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Prediction of fish and sediment mercury in streams using landscape variables and historical mining

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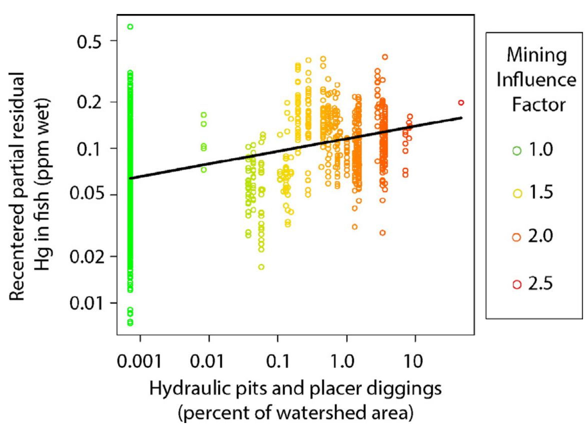
HIGHLIGHTS

- Stream fish Hg positively influenced by Au mines, deciduous forests, urban areas.
- Fish Hg negatively influenced by evergreen forests and wetlands in Sierra Nevada.
- Sediment Hg and MeHg affected by LOI, grain size, land use and cover, Au mines.
- Geospatial model predicts Hg in 5 fish species as a function of length and location.
- Model requiring sediment MeHg slightly better than geospatial-only model.

GRAPHICAL ABSTRACT



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ABSTRACT

Widespread mercury (Hg) contamination of aquatic systems in the Sierra Nevada of California, U.S., is associated with historical use to enhance gold (Au) recovery by amalgamation. In areas affected by historical Au mining operations, including the western slope of the Sierra Nevada and downstream areas in northern California, such as San Francisco Bay and the Sacramento River–San Joaquin River Delta, microbial conversion of Hg to methylmercury (MeHg) leads to bioaccumulation of MeHg in food webs, and increased risks to humans and wildlife. This study focused on developing a predictive model for THg in stream fish tissue based on geospatial data, including land use/land cover data, and the distribution of legacy Au mines. Data on total mercury (THg) and MeHg concentrations in fish tissue and streambed sediment collected during 1980–2012 from stream sites in the Sierra Nevada, California were combined with geospatial data to estimate fish THg concentrations across the landscape. THg concentrations of five fish species (Brown Trout, Rainbow Trout, Sacramento Pikeminnow, Sacramento Sucker, and Smallmouth Bass) within stream sections were predicted using multi-model inference based on Akaike Information Criteria, using geospatial data for mining history and landscape characteristics as well as fish species and length ($r^2 = 0.61$, $p < 0.001$). Including THg concentrations in streambed sediment did not improve the model's fit, however including MeHg concentrations in streambed sediment, organic content (loss on ignition), and sediment grain size resulted in an improved fit ($r^2 = 0.63$, $p < 0.001$). These models can be used to estimate

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THg concentrations in stream fish based on landscape variables in the Sierra Nevada in areas where direct measurements of THg concentration in fish are unavailable.

1. Introduction

Use of mercury (Hg) to enhance gold (Au) and silver (Ag) recovery by amalgamation has resulted in widespread Hg contamination of aquatic systems in many areas worldwide (Hylander and Meili, 2003, 2005; Nriagu, 1994). Microbial conversion of Hg to mono-methylmercury (MeHg), a potent neurotoxin (Wiener et al., 2003), leads to bioaccumulation of MeHg in food webs (e.g. Brigham et al., 2009; Chasar et al., 2009; Driscoll et al., 2013; Grigal 2003; Lavoie et al., 2013; Stewart et al., 2008), causing enhanced risk of MeHg exposure to humans and wildlife in areas affected by historical precious-metal recovery operations. Historical Au mining and processing by amalgamation caused inorganic Hg contamination on the western slope of the Sierra Nevada (Alpers et al., 2005a; Alpers, 2015; Singer et al., 2013), and downstream areas in northern California such as San Francisco Bay and the Sacramento River–San Joaquin River Delta (Davis et al., 2008, 2012; Donovan et al., 2013; Eagles-Smith et al., 2009; Gehrke et al., 2011a,b; Hornberger et al., 1999).

Several previous studies have assessed the distribution of landscape variables relative to Hg in fish and other biota at regional and national scales in North America, with the goal of testing conceptual models regarding biogeochemical and physical processes controlling Hg(II)-methylation and MeHg bioaccumulation. Evers et al. (1998, 2003, 2007, 2011) evaluated spatial trends in northeastern North America, with emphasis on ecosystem characteristics affecting MeHg bioaccumulation in loons. Wiener et al. (2006) used information-theoretic modeling with Akaike Information Criteria (AIC; Burnham and Anderson, 2002) to determine that the following factors influenced MeHg in lake water and fish in the Voyageurs National Park, Minnesota: lake water pH, dissolved sulfate, and total organic carbon, an indicator of wetland influence. Scudder et al. (2009) used a national U.S. database for Hg in fish, plus total mercury (THg) and MeHg in streambed sediment and stream water, to evaluate the influence of Hg sources (atmospheric, Au and Hg mining, and urban), landscape factors including wetlands and other land-use/land-cover types, and ecosystem characteristics with regard to their effects on production and bioaccumulation of MeHg. Other studies have used geospatial landscape variables to evaluate patterns of Hg bioaccumulation in lake fish (Dittman and Driscoll, 2009; Drenner et al., 2011; Shanley et al., 2012; Nagorski et al., 2014; Eagles-Smith et al., 2016), but few studies have addressed Hg in stream fish.

It is well known that MeHg tends to increase with fish length and trophic level, and varies with tissue type (Wiener et al., 2003). Wente (2004) developed a statistical model (National Descriptive Model of Mercury in Fish, NDMMF) that standardizes the concentrations of Hg in fish among different species, individual samples of varying length, and samples of different types.

The spatial distribution of Hg in fish tissue (that occurs predominantly as MeHg: Bloom, 1992; Kuwabara et al., 2007; Saiki et al., 2009) and MeHg in predatory invertebrates has been shown to vary among Sierra Nevada watersheds (Alpers et al., 2005b; May et al., 2000; Slotton et al., 1997); and it has been suggested that historical Au mining intensity and associated Hg losses from amalgamation during Au processing are important factors influencing spatial trends in MeHg bioaccumulation (Alpers and Hunerlach, 2000). Previous studies of spatial variation in fish Hg in the San Francisco Bay, the Sacramento–San Joaquin Delta, and its tributaries (Davis et al., 2008, 2012; Melwani et al., 2007), identified some differences between watersheds draining the Sierra Nevada, but did not identify a clear relationship with historical Au mining intensity. Many of the fish samples analyzed in the previous studies were collected in the lower-elevation reaches of rivers, in areas where there are no physical barriers preventing fish from migrating between watersheds, a phenomenon that may cloud any potential mining signal. In this study, focusing on stream reaches upstream of dams that block fish migration allowed us to isolate the effects of historical Au mining and evaluate the influence of land-use/land-cover characteristics that may affect Hg(II) methylation and MeHg bioaccumulation.

A robust predictive model for Hg in fish in streams is needed in the Sierra Nevada of California to identify stream reaches likely to contain fish with elevated Hg caused by legacy Au mining. The predictive model would be used to prioritize sampling efforts designed to refine lists of impaired water bodies (e.g. California SWRCB, 2012; Fig. 1) and to identify remediation targets to reduce exposure of humans and wildlife to toxic MeHg. The research goal of this study was to develop a predictive model for THg in stream fish tissue based exclusively on geospatial data, including land-use/land-cover data and the distribution of legacy Au mines.

2. Methods

2.1. Study area

The study area for the modeling effort described herein consists of a portion of the western slope of the Sierra Nevada bounded on the south by the Merced River watershed and on the north by the Feather River watershed (Fig. 1). These watersheds contain thousands of historical Au mines (Fig. 1). Within each watershed, river reaches were selected above the lowest elevation dam to avoid problems with fish migration between watersheds. The Cosumnes River (Fig. 1) is the only major river in the study area that does not have a dam blocking fish passage.

The western slope of the Sierra Nevada hosts the Sierra Nevada Foothills (SNFH) Au belt, which includes the Mother Lode, a group of lode mineral deposits consisting of low-sulfide Au-quartz veins (Ashley, 2002). The northern Sierra Nevada also hosts extensive placer Au deposits in Tertiary gravels (Yeend, 1974). The lode Au deposits of the SNFH Au belt were mined primarily by underground methods; Au-quartz ore was crushed by stamp mills where amalgamation with Hg was commonly practiced from the 1860s through the 1930s, resulting in the loss to the environment of approximately 1.3×10^6 kg of Hg associated with the production of about 37×10^6 troy ounces (1.2×10^6 kg) of Au (Churchill, 2000). Placer Au deposits were mined primarily by surface methods including hydraulic mining and dredging; Hg losses from amalgamation are estimated to have been about 4.5×10^6 kg associated with production of about 68×10^6 troy ounces (2.1×10^6 kg) of Au, primarily from the 1850s through the 1930s (Churchill, 2000).

2.2. Data acquisition and database construction

Concentration data for THg and MeHg in streambed sediment and fish were compiled from various sources, including national and state environmental databases, published reports and documents, and previously unpublished research data. Data were imported into a relational database (Microsoft Access, version 2013). Data were retrieved from the USGS National Water Information System (NWIS) and the California SWRCB's California Environmental Data Exchange Network (CEDEN) on February 1, 2012. Previously unpublished data from USGS studies conducted during the 1990s and 2000s were imported into NWIS and the study database. New data were generated for the study by sampling water, streambed sediment, and fish at 25 locations during 2011–12.

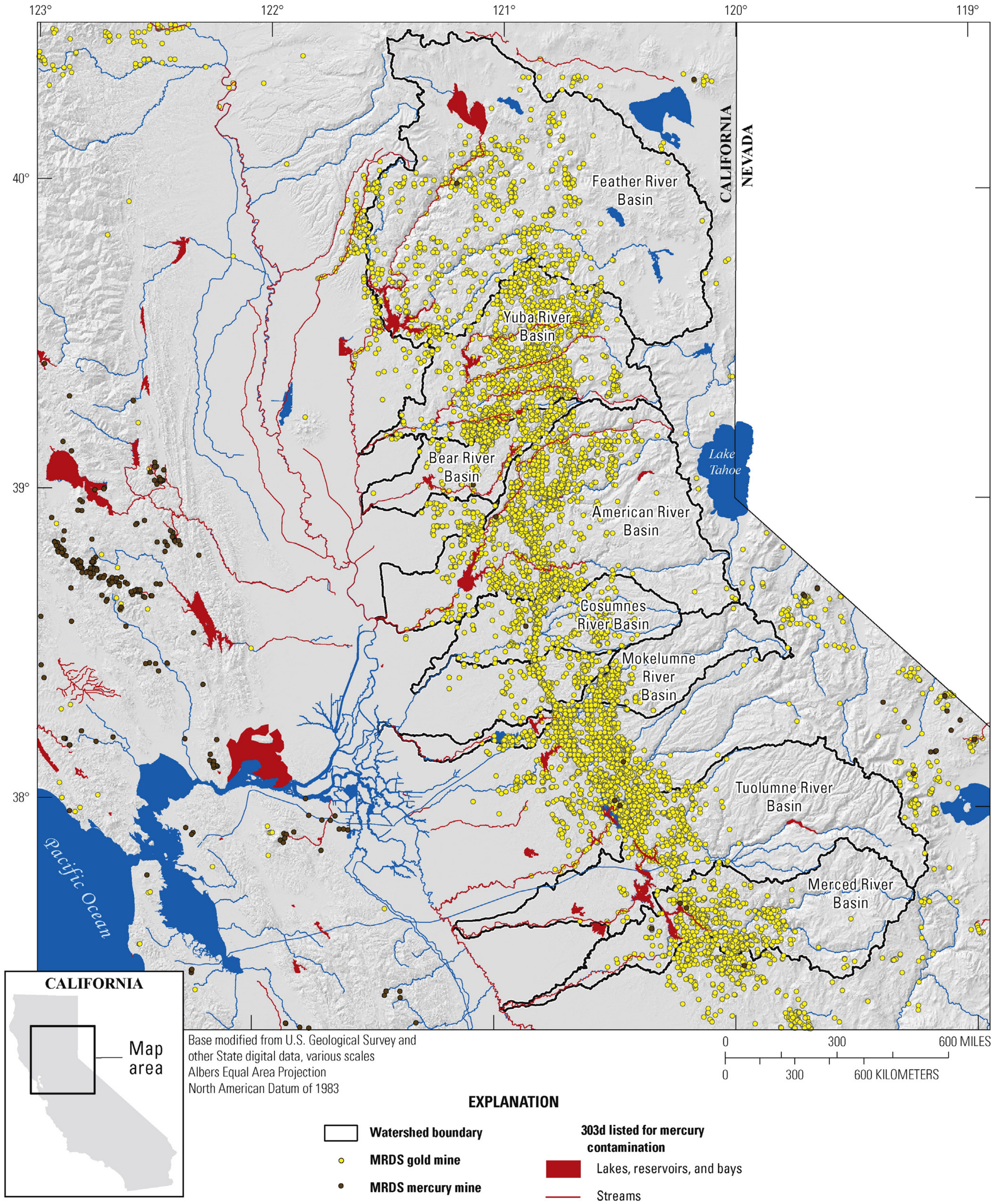

Fig. 1. Map showing locations of historical gold mines in the Sierra Nevada and historical mercury mines in the Coast Ranges, California (MRDS, Mineral Resources Data System; USGS, 2013). Red shading indicates stream segments, lakes, and reservoirs on 303(d) list indicating water-quality impairment caused by mercury (California SWRCB, 2012).

The fish tissue data set included 1399 analyses of 1390 individual fish (including 9 duplicate analyses for individual fish) collected during 1980–2012, representing 17 species (Supplemental material, Fig. S1). Data were compiled for initial modeling, using a guild approach (Fig. S2) (data sources in Supplemental material, Tables S1–S4). It was determined that detailed modeling would work best using the five fish species with the most samples: Brown Trout (210 fish), Rainbow Trout (710 fish), Sacramento Pikeminnow (79 fish), Sacramento Sucker (93 fish), and Smallmouth Bass (179 fish). These five fish species were represented by 1271 individual fish from 103 sites (Fig. S3, Tables S5–S6).

A small number of the fish tissue analyses (20 Rainbow Trout and 2 Brown Trout) were below the method detection limit (mean of 0.025 $\mu g\ g^{-1}$ wet weight, ww). For modeling purposes, a concentration of one-half of the detection limit was used for these censored data prior to any other conversions such as whole body to axial muscle fillet, or dry weight (dw) to ww, as described below. Most of the analyses of mercury in fish tissue were axial muscle fillet without skin. Some whole-body fish analyses were converted to axial muscle fillet equivalent concentration using the following equation, from Peterson et al. (2007):

$$\log(\text{fillet}) = 0.2545 + 1.0623\ \log(\text{whole-body}). \tag{1}$$

For the five species used in the detailed modeling, the following numbers of samples were converted from whole body to axial muscle fillet equivalent: Brown Trout, 55 of 210 analyses (26%); Rainbow Trout, 110 of 710 samples (15%); Sacramento Pikeminnow, 26 of 79 samples (33%); Sacramento Sucker, 69 of 93 samples (74%) and Smallmouth Bass, 100 of 179 samples (56%).

Many of the fish THg analyses were done on a ww basis and moisture content was not determined. For samples for which only dw data were available and moisture content was determined, the fish THg concentration data were converted to ww. If moisture content was not available for an individual fish sample, average percent moisture was calculated by species (Table S7).

After applying the dw-to-ww conversion, 105 individual fish analyses (out of 1399 from all species initially considered) had data for whole-body fish MeHg, but not whole-body fish THg. We fit a linear regression ($r^2 = 0.99$, $p < 0.001$) based on 239 fish samples from 7 species that had both fish MeHg and fish THg values, and used Eq. (2)

$$\log(\text{fishTHg}) = 0.022 + 0.98\ \log(\text{fishMeHg}) \tag{2}$$

where both fishTHg and fishMeHg are in units of $\mu g\ g^{-1}$, to estimate fish THg (ww) for the 105 individual analyses. The average proportion of THg in the MeHg form was 89% (sd 6.0%) for the 239 samples, of which 235 were from the five species used in modeling (Table S8). Modeling of fish tissue mercury concentration in this study was done using ww THg concentrations representing axial muscle fillet tissue without skin. Because THg is commonly analyzed in fish tissue, and almost all mercury present in fish is in the form of MeHg, California regulations refer to THg in fish (California OEHHA, 2013).

Sediment samples in the final data set included 106 THg analyses from 73 sites (Fig. S4). Data for fish tissue and streambed sediment that were used in the modeling came from 133 sites in all: 43 of the sites had data for both fish tissue and sediment, 60 sites had fish tissue data only, and 30 sites had streambed sediment data only. Predictions of mercury in fish tissue were made for the 133 sites with data for fish and (or) sediment, plus an additional 52 sites without fish or sediment data (Fig. S5), a total of 185 sites (Fig. S6).

2.3. Variable estimation and geographic information system methods

A Geographic Information System (GIS) approach was used to create, interpret, and analyze spatial datasets representing potential sources of anthropogenic disturbance for watersheds located within the study area. Watersheds were generated for each sample site using an automated process that leveraged the batch watershed delineation capabilities that exist within the U.S. Geological Survey's StreamStats application (Ries et al., 2009).

Spatial datasets representing landscape metrics of watershed disturbance were created for each watershed from available national and regional datasets (Table S9), and included elevation, slope, land cover (base year 2006; Fry et al., 2011), road networks, soil characteristics, hydrography, dams, Au- and Hg-mine locations, surficial geology, and population density. Additional mining-related metrics derived from both private and public data were also evaluated (Orlando, 2016).

The value of each variable was calculated for each watershed where the fish or sediment sample was collected (Table S10). All work was conducted using ArcGIS, ArcMap 10.2 (Environmental Systems Research Institute, Redlands, CA). Because of limitations in the numbers of variables that could be evaluated within the modeling framework applied during this project, not all landscape metrics were evaluated. A list of variables that were evaluated as well as those retained in the final models is shown in Table S11.

2.4. Statistical analyses and modeling approach

Although GIS information was available at all 133 sites with Hg data for fish and (or) sediment (Table S10), we were unable to model THg in fish directly as a function of THg or MeHg in sediment and GIS variables across all 133 sites because of the uneven sampling of fish and sediment. Instead, a comprehensive model was developed by employing a multiple regression model obtained from a sequence of partial regression models fitted to the same dataset (Neter et al., 1990). Because the partial regressions were performed on overlapping but different subsets of the 133 sites, it was assumed that regressions on these subsets are representative of all 133 sites.

Statistical analyses and model development were done using a three-stage approach: 1) evaluate which variables were correlated with fish THg concentrations, 2) evaluate those variables that were correlated with sediment THg and MeHg concentrations, and 3) determine if sediment THg and (or) MeHg concentrations could be used together with other variables to estimate fish THg concentrations (Fig. 2).

In Stage 1, fish THg was predicted using three different approaches: Stage 1a predicted fish THg using only data for THg in sediment; Stage 1b made predictions of fish THg using only THg and MeHg in sediment; Stage 1c used only geospatial (or GIS) data to predict fish THg. A total of 31 GIS variables were considered in Stage 1c modeling (Table S11).

In Stage 2, the factors influencing sediment THg and MeHg concentrations were assessed using the same 31 potential GIS predictor variables as used in Stage 1c, plus other variables. In Stage 2a, models were derived predicting sediment THg using GIS variables, plus two other ancillary variables: percent fines (<0.063 mm) and log10-transformed loss on ignition (LOI, a measure of organic content) (Table S11). In Stage 2b, sediment MeHg was predicted using the same variables as Stage 2a plus two other variables: sediment THg and sediment THg normalized to LOI. Stage 2c consisted of the same variables as Stage 2b plus sediment reactive mercury (RHg), an operationally defined parameter representing the Hg(II) that is reduced to Hg(0) in a 15-min digestion with $SnCl_2$ (Marvin-DiPasquale et al., 2011). Reactive mercury is considered to approximate the fraction of the inorganic Hg pool that is most prone to microbial methylation (Marvin-DiPasquale et al., 2006; Marvin-DiPasquale and Cox, 2007).

Stage 3 modeling used the residuals from the models in Stages 1c and 2 to determine whether sediment THg and (or) MeHg concentrations could be used to improve the prediction of fish THg beyond that obtained using GIS variables alone (as in Stage 1c).

The three-stage approach allowed use of all available data from all sites and employed the strategy of partial regressions by modeling Hg in fish as a function of GIS variables (Stage 1c, n = 103 sites), Hg in sediment as a function of sediment variables (Stages 2a–b, n = 73 sites), and finally a regression between the residuals of both stages (n = 43 stations) to assemble a full model for Hg in fish as a function of sediment and GIS variables (Stage 3).

In the analysis of models in each stage, AIC was used to select the most parsimonious model from all potential combinations of variables, with the following exceptions. First, some variables that were highly related (Pearson correlation r > 0.75) or that were derived from the same data (e.g. total forest and deciduous forest) were excluded from appearing in the same individual model (Table S12). Pearson

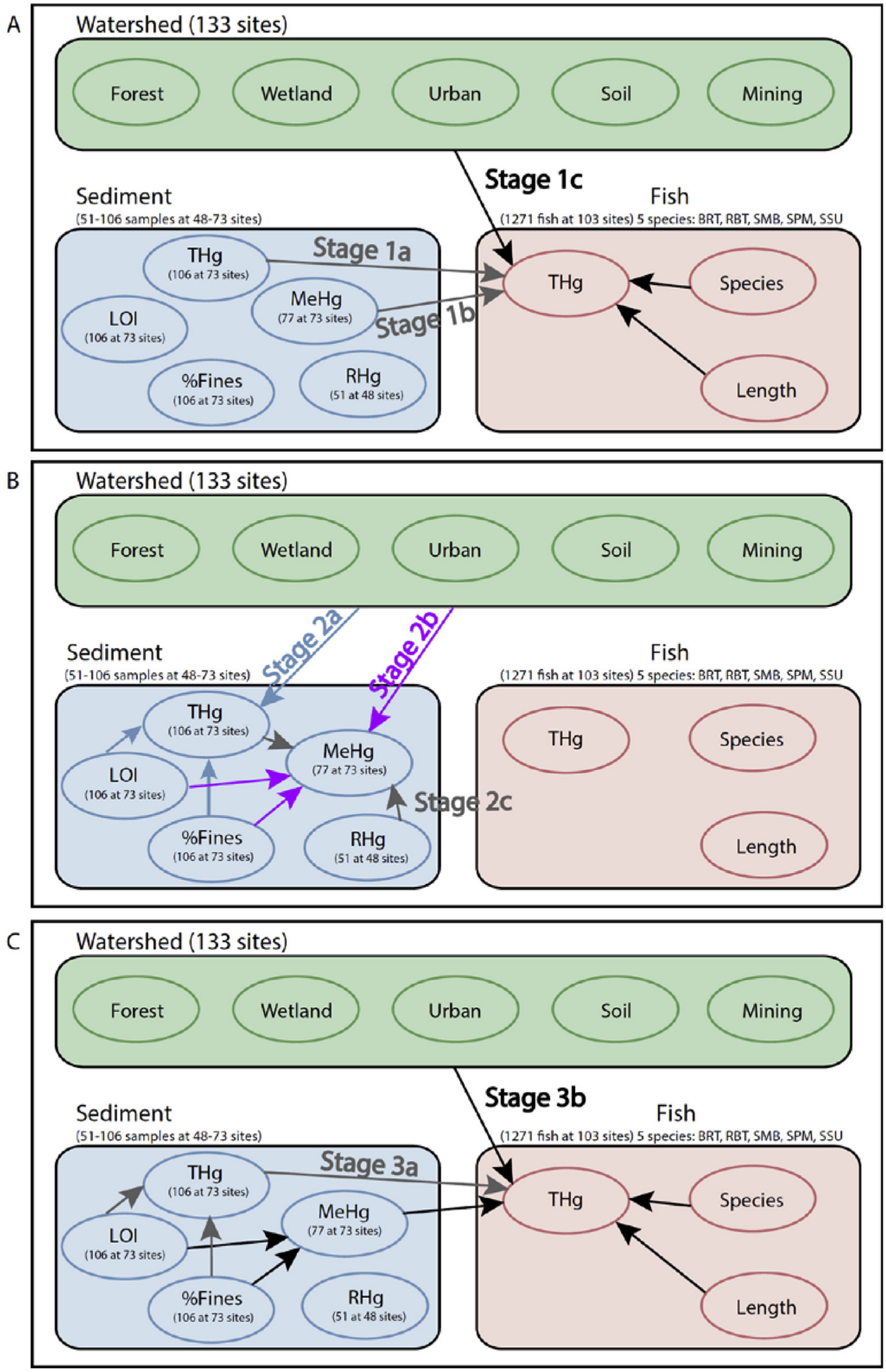

Fig. 2. Flow chart showing available data and multi-stage modeling approach. (A) Stage 1: predicting fish total mercury (THg) in axial fillet using sediment THg (Stage 1a); using sediment methylmercury (MeHg) (Stage 1b), and using geospatial data (Stage 1c); (B) Stage 2: predicting sediment THg using geospatial data, loss on ignition, and percent fines (Stage 2a); predicting sediment MeHg using geospatial data, loss on ignition, and percent fines (Stage 2b); predicting sediment MeHg using geospatial data, sediment THg and reactive mercury (RHg), as well as loss on ignition and percent fines (not shown); Stage 3, predicting fish Hg from residuals in Stage 2a model (Stage 3a), and from residuals in Stage 2b model (Stage 3b).

correlation coefficients between spatial variables are tabulated for non-distance-weighted variables (Table S13) and distance-weighted variables (Table S14), with p values to indicate the degree of statistical significance for correlation between each pair of variables. The two mining-related variables (*HydrPitsPLPct* and *AuMineDens*) were not significantly correlated, so they were allowed to occur in the individual models.

The maximum number of spatial variables in each model stage was determined based on sample size, using guidelines for multivariate modeling (Burnham and Anderson, 2002), as summarized in Table

S15 (see Supplemental material text). Because AIC statistics are only comparable among different models fitted to the same dataset, we used AIC only to compare these models and develop the weighted-average model, and we relied on coefficient of determination (r^2), defined as the proportion of variance explained by the model (Kvalseth, 1985; see Table S16), to compare weighted-average models based on different subsets of the data (e.g. Stages 1a vs. 1b). Negative values of r^2 are possible using this approach. Statistical significance (p) was calculated by permutation test (20,000 random iterations).

All models predicting mercury in fish (Stages 1a, 1b, 1c, 3a, and 3b) included species and length as predictor variables. Length-normalized fish THg was not used as a response variable in any of the models. However, alternative r^2 values based on length-normalized fish THg values were computed for comparison with r^2 values based on non-normalized fish THg (Table S16; see Supplemental material).

3. Results

3.1. Stage 1: models predicting total mercury in fish using either sediment or spatial data

3.1.1. Stage 1a: model predicting total mercury in fish using total mercury in sediment

Prediction of THg in fish (fish THg) using only THg in streambed sediment (sedTHg) was reasonably successful, with an r^2 value of 0.53 ($p < 0.001$, Table S16). The same model predicts length-normalized fish THg with an r^2 value of 0.68 ($p < 0.001$). The Stage 1a modeling was based on data for 43 sites where both sediment and fish were sampled (Table S16).

3.1.2. Stage 1b: model predicting total mercury in fish using total mercury and methylmercury in sediment

Prediction of fish THg using both THg and MeHg concentrations in streambed sediment (Stage 1b) was slightly more successful than the models based only on sediment THg (Stage 1a), with r^2 values of 0.56 ($p < 0.001$) for prediction of non-length-normalized fish THg and 0.70 ($p < 0.001$) for prediction of length-normalized fish THg (Table S16). Stage 1b modeling, like Stage 1a, was based on data for 43 sites where both sediment and fish were sampled. The results from Stage 1a and 1b modeling provide a useful baseline for more complex models, as explained below.

3.1.3. Stage 1c: model predicting total mercury in fish using geospatial data

In the first stage of the analysis using GIS data, factors influencing fish THg concentration among watersheds was examined. First, a preliminary model was derived to determine whether there was more support for one or the other approach among three paired alternatives: (1) species or guild, (2) distance-weighted GIS variables or non-weighted GIS variables, and (3) fish total length or log10-transformed fish total length. For the first of these comparisons, three separate guilds were defined: (a) trophic level 3 (small forage fish, including Brook Trout, Rainbow Trout, and Brown Trout ≤250 mm total length), (b) trophic level 4 (larger, piscivorous fish, including all bass species, Sacramento Pikeminnow, and Brown Trout >250 mm total length), and (c) Sacramento Sucker, which was considered to be its own guild, because it does not fit the definition of either trophic level 3 or 4. Other fish species had an insufficient number of samples (<10) to be considered. The total number of fish samples in the guild models was 1320 (Fig. S2), however for purposes of using AIC to compare guild models to the species-specific models we restricted the data sample to the 1271 fish belonging to the five species represented in the species-specific models (Table S8). Models with species had a relative variable weight of 1.0, whereas those with guild had a relative variable weight of <0.01. Therefore, we excluded the guild approach from all further testing and species was included as a fixed effect for five best-represented fish species in all further fish models (Fig. S1, Table S8).

The evaluation of distance-weighted versus non-distance-weighted (or non-weighted) variables indicated that the relative variable weight for the distance-weighted GIS variables was 0.40 and that for non-weighted GIS variables was 0.60. Therefore, we did not distance-weight any of the GIS variables in the final candidate model set for fish in Stage 1c.

The most robust models using GIS data to predict fish THg (Stage 1c) used data for 1271 fish from 5 species collected at 103 sites during 1980–2012. The individual best model ("top model") subject to parameter limits (Table S15) describing fish THg concentrations among Sierra Nevada watersheds (model 1c.01, Table S17) included four geospatial variables (high intensity of urban development, deciduous forest, woody wetlands, and emergent herbaceous wetlands), and the proportion of the watershed area consisting of hydraulic pits and large placer mines, with species and fish length as fixed effects, and site as a random effect; this model had an Akaike weight of 0.104. Eight other individual models provided a reasonably competitive fit to the data ($\Delta AIC_C < 2.0$), and, similar to the top model, each contained the proportion of cells in a watershed categorized as deciduous forest and the proportion of the watershed area consisting of hydraulic pits and large placer mines. Each of these top nine models included a variable representing urban development (either medium- or high-intensity urban development, or total urban development) and a variable representing wetlands (either woody wetlands or emergent herbaceous wetlands). The proportion of cells in a watershed that were categorized as being evergreen forest also appeared in three of the top nine models. The top model (1c.01, Table S17) was 6.38×10^{13} times more likely than the null model that included only fish species and fish length as fixed effects and site as a random effect.

The weighted-average model for Hg in fish tissue from Stage 1c modeling (GIS data only) is given in Table 1. The weighted-average Stage 1c model (based on 1271 fish at 103 sites) had an r^2 value of 0.61 ($p < 0.001$; Fig. S9, Table S16), indicating that the model explains 61% of the variation in non-length-normalized fish tissue Hg concentration for the 103 sites analyzed. Each observed sample (symbol in Fig. S9)

Table 1
Model equations. Coefficients with additional precision are given in Supplemental material (Tables S18, S27, S31, and S34). Because of differences in units, relative magnitude of coefficients does not indicate relative importance to the model. Data for Variable Importance, Parameter Likelihood, and beta coefficients, which indicate relative importance and influence of each variable, are given in Supplemental material (Tables S24, S29, and S32). Order of variables in each equation is based on variable type (mining, urban development, wetlands, forests). Values of constant denoting fish species: $C_{sp} = 0.39$, Brown Trout; 0.37, Rainbow Trout; 0.031 Sacramento Pikeminnow; 0.14, Sacramento Sucker; and 0, Smallmouth Bass.

Model	Equation
Stage 1c	log(fishTHg) = −0.78 − C_{sp} + 0.0019 length(mm) + 0.081 log(HydrPitsPLPct) + 0.0014 log(AuMineDens) + 0.010 log(TotalUrban) + 0.022 log(DevelopHigh) + 0.0078 log(DevelopMed) + 0.0050 log(PopDens) − 0.0086 log(TotalWetlnd) − 0.046 log(WetlndEmHrb) – 0.030 log(WetlndWoody) + 0.085 log(ForestDecid) − 0.054 log(ForestEvrgr)
Stage 2a	log(sedTHg) = −0.64 + 0.90 log(PctLOI) + 0.00028 pctFines + 0.19 log(HydrPitsPLPct) + 0.000017 log(AuMineDens) + 0.048 log(DevelopHigh) + 0.048 log(PopDens) − 0.0079 log(WetlndEmHrb) + 0.073 log(TotalForest) + 0.058 log(ForestEvrgr) + 0.12 log(ForestMixed) + 0.22 ElevationKm
Stage 2b	log(sedMeHg) = −3.3 + 1.1 log(PctLOI) + 0.0019 pctFines + 0.15 log(HydrPitsPLPct) + 0.014 log(DevelopHigh) + 0.0016 log(DevelopMed) + 0.11 log(PopDens)
Stage 3b	log(fishTHg) = −0.097 − C_{sp} + 0.0019 length(mm) + 0.19 log(sedMeHg) − 0.21 log(sedPctLOI) − 0.00036 sedPctFines + 0.054 log(HydrPitsPLPct) + 0.0012 log(AuMineDens) + 0.012 log(TotalUrban) + 0.023 log(DevelopHigh) + 0.0087 log(DevelopMed) − 0.020 log(PopDen) − 0.0088 log(TotalWetlnd) − 0.045 log(WetlndEmHrb) − 0.030 log(WetlndWoody) + 0.087 log(ForestDecid) − 0.051 log(ForestEvrgr)

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can be compared vertically to the predicted geometric mean and confidence interval obtained from that sample's respective covariate profile.

Results for the Stage 1c model are somewhat better than the results for Stages 1a and 1b, which did not use spatial variables (Table S16). Because Stages 1a and 1b were based on 770 fish at 43 sites, for the purpose of comparison, the performance of Stage 1c was evaluated for the same subset of available data. For non-length-normalized fish THg, the r^2 value for Stage 1c (770 fish at 43 sites) was 0.62 ($p < 0.001$), which was greater than the values for Stages 1a and 1b (0.53 and 0.57, respectively; both $p < 0.001$). For predicting length-normalized fish THg, Stage 1c (770 fish at 43 sites) had an r^2 value of 0.745 ($p < 0.001$), also greater than the values for Stages 1a and 1b (0.675 and 0.702, respectively; both $p < 0.001$).

Predictions from the Stage 1c model were made for five fish species over a range of total length at 185 sites (Table S19). No predictions were made for fish species in areas where suitable habitat is not expected to occur; for Sacramento Pikeminnow, Sacramento Sucker, and Smallmouth Bass, no predictions were made for sites at elevations >1000 m based on the natural range of these species (Moyle, 2002). An example of the predictions compared with available data for a site with data for all five species (Greenhorn Creek at You Bet Road) can be seen in Fig. S8.116. There is good overall agreement between observed concentrations and predicted concentrations, within the 95th percent confidence interval for nearly all of the data points. Plots of predictions for all 185 sites (103 with available fish THg data) are in Figs. S8.1 through S8.185. The performance of the Stage 1c model with regard to predicted versus observed fish THg concentrations (Table S21) and with regard to regulatory criteria (Tables S22 and S23) is discussed in the Supplemental material text.

Fish length, proportion of hydraulic mine pits and placers, and deciduous forest are the three variables with the most influence on predicted fish THg in the Stage 1c model, which can be seen by the relatively steep slopes compared to other variables on plots of partial residual fish THg concentration (Fig. 3). These three variables also have the largest values of Parameter Likelihood and Variable Importance (Table S24); these terms are defined in the Supplemental material. The relative influence of the three variables listed above compared to the other variables in the model can also be seen in the beta coefficients, which indicate mathematical relationships between model variables and calculated predictions of fish THg (Table S24). Variables with negative coefficients in

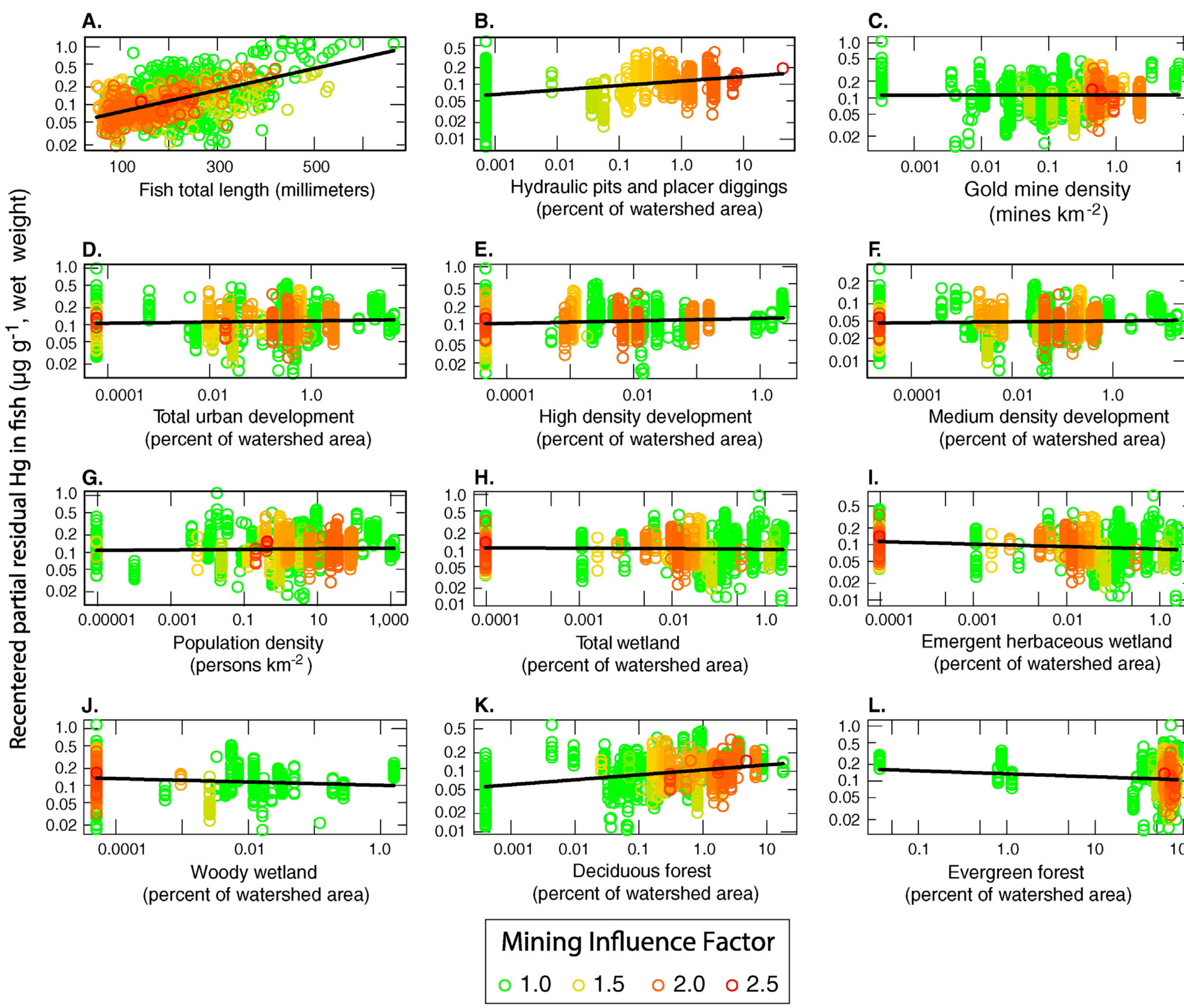

Fig. 3. Plots showing recentered partial residual total mercury (THg) in fish at the individual fish level (n = 1,271) for variables in weighted-average model 1c. (A) fish total length, (B) hydraulic pits and placer areas, (C) gold mine density, (D) total urban development, (E) high density development, (F) medium density development, (G) population density, (H) total wetlands, (I) emergent herbaceous wetlands, (J) woody wetlands, (K) deciduous forest, (L) evergreen forest. Variables in model, except fish length, were adjusted to avoid zero values by adding a small number equal to 0.1 times the smallest actual positive value to facilitate plotting in log space and log-transformation for data analysis. Symbol color indicates value of Mining Influence Factor from Stage 1c model. Partial residual total Hg in fish was recentered by adding the predicted Hg concentration for a 200 mm rainbow trout where all of the watershed covariates were set at mean values.

Table 1) (three wetland variables and evergreen forest) also have negative slopes in the plots of partial residual fish THg (Fig. 3) — see Discussion (Section 4).

3.2. Models predicting THg or MeHg in streambed sediment

In the second stage of our analyses, factors influencing bed sediment concentrations of THg (*sedTHg*) and MeHg (*sedMeHg*) were examined.

3.2.1. Stage 2a: model predicting THg in streambed sediment

To develop the Stage 2a model, data from 106 sediment samples were analyzed for THg from 73 sites (Fig. S4), collected during 1999–2012 (Table S25). First, a preliminary model set was analyzed to determine whether there was more support for (a) distance-weighted versus non-distance-weighted GIS variables, and (b) LOI versus $\log_{10}$(LOI). The relative variable weight for the distance-weighted GIS variables was 0.18 and the non-distance-weighted GIS variables was 0.81. Therefore, none of the GIS variables were distance-weighted in the final candidate Stage 2a model set. LOI had a relative variable weight of <0.01 and the $\log_{10}$-transformed LOI had a relative variable weight of 1.0. Therefore $\log_{10}$-transformed LOI was used in the final candidate Stage 2a model set.

The best individual model describing sediment THg concentrations among watersheds included elevation, the proportion of mixed forest, the proportion of hydraulic pits and placer diggings, the density of people within the watershed, and the LOI of sediment (with site as a random effect; Table S26), and had an Akaike weight of 0.39. One other model provided a reasonably competitive fit to the data ($\Delta AIC_C < 2.0$), and was similar to the top model except that it contained high-intensity urban development instead of population density. The top model in Stage 2a was 3.62×10^{27} times more likely than the null model, which only included site as a random effect.

The weighted-average model for *sedTHg* from Stage 2a is given in Table 1. The weighted-average model for Stage 2a had an r^2 value of 0.73 ($p < 0.001$, Table S28, Fig. S10). Plots of partial residuals of *sedTHg* versus the eleven variables in the Stage 2a model show the extent to which *sedTHg* is influenced by each variable (Fig. S11). Variables LOI (Fig. S11a), and hydraulic pits and placer diggings (Fig. S11c) showed the steepest slopes on the partial residual plots, indicating greatest importance to the model.

3.2.2. Stages 2b and 2c: models predicting methylmercury in streambed sediment

Next, factors influencing *sedMeHg* concentrations were examined among watersheds. MeHg data for 77 sediment samples from 73 sites sampled during 1999–2012 were used (Table S25). First, a preliminary model set was analyzed to determine which transformation had more support for distance-weighted versus non-distance-weighted GIS variables, LOI versus $\log_{10}$(LOI), and *sedTHg* versus *sedTHg*/LOI. The relative variable weight for the distance-weighted GIS variables was 0.30 and for the non-distance-weighted GIS variables was 0.31. For simplicity, we did not distance-weight any of the GIS variables in the final candidate model set. LOI had a relative variable weight of 0.03 and the $\log_{10}$-transformed LOI had a relative variable weight of 0.96. Therefore, $\log_{10}$(LOI) was used in our final candidate model set. Concentration of *sedTHg* had a relative variable weight of 0.07 and the *sedTHg*/LOI transformation had a relative variable weight of 0.04. For simplicity, *sedTHg* was not normalized by LOI in the final candidate model set.

The best Stage 2b model describing *sedMeHg* concentrations among watersheds included the proportion of the watershed area consisting of hydraulic pits and large placer mines, population density, LOI of sediment, and the proportion of fines in sediment (with site as a random effect; Table S30), and had an Akaike weight of 0.46. One other model provided a reasonably competitive fit to the data ($\Delta AIC_C < 2.0$), and was similar to the top model except that it did not include the proportion of fines in sediment. The top model was 1.79×10^{20} times more likely than the null model which included only site as a random effect.

The weighted-average model for *sedMeHg* from Stage 2b is given in Table 1. The weighted-average model for Stage 2b had an r^2 value of 0.71 ($p < 0.001$, Table S28, Fig. S12). Plots of partial residuals of *sedMeHg* versus the six variables in the Stage 2b model (Table 1) show the extent to which *sedTHg* is influenced by each variable (Fig. S13). The variables LOI, hydraulic pits and placer diggings, and population density showed the steepest slopes, indicating their importance to the model.

Stage 2c modeling was an attempt to see if concentration data for sediment reactive mercury (*sedRHg*) would improve the prediction of *sedMeHg* in Stage 2b. In addition to *sedRHg* and GIS variables, candidate variables in Stage 2c models included THg, LOI, and THg normalized by LOI. A total of 51 analyses for *sedRHg* were available from 48 sites. The final Stage 2c model did not contain *sedRHg* as a variable; it did not meet AIC criteria for importance.

3.3. Stage 3: models of fish THg using geospatial and streambed sediment variables

In the third stage of modeling, the first two stages of analyses for fish and sediment, predicted separately, were used to estimate the residual fish THg and bed sediment THg and MeHg concentrations for each sample-defined watershed using model averages for each candidate model set. For this analysis, there were 43 watersheds for which residuals for fish THg, *sedTHg*, and *sedMeHg* concentrations could be estimated.

The r^2 values for the Stage 3a model for fish THg based on *sedTHg* (see Supplemental material) do not represent a significant improvement over the Stage 1c model that does not include bed sediment variables. However, the Stage 3b model for fish THg based on *sedMeHg* does represent a small but significant improvement.

The final predictive Stage 3b model for fish THg within a watershed in the Sierra Nevada based on *sedMeHg* is given in Table 1. The Stage 3b model had an r^2 value of 0.63 ($p < 0.001$) when predicting fish THg, and an r^2 value of 0.75 ($p < 0.001$) when predicting length-normalized fish THg (Table S16); both r^2 values are slightly larger than the corresponding values for the Stage 3a and Stage 1c models.

4. Discussion

Variables that appear in all the models derived in this study are summarized in Table 2. The result from this study with the most general applicability is the Stage 1c model that predicts fish THg using geospatial variables for which data are available throughout the study area. The landscape variables with the most influence on predicted fish THg in the Stage 1c model — those related to historical mining, forests, wetlands, and urban development — are discussed here along with limitations and assumptions of this model, visualization of model results, and potential uses of this model for resource management.

4.1. Influence of historical mining

Of the four variables related to historical mining that were considered in the modeling, two were included in the final Stage 1c model: hydraulic mine pits and placer diggings (*HydrPitPLPct*), and gold mine density (*AuMineDens*). The influence of these two variables was combined to give a Mining Influence Factor (MIF). The MIF was computed so that it represents a multiplication factor for fish THg concentration; that is, one can multiply a fish mercury concentration in a watershed unaffected by mining (with zero values of *HydrPitPLPct* and *AuMineDens*) by the MIF for a given watershed or stream reach to estimate fish mercury concentration in the area corresponding to that MIF, assuming that values of all other variables do not vary. Sites with at least 0.1% of their upstream watershed area consisting of hydraulic mines and placer diggings have MIF values >1.5, and sites with >1.0%

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Table 2
Summary of variables in predictive models. [%Wsarea, percentage of watershed area; NLCD, National Land Cover Dataset; mi^2, square mile; km, kilometer; ft, foot; ha, hectare; lbs, pounds; mm, millimeter; ng, nanogram; g, gram; s, sediment; Hg, mercury; LOI, loss on ignition; RHg, reactive mercury; THg, total mercury; sedTHg, sediment total mercury; sedMeHg, sediment methylmercury; +, indicates variables with positive influence in final model for that stage; −, indicates variables with negative influence in final model for that stage; O, indicates variable that was evaluated but not included in final model for that stage; M, indicates response variable predicted by model]

Short variable name	Units	Long variable name and definition (see Table S10)	transform	Stage 1a: fishTHg-sedTHg	Stage 1b: fishTHg -sedMeHg	Stage 1c: fishTHg-GIS	Stage 2a: sedTHg-GIS	Stage 2b: sedMeHg-GIS	Stage 2c: sedMeHg-RHg-GIS	Stage 3a: fishTHg-sedTHg- GIS	Stage 3b: fishTHg-sedMeHg- GIS
ElevationKm	km	Site elevation				O	+	O	−	−	O
DevelopMed	%Wsarea	NLCD23 (developed, medium intensity)	log10			+	O	+	O	+	+
DevelopHigh	%Wsarea	NLCD24 (developed, high intensity)	log10			+	+	+	O	+	+
TotalUrban	%Wsarea	Combined urban (low, medium, high) (sum of NLCD22, NLCD23, NLCD24)	log10			+	O	O	O	O	+
ForestDecid	%Wsarea	NLCD41 (deciduous forest)	log10			+	O	O	O	+	+
ForestEvrgr	%Wsarea	NLCD42 (evergreen forest)	log10			−	+	O	−	−	−
ForestMixed	%Wsarea	NLCD43 (mixed forest)	log10			O	+	O	O	−	O
TotalForest	%Wsarea	Combined forest (sum of NLCD41, NLCD42, NLCD43)	log10			O	+	O	−	−	O
WetlndWoody	%Wsarea	NLCD90 (woody wetlands)	log10			−	O	O	O	−	−
WetlndEmHrb	%Wsarea	NLCD95 (emergent herbaceous wetlands)	log10			−	−	O	-	−	-
TotalWetlnd	%Wsarea	Combined wetland (sum of NLCD90, NLCD95)	log10			−	O	O	O	−	−
AuMinesDens	km^{-2}	Gold mine density	log10			+	+	O	O	+	+
HydrPitsPLPct	%Wsarea	Hydraulic pits and placer diggings	log10			+	+	+	+	+	+
soilpH	pH units	Area-weighted median soil pH	log10			O	O	O	−	O	O
PopDens	persons km^{-2}	Population density	log10			+	+	+	+	−	−
sedPctFines	%	Percent fines in sediment (<0.063 mm)					+	+	+	−	−-
sedLOI	Weight %	Loss on ignition, log10-transformed	log10				+	+	+	−	−
sedTHg	ng g^{-1}	Total mercury in sediment (dry)	log10	+	+		M	O	+	+	O
sedTHgNorm	ng g^{-1}	Total mercury in sediment normalized by LOI (sedTHg/sedLOI)	log10					O	+	O	O
sedRHg	ng g^{-1}	Reactive mercury in sediment (dry)	log10						O		
sedMeHg	ng g^{-1}	Methylmercury in sediment (dry)	log10		+			M	M		+
fishTHg	μg g^{-1}	Total mercury in fish, axial muscle fillet or equivalent (wet)	log10	M	M	M				M	M
Len	mm	Fish total length		+	+	+				+	+
Spp		Fish species		−	−	−				−	−

have MIF values >2.0. MIF values were computed for 185 stream reaches that were modeled (Table S38). The highest MIF value for a site was 2.56 for Shady Creek at Tyler Foote Road in the South Yuba River watershed (site 74, Fig. S6), a site where 73% of the upstream watershed is composed of historical hydraulic mine workings.

Symbols color-coded by MIF value on various plots help to elucidate the extent of mining influence on fish THg concentrations in the study area. On plots of fish THg concentration (axial muscle fillet or equivalent, log scale) versus total length for each of the five modeled fish species (Fig. 4), the distribution of symbol colors based on MIF clearly shows that sites with higher fish THg for a given length of fish tend to have higher MIF values (red and orange symbols). However, there are some examples of fish from sites with low values of MIF (green symbols in Fig. 4) that have relatively high fish THg for their length, indicating a non-mining source and (or) more efficient methylation and bioaccumulation of Hg.

The MIF-coded color symbols also show the influence of mining on scatter plots of *sedTHg* and *sedMeHg* versus various sediment parameters (Fig. 5 and Figs. S16–S18). The patterns of color symbols in Fig. 5a and b representing MIF value with regard to THg are more systematic than those in Fig. 5c and d relating to MeHg, indicating qualitatively that mining has a stronger influence on THg distribution than on MeHg distribution in streambed sediment.

Numerous other studies have documented Hg contamination in water, sediment and biota associated with losses during amalgamation processing at historical Au and Ag mines in western North America, such as in California (Alpers et al., 2005b; Stewart et al., 2008) and Nevada (Lechler et al., 1997; Stamenkovic et al., 2004) and elsewhere, in areas of historical Au and Ag mining as well as areas where artisanal Au mining with loss of Hg continues (Telmer and Viega, 2009; Viega et al., 2006), such as in Brazil (Belger and Forsberg, 2006; Kehrig et al., 2008; Roulet et al., 1998; Silva-Forsberg et al., 1999), French Guiana (Guedron et al., 2009), Indonesia (Arifin et al., 2015), Suriname (Mol et al., 2001), and Tanzania and Zimbabwe (van Straaten, 2000). This study is novel in that it relates fish Hg concentrations quantitatively to the distribution and density of historical precious metal mining in combination with other geospatial variables including land-use/land-cover data.

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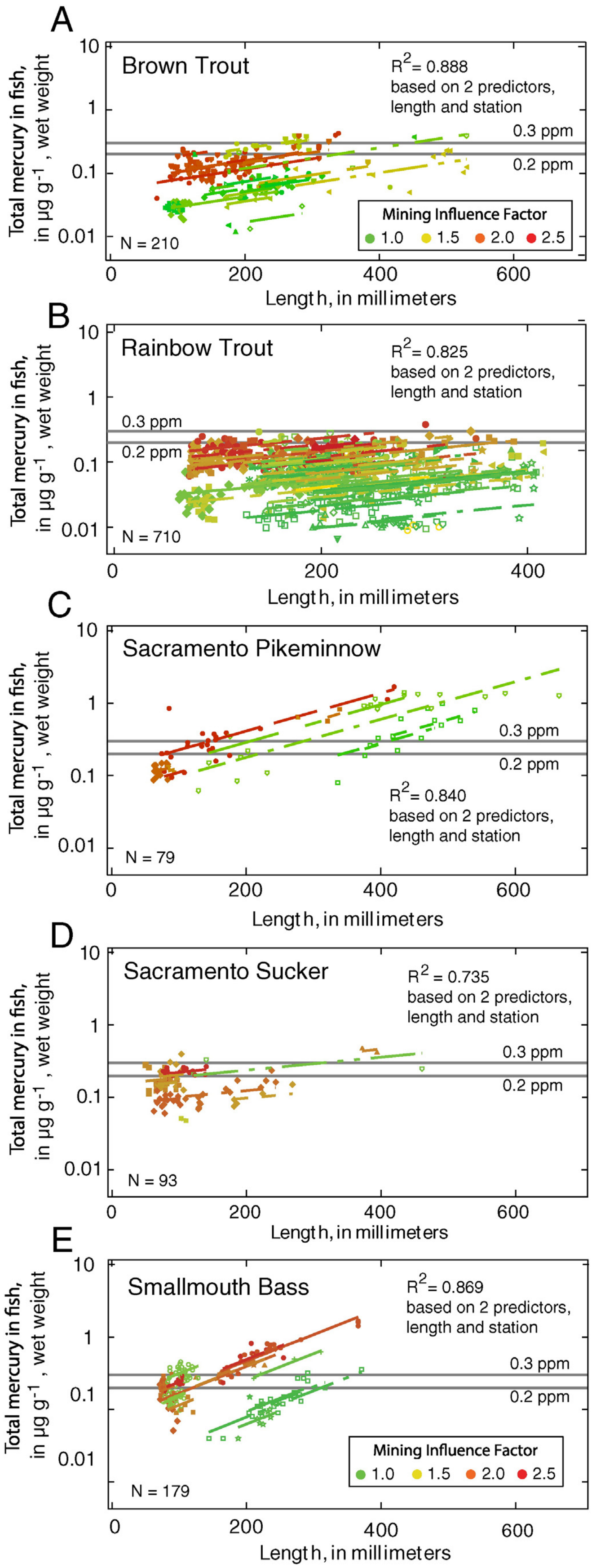

Fig. 4. Plots showing total length versus total mercury concentration in axial-muscle fillet (or equivalent) for five fish species from streams in the Sierra Nevada, California. A) Brown Trout, (B) Rainbow Trout, (C) Sacramento Pikeminnow, (D) Sacramento Sucker, (E) Smallmouth Bass. Symbol color indicates Mining Influence Factor from Stage 1c model. Regression lines are specific to each site with fish THg data; slopes of regression lines were constrained to be parallel for each species. Values of r^2 indicated on each plot represent results of a regression unique to each fish species that considered only fish length and station name as predictors. r^2 values, ranging from 0.735 for Sacramento Sucker to 0.888 for Brown Trout, can be considered as an upper bound for multivariate models such as those derived in this study to predict fish tissue THg concentrations in stream reaches with geospatial data including the distribution of historical Au mines.

4.2. Influence of forests

Models predicting fish THg in this study (Stages 1c, 3a, and 3b) consistently included a positive influence from deciduous forests and a negative influence from evergreen forests (Tables 1 and 2). Other studies have noted differences in THg and MeHg cycling in deciduous versus evergreen (coniferous) forests that may help to explain this effect. For example, leaf litter was found to be higher in MeHg in deciduous forests compared with coniferous forests in the Adirondack Mountains of New York (Munson et al., 2008). Fluxes of THg and MeHg to the forest floor in coniferous forests are typically dominated by throughfall, whereas fluxes in deciduous forests are dominated by litterfall (Demers et al., 2007; Grigal, 2002; Lindberg, 1996). Evergreen (coniferous) forests tend to have higher foliar THg concentrations than deciduous forests (e.g., Grigal, 2002; Hall and St. Louis, 2004; Obrist et al., 2012; Rasmussen et al., 1991), likely caused by longer (multi-year) exposure time and higher surface area for incorporation of dry Hg deposition (Grigal, 2003; Obrist et al., 2016). In a study comparing deciduous and coniferous stands within forests of northern New England, U.S.A., organic soil horizons were higher in THg in the coniferous forests, whereas similar concentrations of THg were found in mineral soil horizons in the two forest types (Richardson and Friedland, 2015). Concentrations of dissolved organic carbon (DOC) in pore water and surface water tend to be higher in coniferous forests compared with deciduous forests, which affects transport of dissolved THg by aqueous complexation (Brigham et al., 2009; Grigal, 2003; Miller et al., 2007). In a study in the Adirondack Mountains, Demers et al. (2007) found that Hg is transferred from soil to decaying leaf litter that concentrates Hg in the organic soil horizons and increases residence time on the forest floor. In the Lake Huron Watershed, Michigan, U.S., Rea et al. (2001) determined that foliar leaching as well as wash-off of dry deposition contributed to net throughfall in deciduous forests. Obrist et al. (2011, 2016) determined that litter is enriched in THg compared to aboveground plant tissues (foliage and bore wood).

In our Sierra Nevada study area, deciduous forests typically occur at lower elevation than evergreen forests. Correlations with elevation are negative for non-distance-weighted deciduous forest ($r = -0.37$, $p < 0.001$) and positive for evergreen forest ($r = 0.20$, $p = 0.01$) (Table S13; similar results for distance-weighted variables in Table S14). Deciduous forests have a weak but significant positive correlation with two mining-related parameters that were ultimately not used in the modeling: Hg losses from Au hard-rock mines ($r = 0.195$, $p = 0.02$) and estimated Hg losses from placer and hard-rock Au mines in the USGS Significant Deposits database (Long et al., 1998) ($r = 0.17$, $p = 0.04$). Correlations between deciduous forest and the mining-related parameters that were used in the modeling were weaker and not significant: $r = 0.15$ and $p = 0.07$ with *AuMineDens*; $r = 0.063$ and $p = 0.45$ with *HydrPitsPLPct* (Table S13). However, the nature of the modeling approach used accounts for variations in each variable separately on partial residual plots (Fig. 3) so the deciduous forest effect is not likely to be merely a proxy for mining influence.

Another important difference between deciduous and evergreen forests is soil pH; it is well known that evergreen forests soils are relatively acidic (e.g. Ste-Marie and Paré, 1999). There is a strong negative correlation in our study area between soil pH and evergreen forest

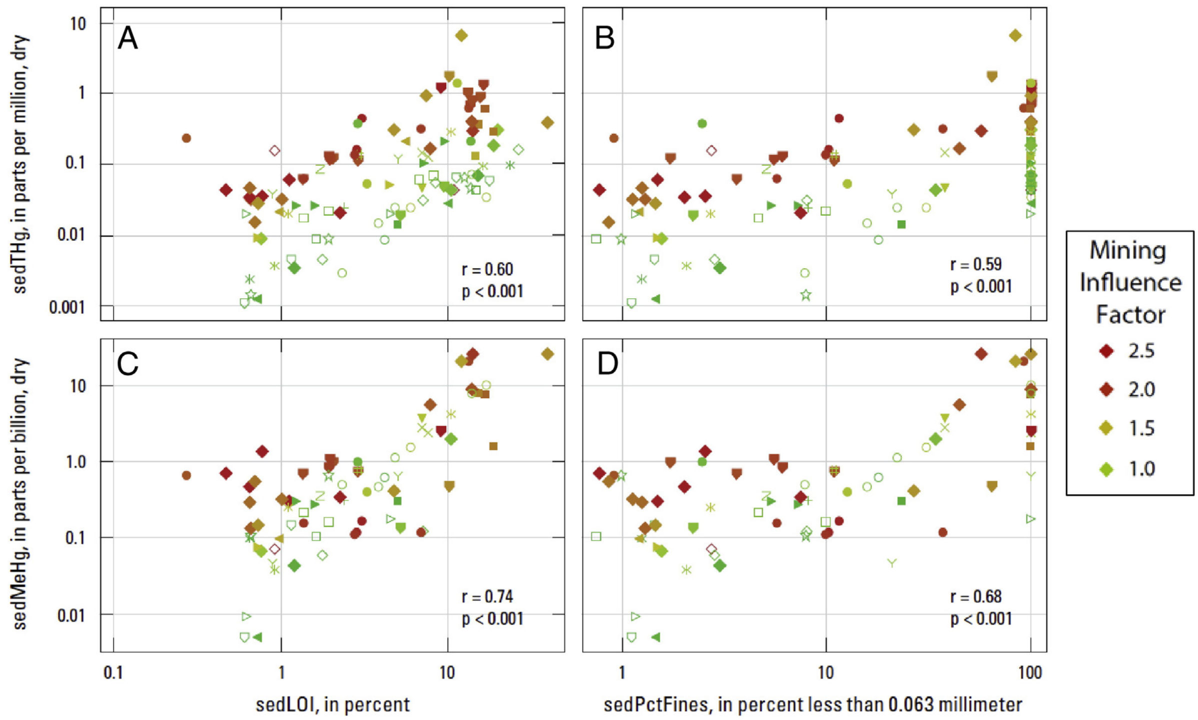

Fig. 5. Plots showing relations between sediment total mercury (sedTHg), sediment methylmercury (sedMeHg), sediment loss on ignition (sedLOI), and sediment percent finer than 0.063 mm (sedPctFines). (A) sedTHg vs. sedLOI, (B) sedTHg vs. sedPctFines, (C) sedMeHg vs. sedLOI, (D) sed MeHg vs. sedPctFines. Symbol color indicates Mining Influence Factor from Stage 1c model. Pearson correlation coefficient (r), and p-value shown for each plot.

($r = -0.77$, $p < 0.001$) and a weaker positive correlation between soil pH and deciduous forest ($r = 0.24$, $p = 0.003$; Table S13). The pH of lakes and reservoirs is known to affect aqueous Hg speciation, and therefore Hg cycling, and MeHg formation and bioaccumulation, however the effects of pH and interactions with DOC can vary from significant to non-significant (e.g. Watras et al., 1998).

Additional studies of deciduous versus evergreen (coniferous) forests in the Sierra Nevada are needed to determine whether forest type has a direct or indirect influence on mercury cycling, methylation, and bioaccumulation in fish. In particular, the effects of elevation, climate, pH, and DOC and their effects on Hg speciation and Hg-organic interactions should be considered in such studies.

4.3. Influence of wetlands

The models derived in this study in Stages 1c, 3a, and 3b each indicate a negative influence of wetlands on fish tissue THg, and the Stage 2a model indicates a negative influence of emergent herbaceous wetlands on sediment THg (Tables 1 and 2). These results were unexpected, given numerous other studies that have found positive correlations between wetland abundance and MeHg formation and bioaccumulation. Previous studies on a national scale for the continental U.S. (e.g. Krabbenhoft et al., 1999; Scudder et al., 2009) showed that watersheds with abundant wetlands tend to have fish with higher THg (predominantly as MeHg; Bloom, 1992). Other studies at a regional scale (e.g. Chasar et al., 2009; Drenner et al., 2011; Shanley et al., 2012) have also shown a positive correlation between wetlands and fish THg, or MeHg in other matrices. It is also well known that wetlands are typically favorable sites for MeHg formation and bioaccumulation (e.g. Krabbenhoft et al., 1999; Lacerda and Fitzgerald, 2001; Langer et al., 2001).

The negative influence of wetlands on fish tissue THg and bed sediment THg in this study may possibly be explained by the distribution of wetlands in the Sierra Nevada, which are typically either (1) at the higher elevations of the watershed, where there are relatively few historical gold mines (e.g., Fig. S7), and where streambed sediment and soils have lower THg concentrations because of the relative absence of mining-related contamination, or (2) at lower elevations in California's Central Valley, outside of the study area. As a consequence of the relatively small amount of wetlands in the vicinity of the historic gold mines in the study area, the overall percentage of wetlands upstream of a given sampling point is not a good predictor of THg in fish. A similar finding was made by Melwani et al. (2007, 2009) who also did spatial analysis of fish mercury data in northern California. It is possible that there are complex interactions between wetlands, elevation, and mining that confounded our ability to estimate their effects individually within the context of the linear models that we applied. Future modeling efforts would need to explore nonlinear effects or interactions between variables to address this possibility.

Plots of partial residual fish THg versus wetland variables (Fig. 3h–j) indicated that sample-defined watersheds with the most abundant wetlands (>0.02% of watershed area) tended to have MIF values near 1.0 (minimal mining influence). Similar trends can be seen on plots of wetland variables versus sedTHg concentrations (Fig. S18). These relationships are consistent with the negative values of the Pearson correlation coefficient (r) in Figs. S18a–b and the negative coefficient for emergent herbaceous wetlands in the Stage 2a model (Table 1). Furthermore, a significant negative correlation was found between emergent herbaceous wetlands and Au mine density ($r = -0.26$, $p = 0.002$; Table S13).

It is expected that watersheds with wetlands in areas affected by historical Au mining would exhibit elevated MeHg. In fact, some historical hydraulic mining sites have ponds that fill abandoned mine pits (Alpers et al., 2005a). These are sites of locally elevated THg and MeHg in water and sediment, and can have elevated MeHg in invertebrates and frogs (Alpers et al., 2005b; Alpers, 2015). Although flooded hydraulic mine pits act as wetlands, they are typically not included in the National Wetland Inventory (NWI) dataset that was used in this study. Using an

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expanded wetland coverage that includes flooded mine features would possibly change the results of the modeling with regard to wetland influence on fish and sediment THg.

4.4. Influence of urban development

Models developed for this study to predict fish THg (Stages 1c, 3a, and 3b) consistently have a positive influence from geospatial variables involving urban development, including high- and medium-density development and total urban area (Table 1). Population density was less consistent, showing a positive influence on the Stage 1c model and a negative influence on the Stage 3a and 3b models (Table 1).

Other studies which have investigated the influence of urban development or human population density on Hg cycling have produced mixed results. In the MERGANSER model (Shanley et al., 2012), human population density has a positive influence on Hg in fish tissue and loon blood in New England lakes; the observed correlation was possibly attributed to enhanced mobilization of Hg related to landscape disturbance, such as timber harvesting. Several studies found that urban settings cause increased yield of atmospherically deposited Hg because of a higher proportion of impervious surfaces (e.g. Brigham et al., 2009; Domagalski et al., 2016; Journey et al., 2012; Shanley et al., 2008; Tsai and Hoenicke, 2001). Urban settings can also be sources of Hg and possibly MeHg from household and industrial waste.

In contrast, several other studies found a negative effect of urban development on MeHg in water, sediment, and fish. On a national scale in the continental U.S., developed watersheds had lower concentrations of MeHg in water, sediment, and fish than undeveloped areas (Brumbaugh et al., 2001; Krabbenhoft et al. 1999; Scudder et al., 2009). These studies emphasized that undeveloped watersheds tend to have higher proportions of forests and wetlands, environments typically favorable to microbial methylation of Hg. Regional-scale studies by Chen et al. (2005), Kamman et al. (2005) and Marvin-DiPasquale et al. (2009) also showed a negative influence of urban development on MeHg in water and sediment. Chen et al. (2005) concluded that higher MeHg bioaccumulation in lakes was associated with forested watersheds where atmospheric deposition is the primary source of Hg and where relatively low pH was coupled with relatively low primary production. Lower concentrations of chlorophyll-*a* in the water column of lakes is typically associated with higher concentrations of MeHg at lower trophic levels, and a lack of biodilution (e.g. Allen et al., 2005; Kamman et al., 2005; Lange et al., 1993; Pickhardt et al., 2002; Simonin et al., 2008); the higher MeHg concentrations propagate up the food chain, resulting in higher MeHg concentrations at higher trophic levels such as piscivorous fish (e.g. Stewart et al., 2008) relative to lakes with higher chlorophyll-*a* concentrations.

In the Sierra Nevada study area, the four variables directly associated with urban development (high- and medium-density development, total urban area, and population density) had negative correlations with evergreen forest ($r = -0.63$ to -0.69; $p < 0.001$) and with elevation ($r = -0.29$ to -0.34; $p < 0.001$; Table S13). Conversely, high-density development had a positive correlation with deciduous forest ($r = 0.34$, $p < 0.001$; Table S13). Therefore, the positive effect of urban development in the models predicting fish Hg in this study may reflect processes in deciduous forests that typically occur at similar elevation as the developed areas, i.e., <1000 m above sea level.

4.5. Implications for resource management

Results of this study include a predictive model that can be used by resource managers and water-quality regulators to prioritize sampling efforts designed to refine lists of impaired water bodies (e.g. California SWRCB, 2012) and to identify remediation targets to reduce exposure of humans and wildlife to toxic MeHg. To evaluate the utility of the model, an analysis was performed of model performance with regard to predicting fish THg over or under 0.2 $\mu g\ g^{-1}$(ww), a regulatory threshold used by the State of California.

4.5.1. Model predictions relative to regulatory threshold

The performance of the Stage 1c model was evaluated with regard to its ability to predict correctly whether or not a fish of a particular species and size range at a specific sampling site would be above or below the threshold concentration of 0.2 $\mu g\ g^{-1}$ ww, a value that is currently being used by the State of California for regulatory purposes. The analysis is similar to that done by Kamman et al. (2004) for fish in lakes of New Hampshire and Vermont with regard to local regulatory criteria. Our analysis was done only for fish >150 mm in total length, and only for fish that were used to calibrate the model. Criteria for agreement between predictions and observed data are described in table S36; results of the evaluation are summarized in Table S37 (additional details in Supplemental materials text). Overall, the Stage 1c model gave an accurate prediction for 89% (108 of 121) of the species-specific site-length bins with regard to whether a fish of a certain length would be above or below 0.2 $\mu g\ g^{-1}$ ww (Table S37).

4.5.2. Visualization of model predictions

Maps showing predicted fish THg concentrations were prepared to visualize the locations of water bodies with elevated THg based on Stage 1c model results. An example of such a map is show in Fig. 6 for 350-mm Rainbow Trout in the Yuba River watershed. The Yuba River watershed has a high proportion of the data used in the modeling: 37 of the 103 sites with fish tissue data (36%) and 73 of the 185 sites where predictions were made (39%). Similar maps for other fish species-length combinations in the Yuba River and other watersheds within the study area are available in the Supplemental material (Fig. S19.1 through S19.56). The maps can be used to visualize differences in fish THg for various lengths of a species, differences between species in the same watershed, or differences between watersheds for various species-length combinations.

Average values of MIF for watersheds in the study area (Fig. 7) were computed using results for the 185 modeled sites (Table S38). The Bear Creek watershed had the highest average MIF value (1.76), followed by Deer Creek, in the southern part of Yuba River watershed (1.70).

4.5.3. Potential uses of predictive models

A potential use of the predictive model for fish THg in Sierra Nevada streams is to prioritize sampling efforts designed to refine lists of impaired water bodies. Maps displaying model results (Fig. 6 and Fig. S19) can be compared with maps showing water bodies listed as impaired for beneficial uses because of Hg contamination (Fig. 1). Stream reaches where fish THg greater than >0.2 $\mu g\ g^{-1}$ ww (or a different regulatory criterion, as needed) is predicted by the model, but are currently not listed as impaired, because of lack of data, can be prioritized for field sampling.

In watersheds where remediation of legacy Au mine sites with Hg contamination is being considered, the model could potentially be used to evaluate the potential benefits of remediation in terms of expected decreases in fish THg. Values of model variables related to historical mining could be reduced to evaluate scenarios in which Hg sources from those mine sites are remediated, so the magnitude of lowering of fish THg concentrations that would result from such remediation can be evaluated. There are typically multiple legacy sources of Hg contamination in watersheds affected by historical Au mining; realistic expectations are needed regarding the benefits of remediating one or more sites in a watershed so that limited resources for cleanups can be used most effectively.

4.5.4. Assumptions and limitations of predictive models

Predictive models derived in this study are based on the assumption that temporal (inter-annual) variations in fish tissue THg and sediment chemistry were small compared with spatial variations. To evaluate

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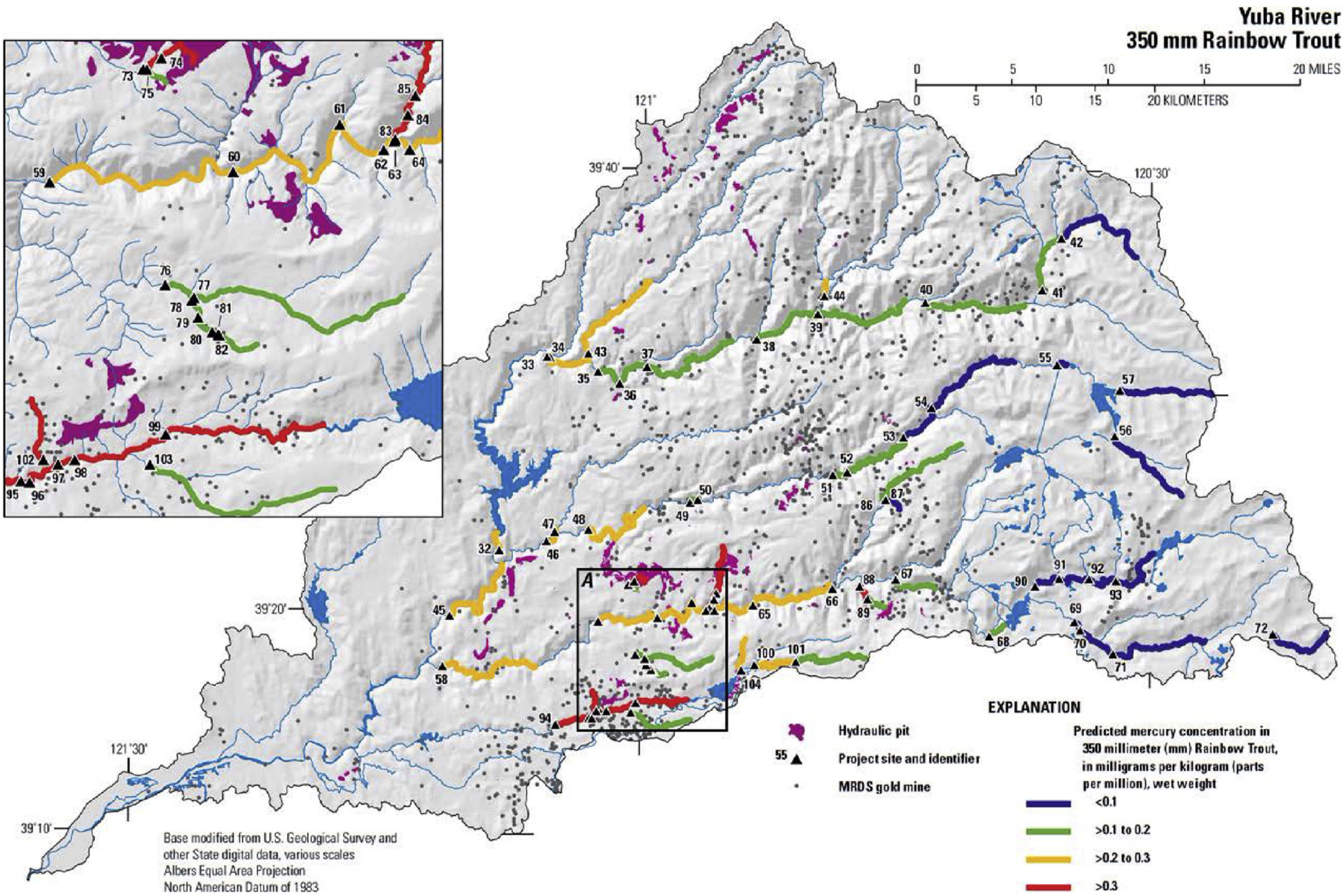

Fig. 6. Map showing Stage 1c model predictions for fish total mercury (in axial fillet) for 350 mm Rainbow Trout in the Yuba River watershed, California. Gold mine locations from Mineral Resources Data System (MRDS; USGS, 2013); hydraulic pit locations from Orlando (2016). Additional maps for five modeled species in Sierra Nevada watersheds in Supplemental material, Figs. S19.1 through S19.56.

year-to-year variations compared with variation among sites, we used a mixed effects model with species, length, and variance components due to site and year. The variance among sample years is about 1/10th the variation among sites, and a little more than 1/2 the variation that occurs between individual fish from the same site in a given year.

Data regarding inter-annual variation of sediment THg and MeHg are limited to the 2011 and 2012 sampling events at 3 sites. Year-to-year variations in THg were <10% in material screened to <0.063 mm, but were higher in material screened to <2 mm. Analyses of replicate samples were also more variable for the THg in the coarser size fraction compared with the finer size fraction. Year-to-year variations in sediment MeHg and MeHg/THg ratio were larger than those for THg, reflecting that MeHg is generally more variable than THg on a seasonal and inter-annual basis. There was no systematic increase or decrease in MeHg or MeHg/THg from 2011 to 2012.

Based on the available data, the assumptions regarding inter-annual variability of fish THg, sediment THg and sediment MeHg appear to be reasonable. Land-use/land-cover data from 2006 were used together with fish data from 1980–2012 and sediment data from 1999–2012 to construct the models. It is also assumed that the spatial data properties did not change dramatically from year to year during these periods. Urban development intensity and population density have increased in some parts of the study area over the past 20 years, especially near major highways. This introduces some bias in the models in that the fish data from the 1990s were compared with land-use/land-cover data from 2006. Because the areas that experienced urban growth during this time period were spatially limited, we infer that impacts to the model based on this assumption are minimal.

Atmospheric Hg deposition was not considered as a variable in this study because reliable data were not available on a sufficiently fine spatial scale for geospatial analysis. Downscaling of wet THg deposition data (e.g. Mercury Deposition Network http://nadp.sws.uiuc.edu/mdn/, using PRISM) could potentially provide data for modeling purposes on a watershed scale (e.g. Domagalski et al., 2016). However, dry Hg deposition is thought to be of equal or greater importance in parts of California, and there is a lack of reliable information or calibrated models on dry THg deposition (Domagalski et al., 2016). A similar modeling effort using atmospheric Hg deposition, when reliable geospatial coverages become available, would be helpful to investigate whether variations in atmospheric deposition can help to explain variability in fish THg, sediment THg, or sediment MeHg that are not explained by the geospatial variables considered in this study.

5. Summary and conclusions

A comprehensive set of statistical calculations was made to use available data for THg and MeHg in fish and bed sediment, together with geospatial data in the Sierra Nevada, to develop predictive models for fish tissue in streams. Results indicated that fish tissue Hg concentrations, accounting for species and length, can be predicted using spatial data for mining history together with other landscape characteristics including land use/land cover.

A model requiring only geospatial data ($r^2 = 0.61$, $p < 0.001$) predicts fish tissue Hg concentrations correctly with respect to over or under 0.2 μg g^{-1} ww (a regulatory threshold used by the State of California) for 89% of size-species combinations tested. Data for THg in

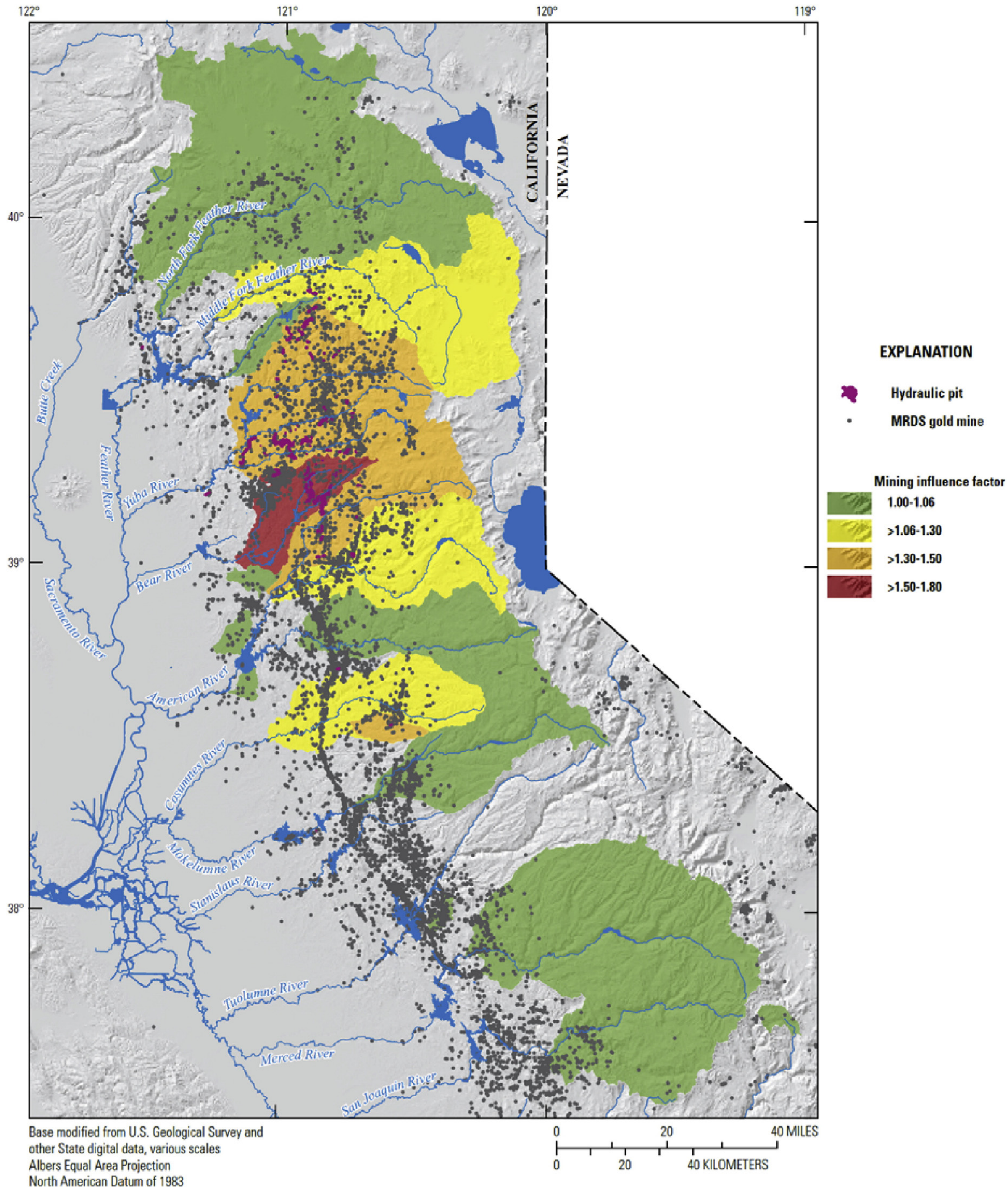

Fig. 7. Map showing distribution of watershed-average values of Mining Influence Factor from Stage 1c model in study area. Gold mine locations from Mineral Resources Data System (MRDS; USGS, 2013); hydraulic pit locations from Orlando (2016).

streambed sediment did not improve the geospatial-only model. However, incorporating data for MeHg in streambed sediment, along with sediment organic content (loss on ignition), grain size, and geospatial data, resulted in an improved model ($r^2 = 0.63$, $p < 0.001$). It is expected that these models will be useful to the State of California and others to predict areas where mercury concentrations in fish are likely to exceed regulatory criteria.

Systematic differences in fish THg were demonstrated between fish species and between sites. A Mining Influence Factor (MIF) was computed for each site considered, based on the contribution of two mining-related variables that appeared in the geospatial-only model. Values of the MIF varied from a minimum of 1.0 (no mining influence) to a maximum of 2.58 at a site in the South Yuba River watershed where placer-mined lands make up more than 70% of the upstream watershed. The MIF represents a multiplier on predicted fish THg concentration. Watershed-average MIF values ranged from 1.00 (Tuolumne River) to 1.77 (Bear River).

Although the models developed in this study are specific to the study area with regard to predictive capability, a similar approach could be used in other areas where there are non-atmospheric sources of mercury such as mining, industrial activity, and/or urban sources. In areas where reliable data are available for wet and dry atmospheric mercury deposition, atmospheric sources could also be included as a geospatial variable in landscape analysis of factors affecting fish THg.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.05.088.

References

Allen, E., Prepas, E., Gabos, S., Strachean, W., Zhang, W., 2005. Methyl mercury concentrations in macroinvertebrates and fish from burned and undisturbed lakes on the Boreal Plain. Can. J. Fish. Aquat. Sci. 62, 1963–1977.

Alpers, C.N., 2015. Arsenic and mercury contamination from historical gold mining in the Sierra Nevada, California. Tucson, AZ: Intl. Appl. Geochem. Symp, pp. 1–25.

Alpers, C.N., Hunerlach, M.P., 2000. Mercury contamination from historic gold mining in California. U.S. Geol. Surv. Fact Sheet FS-061-00 , pp. 1–6http://ca.water.usgs.gov/mercury/fs06100.html.

Alpers, C.N., Hunerlach, M.P., May, J.T., Hothem, R.L., 2005a. Mercury contamination from historical gold mining in California. U.S. Geol. Surv. Fact Sheet. 2005-3014 , pp. 1–6-http://water.usgs.gov/pubs/fs/2005/3014/.

Alpers, C.N., Hunerlach, M.P., May, J.T., Hothem, R.L., Taylor, H.E., Antweiler, R.C., et al., 2005b. Geochemical characterization of water, sediment, and biota affected by mercury contamination and acidic drainage from historical gold mining, Greenhorn Creek, Nevada County, California, 1999–2001. U.S. Geol. Surv. Sci. Invest. Rep. 2004-5251, 1–278http://pubs.usgs.gov/sir/2004/5251/.

Arifin, Y.I., Sakakibara, M., Sera, K., 2015. Impacts of artisanal and small-scale gold mining (ASGM) on environment and human health of Gorontalo Utara Regency, Gorontalo Province, Indonesia. Geosciences 5, 160–176. http://dx.doi.org/10.3390/geosciences5020160.

Ashley, R.P., 2002. Geoenvironmental model for low-sulfide gold-quartz vein deposits. U.S. Geol. Surv. Open-File Rep. 02-195K, 176–195http://pubs.usgs.gov/of/2002/of02-195/OF02-195K.pdf.

Belger, L., Forsberg, B.R., 2006. Factors controlling Hg levels in two predatory fish species in the Negro river basin, Brazilian Amazon. Sci. Total Environ. 367, 451–459.

Bloom, N.S., 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Can. J. Fish. Aquat. Sci. 49, 1010–1017.

Brigham, M.E., Wentz, D.A., Aiken, G.R., Krabbenhoft, D.P., 2009. Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. Environ. Sci. Technol. 43, 2720–2725.

Brumbaugh, W.G., Krabbenhoft, D.P., Helsel, D.R., Wiener, J.G., Echols, K.R., 2001. A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients—bioaccumulation in fish: U.S. Geol. Surv. Biol. Sci. Rep. 2001–0009, 1–25.

Burnham, K.P., Anderson, D.R., 2002. Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach. second ed. Springer-Verlag, Inc., New York, p. 488 http://dx.doi.org/10.1007/b97636.

California OEHHA (Office of Environmental Health Hazard Assessment), 2013s. Statewide Health Advisory and Guidelines for Eating Fish From California's Lakes and Reservoirs. Sacramento, Calif., July, 2013. 48 p http://oehha.ca.gov/fish/pdf/CALakeResAdvisory080113.pdf.

California SWRCB (State Water Resources Control Board), 2012. Final 2012 California Integrated Report (Clean Water Act Section 303(d) List/305(b) Report). Impaired Water Bodies. http://www.waterboards.ca.gov/water_issues/programs/tmdl/integrated2012.shtml (accessed Nov. 30, 2015).

Chasar, L.C., Scudder, B.C., Stewart, A.R., Bell, A.H., Aiken, G.R., 2009. Mercury cycling in stream ecosystems. 3. Trophic dynamics and methylmercury bioaccumulation. Environ. Sci. Technol. 43, 2733–2739.

Chen, C.Y., Stemberger, R.S., Kamman, N.C., Mayes, B.M., Folt, C.L., 2005. Patterns of Hg bioaccumulation and transfer in aquatic food webs across multi-lake studies in the Northeast US. Ecotoxicology 14, 135–147.

Churchill, R.K., 2000. Contributions of mercury to California's environment from mercury and gold mining activities; insights from the historical record. Extended Abstracts for the U.S. EPA Sponsored Meeting, Assessing and Managing Mercury From Historic and Current Mining Activities, November 28 — 30, 2000, San Francisco, Calif. 33 — 36, pp. S35–S48.

Davis, J.A., Greenfield, B.K., Ichikawa, G., Stephenson, M., 2008. Mercury in sport fish from the Sacramento-San Joaquin Delta region, California. Sci. Total Environ. 391, 66–75.

Davis, J.A., Looker, R.E., Yee, D., Marvin-DiPasquale, M., Grenier, J.L., Austin, C.M., et al., 2012. Reducing methylmercury accumulation in the food webs of San Francisco Bay and its local watersheds. Environ. Res. 119, 3–26.

Demers, J.D., Driscoll, C.T., Fahey, T.J., Yavitt, J.B., 2007. Mercury cycling in litter and soil in different forests types in the Adirondack region, New York, USA. Ecol. Appl. 17, 1341–1351.

Dittman, J.A., Driscoll, C.T., 2009. Factors influencing changes in mercury concentrations in lake water and yellow perch (*Perca flavescens*) in Adirondack lakes. Biochemistry 93, 179–196.

Domagalski, J.D., Majewski, M.S., Alpers, C.N., Eckley, C.S., Eagles-Smith, C.A., Schenk, L., et al., 2016. Comparison of mercury mass loading in streams to atmospheric deposition in watersheds in the western U.S.: Evidence for non-atmospheric mercury sources: journal article. Sci. Total Environ. (this issue).

Donovan, P.M., Blum, J.D., Yee, D., Gehrke, G.E., Singer, M.B., 2013. An isotopic record of mercury in San Francisco Bay sediment: chem. Geology 349–350, 87–98. http://dx.doi.org/10.1016/j.chemgeo.2013.04.017.

Drenner, R.W., Chumchal, M.M., Wente, S.P., McGuire, M., Drenner, S.M., 2011. Landscape-level patterns of mercury contamination of fish in north Texas, USA. Environ. Toxicol. Chem. 30, 2041–2045.

Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects: Environ. Sci. Technol. 47, 4967–4983. http://dx.doi.org/10.1021/es305071v.

Eagles-Smith, C.A., Ackerman, J.T., De La Cruz, S.E.W., Takekawa, J.Y., 2009. Mercury bioaccumulation and risk to three waterbird foraging guilds is influenced by foraging ecology and breeding stage. Environ. Pollut. 157, 1993–2002.

Eagles-Smith, C.A., Herring, G., Johnson, B., Graw, R., 2016. Conifer density within lake catchments predicts fish mercury concentrations in remote subalpine lakes. Environ. Pollut. 212, 279–289.

Evers, D.C., Kaplan, J.D., Meyer, M.W., Reaman, P.S., Braselton, W.E., Major, A., et al., 1998. Geographic trend in mercury measured in common loon feathers and blood. Environ. Toxicol. Chem. 17, 173–183.

Evers, D.C., Taylor, K.M., Major, A., Taylor, R.J., Poppenga, R.H., Scheuhammer, A.M., 2003. Common loon eggs as indicators of methylmercury availability in North America. Ecotoxicology 12, 69–81.

Evers, D.C., Han, Y., Driscoll, C.T., Kamman, N.C., Goodale, M.W., Lambert, K.F., et al., 2007. Biological mercury hotspots in the northeastern United States and southeastern Canada. Bioscience 57, 29–43.

Evers, D.C., Williams, K.A., Meyer, M.W., Scheuhammer, A.M., Schoch, N., Gilbert, A.T., et al., 2011. Spatial gradients of methylmercury for breeding common loons in the Laurentian Great Lakes region. Ecotoxicology 20, 1609–1625.

Fry, J., Xian, G., Jin, S., Dewitz, J., Homer, C., Yang, L., et al., 2011. Completion of the 2006 National Land Cover Database for the conterminous United States. Photogramm. Eng. Remote. Sens. 77, 858–864.

Gehrke, G.E., Blum, J.D., Marvin-DiPasquale, M., 2011a. Sources of mercury to San Francisco Bay surface sediment as revealed by mercury stable isotopes. Geochim. Cosmochim. Acta 75, 691–705.

Gehrke, G.E., Blum, J.D., Slotton, D.G., Greenfield, B.K., 2011b. Mercury isotopes link mercury in San Francisco Bay forage fish to surface sediments. Environ. Sci. Technol. 45, 1264–1270. http://dx.doi.org/10.1021/es103053y.

Grigal, D.F., 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. Environ. Rev. 10, 1–39.

Grigal, D.F., 2003. Mercury sequestration in forests and peatlands: a review. J. Environ. Qual. 32, 393–405.

Guedron, S., Grangeon, S., Lanson, B., Grimaldi, M., 2009. Mercury speciation in a tropical soil association; consequence of gold mining on Hg distribution in French Guiana. Geoderma 153, 331–346.

Hall, B., St. Louis, V., 2004. Methylmercury and total mercury in plant litter decomposing in upland forests and flooded landscapes. Environ. Sci. Technol. 38, 5010–5021.

Hornberger, M.I., Luoma, S.N., van Geen, A., Fuller, C., Anima, R., 1999. Historical trends of metals in the sediments of San Francisco Bay, California. Mar. Chem. 64, 39–55.

Hylander, L.D., Meili, M., 2003. 500 years of mercury production: global annual inventory by region until 2000 and associated emissions. Sci. Total Environ. 304, 13–27.

Hylander, L.D., Meili, M., 2005. The rise and fall of mercury: converting a resource to refuse after 500 years of mining and pollution. Crit. Rev. Environ. Sci. Technol. 35, 1–36.

Journey, C.A., Burns, D.A., Riva-Murray, K., Brigham, M.E., Button, D.T., Feaster, T.D., et al., 2012. Fluvial transport of mercury, organic carbon, suspended sediment, and selected major ions in contrasting stream basins in South Carolina and New York, October 2004–September 2009. U.S. Geol. Surv. Sci. Invest. Rep. 2012-5173, 1–125http://pubs.er.usgs.gov/publication/sir20125173.

Kamman, N.C., Burgess, N.M., Driscoll, C.T., Simonin, H.A., Goodale, W., Linehan, J., et al., 2005. Mercury in freshwater fish of northeast North America — a geographic perspective based on fish tissue monitoring databases. Ecotoxicology 14, 163–180.

Kamman, N.C., Lorey, P.M., Driscoll, C.T., Estabrook, R., Major, A., Pientka, B., Glassford, E., 2004. Assessment of mercury in waters, sediments, and biota of New Hampshire and Vermont lakes, USA, sampled using a geographically randomized design. Environ. Toxicol. Chem. 23, 1172–1186. http://dx.doi.org/10.1897/03-170.

Kehrig, H.A., Howard, B.M., Malm, O., 2008. Methylmercury in a predatory fish (*Cichla* spp.) inhabiting the Brazilian Amazon. Environ. Pollut. 154, 68–76.

Krabbenhoft, D.P., Wiener, J.G., Brumbaugh, W.G., Olson, M.L., DeWild, J.F., Sabin, T.J., 1999. A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients. U.S. Geol. Surv. Water-Res. Invest. Rep. 99-4018B, 147–160http://toxics.usgs.gov/pubs/wri99-4018/Volume2/sectionB/2301_Krabbenhoft/.

Kuwabara, J.S., Arai, Y., Topping, B.R., Pickering, I.J., George, G.N., 2007. Mercury speciation in piscivorous fish from mining-impacted reservoirs. Environ. Sci. Technol. 41, 2745–2749.

Kvalseth, T.O., 1985. Cautionary note about R^2. Am. Stat. 39, 279–285.

Lacerda, L.D., Fitzgerald, W.F., 2001. Biogeochemistry of mercury in wetlands. Wetlands Ecol. Mgmt. 9, 291–293.

Lange, T., Royals, H., Connor, L., 1993. Influence of water chemistry on mercury concentrations in largemouth bass in Florida lakes. Trans. Am. Fish. Soc. 122, 74–84.

Langer, C.S., Fitzgerald, W.F., Visscher, P.T., Vandal, G.M., 2001. Biogeochemical cycling of methylmercury at Barn Island Salt Marsh, Stonington, CT, USA. Wetlands Ecol. Mgmt. 9, 295–310.

Lavoie, R.A., Jardine, T.D., Chumchal, M.M., Kidd, K.A., Campbell, L.M., 2013. Biomagnification of mercury in aquatic food webs: a worldwide meta-analysis. Environ. Sci. Technol. 2013 (47), 13385–13394. http://dx.doi.org/10.1021/es403103t.

Lechler, P.J., Miller, J.R., Hsu, L.-C., Desilets, M.O., 1997. Mercury mobility at the Carson River Superfund Site, west-central Nevada, USA: interpretation of mercury speciation data in mill tailings, soils, and sediments. J. Geochem. Explor. 58, 259–267.

Lindberg, S.E., 1996. Forest and the global biogeochemical cycle of mercury: the importance of understanding air/vegetation exchange processes. In: Aeyens, W., Ebinghaus, R., Vasiliev, O. (Eds.), Global and Regional Mercury Cycles: Sources, Fluxes and Mass BalancesNATO ASI Series 21. Kluwer Academic Publishers, Dordreacht, pp. 359–380.

Long, K.R., DeYoung Jr., J.H., Ludington, S.D., 1998. Database of significant deposits of gold, silver, copper, lead, and zinc in the United States. U.S. Geol. Surv. Open-File Rep. 98-206A, 1–33http://pubs.usgs.gov/of/1998/0206a-b/.

Marvin-DiPasquale, M., Cox, M.H., 2007. Legacy mercury in Alviso Slough, South San Francisco Bay, California: Concentration, speciation and mobility. U.S. Geol. Surv. Open-File Rep. 2007-1240, 1–98.

Marvin-DiPasquale, M., Hall, B.D., Flanders, J.R., Ladizinski, N., Agee, J.L., Kieu, L.H., et al., 2006. Ecosystem investigations of benthic methylmercury production: a tin-reduction approach for assessing the inorganic mercury pool available for methylation. Mercury 2006 Abstracts Book: Eighth Intl. Conf. Mercury Global Poll. Madison, WI, Aug. 6–11, 2006.

Marvin-DiPasquale, M., Lutz, M.A., Brigham, M.E., Krabbenhoft, D.P., Aiken, G.R., Orem, W.H., et al., 2009. Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment–porewater partitioning. Environ. Sci. Technol. 43, 2726–2732.

Marvin-DiPasquale, M., Agee, J.L., Kakouros, E., Kieu, L.H., Fleck, J.A., Alpers, C.N., 2011. The effects of sediment and mercury mobilization in the South Yuba River and Humbug Creek confluence area, Nevada County, California: Concentrations, speciation and environmental fate—Part 2: Laboratory experiments. U.S. Geol. Surv. Open-File Rep. 2010-1325B, 2011, 1–54http://pubs.usgs.gov/of/2010/1325B.

May, J.T., Hothem, R.L., Alpers, C.N., Law, M.A., 2000. Mercury bioaccumulation in fish in a region affected by historic gold mining: The South Yuba River, Deer Creek, and Bear River watersheds, California, 1999. U.S. Geol. Surv. Open-File Rep. 00-367, 1–30http://ca.water.usgs.gov/archive/reports/ofr00367/.

Melwani, A.R., Bezalel, S.N., Grenier, J.L., Hunt, J.A., Robinson, A.H., Davis, J.A., 2007. The relationship between landscape features and sport fish mercury in the Sacramento–San Joaquin Delta Watershed. SFEI Contrib. 534. San Fran. Est. Inst., Oakland, CA http://www.sfei.org/documents/relationship-between-landscape-features-and-sport-fish-mercury-sacramento-san-joaquin.

Melwani, A.R., Bezalel, S.N., Hunt, J.A., Grenier, J.L., Ichikawa, G., Heim, W., et al., 2009. Spatial trends and impairment assessment of mercury in sport fish in the –San Joaquin Delta watershed. Environ. Pollut. 157, 3137–3149.

Miller, C.L., Mason, R.P., Gilmour, C.C., Heyes, A., 2007. Influence of dissolved organic matter on the complexation of mercury under sulfidic conditions. Environ. Toxicol. Chem. 26, 624–633.

Mol, J.H., Ramlal, J.S., Lietar, C., Verloo, M., 2001. Mercury contamination in freshwater, estuarine, and marine fishes in relation to small-scale gold mining in Suriname, South America. Environ. Res. Sec. A 86, 183–197.

Moyle, P.B., 2002. Inland fishes of California. University of California Press, Berkeley and Los Angeles, California.

Munson, R., Harris, R., Summers, K., Chen, L., Roy, S.B., Driscoll, C.T., et al., 2008. Mercury in Adirondack wetlands, lakes and terrestrial streams (MAWLTS). Final Report for NY State Energy Research and Development Authority. Tetra Tech Inc. NSERDA Report 08-211.

Nagorski, S.A., Engstrom, D.R., Hudson, J.P., Krabbenhoft, D.P., Hood, E., DeWild, J.F., Aiken, G.F., 2014. Spatial distribution of mercury in southeastern Alaskan streams influenced by glaciers, wetlands, and salmon. Environ. Pollut. 184, 62–72.

Neter, J., Wasserman, W., Kutner, M.H., 1990. Applied Linear Statistical Models: Regression, Analysis of Variance, and Experimental Design. third ed. Richard D. Irwin, Inc., Homewood, IL.

Nriagu, J.O., 1994. Mercury pollution from the past mining of gold and silver in the Americas. Sci. Total Environ. 149, 167–181.

Obrist, D., Johnston, D.W., Lindberg, S.E., Luo, Y., Hararuk, R., Bracho, J.J., et al., 2011. Mercury distribution across 14 US forests. Part I: spatial patterns of concentrations in biomass, litter, and soils. Environ. Sci. Technol. 45, 3974–3981.

Obrist, D., Johnson, D.W., Edmonds, R.L., 2012. Effects of vegetation type of mercury concentrations and pools in two adjacent coniferous and deciduous forests. J. Plant Nutr. Soil Sci. 175, 68–77.

Obrist, D., Pearson, C., Webster, J., Kane, T., Lin, C.-J., Aiken, G.R., Alpers, C.N., 2016. Terrestrial mercury in the western United States: spatial distribution defined by land cover and plant productivity. Sci. Total Environ. (this issue).

Orlando, J., 2016. Hydraulic Mine Pits of California: U.S. Geological Survey data release. http://dx.doi.org/10.5066/F7J38QMD.

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

Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., Blum, J., 2002. Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs. Proc. Natl. Acad. Sci. 99, 4419–4423.

Rasmussen, P.E., Mierle, G., Nriagu, J.O., 1991. The analysis of vegetation for total mercury. Water Air Soil Pollut. 56, 379–390.

Rea, A.W., Lindberg, S.E., Keeler, G.J., 2001. Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall. Atmos. Environ. 35, 3452–3462.

Richardson, J.B., Friedland, A.J., 2015. Mercury in coniferous and deciduous upland forests in northern New England, USA: implications of climate change. Biogeosciences 12, 6737–6749.

Ries III, K.G., Steeves, P.A., Guthrie, J.D., Rea, A.H., Stewart, D.W., 2009. Stream network navigation in the U.S. Geological Survey StreamStats Web Application. 2009 Intl. Conf. Adv. Geog. Info. Syst. Web Serv. , pp. 80–84http://water.usgs.gov/osw/streamstats/Ries-Navigation-Final.pdf

Roulet, M., Lucotte, M., Saint-Aubin, A., Tran, S., Rhéault, I., Farella, N., et al., 1998. The geochemistry of mercury in central Amazonian soils developed on the Alter-do-Chão formation of the lower Tapajós River Valley, Pará state. Brazil. Sci. Tot. Environ. 223, 1–24.

Saiki, M.K., Martin, B.A., May, T.W., Alpers, C.N., 2009. Mercury contamination in fish from a Sierra Nevada foothill reservoir located downstream from historic gold-mining operations. Environ. Monit. Assess. 163, 313–326.

Scudder, B.C., Chasar, L.C., Wentz, D.A., Bauch, N.J., Brigham, M.E., Moran, P.W., et al., 2009. Mercury in fish, bed sediment, and water from streams across the United States, 1998–2005. U.S. Geol. Surv. Sci. Invest. Rep. 2009-5109, 1–74http://pubs.usgs.gov/sir/2009/5109/.

Shanley, J.B., Mast, M.A., Campbell, D.H., Aiken, G.R., Krabbenhoft, D.P., Hunt, R.J., et al., 2008. Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach. Environ. Pollut. 154, 143–154.

Shanley, J.B., Moore, R., Smith, R.A., Miller, E.K., Simcox, A., Kamman, N., et al., 2012. MERGANSER: an empirical model to predict fish and loon mercury in New England lakes. Environ. Sci. Technol. 46, 4641–4648. http://dx.doi.org/10.1021/es300581p.

Silva-Forsberg, M.C., Forsberg, B.R., Zeidemann, V.K., 1999. Mercury contamination in humans linked to river chemistry in the Amazon Basin. Ambio 28, 519–521.

Simonin, H., Loukmas, J., Skinner, L., Roy, K., 2008. Lake variability: key factors controlling mercury concentrations in New York State fish. Environ. Pollut. 154, 107–115.

Singer, M.B., Aalto, R., James, L.A., Kilham, N.E., Higson, J.L., Ghosal, S., 2013. Enduring legacy of a toxic fan via episodic redistribution of California gold mining debris. Proc. Nat. Acad. Sci. USA 110, pp. 18436–18441 http://dx.doi.org/10.1073/pnas.1302295110 (correction 110, 21196).

Slotton, D.G., Ayers, S.M., Reuter, J.E., Goldman, C.R., 1997. Gold mining impacts on food chain mercury in northwestern Sierra Nevada streams. Larry Walker Associates, Sacramento River Watershed Mercury Control Planning Project—Report for the Sacramento Regional County Sanitation District. App. B, pp. 1–74.

Stamenkovic, J., Gustin, M.S., Marvin-DiPasquale, M.C., Thomas, B.A., Agee, J.L., 2004. Distribution of total and methyl mercury in sediments along Steamboat Creek (Nevada, USA). Sci. Total Environ. 322, 167–177.

Ste-Marie, C., Paré, D., 1999. Soil, pH and N availability effects on net nitrifcation in the forest floors of a range of boreal forest stands. Soil Biol. Biochem. 31, 1579–1589.

Stewart, A.R., Saiki, M.K., Kuwabara, J.S., Alpers, C.N., Marvin-DiPasquale, M., Krabbenhoft, D.P., 2008. Influence of plankton mercury dynamics and trophic pathways on mercury concentrations of top predator fish of a mining-impacted reservoir. Can. J. Fish. Aquat. Sci. 65, 2351–2366.

Telmer, K.H., Veiga, M.M., 2009. World emissions of mercury from artisanal and small scale gold mining. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, New York.

Tsai, P., Hoenicke, R., 2001. San Francisco Bay atmospheric deposition pilot study part 1: mercury. San Francisco Estuary Institute, SFEI Contribution. 72 , pp. 1–45. http://www.sfei.org/documents/san-francisco-bay-atmospheric-deposition-pilot-study-part-1-mercury.

USGS (U.S. Geological Survey), 2013. Mineral Resources Data System (MRDS); Mines of California, Digital data. accessed February 4, 2013 from URL http://mrdata.usgs.gov/mrds/select.php.

Van Straaten, P., 2000. Mercury contamination associated with small-scale gold mining in Tanzania and Zimbabwe. Sci. Total Environ. 259, 105–113.

Viega, M.M., Maxson, P.A., Hylander, L.D., 2006. Origin and consumption of mercury in small-scale gold mining. J. Clean. Prod. 14, 436–447.

Watras, C.J., Back, R.C., Halvorsen, S., Hudson, R.J.M., Morrison, K.A., Wente, S.P., 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Sci. Total Environ. 219, 183–208.

Wiener, J.G., Knights, B.C., Sandheinrich, M.B., Jeremiason, J.D., Brigham, M.E., Engstrom, D.R., et al., 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. Environ. Sci. Technol. 40, 6261–6268.

Wiener, J.G., Krabbenhoft, D.P., Heinz, G.H., Scheuhammer, A.M., 2003. Ecotoxicology of mercury. Handbook of Ecotoxicology. Lewis Publishers, Boca Raton, FL, pp. 409–463.

Wente, S.P., 2004. A statistical model and national data set for partitioning fish-tissue mercury concentration between spatiotemporal and sample characteristic effects, U.S. Geol. Surv. Sci. Invest. Rep. 2004-5199, 1–21.

Yeend, W.E., 1974. Gold-bearing gravel of the ancestral Yuba River, Sierra Nevada, California. U. S. Geol. Surv. Prof. Pap. 772, 1–44 2 plates http://pubs.er.usgs.gov/publication/pp772.

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