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4 **Terrestrial mercury in the Western United States: Spatial distribution defined by land**
5 **cover and plant productivity**
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Abstract

Analysis of vegetation mercury (Hg) distribution across 11 contiguous states in the Western United States showed that aboveground biomass concentrations followed the order: leaves ($26 \mu\text{g kg}^{-1}$) > branches ($26 \mu\text{g kg}^{-1}$) > bark ($16 \mu\text{g kg}^{-1}$) > bole wood ($1 \mu\text{g kg}^{-1}$). No spatial trends of Hg in aboveground biomass distribution were detected, which likely is due to very sparse data coverage and different sampling protocols. Vegetation data are largely lacking for important functional vegetation types such as shrubs, herbaceous species, and grasses.

Soil concentrations collected from published literature were high, with 12% of observations exceeding $100 \mu\text{g kg}^{-1}$, reflecting a bias toward investigations in Hg-enriched sites. In contrast, soil Hg concentrations from a randomly distributed data set (1,911 sampling points; Smith et al., 2013a) averaged $24 \mu\text{g kg}^{-1}$ (A-horizon) and $22 \mu\text{g kg}^{-1}$ (C-horizon), and only 2.6% of data exceeded $100 \mu\text{g kg}^{-1}$. Soil Hg concentrations significantly differed among land covers, following the order: forested upland > planted/cultivated > herbaceous upland/shrubland > barren soils. Concentrations in forests were on average 2.5 times higher than in barren locations. Principal component analyses showed that soil Hg concentrations were not or weakly related to modeled dry and wet Hg deposition and proximity to mining, geothermal areas, and coal-fired power plants. Soil Hg distribution also was not closely related to other trace metals, but strongly associated with organic carbon, precipitation, canopy greenness, and foliar Hg pools of overlying vegetation. These patterns indicate that soil Hg concentrations are related to atmospheric deposition and reflect an overwhelming influence of plant productivity — driven by water availability — with productive landscapes showing high soil Hg accumulation and unproductive barren soils and shrublands showing low soil Hg values. Large expanses of low-productivity, arid ecosystems across the Western U.S. result in some of the lowest soil Hg concentrations observed worldwide.

Keywords: Western North American Mercury Synthesis, WNAMS, landscape gradients, soil pollution, plant pump, trace metals

1. Introduction

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4 Terrestrial ecosystems accumulate substantial amounts of mercury (Hg; Grigal, 2003; Obrist et
5 al., 2011) with the main source in remote ecosystems originating from atmospheric deposition
6 (Fitzgerald et al., 1998). Terrestrial runoff is the main Hg source to streams and lakes (Hermanns
7 et al., 2013; Lorey and Driscoll, 1999; Teisserenc et al., 2011), where Hg pollution impacts
8 wildlife and humans primarily through fish consumption. Elevated Hg, however, also is observed
9 in the terrestrial food chain (Richardson et al., 2014; Townsend and Driscoll, 2013). Hg
10 sequestered in terrestrial ecosystems represents a legacy of past natural and anthropogenic
11 emissions that likely have been deposited and accumulated for decades and even centuries
12 (Amos et al., 2013; Grigal, 2003; Obrist, 2012). These legacy Hg pools are expected to be
13 important sources of runoff for long time periods (Harris et al., 2007), and terrestrial ecosystems
14 therefore continue to play an important regulating function for mobilization and transfer of Hg to
15 water bodies.
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18 Soils generally account for more than 90% of Hg stored at the whole ecosystem level in
19 terrestrial ecosystems (Engle et al., 2006; Grigal, 2003; Obrist, 2012; Schwesig and Matzner,
20 2000) and form one of the largest actively cycling reservoirs in the biogeochemical cycle of Hg,
21 with pool sizes estimated at 15230 Mg in the United States (U.S.). (Hararuk et al., 2013), and up
22 to 300000 Mg globally (Amos et al., 2013; Corbitt et al., 2011; Hararuk et al., 2013). Soils
23 contain natural (geogenic or lithospheric) levels of Hg — particularly in areas naturally-enriched
24 in Hg such as geothermal systems and mining sites (Barnes and Seward, 1997). However, the
25 main soil source (generally >80%) is from “exogenic” (i.e., atmospheric) inputs (Fiorentino et
26 al., 2011; Grimaldi et al., 2008; Peña-Rodríguez et al., 2012; Peña-Rodríguez et al., 2014;
27 Reimann et al., 2009). The retention of atmospheric Hg in soils is largely due to strong binding
28 interactions with soil organic matter functional groups (Meili, 1991; Schluter, 2000; Schuster,
29 1991; Yin et al., 1996), in particular with thiols (Schuster, 1991; Skjellberg et al., 2006; Skjellberg
30 et al., 2000) as well as with clay minerals and oxides (Yin et al., 1996).
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33 Although lower in pool sizes, vegetation also plays an important role in Hg cycling (Grigal,
34 2003; Obrist, 2012). Vascular plants, lichen, and mosses sorb Hg from the atmosphere through
35 various deposition pathways, including internal uptake through stomata (Rutter et al., 2011).
36 Therefore, vegetation enhances atmosphere-surface transfer of Hg via litterfall and throughfall
37 deposition, which in many areas exceeds other deposition pathways such as wet deposition
38 (Grigal et al., 2000; Grigal, 2003; Iverfeldt, 1991; Munthe et al., 1995; St. Louis et al., 2001).
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As part of the Western North American Mercury Synthesis (WNAMS), the goal of this study was to collect and spatially analyze Hg distribution patterns across terrestrial ecosystems — including in aboveground tissues of plants, and organic and mineral layers of soils — in the contiguous U.S. from the west coast to the states encompassing the Rocky Mountains (Montana, Wyoming, Colorado, and New Mexico). The study domain is characterized by varied topography with large mountain ranges resulting in strong environmental gradients, thereby providing an ideal spatial domain to study Hg differences across landscape gradients. For example, western landscapes include the following: arid and semiarid deserts with some of the driest locations such as the Great Basin, Mojave, and Chihuahua deserts; mountain ranges such as the Coastal Range, the Cascade Mountains, the Sierra Nevada, and Rocky Mountains; coastal and near-coastal landscapes with high precipitation amounts; and the Central Valley of California with its productive Sacramento and San Joaquin agricultural basins. Across relatively short distances in these regions, there are strong gradients in geographic, climatic, and ecosystem variables — including pronounced precipitation gradients such as from the western to eastern slopes of the Sierra Nevada where annual precipitation changes from $>150 \text{ cm yr}^{-1}$ to $<25 \text{ cm yr}^{-1}$ across a distance of just a few dozen kilometers (WRCC, 2014). The broad range of climate and ecosystem types also leads to shifts in wet versus dry deposition of nutrients and pollutants (Pearson et al., 2015) and is associated with distinct patterns of soil development, plant productivity, as well as carbon and nutrient dynamics, aspects with known implications for the biogeochemistry of Hg. Further, the western U.S. is impacted by long-range Hg transport from global sources including east Asia (Obrist et al., 2008; Strode et al., 2008; Weiss-Penzias et al., 2006), while specific local and regional sources also exist in the West such as from natural emissions, precious metal mining, coal-fired power plants, and other urban and industrial activities (e.g., EPA, 2015; Zehner and Gustin, 2002).

2. Materials and Methods

2.1. Data collection and mapping

Aboveground biomass and organic and mineral soil Hg data were collected from peer-reviewed journals, publically released and peer-reviewed databases, and one previously unpublished data source. For aboveground biomass, data was obtained from seven peer-reviewed publications (Engle et al., 2006; Friedli et al., 2007; Obrist, 2012; Obrist et al., 2011; Obrist et al., 2012; Obrist et al., 2009; Wright et al., 2014) and one available data set on lichen Hg concentrations for air quality monitoring (USFW Lichen Air Monitoring; data from Washington and Oregon). Collection dates of leaf foliage varied between July and November, i.e., generally between the peak and the end of the vegetation periods, with the exception of a blue oak site in the California where foliage was collected in May prior to summer leaf senescence. For organic and mineral soil layers, data were collected both from published literature and a recent, large-scale sampling campaign by the U.S. Geological Survey (U.S.G.S.; Smith et al., 2014; Smith et al., 2013a; Smith et al., 2013b). Soil Hg concentrations retrieved from the literature were from 16 peer-reviewed publications (Biswas et al., 2008; Biswas et al., 2007; Dudas and Pawluk, 1976; Engle et al., 2006; Ericksen et al., 2006; Faïn et al., 2011; Friedli et al., 2007; Harden et al., 2004; Nacht and Gustin, 2004; Obrist, 2012; Obrist et al., 2011; Obrist et al., 2012; Obrist et al., 2009; Turetsky et al., 2006; Woodruff et al., 2009; Zehner and Gustin, 2002), and an additional unpublished soil Hg data set collected in California and Nevada (195 data points) by the first author (D. Obrist). The U.S.G.S. data set was part of a large geochemical characterization study across the entire contiguous U.S. (Smith et al., 2014; Smith et al., 2013a; Smith et al., 2013b) with a total of 4,857 sampling points of which 1,911 sampling locations were located in the western U.S. study domain.

All data were integrated into Microsoft Excel® and ArcGIS® programs for further analyses. Spatial data processing and mapping were accomplished using ArcGIS® and ArcMAP® software (Esri, Redlands, California, USA). Inverse distance weighting (IDW; $n=12$) was used for spatial interpolation and plotting of Hg concentrations across the Western U.S. Prior to IDW, outliers with concentrations $>200 \mu\text{g kg}^{-1}$ were replaced with $200 \mu\text{g kg}^{-1}$ to reduce the influence of extreme values for the purpose of mapping. However, no data points were removed for analysis of spatial distribution patterns (e.g., for principal component analysis, see below).

2.2. Auxiliary data layers

The following additional spatial data layers for analyses of Hg distribution data were used: (i) ecoregions were retrieved from Level 1 of the U.S. Environmental Protection Agency assignments for Ecological Regions of North America (<ftp://ftp.epa.gov/wed/ecoregions/>); (ii) annual precipitation and temperature were obtained from the PRISM 30-year (800 m resolution) data set (<http://www.prism.oregonstate.edu/normals/>); (iii) surface soil erodibility (K_{fact}) was based on the USDA-NRCS State Soil Geographic Database (STATSGO) through the Soil Information for Environmental Modeling and Ecosystem Management database (<http://www.soilinfo.psu.edu/>); (iv) solar radiation was based on 22-year annual average (July 1983–June 2005) values from NASA Surface meteorology and Solar Energy (SSE) data set (<http://en.openei.org/>); (v) Normalized Difference Vegetation Index (NDVI) was compiled using Google Earth Engine from the MDC43A4 MODIS TERRA/Aqua 16-day composite (2000–2014), taking the maximum observed value for each sampling site; (vi) simulated mercury wet and dry deposition obtained from the Hg model of Community Multi-scale Air Quality system (CMAQ/Hg v.4.7.1) using US EPA’s national emission inventory (NEI 2008) and WRF meteorology (Bash, 2010; Lin et al., 2006); (vii) mining layers for Hg, Ag, and Au mines (active as of the mid-1990s, plus historic and abandoned) were obtained from the U.S.G.S. Mineral Resources Data System (MRDS) database (<http://mrdata.usgs.gov/mrds/>), and closest distances to mines were calculated for each Hg data point; (viii) Distances to geothermal systems were based on data available at the U.S.G.S Energy Resources Program (<http://energy.usgs.gov/OtherEnergy/Geothermal.aspx>; Williams et al. (2008); Williams and DeAngelo (2008); and (ix) foliar Hg mass across the study domain was calculated for different land cover types (coniferous forests, deciduous forests, shrublands, grasslands, and barren regions; urban areas, waterways, wetlands, and ice were excluded), based on satellite-derived leaf area index (LAI) for July, 2013. Mass of foliar Hg was calculated for each pixel with the following relationship:

$$M_{\text{Hg}} = [\text{Hg}] \left(\frac{\text{LAI}}{\text{SLA}} \right) \quad \text{Equation 1}$$

where $[\text{Hg}]$ is the concentration of Hg found for leaves and needles, LAI is the leaf area index, SLA is the specific leaf area; and M_{Hg} is the total mass of Hg stored in leaves. Leaf Hg

concentrations were used from the summary statistics of foliar concentration from the study domain (Table 2A; coniferous forests: 28 $\mu\text{g kg}^{-1}$; deciduous forests: 19 $\mu\text{g kg}^{-1}$); a value of 55 $\mu\text{g kg}^{-1}$ was used for shrub leaves based on Engle et al. (2006), and an average Hg value of coniferous and deciduous leaves (24 $\mu\text{g kg}^{-1}$) was used where data were missing (i.e., for grassland, croplands, barren). SLA (i.e., leaf surface area per unit mass) values used were 38 $\text{cm}^2 \text{g}^{-1}$ for coniferous trees, 137 $\text{cm}^2 \text{g}^{-1}$ for deciduous trees, and 112 $\text{cm}^2 \text{g}^{-1}$ for shrublands based on Reich et al. (2007). SLA values for grassland regions were calculated as an average of forb and graminoid species (247 $\text{cm}^2 \text{g}^{-1}$) based on Vile et al. (2005), and the same values were applied for croplands and barren regions.

2.3. Statistical and spatial analyses

For literature data and the unpublished dataset, summary statistics (including means, medians, and variances) were performed using a statistical and data analysis package (STATA® 12.0, StataCorp, College Station, Texas, USA). Due to its large spatial coverage with 4,857 sampling points across the contiguous U.S. and 1,911 sampling points located in the Western U.S. study domain, detailed spatial analyses were performed with this U.S.G.S. data set. Because a significant number of observations fell below detection limits, statistics (mean, median, variance) for this data set were calculated using maximum likelihood estimation (MLE) techniques using the NADA package (Lee, 2013) of the statistical software program “R” (R-Core-Team, 2014). MLE and non-parametric techniques are used to deal with non-detect values since replacement of data (e.g., using $\frac{1}{2}$ detection limits) has been shown to be problematic (Helsel, 2012). MLE has been shown to produce unbiased estimates of mean, median, and standard deviation without substitution for minimally censored data sets with $n > 50$ (Helsel, 2012). A lognormal distribution was assumed for MLE estimation. MLE can be sensitive to outlier concentrations, and summary statistics were calculated (Table 2) both with and without removal of data points above Hg concentrations $> 200 \mu\text{g kg}^{-1}$ (1.1% of data in the study region). Differences in the distribution of Hg concentration between land cover types were assessed using the Kolmogorov-Smirnov test. Since multiple comparisons among land cover types were performed (i.e., 10 comparisons), the statistical significance levels were adjusted to P -values of 0.005 ($\alpha=0.995$) using the Bonferroni correction for performing multiple tests.

Three ranked-based principal component analyses (PCA) were performed including all data (i.e., no outlier removal) using R packages “ade4” (Dray and Dufour, 2007) and “psych” (Revelle, 2014). PCAs were performed for A-horizon Hg concentrations and included the following variables: PCA 1 – “Environmental Variables”, including A-horizon organic carbon concentrations, precipitation, elevation, latitude, temperature, solar radiation, NDVI, and erodibility factor “K”; PCA 2 – “Potential Sources” including modelled Hg wet and dry deposition, precipitation, distance to Hg, Ag, and Au mines, distance to coal-fired power plants, distance to geothermal areas, and canopy Hg pools. PCA 3 – “Soil Metals” including A-horizon Fe, Ti, V, Al, Mn, Cr, Zn, Sn, and Pb concentrations plus organic carbon content; PROMAX oblique rotations were applied to all PCAs. Variances in text and figures are expressed as standard deviations.

3. Results and Discussion

3.1. Aboveground biomass Hg concentrations

Published aboveground biomass data on Hg concentrations across the western U.S. are sparse and clustered around only a few locations; for example, data for vascular plants were found at 19 sites representing 16 tree species and one shrub species, but these were located in only four of the 11 western U.S. states (Washington, California, Nevada, and Colorado). Vascular plant foliage Hg concentrations (Table 1A; Figure 1A) ranged from a minimum of 7 $\mu\text{g kg}^{-1}$ (in Lodgepole Pine needles in the Rocky Mountains) to 64 $\mu\text{g kg}^{-1}$ (Douglas Fir needles in Washington State), with a mean concentration of $26 \pm 17 \mu\text{g kg}^{-1}$ (mean $\pm$ std.dev.).

Although concentrations differed by almost a factor of 10, most values were in the range of 10–20 $\mu\text{g kg}^{-1}$ (31% of data), followed by the two adjacent concentration brackets (0–10 $\mu\text{g kg}^{-1}$: 18%; 20–30 $\mu\text{g kg}^{-1}$: 16%; Figure 1A). About a quarter of observations exceeded concentrations of 40 $\mu\text{g kg}^{-1}$. These foliar Hg concentrations were in similar ranges as concentrations observed in other areas in North America, including the Adirondacks (Blackwell and Driscoll, 2015), Ontario, Canada (Siwik et al., 2009; St. Louis et al., 2001), and across 14 distributed forest sites in the contiguous U.S. (Obrist et al., 2011).

Figure 1: Histograms of Hg concentrations in foliage (A, all species) and soils (B) across the western U.S. study domain with data collected from the literature. Soil Hg values $>200 \mu\text{g kg}^{-1}$ are combined into a single group.

No spatial trends in aboveground Hg concentrations were detected across the study domain. For example, an unpaired t-test of foliar Hg concentrations grouped into the three main sampling areas (i.e., Washington State: mean of 26 $\mu\text{g kg}^{-1}$; Nevada and California: mean of 27 $\mu\text{g kg}^{-1}$; and Colorado: mean of 24 $\mu\text{g kg}^{-1}$) revealed no statistically significant differences among these locations. The lack of spatial patterns may be due to a sparse data coverage as well as

the strong variability in tissue Hg concentrations. Based on the data available, it is not possible to clarify the reasons for the high variability in Hg concentrations among tissues. However, reasons may include the presence of many different species (i.e., 16 different tree species in this data summary), different field sampling protocols, and different collection dates among studies. For example, a major source of variability in leaf Hg concentrations may be a strong effect of leaf age (Rea et al., 2002), whereby different collection times would add variability due to the presence of different foliage ages; however, foliar samples in this dataset were generally collected during peak vegetation period or close to leaf senescence, so that most data represent fully leaved-out, mature leaves and needles. It has further been shown that concentrations of Hg differ between species and functional groups (Hall and St. Louis, 2004a; Melieres et al., 2003; Rasmussen, 1995; Rasmussen et al., 1991; Schwesig and Krebs, 2003; Siwik et al., 2009). Further, even within-canopy variability has been reported in trees (Barghigiani et al., 1991; Bushey et al., 2008; Rasmussen, 1995; Rea et al., 2002; Siwik et al., 2009).

Table 1A. Mercury (Hg) concentrations in aboveground biomass (A) and soils (B) across the western U.S. Data were collected from the published literature. (C) Comparison of vertical distribution patterns of Hg in different organic and mineral soil layers and comparison to aboveground Hg foliage concentrations of the dominant species. These data are based on eight selected sites from Obrist et al. (2011).

A. Tissue/sample type	N	Hg concentrations ($\mu\text{g kg}^{-1}$)			
		Mean	Std.Dev.	Min.	Max.
Leaves	74				
Coniferous	56	27.8	16.3	6.7	63.8
Deciduous	17	19.3	15.8	7.8	50.2
Branches	44	25.9	27.9	0.7	160.9
Bark	18	16.0	7.6	5.9	38.6
Bole Wood	53	1.0	1.8	< d.l.	5.8
other					
Lichen	138	647.3	824.0	30.6	7195.0
Mosses	4	90.3	16.6	68.0	108.0

B. Soil Horizon	N	Sign.*	Hg concentrations ($\mu\text{g kg}^{-1}$)			
			Mean	Median	Std.Dev.	Min. Max.
Top soils (A-horizon)	494	A	1,814	31	12,462	< d.l. 231,000
Subsurface soils (B & C horizons)	347	B	35	25	37	3 420
All	841		1,080	29	9,587	< d.l. 231,000

C. Vertical concentration patterns	N	Sign.*	Hg concentrations ($\mu\text{g kg}^{-1}$)			
			Mean	Std.Dev.	Min.	Max. Enrichment
8 select sites across the western U.S.						
Foliage (dominant trees)	8	A	23.8	12.3	9.4	43.2
Oi horizon	8	B	33.9	14.4	21.6	66.4 66%**
Oe horizon	8	C	84.5	49.0	45.9	194.8 318%**
Oa horizon	5	D	206.8	106.0	126.4	385.4 907%**
A horizon (top 20 cm)	8	E	58.6	61.7	10.7	161.1 3,863%***
B horizon (>20 cm)	8	E	47.3	51.8	7.5	132.9 4,203%***

* Statistical differences ($P < 0.05$): different letters are statistically different. All tests were based on Hg concentrations, with the exception of Table C where Hg/C was used for soil comparisons.

** Concentration enrichments compared to foliar concentrations at the sites

*** Enrichment factors of Hg/C ratios compared to foliar Hg/C ratios at the sites

Surprisingly, only small differences between concentrations of deciduous leaves versus coniferous needles were observed across the study domain (Table 1A): coniferous foliage tissues averaged $28 \pm 16 \mu\text{g kg}^{-1}$ compared to deciduous foliage of $19 \pm 16 \mu\text{g kg}^{-1}$, but this difference was not statistically significant at the 5% level ($P = 0.065$). Many studies report much higher aboveground tissue Hg concentrations in coniferous species compared to deciduous species: for example, Rasmussen et al. (1991) reported 70% higher concentrations in foliage of balsam and spruce needles compared to three deciduous species; Hall and St. Louis (2004b) reported about double the concentrations in pine needles versus birch leaves; and Obrist et al. (2012) reported four times the concentrations in Douglas fir needles compared to adjacent red alder leaves. Differences in Hg concentrations between coniferous and deciduous species at individual study sites are generally attributed to increased foliage age as well as lower canopy resistance of needles compared to leaves increasing atmospheric uptake. Using the data set collected for this study, it seems that forest canopies are poor proxy surfaces to assess atmospheric exposure or pollution impacts across large spatial scales, unless factors contributing to data variability, such as sampling protocols, species, and foliage locations within tree canopies, can be constrained. A potential value of using tree canopies as atmospheric Hg deposition monitors, however, has recently been proposed using hardwood foliage in 45 sites in the Adirondack Park located across varied topography (Blackwell and Driscoll, 2015). Others report that biotic surfaces have not been calibrated as passive samplers and little variability in concentrations may be expected due to relatively homogenous concentrations of gaseous elemental Hg in air (Huang et al., 2014).

Tree branches across the western study domain (Table 1A) showed similar mean Hg concentrations as foliage but were even more variable (e.g., concentrations ranged from 1 to $161 \mu\text{g kg}^{-1}$). This may be attributable to varying branch diameters with different contributions of bole wood versus bark that differ in concentrations. Hg concentrations in tree bark averaged $16 \pm 8 \mu\text{g kg}^{-1}$, and lowest Hg concentrations were found in bole wood ($1 \pm 2 \mu\text{g kg}^{-1}$), in accordance with a review by (Grigal, 2003) that showed bole wood concentrations generally below $3 \mu\text{g kg}^{-1}$ with the largest proportions between 1 to $2 \mu\text{g kg}^{-1}$. The sequence of Hg tissue concentrations observed (leaves > branches > bark > bole wood) was similar to other studies (Grigal, 2003) with tissues of low surface area generally showing low concentrations due to lower atmospheric uptake — the dominant source of Hg in aboveground tissues (Beauford et al., 1977; Frescholtz et al., 2003; Grigal, 2003; Lindberg et al., 1979; Millhollen et al., 2006a;

Millhollen et al., 2006b; Rutter et al., 2011). Finally, aboveground biomass components with by far the highest Hg concentrations in the study domain were lichen ($647 \pm 824 \mu\text{g kg}^{-1}$) and mosses ($90 \pm 17 \mu\text{g kg}^{-1}$; Table 1A), supporting other studies that reported high Hg levels in non-vascular plants such as mosses, lichen, and mushrooms both in North America as well as in Europe (Grigal, 2003; Hall and St. Louis, 2004a; Harmens et al., 2010; Rasmussen et al., 1991). The concentration distribution of Hg in lichen and mosses across the western U.S. was not further analyzed in this paper because available Hg concentration data are sparse and limited to National Park areas in Washington and Oregon.

Foliar Hg mass was estimated across the study domain based on satellite-derived leaf areas and land-cover specific SLA and Hg concentrations (Figure 2; see methods). Calculated Hg pools associated with foliar canopies range from $0 \mu\text{g m}^{-2}$ to $44 \mu\text{g m}^{-2}$, with a mean foliar Hg mass of $4.4 \mu\text{g m}^{-2}$. The magnitude of estimated foliar Hg pool is similar to that of field measurements across six forest sites across the western U.S. by Obrist et al. (2011) and Obrist (2012) that showed foliar Hg pools ranging from 3 to $58 \mu\text{g m}^{-2}$. Based on Figure 2, foliage was estimated to retain 13 Mg of Hg during peak

vegetation periods across the Western U.S., a value close to the 15 Mg of annual foliar Hg uptake estimated for three specific biomes (semiarid deserts, grasslands, and deciduous forests) across the continental U.S. (Hartman et al., 2009). A recent study (Yang et al., 2014) showed that, despite low concentrations, tree trunks further add substantially to the standing Hg pool size in forests, with hardwood Hg pool sizes similar to those of forest canopies. Therefore, total aboveground pools across the West are likely at least double of these calculated foliar pools.

Figure 2: Estimated peak summertime (July) foliar Hg pool sizes across the western U.S. study domain. Hg pools were calculated based on satellite-derived leaf area estimates, specific leaf area (surface area per mass) of different land cover types, as well as corresponding leaf Hg concentrations of these land cover types.

Much of these aboveground Hg pools, particularly leaves and understory vegetation, are cycled annually via growth and senescence, while others (e.g., coniferous needles and woody tissues) have turnover rates of several to many years. These pool sizes therefore show the importance of vegetation as a transfer pathway of atmospheric Hg to underlying ecosystems. For example, calculated foliar pool sizes (with a peak $44 \mu\text{g m}^{-2}$) are large compared to annual wet deposition loads that generally are below $6 \mu\text{g m}^{-2} \text{yr}^{-1}$ across the western U.S. (NADP, 2013), and also are large compared to dry deposition estimates (1.3 to $10 \mu\text{g m}^{-2} \text{yr}^{-1}$) at sites in the study domain (Lyman et al., 2007). Thus, plant-derived Hg deposition is likely the dominant deposition pathway and significantly drives soil Hg distribution across the Western U.S. (see section 3.5.). Given a relatively high uncertainty in estimating foliar Hg stocks and fluxes (e.g., due to differences in SLA: Hartman et al., 2009), which in the Western U.S. is further driven by a lack of Hg vegetation data for important functional groups (e.g., only 2 out of 172 foliar samples originated from desert shrubs, and there was a complete lack of Hg data from grasses and forbs), vegetation-derived Hg deposition is still a key uncertainty in estimating atmospheric Hg deposition in the Western U.S.

3.2. Concentration increases from aboveground biomass to organic and mineral soil layers

For 8 western forest sites with corresponding characterization of vegetation, organic, and mineral soil Hg concentrations and pools (Obrist, 2012; Obrist et al., 2011), vertical concentration patterns we re-analyzed from aboveground biomass into organic and mineral soil layers (Table 1C). Across these sites, Hg concentrations increased from undecomposed surface organic layers (Oi horizon: $34 \mu\text{g kg}^{-1}$), to partially decomposed, deeper organic layers (Oe: $85 \mu\text{g kg}^{-1}$) and to well humidified Oa layers ($207 \mu\text{g kg}^{-1}$; Table 1C). Oi organic layers were enhanced in Hg compared to aboveground biomass (+66%; compared to foliage of the dominant tree species which are mainly forming this layer), and greater enrichments were observed in partially decomposed, deeper organic layers (Oe: +318%) and fully humidified Oa layers (+907%); similar increases were observed for median values across sites (+37%, +287%, and +1010%, respectively). Therefore, Hg concentrations increased about 10-fold from fresh biomass to decomposed plant detritus; such concentration increases have been reported before in forest floors (Grigal, 2003; Obrist et al., 2011; Schwesig and Matzner, 2000) and in litter

decomposition studies (Demers et al., 2007; Hall and St. Louis, 2004b; Pokharel and Obrist, 2011). The increases are attributed to decomposition of organic carbon (and associated losses as CO₂) under comparably higher retention of Hg, as well as additional sorption of Hg from atmospheric deposition in decomposing organic matter (Pokharel and Obrist, 2011). Therefore, organic soil horizons are considered efficient horizons to sorb atmospheric deposition which accumulate in surface organic and mineral soils.

Compared to organic horizons, mineral soil Hg concentrations generally show Hg concentration declines compared to organic layers above (-72% across these eight sites), attributable to higher soil bulk densities resulting in a dilution effect. Further concentration declines are generally observed with depth in the mineral soils (e.g., -24% on average across the eight sites for soils deeper than 20 cm) which follow concentration declines of organic C content with depth (Grigal, 2003). If mineral soil Hg levels were expressed as Hg/C ratios, however, Hg/C ratios generally continue to increase in mineral soils compared to Hg/C ratios of aboveground tissues (i.e., before the onset of mineralization), e.g., showing enhancement of Hg/C ratios of +3860% in the top 20 cm mineral soils and +4290% in the mineral soils below 20 cm depth across these eight study sites.

The key point pertaining to these vertical concentration and Hg/C ratio patterns is that high vertical variability in concentrations across organic and mineral soil layers can greatly exceed variability across horizontal scales, and this needs to be carefully considered when analyzing spatial data sets. It is therefore critical to note depth of sampling horizons, if samples include organic or mineral soils, and provide auxiliary measures, such as carbon concentrations or bulk densities, to help standardization across sites. Information on vertical concentration patterns also are critical in regard to runoff and mobilization, because different hydrologic pathways (e.g., overland versus belowground runoff) affect different Hg source horizons. For example, using a unique analysis of lignin biomarkers in sediments to fingerprint terrestrial Hg sources, Teisserenc et al. (2011) observed that Hg mobilization from humidified horizons was a main upland source of Hg to lakes, supporting the strong source potential of humidified organic soil horizons with high Hg concentrations.

3.3. Mineral soil Hg concentrations across the western U.S. – literature data

Mineral soil Hg concentrations compiled from the literature were based on 16 published studies and one additional unpublished soil Hg data set (Table 1B). Figure 1B shows the frequency distribution of soil Hg data (841 sample points, including surface and subsurface soil samples). Of these observations, 12% exceeded 100 $\mu\text{g kg}^{-1}$ (101 observations), a value which has been considered a threshold value for “background” concentrations (Gustin et al., 2000), and 7% were above a value of 200 $\mu\text{g kg}^{-1}$ (55 observations). Other studies, however, have considered lower concentrations as background (Andersson, 1979; Yu et al., 2014) while others have reported higher Hg concentrations (i.e., > 150 $\mu\text{g kg}^{-1}$) in upper mineral soils at sites not affected by specific pollution sources (Obrist, 2012).

Surface soil samples (494 sample points; considered A-horizon samples, although samples were taken at various depths and often lacked clear pedogenic horizon determination) averaged 1,814 $\mu\text{g kg}^{-1}$ with a median value of 31

$\mu\text{g kg}^{-1}$. This shows that a few samples had extremely high Hg concentrations (e.g., as high as 231000 $\mu\text{g kg}^{-1}$ in a mining site in Nevada; Zehner and Gustin, 2002). Hg concentrations collected from deeper soils (347 sample points; considered B- or C-horizons) averaged 35 $\mu\text{g kg}^{-1}$ (median value of 25 $\mu\text{g kg}^{-1}$), with a maximum value of 420 $\mu\text{g kg}^{-1}$. The mean concentrations were much higher than concentration ranges and means reported across other areas. For example, a large U.S.G.S. data reported much lower concentrations (see section 3.4.), and Amos et al. (2015;

Table 2: Summary tables of soil Hg concentrations across the western U.S. using a recent U.S.G.S data set (Smith et al., 2013b) based on Maximum Likelihood Estimation (MLE) statistics using NADA package in R. (A) Soil Hg concentrations separated by horizons. (B) A-horizon Hg concentrations separated by major ecoregions of the West. (C) A-horizon Hg concentrations separated by land covers. (D) Statistical differences in A-horizon Hg concentrations among different land cover types based on a Kolmogorov-Smirnov test. Statistical significance levels of individual land cover type comparisons (n=10) were adjusted to a p-value of 0.005 (alpha=0.995) using the Bonferroni correction for performing multiple tests.

A. Soil Horizons	N	P*	Hg concentrations ($\mu\text{g kg}^{-1}$)		
			Median	Mean	Std.Dev.
Top 5 cm	1881 (1911)	AB	20.0 (20.5)	25.9 (28.6)	21.3 (27.7)
A Horizon	1882 (1911)	A	19.1 (19.7)	24.1 (27.0)	18.6 (25.3)
C Horizon	1874 (1911)	B	16.4 (16.7)	21.9 (23.7)	19.3 (23.7)

Parenthesis: no outliers (>200 $\mu\text{g kg}^{-1}$) removed. Statistical differences based on non-parametric test for difference (Wilcoxon Sign Ranked Test). Different letters are statistically different ($P < 0.05$).

B. Ecoregions	N	Hg concentrations ($\mu\text{g kg}^{-1}$)		
		Median	Mean	Std.Dev.
Marine West Coast Forests	56	25.3	35.1	33.7
Northwestern Forested Mountains	502	20.5	26.6	22.0
Mediterranean California	95	19.1	24.4	19.2
Great Plains	334	18.8	22.5	14.9
North American Deserts	804	18.7	23.5	17.9
Temperate Sierra	63	15.1	17.6	10.5
Southern Semiarid Highlands	28	14.0	15.2	6.5

C. Land Cover Types	N	P*	Hg concentrations ($\mu\text{g kg}^{-1}$)		
			Median	Mean	Std.Dev.
Forested Upland	457	A	27.7	35.6	28.7
Planted/Cultivated	123	B	22.3	29.9	26.9
Herbaceous Upland	373	C	17.6	20.9	13.6
Shrubland	850	C	16.3	19.3	12.1
Barren	58	D	11.8	13.3	7.0

D. Statistical differences among land cover types					
	Barren	Forested Upland	Herbac. Upland	Planted/Cultivated	Shrub-land
Barren	1.00E+00				
Forested Upland	2.74E-14	1.00E+00			
Herb. Upland	1.26E-06	0.00E+00	1.00E+00		
Planted/Cultivated	2.24E-08	1.01E-03	1.05E-03	1.00E+00	
Shrubland	9.46E-05	0.00E+00	1.35E-01	7.36E-06	1.00E+00

supplemental information) reported mean soil Hg concentrations from North America in a range of 7 to 50 $\mu\text{g kg}^{-1}$ and an average of 47 $\mu\text{g kg}^{-1}$. Similarly, Grigal (2003) reported average Hg concentrations from European soils of 40 $\mu\text{g kg}^{-1}$, and Lado et al. (2008) reported median values of 41 $\mu\text{g kg}^{-1}$ across 26 European countries. The main reason for higher soil Hg concentrations in the literature data from the western U.S. compared to a systematic soil investigation in the same area (see below) includes a strong sampling bias toward sites with high Hg concentrations, particularly because many studies focused on investigating naturally-enriched Hg areas (such as the global Hg belts) and mining sites with locally very high Hg levels.

3.4. Soil Hg concentrations and stocks across the western U.S. – data from a U.S.G.S. geochemical database

A systematic, large-scale geochemical soil data set was recently collected, analyzed, and made public by the U.S.G.S. (Smith et al., 2013b) with 4857 sampling points across the contiguous U.S., of which 1911 sampling points were located in the Western U.S. study domain. In addition to an unprecedented number of sampling points, this campaign used consistent sampling protocols, separated samples into well-defined soil horizons, used random selection of sampling points to avoid spatial sampling bias, and provided a comprehensive set of other elements and soil characteristics. These data provide a foundation for a unique analysis of spatial patterns of Hg in soils. Figures 3A and 3B show Hg concentrations in soil A- and C-horizons using IDW, and figure inserts show respective frequency distributions. Hg concentrations (Table 2A) ranged from below the method detection limit ($<\text{MDL}$; 10 $\mu\text{g kg}^{-1}$) to 8240 $\mu\text{g kg}^{-1}$ in A-horizons and from $<\text{MDL}$ to 1750 $\mu\text{g kg}^{-1}$ in C-horizons. Hg concentrations and distribution in the top 5 cm-horizons (Table 2A) were similar to those of A-horizons. The top 5 cm-horizon represents the uppermost layer that supports plant and root growth that at some sites included fully organic horizons, whereas at other sites, represented the first mineral soil horizon. This layer therefore included varying degrees of organic versus mineral horizons that complicated interpretation of Hg concentrations given the strong vertical Hg concentration gradient from organic to mineral soil horizons discussed in section 3.2. Therefore, discussions of soil Hg distribution patterns were focused on data from clearly defined A- and C-horizons.

In contrast to data collected from the literature, the randomly collected U.S.G.S. data set shows very few A- and C-horizon samples with high soil Hg concentrations. The histograms in Figures 3 show that data points exceeding 200 $\mu\text{g kg}^{-1}$ account for 21 and 17 observations in A- and C-horizons, respectively, out of more than 1900 observation points (about 1%), compared to 7% when using literature data. Similarly, only 2.6% of the data exceeded “background” concentrations of 100 $\mu\text{g kg}^{-1}$. This confirms a strong sampling bias of the collected from the literature (section 3.3). At the low end of concentrations, we found a significant number of observations falling below the MDL of 10 $\mu\text{g kg}^{-1}$, i.e., 175

points (or 9%) in A-horizons and 312 points (16%) in C-horizons. Resulting mean concentrations and standard deviations of soil Hg concentration across the Western U.S. (Table 2A) were 24 ± 19 $\mu\text{g kg}^{-1}$ (A-horizon) and 22 ± 19 $\mu\text{g kg}^{-1}$ (C-horizon), with median values of 19 $\mu\text{g kg}^{-1}$ and 16 $\mu\text{g kg}^{-1}$, respectively. Median and mean concentrations without the removal of outliers suggested by MLE techniques (we chose >200 $\mu\text{g kg}^{-1}$ for outliers, ~1% of all data) were very similar (Table 2A). These soil Hg concentrations are considerably lower (about half) compared to values found

Figure 3: Soil Hg concentrations from Smith et al. (2013b) for the western U.S. study domain. A. Hg concentrations for A-horizons across the western U.S. study domain. Distribution map is based on spatial interpolation of 1881 sampling points using inverse distance weighting (IDW; $n=12$) using ArcGIS® and ArcMAP® software. Outliers with concentrations >200 $\mu\text{g kg}^{-1}$ were replaced with 200 $\mu\text{g kg}^{-1}$ in order to reduce influence of extreme values. Figure insert shows a histogram of A-horizon Hg concentrations. B. Same as A but for C-horizon soil Hg concentrations. C. Delineation of ecoregions based on Level 1 of the U.S. Environmental Protection Agency assignments for Ecological Regions of North America (http://ftp.epa.gov/wed/ecoregions/cec_na/NA_LEVEL_I.pdf).

in other areas across the U.S. and other regions, indicating that Western U.S. soil Hg concentrations are some of the lowest observed anywhere.

3.5. Concentration differences between ecoregions and land cover types

Spatial distribution patterns follow landscape patterns as indicated in Figure 3 delineating major ecoregions. Summarizing data based on ecoregions, highest soil Hg concentrations (Table 2B) were found in Marine West Coast Forests ($35 \pm 34 \mu\text{g kg}^{-1}$) and Northwestern Forested Mountains ($27 \pm 22 \mu\text{g kg}^{-1}$), with lower values in Mediterranean California landscapes ($24 \pm 19 \mu\text{g kg}^{-1}$). Lowest Hg concentrations were observed in Southern Semiarid Highlands (15 ± 7) and the Temperate Sierras ($18 \pm 11 \mu\text{g kg}^{-1}$), with generally only about half the concentrations of forested landscapes. We further analyzed data based on different land cover types (Table 2C) because unlike ecoregions, land cover types are more randomly distributed across the western U.S. (although they also are not fully randomly distributed either). Soil Hg concentrations of the major land cover classes were in the following order: forested upland > planted/cultivated > herbaceous upland/shrubland >

barren, and differences were significant (except between herbaceous uplands and shrublands; Table 2D). Differences between land cover types were in fact very pronounced: forested upland locations showed more than 2.5 times the soil Hg concentrations of barren locations, indicating a pronounced role of land cover types in determining soil Hg concentrations. Strong differences in soil Hg concentrations were also evident in the cumulative

Figure 4. Cumulative probability function of A-horizon Hg concentrations of different land cover types. Large differences exist among different land cover types, such as barren soils where almost 80% of samples show concentrations $<20 \mu\text{g kg}^{-1}$, whereas more than 80% of forested upland soils have Hg concentrations $>20 \mu\text{g kg}^{-1}$. The bin size of $10 \mu\text{g kg}^{-1}$ reflects the analytical measurement resolution. Statistical differences among land cover types are provided in Tables 2C and 2D.

probability functions of soil concentrations in different land cover types (Figure 4). For example,

almost 80% of barren soils showed concentrations $<20 \mu\text{g kg}^{-1}$, whereas more than 80% of forested upland soils show Hg concentrations $>20 \mu\text{g kg}^{-1}$. Intermediate land cover types – such as herbaceous sites, shrublands, and cultivated sites – are between forested and barren landscapes. These patterns indicate a pronounced role of vegetation cover with regard to soil Hg distribution.

3.6. Relationships of soil Hg concentrations to ecosystem properties, sources, and other soil elements

To analyze underlying parameters that define differences in land cover types and shape spatial patterns, principal component analyses (PCA) were done. In particular, PCAs were performed to assess correlations between soil Hg concentrations, ecosystem and source variables, and other soil metals (note that all PCAs were performed with all data without any removal of high values). Correlation matrices among all variables of these PCA analyses are provided in Supplemental Table 1.

In a first PCA, we included “Ecosystem” variables, including latitude, elevation, mean annual

Figure 5. Rank-based Principal Component Analyses (PCA) with PROMAX oblique rotation performed for A-horizon Hg concentrations. A. PCA 1 includes “Environmental Variables”: organic carbon concentrations, precipitation, elevation, latitude, temperature, solar radiation, NDVI, canopy Hg area, and erodibility factor “K”. B. PCA 2 includes “Potential Hg Sources”: Modelled Hg wet and dry deposition, precipitation, distance to Hg, Ag, and Au mines, distance to power plants, and distance to geothermal areas. PCA 3 includes “Metals” such as Fe, Ti, V, Al, Mn, Cr, Zn, Sn, Pb concentrations plus organic C. C.

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4 temperature, and solar radiation, annual precipitation, peak NDVI (a “greenness” factor
5 representing vegetation coverage), soil organic carbon, and a soil erosion index (K_{fact}). PCA
6 analysis (Promax-rotated) showed three principal components with eigenvalues above 1,
7 whereby the first and second most important factors are shown in Figure 5A. The first
8 component (horizontal axis) included soil Hg concentrations with organic carbon, precipitation,
9 and NDVI, with a normalized loading of 0.78 for Hg. The second eigenvector grouped together
10 variables including solar radiation, temperature, and elevation, and shows negative loadings for
11 latitude and K_{fact} . The result of this PCA indicated that soil Hg distribution is strongly co-
12 determined by ecosystem properties – in particular organic carbon concentrations and NDVI –
13 and climatic variables, particularly precipitation. A key feature of Western U.S. landscapes is
14 that plant productivity and vegetation cover are strongly limited by water availability, and this
15 linkage is likely the reason that NDVI, soil organic carbon content, and precipitation are
16 correlated (representing the first Eigenvector; see also Suppl. Table 1). We propose that this set
17 of variables also determines Hg accumulation and leads to different Hg concentrations in
18 ecoregions and land cover types. To visualize this, a scatter plot of land cover types along the
19 two principal components of PCA 1 shows a separation of land covers particularly along
20 eigenvector 1 (which basically represents an “aridity” gradient; Figure 6). Productive forested
21 upland sites are clustered along the positive axis of this component following high precipitation,
22 NDVI, soil organic carbon content, and, interestingly, high soil Hg concentrations. In contrast,
23 arid barren locations and shrublands are located on the opposite loading of this eigenvector, and
24 intermediary land cover types (planted/cultivated sites and herbaceous upland sites) are in-
25 between. Based on continental-scale distributions of Hg across 14 forest sites, Obrist et al.
26 (2011) previously showed correlations of soil Hg to precipitation, latitude, clay content, and
27 organic carbon content, that together explained between 85% and 94% of the concentration
28 variability in soils. This analysis of Hg content across the western U.S. supports the idea that soil
29 Hg concentrations are linked to precipitation (i.e., soil moisture) and soil organic carbon.
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A second PCA (Fig. 5B) analysis included variables representing potential Hg sources in the Western U.S., including proximity to coal-fired power plants, Hg and precious metal (Au and Ag) mining operations, and geothermal areas. Atmospheric Hg wet and dry deposition was modeled using the CMAQ-Hg model (Bash, 2010; Lin et al., 2006), and canopy Hg mass as a measure of potential plant-derived Hg deposition (Figure 2). The first of three principal components with eigenvalues >1 showed high loading for distance to Hg and precious metal

mining locations as well as distance to geothermal areas. It is to be expected that the spatial distribution of Hg, Au, and Ag mines would to some extent be associated with each other and with that of geothermal areas because of similarities in geologic settings. Most Hg, Au, and Ag deposit types (e.g., hot-spring and epithermal) represent geothermal systems typically associated with volcanic rocks (White, 1981; White and Hedenquist, 1990), although other Au and Ag deposit types (e.g., sediment-hosted) are less associated with zones of currently elevated heat flow (Bonham and Giles, 1983). A second component showed strong positive loadings for Hg concentration, precipitation, and canopy Hg mass, while at the same time only showed very minor loadings for modeled wet deposition and even negative association with dry deposition. However, model results of dry deposition across the western U.S. are may be uncertain because of a lack of field data for verifying model results. The Western U.S. is home to several of the 26 known globally distributed mercury mineral belts (Rytuba, 2003), and emission from these belts, as well as from mining and geothermal areas, are significant sources of atmospheric Hg through degassing of gaseous elemental Hg (Zehner and Gustin, 2002). Despite this, the spatial distribution of soil Hg is largely unrelated to proximity to mining and geothermal areas and that proximity to these does not result in significant soil Hg accumulation. Of course locally

Figure 6. Factor loadings for PCA 1 projected for each land cover data point across the western U.S. The plot shows clear separation of land cover types along an aridity gradient (Factor 1) and a latitudinal/radiation gradient (Factor 2). High Hg concentrations are located along Factor 1 (positive loading) along with high precipitation, NDVI, and organic C values.

enhanced Hg concentrations due to geogenic contributions are well known in mining and geothermal areas as discussed in section 3.3. Similarly, no effects of proximity to coal-fired power plants on soil Hg levels were found. This is not to say that point-source emissions are not significant sources of Hg across the Western U.S., as it is possible that the scale of the available data set may not allow assessing localized pollution impacts at smaller scales. However, PCA results indicated a strong control of canopy Hg contribution for soil Hg accumulation, as expressed by the strong link of soil Hg to canopy Hg pool sizes. Weaker correlations to Hg wet deposition suggest that the associations shown in PCA 1 (between soil Hg and precipitation, NDVI, and organic C) are indeed driven by plant productivity, rather than direct contributions by wet deposition. A key factor shaping spatial Hg distribution across the West is site productivity and plant-derived Hg deposition such as litterfall and throughfall deposition (Bishop and Lee, 1997; Grigal et al., 2000; Iverfeldt, 1991; Lindberg, 1996; Munthe et al., 1995; Rea et al., 1996a; St. Louis et al., 2001). Many studies have shown that litterfall deposition contributes the major deposition flux to ecosystems (Graydon et al., 2008; Iverfeldt, 1991; Lindberg, 1996; Munthe et al., 1995; Rea et al., 1996b), and others also have shown additional deposition via throughfall (Grigal et al., 2000; Grigal, 2003; Hall and St. Louis, 2004a; Iverfeldt, 1991; Lindberg, 1996; St. Louis et al., 2001). Much of the plant-derived deposition is considered derived from atmospheric elemental Hg uptake by vegetation (Demers et al., 2013; Ericksen et al., 2003; Jiskra et al., 2015; Obrist, 2007; Zheng et al.).

A third PCA (Figure 5C) included other elements that were measured along with Hg in the U.S.G.S. soil data set, including transition and post-transition metal concentrations (Al, Cr, Fe, Hg, Mn, Pb, Sn, Ti, V, and Zn) and organic carbon content. Of the strongest two eigenvectors, the first groups most metals including those considered of geologic origin (such as Fe, Ti, Al, and V) and trace elements with possibly mixed geologic and anthropogenic origins (such as Zn or Sn). A second principal component shows significant loading for organic carbon and Hg, and to a smaller degree Pb, with normalized loadings of 0.80 for Hg and 0.79 for carbon. This analysis highlights that the distribution of soil Hg is very different than that of most other metals and that the key factor separating Hg—and to some degree Pb as well—is its atmospheric deposition and strong association with organic carbon, as opposed to geogenic origin for many other trace metals. Pb is also a metal subject to atmospheric transport and deposition, primarily as PbCO_3 and PbSO_4 (Steinnes and Friedland, 2006) and it also interacts with OM (Friedland

and Johnson, 1985; Siccama and Smith, 1978). Many studies from different parts of the world have shown that, although soils contain some level of natural (geogenic or lithospheric) Hg, the vast majority of soil Hg (generally 80% to 90%) stems from exogenic (i.e., atmospheric) inputs (Fiorentino et al., 2011; Grimaldi et al., 2008; Peña-Rodríguez et al., 2012; Peña-Rodríguez et al., 2014; Reimann et al., 2009).

Similar to the results of the analysis in PCA 3, other studies found strong evidence of atmospheric Hg enrichment in surface organic and mineral soil layers, which in part also applies to other trace elements. For example, across Norwegian humus layers, Låg and Steinnes (1978) observed strong correlation coefficients of Hg and organic carbon (r^2 of 0.55 to 0.58), but weaker than anticipated correlations of Hg with other “chalcophilic” elements that generally are associated with sulfides (such as Pb, Zn, and Cd; r^2 between 0.24 and 0.39). Reimann et al. (2009) observed that organic layers along transects in Norway were strongly enriched in Hg (about nine times) compared to underlying C-horizons, but also enriched in other trace metals (including Cd, Ag, Pb, As) and other elements (K, C and P). They also observed that Hg concentrations (and other trace metals) increased with decreasing altitude and precipitation. These authors actually attributed trace metal enhancements in surface soils to a biological or vascular pump (i.e., Goldschmidt’s plant pump; Goldschmidt, 1937), and refer to Goldschmidt (1937) that showed that many elements are enriched in organic horizons due to plant uptake (from soils) and leaf litterfall. Unlike many other trace Hg that originate from soil uptake, however, soil-plant transfer of Hg is very limited and plant-derived Hg deposition is mainly attributable to direct atmospheric uptake (Bishop et al., 1998; Frescholtz and Gustin, 2004; Millhollen et al., 2006a). This analysis demonstrated that mineral soil Hg concentrations strongly followed productivity gradients (PCA 1) and leaf canopy Hg pools (PCA 2), resulting in distinctly different spatial patterns compared to other trace metals (PCA 3), and indicated control of soil Hg accumulation from vegetation (i.e., plant-derived atmospheric deposition), an effect that is even stronger than that of Goldschmidt’s plant pump that applies to other metals.

3.7. C-horizon Hg concentrations

Similar soil Hg concentration ranges and spatial patterns as observed in A-horizons were also observed in C-horizon across the western U.S (Figure 3B). The similarity in distributions between A and C horizons (rank-based coefficient of determination, r^2 , of 0.58; $P<0.01$) suggests

that similar to A-horizon patterns (see discussion above), C horizon Hg concentrations also are driven by atmospheric (particularly vegetation-derived) deposition. Supporting evidence for this is the fact that C-horizon Hg concentrations also are strongly enhanced at vegetated sites compared to barren sites (e.g., 2.9 times higher; $P<0.05$; data not shown). Therefore, we suggest that enhanced atmospheric Hg deposition is to some degree vertically translocated to deeper soil horizons as well. Caution, therefore, is warranted when calculating exogenic contributions via application of geochemical methods based on enhancement of concentration ratios of Hg to those of other metals such as Ti or Al (Guedron et al., 2006; Hissler and Probst, 2006). In particular, we recommend using data from parent material for calculation of baseline geogenic ratios—rather than using C-horizon soil concentrations as these may already be considerably affected by atmospheric deposition.

From A- to C-horizons, observed Hg concentration declined by $2 \mu\text{g kg}^{-1}$, or -8% on average (statistically significant; Table 2A). This concentration decline across the study domain was surprisingly small given that stronger concentration declines between surface and subsurface soils have been reported in many other studies, such as -31% by (Obrist, 2012) across 14 forest soils; -35% in organic-rich soils (Chernozems; (Grigal, 2003); and even more pronounced concentration decline in non-podzol soils contaminated by regional pollution (Schwesig and Matzner, 2000). The smaller concentration declines in this data set may be due to generally lower Hg concentrations in soils, or due to similarly lower vertical OM gradients in Western U.S. soils. Interestingly, however, the vertical patterns also follow land cover categories: for example, in forested sites, concentration declines from A- ($35 \mu\text{g kg}^{-1}$) to C-horizons ($29 \mu\text{g kg}^{-1}$) averaged -15%, but only about half this concentration decline was observed in vegetated, herbaceous upland (-8%) sites. Sparsely vegetated and non-vegetated sites showed only minor or no concentration differences at all, e.g., barren landscapes (-1%) or shrublands (+3%). Therefore, vertical concentration differences between upper and deeper mineral soil horizons were more pronounced in densely vegetated ecosystems with more precipitation with highest productivity (and therefore largest contributions of plant-derived Hg inputs) and with higher OM contents in the A-horizon.

4. Conclusion

This data synthesis and analyses for the study domain of the Western contiguous U.S. utilized available data on vegetation Hg concentration in four of 11 states only, from 19 sites representing 16 tree and 1 shrub species. Hg data from important functional vegetation types such as shrubs, herbaceous species, and grasses were largely lacking, providing uncertainties with regards to the role of vegetation in Hg cycling. No apparent spatial differences in Hg concentrations were observed, which likely was due to a dearth of data and high variability induced by the presence of different species and relatively constant gaseous air Hg concentration as a source of leaf Hg. Calculated pool sizes of Hg contained in aboveground vegetation, with a peak of $44 \mu\text{g m}^{-2}$, however, indicate that the turnover of these vegetation pools (e.g., via leaf senescence and litterfall) constitutes a large deposition pathway, e.g. compared to other deposition processes such as wet deposition that generally is below $6 \mu\text{g m}^{-2} \text{yr}^{-1}$ across the Western U.S.

Across 8 western forest sites, Hg concentrations increased significantly from aboveground vegetation to organic soil layers (composed of plant detritus), with increases compared to dominant foliage of +66% (Oi-layer); +318% (Oe-layer), and +907% (Oa-layer), indicating approximately a 10-fold concentration increase from live vegetation to decomposed organic soil layers. Although surface mineral soil (0-20 cm) concentrations decreased compared to organic layers above (-72% compared to Oa) and further decreased with depth (-24% for soils deeper than 20 cm compared to the top 20 cm), Hg/C ratios continued to increase with depth (with Hg/C ratios increasing +3860% in the top 20 cm mineral soils and +4290% in the mineral soils below 20 cm depth compared to Hg/C ratios of vegetation). These pronounced vertical concentration and Hg/C ratio profiles show an extremely high vertical variability of Hg levels that greatly exceed variability across horizontal scales, so that the depth of sampling needs to be considered when comparing spatial data sets.

In mineral soils, analyses of two different data sources provided different results. Hg concentrations compiled from the literature showed that of 841 sample points, 12% exceeded $100 \mu\text{g kg}^{-1}$, a value which has been considered a threshold value for “background” concentrations, and concentrations reached as high as $231,000 \mu\text{g kg}^{-1}$ at a mining site. The high number of samples above background Hg levels is driven by a bias of published soil investigations towards Hg-enriched areas, such as geothermal systems and mining sites. In

contrast, data from a large-scale U.S.G.S. soil data set with more than 1,900 randomly selected sampling points across the western states showed some of the lowest Hg concentrations in western U.S. soils worldwide, with median Hg concentrations of 19 $\mu\text{g kg}^{-1}$ (A-horizon) and 16 $\mu\text{g kg}^{-1}$ (C-horizon), and only 1% of soil samples exceeding background values (i.e., $>100 \mu\text{g kg}^{-1}$). Spatial patterns of soil Hg concentrations strongly differed among land cover types, with Hg concentrations increasing in the order of: barren soils < herbaceous upland/shrubland < planted/cultivated < forested upland sites. Soil Hg concentrations in forests were on average 2.5 times higher than those at barren soil locations. Soil Hg concentrations were unrelated, or weakly related, to other soil trace metals, to potential pollution sources such as proximity to mines, geothermal areas, power plants, and to modelled dry and wet deposition. Instead, soil Hg concentrations strongly correlated with organic carbon, precipitation, vegetation greenness, and foliar Hg mass contained in aboveground biomass. These results suggest a dominant influence of plant productivity — driven by water availability — on soil Hg concentrations via leaf-derived atmospheric Hg deposition, with productive landscapes leading to high soil Hg accumulation, whereas unproductive, barren soils and shrublands result in low soil Hg levels.

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