study focused on Hg in small-bodied fishes and seining is an effective collection method for these taxa, and specific conductance at many of the sampling sites is relatively high (>2000 $\mu S\ cm^{-1}$), preventing effective use of electrofishing as a capture technique. After collection, fish were anesthetized with MS-222 and preserved in 70% ethanol. In the field, jars containing preserved fish were kept on ice in coolers and transported to Texas State University-San Marcos. Once in the laboratory, fillet muscle (mostly apaxial muscle) was removed from individual fish, dried at 60°C for 48 hours, homogenized with a thoroughly cleaned mortar and pestle, and analyzed for total Hg (THg) with a direct mercury analyzer (DMA-80, Milestone, Inc., Monroe, Connecticut) that uses thermal decomposition, gold amalgamation, and atomic absorption spectrometry (USEPA 1998). Concentrations are reported as μg THg/kg wet weight (ww) of fish. Because more than 90% THg in fish muscle is MeHg (Bloom 1992, Weiner et al. 2003, Paller and Littrell 2007), measurement of THg is a suitable estimate of MeHg in fish fillets. Individual fish too small to yield adequate fillet material for analysis were dried whole and homogenized and a published

regression equation was used to estimate THg in whole fish (Peterson et al. 2007). A subset of fish samples analyzed for THg was also analyzed for stable isotopes of nitrogen and carbon (see below).

For each fish Hg analysis run, a calibration curve was generated using three reference materials from the Institute for National Measurement Standards (National Research Council of Canada): MESS-3 (marine sediment, certified value 91 ± 9 ng mercury/g DW (average ± 95% confidence interval [CI]), PACS-2 (marine sediment, certified value = 3,040 ± 200 ng mercury/g DW), and DORM-2 (dogfish *Squalus* spp. muscle, certified value = 4,640 ± 260 ng mercury/g DW). Quality assurance included reference and duplicate samples. At approximately every 10th sample during mercury analyses, reference samples of MESS-3 or DORM-2 were analyzed and the mean percent recovery was 100 ± 1% (range = 92–107%, n = 41) and 100 ± 2% (range = 95–104%, n = 11), respectively. Duplicate samples were analyzed at approximately every 20th sample, and the mean relative percent difference was 7.85% (range = 0.3–11.4%, n = 28). THg concentrations in fishes were explicitly compared to EPA human consumption thresholds (EPA HC = 300 µg/kg wet tissue mass) and EPA criteria for piscivorous wildlife (EPA WC ≥77 µg/kg wet tissue mass, USEPA 1997, McClain et. al. 2006). I analyzed, on average, 107 fish samples for THg at each site.

2.3 Determination of Fish Trophic Guild and Trophic Position

Variation in Hg content among fishes is often a reflection of the primary food sources and trophic position in a food web (Power and Dietrich 2002, McIntyre and Beauchamp 2007, Chumchal et al. 2008) and one of the primary goals of my study is to determine whether Hg of trophically-similar fishes differs between sites along the Rio Grande drainage. Thus, in order to assess how Hg content varied among trophically-similar fishes among sites I determined trophic ecology of the various fishes using two methods. First, I grouped fish together into trophic guilds (TGs) based on literature-defined feeding ecologies (Simon 1998, Table 2). Previous studies also use trophic guilds to compare differences in levels of Hg among fish collected at the same site or at different sites (Chen et al. 2005, Paller and Littrell 2007, Peterson et al. 2007). For this study, fish were categorized into three TGs: Herbivore/Benthivore/Omnivore (H/B/O), Invertivore (INV), and Invertivore/Piscivore (INV/P). Herbivorous, omnivorous and benthivorous fishes were grouped into a single trophic guild for this study because these guilds often exhibit substantial dietary overlap (Anderson 1976, Parker and Voshell 1983, Haroon 1998, Plague et al. 1998, Anderson and Cabana 2007) and sample sizes at some sites for these individual guilds was occasionally small.

I additionally determined the trophic position of fishes via stable isotope analysis (SIA). This analysis allowed me to compare Hg concentration in fishes (regardless of species) from different sites that are within the same trophic level. To estimate trophic position of fishes at the various sites, stream algae and invertebrates were collected and

analyzed for $\delta^{15}N$ and $\delta^{13}C$ so that site-specific food webs were created (Anderson and Cabana 2007). $\delta^{15}N$ values are used to estimate trophic position, while $\delta^{13}C$ can be used to estimate the food source of organisms when the isotopic signature of food sources differ (Minagawa and Wada 1984, Post 2002, Anderson and Cabana 2007).

At each site on each sampling date, periphyton, macroinvertebrates, and fishes were collected for SIA. For periphyton analyses, microalgae collected from relatively slow (e.g., runs) and fast-flowing (e.g., riffle) habitats at each site. Duplicate samples of microalgae were collected from each habitat type as a composite from several rocks from the habitat type. Rocks were scrubbed with a clean nylon brush, rinsed into acid-washed high density polyethylene (HDPE) centrifuge tubes with Milli-Q water, placed into a cooler, and transported to the laboratory at Texas State. Macroinvertebrates were collected from fast and slow-flowing habitats with a combination of Hess samples, kick-netting, and hand-picking, placed into plastic bags with stream water, kept for ~2 h to allow gut content passage, and preserved in 70% EtOH. On average, 47 fish were analyzed at each site for both THg and stable isotopes.

Algae samples were filtered onto pre-combusted glass fiber filters (Whatman GF/F). Filters were dried at 60°C in an oven for 48 h. Many of the sites are spring-fed and are part of limestone-dominated aquifers (Dolan Creek, Pinto Creek, Independence Creek) or have substantial aqueous calcium carbonate concentrations, thus I placed dried microalgae filters in a fuming HCl chamber for 24 h to remove inorganic carbon that affects algal ^{13}C:^{12}C ratios (W.H. Nowlin, unpublished data). Macroinvertebrate samples

were sorted into taxonomic groups (largely to family) and rinsed with Milli-Q to remove attached organic matter. Prior to drying, foot regions were removed from gastropods with a clean scalpel and larger invertebrates (Odonata, large Hemiptera, Megaloptera) had guts removed. 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. Material from taxa that contained adequate mass for SIA after drying (~2 mg) was prepared. Fish fillet muscle was removed from individual fish, dried at 60°C for 48 hours, homogenized with a thoroughly cleaned mortar and pestle.

All samples were packaged in tin capsules and sent to University of California-Davis Stable Isotope Laboratory for analysis. Samples were analyzed for $\delta^{13}C$ and $\delta^{15}N$ and duplicates were run approximately every 10-20 samples with a mean standard error of <0.10‰. All stable isotope values are reported with δ notation, where $\delta^{13}C$ and $\delta^{15}N$ values are equivalent to $([R_{SAMPLE}/R_{STANDARD}] - 1) * 1000$, where R is the $^{13}C:^{12}C$ or the $^{15}N:^{14}N$ of the sample and standards. The universal standards PeeDee Belemnite ($\delta^{13}C$) and atmospheric N ($\delta^{15}N$) were used.

$\delta^{15}N$ values were used to estimate trophic position of all invertebrates and fishes, where each organism is considered ~1 trophic position above its direct prey. $\delta^{15}N$ values of consumers become enriched with each trophic transfer, thus $\delta^{15}N$ can be used to estimate trophic position of consumers (Post 2002). Because algal $\delta^{15}N$ values can be highly variable in space and time, I used an approach in which the organism with the

lowest $\delta^{15}N$ value in the community was designated as the baseline consumer with a trophic position = 2 (Post 2002, Anderson and Cabana 2007). The $\delta^{15}N$ of the baseline organism was subsequently used to estimate trophic position for all other invertebrate and vertebrate consumers in the food web using the equation:

$$\text{Trophic position}_{\text{Consumer}} = ([\delta^{15}N_{\text{Consumer}} - \delta^{15}N_{\text{Baseline}}]/f) + 2$$

Where, $\delta^{15}N_{\text{Consumer}}$ is the $\delta^{15}N$ value for consumer for which trophic position is estimated, $\delta^{15}N_{\text{Baseline}}$ is the $\delta^{15}N$ value of baseline organism, 2 is the expected trophic position of the organism used to estimate baseline $\delta^{15}N$, and f is the $\delta^{15}N$ fractionation factor expected between a predator and its direct prey (3.4‰, Post 2002, Anderson and Cabana 2007). Trophic position of each consumer in the food web was determined by standardizing each site with a site-specific $\delta^{15}N$ "baseline" organism (Anderson and Cabana 2007) which was established by determining the consumer that exhibits the lowest $\delta^{15}N$ values at that site on a specific date. In this study, "base line" organisms at each site were found to be invertebrates mostly consisting of the following groups: Naucoridae, Psephenidae, Leptophlebiidae, and Baetidae. Using $\delta^{15}N$-inferred trophic positions for each fish, fishes 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+).

2.4 Site-Specific Environmental Conditions

Environmental conditions were assessed on each sampling date at each site. Water temperature, dissolved oxygen (mg/L), specific conductance (μS/cm), and salinity (ppt) at each site was determined with a YSI model 85 or 650 MDS sonde. To analyze concentration of DOC and SO_4^{3-}, nitrate (NO_3^-), and phosphate (PO_4^{3-}) water was collected at each site as triplicate "grab" samples in clean opaque high-density polyethylene (HDPE) bottles, stored in a cooler on ice and transported to Texas State. Water for DOC, SO_4^{3-}, NO_3^-, and PO_4^{3-} analyses was filtered through ashed Whatman GF/Fs and was analyzed within 2 days of collection (DOC and SO_4^{3-}) or was acid-preserved for later analysis (NO_3^- and PO_4^{3-}). DOC and SO_4^{3-} were determined on a Shimadzu TOC-V_{CSH} Analyzer and a Lachat FIA Quickchem Autoanalyzer, respectively. PO_4^{3-} was measured as soluble reactive phosphorus (SRP) using the molybdenum blue method (Wetzel and Likens 2000) on a Varian Cary 50 UV-Vis spectrophotometer. NO_3^- was determined with second derivative UV spectroscopy (Crumpton et al. 1992).

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 3 to 4 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 ~5 cm of underlying sediment was collected so that mostly anoxic, reduced sediments were collected. Sediments from each of the 3 – 4 locations in each replicate sample was combined in an acid-washed HDPE tub and thoroughly mixed. Sediment

samples for THg and MeHg were immediately placed into acid washed glass bottles with Teflon-lined caps. Sediments for THg and MeHg were handled using clean techniques and bottles were double bagged. The remaining sediments were placed into large (50 mL) acid-washed HDPE screw cap test tubes for determination of %OM and the carbon (C) and nitrogen (N) content. All sediment samples were kept on ice in a cooler and transported to Texas State. Sediments for Hg analyses were stored at -80°C until they were freeze dried with a Labconco Freeze Dry System – Freezone 6, and THg was determined with a Milestone DMA-80 using the same methods as for fish samples and MeHg was determined with EPA method 1630 (DeWild et al. 2004). Sediment % OM was determined via loss-on-ignition (Robertson and Taylor 2007). Sediment C and N content, and C:N (molar) ratios were determined on a CE Elantech CN Soil Analyzer.

2.5 Data Analysis

In order to determine if Hg content of fishes within the same TG and TL fishes differed between sites in the Rio Grande drainage, I compared Hg in fishes across sites from each TG (H/B/O, INV, and INV/P) and each TL (TL2, TL3, and TL4+) among sites using one-way analysis of variance (ANOVA). Prior to analyses, fish Hg from three sites along the mainstem of the Rio Grande in the Big Bend Area were combined (Contrabando, Santa Elena, and Hot Springs) because I was mainly interested in broad-scale patterns in the potential spatial differences in fish Hg concentrations and these three sites spanned ~70 km, a much shorter distance than the intervals between the remaining

Rio Grande mainstem sites (Fig. 1). I also combined fish Hg data from the three sites along Terlingua Creek, and the two sites along Independence Creek. Again, multiple sites along these tributaries were combined because they were in relatively close proximity and I was interested in assessing broad-scale differences within the drainage. Combining the Big Bend mainstem sites, the three Terlingua Creek sites, and the two Independence Creek sites, yielded a total of 10 sites for analyses. Site was used as the independent variable (factor) and the Hg concentration of fishes 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 homoscedacticity. Significance (α) was set at $p \leq 0.05$, but because multiple comparisons were made I used a sequential Bonferroni procedure to adjust α (Rice 1989, Moran 2003) in which I ranked response variable p-values from least to greatest and compared the lowest p-value to α/j, where j 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. I compared greater p-values progressively to $j - 1, j - 2$, 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 fishes were related to environmental factors that can affect Hg accumulation in fishes, I first used principal

components analysis (PCA) to summarize variation in environmental factors among the 15 sites in the Rio Grande 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) were z-score transformed (Krebs 1999). I did not include specific conductance, pH, temperature or dissolved oxygen (DO) in the PCA because I wanted to avoid an inverted matrix in the PCA (McCune et al. 2002). Thus, I eliminated some variables prior to analyses. DO was always >5 mg/L and pH was always circumneutral (~7) across all sites. I did not include specific conductance because it was not consistently recorded at all sites due to issues with the YSI Sonde and temperature was not utilized because I was not interested in examining seasonality in this study. To examine if Hg in fishes of the various TGs and TLs were related to the variation among sites in environmental parameters, I regressed the mean Hg of each group of fishes at each site as a function of the PCA axis scores for each site using ordinary least squares (OLS) linear regression. PCA axis scores (PCA I, II, and III) represent a linear combination of environmental variables for each site, thus this analysis allows me to examine the cumulative influence of environmental factors expressed along each PCA axis on Hg in fishes. Again, I used a sequential Bonferroni procedure to adjust α. All analyses were performed using SPSS version 15.0.

3. RESULTS

3.1 Spatial Variation in Hg Content of Rio Grande Fishes

When THg of fishes among the ten sites was examined, there was a significant effect of site (ANOVA, $p \leq 0.005$, Table 3) across all TGs (Fig. 2a, Table 4). In general, mean Hg of all TGs at Big Bend area sites exhibited the highest Hg content (Table 5). Mean H/B/O Hg levels exceeded EPA WC at two sites; mean (± SE) H/B/O Hg in content in the Big Bend mainstem (BBMS) and Terlingua Creek sites were 105.5 ± 23.0 µg/kg and 110.2 ± 13.5 µg/kg, respectively. Mean INV Hg content exceeded EPA WC at six sites: BBMS, Terlingua Creek, Tornillo Creek, Pecos, Pinto Creek, and San Ygnacio. Mean INV/P Hg content exceeded EPA WC at every site where fish within this TG were captured (e.g., no INV/P were captured at Roma). Tornillo Creek was the only site in which fish Hg levels exceeded EPA human consumption criteria (INV/P Hg = 387.4 ± 100.0 µg/kg), but INV/P Hg at other sites within the Big Bend reach were also relatively high (BBMS = 263.8 ± 57.6 µg/kg, Terlingua Creek = 278.8 ± 80.5 µg/kg).

There was a significant overall difference between sites in Hg content of fishes within stable isotope-defined TLs (Fig. 2b, Table 3, 4). As observed in the results for Hg content of TGs, the sites with the highest Hg in fish tissues were located within the Big Bend reach of the Rio Grande. Fishes within TL2 (e.g., herbivores) were found at only five sites, but TL2 fish at Terlingua Creek exceeded EPA WC (122.0 ± 86.2 µg/kg, Table 2). Mean Hg content of TL3 fishes exceeded EPA WC at five sites (BBMS, Terlingua

Creek, Tornillo Creek, Pinto Creek, and Quemado) and Hg levels in TL4+ fishes exceeded EPA WC at six sites: BBMS, Tornillo Creek, Terlingua Creek, and the Pecos River. Mean Hg concentration of fishes that were collected and had both stable isotope and Hg analyses performed did not exceed EPA HC Criteria at any site.

3.2 Spatial Variation in Environmental Gradients

PCA revealed substantial variation between sites along environmental gradients known to influence Hg concentrations in food webs (Fig. 3). PCA axis I explained 33% of the variation among sites and exhibited relatively large positive loadings for THg and MeHg concentration in sediments (0.46 and 0.41, respectively) and water DOC concentration (0.42), while sediment C:N ratio and NO_3^{2-} concentration had relatively large negative loadings (-0.38 and -0.36, respectively). Ordination of the fifteen sites along PCA axis I revealed that the Big Bend area Rio Grande and Terlingua Creek sites grouped together, indicating that these sites had higher sediment THg, sediment MeHg, and DOC. In contrast, the relatively undisturbed spring-fed tributary sites (Independence Creek, Dolan Creek) were clustered on the left side of axis I, and were associated with lower sediment Hg and DOC and higher NO_3^{2-} concentrations. The downstream main stem sites (Quemado, San Ygnacio and Roma) and Pinto Creek are intermediate to the Big Bend and undisturbed spring sites on PCA axis I. Interestingly, Tornillo Creek in the Big Bend area does not group with the rest of the Big Bend sites; it is ordinated in the middle region of PCA axis I.

PCA axis II explained an additional 22% of the variation among sites, with relatively high positive loadings for aqueous concentration of SO_4^{2-} and DOC (0.65 and 0.48, respectively), and negative loadings for SRP and % OM of sediments (-0.28 and -0.21, respectively). Almost all sites were distributed in the middle portion of axis II, indicating a smaller variation among sites along the variables associated with this axis. The only exception was the Pecos River site, which had relatively high SO_4^{2-} and DOC concentrations. PCA axis III explained an additional 14% of the variation among sites, with a high loading for positive loadings for SRP (0.08) and a negative loading for sediment % OM (-0.29). Again, most of the sites fall in the middle of the axis, with only the San Ygnacio site exhibiting substantial variation from the other sites because of its relatively high SRP concentration (169.4 µg/L, Table 1).

3.3 Influence of Environmental Gradients on Fish Hg Levels

Mercury concentrations of fishes in most of the TGs and TLs were a function of the environmental gradient differences expressed along PCA axis I (Fig. 4a-f, Table 6). Across all sites, mean Hg concentration of H/B/O, INV, and TL3 fishes were a positive function of PCA axis I scores ($p \leq 0.004$, Table 6), indicating that Hg concentration of these groups of fishes in the Rio Grande drainage increased with sediment THg, sediment MeHg, and DOC (Fig. 4a, b, c, and e). However, mean Hg concentration of INV/P and TL4+ fishes were not a significant function of PCA I scores (Table 6). Mean Hg concentration of H/B/O, INV, INV/P, TL3, and TL4+ fishes were not a significant

function of the PCA II and III scores ($p = 0.072$ to 0.962, respectively). I did not examine patterns of TL2 fishes in relation to the environmental gradients expressed along PCA axes because this group was only found at five sites and there was limited variation in conditions among the sites where these fishes were found.

I wanted to further explore the relationship between H/B/O, INV, and TL3 fish Hg concentrations and the various components of PCA axis I. Significant positive relationships between Hg content of these groups of fishes and PCA axis I scores provide information on the cumulative role of environmental gradients because PCA scores are a result of the linear combination of all variables along the axis. However, this analysis provides little information on the relative strengths of individual variables in predicting Hg concentration in these groups of fishes and the nature of these univariate relationships. Thus, I examined the relationship between Hg of fishes in the various TGs and TLs in relation to three variables included in PCA axis I: sediment THg, sediment MeHg, and DOC. I wanted to explore the relative strengths of sediment THg, sediment MeHg, and DOC as predictors of mean Hg in the in the various TGs and TLs (e.g., proportion of variation in Hg in fishes of the various trophic groups explained by the relationship) and the nature of the relationship between Hg in the in the various TGs and TLs and these variables (e.g., a linear, quadratic, or exponential relationship). Thus, I performed regression analyses and examined if the mean Hg of each fish trophic group was a function of the three environmental variables (DOC, sediment THg, and sediment MeHg) that are often associated with elevated Hg in fishes (Morel et al. 1998, Dennis et

al. 2005, Paller and Littrell 2007) and had high positive loadings on PCA axis I. DOC was a strong predictor of Hg in four trophic groups (Table 6): H/B/O ($r^2 = 0.73$, $p = 0.001$), INV ($r^2 = 0.61$, $p = 0.004$), INV/P ($r^2 = 0.51$, $p = 0.014$), TL3 ($r^2 = 0.62$, $p = 0.005$) and sediment THg ($r^2 = 0.72$, $p = 0.002$). Sediment THg tended to be an equally strong predictor of Hg in fishes across a number of trophic groups including H/B/O ($r^2 = 0.72$, $p = 0.002$), TL3 ($r^2 = 0.62$, $p = 0.005$), and TL4+ fishes ($r^2 = 0.47$, $p = 0.031$). In all cases where a significant relationship was detected, a unimodal (quadratic) function was the best descriptor of the relationship between fish Hg and the environmental variable (DOC or THg). Mercury in fishes across all trophic groups did not exhibit a significant relationship with sediment MeHg (Table 7).

4. DISCUSSION

4.1 Spatial Variation in Hg in Rio Grande Fishes and Sensitivity of Sites to Hg Loading

In the present study, I found Hg at detectable levels in fishes throughout the Lower Rio Grande drainage, demonstrating that Hg bioaccumulation is fairly wide spread in aquatic communities across the basin. Among the 1073 fish samples analyzed for Hg across all sites, 52% of fishes exceeded EPA Wildlife Criteria and 3% exceeded EPA Human Consumption Levels. While the large percentage of fishes that exceed EPA WC presents a concern for piscivorous wildlife in the basin, the low incidence of fishes exceeding EPA HC levels is not surprising given that I did not sample large-bodied piscivorous taxa which humans tend to consume. In addition, I found that Hg levels in fishes 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 levels. In general, the Big Bend region exhibited relatively higher Hg levels and these levels are associated with several environmental factors which are known to influence Hg methylation and biomagnificantion in food weds (Downs et al. 1998, Dennis et al. 2005, Hammerschmidt and Fitzgerald 2006).

Previous studies have examined Hg levels in the lower Rio Grande aquatic communities (IBWC 1994, Van Metre et al. 1997, Lee and Wilson 1997, IBWC 2004, Schmitt et al. 2004) and in general, the fish Hg levels I report here are similar to these other basin-level studies. Schmitt et al. (2004, 2005) performed a basin-wide survey of

contaminant levels in the Rio Grande drainage and also found that Hg levels in common carp (*Cyprinus carpio*), basses (*Micropterus* spp.), and catfishes (*Ictalurus* spp.) from throughout the basin frequently exceeded wildlife criteria. In addition, some basin-scale studies have identified the Big Bend are as an area of potentially high Hg concentrations in fishes (IBWC 1994, 2004). Hg levels in large predatory fish (flathead catfish, *Pylodictis olivaris*) and shiners (*Cyprinella* spp.) were relatively high (i.e., flathead catfish Hg ≈600 µg/kg ww) in the Big Bend reach of the Rio Grande, indicating Hg contamination of the Big Bend fish community (IBWC 2004). Thus, my results are consistent with other basin-scale studies of the Rio Grande and show that fishes frequently exceed EPA WC throughout the basin.

While the Big Bend region of the lower Rio Grande appears to contain relatively elevated Hg levels when compared to other sites within the lower Rio Grande, Big Bend Hg levels are not substantially different from mean Hg levels of fishes from throughout the western United States (Peterson et al. 2007). In a large scale study of Hg in fishes from 626 Western U.S. streams across 12 states, Peterson et al. (2007) reported a mean invertivore Hg level of 167.4 µg/kg (wet fillet weight) and a mean invertivore-piscivore Hg concentration of 256.8 µg/kg (wet fillet weight). These values are comparable to mean INV and INV/P values from all sites within the Big Bend area of the Rio Grande (INV = 141.1 µg/kg, INV/P = 306.2 µg/kg). In addition, the lower sites of the Rio Grande (Quemado, San Ygnacio, and Roma) and the spring-fed tributary sites (Dolan and Independence Creeks) have much lower mean fish Hg levels (INV = 69.3 µg/kg, INV/P =

140.8 μg/kg) when compared to the Big Bend area and the mean for the western US (Petersons et al. 2007). Thus, in the present study, Hg levels in the Big Bend area are elevated when compared to downstream sections of the drainage, but are close to the mean Hg levels reported across the western US. These findings also suggest that Hg contamination of lotic fish communities is widespread in the western US and can affect sites thought to be isolated from Hg sources (Peterson et al. 2007).

Environmental toxicologists have recently called for increased examination of the spatial distribution of Hg levels in biota within landscapes (Peterson, 2007) and the identification of so-called "biological Hg hotspots" (*sensu* Evers et al. 2007). Evers et al. (2007) 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 levels in yellow perch (*Perca flavescens*) from approximately 4000 water bodies to EPA human health criteria (HC = 300 μg/kg), Evers (2007) identified hotspots in Northeastern U.S and Southeastern Canada. In the present study I do not have an adequate number of sampling sites and the required spatial resolution of sites to detect biological Hg hotspots in lower Rio Grande drainage. However, I compared mean INV and INV/P Hg levels at sites across the Rio Grande drainage to HC criteria to identify locales that would qualify as areas of elevated Hg levels in fishes. Using EPA HC, the Big Bend region is a zone of elevated fish Hg levels in the landscape (mean INV/P = 306 μg/kg). However, if I attempt to identify areas of elevated Hg within the lower Rio Grande drainage by

utilizing established wildlife criteria levels (77 μg/kg), all 10 sites across the drainage have INV and TL3 levels >77 μg/kg. Furthermore, if Peterson et al.'s (2007) data set were compared to WC levels, much of the Western U.S. would qualify as such. Thus, identification of areas of relatively elevated Hg where piscivorous wildlife are most at risk between and within drainages using EPA WC may present difficulties when substantial amounts of Hg are present in landscapes.

In the present study spatial variation of Hg in several trophic groups of fishes throughout the lower Rio Grande drainage was related to local environmental variables, specifically concentrations of sediment Hg and DOC. Previous studies have also found that these environmental variables can influence bioaccumulation and biomagnification of Hg in fish communities (Grieb et al. 1990, Brumbaugh et al. 2001, Kamman et al. 2005). 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 levels. This is because both sediment THg and DOC co-varied across sites; sites with higher sediment THg also had higher DOC. The combination of high Hg levels in sediments and DOC in the Big Bend reach likely make many locations in this portion of the drainage "sensitive" to Hg loading (Driscoll et al. 2007, Evers et al. 2007). Relatively high Hg loading to an ecosystem alone does not necessarily lead to Hg bioaccumulation or its status as a biological hotspot; conditions within the ecosystem must be conducive to

the methylation and bioaccumulation of Hg in biota (e.g., sensitivity, Driscoll et al. 2007). 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 (Driscoll et al. 2007, Evers et al. 2007). While sensitivity criteria for river systems likely differ from lake systems, it is predicted that lakes will be sensitive to Hg loadings when DOC >4 mg/L, pH <6, ANC <100 (μeq/L), and water level fluctuations are pronounced (Driscoll et al. 2007, Evers et al. 2007). 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 I did not measure ANC in the present study. However, sites within the Big Bend reach experience substantial seasonal water level fluctuations because arid river systems experience highly variable flows (Bunn et al. 2006). I hypothesize that the Big Bend reach of the lower Rio Grande appears to be a biological hotspot because it has relatively abundant Hg sources and environmental conditions (i.e., DOC, water level fluctuation) make it sensitive to these Hg loadings.

The Big Bend sites exhibited relatively high THg sediment concentrations ($\bar{x} \pm 1$ SE = 49 ± 15 μg/kg dw) when compared to the other study sites. Areas of the Big Bend region have naturally occurring Hg in the geologic formations and numerous abandoned Hg mines sites are distributed throughout this region (Gray et al. 2006). Mine wastes at some sites in the Terlingua area exhibit high MeHg concentrations (up to 79 ng MeHg/g

sediment) and rapid Hg methylation rates (Gray et al. 2003). Levels of Hg in sediments are often reflected Hg concentrations observed in biota; however, extremely high sediment Hg levels can lead to lower than predicted Hg bioaccumulation in biota (Suchanek et al. 2000). Interestingly, the significant univariate relationships I observed between sediment THg and several groups of fishes (H/B/O, TL3, and TL4+) were unimodal in nature, but THg and MeHg levels at my most Hg-rich sites were not elevated enough to be considered highly contaminated (Suchanek et al. 2000, Eisler 2006) and it is unlikely that sediment Hg levels at some of my sites led to suppression of Hg bioaccumulation in some groups of fishes.

Dissolved organic matter is often cited as having a major influence on Hg levels in biota, but the relationship between DOC, MeHg production, and Hg bioaccumulation is complex (Ullrich et al. 2001). Microbes, including some known methylating taxa, can use DOC as an energetic source (Ullrich et al. 2001, Ekstrom et al. 2003) and there is substantial evidence of increasing MeHg levels and Hg in biota increases with DOC concentrations (Grieb et al. 1990, Chen et al. 2005). In addition, a portion of the DOC pool (i.e., fulvic and humic substances) can lead to the direct abiotic methylation of inorganic Hg (Ullrich et al. 2001). However, higher levels of DOC and/or high molecular weight DOC constituents can limit Hg bioavailability by binding MeHg. In the present study, I observed significant, strong non-linear (e.g., unimodal) relationships between DOC concentration and Hg levels in several groups of fishes (H/B/O, INV, INV/P, TL3), with fish Hg concentrations leveling off around ~3.0 mg DOC/L and the

interaction between DOC composition, methylation rates, and chemical binding processes in our study remain unknown. In addition, the Big Bend area sites generally exhibited higher in 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 landscape is typically low (Sponseller and Fisher 2006). It is possible that the relatively high DOC in these sites is autochthonously-generated (e.g., from riverine production) or from upstream point sources such as waste water discharges, but the relative roles of theses sources remains unknown at this time.

Identification of 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 (e.g., Wiener et al. 2006, Peterson et al. 2007). However, identification of locations within an individual site that contribute to the bioaccumulation of Hg in biota at may also be important for the management and restoration of Hg-contaminated ecosystems. It has been hypothesized that wetlands located in adjacent riparian or headwater areas serve as Hg sources for the main river channel because conditions within these wetlands are more favorable for microbial Hg methylation (i.e., warm temperatures, low pH, high OM, and anoxic sediments) (Paller et al. 2007). This conceptual model was developed to describe Hg dynamics in southeastern US river systems. In the present study, however, much of the lower Rio Grande drainage contains very little wetland area, especially the arid Big Bend reach.

The only sites with substantial wetland area and macrophyte development are the headwaters sections of the two spring-fed sites (Dolan and Independence Creeks), which also have some of the lowest fish Hg levels. I hypothesize that Hg dynamics in the Rio Grande differs from the conceptual models describing southeastern US rivers; in the Rio Grande and its tributaries, a majority of Hg methylation occurs within the main stream or river channel in sediment accumulating areas under reduced conditions. 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 (Schmidt 2003). These conditions may have led to an increase *in situ* Hg methylation in the main river and stream channels and subsequent bioaccumulation in the fish community.

4.2 Implications for Human and Wildlife Health

In this study I focused my attention on Hg levels in smaller-bodied riverine fishes, most of which are not utilized by humans as a food source. However, given the Hg levels of these smaller-bodied fishes at some sites and trends in Hg biomagnification in aquatic food webs, it is likely that large bodied, longer-lived piscivorous fish species exceed EPA HC at multiple sites in the Rio Grande drainage, in particular the Big Bend area. Indeed, I captured two piscivorous longnose gar (*Lepisosteus osseus*) at Santa Elena Canyon (506mm and 540 mm total length) and fillet Hg levels of these two fish were much

greater than EPA HC (1038.7 and 1109.7 μg/kg wet weight, respectively). Previous studies have also collected a small number of large-bodied piscivores from the Big Bend region that exceed EPA HC (i.e., longnose gar and flathead catfish at Santa Elena Canyon) (IBWC 2004). Thus, it is highly likely that large piscivorous fish in the Big Bend reach of the Rio Grande contain Hg levels that exceed EPA HC; however, a focused effort to collect more fish of this trophic group is required before any conclusion can be drawn about this prediction.

As stated previously, I partly 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 I collected as a part of this study, 16% are designated as endangered, imperiled, or at risk (Table 2). While fish Hg levels I observed were below known tissue burdens that cause acute effects on growth and reproduction (6000 – 20,000 μg/kg fillet ww) (Scheuhammer et al. 2007), muscle tissue Hg burdens of fishes from multiple sites are high enough to be associated with the effects of chronic, non-lethal Hg exposure. For example, decreased spawning success in several species of freshwater fishes has been observed Hg burdens of ~600 μg/kg (ww) and tissue levels of as low as 90 μg/kg (ww) can lead to suppression of sex hormone production (Webb et al. 2006, Schuehammer et al. 2007). Of the sites sampled for my study, < 1% of fishes had fillet Hg burdens greater than 600 μg/kg and 44% had burdens greater than 90 μg/kg. In particular, the Big Bend area had the highest incidence of fish Hg levels that exceeded these levels (< 1% % and

73%, respectively). Despite the high probability that a portion of the Rio Grande fish community at some sites in the drainage experience some level of chronic Hg exposure effects, the population- and community-level implications of these levels of Hg burdens remains unknown. These levels 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*) (USFWS 2007).

4.3 Summary and Conclusions

The study presented shows that there is substantial spatial variation in fish Hg across the lower Rio Grande drainage and that fish Hg levels are related to specific environmental conditions. In addition, according to Evers et al.'s (2007) definition of a biological Hg hotspot, the Big Bend Area would indeed qualify as such. Understanding how environmental gradients affect Hg bioaccumulation in food webs is critical for predicting and managing wildlife populations and protection human health (Peterson et al. 2007) and my study represents one of the first efforts to relate Hg levels in riverine fish communities to regional variation in environmental factors that affect Hg bioaccumulation. To date, studies of spatial patterns of Hg levels in riverine fishes 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 levels in a given system (Peterson et al. 2007). Here, I confined the scale of my study

to a single relatively large drainage and detected strong influences of environmental variables which are known to affect bioaccumulation of Hg in fishes. Future studies of Hg dynamics in the Rio Grande drainage should focus efforts on sampling larger piscivorous fishes, assessment of temporal patterns of Hg levels in sediments and the biota, and the location within sites that actually produce MeHg.

Table 1. Coordinates, site type (mainstem or tributary), sampling dates, and mean values of environmental variables for each site. Su = Summer, Fa = Fall, Sp = Spring, Wi = Winter. 06 = 2006, 07 = 2007.

Site	Coordinates	Site type	Sampling Dates	DOC (mg L)	SO_4 (mg L)	NO_3 (ug L)	SRP (ug L)	% OM	C:N (molar)	THg (µg kg dw)	MeHg (µg kg dw)
Contrabando	29°16'45.30" N, 103°50'31.01" W	Mainstem	Su 06 Su 07 Fa 07	3.48	485	224.86	41.09	3.35	46.32	18.96	0.073
Santa Elena Canyon	29°09'51.24" N, 103°36'35.34" W	Mainstem	Su 07 Fa 07	3.34	494	261.36	46.50	2.11	83.39	120.00	0.106
Hot Springs	29°10'38.90" N, 102°59'47.79" W	Mainstem	Su 06 Su 07 Fa 07	2.65	493	360.59	60.99	2.18	54.28	23.58	0.186
Terlingua Creek at Study Butte	29°19'37.70" N, 103°33'12.31" W	Tributary	Fa 06 Sp 07 Su 07 Fa 07	2.64	320	470.45	19.28	3.49	88.91	59.69	0.134
Terlingua Creek at Terlingua Abajo	29°11'58.18" N, 103°36'09.76" W	Tributary	Su 07 Fa 07	3.55	353	343.29	36.75	4.04	45.83	79.59	1.151
Terlingua Creek at Santa Elena Canyon	29°10'02.43" N, 103°36'44.60" W	Tributary	Fa 06 Sp 07 Su 07 Fa 07	2.73	407	291.22	0.81	2.76	97.22	29.04	0.038
Tornillo Creek	29°10'37.33" N, 103°00'02.95" W	Tributary	Fa 06 Sp 07 Su 07 Fa 07	0.49	386	378.04	4.49	1.18	30.12	8.48	0.019
Lower Independence Creek	30°27'52.68" N, 101°46'50.34" W	Tributary	Fa 06 Sp 07 Su 07 Fa 07	1.30	184	795.56	9.36	0.82	213.49	0.90	0.025
Upper Independence Creek	30°27'55.69" N, 101°49'33.06" W	Tributary	Su 06 Fa 06 Sp 07 Su 07 Fa 07	0.57	215	878.76	1.05	1.25	166.58	2.91	0.036
Pecos River	30°26'36.34" N, 101°43'04.39" W	Tributary	Su 06 Fa 06 Sp 07 Su 07 Fa 07	3.85	1340	836.09	2.52	1.74	160.70	1.68	0.059
Dolan Creek	29°53'05.16" N, 100°59'37.11" W	Tributary	Fa 06 Sp 07 Su 07 Fa 07 Wi 07	0.58	124	1406.88	36.04	2.61	110.53	6.43	0.166
Pinto Creek	29°24'10.80" N, 100°28'21.89" W	Tributary	Fa 06 Sp 07 Su 07 Fa 07 Wi 07	1.22	133	398.79	0.68	5.85	65.79	9.12	0.149
Quemado	28°56'30.22" N, 100°38'38.81" W	Mainstem	Sp 07 Su 07 Fa 07	1.08	57	231.00	32.36	1.64	133.85	19.30	0.047
San Ygnacio	27°09'56.57" N, 99°25'04.55" W	Mainstem	Sp 07 Su 07	1.27	37	760.59	166.94	2.13	40.87	13.98	0.047
Roma	26°24'06.51" N, 99°00'08.94" W	Mainstem	Fa 07 Wi 07	0.38	16	79.15	4.91	2.62	29.65	8.67	0.047

Table 2. Trophic guilds (TG) and total lengths (mean, min-max) of fishes captured in this study. TGs based upon Simon (1998).

Genus	species	Common name	Total length (mm)	Trophic Guild
Astyanax	*mexicanus*	Mexican tetra	53 (20-91)	INV/P
Campostoma	*ornatum*	Mexican stoneroller	56 (40-80)	H/B/O
Carpiodes	*carpio*	River carpsucker	43 (19-175)	H/B/O
Cichlasoma	*cyanoguttatum*	Rio Grande cichlid	31 (13-115)	H/B/O
Cyprinella	*lutrensis*	Red shiner	38 (15-133)	INV
Cyprinella	*proserpina*	Proserpine shiner	42 (17-66)	INV
Cyprinella	*venusta*	Blacktail shiner	46 (17-66)	INV
Cyprinodon	*variegatus*	Sheepshead minnow	40 (34-50)	INV
Dionda	*argentosa*	Manatial roundnose minnow	36 (28-61)	H/B/O
Dionda	*episcopa*	Roundnose minnow	43 (13-92)	H/B/O
Dorosoma	*cepedianum*	Gizzard shad	106 (90-126)	H/B/O
Dorosoma	*petenense*	Threadfin shad	42 (23-87)	INV
Etheostoma	*grahami*	Rio Grande darter	41(36-16)	INV
Fundulus	*grandis*	Gulf killifish	67 (57-88)	INV
Fundulus	*zebrinus*	Plains killifish	40 (19-70)	INV
Gambusia	*affinis*	Western Mosquitofish	32 (12-52)	INV
Ictalurus	*furcatus*	Blue catfish	46 (22-107)	H/B/O
Ictalurus	*lupus*	Headwater catfish	134 (63-237)	H/B/O
Ictalurus	*punctatus*	Channel catfish	53 (23-167)	H/B/O
Lepisosteus	*osseus*	Longnose gar	531 (506-546)	INV/P
Lepomis	*auritus*	Redbreast Sunfish	87 (71-130)	INV
Lepomis	*cyanellus*	Green sunfish	62 (49-59)	INV/P
Lepomis	*macrochirus*	Bluegill	59 (25-98)	INV
Lepomis	*megalotis*	Longear sunfish	81 (32-95)	INV
Lepomis	*microlophus*	Redear sunfish	54 (39-87)	INV
Lucania	*parva*	Rainwater killifish	54 (29-73)	INV
Menidia	*beryllina*	Inland silverside	48 (28-76)	INV
Micropterus	*salmoides*	Largemouth bass	92 (26-343)	INV
Moxostoma	*congestum*	Gray redhorse	184 (46-419)	H/B/O
Notropis	*amabilis*	Texas shiner	48 (17-65)	INV
Notropis	*braytoni*	Tamaulipas shiner	38 (24-57)	INV
Notropis	*chihuahua*	Chihuahua shiner	45 (45-45)	INV
Notropis	*stramineus*	Sand shiner	53 (46-59)	INV
Pimephales	*vigilax*	Bullhead minnow	49 (20-75)	INV
Poecilia	*latipinna*	Sailfin molly	35 (24-46)	H/B/O
Pomoxis	*nigromaculatus*	Black crappie	80 (80-80)	INV/P
Pylodictis	*olivaris*	Flathead catfish	57 (42-86)	INV

Table 3. One-way ANOVA summary statistics for the effect of site on Hg concentration of fishes in the various trophic groups.

Trophic Group	df	F	P
H B O	8, 281	25.3	< 0.001 *
INV	9, 681	37.8	< 0.001 *
INV P	8, 107	2.7	0.005 *
TL3	9, 208	6.9	< 0.001 *
TL4+	9, 251	13.6	< 0.001 *

* Significant at sequential Bonferroni adjusted α

Table 4. Results of Post Tukey HSD tests. Homogenous groups are designated with the same letter (A - F).

Site	H/B/O	INV	INV/P	TL2	TL3	TL4+
01 BBMS	A	A,B	A	-	A	A,B
02 Terlingua	A	A	A	A	A,B	A
03 Tornillo	A,B	A,B,C	A	-	A,B,C	A,B
04 Independence	B	E,F	A	A	B,C	D,E
05 Pecos	A,B	B,C,D	A	B	A,B,C	A,B,C
06 Dolan	B	D,E	A	-	C	B,C,D,E
07 Pinto	A,B	A,B,C	A	-	A,B,C	A,B
08 Quemado	B	D,E	A	A	A,B,C	C,D,E
09 San Ygnacio	-	C,D	A	-	B,C	A,B,C,D
10 Roma	B	F	A	A	C	E

Table 5. Mean (± SE) Hg levels for each fish trophic group at each site and the number of fish sampled at each site. Values are µg/kg (ww).

Site	H B O Hg Mean	INV Hg Mean	INV P Hg Mean	TP2 Hg Mean	TP3 Hg Mean	TP4+ Hg Mean
Contrabando	-	105.0 ± 21.4	265.4 ± 132.7	-	-	110.7 ± 49.5
Santa Elena Canyon	141.6 ± 63.3	129.9 ± 23.0	-	-	167.3 ± 96.6	136.8 ± 45.6
Hot Springs	96.9 ± 25.0	135.1 ± 25.5	263.4 ± 63.9	-	156.5 ± 63.9	182.9 ± 42.0
Terlingua Creek at Study Butte	103.8 ± 18.1	154.1 ± 23.5	465.6 ± 208.2	-	130.4 ± 27.2	368.1 ± 130.1
Terlingua Creek at Terlingua Abajo	137.9 ± 43.6	161.0 ± 34.3	158.9 ± 91.7	-	172.7 ± 57.6	218.2 ± 97.6
Terlingua Creek at Santa Elena Canyon	107.4 ± 21.9	163.8 ± 31.5	135.3 ± 67.7	122.0 ± 86.2	107.3 ± 35.8	183.8 ± 53.0
Tornillo Creek	65.4 ± 9.9	121.3 ± 36.6	387.4 ± 100.0	-	87.3 ± 23.3	198.5 ± 48.1
Lower Independence Creek	61.7 ± 15.0	80.9 ± 8.4	217.69 ± 62.9	-	98.5 ± 21.0	93.5 ± 17.7
Upper Independence Creek	19.8 ± 3.1	29.5 ± 3.4	-	51.0 ± 22.8	20.2 ± 6.7	56.9 ± 9.5
Pecos River	74.8 ± 11.0	110.5 ± 10.2	120.2 ± 49.1	11.3 ± 6.5	69.7 ± 10.1	145.5 ± 24.9
Dolan Creek	39.8 ± 8.3	71.7 ± 12.1	105.0 ± 27.1	-	48.6 ± 13.0	76.4 ± 12.6
Pinto Creek	69.5 ± 31.1	111.0 ± 12.9	118.0 ± 41.7	-	117.1 ± 21.0	126.5 ± 28.3
Quemado	36.3 ± 25.7	60.0 ± 8.8	191.8 ± 135.6	74.3 ± 24.8	94.9 ± 33.6	51.7 ± 16.4
San Ygnacio	-	86.5 ± 17.0	210.5 ± 105.2	-	61.9 ± 20.6	91.7 ± 41.0
Roma	35.2 ± 8.5	37.0 ± 6.9	-	39.2 ± 14.8	43.6 ± 25.2	31.3 ± 11.8

Table 6. Results of the regression of the analyses for PCA I scores and Hg content of the various trophic groups.

	PCA1				
Trophic Group	r^2	equation	df	F	P
HBO	0.71	y = 19.35x − 77.1	1, 12	27.2	< 0.001 *
INV	0.49	y = 18.4x − 103.6	1, 14	12.6	0.004 *
INV P	0.02	-	1, 14	1.3	0.281
TL3	0.64	y = 22.7x − 100.7	1, 13	21.0	0.001 *
TL4+	0.21	-	1, 13	3.1	0.101

* Significant at sequential Bonferroni adjusted α

Table 7. Regression equations for DOC, THg, and MeHg and Hg content of fishes in the various trophic groups.

Trophic Groups		Environmental Variables DOC	THg	MeHg
	r^2	0.73	0.72	0.30
H/B/0	P	0.001	0.002	0.170
	equation	$y = -7.3x^2 + 55.3x + 8.9$	$y = -0.006x^2 + 1.6x + 43.3$	-
	r^2	0.61	0.22	0.20
INV	P	0.004	0.226	0.293
	equation	$y = -14.1x^2 + 82.2x + 18.4$	-	-
	r^2	0.51	0.15	0.02
INV/P	P	0.014	0.417	0.889
	equation	$y = -0.02x^2 + 2.6x + 63.9$	-	-
	r^2	0.62	0.62	0.37
TL3	P	0.005	0.005	0.076
	equation	$y = -16.5x^2 + 93.8x + 5.7$	$y = -0.01x^2 + 2.2x + 59.3$	-
	r^2	0.31	0.47	0.10
TL4+	P	0.130	0.031	0.574
	equation	-	$y = -0.05x^2 + 6.4x + 53.7$	-

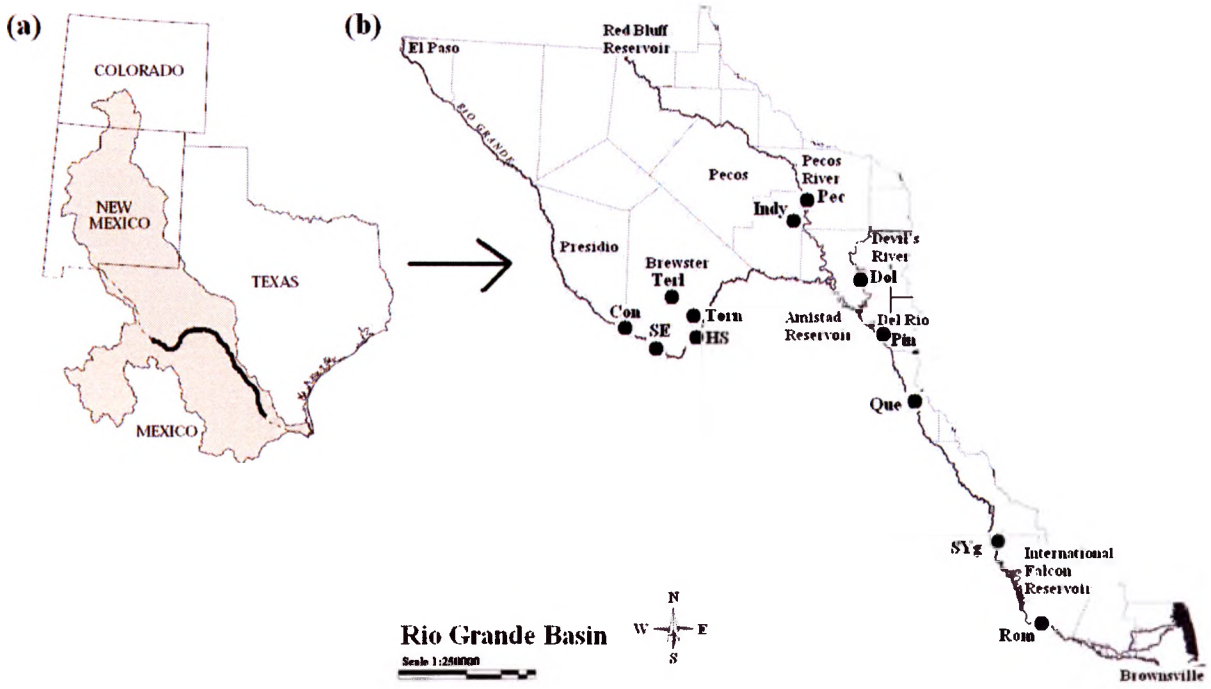

Figure 1. Map of the Rio Grande drainage and sampling sites utilized in this study. Each dot represents a site or set of sites (e.g., Terlingua and Independence Creeks). Site abbreviations are as follows: Con = Contrabando, Santa Elena = SE, Hot Springs = HS, Terlingua Creek = Terl, Tornillo Creek = Torn, Independence Creek = Indy, Pecos River = Pec, Dolan Creek = Dol, Pinto Creek = Pin, Quemado = Que, San Ygnacio = SYg, and Roma = Rom. Maps are modified from Van Metre (1997) and TNRCC (1994).

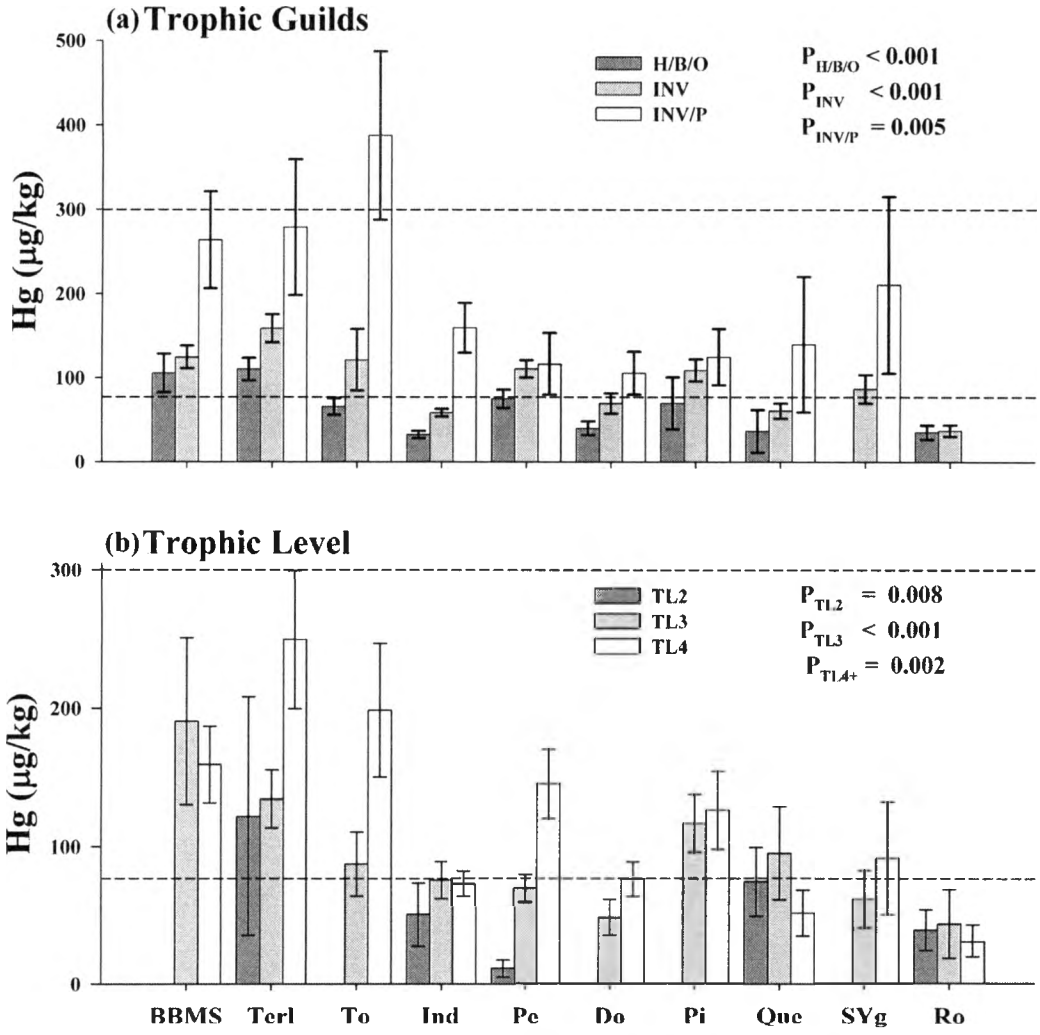

Figure 2. Mean Hg concentrations (µg/kg ww) in fish fillets at each site grouped as literature-defined trophic guilds (a) and stable-isotope defined trophic levels (b). Error bars are ± 1 SE. The dashed lines that run parallel to the x-axis denote the EPA Wildlife Criteria (77 µg/kg) and the Human Consumption Criteria (300 µg/kg). Note the difference in y-axis scales for (a) and (b).

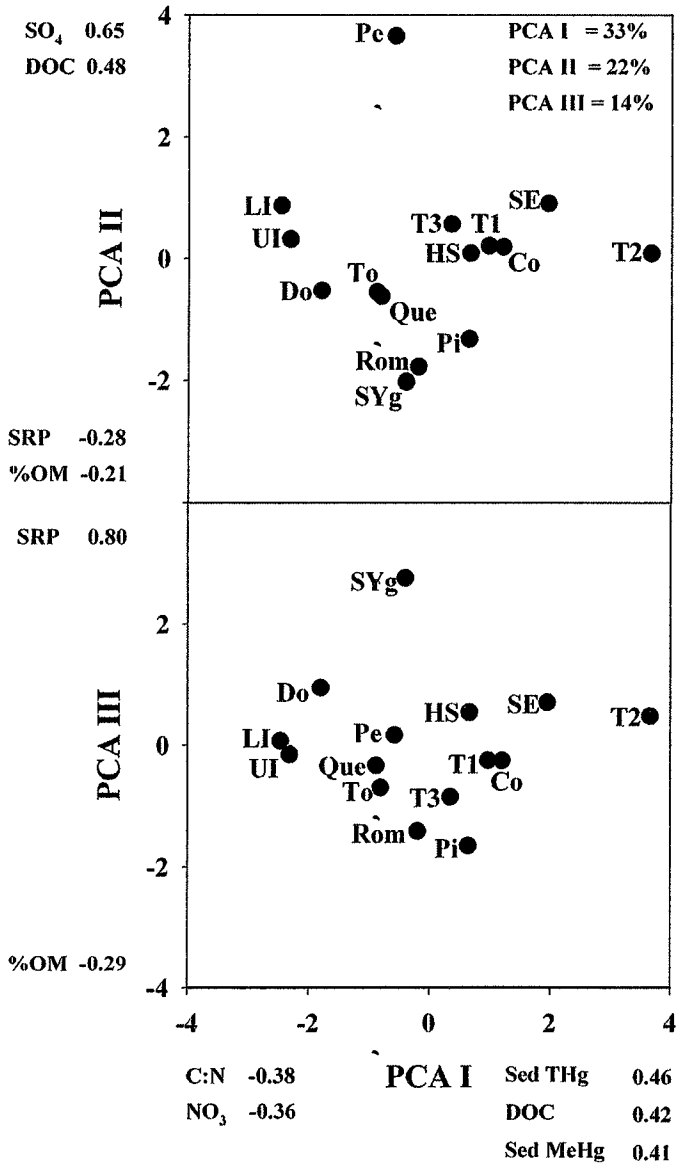

Figure 3. PCA results showing axes I, II, and III with each site denoted in multivariate space. The percent of variation among sites explained by each axis is provided as are the loadings for individual environmental variables associated with the different axes. Site abbreviations are as follows: Co = Contrabando, SE = Santa Elena Canyon, HS = Hot Springs, T1 = Terlingua Creek at Study Butte, T2 = Terlingua Creek at Terlingua Abajo, T3 = Terlingua Creek at Santa Elena Canyon, To = Tornillo Creek, LI = Lower Independence Creek, UI = Upper Independence Creek, Pe = Pecos River, Do = Dolan Creek, Pi = Pinto Creek, Que = Quemado, SYg = San Ygnacio, and Rom = Roma.

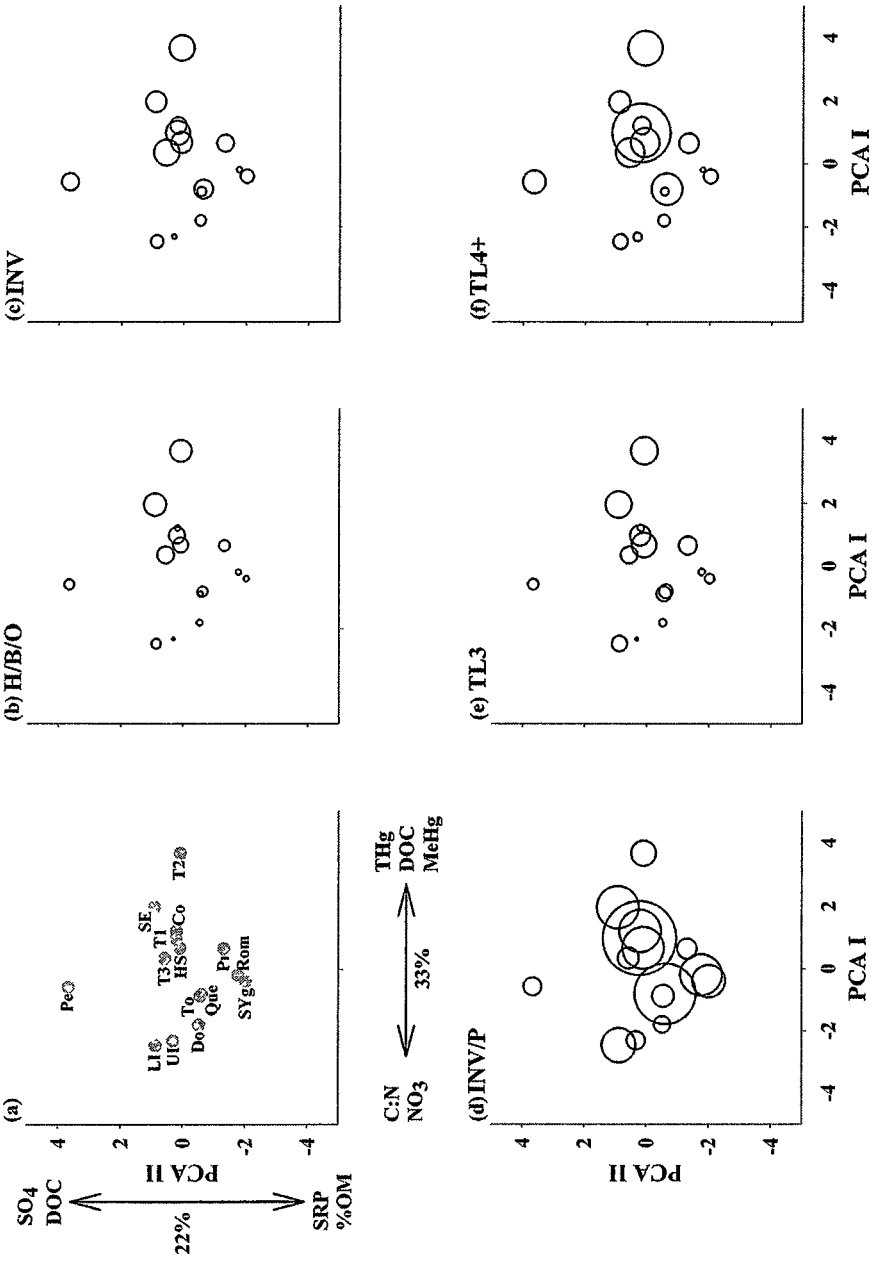

Figure 4. An overall summary of the ordination of sites in multivariate space and the individual loading variables (a), and bubble graphs of PCA axes I and II and the mean Hg of fishes within each trophic group (b – f). The size of a bubble indicates the mean fish Hg concentration of each trophic group at each site (e.g., a larger the bubble denotes a higher Hg concentration).

REFERENCES

Anderson, N.H. 1976. Carnivory by an aquatic detritivore, *Clistoronia magnifica* (Trichoptera: Limnephilidae). Ecology 57: 1081 – 1085.

Anderson, C., G. Cabana. 2007. Estimating the trophic position of aquatic consumers in river food webs using stable nitrogen isotopes. Journal of the North American Benthological Society 26(2): 273 – 285.

Avery, D.W., P.R. Moyle, R.M. Reisenburg, J.M. Fay. 1996. Preliminary assessment and site inspection, the Mariscal mine and mill site, Big Bend National Park, Brewster County, Texas. US Bureau of Mines, Site Characterization Section, E.

Bender, S., S. Shelton, K. Bender, A. Kalmbach (Eds). 2005. Texas Comprehensive Wildlife Conservation Strategy 2005-2010. Texas Parks and Wildlife Department.

Bloom, N.S. 1992. On the Chemical form of Mercury in Edible Fish and Marine Invertebrate Tissue. Canadian Journal of Fisheries and Aquatic Sciences 49(5): 1010 – 1017.

Bodaly, R.A., R.J.P Fudge. 1999. Uptake of Mercury by Fish in an Experimental Boreal Reservoir. Archives of Environmental Contamination and Toxicology 37: 103 – 109.

Bunn S.E., M.C. Thoms, S.K. Hamilton, J. Samantha. 2006. Flow variability in dryland rivers: Boom, bust and the bits in between. River Research and Applications 22(2): 179 – 186.

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

Chen, C.Y., R.S. Stemberger, N.C. Kamman, B.M. Mayes, C.L. Folt. 2005. Patterns of Hg Bioaccumulation and Transfer in Aquatic Food Webs Across Multi-Lake Studies in the Northeast US. Ecotoxicology 14: 135 – 147.

Chumchal, M.M, R.W. Drenner, B. Fry, K.D. Hambright, L.W. Newland. 2008. Habitat-Specific Differences in Mercury Concentration in a Top Predator from a Shallow Lake. Transactions of the American Fisheries Society 137: 195 – 208.

Crumpton, W.G., T.M. Isenhart, P.D. Mitchell. 1992. Nitrate and organic N analyses with second-derivative spectroscopy. Limnology and Oceanography 37: 907 – 913.

Dennis, I.F., T.A. Clair, C.T. Driscoll, N. Kamman, A. Chalmers, J. Shanley, S.A. Norton, S. Kahl. 2005. Distribution Patterns of Mercury in Lakes and Rivers of Northeastern North America. Ecotoxicology 14: 113 – 123.

DeWild, J.F., S.D. Olund, M.L. Olson, M.T. Tate. United States Geological Survey. 2004. Methods for the Preparation and Analysis of Solids and Suspended Solids for Methylmercury. USGS Techniques and Methods 5 A-7.

Downs, S.G., C.L. Macleod, J.N. Lester. 1998. Mercury in Precipitation and its Relation to Bioaccumulation in Fish: A Literature Review. Water, Air, and Soil Pollution 108: 149 – 187.

Eisler, R. 1987. Mercury Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Fish and Wildlife Service Patuxent Wildlife Research Center, Laurel, MD. Biological Report 85(1.10) April 1987 Contaminant Hazard Reviews Report No. 10.

Eisler, R. 2006. Mercury Hazards to Living Organisms. Eds. CRC Press, Taylor & Francis Group, Boca Raton, Florida. 312 pages.

Ekstrom, E.B., F.M.M. Morel, J.M. Benoit. 2003. Mercury Methylation Independent of the Acetyl-Coenzyme A Pathway in Sulfate-Reducing Bacteria. Applied and Environmental Microbiology 69(9): 5414 – 5422.

Evers, D.C., Y.J. Han, C.T. Driscoll, N.C. Kamman, M.W. Goodale, K.F. Lambert, T.M. Holsen, C.Y. Chen, T.A. Clair, T. Butler. 2007. Biological mercury hotspots in the northeastern United States and southeastern Canada. Bioscience 57(1): 29 – 43.

Fitzgerald, W.F., T.W. Clarkson. 1991, Mercury and monomethylmercury-Present and future concerns: Environmental Health Perspectives 96: 159 – 166.

Franssen, N.R., K.B. Gido. 2006. Use of Stable Isotopes to Test Literature-based Trophic Classifications of Small-bodied Stream Fishes. The American Midland Naturalist 156(1): 1 – 10.

Gilmour, C.C., E.A.Henry, R. Mitchell. 1992. Sulfate stimulation of mercury methylation in fresh-water sediments. Environmental Science and Technology 26: 2281 – 2287.

Gray, J.E., M.E. Hines, H. Biester. B.K. Lasorsa. 2003. Mercury methylation in mine wastes collected from abandoned mercury mines in the USA. *J. Phys. IV France.* 107. 573 – 576.

Gray, J.E., M.E. Hines, H. Biester. 2006. Mercury methylation influenced by areas of past mercury mining in the Terlingua district, Southwest Texas, USA. Applied Geochemistry. 21: 1940 – 1954.

Hall, B.D., D.M. Rosenberg, A.P. Wlens. 1998. Methyl mercury in aquatic insects from an experimental reservoir. Canadian Journal of Fisheries and Aquatic Sciences. 55: 2036 – 2047.

Hammerschmidt, C.R., W.F. Fitzgerald. 2006. Methylmercury cycling in sediments on the continental shelf of southern New England. Geochimica et Cosmochimica Acta 70: 918 – 930.

Haroon, A.K.Y, K.A. Pittman, G. Blom. 1998. Diel Feeding Pattern and Ration of Two Sizes of Tilapia, *Oreochromis* spp. in Pond and Paddy Field. Asian Fisheries Science 10: 281 – 301.

Harris, R.C. (editor), D.P. Krabbenhoft (editor), R. Mason (editor), M.W. Murray (editor), R. Reash (editor), T. Saltman (editor). 2007. Ecosystem Responses to Mercury Contamination: Indicators of Change. 219 pages.

Hubbs, C., R.J. Edwards, G.P. Garrett. 2008. An annotated checklist of the freshwater fishes of Texas, with keys to identification of species. Texas Journal of Science 43: 3 – 87.

International Boundary Waters Commission. 1994. Binational Study Regarding the Presence of Toxic Substances in the Rio Grande/Rio Bravo and its Tributaries Along the Boundary Portion Between the United States and Mexico. Final Report, September 1994.

International Boundary Waters Commission. 2004. Third Phase of the Binational Study Regarding the Presence of Toxic Substances in the Upper Portion of the Rio Grande/Rio Bravo Between the United States and Mexico. Final Report, June 2004.

Klinck, J., M. Dunbar, S. Brown, et al. 2005. Influence of water chemistry and natural organic matter on active and passive uptake of inorganic mercury by gills of rainbow trout (*Oncorhynchus mykiss*). Aquatic Toxicology 72(1-2): 161 – 175.

Krebs, C.J. 1999. Ecological methodology, 2nd ed. Addison-Welsey Education Pubishers, Inc., Menlo Park California. 620 pages.

Lee, R.W., J.T. Wilson. 1997. Trace elements and organic compounds associated with riverbed sediments in the Rio Grande/Rio Bravo basin, Mexico and Texas. U.S. Geological Survey Fact Sheet FS-098-97.

Marrugo-Negrete, J, J.O. Verbel, E.L. Ceballos, L.N. Benitez. 2008. Total mercury and methylmercury concentrations in fish from the Mojana region of Colombia. Environmental Geochemistry Health. 30: 21 – 30.

McClain, W.C., M.M. Chumchal, R.W. Drenner, L.W. Newland. 2006. Mercury concentrations in fish from Lake Meredith, Texas: Implications for the issuance of fish consumption advisories. Environmental Monitoring and Assessment. 123: 249 – 258.

McCune, B., J.B. Grace, D.L. Urban. 2002. Analysis of Ecological Communities. MjM Software Design, Glenden Beach, Oregon, USA.

McIntyre, J.K., D.A. Beauchamp. 2007. Age and trophic position dominate bioaccumulation of mercury and organochlorines in the food web of Lake Washington. Science of the Total Environment. 372: 571 – 584.

Minagawa, M., E. Wada. 1984. Stepwise enrichment of δ15N along food chains: further evidence and the relation between d15N and age. Geochimica et Cosmochimica Acta 48: 1135 – 1140.

Mora, M.A., R. Skiles, B. McKinney, M. Parades, D. Buckler, D. Papoulias, D. Klein. 2002. Environmental contaminants in prey and tissues of the peregrine falcon in the Big Bend Region, Texas, USA. Environmental Pollution. 116: 169 – 176.

Mora, M.A., D. Musquiz, J.W. Bickham, D.S. Macknzie, M.J. Hooper, J.K. Szabo, C.W. Matson. 2006. Biomarkers of exposure and effects of environmental contaminants on swallows nesting along the Rio Grande, Texas, USA. Environmental Toxicology and Chemistry. 25(6): 1574 – 1584.

Mora, M.A., R.S. Skiles, M. Paredes. 2007. Further assessment of environmental contaminants in avian prey of the peregrine falcon in Big Bend National Park, Texas. Southwestern Naturalist. 52(1): 54 – 59.

Morel, F.M.M., A.M.L. Kraepiel, M. Amyot. 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics 29: 543 – 566.

Moran, M.D. 2003. Arguments for rejecting the sequential Bonferroni in ecological studies. Oikos 100: 403 – 405.

National Geographic Society. 1987. Field guide to birds of North America. National Geographic Society, Washington DC, USA.

Orihel, D.M., M.J. Paterson, C.C. Gilmour, R.A (Drew) Bodaly, P.J. Blanchfield, H. Hintelmann, H.C. Harris, J.W. Rudd. 2006. Effect of Loading Rate of the Fate of Mercury in Littoral Mesocosms. Environmental Science and Technology 40(19): 5992 – 6000.

Paller, M.H., J.W. Littrell. 2007. Long-term changes in mercury concentrations in fish from the middle Savannah River. Science of the Total Environment 382: 375 – 382.

Parker, C.R., J.R. Voshell. 1983. Production of filter feeding Trichoptera in an impounded and free-flowing river. Canadian Journal of Zoology 61: 70 – 87.

Pennuto, C.M., O.P. Lane, D.C. Evers, R.J. Taylor, J. Loukmas. 2005. Mercury in the Northern Crayfish, *Orconectes virilis* (Hagen), in New England, USA. *Ecotoxicology*, 14: 149 – 162.

Peterson, S.A., J. Van Sickle, A.T. Herlihy, R.M. Hughes. 2007. Mercury concentration in fish from streams and rivers throughout the western United States. Environmental Science and Technology 41: 58 – 65.

Plague, G.R., J.B. Wallace, J.W. Grubauch. 1998. Linkages between trophic variability and distribution of *Pteronarcys* spp (Plecoptera: Pteronarcyidae) along a stream continuum. American Midland Naturalist 139: 224 – 234.

Post, D.M., J.P. Taylor, J.F. Kitchell, M.H. Olson, D.E. Schindler, B.R. Herwig. 1998. The role of Migratory Waterfowl as Nutrient Vectors in a Managed Wetland. Conservation Biology 12(4): 910 – 920.

Post, D.M. (2002). Using stable isotopes to estimate trophic position: Models, methods, and assumptions. Ecology 83(3): 703 – 718.

Power, M.E., W.E. Dietrich. 2002. Food webs in river networks. Ecological Research 17: 451 – 471.

Robertson, D.J., K.G. Taylor. 2007. Temporal Variability of Metal Contamination in Urban Road-deposited Sediment in Manchester, UK: Implications for Urban Pollution Monitoring. Water, Air, & Soil Pollution 186: 209 – 220.

Rice, W.R. 1989. Analyzing tables of statistical tests. Evolution 43: 223 – 225.

Rypel, A.L, D.A. Arrington, R.H. Findlay. 2008. Mercury in Southeastern U.S. Riverine Fish Populations Linked to Water Body Type. Environmental Science and Technology 42: 5118 – 5124.

Scheuhammer, A.M., M.W. Meyer, M.B. Sandheinrich, M.W. Murray. 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. AMBIO 36(1): 12 – 18.

Schierow, L. 2004. Mercury in the Environment: Sources and Health Risks. CRS Report for Congress. United States. http://www.ncseonline.org/NLE/CRSreports/04Jun/RL32420.pdf

Schmidt, J.C., B.L. Everitt, G.A. Richard. 2003 Hydrology and Geomorphology of the Rio Grande and Implications for River Rehabilitation. Aquatic Fauna of the Northern Chihuahuan Desert, Special Publications, Museum of Texas Tech University, Lubbock Texas, 46: 25 – 45.

Schmitt, C.J., G.M. Dethloff, J.E. Hinck, T.M. Bartish, V.S. Blazer, J.J. Coyle, N.D. Denslow, D.E. Tillitt. 2004. Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental Contaminants and their Effects on Fish in the Rio Grande Basin. USGS Scientific Investigations Report 2004-5108.

Schmitt, C.J., J.E. Hinck, V.S. Blazer, N.D. Denslow, G.M. Dethloff, T.M. Bartish, J.J. Coyle, D.E. Tillitt. 2005. Environmental contaminants and biomarker responses in fish from the Rio Grande and its U.S. tributaries: Spatial and temporal trends. Science of the Total Environment 350: 161 – 193.

Shanley, J.B., N.C. Kamman, T.A. Clair, A. Chalmers. 2005. Physical Controls on Total and Methylmercury Concentrations in Streams and Lakes of the Northeastern USA. Ecotoxicology 14: 125 – 134.

Sharp, R.D. 1980. Development of the mercury mining industry, Trans-Pecos Texas. Published by Mining and Mineral Resources Institute, Bureau of Economic Geology, University of Texas at Austin. 32 pages

Simon, T.P. 1998. Assessing the Sustainability and Biological Integrity of Water Resources. CRC Press. 671 pages.

Sponseller RA, and SG Fisher. 2006. Drainage size, stream intermittency, and ecosystem function in a Sonoran Desert landscape. Ecosystems 9: 344 – 356.

Suchanek, TH, BA Lamphere, LH Mullen, CE Woodmansee, PJ Richerson, DG Slotton, LA Woodward, and EJ Horner. 2000. Mercury in lower trophic levels of the Clear Lake aquatic ecosystem, California. In: Integrated Assessment of Ecosystem Health, pp 249-268. eds. KM Scow, GE Fogg, DE Hinton, and ML Johnson. Lewis Publishers, Inc., Boca Raton, Florida

Texas Commission on Environmental Quality. 1994. Regional assessment of water quality in the Rio Grande Basin. Watershed Management Division, Texas Natural Resource Conservation Commission, 1994,: Austin, Tex., Texas Natural Resource Conservation Commission Publication AS–34, 377 pages.

Texas Commission on Environmental Quality. 2006. Mercury in Texas: Background, federal rules, control technologies, and fiscal implications. Implementation of Section 2, HB 2481 (79th Legislature) – A Report to the Texas Legislature. Texas Commission on Environmental Quality.

Ullrich, S.M., T.W. Tanton, S.A. Abdrashitova. 2001. Mercury in the Aquatic Environment: A Review of Factors Affecting Methylation. Critical Reviews in Environmental Science and Technology 31(3): 241 – 293.

United States Environmental Protection Agency. 1997. Mercury Report to Congress, Volume VII: Characterization of human health and wildlife risks from mercury exposure in the United States. United States Environmental Protection Agency EPA-452/R-97-009.

United States Geological Survey. 1998. Monitoring the Water Quality of the Nation's Large Rivers: Rio Grande NASQAN Program. USGS Fact Sheet FS-083-98. http://water.usgs.gov/nasqan/progdocs/factsheets/riogfact/engl.html

United States Environmental Protection Agency. 2002. Website: http://www.epa.gov/waterscience/presentations/fish/maps_ graphics_files/frame.htm. (viewed January 9, 2008).

Van Metre, P.C., B.J. Mahler, E. Callender. 1997. Water-quality trends in the Rio Grande/Rio Bravo basin using sediment cores from reservoirs. U.S. Geological Survey Fact Sheet FS-221-96.

Watras, C.J., R.C. Black, S. Halvorsen, R.J.M. Hudson, K.A. Morrison, S.P. Wente. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Science of the Total Environment 219: 183 – 208.

Webb, M.A.H., G.W. Feist, M.S. Fitzpatrick, E.P. Foster, C.B. Schreck, M. Plumlee, C. Wong, D.T. Gundersen. 2006. Mercury concentrations in gonad, liver, and muscle of white sturgeon Acipenser transmontanus in the lower Columbia River. Archives of Environmental Contamination and Toxicology 50: 443 – 451.

Wetzel, R.G., G.E. Likens. 2000. Limnological Analyses. Springer Publishers. 429 pages.

Wiener, J.G., D.P. Krabbenhoft, G.H. Heinz, A.M. Scheuhammer. 2003. Ecotoxicology of Mercury. In: Handbook of Ecotoxicology. Eds. D.J. Hoffman, B.A. Rattner, G.A. Burton, Jr., J. Cairns, Jr. Lewis Publishers, Boca Raton, Florida. pages 409 – 443.

Wiener, J.G., B.C. Knights, M.B. Sandheinrich, J.D. Jeremiason, M.E. Brigham, D.R. Engstrom, L.G. Woodruff, W.F. Cannon, and S.J. Balogh. 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. Environmental Science and Technology 40: 6261 – 6268.

VITA

Alexandra Smith was born in Dallas, Texas, on May 15, 1976, the daughter of Patsy Lucille Smith and Jesse Dean Smith. After graduating from Rockdale High School, Rockdale, Texas, in 1994, she attended Stephen F. Austin State University in Nacogdoches, Texas before transferring to Texas State University-San Marcos in 1996. She received the degree of Bachelor of Science from Texas State in December 2000. After graduating, she was employed by the United States Geological Survey. In August 2006, she entered the Graduate College of Texas State University-San Marcos.

Permanent Address: 211 Windrock Dr.

Victoria, TX 77904

This thesis was typed by Alexandra Smith