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Mercury Speciation in Piscivorous Fish from Mining-Impacted Reservoirs

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Guadalupe Reservoir (GUA), California, and Lahontan Reservoir (LAH), Nevada, U.S. are both affected either directly or indirectly by the legacy of gold and silver mining in the Sierra Nevada during the nineteenth century. Analysis of total mercury in fish from these lentic systems consistently indicate elevated concentrations (>1 $\mu g \cdot g^{-1}$ wet weight; hereinafter, all concentrations are reported as wet weight unless indicated otherwise) well above the U.S. Environmenal Protection Agency's human consumption advisory level for fish (<0.3 $\mu g \cdot g^{-1}$). Replicate X-ray absorption near edge structure (XANES) analyses on largemouth bass and hybrid striped bass from GUA and LAH were performed to determine predominant chemical species of mercury accumulated by these high-trophic-level piscivores that are exposed to elevated mercury through trophic transfer in mining-impacted lentic systems. Despite distinct differences in mercury source, the proximity of the source, and concentrations of complexing ligands, results of XANES analysis clearly indicated that mercury accumulated in these individual fish from the two reservoirs were dominated by methylmercury cysteine complexes. These findings are consistent with results from commercial fish species inhabiting marine environments which are presumed to include differing mercury sources (e.g., atmospheric, hydrothermal, or benthic). The dominance of methylmercury cysteine complexes in muscle tissues of fish obtained from such contrasting environments and exposure conditions suggests that a generic toxicological model for the consumption of fish could be applicable over a wide range of ecologic settings.

Introduction

Toxicological pathways and effects of mercury, particularly methylmercury, have become a burgeoning environmental concern because methylmercury biomagnifies through terrestrial and aquatic food webs (*1*−*4*). At the apex of many freshwater food webs, piscivorous fish can then extend that trophic transfer and potential for neurotoxcity to wildlife and humans (*5*−*7*). Understanding mercury trophic transfer is complicated by the diversity of point and non-point sources spanning multiple spatial and temporal scales (*8*−*10*). Mining activities can generate both point and non-point mercury sources (*10*−*13*).

Guadalupe Reservoir (GUA) is adjacent to the New Almaden Mercury Quicksilver Mines (NAMQM) in San Jose, CA and, hence, is affected by its drainage (*12*, *14*). The positive economic, historic, and geochemical contributions of these mines over regional, national, and global scales during the nineteenth century (*15*−*21*) have been adversely offset by a legacy of mercury contamination in sediment, water, and biota from the cinnabar and calcine deposits. Fish consumption advisories (i.e., no consumption) for the reservoir were initially recommended in 1987. As an environmentally important component of the Guadalupe River watershed, biogeochemical studies have intensified within the past decade to facilitate the development of management strategies (e.g., total maximum daily load, TMDL) for the watershed and the southern component of San Francisco Bay, down gradient of the watershed.

Lahontan Reservoir (LAH) is located within the Carson River Mercury Site, the only site in the State of Nevada on the Superfund National Priorities List. Like GUA, LAH's contamination is a mining legacy from the nineteenth century. However, contamination at LAH is derived from elemental mercury imported from mines in the San Francisco Bay area (e.g., the NAMQM) and used at mill sites to refine gold and silver ore from the Comstock Lode (*22*). Mercury-contaminated mine tailings from the historic mill operations continue to discharge into the Carson River system and accumulate in lentic environments like LAH (*22*, *23*). A "no consumption" advisory for fish has been in place since 1997.

Examination of an array of commercially sold marine fish (*24*) determined that the predominant chemical form of mercury in these fish was "methylmercury-cysteine (or structurally related species)". This finding not only motivated an energized discussion about the health hazards of ingesting mercury doses from marine fish, but also analytically paved the way for new synchrotron-based X-ray analysis of solid-state mercury speciation at much lower (i.e., $\mu g \cdot g^{-1}$) concentrations than had previously been attainable. Traditional analytical (cold-vapor atomic fluorescence spectroscopy; *25*, *26*) methods for mercury provide low ($ng \cdot g^{-1}$) detection limits for total mercury and methylmercury in biological samples, but the synchrotron-based X-ray analysis provides detailed mercury speciation (e.g., coordination with protein structures) that can complement traditional methods to more accurately assess risks to human and ecosystem health. As described above, GUA and LAH have distinctly different mercury sources, but both are mining-impacted, mineralogically based, proximal sources in freshwater. In contrast, an extensive survey of fish throughout the western United States suggested the importance of atmospheric sources to most freshwater systems (*27*). Although it is unclear if atmospheric, hydrothermal, or benthic sources of mercury (*28*, *29*) dominate the environment where previously examined marine fish were caught (*24*), these marine sources are clearly different from those for GUA and LAH. It is generally assumed that fish accumulate mercury in their tissues predominantly as methylmercury (*30*), but notable exceptions showing significant inorganic-mercury tissue concentrations have been recently reported (*31*). Therefore, mercury speciation at GUA and LAH is examined in tissues of piscivorous

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TABLE 1. Mercury in Freshwater Fish Samples Used for XANES Analyses

species	source	fish sample no. and name	dissolved total Hg in water column (pM)	dissolved methyl-Hg in water column (pM)	total length (mm)	total mercury concentration[a] (wet wt.; $\mu g \cdot g^{-1}$)	Log BAF ($L \cdot kg^{-1}$)
largemouth bass (*Micropterus salmoides)*	Guadalupe Reservoir, CA	1 GUA LMB_A	6.0 ± 0.4	0.4 ± 0.1	346	2.42	7.4
largemouth bass (*Micropterus salmoides)*	Guadalupe Reservoir, CA	2 GUA LMB_B			410	3.74	7.6
largemouth bass (*Micropterus salmoides)*	Lahontan Reservoir, NV	3 LAH LMB	732 ± 78	0.4 ± 0.2	320	1.74	7.3
hybrid striped bass (*Morone saxatilis x Morone chrysops*)	Lahontan Reservoir, NV	4 LAH Wiper			767	8.28	8.0

[a] For wet to dry weight conversion, the percent solids were 21−22%. The USEPA Water Quality Criterion is 0.3 $\mu g \cdot \times d7g^{-1}$ (*19*) for human consumption of fish.

fish collected from two reservoirs severely impacted by mining to compare with mercury speciation previously reported for marine fish (*24*).

Experimental Section

Mercury Determinations. Piscivorous fish (largemouth bass and hybrid striped bass), all exceeding 300 mm in total length, were collected by angling in GUA, or by electroshocking in LAH in August 2005 (Table 1). Foil-wrapped samples were stored in a cooler with ice until transported to the laboratory for freezing. Sampling plugs (a disk of muscle tissue measuring 6 mm i.d. × 8 mm depth) were analyzed for total mercury by atomic absorption spectroscopy (*32*). Concentrations of total methylmercury in fish were not determined. Mercury and methylmercury concentrations in water were determined by cold-vapor atomic fluorescence spectrometry (*33*, *34*).

XAS Analyses. In situ X-ray absorption spectroscopy (XAS) measurements of fish tissue samples and reference compounds were performed at beamline 9−3 at the Stanford Synchrotron Radiation Laboratory (SSRL), Menlo Park, CA. The electron storage ring was operated at 3 GeV with a current range of 80−100 mA. The Hg L_{III} edge XAS spectra were collected in fluorescence mode by monitoring the Hg−Hg Lα1 fluorescence using a 30 element Ge array detector equipped with a Ga_2O_3 9 absorption-length filter and Soller-slits. The muscle tissue samples were loaded on Teflon sample holders sealed with 38 μm Kapton tape. The energy was calibrated at the lowest energy inflection point of a Hg−Sn amalgam foil (12285.0 eV). Sample temperature was maintained at 10 Kelvin to minimize the radiation damage during scans (18−25 scans for fish samples). Model compound spectra were recorded on red HgS(cinnabar), black HgS (metacinnabar), methylmercuric hydroxide(CH_3HgOH) (aq), Hg-2,3-dimercapto-1-propanesulfonic acid $(DMPS)_4$ (aq), Hg-2,3-dimercapto-1-propanesulfonic acid $(DMPS)_2$ (aq), diphenylmercury ($HgPh_2$) (s), mercuric oxide (HgO) (s), Hg-$(NO_3)_2$(aq), Hg(II)$(Cysteine)_2Cl$ (s), $[HgCl_4]^{2-}$ (aq), $HgCl_2$ (aq), Hg_2Cl_2 (s), $[nBu_4N][Hg(SPh)_3]$ (s), $CH_3HgC_3H_4N_2$(imidazole) (aq), and CH_3HgS(Cys) (aq). Spectra of solids (s) were recorded on material appropriately diluted by mixing with boron nitride (to give an edge-jump of 2 absorbance units) in transmittance, while spectra of aqueous solutions (1−5 mM Hg, in 50 mM HEPES buffer 30% v/v glycerol, pH 7) were recorded using fluorescence detection. The XAS data reduction and analysis were performed either with the SiXPACK (*35*) or using EXAFSPAK (http://ssrl.slac.stanford-.edu/exafspak.html).

Results and Discussion

Mercury in Fish and Water. The U.S. Environmental Protection Agency's human consumption threshold for mercury in fish is 0.3 $\mu g \cdot g^{-1}$ (*3*). By comparison, the concentrations in the four fish analyzed for total mercury ranged from 1.74 to 8.28 $\mu g \cdot g^{-1}$ (Table 1). The mean (4.05 $\mu g \cdot g^{-1}$) is an order of magnitude greater than the mean mercury concentration reported for piscivores of the Western United States (0.26 $\mu g \cdot g^{-1}$; *27*). In these mining-affected watersheds, extraordinary concentrations of mercury are common even for lower-trophic level organisms such as zooplankton and planktivorous fish (*14*). A comparison of dissolved concentrations in each reservoir (Table 1, *36*) reveals that methylmercury concentrations are essentially equal, while total mercury is orders of magnitude higher in LAH. A bioaccumulation factor (BAF; units of $L \cdot kg^{-1}$) can be determined as the ratio of methylmercury concentration in the fish tissue ($mg \cdot kg^{-1}$) over the dissolved methylmercury concentration in the water ($mg \cdot L^{-1}$). Log BAF values between 6.0 and 6.8 have been reported for largemouth bass by others (*37*, *38*). Higher log BAF values are associated with our samples (a range of 7.3−8.0; Table 1), suggesting efficient methylmercury trophic transfer in both GUA and LAH reservoirs.

XANES Analyses. XAS is a spectroscopic technique that uses synchrotron based X-rays to probe the physical and chemical structure of matter at an atomic scale. The XANES spectrum can be used as a "fingerprint" to understand qualitative and semi-qualitative information of the local bonding environment of the measured element in the sample, in this case Hg (*39*). Figure-1a shows Hg L_{III} XANES spectra of a largemouth bass (LMB) sample from LAH and 10 model compounds. While spectral features of CH_3HgS(Cys) show a striking resemblance to our fresh fish samples at pre- and postedge regions (as indicated by two arrows at the preedge and a vertical dotted line at the postedge), the features of other model compounds are dissimilar to those in this fish-tissue sample. Six other model compounds ($[HgCl_4]^{2-}$(aq), Hg_2Cl_2(s), $[nBu_4N][Hg(SPh)_3]$, $CH_3HgC_3H_4N_2$ (imidazole) (aq), Hg(II)$(Cysteine)_2Cl$ (s), and diphenylmercury ($HgPh_2$) (s) (data not shown)) did not match the spectral features of the fish samples. As an indication of the consistency of mercury speciation in all specimens, the spectra of CH_3HgS(Cys) were overlaid on each fish-tissue spectra (Figure-1b). Regardless of bass species or sampling locations, the predominant mercury species was CH_3HgS(Cys), which contains linear two-coordinate Hg with methyl and cysteinyl sulfur donors. Our findings are consistent with previous work on commercial marine species (*24*) which reported the presence of CH_3-HgS(Cys), but we acknowledge that four individual fish represent a relatively small sample-size.

The two aquatic systems sampled here represent conditions induced by tremendous non-atmospheric inorganic-mercury pollution (viz., proximal mining operations). Aqueous and sediment mercury concentrations are elevated at both GUA and LAH (*12*, *14*, *22*, *23*, *36*). For example, the range of dissolved Hg in a survey of 23 lakes in Wisconsin

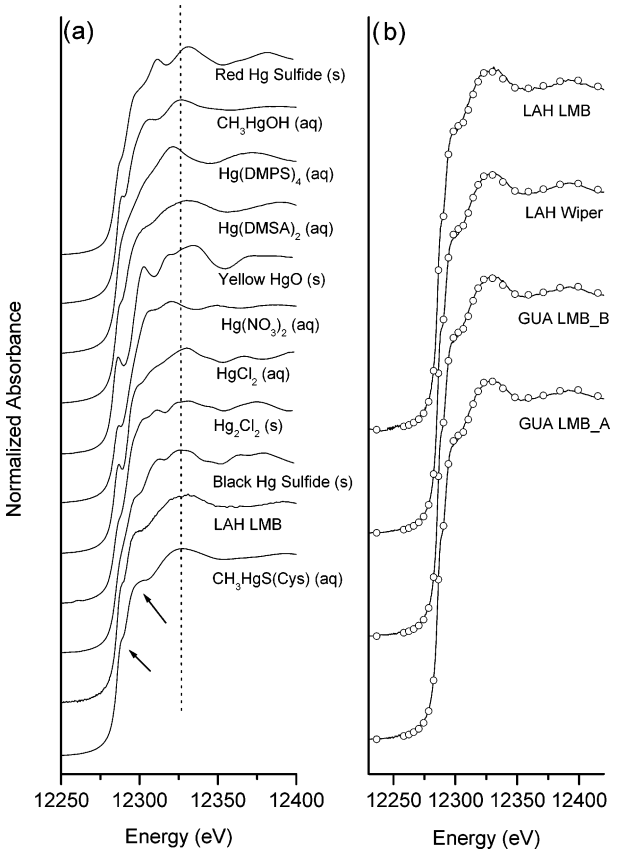

FIGURE 1. (a) Comparison of normalized Hg L_{III} XANES of large mouth bass (LMB) with ten selected model compounds (red HgS-(cinnabar), black HgS (metacinnabar), methylmercuric hydroxide (CH_3HgOH), Hg-2,3-dimercapto-1-propanesulfonic acid [$Hg(DMPS)_4$], Hg-2,3-dimercapto-1-propanesulfonic acid [$Hg(DMPS)_2$], mercuric oxide (HgO) (s), $Hg(NO_3)_2$ (aq), $HgCl_2$ (aq), Hg_2Cl_2 (s), and CH_3HgS-(Cys) (aq). (b) Comparison, using overlays, of normalized Hg L_{III} XANES of largemouth bass (LMB) A and B (LMB_A and LMB_B) and hybrid-striped (Wiper) bass collected at Lahontan Reservoir (LAH), NV, and at Guadalupe (GUA) reservoir, CA, with that of CH_3HgS-(Cys). Solid lines and open circles represent fish tissue samples and CH_3HgS(Cys), respectively.

was 0.15−4.8 ng-L^{-1} (*40*). By comparison, reported ranges for dissolved-mercury concentrations in GUA and LAH are 1.2−6.3 and 75−387 ng-L^{-1}, respectively (*14*, *36*, *41*). One might, therefore, consider conditions in GUA and LAH conducive to the bioaccumulation of inorganic mercury in fish tissues, yet no evidence of inorganic mercury was observed. Previous studies reported significant inorganic mercury (up to 72% of total Hg) in fish from estuaries as well as from the Adriatic Sea (*31*, *42*, *43*). Digestive demethylation to detoxify methylmercury ingestion, and dietary sources elevated in inorganic mercury have been hypothesized as mechanisms for lowering the percentage of methylmercury (*31*). Although we analyzed freshwater fish, our results do not support the demethylation hypothesis because fish species that have come to survive in GUA and LAH since mining activities commenced over a century ago would clearly have benefited from evolving such an ability. Dietary sources also do not appear to be a suitable explanation. Inorganic mercury in zooplankton (*14*) is excluded after being consumed by planktivorous fish and then by piscivorous fish. It is, therefore, challenging to speculate how other aquatic habitats, less polluted by inorganic mercury, can produce fish tissues having significant concentrations of inorganic mercury.

Management Implications. Results presented herein demonstrate that mercury is accumulated almost exclusively as methylmercury−cysteine complexes in the muscle tissues of piscivorous freshwater fish from two mining-impacted reservoirs. This result, consistent with observations for several marketed marine fish species (*24*), suggests that speciation of bioaccumulated mercury at high trophic levels is consistent over a wide range of ionic strengths and mercury sources. As one might expect, GUA and LAH have fish-consumption advisories, and both have remediation strategies (e.g., TMDL programs) in development. These strategies face some critical questions associated with mercury transport and transformation, not the least of which is, "How does one develop and justify biological targets for ecosystem remediation?" Because sulfhydryl complexes with methylmercury are more thermodynamically stable than chloride complexes, the consistency of mercury speciation in muscle tissue from a wide variety of fish species highlights the management importance of quantitatively understanding (modeling) the underlying mechanisms of trophic transfer of mercury through aquatic food webs to wildlife and humans. Recognizing that mercury bioaccumulation rates can vary among fish species, our results, combined with similar findings for marine fishes (*24*), suggest that toxicological models for fish consumption, over wide-ranging aquatic habitats, can be simplified by assuming that piscivorous fishes, a food source for wildlife and humans, consistently accumulate mercury as cysteine complexes in their tissues. Synchrotron-based studies, particularly of biological samples, are resource intensive and, hence, constrained our replicated analyses to tissues from four fish. Our hypothesis could, therefore, be strengthened if similar analyses were performed on other predatory freshwater fish species (e.g., walleye and northern pike) and other types of freshwater ecosystems (e.g., wetlands-dominated lowlands and glaciated lakes with primarily atmospheric mercury sources). Chloro-complexes of methylmercury have long been used as the mercury species of toxicological concern for trophic transfer (*24*, *44*, *45*). Therefore, this work highlights the importance of describing processes that intra- or extracellularly transform mercury coordination between complexes that are toxicologically labile (e.g., chloro-methylmercury complexes) and others that are more inert (e.g., inorganic mercury or sulfhydryl-methylmercury complexes).

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