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Mercury and methylmercury in aquatic sediment across western North America

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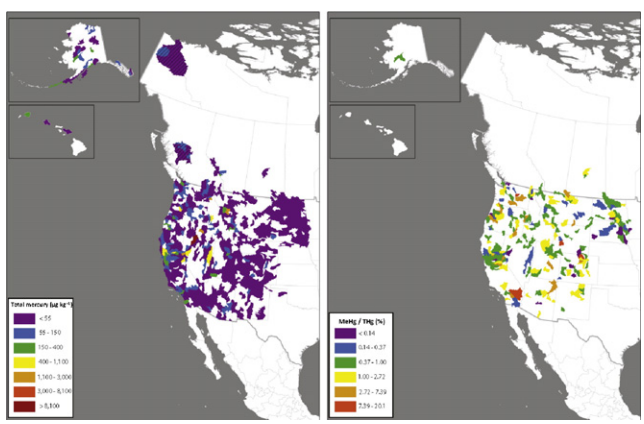
HIGHLIGHTS

- THg and MeHg concentrations of aquatic sediment compiled from >11000 western sites
- Geospatial attributes were integrated with Hg and MeHg concentrations
- MeHg concentrations differed among landscape categories, trends differed from THg
- THg - MeHg relationship was weak ($r^2 = 0.25$) but significant across the landscape
- 51% of MeHg variation explained by within-site variability and landscape categories

GRAPHICAL ABSTRACT



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ABSTRACT

Large-scale assessments are valuable in identifying primary factors controlling total mercury (THg) and monomethyl mercury (MeHg) concentrations, and distribution in aquatic ecosystems. Bed sediment THg and MeHg concentrations were compiled for >16,000 samples collected from aquatic habitats throughout the West between 1965 and 2013. The influence of aquatic feature type (canals, estuaries, lakes, and streams), and environmental setting (agriculture, forest, open-water, range, wetland, and urban) on THg and MeHg concentrations was examined. THg concentrations were highest in lake (29.3 ± 6.5 μg kg^{-1}) and canal (28.6 ± 6.9 μg kg^{-1}) sites, and lowest in stream (20.7 ± 4.6 μg kg^{-1}) and estuarine (23.6 ± 5.6 μg kg^{-1}) sites, which was partially a result of differences in grain size related to hydrologic gradients. By environmental setting, open-water (36.8 ± 2.2 μg kg^{-1}) and forested (32.0 ± 2.7 μg kg^{-1}) sites generally had the highest THg concentrations, followed by wetland sites (28.9 ± 1.7 μg kg^{-1}), rangeland (25.5 ± 1.5 μg kg^{-1}), agriculture (23.4 ± 2.0 μg kg^{-1}), and urban (22.7 ± 2.1 μg kg^{-1}) sites. MeHg concentrations also were highest in lakes (0.55 ± 0.05 μg kg^{-1}) and

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canals (0.54 ± 0.11 μg kg^{-1}), but, in contrast to THg, MeHg concentrations were lowest in open-water sites (0.22 ± 0.03 μg kg^{-1}). The median percent MeHg (relative to THg) for the western region was 0.7%, indicating an overall low methylation efficiency; however, a significant subset of data (n > 100) had percentages that represent elevated methylation efficiency (>6%). MeHg concentrations were weakly correlated with THg ($r^2 = 0.25$) across western North America. Overall, these results highlight the large spatial variability in sediment THg and MeHg concentrations throughout western North America and underscore the important roles that landscape and land-use characteristics have on the MeHg cycle.

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1. Introduction

Aquatic bed sediment is an important zone of mercury (Hg) methylation, the microbially-mediated process whereby inorganic Hg is converted to the more bioavailable form monomethyl mercury (MeHg) (Morel et al., 1998). Once converted to MeHg, this powerful neurotoxin can enter the food web and biomagnify up the food chain to concentrations that can threaten both human health and ecosystem function (Mergler et al., 2007; Wiener et al., 2003). Although MeHg concentrations generally correlate with total mercury (THg) concentrations over large spatial scales (e.g., Krabbenhoft et al., 1999), the strength of the correlation depends upon a number of factors. First, some fraction of the inorganic Hg must be available to the microbial populations that can methylate it, and the proportion of THg that is available for methylation is determined not only by the amount of inorganic Hg but also the biogeochemical conditions that affect its speciation (Bloom et al., 2003; Hsu-Kim et al., 2013; Jonsson et al., 2012; Sunderlund et al., 2006). Also, biogeochemical conditions also affect the microbial activity that leads to MeHg production, as well as its degradation (Lambertsson and Nilsson, 2006; Ullrich et al., 2001). Then, physical transport processes may either concentrate MeHg in the area where it is produced leading to high MeHg concentrations or flush the MeHg away from the site of production at a greater rate than it can be replenished leading to low MeHg concentrations independent of net MeHg production rates.

Large-scale assessments have proven valuable in identifying primary factors controlling THg and MeHg concentrations in aquatic systems (Evers and Clair, 2005; Wiener et al., 2012). A national pilot study of 106 sites in 21 large river basins across the USA identified the importance of wetlands to MeHg concentrations in aquatic ecosystems (Brumbaugh et al., 2001; Krabbenhoft et al., 1999). Subsequent assessments have further identified the influence of urban development and forest cover in US watersheds on THg and MeHg concentrations in both sediment and biota (Eagles-Smith et al., 2016a; Horowitz and Stephens, 2008; Wentz et al., 2014). Other studies have evaluated large-scale spatial effects on the geochemical factors controlling MeHg production in specific ecosystem types (Hall et al., 2008; Marvin-DiPasquale et al., 2009; Scudder et al., 2009).

The western North American landscape provides a unique setting with extremes in geological, geographical, and climatological characteristics. The combination of diverse Hg sources, habitat types, and geology, and extremes in topography, geography, and climate, create a complex mosaic of processes driving Hg cycling and bioaccumulation. One of the unique aspects of the West is the vast expanse of arid landscapes where water is scarce and extensively manipulated through a network of reservoirs, canals, and pipelines. Additionally, public lands comprise more than 60% of the total surface area in the American West, which includes numerous wildlife refuges, conservation areas, and preserves, where wetlands are managed to provide habitat for a diverse group of trust resources and endangered species. Because so much land is in the public domain, management efforts to reduce Hg risk may be more plausible in the West than in other geographic regions of North America. A better understanding of the distribution of MeHg across the landscape, and its relationship with THg, would benefit attempts to manage MeHg risk.

In this paper, the distribution of THg and MeHg concentrations compiled from a number of publicly available databases and literature for bed sediment are evaluated across a broad range of aquatic habitat types and environmental settings. Data are placed in the context of regulatory and advisory benchmarks as a means to assess areas of relative concern with respect to Hg contamination. Then, the relationship between MeHg and THg concentrations in bed sediment were examined across broad habitat types and environmental settings. These results further the understanding of THg and MeHg distribution across western North America, and affirm the importance of landscape factors in controlling MeHg concentrations.

2. Methods

2.1. Database compilation

Aquatic bed sediment THg and MeHg concentration data sets from a wide variety of sources, including publicly available federal, state, and provincial databases, as well as published and unpublished data from individual laboratories and research projects were compiled in a single database (Table S1). The geographic scope of the data compilation encompassed 15 Western United States (US) states and five Canadian provinces (Fig. 1), which included all states and provinces containing land west of the front ranges of the Rocky Mountains, including Alaska and Hawaii, as well as those containing prairie potholes (Saskatchewan, North Dakota, and South Dakota). Data from Mexico were not available for inclusion except for a few values from lake sediment cores (Ontiveros-Cuadras et al., 2014). All results compiled in the data set were evaluated for comparability. To achieve this, THg data results were constrained to include only total digests, whereas MeHg methods were generally more comparable across the databases. Despite attempts to include only THg results from complete digests with comparable Hg recoveries, the possibility of differences in the methodological recoveries of each database cannot be ruled out, although such an effect would likely only contribute to greater variation in the data set rather than a bias. All THg results with detection limits > 10 μg kg^{-1} (0.04 μg kg^{-1} for MeHg) or where data quality could not be effectively evaluated were then removed. This process eliminated nearly all data prior to 1990. Some pre-1990 data were retained in the data set where sufficient documentation was provided for sample aliquots large enough to lower the effective THg detection limits to ≤10 μg kg^{-1}. Data were then cross-checked using database codes that contained information about sample types, eliminating data where contradictions occurred that could not be resolved with the available metadata. For instance, it was not uncommon for sediment core samples to be labeled as "soil" and for soil samples to be labeled "bed sediment" in the databases. Because wetland environments represent the transition between aquatic and terrestrial systems, this distinction remains a challenge to consistency within and between all the databases queried. For the USGS National Water Information System (NWIS) database, some parameter codes explicitly state the matrix (e.g., suspended sediment versus bed sediment) and may have contradicted the selected matrix code for a specific result. In many cases, results with these contradictions were simply eliminated from the database unless there was clear evidence of the proper assignment to the bed sediment category to be included in this analysis.

Bed sediment results were then grouped by sieve sizes. For this effort, "unsieved", "<2 mm", and "not reported" were grouped as "bulk sediment", whereas other sieve fractions were excluded for this

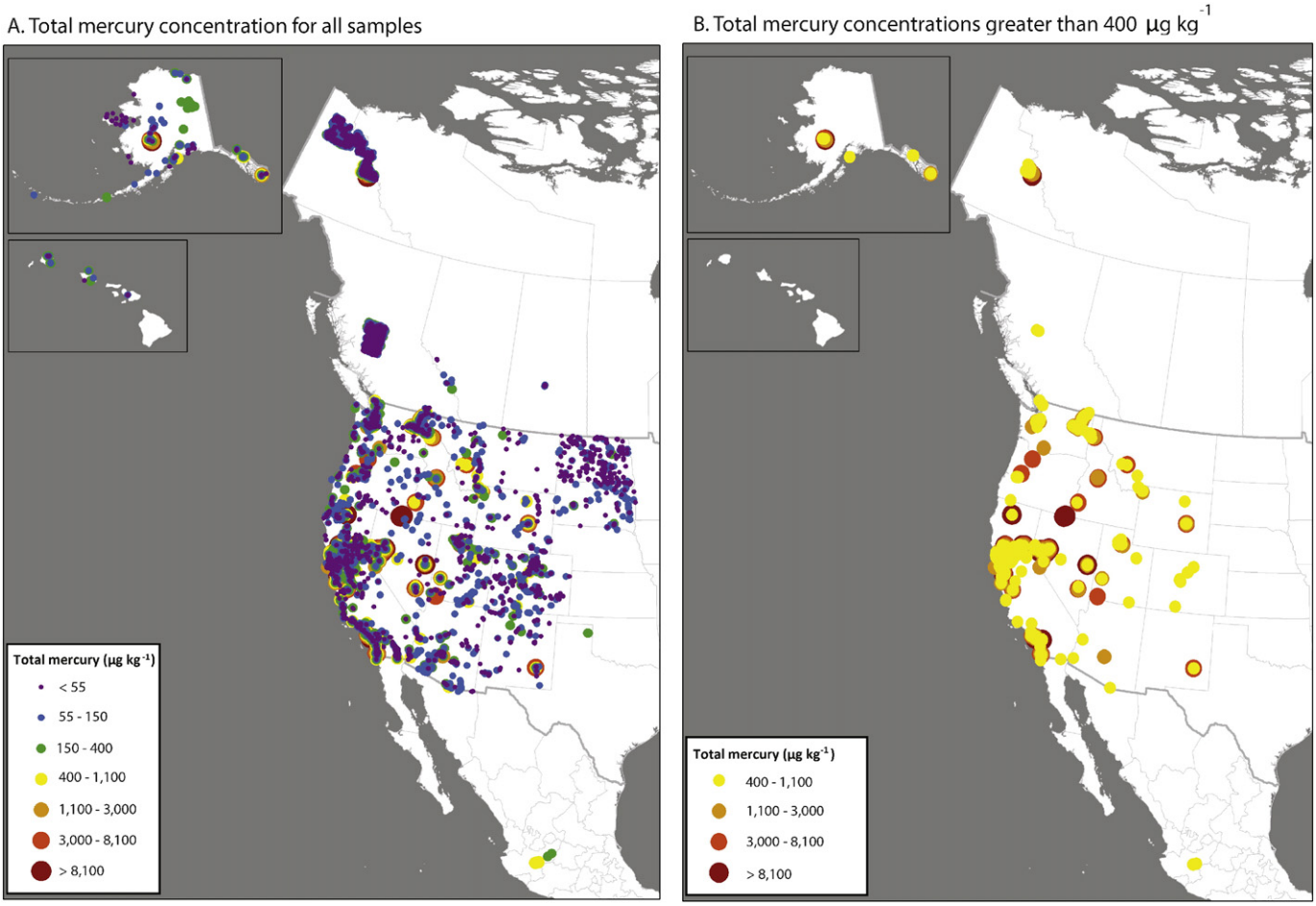

Fig. 1. Map showing the distribution of THg concentrations of individual aquatic bed sediment samples across the western North American landscape. Figure A shows concentration data for all samples with low values overlaid on top of higher values. Figure B shows data for samples with concentrations > 400 µg kg^{-1} for easier visualization of the higher concentration locations. Symbol size and color are for visualization purposes only. Symbol colors reflect regulatory targets and benchmark screening levels, as summarized in Table 1, but also closely reflect the natural log distribution across the entire data set. Despite the linkage to regulatory and benchmark concentrations, the concentration bins used in this assessment are not meant to imply risk but to provide a standardized framework for comparison.

analysis. One exception was the Canadian provincial databases where nearly all samples were sieved to <177 µm (Heon, 2003). Finally, all results were restricted to the surface sediment layer, for which 0–2 cm and 0–5 cm depth increments were most common. For results at or below the selected reporting levels (15% of all THg data; 3% of all MeHg data), results were included as reported from data sources with lower reporting levels. For results reported as "<" or "detected, not quantifiable" (DNQ) half the detection limit was assigned for the purpose of statistical analysis. All final compiled data were integrated into Microsoft Excel®, JMP® and ArcGIS® programs for further analysis. Spatial data processing and mapping were accomplished using ArcGIS® and ArcMAP® software (Esri, Redlands, California, USA).

2.2. Attribute and geospatial variable assignments

Extracting data from a number of databases resulted in a diverse range of supporting information for the THg results. There was a wide range in the level of descriptive metadata and relative quality with respect to accuracy and precision. Many THg results from the data compilation had little to no supporting information with respect to the site characteristics and sampling location. Therefore, to examine the compiled data in a consistent manner, only the THg and MeHg concentrations and GPS coordinates were included in the final compiled database. For each geo-referenced result, point-intersection attributes were assigned using a suite of GIS-based landscape coverages available on the web (Table S1-2). No single geospatial resource provided a consistent classification for habitat, land coverage, or water body type across the full data set. To achieve a consistently coded data set, a step-wise approach was used, illustrated in Fig. S1-1a, assigning four general classes of aquatic 'feature type' loosely analogous to water body types (canal, estuary, lake, and stream). Those that were not classified by any of the geospatial layers or had conflicting classifications (a relatively small subset of the total) were cross-checked with site names and Google Maps (http://www.google.com/maps). Those with insufficient metadata and location uncertainty were left as "Unclassified" (Fig. S1-1). Canadian data were limited to lakes and streams and were kept as reported in the data set, except prairie pothole wetlands which were included in the lake (closed drainage) feature category. Sites were then further categorized into six generalized classes of 'environmental setting' (agriculture, range, forested, open-water, urban, and wetland), which described a combination of habitat type and land cover as illustrated in Fig. S1-2. The range category included all barren, shrubland and grassland categories identified in the land cover database. Environmental setting results that were not classified by any of the geospatial layers and/or available metadata were labeled as "not determined" (Fig. S1-1b). All data were included in the subsequent development of maps, but those that were not classified were not included in statistical comparisons between groups.

To account for repeated measurements at the same location, all results were assigned a unique site ID as determined by the reported

coordinates (latitude and longitude, in decimal degrees) in their respective databases. Coordinates were converted where necessary into decimal degrees. It is possible that samples from a single site may be represented as separate sites, if different location coordinates were reported for the individual results imposed by differing precision and accuracy of the location data ranging from hundredths to hundred-thousands of decimal degrees in the data set. However, this was expected to have occurred for only a small fraction of the data and that this

Table 1
Relation of total Hg (THg) sediment quality guidelines (SQLs, compiled from MacDonald et al., 2000 and Randall and Chattopadhyay, 2013) and other benchmarks to map colors in Figs. 1 and 2.

Map color	Concentration range (μg kg^{-1})	Percent of THg results in bin	Percent of HUC8 LSMs in bin	Abbreviation	Name	Description	Value (μg kg^{-1})	Citation
	< 55	41.3%	76.7%	NA	Background	Terrestrial soil–mean of western USA	24	Obrist et al., this issue
				NA	Background	Terrestrial soil–Europe	30	Ottesen et al., 2013
	55 – 150	29.8%	17.1%	NA	Background	Upper limit of terrestrial soil, non–outlier western USA	86	Obrist et al., this issue
				TEL–freshwater	Threshold Effects Level–freshwater	Represents the concentration below which adverse effects are expected to occur only rarely.	130	Smith et al., 1996; Canadian Council of Ministers of the Environment, 2003; Environment Canada, 2007
	150 – 400	19.9%	3.9%	ERL	Effects Range–Low	Adverse effects seen rarely (<10% of study)	150	Long et al. 1995; Long and Morgan 1991
				TEL–marine	Threshold Effects Level–marine	Represents the concentration below which adverse effects are expected to occur only rarely.	170	Smith et al., 1996; Canadian Council of Ministers of the Environment, 2003; Environment Canada, 2007
				TEC–c	Threshold Effect Concentration, consensus–based	More than 75% of sediment samples were correctly predicted to be not toxic	180	Massachusetts Department of Environmental Protection,2002; Wells and Hill, 2004
				LEL, MET	Lower Effect Limit, Minimal Effect Threshold	Sediments are considered to be clean to marginally polluted. No effects on the majority of sediment–dwelling organisms are expected below this concentration.	200	Persaud et al. 1993; EC and MENVIQ, 1992
	400 – 1,100	6.2%	1.5%	AET	Apparent Effects Threshold		410	Massachusetts Department of Environmental Protection, 2002; Wells and Hill, 2004
				PEL–fresh	Probable Effects Level for freshwater sediment	Represents the concentration above which adverse effects are expected to occur frequently.	490	Smith et al., 1996; Canadian Council of Ministers of the Environment, 2003; Environment Canada, 2007
				PEL–marine	Probable Effects Level for marine sediment	Represents the concentration above which adverse effects are expected to occur frequently.	700	Smith et al., 1996; Canadian Council of Ministers of the Environment, 2003; Environment Canada, 2007
				ERM	Effects Range–Medium	Adverse effects seen frequently (50% of study)	710	Massachusetts Department of Environmental Protection, 2002; Wells and Hill, 2004
				ERM	Effects Range–Median	Represents the chemical concentration above which adverse effects would frequently occur.	1000	Long and Morgan 1991

Table 1 (*continued*)

	1,100 – 3,000	1.5%	0.7%	PEC–c	Probable Effects Concentration, consensus–based	Represents the concentration above which adverse effects are expected to occur frequently (>75%)	1060	Long et al., 1998
				TET	Toxic Effect Threshold	Sediments are considered to be heavily polluted. Adverse effects on sediment–dwelling organisms are expected when this concentration is exceeded	1300	EC and MENVIQ, 1992
				SEL	Severe Effect Level	Sediments are considered to be heavily polluted. Adverse effects on the majority of sediment–dwelling organisms are expected when this concentration is exceeded.	2000	Persaud et al., 1993
	3,000 – 8,100	0.5%	0.0%	NA	None identified between 2100 and 8000	Heavily polluted, between screening levels for organisms/indirect human and direct human effects		
				RMC–median	BLM median wildlife Risk Management Criteria–soil		8000	BLM
	> 8,100	0.7%	0.2%		EPA Superfund screening level–residential	Human effects risk, residential	9400	EPA Superfund, http://www.epa.gov/region9/superfund/navajo–nation/
					EPA Superfund screening level–industrial	Human effects risk, industrial	40,000	EPA Superfund, http://www.epa.gov/region9/superfund/navajo–nation/
				RMC–secondary	Secondary action level–risk management criteria–recreational user–camper	Human effects risk, recreational	46,000	BLM
					EPA Superfund clean–up level	Site–specific cleanup level for contaminated soils in residential areas –New Almaden, California	80,000	EPA Superfund

variability would be accounted for through a spatial binning. The binning was performed by assigning each geo-referenced result in the database to its appropriate hydrologic unit code (HUC). There are different levels of HUCs, from HUC2 to HUC12 (largest to smallest in areal coverage). The HUC8 scale represents a relatively uniform watershed unit approximately 1800 km^2 (700 mi^2) in size, although the actual size varies according to specific topographic and hydrologic factors. Geospatial attributes in the public domain were well represented at the spatial scale of the HUC8 compared to the other HUC scales. This normalization of scale also addressed concerns related to evaluating data over differing spatial scales (Bradley et al., 2013; Horowitz and Stephens, 2008). Also, recent efforts extended the HUC8 level boundaries into Canada, allowing the data to be binned at the HUC8 level across both the USA and Canada. This analysis was not applied to the few data located in Mexico.

2.3. Statistical analyses

All statistical analyses were conducted using JMP statistical software (Version 11.2, SAS, Cary, North Carolina). The first step was to use basic summary statistics to examine the occurrence and distribution of THg and MeHg concentrations in all bed sediment samples collected across the landscape, regardless of the spatial distribution of the sites and the number of repeated measurements at any single site. Because data sets for THg and MeHg differed substantially in spatial coverage, the THg data set was evaluated first, then the MeHg data set, followed by a separate analysis of the subset of data where both THg and MeHg were co-collected. There were only 68 MeHg results from Canada, all from a single study in the prairie pothole region of the Great Plains (Table S1-1). Because the collection and analysis procedures for these Canadian samples match those

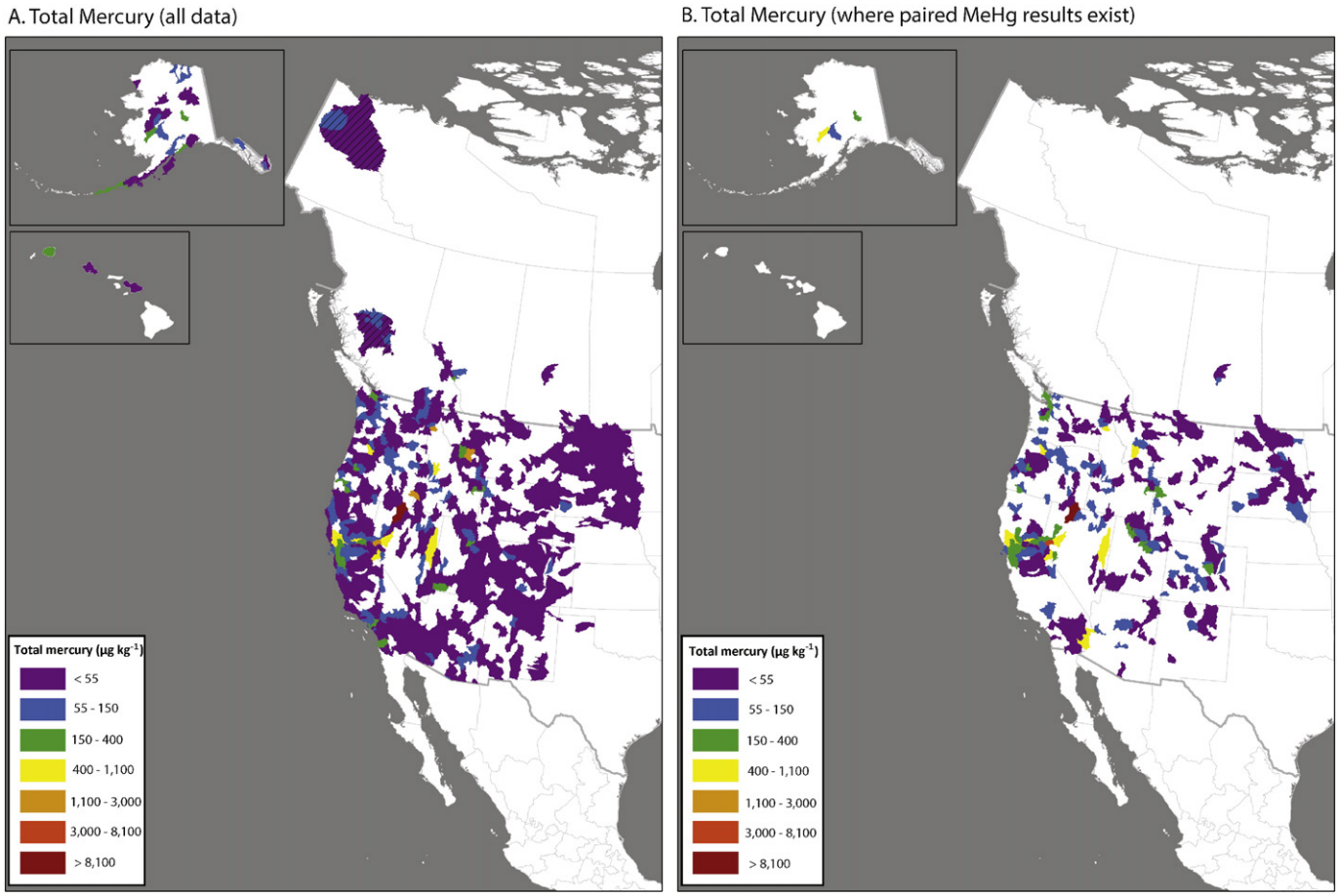

Fig. 2. Map showing the spatial distribution of HUC8-based least squares mean THg concentrations for A) the complete THg data set and B) the subset of the THg data where MeHg was also measured. Cross-hatching indicates HUCs where all samples were sieved.

for the US data set, all MeHg data were pooled for further analysis and discussion of MeHg statistics.

Next, a global Linear Mixed Effect (LME) ANCOVA model was developed to assess statistical differences, while simultaneously accounting for: a) within-site temporal variation where multiple samples were collected; b) among-site spatial variation across the landscape (at an approximate 1800 km^2 scale, including intrinsic larger-scale effects such as longitudinal, latitudinal, ecoregion, climatological, and altitudinal characteristics); c) differences in temporal resolution of sampling efforts; and d) variation in repeated measures at specific sites. The global model included natural log (Ln) transformed concentration as the dependent variable, the sample HUC8 ID, feature type, and environmental setting classifications as fixed effects, and the unique site identifiers as a random effect. This approach allowed the creation of spatial maps representing least squares mean concentrations for HUC8s, and a statistical basis for comparison of the least squares means by classification groups. The HUC-based maps provide a statistically-based spatial visualization of concentration, accounting for repeated measurements, site type, and the integrated characteristics of the HUC8 grouping (e.g., elevation, precipitation, temperature), thus reducing the bias related to these factors in the visualization of the compiled database. Differences between categorical variables were evaluated at $\alpha = 0.05$ using Tukey's Honest Significant Difference test.

Finally, the relationship between THg and MeHg was evaluated where data were paired within the original databases. First, simple bivariate linear regressions were evaluated for all data followed by a separate model, which included feature type and environmental setting as factors. The bivariate regression was then compared with the global ANCOVA model, using a likelihood ratio test, to determine if the additional variables significantly improved the model fit to the data. For this comparison, LnTHg and interactions between LnTHg and feature type and environmental setting were added as fixed effects in the global MeHg model.

3. Results and discussion

The final compiled database included total of 16,418 THg results from 11,103 unique sites located in 545 HUC8s; 3233 MeHg results from 1877 sites in 244 HUC8s; and 2474 sample pairs where both THg and MeHg were collected from 1516 sites in 236 HUC8s across western North America. Each unique site, as identified by unique GPS coordinates, was represented by anywhere from one to 114 sample results for THg and one to 68 sample results for MeHg, and each HUC8 was represented by one to 761 unique sites for THg and one to 450 unique sites for MeHg.

3.1. Total mercury

Bed sediment THg concentrations ranged over five orders in magnitude, from <10 µg kg^{-1} (lower limit of reporting) widely scattered across the entire landscape to 303,255 µg kg^{-1} at a lake in eastern Nevada. A number of gold and mercury mine sites in California, Nevada, and Alaska also had concentrations near to or exceeding 100,000 µg kg^{-1} (Fig. 1). United States databases contained the vast majority of the high THg concentrations in the compiled data set; however, there was a maximum concentration of 13,902 µg kg^{-1} at a forested stream site in the Mackenzie and Selwyn Mountains of the Yukon Territory. Median and 90th percentile THg values were higher in the

bulk sediment than in the sieved sediment from the provincial databases. The sieved (<177 μm) sample data set had a median THg of 58 μg kg^{-1} and a 90th percentile of 130 μg kg^{-1}. Median THg for bulk sediment (91 μg kg^{-1}) was 57% higher than the median THg for the sieved data set; the 90th percentile (513 μg kg^{-1}; N = 1861) was nearly four times higher.

There are a number of sediment THg concentration-based screening levels established for the protection of wildlife and human health that provide context to these concentrations and distributions (Canadian Council of Ministers of the Environment, 1995; EC MENVIQ (Environment Canada and Ministere de l'Envionnement du Quebec), 1992; Environment Canada, 2007; Long and Morgan, 1991; Long et al., 1998a; Long et al., 1998b; MacDonald et al., 2000; Massachusetts Department of Environmental Protection, 2002; Ottesen et al., 2013; Persaud et al., 1993; Randall and Chattopadhyay 2013; Smith et al., 1996; Wells and Hill, 2004). Overall, the compiled data set is heavily weighted toward the low end of the concentration range and many of the results are below any screening or advisory levels, but a substantial number of results were above benchmarks for potential risk to both wildlife and human health (Table 1). Fewer than 10% of the sieved samples exceeded the benchmark effects level, the lowest screening level for aquatic health effects (170 μg kg^{-1}) and only three out of 5045 exceeded the severe, or adverse, benchmark effect level (2000 μg kg^{-1}). By comparison, the bulk sediment set had at least 10% of samples exceed the probable effect level for freshwater sediment in Canada (490 μg kg^{-1}) and the clean-up screening level for the state of Washington (590 μg kg^{-1}) and nearly 2% (more than 200 of 11,000 samples) exceed the adverse benchmark effect level (2000 μg kg^{-1}). When comparing the distribution of the results with the spatial distribution in the map, it appeared that the data set is heavily weighted by a bias in sampling frequency and/or data density in contaminated locales, such as was observed in the soil THg data sets (Obrist et al., 2016–in this issue).

When accounting for repeated measurements at a single sampling location, significant differences among HUC8 units were evident across the landscape (bulk sediment: $F_{519,5711} = 11.19$, $p < 0.0001$; sieved sediment: $F_{24,4729} = 50.41$, $p < 0.0001$). It should be noted that a high degree of uncertainty existed within the modeled least squares mean THg concentrations for some HUC8s (Fig. S2-1). Least squares mean THg concentrations exceeded the 200 μg kg^{-1} benchmark in only 5% of the HUC8s (6% in US and 0% in Canada), a result aligned with the distribution of soil THg across this region (Obrist et al., 2016–in this issue), and the highest concentrations occur in areas of known native cinnabar deposits and/or historic Hg, gold or silver mining activity (Alpers et al., 2005; Bouse et al., 2010; Gray et al., 2000; Lawrence, 2003; Rytuba, 2003; Singer et al., 2013).

HUC8-based least squares mean THg concentrations indicate a potential grain-size effect between the bulk sediment and the sieved sediment. The act of sieving effectively removed the coarse and medium sand fractions from the samples, which are typically lower in THg concentration than finer grained particles, leading to elevated THg concentrations in sieved samples (Fleck et al., 2011; Nater and Grigal, 1992). However, lack of a grain-size effect on THg concentration has been observed in stream sediment downstream from natural sources (e.g., Bosworth and Morris, 2009). Although there are large areas where natural geologic sources of THg determine aquatic sediment concentrations in the Western U. S., only a small portion of the entire western landscape is represented by this condition, particularly the Hg ore belts located in the Coast Ranges along the Pacific coast and isolated deposits in the Great Basin and Rocky Mountains (Rytuba, 2003). Even areas contaminated from historical mining activities, where elemental Hg was used to recover gold and silver from non-Hg bearing deposits, exhibit a grain-size effect with increasing THg concentration associated with finer grain sizes (Alpers et al., 2006; Fleck et al., 2011; Hunerlach et al., 2004).

Significant differences in THg concentrations were observed among the general categories of feature type and environmental setting (Fig. 3). Among feature types, lake (29.3 ± 6.5 μg kg^{-1}) and canal (28.6 ± 6.9 μg kg^{-1}) had the highest THg concentrations, whereas stream (20.7 ± 4.6 μg kg^{-1}) and estuarine (23.6 ± 5.6 μg kg^{-1}) sites had the lowest ($F_{4,5497} = 14.44$, $p < 0.0001$; Fig. 3A). No difference was observed between lakes (41.5 ± 6.2 μg kg^{-1}) and streams (46.0 ± 6.8 μg kg^{-1}) in the sieved data set from Canada ($F_{2,4736} = 1.28$, $p = 0.28$; Fig. 3A). The difference between lakes and streams in the bulk sediment, and the lack of a difference in the sieved samples, may be due to the grain size effect noted above, because streams tend to have larger grain size sediment than lakes due to the relative hydraulic gradients in these landscape feature types, with lakes representing lentic and streams representing lotic systems. Sieving the samples removed this feature-based grain size effect from the Canada data set. Canals and ditches tend to be relatively low-gradient environments (lentic) as well, explaining why this feature type may resemble lakes more than streams in terms of THg concentration.

General trends in differences among environmental settings were similar for the bulk ($F_{6,5402} = 9.31$, $p < 0.0001$) and sieved ($F_{4,4736} = 14.66$, $p < 0.0001$) data sets, although not all settings were represented in the sieved data set. Forested (bulk = 32.0 ± 2.7 μg kg^{-1}; sieved = 47.6 ± 11.2 μg kg^{-1}) and open-water (bulk = 36.8 ± 2.2 μg kg^{-1}; sieved = 48.0 ± 11.4 μg kg^{-1}) sites generally had the highest least squares mean THg concentrations followed by wetland sites (bulk = 28.9 ± 1.7 μg kg^{-1}; sieved = 45.4 ± 11.0 μg kg^{-1}; Fig. 3B), whereas rangeland (bulk = 25.5 ± 1.5 μg kg^{-1}; sieved = 39.7 ± 9.4 μg kg^{-1}), agriculture (bulk = 23.4 ± 2.0 μg kg^{-1}; sieved = 15.8 ± 11.6 μg kg^{-1}) and urban (bulk = 22.7 ± 2.1 μg kg^{-1}; sieved = no data) sites generally had the lowest THg concentrations, a trend opposite of that observed in previous assessments across the US where urban settings were elevated in THg (Horowitz and Stephens, 2008; Marvin-DiPasquale et al., 2009). It is difficult to speculate why THg concentration would differ between the broad characteristics that define the environmental settings categories; however, open-water sites and wetlands are depositional environments where finer-grained materials accumulate which may explain their relatively high THg concentrations. Forested sites are likely to have elevated THg relative to the rangeland and agricultural sites, because of the greater productivity and higher organic content of the forested sites which facilitates greater delivery and storage of Hg to these systems, leading to higher THg concentrations in the terrestrial soils (Obrist et al., 2016–in this issue).

3.2. Methylmercury

Sediment MeHg concentrations ranged over three orders of magnitude from below the reporting limit (0.04 μg kg^{-1}) to 91 μg kg^{-1} at the Alpha Mine tunnel and pit in California's Sierra Nevada gold mining region; however, sites in South San Francisco Bay, other gold mines in the Sierra Nevada, California, and the Great Salt Lake, Utah also had MeHg concentrations between 20 and 80 μg kg^{-1} (Fig. 4A). Importantly, some of the highest MeHg concentrations occurred in areas with relatively low THg concentrations, particularly in the prairie pothole region of the Great Plains, parts of the Rocky Mountains, and the Great Basin. The Canadian provincial databases did not include MeHg (Table S1-1). MeHg concentrations were more evenly distributed across the landscape than THg, as indicated in the representation of the colors in each concentration bin (Fig. 4A). The median MeHg concentration was 0.70 μg kg^{-1} with a 90th percentile value of 4.51 μg kg^{-1}. It should be noted that the locations where MeHg was measured had generally higher THg concentrations than the larger THg data set, indicating a bias toward more contaminated sites for the sampling locations where data for MeHg were also collected (median = 129 μg kg^{-1} vs 90 μg kg^{-1}, respectively); however, the general spatial trends for THg in the full data set and the subset where MeHg data exist were similar (Fig. 2A and B).

Unlike THg, there are no established environmentally-relevant screening levels for MeHg in aquatic bed sediment; however, MeHg/

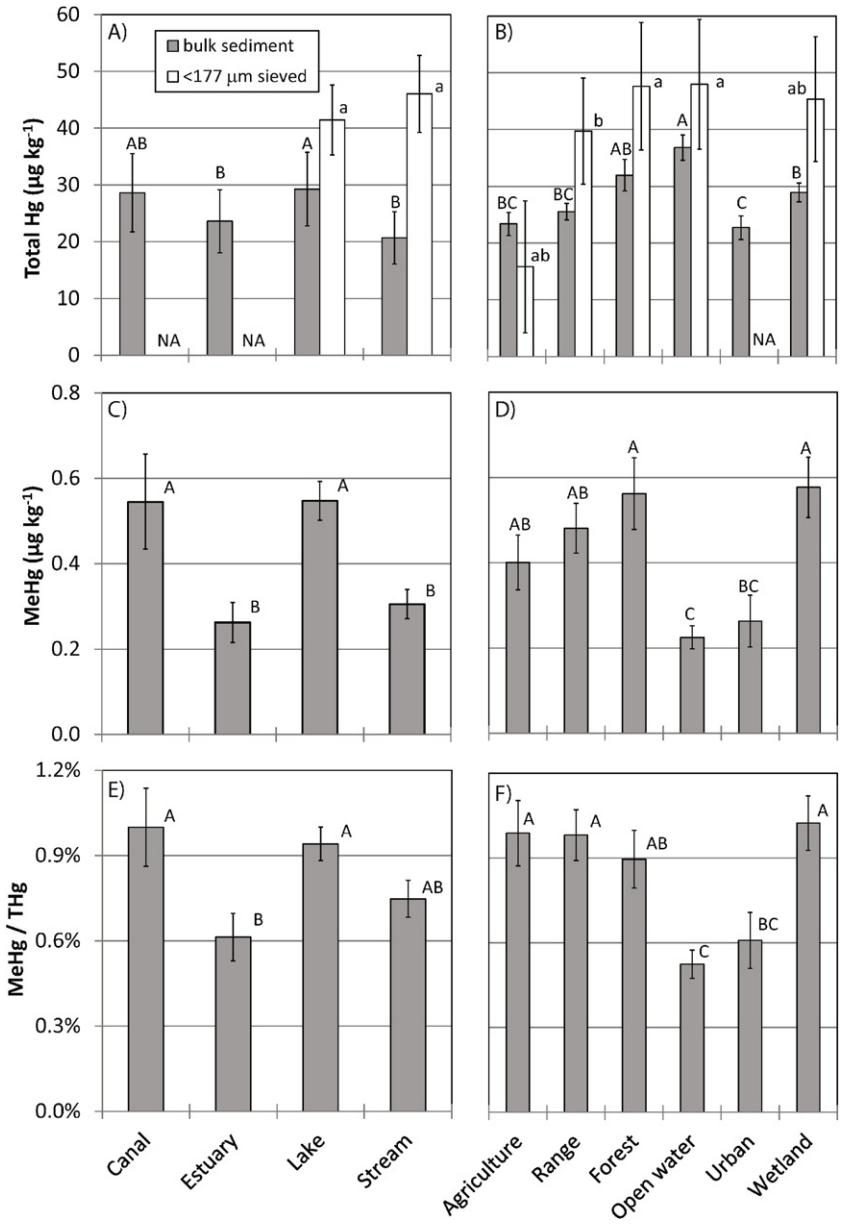

Fig. 3. Comparison of least squares mean concentration for A) THg by feature type, B) THg by environmental setting, C) MeHg by feature type, D) MeHg by environmental setting, E) MeHg/THg by feature type, and F) MeHg/THg by environmental setting. Different letters next to the bars on the chart indicate significant differences between categories, capital letters were used for the bulk data set and small letters were used for the sieved data set.

THg ratios are often used to determine the relative "methylation efficiency" of a system to identify areas of greater concern with respect to ecosystem risk (Kelly et al., 1995, Gilmour et al., 1998; Krabbenhoft et al., 1999; Sunderlund et al., 2006). In the previous USGS national assessment, locations where %MeHg relative to THg concentrations were >6% corresponded with elevated MeHg concentrations in biota (Krabbenhoft et al., 1999). The MeHg/THg ratio in this compilation was generally low across the landscape with a median value of 0.7% and a 90th percentile of 3.1%, although more than 100 locations exceeded the 6% benchmark (Fig. 4B). Several other studies have reported similar central tendencies for MeHg/THg ratios: estuarine sediment in southern Florida (0.8%, Kannan et al., 1998), estuarine sites in New England (0.4%, Taylor et al., 2012), reservoirs in Colorado (0.2% to 0.3%, Gray et al., 2014), and mine-dominated large-scale watersheds in the USA (1%, Krabbenhoft et al., 1999). However, much higher mean MeHg/THg ratios were reported in northeastern lakes and streams (4%, Loukmas et al., 2006) and watersheds across the USA (3.2%, Scudder et al., 2009), particularly in mixed agricultural-forested watersheds (10%, Krabbenhoft et al., 1999).

Modeled MeHg concentrations differed significantly among HUC8s across the landscape ($F_{243,1856} = 3.06$, $p < 0.0001$). Accounting for repeated measurements at the same locations did not alter the apparent distribution of MeHg across the landscape. As noted above for HUC8-based least squares mean THg concentrations, there is a large range in uncertainty based on internal variability and number of measurements at any site or HUC8 (Fig. S2-3). Generally speaking, least squares mean MeHg concentrations were distributed more extensively across the landscape than were THg concentrations, illustrated in the MeHg/THg ratio (Fig. 5). However, some of the locations where high individual MeHg concentrations were observed contained low to moderate THg concentrations (e.g., prairie potholes in Canada). In this particular case, large temporal variations might be expected between repeated measures of MeHg at a single site due to hydrologic and climatological effects (e.g., Bradley et al., 2013; Heim et al., 2007; Ullrich et al., 2001),

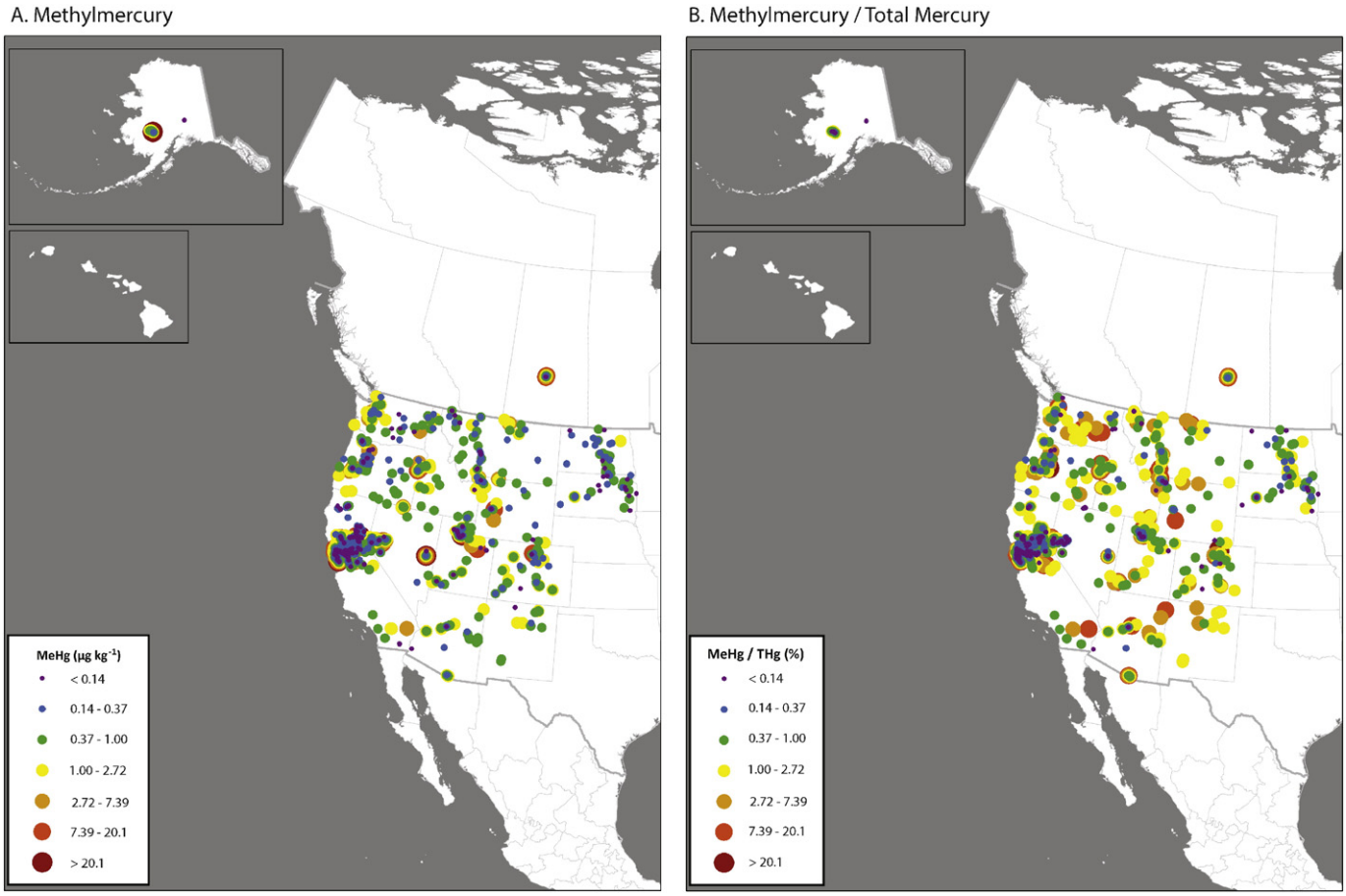

Fig. 4. Map showing the spatial distribution of individual sample results for A) surface sediment MeHg concentration and B) the ratio of MeHg to THg, shown as a percentage, across western North America.

and extreme small-scale spatial variation in MeHg concentrations may be expected along a hillslope due to "hot spots" associated with unique biogeochemical conditions in edge environments (Lambertsson and Nilsson, 2006; Mitchell et al., 2009). However, it is important to note that analysis of a compiled data set at this scale cannot discriminate between these drivers of MeHg concentration. The HUC8-based least squares mean MeHg concentrations should be viewed as an indicator of the potential for any aquatic habitat within a specific HUC8 boundary to have a higher or lower MeHg concentration relative to the other similar aquatic habitats within other HUC8s as represented on the map.

Significant differences in MeHg concentration and MeHg/THg ratios were observed among our general categories of feature type (MeHg, $F_{3,1497} = 17.27$, $p < 0.0001$; MeHg/THg, $F_{3,1060} = 7.80$, $p < 0.0001$) and environmental setting (MeHg, $F_{5,1574} = 24.51$, $p < 0.0001$; MeHg/THg, $F_{5,1095} = 10.76$, $p < 0.0001$). Least squares mean MeHg concentrations for lakes (0.55 ± 0.05 µg kg^{-1}) and canals (0.54 ± 0.11 µg kg^{-1}) were approximately twice that of estuarine (0.26 ± 0.05 µg kg^{-1}) and stream sites (0.31 ± 0.03 µg kg^{-1}; Fig. 3C). Ratios of MeHg/THg by feature followed the same general ranking as MeHg concentration, but the differences were less pronounced (Fig. 3D). For the least squares mean MeHg/THg ratio, lakes ($0.9\% \pm 0.1\%$) and canals ($1.0\% \pm 0.1\%$) were higher than estuarine ($0.6\% \pm 0.1\%$) sites and streams ($0.7\% \pm 0.1\%$), a non-significant difference for this data set. The trends observed in least squares mean MeHg concentration (Fig. 3E) were similar to those for MeHg/THg ratio (Fig. 3F) among environmental setting, with open water (0.22 ± 0.03 µg kg^{-1}; $0.5\% \pm 0.0\%$) and urban (0.26 ± 0.06 µg kg^{-1}; $0.6\% \pm 0.1\%$) sites lowest among the environmental setting categories, whereas wetland (0.58 ± 0.07 µg kg^{-1}; $1.0\% \pm 0.1\%$) and forested (0.56 ± 0.08 µg kg^{-1}; $0.9\% \pm 0.1\%$) were the highest. There are numerous landscape, climatological, and biogeochemical variables integrated within these general categories that likely contribute to these trends. Unfortunately, the wide range in scope and quality in the databases ancillary data and metadata limited the ability to examine these trends in a deterministic manner.

3.3. Methylmercury and THg relationships

The relationship between MeHg and THg has been used extensively to evaluate the relative risk between habitats without the difficulties and expense of measuring both MeHg and THg and methylation rates, which can be cost-prohibitive if applied across the landscape (Krabbenhoft et al., 1999). The benefit of a predictive relationship between the two variables is clear when comparing the number of results and the spatial coverage of the THg data set with that of the MeHg data set (Fig. 2). However, numerous studies have shown inconsistency in the MeHg-THg relationships across habitats and seasons (Davis et al., 2012; Gilmour et al., 1998; Heim et al., 2007; Kannan et al., 1998; Kelly et al., 1995; Lambertsson and Nilsson, 2006). Examining the overall relationship and how it differs across the landscape may provide a more robust foundation for identifying, if not predicting, areas of greater concern.

This study addresses the relationship between sediment MeHg and THg concentrations across a larger spatial scale and greater variety of aquatic habitats, settings, and landscape characteristics than previous studies. Across these extensive gradients, a weak positive relationship between MeHg and THg concentrations was observed ($r^2 = 0.25$; $p < 0.0001$, Fig. S3-1). Additionally, the slope and intercept of the relationship differed among feature type and environmental setting (Fig. S3-1). Rangeland sites had a significantly lower slope (0.32 ±

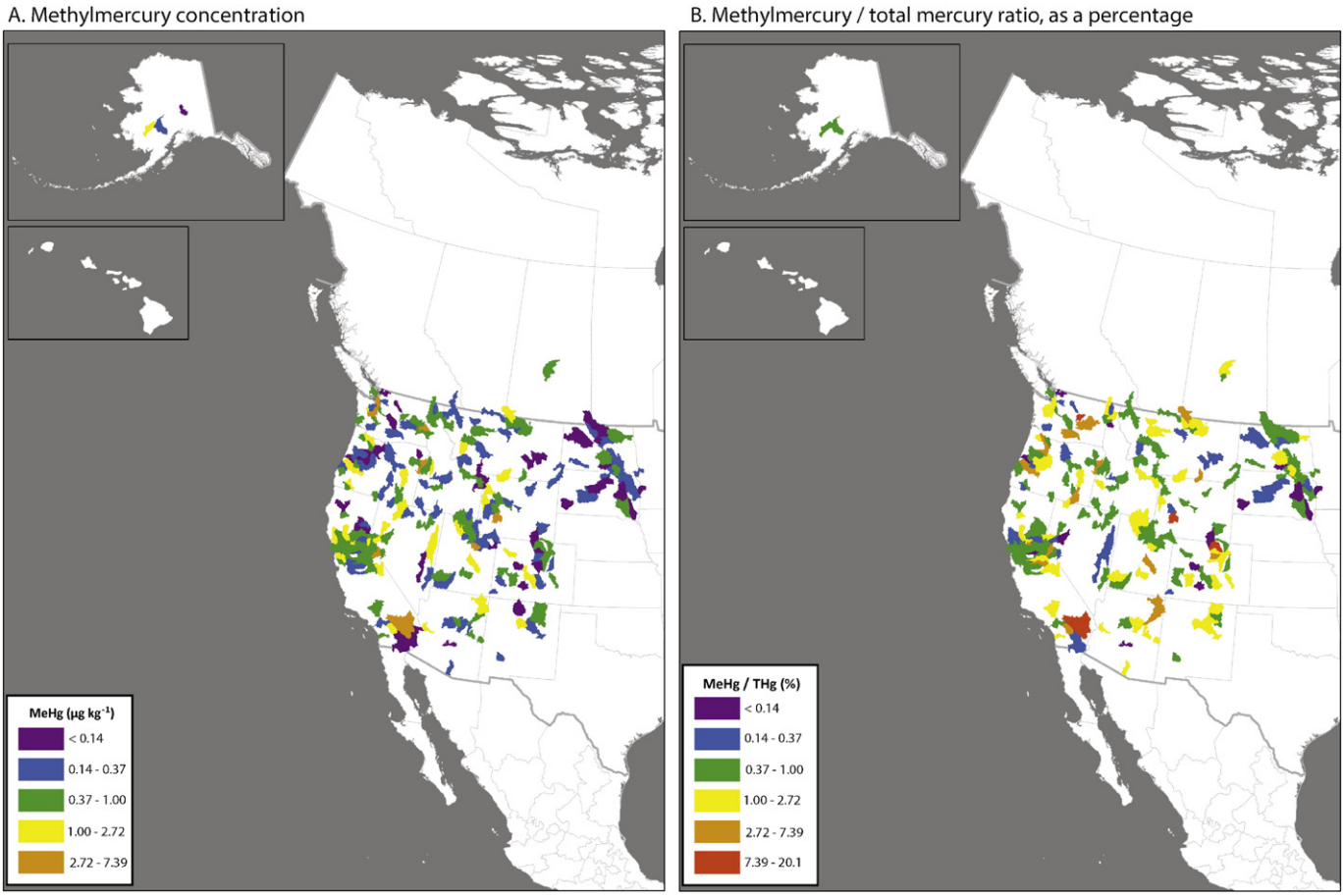

Fig. 5. Map showing the spatial distribution of HUC8 least squares mean for A) MeHg concentrations and B) the ratio of MeHg to THg, shown as a percentage.

0.03) than the other environmental settings that were similar to each other (e.g., wetland = 0.54 ± 0.03, open water = 0.50 ± 0.04), indicating the relatively low MeHg producing capacity of rangelands. The slope was highest in the urban setting (0.65 ± 0.12), but the difference was not significant among environmental settings except when compared to the rangeland slope. When accounting for feature type ($F_{3,1808} = 0.54$, $p = 0.65$) and environmental setting ($F_{5,1803} = 2.22$, $p = 0.05$), the global model was able to explain 76% of the variation in the MeHg data. These results indicate that THg concentrations are generally a weak determinant of resulting MeHg concentrations in sediment across western North American aquatic habitats, and indicate that local biogeochemical drivers, such as feature type and environmental setting, are likely more important in determining MeHg concentrations. The full model better explained the MeHg data than THg alone ($D_{243} = 937$, $p < 0.0001$). Further analysis of the within-HUC8 spatial attributes is warranted to identify and characterize the specific driving variables implicit in our categorization scheme and further the goal of predictive landscape-based models for MeHg concentrations and ecosystem risk.

3.4. Implications

The extensive landscape and water management activities that are commonplace in western North America present a potential opportunity to minimize the threats posed by mercury contamination. Because THg is a poor predictor of MeHg across the habitats in this vast region, management approaches focused on THg concentration as the means to reduce risk are likely to have limited effects. Although this decoupling between THg and MeHg has been recognized previously within specific studies, there has been general agreement on the effects that THg concentrations impose upon MeHg concentrations within and between habitats observed over large spatial scales. This phenomenon was not observed across the expanse of western North America and its diverse range of habitats. Instead, the importance of local environmental factors on MeHg concentrations highlights the need for a greater understanding of the environmental conditions that influence MeHg production, degradation, and transport across the landscape. Therefore, to further the understanding of health and environmental risks due to Hg contamination across the landscape, attention should be given to more comprehensive characterization of the aquatic habitats where Hg cycling is being investigated. Based on the degree of influence imposed by the coarse habitat categories available for use in this assessment, even a modest improvement in site characterization within, and its standardization across, studies would likely improve our predictive capability in assessing MeHg concentrations across the landscape. Simple site characteristics including: a) a standardized and detailed classification scheme for water body or wetland type (e.g., Cowardin et al., 1979); b) information about the location within the water body or wetland to address the issue of 'hot spots' in edge environments; c) water depth (both the overall maximum and average of the water body and the specific depth at the sampling location); d) an estimate of water velocity at the sampling location during collection to address variability imposed by transport; and e) land cover (both within the general area and at the specific sampling location) would provide a robust assessment of factors controlling MeHg concentrations. Addition of these site characteristics, combined with the recent advancements in geospatial information and analysis, as well as ancillary chemical measurements recommended in previous synthesis efforts (e.g., organic matter content, sulfate concentration, pH), would greatly improve the understanding of habitat-related processes that affect MeHg production (e.g., Hall

et al., 2008; Marvin-DiPasquale et al., 2009) and its ultimate fate in the food web (Eagles-Smith et al., 2016b–in this issue).

4. Conclusions

Aquatic bed sediment THg and MeHg concentrations from a wide array of aquatic habitats across western North America were compiled and statistically analyzed. Results indicated that MeHg concentrations at levels that pose a potential concern to the food web were more widespread across the landscape than THg concentrations were. As a result, MeHg concentrations were weakly ($r^2 = 0.25$; $p < 0.0001$) related to THg concentrations. Landscape features (e.g., lakes, streams) and environmental setting (e.g., wetland, forested, rangeland, urban) accounted for an additional 51% of the variation in MeHg concentrations, indicating that local biogeochemical conditions associated with habitat characteristics impose a predominant influence on the spatial distribution of MeHg in sediment across western North America, independent of THg concentration. Future efforts to elucidate factors controlling MeHg concentration in sediment would be improved with simple metrics aimed to characterize the habitat and its biogeochemical attributes during sample collection.

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Supplementary Information for Mercury and methylmercury in aquatic sediment across western North America

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6 multi-paneled figures

2 Tables

6 References

Section 1: Tables (S1-1, S1-2) and Figures (S1-1, S1-2) supporting data sources, compilation and processing

Section 2: Maps showing a) coefficient of variation in HUC8 least squares mean values, b) number of samples per HUC8 and c) number of sites per HUC8 for all THg results (S2-1), THg results with paired MeHg results (S2-2), all MeHg results (S2-3), and all MeHg/THg results (S2-4)

Section 3: Biplots showing THg-MeHg relationships by feature and environmental setting (S3-1)

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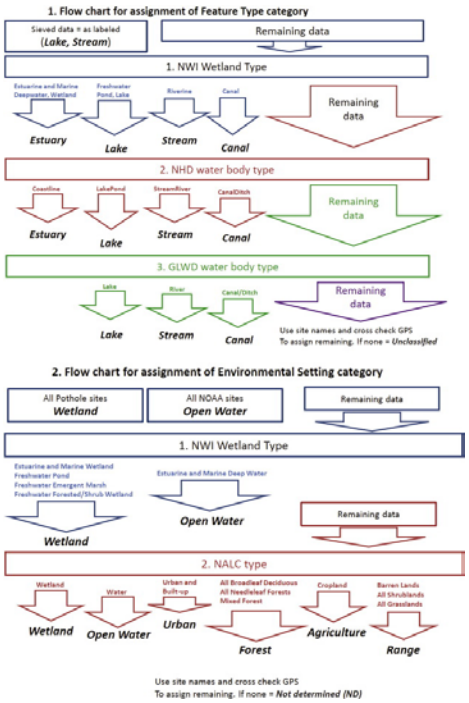

Fig. S1-1. Flow chart for assignment of Feature Type category. Fig. S1-2. Flow chart for assignment of Environmental Setting category.

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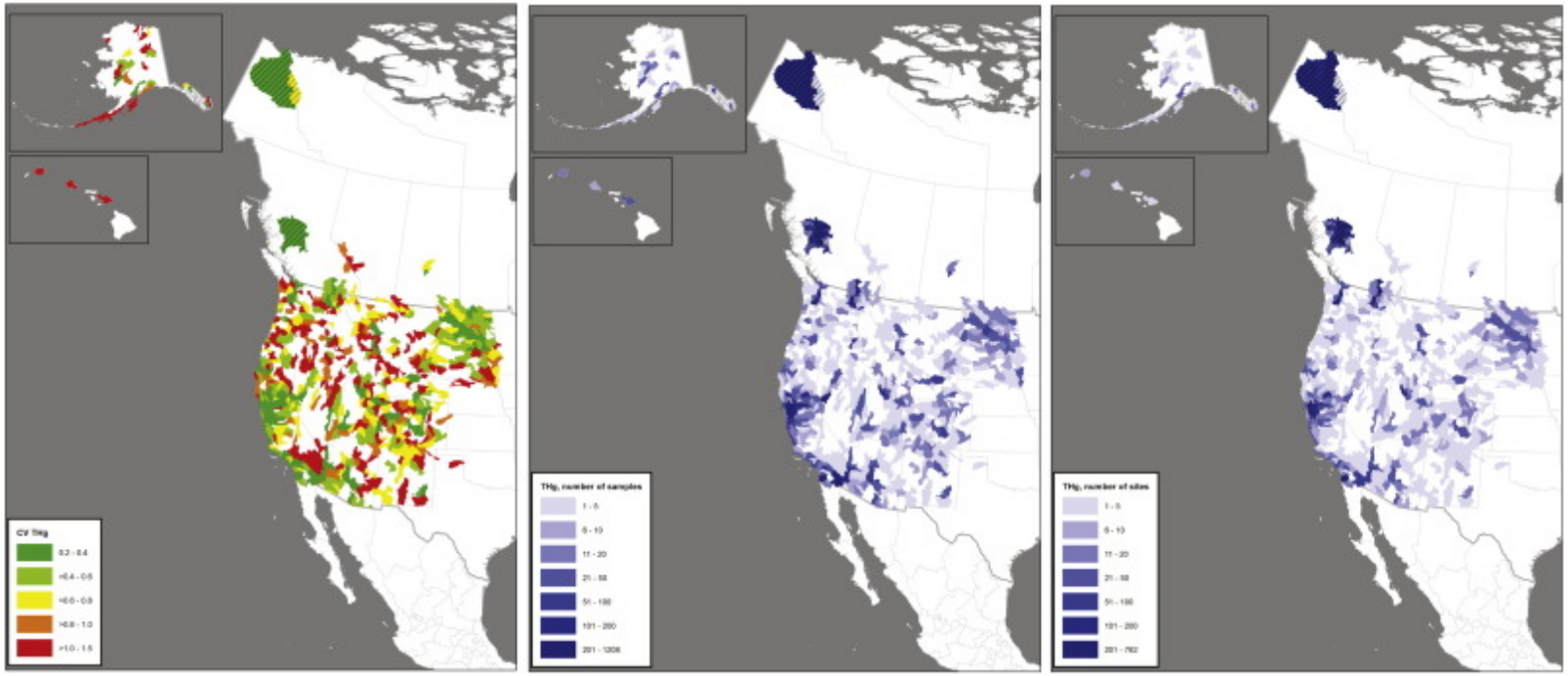

Fig. S2-1. Supporting information for statistical calculation of HUC8 least squares mean THg for all sample results. Figure a) coefficient of variation (CV), figure b) number of samples within each HUC8 and c) number of sites within each HUC8. The HUC8s with h...

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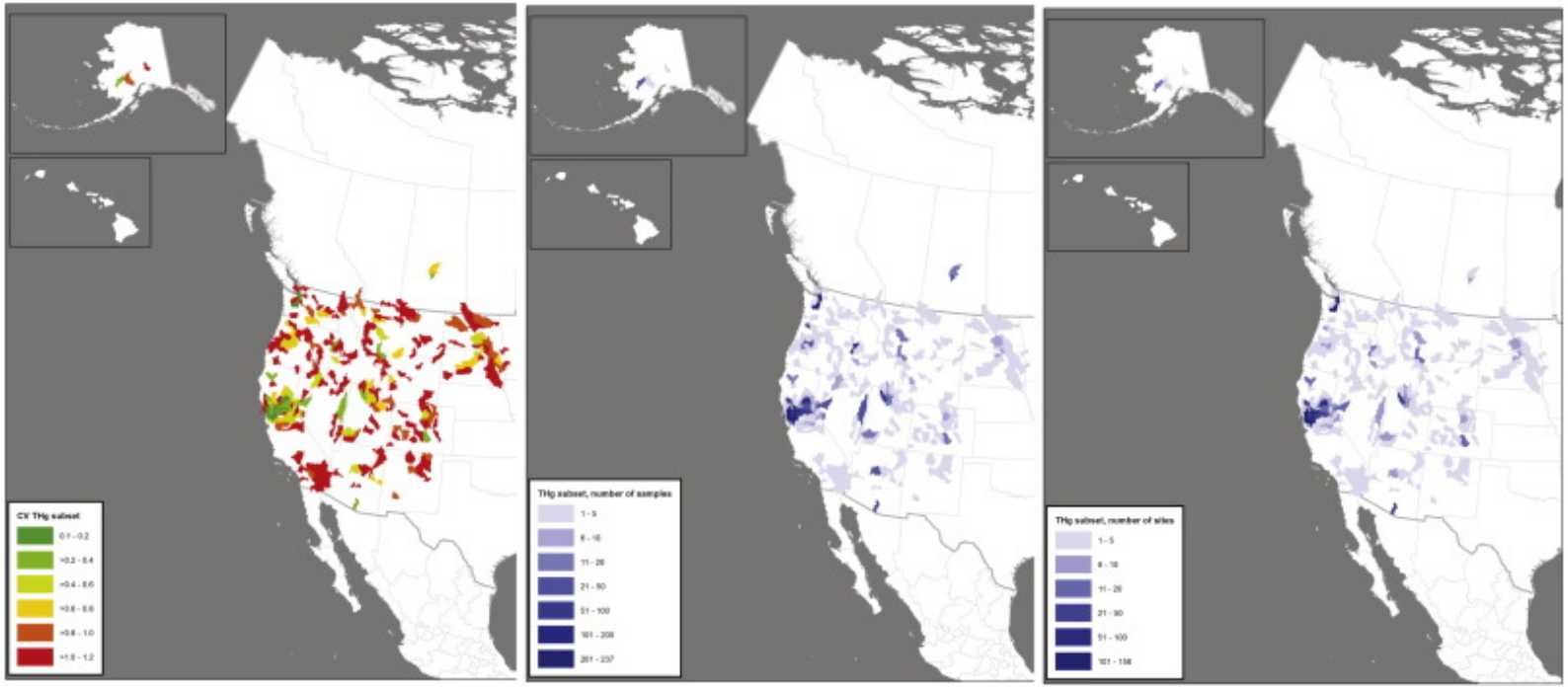

Fig. S2-2. Supporting information for statistical calculation of HUC8 least squares mean THg for samples with paired MeHg results. Figure a) coefficient of variation (CV), figure b) number of samples within each HUC8 and c) number of sites within each HUC8. Th...

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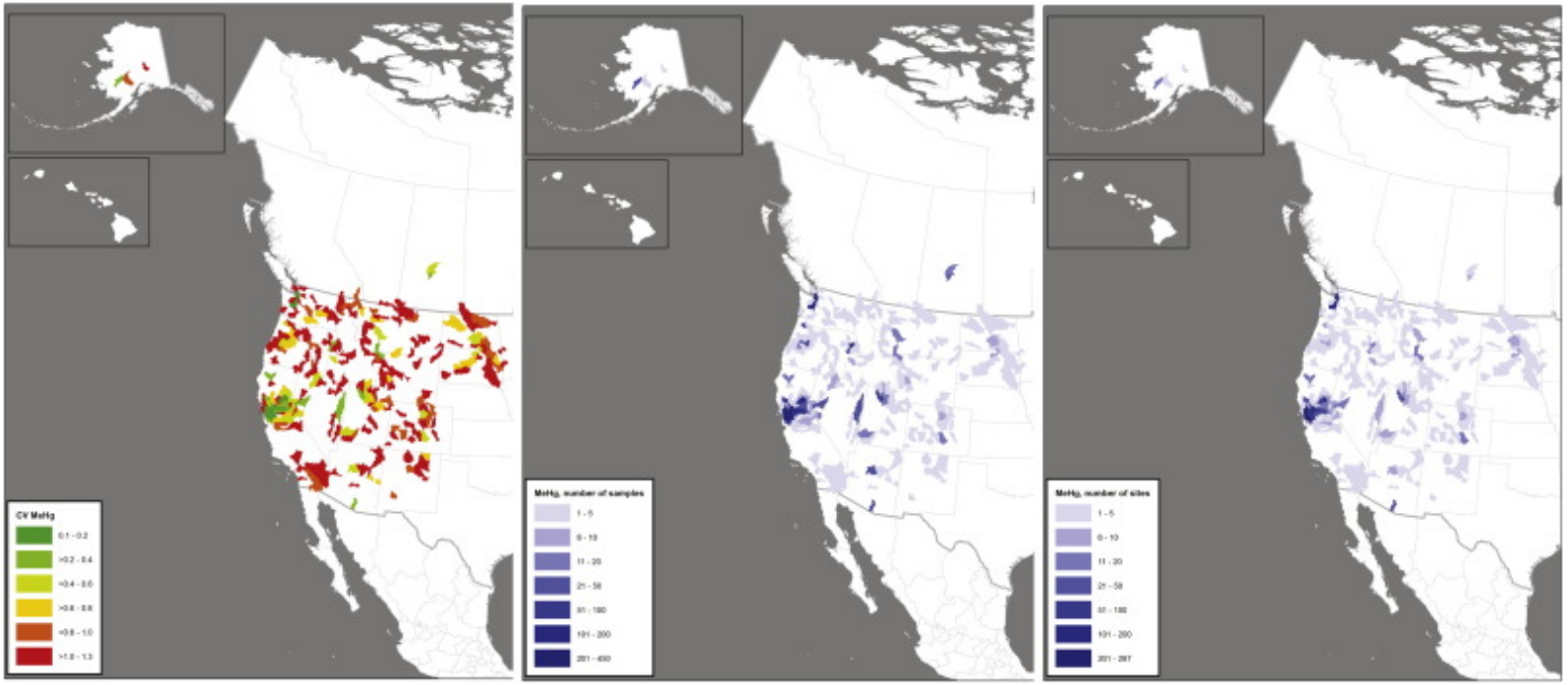

Fig. S2-3. Supporting information for statistical calculation of HUC8 least squares mean MeHg for all sample results. Figure a) coefficient of variation (CV), figure b) number of samples within each HUC8 and c) number of sites within each HUC8. The HUC8s with ...

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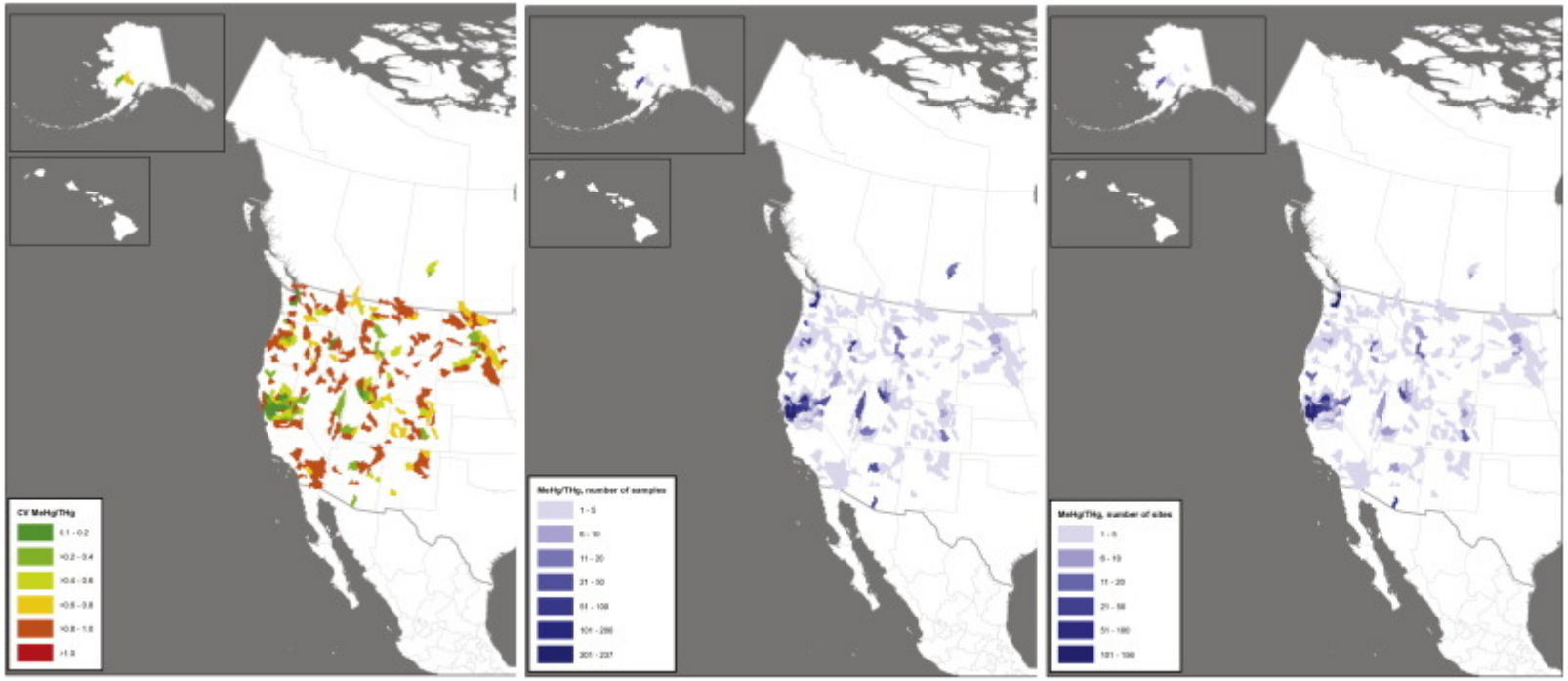

Fig. S2-4. Supporting information for statistical calculation of HUC8 least squares mean MeHg to THg ratios for all sample results. Figure a) coefficient of variation (CV), figure b) number of samples within each HUC8 and c) number of sites within each HUC8. T...

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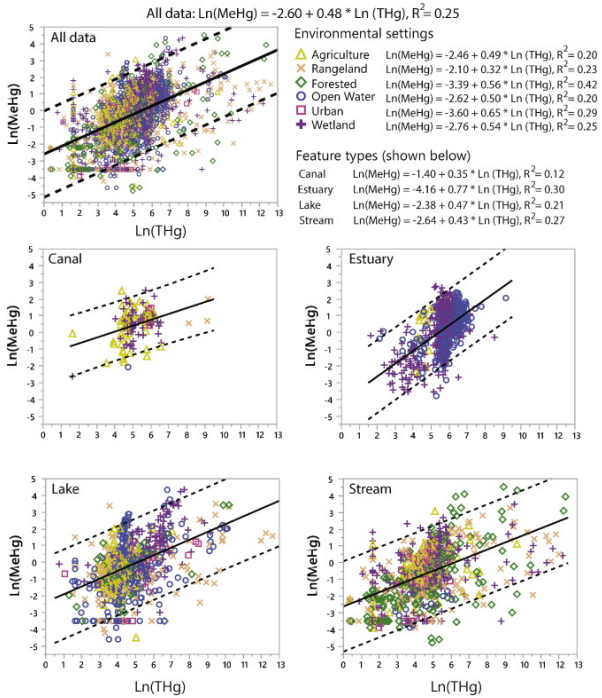

Fig. S3-1. Biplots showing the relationships between THg and MeHg by feature type and by environmental setting. The solid lines are the regression lines, dashed lines are the confidence intervals for individual values. Concentrations were μg kg− 1 prior to tra...

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Data Source	full or partial databases included	period of record for matrix	owner/contact	matrix lines in database	QA'd THg results count	THg quant-itative	THg non-quant; Qual/RMK coded	QA'd MeHg results count	MeHg quant-itative	MeHg non-quant; Qual/RMK coded	notes
United States											
MercNet	EPA STORage and RETrieval (STORET) Data Warehouse, California Environmental Data Exchange Network (CEDEN), USGS National Water Information System (NWIS), USGS National Water Quality Assessment (NAWQA), USGS National Lake Assessment (NLA), individual state Departments of Environmental Quality (DEQ)	1986-2010	Biodiversity Research Institute, http://mercnet.brloon.org/	18181	4564	1860	2704	804	769	35	Primary compiled database served as starting point for compiling this data set. Many results removed due to mislabeled matrix codes, core materials >5 cm, etc. Many removed due to high detection limits related to old methods
United States Environmental Protection Agency	STORET legacy	1965-1998	http://www3.epa.gov/storet/dbtop.html	87	87	0	0	0	0	0	STORET Legacy data difficult to retrieve and included no additional quantitative data.
United States Geological Survey (USGS)	National Water Information System (NWIS)	1983-2012	http://waterdata.usgs.gov/nwis	2041	970	888	82	316	258	58	Many results removed due to mislabeled matrix codes (suspended sediment, core materials >5 cm depth, sieve classes, etc) - many removed due to high detection limit, old methods
United States Fish and Wildlife Service	Environmental Contaminant Data Management System (ECDMS)	1975-2010	http://www.fws.gov/chemistry/ecf_ecdms.html	2776	2769	1456	1313	111	87	24	Generally a better record and retrieval success of ancillary data and site descriptions than most other public databases
USGS Wisconsin Mercury Research Laboratory	Laboratory database	2001-2012	http://wi.water.usgs.gov/mercury-lab/	379	307	307	0	283	279	4	Data retrieval is by request and availability is project-specific
USGS Menlo Park Mercury Research Laboratory	Laboratory database and numerous partner data	1998-2013	Mark Marvin-DiPasquale	1041	966	862	104	908	744	164	Data retrieval is by request and availability is project-specific
USGS Sierra Nevada Impairment Project (SNIP) database	STORET, CEDEN, NWIS, NAWQA, NLA, state DEQs	1977-2013	Charlie Alpers	2374	1732	1441	291	531	529	2	Compiled from other databases in the compilation - duplicate results were removed in most cases. Contained a number of unique contributions to the compilation - exclusively from California
California Environmental Data Exchange Network	CEDEN	post-2012	http://ceden.org/	120	120	116	4	209	209	0	Data queried after MercNet and SNIP databases already compiled.
Reports and Journal Articles	Bausch et al., 2006		http://pubs.er.usgs.gov/	119	115	115	0	116	116	0	
	Bosworth and Morris, 2009		http://www.waterboards.ca.gov/centralvalley/	64	64	64	0	0	0	0	Bulk sediment values were calculated by recombining the percent weight and Hg concentration of each of the 3 size fractions reported
Canada											
Yukon Geological Survey	Yukon Regional Geochemical Database 2003, (Héon, D. (compiler), 2003)	1976 - 2001	http://www.geology.gov.yk.ca	31104	0	0	0	0	0	0	All data are sieved <177 µm. These data not included in analysis. Partially represented in smaller RGS file. May be included in future data analyses after further review is conducted
Yukon Geological Survey	New North Yukon 2003, (Héon, D. (compiler), 2003)	1995 - 2001	http://www.geology.gov.yk.ca	3015	2373	2373	0	0	0	0	All data are sieved <177 µm. These data are included in the larger database but are of more recent era. Data were reviewed and included in the compilation.
British Columbia Geological Survey	1993LAKE, 2005LAKE, 2005STRM	1993, 2005	http://www.em.gov.bc.ca/Mining/Geoscience/Geochemistry/IssuedGeochemicalSurveys/LakeSedimentWater/Pages/default.aspx	2557	2557	2557	0	0	0	0	All data are sieved <177 µm. Three databases downloaded. Project-level analysis was performed and maps generated. Data were reviewed and included in the compilation. Other databases may be included in future data analyses.
Alberta Geological Survey	Prior et al., 2005	2004	www.ags.gov.ab.ca	122	0	0	0	0	0	0	All data are sieved <177 µm. Samples were left out of analysis because of a caution about QA. May be included in future data analyses after review. Project-level analysis was performed and maps generated
University of Regina	Prairie potholes		Britt Hall	76	76	76	0	68	68	0	Methods of collection and analysis are comparable to USA bulk sediment.
Literature	Phillips et al., 2011		http://dx.doi.org/10.1021/es1031135	9	9	9	0	0	0	0	Values are semi-quantitative, estimated from Figure 2, surface layer
Mexico											
Literature	Ontiveros-Cuadras et al., 2014		http://dx.doi.org/10.1016/j.scitotenv.2013.08.071	6	6	6	0	0	0	0	Values are semi-quantitative, estimated from Figure 3, surface layer

Supplementary Table S1. Summary of mercury data sources and number of results from each source compiled for this analysis.

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Geospatial attribute layer database name	Purpose	date / period	coverage area	scale	Attribute layer descriptions	Source
North American Land Cover	feature and setting classification	2005	WNA	250m grid	19 land cover types across North America based on spectral satellite data	http://www.cec.org/Page.asp?PageID=924&ContentID=2819&AA_SiteLanguageID=1
NHDPlus	feature and setting classification	2012	CONUS and HI	1:100k	Attributes describing waterbody type (13 codes), and further characteristics including permanency (106 codes)	http://www.horizon-systems.com/NHDPlus/index.php
National Hydrography Dataset - High Resolution	feature and setting classification	various	Alaska	1:24k	Attributes describing waterbody type (13 codes), and further characteristics including permanency (106 codes)	http://nhd.usgs.gov/data.html
National Hydro Network	feature and setting classification	various	Canada	1:50k	Attributes describing waterbody type (12 codes), permanency of the waterbody feature (3 codes), and whether the waterbody is isolated or not (2 codes)	http://databasin.org/datasets/dda81e7c146049259097c1e7aade60ba
Watershed Boundary Dataset	HUC8 designation	various	USA	1:24k	12-digit Hydrologic Units (HUC), from which larger (e.g., 8-digit) HUCs were derived	http://nhd.usgs.gov/wbd.html
National Hydro Network Index Dataset	HUC8 designation	various	Canada	1:50k	A national index that groups together all NHN Work Unit (WU) limits covering the entire Canadian landmass; boundaries approximated the size of 8-digit HUCs in the US	http://databasin.org/datasets/dda81e7c146049259097c1e7aade60ba
Global Lakes and Wetlands Database	feature and setting classification	1992 - 2000	WNA	30 second grid	**Level 3** (GLWD-3) comprises lakes, reservoirs, rivers and different wetland types in the form of a global raster map at 30-second resolution.	http://www.worldwildlife.org/pages/global-lakes and-wetlands-database
National Wetland Inventory	feature and setting classification	various	USA	various	8 types: Estuarine and Marine Deepwater, Estuarine and Marine Wetland, Freshwater Emergent Wetland, Freshwater Forested/Shrub Wetland, Freshwater Pond, Other, Lake, Riverine	http://www.fws.gov/Wetlands/NWI/index.html
National Land Cover Database	feature and setting classification	2011	L48	30m grid	20-class land cover classification scheme that has been applied consistently across the United States at a spatial resolution of 30 meters Based on Landsat satellite data.	http://www.mrlc.gov/nlcd2011.php

Supplementary Table S2. Geospatial attributes and sources used in the analysis.

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