Article

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Isotopic composition of inorganic mercury and methylmercury downstream of a historical gold mining region

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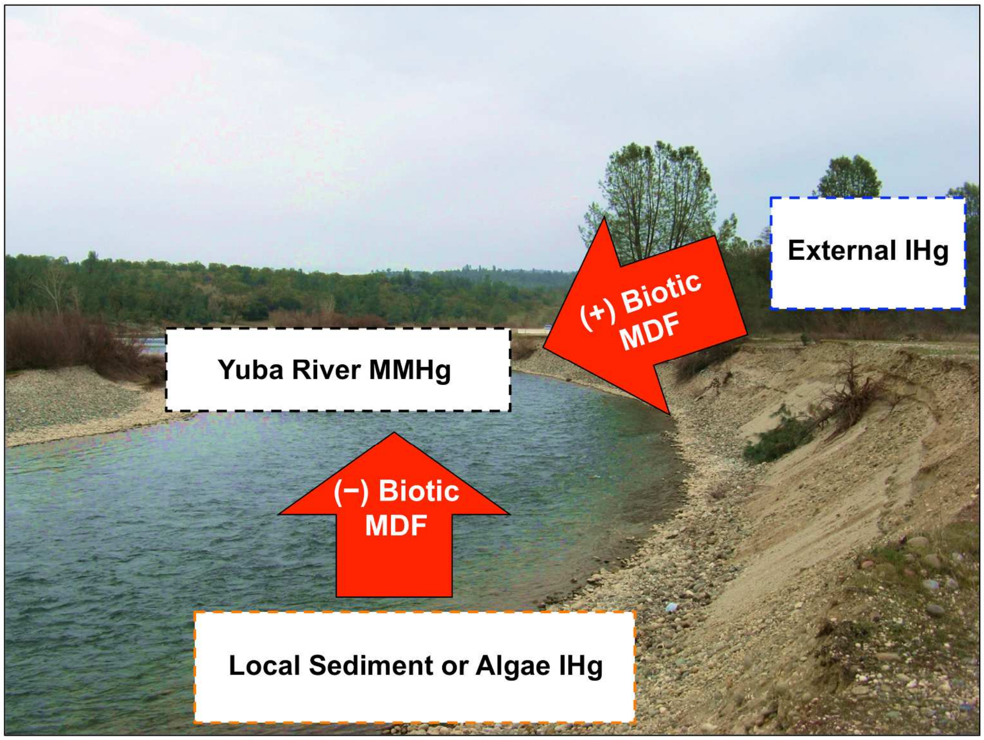
Keywords

Mercury Isotopes, Yuba River, Feather River, Sediment, Benthic Macroinvertebrates

Abstract

We measured total mercury (THg) and monomethyl mercury (MMHg) concentrations and mercury (Hg) isotopic compositions in sediment and aquatic organisms from the Yuba River (California, USA) to identify Hg sources and biogeochemical transformations downstream of a historical gold mining region. Sediment THg concentrations and δ^{202}Hg decreased from the upper Yuba Fan to the lower Yuba Fan and the Feather River. These results are consistent with the release of Hg during gold mining followed by downstream mixing and dilution. The Hg isotopic composition of Yuba Fan sediment (δ^{202}Hg = -0.38 ± 0.17‰ and Δ^{199}Hg = 0.04 ± 0.03‰; mean ± 1SD, n=7) provides a fingerprint of inorganic Hg (IHg) that could be methylated locally or after transport downstream. The isotopic composition of MMHg in the Yuba River food web was estimated using biota with a range of %MMHg (the percent of THg present as MMHg) and compared to IHg in sediment, algae and the food web. The estimated δ^{202}Hg of MMHg prior to photodegradation (−1.29 to −1.07‰) was lower than that of IHg and we suggest this is due to mass-dependent fractionation (MDF) of up to −0.9‰ between IHg and MMHg. This result is in contrast to net positive MDF (+0.4 to +0.8‰) previously observed in lakes, estuaries, coastal oceans and forests. We hypothesize that this unique relationship could be due to differences in the extent or pathway of biotic MMHg degradation in stream environments.

TOC Art


External IHg
(+) Biotic MDF
Yuba River MMHg
(−) Biotic MDF
Local Sediment or Algae IHg

Introduction

Mercury (Hg) is a globally distributed neurotoxic pollutant that bioaccumulates in food webs as monomethyl mercury (MMHg). The amount of Hg actively cycling in the environment has increased due to anthropogenic activities such as mining, coal combustion, and industrial Hg use.[1] In the 19th century, metallic Hg was widely used to enhance gold (Au) recovery during hydraulic mining of placer deposits throughout the Sierra Nevada Mountain Range in California. During hydraulic mining, large volumes of sediment were washed through sluices containing Hg to amalgamate fine particles of Au and up to 30% of the Hg used was released to the environment.[2] The Hg-contaminated sediment was released downstream and deposited in river valleys along the western front of the Sierra Nevada, with significant amounts of sediment entering lowland channels and reaching San Francisco Bay (SF Bay).[3] Sediment from Au mining persists in anthropogenic fan deposits evident in terraces and banks alongside rivers draining former mining districts.[4] One of the largest of these is the Yuba Fan, a massive deposit of mining derived sediment (252×10^6 m^3) which grades from the Sierra Nevada piedmont to the Central Valley.[4, 5] This sediment has total Hg concentrations (THg) consistently two to three times higher than pre-mining sediment.[4, 5] The lower Yuba River, between Englebright Dam and the Feather River, flows through this sediment deposit. Erosion of the Yuba Fan supplies inorganic Hg (IHg) laden sediment to local and downstream environments, particularly during major flood events.[4]

IHg in sediment can be transformed by methylating microbes (e.g., sulfate and iron reducing bacteria) into bioaccumulative MMHg and this process is controlled by a variety of geochemical parameters (e.g., nutrient and organic matter availability, redox conditions, Hg speciation, etc.).[6] In general, conditions that promote IHg methylation are often found in wetlands or estuarine environments,[7] such as in San Francisco Bay where MMHg production and bioaccumulation is well documented.[8-10] MMHg formation and distribution in rivers is more difficult to predict because it can be a function of both watershed landscape characteristics (i.e., wetland density, land use, etc.)[11, 12] and in-stream processes (i.e., microbial community, hydrology, productivity).[13-15] Thus, in watersheds with multiple potential IHg inputs, it is difficult to identify the origin of bioaccumulated MMHg using MMHg or THg concentrations alone. Nonetheless, MMHg biomagnifies in many riverine food webs[11] and processes that govern MMHg formation and degradation in streams are of great interest.[14]

In the Yuba River upstream of Englebright Dam (built in 1941 to trap hydraulic mining sediment), the spatial distribution, speciation and reactivity of Hg in sediment was previously documented,[16, 17] as were fish THg concentrations,[18] and invertebrate THg and MMHg concentrations.[16] Downstream of Englebright Dam, where the Yuba River flows through the Yuba Fan, previous work has shown high THg in bar, bank, terrace, and floodplain sediment.[4] THg concentrations were also measured in sediment deposited behind Daguerre Point Dam (built in 1910), a 7.3 m high overflow spillway dam located midway between Englebright Dam and the Feather River.[5] However, no prior studies have investigated MMHg bioaccumulation in the lower Yuba River and the importance of high THg Yuba Fan sediment to MMHg bioaccumulation in resident biota was unknown. We hypothesized that sediment IHg could be methylated in situ, resulting in MMHg bioaccumulation in the local food web. We also considered whether MMHg might be derived from watershed sources upstream of the Yuba Fan and Englebright Dam. To better understand the processes by which MMHg enters riverine food webs we measured Hg stable isotope ratios in lower Yuba River sediment and biota.

Mercury has seven stable isotopes that undergo mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) in the environment. Hg stable isotope ratios have become a useful tool for identifying anthropogenic Hg sources and tracing their transport and deposition in stream systems.[19-23] Comparisons of Hg isotopes in sediment (mostly IHg) with fish or other biota (containing MMHg) have been used to infer transformations between IHg and MMHg (e.g., microbial IHg methylation, microbial MMHg degradation, and photochemical MMHg degradation).[24, 25] More recent studies have estimated the isotopic composition of IHg and MMHg in food webs by measuring Hg isotopes in biota with a range of %MMHg values (percent of THg present as MMHg).[26-28] This approach tests whether mixing of isotopically distinct IHg and MMHg pools can explain the Hg isotopic composition of all biota at a particular location, assuming these pools do not vary widely during the study time period. Using this method, Kwon et al. ([27]) measured Hg isotope ratios in estuarine sediment and biota along the U.S. northeast coast. From the estimated isotopic composition of MMHg, the authors were able to determine that organisms were primarily exposed to MMHg from local sediment. In another study, MMHg isotopic composition was estimated in the South Fork Eel River (California) to evaluate Hg exchange across ecosystem boundaries via organismal movement,[29 28] and longitudinal changes in MMHg photochemical degradation.[30] So far, investigation of MMHg in stream ecosystems using Hg isotopes has been limited to the Eel River, which is a relatively remote, bedrock-dominated, free flowing river where Hg is derived mainly from atmospheric deposition and there are no local Hg point sources.

Here we present the first Hg isotope study to investigate Hg sources and biogeochemical transformations in sediment and biota in a river contaminated by historical Au mining. We report THg and MMHg concentrations and Hg isotopic compositions of sediment, filamentous algae and aquatic organisms from the lower Yuba River (six sites) and the Feather River (one site; SI Figure 1). A diverse suite of organisms was analyzed, including five types of benthic macroinvertebrates: stonefly larva (*Perlidae*), caddisfly larva (*Hydropsychidae*), mayfly larva (*Heptageniidae* and *Ephemerellidae*), aquatic worm (*Oligochaeta*), Asian clam (*Corbicula fluminea*), and two fish species: riffle sculpin (*Cottus gulosus*) and speckled dace (*Rhinichthys osculus*). We estimated the isotopic composition of both IHg and MMHg in the food web to (1) determine the source of bioaccumulated

MMHg and (2) identify important microbial and photochemical processes governing Hg cycling in this river system.

Materials and Methods

Sample Collection and Processing

Twelve sediment samples were analyzed from subaerial riverbanks and terraces at eight locations in the Yuba and Feather Rivers (Figure 1). Nine sediment samples were collected between 2006 and 2008 by Singer et al.[4] and three additional samples were collected in March 2013. Prior to analysis, all sediment was either air dried (n=9; from Singer et al.[4]) or freeze-dried (n=3 from March 2013) and dry-sieved to <63μm. Aquatic organisms were collected from five sites in the Yuba River: Rose Bar (RB), Parks Bar (PB), Hammon Grove (HG), Dantoni (Da), and Simpson Bridge (SB), and one site downstream in the Feather River (FR; SI Figure 1). All organisms were collected using a kick net, dip net or directly off gravel cobbles during sampling campaigns in March 2013 (at RB, Da and FR) and June 2014 (all sites). Individual organisms were removed with clean stainless steel tweezers, identified, sorted into composite samples (five or more individuals per sample, except for riffle sculpin) and immediately frozen on dry ice. When individual organisms were plentiful (i.e., more than ~50 individuals) they were collected as multiple composite samples and analyzed separately (e.g., four stonefly samples at PB). Biotic samples were freeze-dried and then ground into a powder with either an agate mortar and pestle or an alumina ball mixer mill prior to analysis. Additional sample collection details are available in the Supporting Information.

MMHg Concentration Analysis

The concentration of MMHg (dry wt.) in freeze-dried sediment and biota was measured at the U.S. Geological Survey (USGS; Menlo Park, CA). Sediment was sub-sampled (20–30 mg) and extracted for MMHg using 25% KOH/methanol (25 g of KOH in 100 mL methanol) at 60°C for four hours.[17] Biota was sub-sampled (3–7 mg) and extracted for MMHg using 30% HNO_3 at 60°C (12-16 h), as adapted from ([31]). Sediment and biota extract sub-samples were diluted, pH was adjusted with citrate buffer and they were analyzed for MMHg by aqueous phase ethylation (with sodium tetraethylborate) on an automated MMHg analyzer (MERX, Brooks Rand).[32] For sediment MMHg (analyzed in a single batch), the relative percent deviation (RPD) of analytical duplicates was 8.4% (n=1 pair), matrix spike recovery was 107 ± 1% (n=2), and certified reference material (CRM) ERM-CC580 (estuarine sediment) recovery was 95% (n=1). For biota, the mean RPD of analytical duplicates was 3.0% (n=12 pairs), matrix spike recoveries were 105 ± 1% (mean ± SE, n=26), and recoveries from NRC Tort-3 (lobster hepatopancreas) were 86 ± 2% (mean ± SE, n=7) and from NIST-2967 (marine mussel tissue) were 94 ± 3% (mean ± SE, n=7).

THg Concentration and Hg Isotope Analysis

Hg was separated for THg concentration and Hg stable isotope measurements by offline combustion, as described in detail elsewhere (e.g., [28, 33]). Briefly, up to 1 g of sample was placed into the first furnace of a two-furnace combustion system. The temperature of the first furnace was increased to 750°C over six hours with the second furnace held at 1000°C. Hg was released and carried in a flow of Hg-free O_2 through the second furnace and into a 24 g trapping solution of 1% $KMnO_4$ in 10% H_2SO_4. These solutions were partially reduced with 2% (w/w) of a 30% solution of NH_2OH•HCl and an aliquot was measured for THg by CV-AAS (Nippon MA-2000) to calculate the sample dry wt THg concentration (based on the mass of Hg in solution and the sample mass combusted). Compared to independent analysis by hot concentrated acid digestion and CV-AFS at

USGS-Menlo Park, offline combustion recovered 107 ± 11% (1SD, n=6) of Hg from biotic samples and 97 ± 11% (1SD, n=15) of Hg from sediment samples. The content of each trap was then divided into 1-5 g aliquots, treated with 0.3 ml of 20% $SnCl_2$ and 0.3 ml of 50% H_2SO_4 and Hg was purged into a secondary 1% $KMnO_4$ trap to isolate Hg from combustion residues and concentrate Hg for isotopic analysis. An aliquot of this secondary trap solution was analyzed by CV-AAS (Nippon MA-2000) and recoveries averaged 98 ± 3% (1SD; n=36) for biota and 99 ± 2% (1SD; n=15) for sediment. The Hg isotopic composition of the secondary trap solution was then measured by cold vapor multi-collector inductively coupled plasma mass spectrometry (CV-MC-ICP-MS; Nu Instruments). Solutions were partially reduced with 2% (w/w) of a 30% solution of NH_2OH•HCl and diluted to between 0.9 and 5 ng/g. All Hg was reduced to Hg(0) online by the addition of 2% (w/w) $SnCl_2$ and carried in a stream of Ar gas to the MC-ICP-MS inlet. Instrumental mass bias was corrected by introduction of an internal Tl standard (NIST 997) as a dry aerosol to the gas stream and by strict sample standard bracketing using NIST 3133 with a matching concentration (±10%) and solution matrix.[34]

Mercury stable isotope compositions are reported in permil (‰) using delta notation (δ^{xxx}Hg) relative to NIST SRM 3133 (Eq. 1), with MDF based on the ^{202}Hg/^{198}Hg ratio (δ^{202}Hg).[34] MIF is the deviation from theoretically predicted MDF and is reported in permil (‰) using capital delta (Δ^{xxx}Hg) notation (Eq. 2). In this study, we use Δ^{199}Hg and Δ^{201}Hg to report MIF where $\beta = 0.252$ for Δ^{199}Hg and $\beta = 0.752$ for Δ^{201}Hg.[34] All δ^{xxx}Hg and Δ^{xxx}Hg values are available in SI Tables 1, 2, and 3.

Equation [1]: $\delta^{xxx}\text{Hg}\ (‰) = ([(^{xxx}\text{Hg}/^{198}\text{Hg})_{sample}/(^{xxx}\text{Hg}/^{198}\text{Hg})_{NIST3133}]-1) * 1000$

Equation [2]: $\Delta^{xxx}\text{Hg} = \delta^{xxx}\text{Hg} - (\delta^{202}\text{Hg} * \beta)$

Procedural blanks and CRMs (NRC TORT-2: lobster hepatopancreas and NIST 1944: New York/New Jersey waterway sediment) were processed for THg and Hg isotopic composition in an identical manner to samples. Process blanks for sediment and biota averaged 95 ± 15 pg (1SD, n=8) and 104 ± 30 pg (1SD, n=6), respectively and accounted for between 0.2% to 1.8% of Hg in the final trap solutions. THg for CRMs was within 5% of certified values (SI Table 3) and recoveries during secondary purge and trap were 94 ± 4% (1SD, n=6, min=87%) for NIST 1944 and 96 ± 7% (1SD, n=11, min=80%) for NRC Tort-2. The Hg isotopic composition of both CRMs was consistent with previously reported values (SI Table 3).[21, 24, 27-29, 35-39] The long-term analytical uncertainty of Hg isotope ratio measurements was estimated from the standard deviation (2SD) of the mean Hg isotopic composition of the secondary UM-Almadén standard over multiple analytical sessions. We also estimated external reproducibility from replicate measurements of CRMs. The uncertainty associated with CRMs was greater than uncertainty associated with the UM- Almadén standard (SI Table 3). Therefore, we use the 2SD of mean Hg isotope values of replicate CRM measurements to approximate uncertainty for sample measurements in this study (±0.08‰ for δ^{202}Hg and ±0.05‰ for Δ^{199}Hg).

Results & Discussion

Sediment THg and Hg Isotopic Composition

Yuba River and Feather River sediment THg concentrations ranged from 170 to 6,820 ng/g, δ^{202}Hg values ranged from −0.95 to 0.72‰ and Δ^{199}Hg values were near zero (mean=0.04 ± 0.03‰; 1SD, n=12; SI Table 1). Sediment THg and δ^{202}Hg generally decreased from the upper Yuba Fan (~0 to 20 km downstream of Englebright Dam) to the lower Yuba Fan (20 to 36 km downstream of Englebright Dam) and into the Feather River (>36 km downstream of Englebright Dam; Figure 1). Metallic Hg(0) was used during the hydraulic mining of placer deposits in the upper fan adjacent to Rose Bar between 1850 and the early 1900's. Upper fan sediment (n=4) had the highest THg concentrations (up to 6,820 ng/g) and somewhat variable δ^{202}Hg (δ^{202}Hg = −0.04 ± 0.52‰; mean±1SD) due to one of the four sediment samples having an anomalous δ^{202}Hg of

+0.71‰. The remaining three upper fan sediment samples had δ^{202}Hg between -0.50 and -0.18‰, similar to previously analyzed sediment from a single tailings pile at Rose Bar (−0.50‰ and −0.64‰).[40] The δ^{202}Hg value of metallic Hg(0) has been reported to vary globally from −1.06 to 0.00‰ (mean=−0.39 ± 0.37‰, 1SD, n=7),[41] and is often similar to the δ^{202}Hg of the Hg ore from which it is derived.[42] Sierra Nevada Au mining operations obtained metallic Hg from the CA Coast Range,[2] where Hg ore deposits exhibit a wide range in δ^{202}Hg (−0.64 ± 0.84‰; mean ± 1SD, n=91).[43] Metallic Hg(0) has also been shown to undergo complex transformations (i.e., dissolution, oxidation, volatilization and sorption) upon its release during Au mining.[44] Thus, the single high δ^{202}Hg sediment sample could reflect metallic Hg(0) from a specific Au mine or during a specific mining period or could have been fractionated by loss of isotopically light Hg in the stream environment. Downstream in the lower Yuba Fan, THg concentrations decrease and δ^{202}Hg values are less variable. Lower fan sediment had THg between 170 and 309 ng/g and a mean δ^{202}Hg of −0.44 ± 0.16‰ (1SD, n=4). The smaller isotopic variability in this stream section suggests that various Hg sources are relatively well homogenized. Although we did not measure the speciation of Hg in Yuba Fan sediment here, previous work in the Upper Yuba River[16, 17] and elsewhere (e.g.,[45]) has suggested that a significant proportion of Hg in Au mining derived sediment is present as Hg(0). Our results are consistent with the presence of a metallic Hg(0) source: the mean Hg isotopic composition of all Yuba Fan sediment (δ^{202}Hg = −0.38 ± 0.17‰ and Δ^{199}Hg = 0.04 ± 0.03‰; 1SD, n=7, excluding one sample treated as an outlier) is similar to the mean δ^{202}Hg of metallic Hg globally (-0.39‰)[41] and to the average δ^{202}Hg of Hg-ore in the CA Coast Range (-0.64‰).[43]

Downstream of the Yuba River, Feather River sediment had THg (218-413 ng/g) and mean δ^{202}Hg values (−0.66 ± 0.26‰, 1SD, n=4) similar to the Yuba Fan. Multiple studies have shown that sediment Hg isotopic compositions can be used to trace downstream Hg transport and mixing in rivers.[19-21, 23, 46] Pre-mining sediment (i.e., less than 60 ng/g) in subtidal sediment cores from SF Bay had an average δ^{202}Hg of −0.98 ± 0.06‰ and Δ^{199}Hg of 0.17 ± 0.03‰ (1SD, n=5).[40] Pre-mining sediment in SF Bay was likely derived from watersheds draining the Sierra Nevada, including the Yuba and Feather Rivers. If we assume this pre-mining sediment isotopic composition is similar to uncontaminated sediment in the Yuba-Feather watershed, then the downstream decrease in THg and gradual shift toward lower δ^{202}Hg suggests dilution of mining derived Hg with uncontaminated sediment (SI Figure 3). This is consistent with the model of progressively diluted hydraulic mining sediment being remobilized and redeposited within the fan and exported from it.[4, 47, 48] We use the Hg isotope signature of Yuba Fan sediment (δ^{202}Hg = −0.38 ± 0.17‰ and Δ^{199}Hg = 0.04 ± 0.03‰; mean ± 1SD, n=7, excluding one sample treated as an outlier) as a fingerprint of the large volume of IHg that could be methylated within the Yuba River or exported downstream.

Yuba and Feather River Biota

Biota THg and MMHg Concentrations

Biota THg and MMHg concentrations in the Yuba and Feather Rivers were similar to previous studies downstream of Au mining regions in the Sierra Nevada (e.g.,[16, 49, 50]). The concentrations in this study also overlap with THg and MMHg reported for biota in streams without any local Hg point sources (e.g, [11, 51]). Algae THg ranged from 57 to 186 ng/g, likely due to the variable accumulation of high THg Yuba Fan sediment. However MMHg levels in filamentous algae increased with distance downstream in the Yuba River, from 2.4 ng/g at Rose Bar to 17 ng/g at Dantoni and 15 ng/g at Simpson Bridge. Algae MMHg levels were similar to the Eel River in the northern California Coast Range (3 to 34 ng/g), where the authors suggested that microbial communities associated with algae might mediate in situ methylation of IHg.[13, 51] Benthic macroinvertebrate MMHg concentrations ranged from 37 to 271 ng/g and there was no systematic change in MMHg or %MMHg between sampling locations. These concentrations were more similar to macroinvertebrates from streams affected by atmospheric deposition (e.g., Eel River[51] and others across the US[11]) than streams with significant Hg point sources (e.g., Cache Creek[52] or streams near Oak Ridge, TN[53]). The highest MMHg and THg concentrations in this study were measured in Asian clam (79 to 271 ng/g and 168 to 426 ng/g, respectively) and forage fish (380 to 406 ng/g and 377 to 436 ng/g, respectively). Fish THg concentrations were within the reported range for these species in US streams unaffected by Hg point sources.[11] Consistent differences in %MMHg were observed among the organisms sampled, depending on their feeding behavior and presumed trophic position. The %MMHg (mean ± 1SD) increased in the order: sediment (1%, n=4), filamentous algae (6 ± 6%, n=7), aquatic worm (30 ± 9%, n=4), Asian clam (49 ± 20%, n=3), caddisfly larva (66 ± 7%, n=6), mayfly larva (73 ± 2%, n=3), stonefly larva (80 ± 9%, n=10), speckled dace (93%, n=1) and riffle sculpin (100%, n=1). This trend is strongly indicative of the preferential trophic transfer of MMHg via biomagnification in the Yuba River.

Biota Hg Isotopic Compositions

Aquatic organisms displayed a relatively narrow range in δ^{202}Hg (−0.84 to −0.42‰) but a wide range in Δ^{199}Hg (0.06 to 1.17‰; SI Table 2). Following the approach of Tsui et al.,[28] we performed linear regressions between %MMHg and Hg isotope values to determine whether δ^{202}Hg and Δ^{199}Hg values in biota change with increasing %MMHg (i.e., to test whether IHg and MMHg pools are isotopically distinct). Sediment was excluded from these regressions to compare IHg in the food web with IHg in sediment. In all biota (2013 and 2014) we observed a significant positive relationship between Δ^{199}Hg and %MMHg ($r^2 = 0.78$; $p<0.001$), but a significant relationship was not observed for δ^{202}Hg ($r^2 = 0.01$; $p = 0.61$). Because IHg and MMHg isotopic compositions could vary across sampling seasons, benthic macroinvertebrates were grouped by collection year (2013 and 2014) and the relationship between $\Delta^{199}Hg$ and %MMHg strengthened ($r^2 = 0.96$ for 2013 and $r^2 = 0.94$ for 2014). Positive relationships between $\Delta^{199}Hg$ and %MMHg have previously been reported for biota in stream, lake and estuarine food webs.[26-28] Although studies of lake, forest and estuary food webs have also consistently found significant positive relationships between $\delta^{202}Hg$ and %MMHg,[26-28] no such relationship was observed here (Yuba River) or in previous studies of the Eel River.[28] Overall, these results demonstrate the presence of isotopically distinct pools of IHg and MMHg within the food web and are consistent with a model of binary mixing. Therefore, we use these relationships to estimate the isotopic composition of the IHg and MMHg in the food web.

We estimated the isotopic composition of IHg and MMHg in the food web by extrapolation to 100% IHg and 100% MMHg for $\Delta^{199}Hg$ and $\delta^{202}Hg$ (Figure 2a,b). Because there was no significant relationship between $\delta^{202}Hg$ and %MMHg, we also compared the estimated $\delta^{202}Hg$ values for MMHg and IHg with the mean $\delta^{202}Hg$ of organisms containing more than 70% MMHg (i.e., predatory macroinvertebrates, following Tsui et al. [28]) and less than 15% MMHg (i.e., filamentous algae). The mean $\delta^{202}Hg$ of high %MMHg biota (−0.69 ± 0.12‰ for MMHg) and low %MMHg biota (−0.70 ± 0.08‰ for IHg) were not significantly different than linear regression estimates. Thus, these methods result in similar $\delta^{202}Hg$ values for MMHg and IHg and for consistency (with $\Delta^{199}Hg$) we use $\delta^{202}Hg$ values that were estimated by linear regression. We estimate that in 2013 MMHg had $\delta^{202}Hg$ of −0.72 ± 0.05‰ and $\Delta^{199}Hg$ of 0.90 ± 0.04‰ and IHg had $\delta^{202}Hg$ of −0.63 ± 0.06‰ and $\Delta^{199}Hg$ of 0.05 ± 0.04‰. We estimate that in 2014 MMHg had $\delta^{202}Hg$ of −0.72 ± 0.04‰ and $\Delta^{199}Hg$ of 1.44 ± 0.04‰ while IHg had $\delta^{202}Hg$ of −0.70 ± 0.05‰ and $\Delta^{199}Hg$ of −0.04 ± 0.05‰. The error reported for these estimates is the ±1SE of the intercept of the linear regression (i.e., at 100% IHg or MMHg). These estimates for the isotopic compositions of MMHg and IHg are employed throughout the following discussion.

MMHg Photodegradation

The estimated isotopic composition of bioaccumulated MMHg in the Yuba River reflects the isotopic composition of Hg source(s) and any fractionation that occurs during biogeochemical processes prior to entering the food web.[54] The Δ^{199}Hg:Δ^{201}Hg ratio in environmental samples such as fish and other biota is often compared to experimental ratios (e.g.,[55-57]) to differentiate between photochemical MMHg degradation (slope of ~1.3) and photochemical Hg(II) reduction (slope of ~1.0).[56] Biota from the Yuba and Feather Rivers had a Δ^{199}Hg:Δ^{201}Hg ratio of 1.27 ± 0.05 (1SE, n=35; SI Figure 4), which is comparable to freshwater fish from lakes (1.28 ± 0.01; 1SE, n=135)[58] and consistent with other freshwater food web studies.[26-29] This implies that the Δ^{199}Hg and Δ^{201}Hg values in biota result from MIF during photochemical MMHg degradation.[56] Significant MMHg photodegradation likely occurs in the highly exposed, nearly treeless Yuba-Feather riparian zone and the residual MMHg (with positive Δ^{199}Hg and Δ^{201}Hg) could then be incorporated into the food web. It is believed that the magnitude of MIF is directly proportional to the extent of photochemical MMHg degradation.[56] Experimental studies have found the observed MIF is sensitive to DOC concentrations,[56, 57] MMHg:DOC ratios,[59] and the wavelength of incident radiation.[55] However, we should note that all experiments to date have used Hg concentrations (and thus Hg:DOC ratios) that are higher than typically found in the environment. During a recent 4-year period (1999-2003), dissolved organic carbon (DOC) concentrations in lower Yuba River surface water averaged 1.16 ± 0.05 mg/L (1SE, n=104).[60] Therefore, we use the experimental isotope fractionation data for 1 mg/L DOC, and the estimated Δ^{199}Hg of MMHg, to calculate that 24% of the MMHg in the river had undergone photodegradation in 2013 prior to incorporation into the food web, while 35% was photodegraded in 2014.

In aquatic systems, MIF from photochemical MMHg degradation has been shown to vary with environmental characteristics such as water clarity,[24] water depth,[61] and canopy cover.[26, 30] In this study we observed significant differences in the extent of MMHg photodegradation between March 2013 (24%) and June 2014 (35%), but not between sampling locations within each time period. Such differences could have resulted from different environmental conditions (e.g., streamflow, water depth, or shading) or the timing of sampling (e.g., early spring vs. early summer), but we are unable to identify the relative importance of these factors. However, we did observe that fish sampled in 2014 (93-100% MMHg) had Δ^{199}Hg values of 0.79 and 0.84‰, which are nearly identical to the estimated Δ^{199}Hg of MMHg in 2013 (0.90‰). We suspect this similarity results because the fish sampled are relatively long lived (1-3 years) and integrate the MMHg across multiple years, in contrast to the seasonal growth and MMHg bioaccumulation of benthic macroinvertebrates.

To isolate photochemical and non-photochemical processes in aquatic environments Gehrke et al. ([25]) used experimental relationships to subtract the known MDF and MIF that occurs during photochemical MMHg degradation. Subsequently, this approach has been used to infer MDF from non-photochemical processes in many different field studies (e.g., in lakes, forests, and the ocean).[24, 26-28, 61, 62] These studies have consistently found a positive δ^{202}Hg offset between MMHg prior to photodegradation ("pre-photodegraded MMHg") and IHg ($\delta^{202}Hg_{pre\text{-}photodegraded\ MMHg}$ – $\delta^{202}Hg_{IHg}$) which has been interpreted to result from biotic MDF (e.g., the net result of biotic methylation and biotic degradation) in the environment.[24, 25, 27] For a similar comparison in the Yuba River, we begin with the estimated MMHg isotopic composition and use experimentally derived Δ^{199}Hg/δ^{202}Hg slopes (2.43 for 1 mg/L DOC)[56] to obtain an estimated δ^{202}Hg value for pre-photodegraded MMHg. Assuming that pre-photodegraded MMHg has Δ^{199}Hg values near zero, consistent with methylation of IHg in sediment, algae or the food web, the δ^{202}Hg of pre-photodegraded MMHg is estimated as −1.07‰ in 2013 and −1.29‰ in 2014. These values are much lower than the δ^{202}Hg of IHg estimated in the food web (-0.63 ± 0.06‰ in 2013 and -0.70±0.05‰ in 2014) or measured in sediment (−0.38 ± 0.17‰) or algae (−0.70 ± 0.08‰). Thus, there is a negative offset in δ^{202}Hg between IHg and estimated pre-photodegraded MMHg in this system (Figure 3). A negative δ^{202}Hg offset has not been previously observed and we examine possible explanations for this unique relationship below.

Hg Sources in the Yuba River

The Yuba River contains large quantities of IHg in streambed, bank and terrace sediment providing a persistent source of IHg to the river. The isotopic composition of two IHg pools were characterized in this study: Yuba Fan sediment (>95% IHg) has a mean δ^{202}Hg of −0.38 ± 0.17‰ and Δ^{199}Hg of 0.04 ± 0.03‰ (1SD, n=7; excluding one sample treated as an outlier) and filamentous algae (85-98% IHg) has a mean δ^{202}Hg of −0.70 ± 0.08‰ and Δ^{199}Hg of 0.11 ± 0.04‰ (1SD, n=7). As described above, we estimated the isotopic composition of IHg in the food web (δ^{202}Hg = −0.70 ± 0.04‰ and Δ^{199}Hg = 0.05 ± 0.07‰) and these δ^{202}Hg values are similar to algae and slightly lower than Yuba Fan sediment (Figure 3). Therefore, we suggest that IHg in the food web is directly accumulated from sediment and algae, likely because these materials provide a direct dietary resource for benthic macroinvertebrates.

We have estimated the isotopic composition of MMHg (by linear regression) and pre-photodegraded MMHg (MMHg minus the MIF and MDF from MMHg photodegradation) in the Yuba River. MMHg could be produced in situ by methylation of sediment IHg in the hyporheic zone or associated with benthic biofilms and filamentous algae.[13, 63-65] If so, then either a bioavailable pool of IHg with a δ^{202}Hg lower than bulk sediment is preferentially methylated or net negative MDF (of up to −0.9‰) occurs between IHg and pre-photodegraded MMHg (Figure 4a). Alternatively, the presence and bioaccumulation of MMHg in some streams can be a function of watershed characteristics that promote Hg deposition and methylation.[11, 12, 14, 66] If MMHg in the lower Yuba

River were derived from external or upstream sources, and not produced in situ, then Yuba Fan sediment might only be a source of IHg (not MMHg) to the food web.

We explore potential external Hg sources by comparing known isotopic compositions of these sources with the estimated isotopic composition of Yuba River MMHg and pre-photodegraded MMHg. In lakes and oceans, atmospheric deposition may provide a readily reactive IHg source that can be methylated leading to MMHg in the food web.[67] [61] In a previous study, precipitation collected near coastal CA and SF Bay had a Hg isotopic composition (δ^{202}Hg = 0.06 ± 0.03 ‰ and Δ^{199}Hg = 0.30 ± 0.05‰; mean ± 1SD, n=3)[40] consistent with studies of precipitation unaffected by local Hg point sources (i.e., δ^{202}Hg near zero and significant positive Δ^{199}Hg).[33, 68-70] Significant positive Δ^{199}Hg in regional precipitation (Δ^{199}Hg = 0.30 ± 0.05‰), but a lack of significant positive Δ^{199}Hg estimated for IHg in the food web (Δ^{199}Hg of 0.05±0.07‰), suggests that biota in the Yuba River do not obtain IHg from precipitation. If IHg in precipitation was the precursor to MMHg in Yuba River biota, then significant MDF of approximately -1 ‰ would be required to link precipitation IHg to pre-photodegraded MMHg. Furthermore, this IHg source would have to be preferentially methylated despite the presence of large volumes of IHg in Yuba Fan sediment.

It is also possible that IHg accumulated in the watershed (i.e., upstream of Englebright Dam) could be a source of MMHg to the lower Yuba River. Forest soils accumulate Hg from dry deposition, leaf litter, and precipitation.[33, 71] This IHg could be methylated in wetlands, floodplains or reservoirs and transported to aquatic environments during runoff events.[72-74] Basal resources (foliage, soil, and submerged leaf litter) from the Eel River in northern California had relatively low δ^{202}Hg (−2.53 to −1.54‰) and negative Δ^{199}Hg (−0.37 to −0.15‰).[28] Similar Hg isotopic compositions have been found in forest floor samples from the upper Midwest (δ^{202}Hg = −1.05 to −1.88‰ and Δ^{199}Hg = −0.15 to −0.25‰)[33] and in low THg sediment from Tennessee streams (δ^{202}Hg = −1.40 ± 0.06‰ and Δ^{199}Hg = −0.26 ± 0.03‰, mean ± 1SD, n=6).[21] Without Au mining impacts, we would expect the isotopic composition of geogenic and atmospheric Hg sources accumulated in the Yuba River watershed to have a similar range in isotopic composition (i.e., δ^{202}Hg between −1 and −2.5 ‰ and slight negative Δ^{199}Hg). Because the estimated δ^{202}Hg of pre-photodegraded MMHg in the Yuba River overlaps with these IHg pools (Figure 4b), we cannot rule out upstream or terrestrial IHg as a possible source of MMHg in the Yuba River. However, THg in Yuba Fan sediment is at least three times, and up to 100 times, higher than background sediment and is found in locations where methylation is thought to occur (e.g., streambed, floodplains, hyporheic zone, and associated with filamentous algae).[12, 13, 65, 75, 76] The Hg isotope data suggest that IHg in the food web is directly accumulated from sediment and algae (Figure 3) and it follows that MMHg is also accumulated from dietary resources. From Hg isotope data alone, we cannot rule out the possibility that external sources of MMHg (e.g., upstream reservoirs, precipitation) become associated with lower Yuba River sediment or algae (which could then be accumulated in the Yuba River food web). Nonetheless, below we consider the scenario where IHg in co-located sediment and algae is methylated in situ and then bioaccumulated as MMHg in the lower Yuba River.

In Stream Processes and MDF

Labile Hg in Sediment

It is likely that only a fraction of the IHg in sediment is in a chemical form that is available for microbial methylation.[12, 17, 77-79] If this fraction has lower δ^{202}Hg values than bulk sediment, then the negative δ^{202}Hg offset between sediment IHg and pre-photodegraded MMHg may be an artifact of the difference between bulk sediment δ^{202}Hg and the δ^{202}Hg of labile IHg. If we assume biotic MDF occurs in a consistent manner to that observed in previous studies (i.e., MDF of +0.4‰ to +0.8‰),[24, 25, 27, 62] then from the estimated pre-photodegraded MMHg δ^{202}Hg value (−1.29 to −1.07‰) we would predict that the labile IHg fraction would have δ^{202}Hg between −1.5 and

−2.1‰. Multiple experiments have shown that leachates (water soluble, thiosulfate soluble and weak acid soluble) have consistently higher δ^{202}Hg (up to 1.3‰) than bulk sediment and mine wastes.[80-82] HgS species and Hg sorbed to colloids, both of which could be present in Yuba Fan Au mine tailings,[17] are susceptible to methylation in the hyporheic zone or inundated floodplains.[45] Studies have demonstrated that precipitation of HgS, β-HgS and HgO from solution,[19, 83] sorption of Hg to goethite,[84] and binding of Hg to thiol groups in natural organic matter,[85] all result in a lower δ^{202}Hg value for the product (e.g., HgS or goethite-Hg). However, a separate investigation of sediment contaminated by metallic Hg suggests that sulfide bound Hg displays higher δ^{202}Hg values (up to 1‰ higher) than bulk sediment.[86] These studies demonstrate that Hg fractions in sediment may have different δ^{202}Hg values and future investigations of the isotopic composition of different Hg species in Yuba Fan sediment could prove valuable. However, at present we are unable to identify a specific labile Hg fraction, with consistently low δ^{202}Hg, that could explain the observed IHg-MMHg relationship. Thus, we use bulk Hg isotope measurements of sediment and algae, or the estimated IHg in the food web, to compare with MMHg in the Yuba River.

Net MDF during Biotic Processes

Previous studies have found a net positive offset in δ^{202}Hg ($\delta^{202}Hg_{\text{pre-photodegraded MMHg}}$ – $\delta^{202}Hg_{IHg}$), between bulk sediment (IHg) and estimated pre-photodegraded MMHg, which ranged from +0.4 to +0.8‰ in coastal oceans (San Francisco Bay, East Coast estuaries, Minamata Bay) and freshwater lakes (Michigan and Florida).[24, 25, 27, 62] Biotic methylation preferentially methylates the light isotopes of Hg, resulting in MMHg that displays lower δ^{202}Hg values than the IHg substrate (-MDF).[87, 88] In contrast, biotic degradation of MMHg by the mercury reductase mechanism leads to higher δ^{202}Hg values for the residual MMHg (+MDF).[89] Therefore, the previously observed positive offset was suggested to result from processing of Hg in sediment where biotic methylation is followed by significant biotic MMHg degradation,[24, 25] leading to a δ^{202}Hg value for residual MMHg that is higher than the original sediment. This residual MMHg is subsequently photodegraded (+MIF and +MDF)[56, 57] and bioaccumulated (no MIF or MDF).[35, 54] In contrast, in this study the estimated δ^{202}Hg of pre-photodegraded MMHg in the Yuba River is significantly lower (at least 0.4‰ in 2013 and at least 0.6‰ in 2014) than estimated δ^{202}Hg of IHg in the food web or the measured δ^{202}Hg of sediment or filamentous algae. Therefore, we suggest that if MMHg is formed from sediment or algae, then there is a fundamental difference in Hg biogeochemistry and resulting isotope fractionation in this system. We note that all of the previous studies were in lakes, coastal oceans or estuaries, whereas this is the first such study to compare IHg and estimated MMHg isotopic compositions in a river system.

In general, a number of environmental characteristics (e.g., DOC, redox, turbulence, suspended solids, etc.) that affect MMHg formation and degradation differ between 1) rivers (flowing water) and 2) lakes or marine coastal (non-flowing water) environments. These characteristics might affect net MDF between IHg and MMHg by changing the extent of methylation or MMHg degradation. In streams, in-situ Hg methylation in sediment, hyporheic zones, benthic biofilms or filamentous algae (e.g.,[13, 63, 65, 75]) would be followed by MMHg advection from the substrate into the water column. We would expect this transport to be greater in flowing water (i.e., rivers) than in non-flowing water environments (i.e., lakes or estuaries). Turbulent diffusion of MMHg has been hypothesized to increase MDF during experimental studies of net biotic methylation and degradation.[88] Similarly, in-situ methylation in flowing water could lead to continuous removal of the MMHg product from the site of methylation and decrease the amount of MMHg available for biotic degradation. This would result in less biotic degradation (less +MDF) of the MMHg exported to the water column, and therefore lower δ^{202}Hg values for MMHg compared to the IHg substrate. Conversely, when MMHg resides for a relatively long period of time in sediment, as might be the case in standing water, it could be biotically degraded to a greater extent (more

+MDF). Significant biotic MMHg degradation would drive the residual MMHg to higher δ^{202}Hg values than the sediment, as has been observed in lakes and coastal marine environments. Thus, the extent of biotic MMHg degradation could cause the different δ^{202}Hg offset between flowing and non-flowing water environments. If so, our data suggests that relatively little biotic MMHg degradation occurs, and photochemical degradation is a relatively more dominant degradation pathway, in the Yuba River.

It is also possible that non-*mer* mediated biotic degradation pathways could result in different MDF patterns, leading to the observed negative δ^{202}Hg offset. Biotic MMHg degradation can occur through either *mer*-mediated degradation or oxidative demethylation pathways.[90, 91] During *mer*-mediated degradation, MMHg is converted to Hg(0), which is volatile and could be more easily removed from the substrate,[91] resulting in residual MMHg with higher δ^{202}Hg (+MDF).[89] Oxidative demethylation, which is considered a byproduct of microbial metabolism, likely converts MMHg to Hg(II).[6, 7, 92] Isotopic fractionation during oxidative demethylation has not yet been measured, but during this process the Hg(II) product could undergo remethylation. We hypothesize that during biotic cycling, when oxidative MMHg degradation is the dominant pathway, MMHg would become enriched in light Hg isotopes through successive remethylation (−MDF) of the degraded MMHg. Environmental conditions that determine preferred degradation pathways might differ between flowing and non-flowing water environments. In general, oxidative demethylation is expected to be dominant when bioavailable Hg is not at a high enough concentration to induce *mer*-enzyme expression (i.e., low THg environments).[90, 92] However, in high THg environments, geochemical conditions such as redox state, organic matter content and sulfide can control Hg bioavailability and change the dominant degradation pathway.[90] Although we cannot pinpoint the specific mechanism, changes in the extent or the pathway of biotic MMHg degradation are plausible explanations for the observed net negative MDF between IHg and MMHg in the Yuba River.

Implications for Future Work

This study is the first to use Hg isotopes to identify MMHg sources and infer biogeochemical transformations in a stream contaminated by historical Au mining. We have characterized the isotopic composition of sediment in the Yuba Fan, which may enable future tracing of sediment-bound IHg to downstream floodplains and wetlands in the Sacramento Valley. We also estimated the isotopic composition of Yuba River MMHg, which might be valuable for future studies that investigate whether this MMHg is exported downstream[79, 93] or to the terrestrial food web. Comparisons of the isotopic compositions of IHg with MMHg and pre-photodegraded MMHg provided useful insight into Hg biogeochemistry in the Yuba River. The Hg isotope data suggest that benthic macroinvertebrates obtain IHg from filamentous algae and sediment (i.e., through their diet). Although we cannot rule out the possibility for external inputs of MMHg, we think it likely that MMHg is accumulated directly from sediment and algae in the Yuba River. If this MMHg is formed in situ, then the relationship between IHg (in the food web, sediment or algae) and MMHg in this study is different than previous studies of lakes, estuaries and forests. We hypothesize that this could be due to differences in net MDF resulting from the extent or the pathway of biotic MMHg degradation in the Yuba River. If changes in biotic MMHg degradation result from characteristic differences between flowing and non-flowing water environments, we would expect similar net negative MDF to be observed between IHg and MMHg in other stream systems.

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Supporting Information

Sample collection details, regional sampling map, a detailed figure legend, complementary figures and three data tables. This information is available free of charge via the Internet at http://pubs.acs.org/.

Figures

Figure 1: Sediment δ^{202}Hg and THg vs. Distance in the Yuba and Feather Rivers. All diamonds represent sediment analyzed in this study, with grey symbols indicating THg and black symbols indicating the corresponding δ^{202}Hg values (±0.08‰). Circles represent two sediment samples previously analyzed by Donovan et al. ([40]) from Rose Bar. Biota sampling sites are noted at the bottom of the figure at their approximate location in the river system.

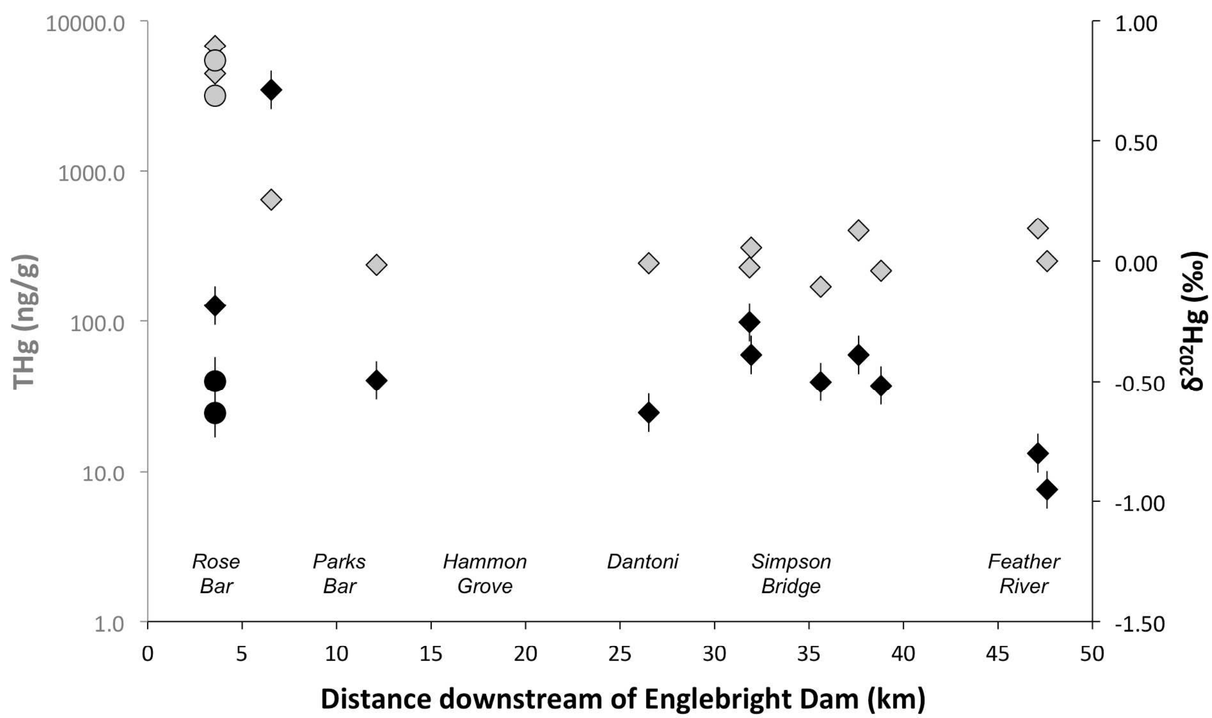
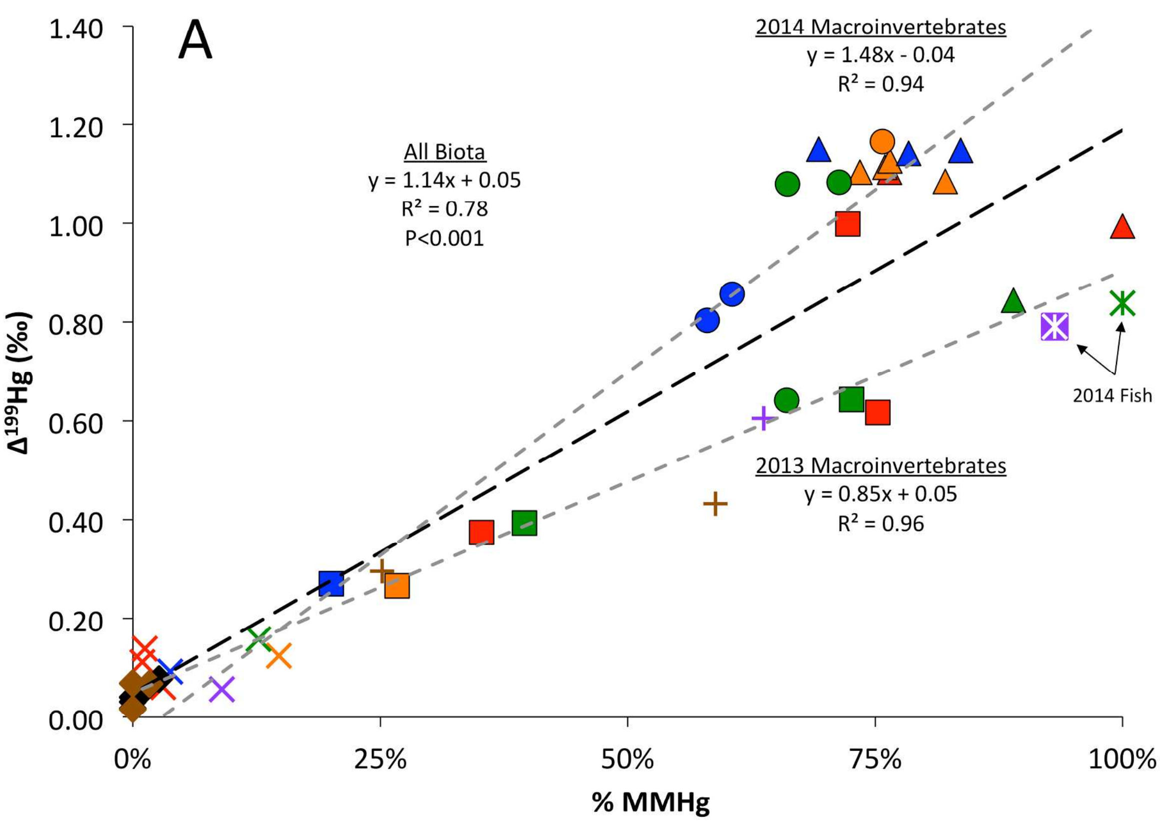
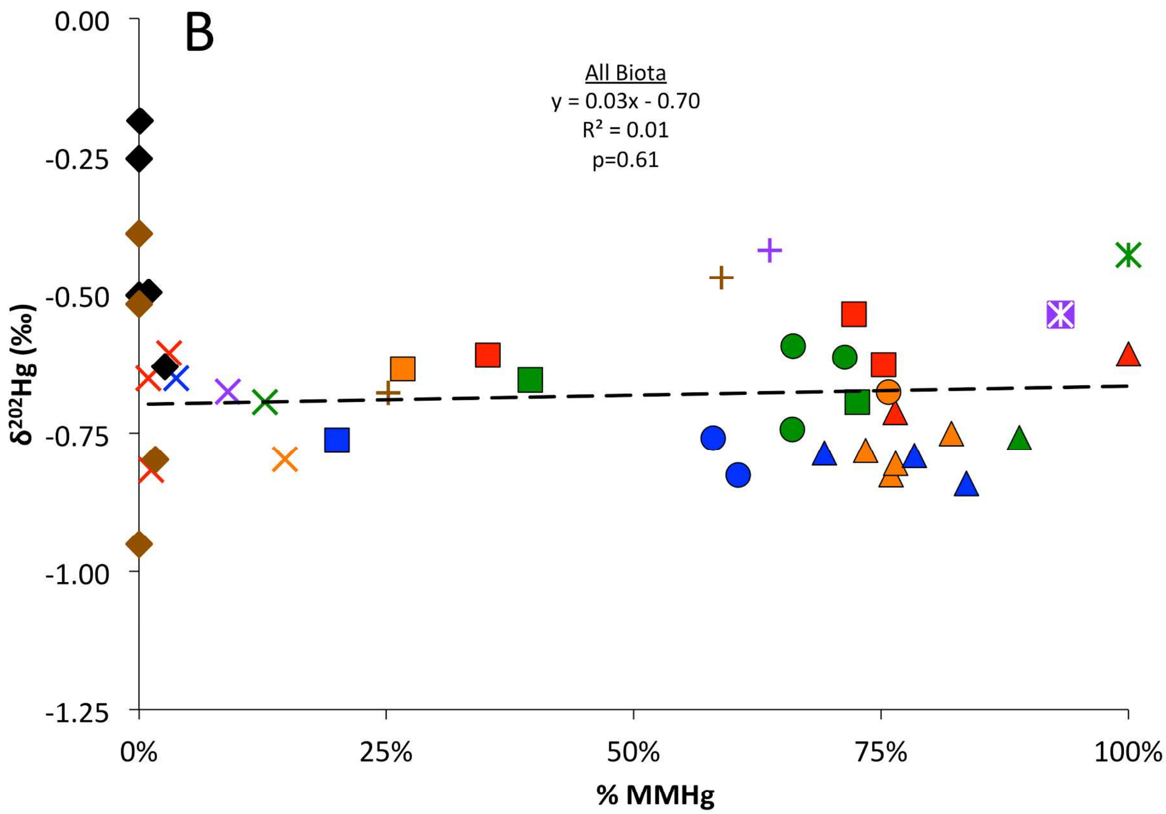


Figure 2: %MMHg vs. Δ^{199}Hg (A, top) and δ^{202}Hg (B, bottom) for all biota. Dark dashed lines represent linear relationships for all biota samples and light grey lines (in A only) represent specific sampling years. Biota are colored corresponding to their sampling location (RB = red, PB = orange, HG = blue, Da = green, SB = purple, FR = brown). Symbols represent the sample type (stonefly = triangle, caddisfly = circle, mayfly and aq. worm= square, clam = +, fish = asterisk and filamentous algae = x). Sediment symbols are colored by stream with solid black diamonds representing Yuba River sediment and solid brown diamonds representing Feather River sediment. A detailed legend can be found in the Supporting Information (SI Figure 2).




B
All Biota
y = 0.03x - 0.70
R² = 0.01
p=0.61
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
δ202Hg (‰)
0%
25%
50%
75%
100%
% MMHg

534

Figure 3: Hg isotopic composition ($\delta^{202}Hg$ vs. $\Delta^{199}Hg$) for biota and sediment in the Yuba and Feather Rivers. Symbols are identical to Figure 2 and the representative uncertainty for individual samples is indicated in the upper left hand corner (±0.08‰ for $\delta^{202}Hg$ and ±0.05‰ for $\Delta^{199}Hg$). Estimated MMHg and IHg isotopic compositions (from linear regression) are black crosses and their size is representative of the 1SE uncertainty of these estimates. The 1 mg/L DOC MMHg photochemical degradation slope, from ([56]), is included as a black dashed line drawn from each estimated MMHg.

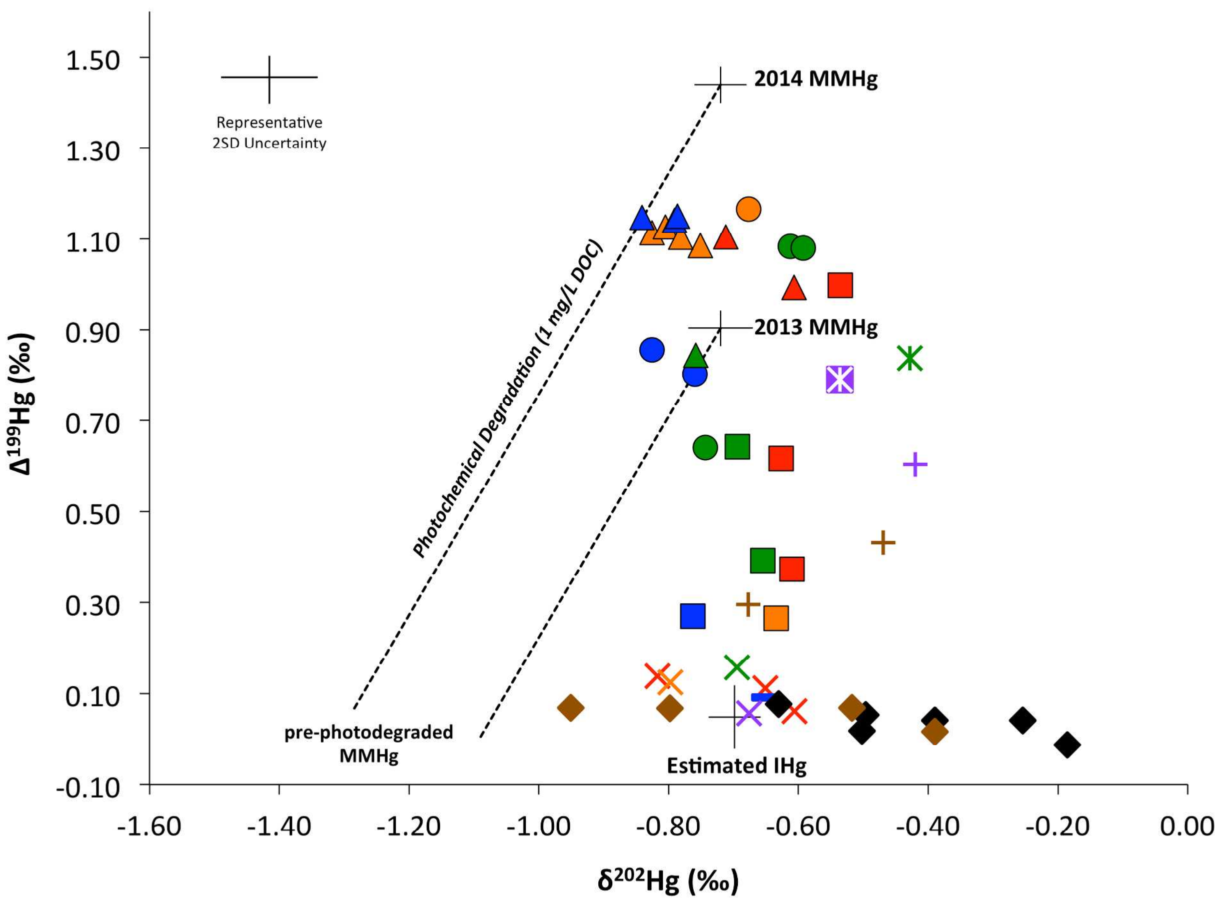
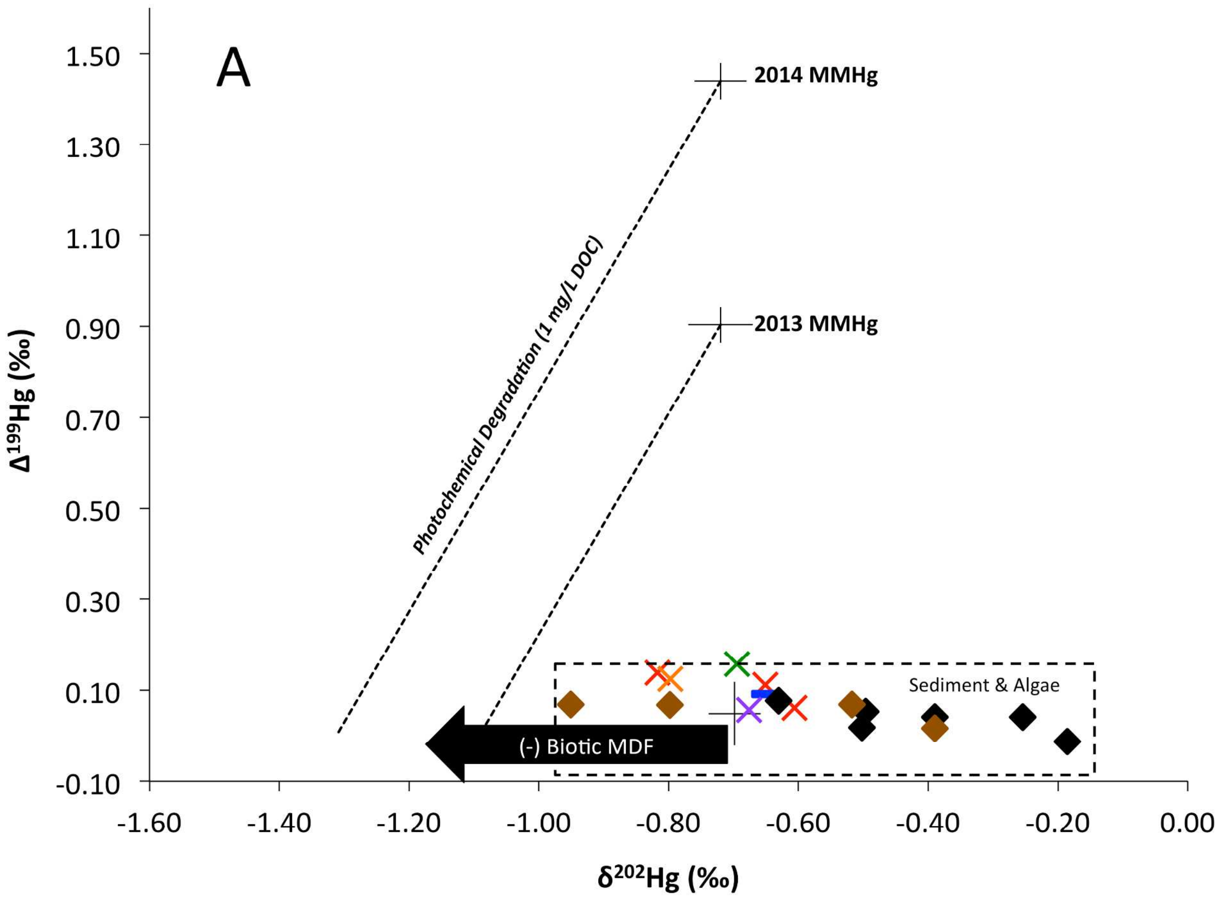
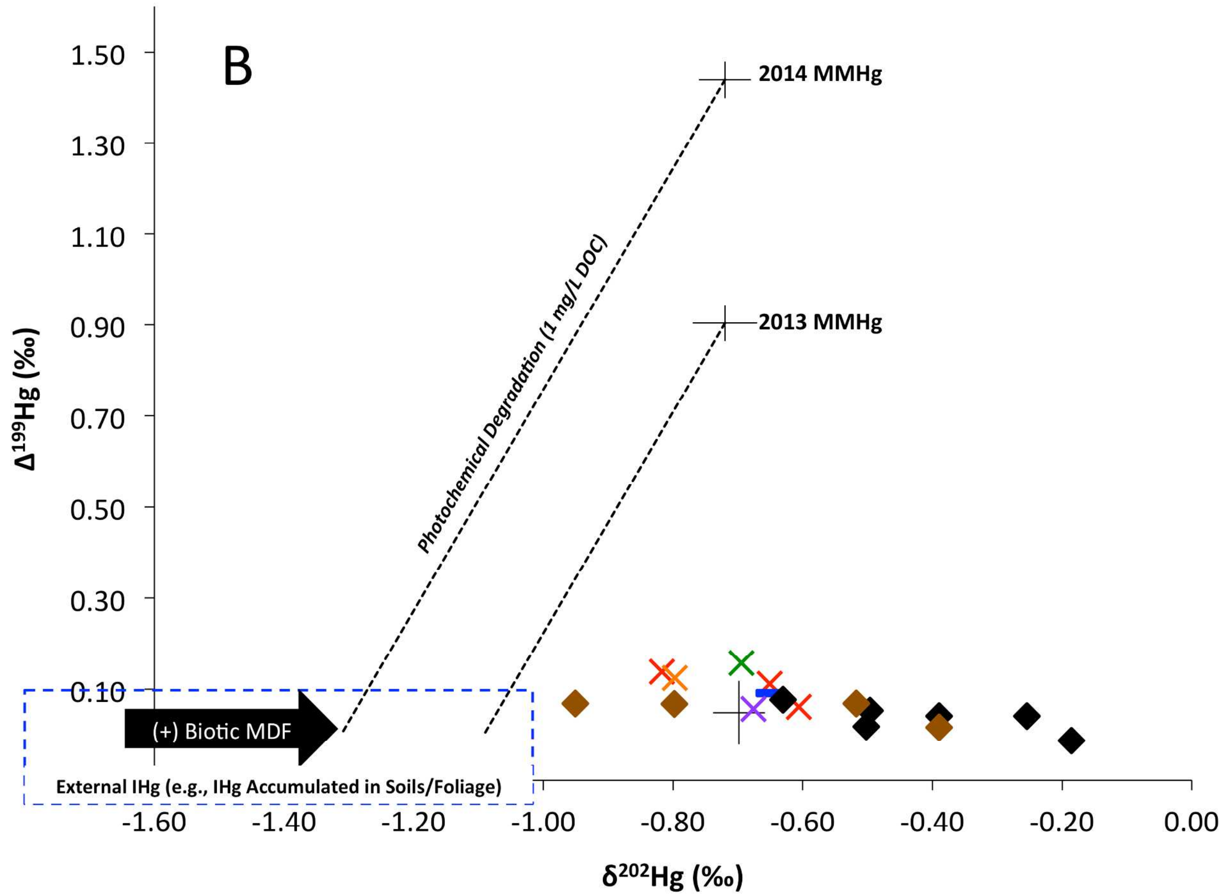


Figure 4: Possible explanations for the origin of MMHg in the Yuba and Feather Rivers. Either (A) methylation of sediment and algae IHg sources result in net negative biotic MDF or (B) external, watershed IHg sources (~δ^{202}Hg of −1 to −2.5‰) are methylated and input to the Yuba-Feather River and net positive biotic MDF is consistent with previous studies.




B
1.50
1.30
1.10
0.90
0.70
0.50
0.30
0.10
Δ199Hg (‰)
2014 MMHg
2013 MMHg
Photochemical Degradation (1 mg/L DOC)
(+) Biotic MDF
External IHg (e.g., IHg Accumulated in Soils/Foliage)
-1.60
-1.40
-1.20
-1.00
-0.80
-0.60
-0.40
-0.20
0.00
δ202Hg (‰)

551

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