Mercury Distribution Across 14 U.S. Forests. Part I: Spatial Patterns of Concentrations in Biomass, Litter, and Soils

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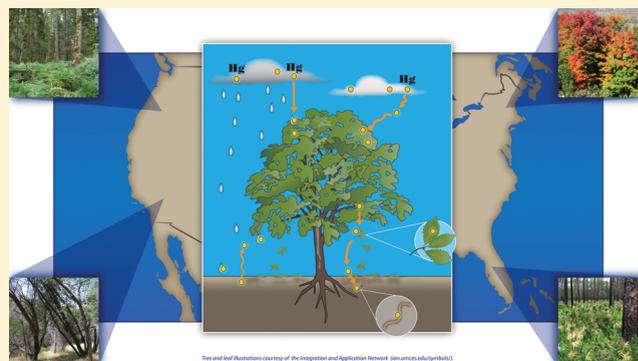[◆]University of Colorado, Boulder, CO, USA

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S *Supporting Information*

ABSTRACT: Results from a systematic investigation of mercury (Hg) concentrations across 14 forest sites in the United States show highest concentrations in litter layers, strongly enriched in Hg compared to aboveground tissues and indicative of substantial postdepositional sorption of Hg. Soil Hg concentrations were lower than in litter, with highest concentrations in surface soils. Aboveground tissues showed no detectable spatial patterns, likely due to 17 different tree species present across sites. Litter and soil Hg concentrations positively correlated with carbon (C), latitude, precipitation, and clay (in soil), which together explained up to 94% of concentration variability. We observed strong latitudinal increases in Hg in soils and litter, in contrast to inverse latitudinal gradients of atmospheric deposition measures. Soil and litter Hg concentrations were closely linked to C contents, consistent with well-known associations between organic matter and Hg, and we propose that C also shapes distribution of Hg in forests at continental scales. The consistent link between C and Hg distribution may reflect a long-term legacy whereby old, C-rich soil and litter layers sequester atmospheric Hg depositions over long time periods. Based on a multiregression model, we present a distribution map of Hg concentrations in surface soils of the United States.

Tree and leaf illustrations courtesy of the Integration and Application Network (ian.umces.edu/symbols/).

INTRODUCTION

Mercury (Hg) is a potent environmental pollutant which can cause significant damages to the central nervous system, kidneys, and other organs in humans.[1] The effects of Hg pollution are of greatest concern in aquatic systems where Hg can be methylated and biomagnified.[2] Hg loads in remote ecosystems are considered dominated by atmospheric deposition,[3] and due to large surface areas catchments surrounding lakes and rivers represent important receptor areas for atmospheric deposition that may ultimately reach aquatic environments.[4] Hence, it is important to understand the spatial distribution of Hg in terrestrial ecosystems and the factors that affect its distribution therein.

Studies addressing the spatial patterns of Hg in remote terrestrial sites are limited. Almost 20 years ago, Nater and Grigal[5] attributed Hg enrichments in litter and surface soils across a 1000 km transect in the north-central U.S. to regional and local sources of atmospheric Hg inputs, possibly driven by nearby Hg emissions in particulate form. Similarly, Hakanson et al.[6]

attributed elevated Hg levels in mor layers over about 900 km distance in Sweden to regional emission sources and proposed that continental European emissions lead to higher Hg levels in the south. In contrast, Lag and Steinnes[7] observed no Hg enrichment in surface humus due to anthropogenic activities in a 650-km north—south transect across Norway. Hence, spatial studies provide conflicting results in regards to the importance of regional contributions to observed Hg loads. To our knowledge, no study has yet addressed larger-scale distribution patterns, for example, at continental scales, of Hg in terrestrial ecosystems.

We performed a systematic investigation of Hg concentrations and pools in 14 forests (Supporting Information (SI) Figure S1) across the contiguous United States. Sites span 6000 km in longitude and 2000 km in latitude. Sites represent a wide range of forest types, elevations, geographic, and climatic conditions, and atmospheric Hg exposures, including an estimated 3-fold difference in atmospheric wet deposition loads and an 18-fold difference in exposure to oxidized atmospheric Hg. We characterized Hg concentrations in all major aboveground and belowground ecosystem components, including tree foliage, branches, bark, and bole wood of dominant tree species, organic litter horizons, and soils at different depths. We characterized a series of auxiliary variables in samples and on sites, including organic carbon (C) levels due to expected associations between Hg and C.[8,9] Accurate replication (12 sampling locations per site) and consistent sampling protocols allowed for a systematic comparison of Hg distribution across these sites. A companion paper[10] describes methyl-Hg patterns and pools of Hg at the ecosystem level determined by scaling up concentrations with detailed inventories of biomass, litter, soil mass, and C.

MATERIALS AND METHODS

Site Descriptions. Fourteen forest sites in the United States were selected for sampling based on site access, availability of background information, access, and existing inventories of biomass, litter, soil mass, and C pools. The 14 selected sites are listed and described in the SI, including Figure S1 and Table S1.

Sample Collections. Field samples at all sites were taken in four replicate plots (exception of three plots in site S4). Plot diameters approximately ranged between 20 and 100 m, and were generally over 200 m apart. Three randomly selected locations were sampled and pooled per plot, resulting in 12 sampling locations per site. Ecosystem compartments sampled included green leaves/needles and dry leaves/needles, branches, bark, and bole wood of the dominant tree species (1—3 species, depending on site), plus understory vegetation. Litter samples were collected and visually separated by litter horizons (Oi: fresh undecomposed surface litter; Oe: partially decomposed litter; Oa: strongly decomposed, humic substance; and coarse woody debris). Soils were collected to depths of 20 cm (Florida site) to 60 cm (Tennessee site) separated into depth horizons (see SI), and soil data were separated into 10 cm depths intervals for comparison across sites. Sampling was conducted using clean latex gloves and sampling equipment made of stainless steel, washed prior to use in the field using deionized water. All samples were immediately double-bagged in plastic freezer bags and stored on ice until transport to the laboratory. Green and dry needles and leaves and branches were directly cut and picked from trees using scissors and clippers, bark was removed using knives, and bole wood was cored (after removal of bark) using a tree borer. Forest surface litter was picked directly from the floor using clean gloves and a spade. Soils at different depths were sampled using stainless-steel hand-shovels from soil pits.

Analytical Methods. All samples were freeze-dried in acid-cleaned test tubes. Samples were milled and homogenized using stainless steel coffee mills. Hg concentrations were analyzed using a Nippon model MA-2000 total Hg analyzer in accordance with U.S. EPA Method 7473. National Institute of Standards and Technology (NIST) solid standard reference materials (Nos. 1515 and 1575) were run after every eight samples, and analyzer was recalibrated when NIST standards deviated >5%. All samples were analyzed in duplicates, and analyses were repeated when the CV exceeded 10% (and 20% for concentrations <10 ng g^{-1}). Total C and nitrogen (N) concentrations and C/N ratios were analyzed using a Leco Truspec C/nitrogen analyzer (LECO, St. Joseph, MI) at the Soil Forage and Water Analysis Laboratory at Oklahoma State University. Soil texture was analyzed at the same laboratory by a ASTM 152-type hydrometer.

Regression Analyses and Spatial Modeling. We performed principal component analyses, stepwise (forward) multiregression analyses, and individual linear regression analyses between Hg concentrations and all available variables to determine the major variables that correlated with the distribution of Hg. One site near Oak Ridge, Tennessee, was excluded from these analyses as we consider this site affected by local pollution (see Results and Discussion). Independent variables tested included: latitude and longitude; elevation; annual precipitation; C and N contents; C/N ratio; soil clay, silt, and sand contents (for soils only); ecosystem data previously assessed by site investigators such as annual litterflux mass and standing above-ground and foliage biomass; and estimated Hg deposition data including litterflux deposition, wet deposition concentration and wet deposition fluxes interpolated from ref 11; Hg air emissions interpolated from ref 12; and atmospheric gaseous and oxidized Hg levels and deposition based on modeled Hg distribution maps.[13] Based on these analyses, we found that four variables (latitude, precipitation, percent soil C, percent soil clay content) exhibited consistent correlations with Hg concentrations across multiple ecosystem components and across all sites. Other variables either showed lack of correlations or were disregarded due to collinearity (e.g., between sand, silt, and clay). A multi-regression using the four variables showed a coefficient of determination, r^2, of 0.87 for all soil samples (0—40 depths) across the 13 sites, indicating that the model captured most of the observed concentration variability in soils. Based on this multi-regression model, we extrapolated soil Hg concentrations to the contiguous United States. We used and modified the Community Land Model (Version 3.5) to model the underlying soil C distribution and then predicted soil Hg concentration based on the above multiregression model. Details are presented in the SI.

RESULTS AND DISCUSSION

Hg Concentrations and Hg/C Ratios in Aboveground Biomass, Litter, And soils. Observed Hg concentrations in aboveground tissue (Figure 1A, SI Table S2) generally showed increasing values in the order of bole wood, branches, leaves, and bark. No consistent differences were observed between species (17 different tree species), functional groups (deciduous versus coniferous), or tissue age (fresh versus senesced foliage). Species-level Hg concentrations were hence pooled to calculate one average value per tissue and site. Tissues with high surface areas directly exposed to the atmosphere showed highest Hg levels, consistent with atmospheric Hg as the main source of Hg to aboveground tissues.[14,15] Hg levels in underlying litter layers (Figure 1B),
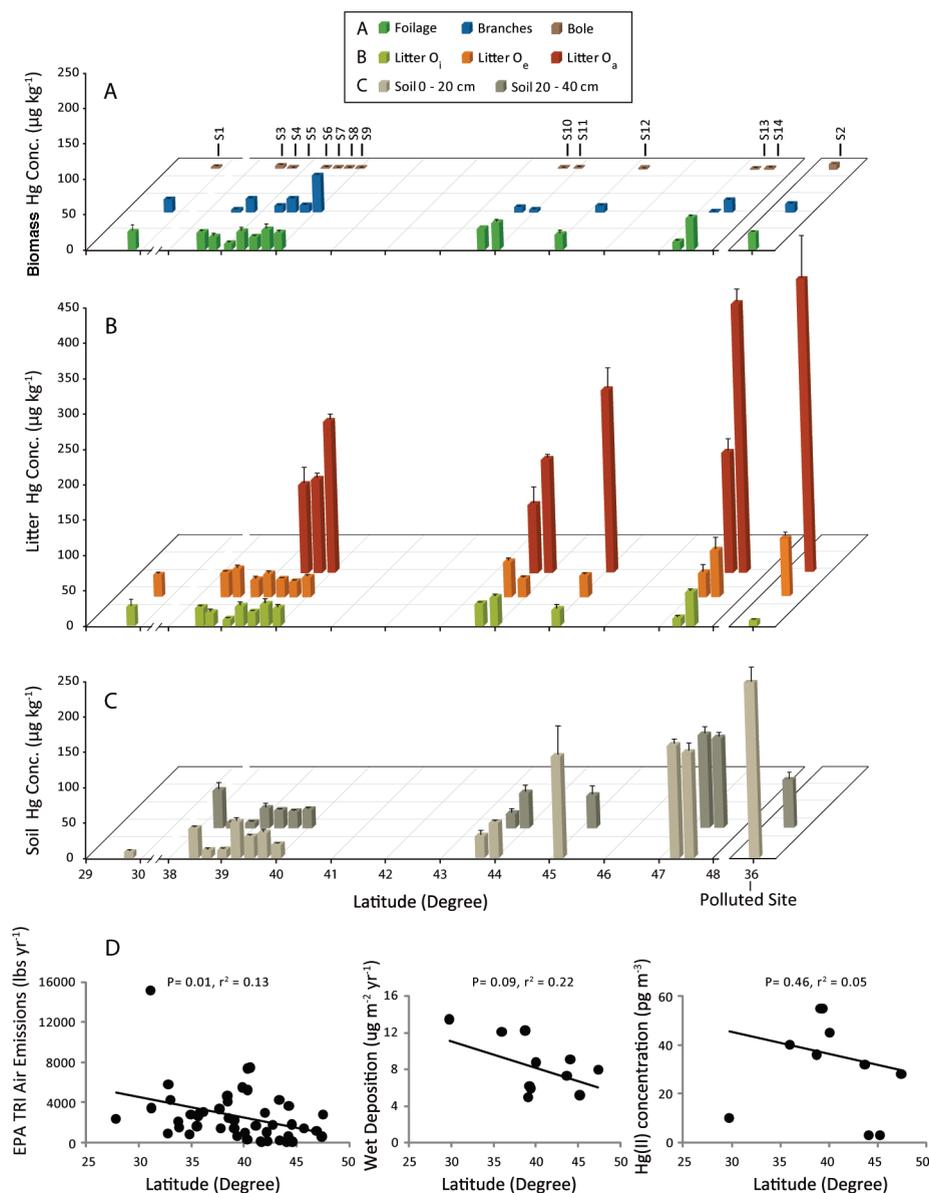
Figure 1. Hg concentrations (in μg kg^{-1}) of major ecosystem components (Panels A–C). Each bar represents average concentration plus standard error of four replicate plots. Sites are numbered S1–S14 according to site names in SI Figure S1 and Table S1 and are ordered by latitude (exception of site S2 which is influenced by local Hg pollution). A: Hg concentrations in aboveground biomass tissues. Values represent average of dominant tree species on sites (i.e., 1–4 species per site). B: Litter Hg concentrations, separated into Oi (fresh), Oe (partially decomposed), and Oa (strongly decomposed) layer. C: Concentrations in soils, averaged for top 0–20 cm and 20–40 cm depths. D: Latitudinal trends of atmospheric pollution proxies. These data were extrapolated from other data sets.[11,13,21] For wet deposition and Hg(II) concentrations, only values for the 13 sites were extrapolated.

separated into variously decomposed layers (Oi, Oe, and Oa), were consistently higher than in aboveground tissues which originally formed these layers, and similar enrichments were observed in soils (Figure 1C). Compared to fresh foliage, litter layers were enriched in Hg by 50–800% (depending on horizon), and soil concentrations were 135% higher compared to foliage samples. Expressed per unit C, Hg enrichments in surface litter and in soils were even stronger (e.g., $55 \pm 7 \mu$g Hg kg^{-1} C in foliage; $730 \pm 207 \mu$g Hg kg^{-1} C in Oa litter; $3147 \pm 909 \mu$g Hg kg^{-1} C in soils). These Hg enrichments show that forest litter on the surface and organic C in top soils strongly accumulate Hg after their initial deposition as plant detritus, as is generally shown in forest litter decomposition studies.[16–18] Highest Hg concentrations observed in litter and upper soils are

in support of previous studies[9] and indicative of Hg sorption from atmospheric deposition to upper litter and soil layers.

Spatial Patterns Across the 14 Forest Sites. For aboveground tissues, we found no relationships to environmental parameters and no clear spatial distribution patterns. This absence of spatial patterns is likely due to the dependence of Hg concentrations on plant species, tissue age, and canopy exposure.[19] Across the 14 sites, we sampled 17 different tree species and used tissues of different exposure and age (although most sites were sampled close to litterfall), which could have masked potential spatial patterns. In litter and soils, however, we found that four variables – latitude, precipitation, soil C and clay content—consistently correlated with Hg concentrations across

Table 1. Linear Regression Analyses Between total Hg[a] and Selected Variables

ecosystem component	latitude		annual precipitation		soil C[a]		soil clay content		multiple regression (latitude, precipitation, clay, carbon[a]	
	P	r^2	P	r^2	P	r^2	P	r^2	P	r^2
foliage	ns		<0.01	0.10					<0.01	0.10
litter Oi	0.04	0.08	0.03	0.09					0.03	0.14
litter Oe	<0.01	0.40	<0.01	0.21					<0.01	0.51
litter Oa	<0.01	0.21	<0.01	0.23					0.02	0.24
soil 0−10	<0.01	0.57	0.02	0.09	<0.01	0.39	<0.01	0.23	<0.01	0.85
soil 10−20	<0.01	0.72	ns		<0.01	0.46	0.02	0.15	<0.01	0.94
soil 20−40	<0.01	0.60	<0.01	0.65	<0.01	0.33	ns		<0.01	0.86
soil 0−40	<0.01	0.60	<0.01	0.23	<0.01	0.36	<0.01	0.10	<0.01	0.88

[a] Log-transformed values; ns means not significant.

13 of the 14 sites (Table 1). One site did not fit within these correlations, a site near Oakridge, Tennessee which showed highly enriched Hg concentrations in soil and litter. This site is nearby a former large-scale mercury contamination source where previous research has shown consistently enriched levels of atmospheric Hg.[20] We believe this site is affected by strong local Hg pollution and excluded it from spatial analyses of the remaining 13 forest sites that we consider remote, background sites.

In litter and soils, we found significant Hg concentration enhancements at higher latitude sites (Figure 1; Table 1). South-to-north gradients became increasingly pronounced with increasing stage of litter decomposition (from Oi to Oa) and were most pronounced in soils where latitude alone explained up to 72% of the concentration variability. Precipitation was another climatic variable that positively correlated with Hg concentrations in litter and soil (although weaker regression fits). In soils, Hg concentrations were positively related to soil C and clay content (details below). Multiregression analyses combining the variables latitude, precipitation, C, and clay content (for soils only) explained 14−51% of the variability of Hg concentrations in litter, and a full 85−94% in soils. Using all soil samples collected in the upper 40 cm in all remote sites, the above multilinear regression model explained the dominant part of the concentration variability ($r^2 = 0.87$).

An interesting finding was that spatial distribution of Hg showed no relationships, or only inverse correlations, to metrics representing current atmospheric Hg exposure or deposition (Figure 1D), including (i) Hg air emissions based on EPA Toxics Release Inventory;[21] (ii) Hg wet deposition based on the National Atmospheric Deposition Program;[11] or (iii) atmospheric gaseous and oxidized Hg levels and depositions based on modeled maps.[13] For litter and soils this was surprising given that they are considered efficient storage pools for atmospheric Hg, retaining up to 90%, and possibly more, of deposited Hg.[4,22,23] Our observations suggest that current atmospheric Hg exposure and deposition—as assessed by the metrics mentioned above—are not directly reflected by Hg concentrations in remote forests, and that at continental scales, Hg distribution is driven by other factors. There are two caveats to this notion; however, first, the site near Oak Ridge, Tennessee, showed enhanced Hg concentrations in litter and soils, likely due to local atmospheric pollution; second, metrics reflecting atmospheric exposure were not directly measured at the sampling sites but were extrapolated from other databases, hence likely including large uncertainties. Still, many atmospheric pollution proxies showed decreasing trends at higher latitude, in contrast to strong latitudinal increases in Hg concentrations across the 13 remote sites. In addition, Hg concentrations did not increase in the Eastern U.S. as might be expected based on higher wet deposition loads.[11] Hg concentrations were also unrelated, or were inversely correlated, to measures of plant-derived Hg inputs, including leaf litterfall mass fluxes, annual litterfall Hg deposition, and standing forest foliar biomass (data not shown). Plant-derived Hg inputs by means of litterfall Hg deposition and wash-off of canopy surfaces (i.e., throughfall) are considered important deposition pathways for Hg in forests and can exceed direct wet-only deposition.[24,25] A possible reason for above patterns is that residence time and retention of Hg in soils and litter as discussed below are more important in shaping spatial patterns of Hg concentrations than direct exposure to atmospheric deposition or plant-derived inputs.

Reasons and Implications of Observed Spatial Patterns. Regressions between Hg concentrations and the four variables are not proof of causal relationships, but we find that the relationships are consistent with well-known biogeochemical processes. We observed strong relationships between organic C and Hg concentrations across all sites and soil depths, and soil C alone explained up to 46% of Hg concentration variability in soils. Naturally, no C-relationships existed in aboveground tissue or litter given their stable C range (45−50%). However, northern sites with deeper and more decomposed litter layers and presence of well-developed Oa-litter horizons showed highest Hg litter concentrations. Close associations between Hg and soil organic matter have been reported previously in soils[9,26,27] and litter,[5−7] and are attributed to the strong binding of divalent Hg to reduced sulfur groups or O and N groups in organic molecules.[28,29] Our results show that soil Hg−C relationships were surprisingly consistent across sites, as evident by consistent linear slopes between C and Hg at different soil depths across the sites (Figure 2A; no statistical slope differences between depths). We suggest that organic C is a key variable that determines the spatial distribution of Hg across terrestrial ecosystems, and that C distribution likely also influences other observed relationships, including dependence to latitude and precipitation (see below).

Vegetation and soils are known to have a high capacity to sorb atmospheric deposition;[23,30] runoff generally account only for a small fraction of annual atmospheric Hg deposition in watersheds (possibly as low as ∼1% of wet deposition[23,31]), and atmospheric re-emissions are considered <10% of deposited wet Hg within a year after deposition.[23,32] Smith-Downey et al.[33] calculated that the number of sorption sites in soils should exceed

A: Hg to Carbon correlations in soils

B: Hg/C ratio to C/N ratio correlation in litter and soils
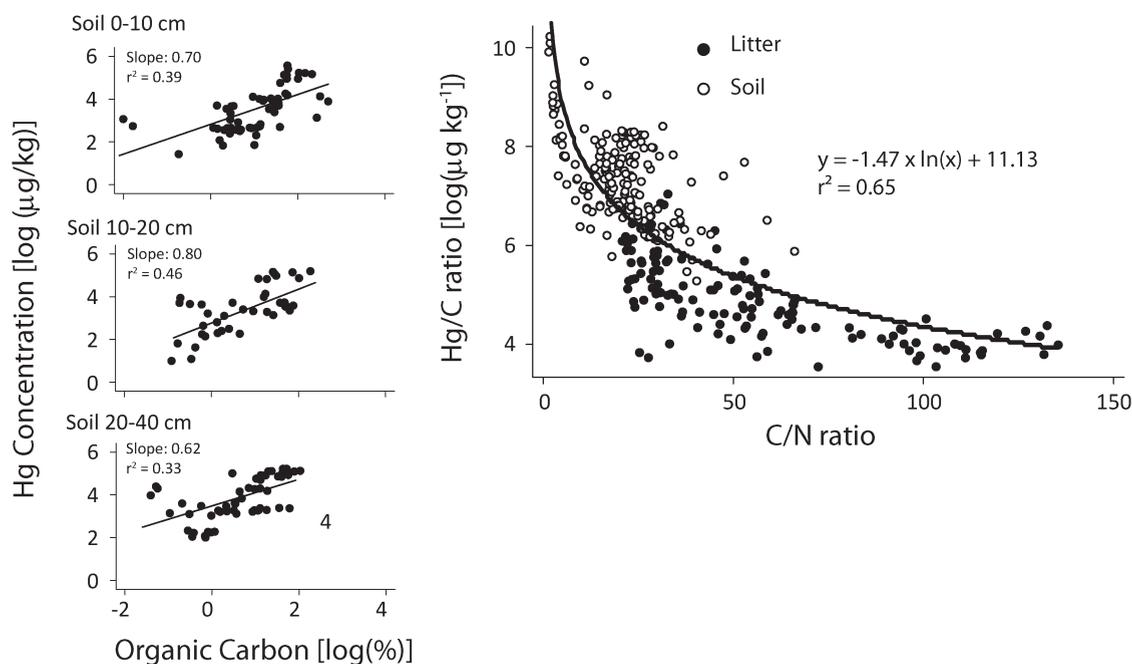

Figure 2. Hg to C relationships observed in soils and litter. A. Linear correlations between soil Hg and C concentrations for all samples taken from the 13 remote sites at depths of 0−10 cm, 10−20 cm, and 20−40 cm. We used multiregression analyses (with dummy variables) to test for differences in slopes and intercepts of regressions between Hg and C for various soil depths. B. Relationships between Hg/C ratios in all litter and soil samples (0−40 cm) and respective C/N ratios of samples.

the amount of Hg present (e.g., storage capacity of 2.4×10^{-2} g Hg g^{-1}C, based on presence of reduced sulfur groups). Using this number, the Hg sorption capacity calculated in our sites should be about 3 orders of magnitude higher than highest soil Hg/C levels in any of the 13 remote forest soils. If these calculations are correct, then it would be difficult to explain why soils high in C contents show correspondingly high Hg concentrations, since even C-poor soils should have enough sorption sites to retain the main bulk of atmospheric deposition.

It is possible that the dependence of soil Hg—and litter Hg—to organic C may reflect a historic legacy. We analyzed Hg/C ratios as a function of C/N ratios in litter and soils (Figure 2B; note that we used Hg/C ratios instead of concentrations to combine both soil and litter samples). C/N ratios are indicative of the degree of decomposition, where high C/N ratios generally represent fresh, undecomposed organic C while low C/N ratios are indicative of older, decomposed fractions.[34] Hg/C ratios (and Hg concentrations) exponentially increase with decreasing C/N ratios, for example increasing from 75 to 600 μg Hg g^{-1}C (or from 4.3 to 6.4 when log-transformed) when C/N decreased from 100 to 25. These patterns suggest that older, highly decomposed litter fractions show particularly high levels of Hg, which we attribute to a long-term (possibly decades to centuries) exposure to Hg depositions. An alternate, or supplemental, explanation for these patterns include "internal" processes: that during mineralization, Hg is efficiently retained in organic matter while C is lost, hence leading to increasing Hg/C levels.[18] We consider this process alone unlikely the sole reason for the strong Hg/C increases for two reasons: first, Hg concentrations and Hg/C ratios increase strongly (orders of magnitude) during even small C/N decreases; second, laboratory litter incubation studies

show pronounced Hg/C ratio increases particularly in the field but not in the laboratory,[18] indicating that Hg accumulation due to sorption may be more important than "internal" accumulation. Other possible reasons for increasing Hg and Hg/C levels in decomposing litter and C pools include selective Hg sorption to different organic matter fractions; for example, Hg may preferentially sorb to high-density metal-binding functional groups and show different selectivity to different hydrophilic fractions or molecular weights.[35−37] The hypothesis that soils and litter age may be an important determinant for Hg contents is supported by recent observations of increasing Hg concentrations with increasing time since occurrence of wildfires.[38] We propose that the effect of such "legacy" sequestration of atmospheric Hg deposition within C pools is strong enough to shape the spatial distribution of Hg at the continental scale.

The link between C and Hg may also shape latitudinal increases in Hg concentrations as soil and litter C stocks are known to increase at higher latitudes. For example, turnover rate of C decreases with increasing latitude,[39] which increases C residence time. Older organic C fractions at higher latitudes may hence contain higher Hg levels due to longer exposure time. However, latitudinal trends still persisted in our study when Hg concentrations were standardized per unit C (Hg/C ratios, Table 2), indicating that latitudinal gradients were not solely driven by higher C levels. Latitudinal gradients—often inversely related to gradients of emissions—have been reported for organic air pollutants and have been attributed to long-range transport and a "global distillation" or "grasshopper" effect,[40] whereby semivolatile pollutants preferentially condense and deposit at the higher, colder latitudes and preferentially evaporate at low latitudes.[41] It is unclear if Hg may be subject to such

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Table 2. Linear Regression Analyses between Total Hg, Hg/C Ratios, Soil Carbon (C), and Latitude

ecosystem component	Hg[*] and Latitude		Hg/C ratio[*] and latitude		soil C[*] and latitude		Hg[*] and soil C[*]	
	P	r^2	P	r^2	P	r^2	P	r^2
foliage	ns		ns					
litter Oi	0.04	0.08	ns					
litter Oe	<0.01	0.40	<0.01	0.37				
litter Oa	<0.01	0.21	<0.01	0.23				
soil 0—10	<0.01	0.57	<0.01	0.27	<0.01	0.14	<0.01	0.39
soil 10—20	<0.01	0.72	<0.01	0.17	<0.01	0.40	<0.01	0.46
soil 20—40	<0.01	0.60	0.04	0.08	<0.01	0.33	<0.01	0.33

[*] Log-transformed values; ns means not significant.

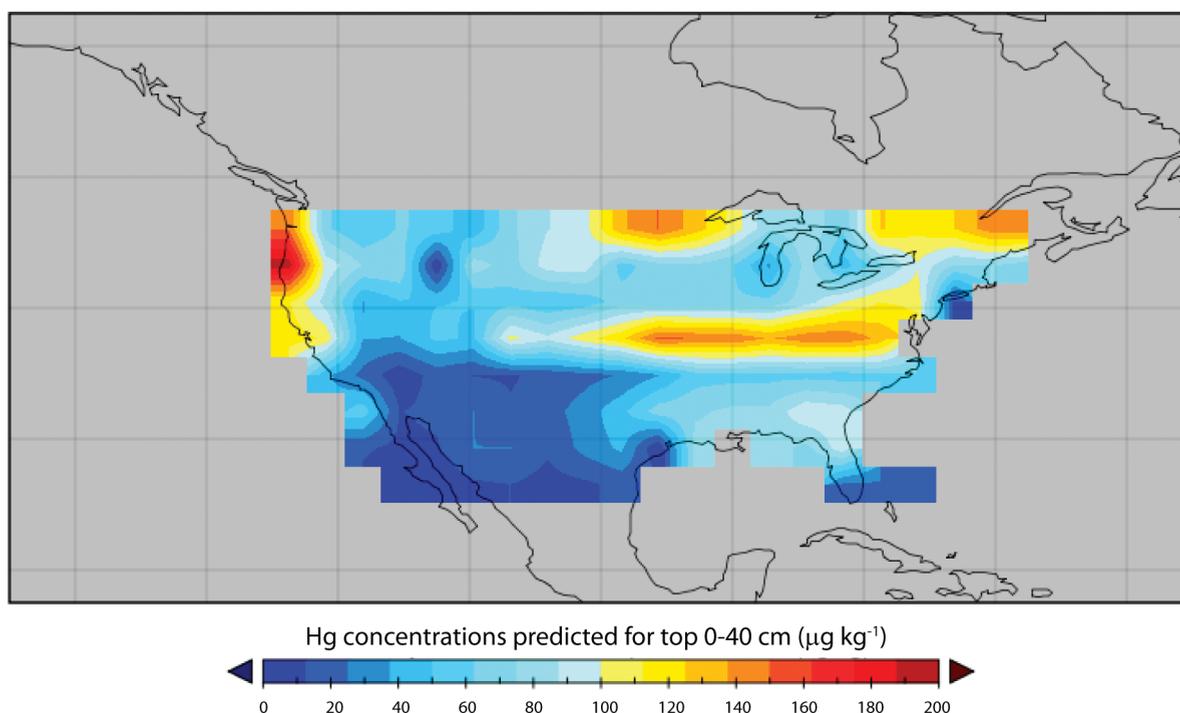Hg concentrations predicted for top 0-40 cm (µg kg^{-1})

Figure 3. Spatial extrapolation of top soil (0—40 cm) Hg concentrations based on multiregression modeling using independent variables latitude, precipitation, soil C content, and clay content ($r^2 = 0.88$; SI Table 2A). Underlying soil C distribution was calculated using the Community Land Model (CLM) with the Carnegie-Ames-Stanford Approach to simulate equilibrium carbon densities in soils. Note that due to grid resolution, the map extrapolates Hg concentrations also over areas with no soils such as the Great Lakes and along coastal waters.

"global distillation" given its complex redox chemistry in the atmosphere. However, instead of temperature effects, "grasshopping" of Hg may be linked to other factors such as solar and UV radiation which promote photoreduction of Hg and subsequent volatilization losses[42] and which show strong latitudinal gradients.

Positive correlation of Hg concentrations to annual precipitation—albeit not to estimated wet deposition—may be codetermined by higher soil C contents in sites of high precipitation. Other possible reasons include increased canopy wash-off (throughfall deposition) where precipitation is frequent. The positive correlation between clay content and soil Hg concentrations—and to a lesser degree to silt content (data not shown)—may be due to a combination of high C retention in clayey soils[34] and strong Hg sorption to clay minerals.[43]

Spatial Extrapolation of Hg Concentrations. Based on the multiregression model developed for soils ($r^2 = 0.89$), we extrapolated

data to predict top soil Hg soil concentrations across the United States. We used the Community Land Model (CLM) to calculate the distribution of soil C, and then implemented the three parameters latitude, precipitation, and soil texture (i.e., clay content) using national databases (see SI). The resulting spatial distribution of Hg concentrations (Figure 3), based on observations from our 13 remote forest sites, reflects the significant influence of latitude and shows high Hg concentrations in areas characterized by high precipitation and high soil carbon contents. As a result, most of the southwestern and western U.S., as well as the Intermountain West, is characterized by relatively low Hg concentrations. Northern sites show high Hg concentrations in agreement with observations,[44] and coastal areas along coasts and Midwestern areas show some of the highest levels due to a combination of high precipitation, high soil C, and northern location. Predicted spatial patterns agree well with soil Hg concentrations observed across the 13 sites (SI Table S2), but predicted spatial distribution patterns

are not in agreement with a map modeled by Smith-Downey et al.;[33] they predict low Hg concentrations at northern latitudes and highest Hg concentrations in western U.S. soils. It is possible that important model constraints of that mechanistic model, including re-emission estimates of depositions, Hg turnover rates, and Hg residence times, may cause discrepancies between our observations and predictions and theirs.

ASSOCIATED CONTENT

S **Supporting Information.** Detailed description of sites (in text, Figure S1 and Table S1), and description of spatial modeling. The secrtion also includes a table with detailed, site-averaged Hg concentrations of all sites and ecosystem components (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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