Environmental Science & Technology

Article

pubs.acs.org/est

Threshold Increases in Soil Lead and Mercury from Tropospheric Deposition Across an Elevational Gradient

Clare Stankwitz,[†,‡] James M. Kaste,*[,†] and Andrew J. Friedland[§]

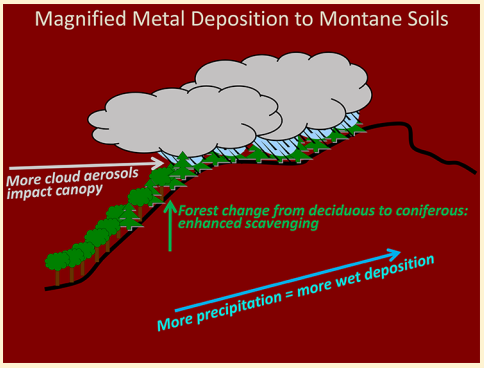
[†]Geology Department, College of William and Mary, Williamsburg, Virginia 23187, United States

[‡]The Cadmus Group, Inc., Arlington, Virginia 22209, United States

[§]Environmental Studies Program, Dartmouth College, Hanover, New Hampshire 03755, United States

Supporting Information

ABSTRACT: Atmospheric deposition is the primary mechanism by which remote ecosystems are contaminated, but few data sets show how fluxes change and control soil metal burdens at the landform scale. We present mercury (Hg), lead (^{210}Pb and total Pb), and cosmogenic beryllium-7 (^{7}Be) measurements in organic (O) soil horizons at high-resolution elevation intervals of ∼60 m from 540 to 1160 m on Camels Hump in northern Vermont, USA. Across this gradient, average O horizon Hg ranges from 0.99 mg m^{-2} in the low elevation deciduous forest zone to 7.6 mg m^{-2} in the higher elevation coniferous forest at 1030 m. We measure two pronounced threshold increases in soil metal burdens above 801 and 934 m, corresponding to the two most common altitudes of cloud base, which coincide with changes in vegetation species. Lead-210, a unique tracer of tropospheric deposition, also increased from 3200 Bq m^{-2} to 11 500 Bq m^{-2} in O horizons, exhibiting threshold responses at the same elevations as Hg and total Pb. Concentrations of ^{210}Pb and Hg in foliage double from 760 to 900 m elevation, indicating enhanced deposition across the transition from deciduous to coniferous forest. In contrast, ^{7}Be is constant across the entire elevational gradient because of its upper atmospheric source. This indicates that the effects of orographic precipitation have a smaller control on soil contaminant burdens than the coupled cloudwater deposition−vegetation scavenging effect in the presence of upwind sources. By measuring soil contaminants and unique tracers of atmospheric deposition, we show that tropospheric fluxes of Hg and Pb are higher by a factor of 2 in high-elevation coniferous forests than in adjacent lowlands. Total O horizon Hg and Pb burdens increase by over 4-fold with elevation because of the compounding effects of enhanced deposition and longer metal residence times at higher elevations (>50 years).



INTRODUCTION

Lead (Pb) and mercury (Hg) are two of the most widely dispersed heavy metals in the environment, historically having anthropogenic emissions to the atmosphere exceeding natural emissions by a factor of 3.9 or more.[1,2] The complex upper and lower atmospheric processes driving the transfer of these metals from the air to watersheds are dynamic and difficult to measure directly. Wet deposition (rain and snow) is one of the principal mechanisms delivering Pb and Hg from the atmosphere to landscapes. Strong convective storms are particularly effective at tapping reactive gaseous mercury (RGM) from the upper atmosphere, enhancing mercury deposition in certain regions.[3] In the presence of upwind pollution sources, however, cloudwater scavenges Pb- and Hg-bearing particulates from the lower troposphere, magnifying the air-to-land flux as droplets enriched in metals impact vegetation.[4,5] Furthermore, Hg is unique in that plants directly assimilate gaseous elemental mercury (GEM, as Hg^{0}) through stomates and across the cuticle;[6] Hg absorbed by forests is ultimately delivered to soils by litterfall.[7,8] Large-scale regional models aiming to project contaminant fluxes rely on a detailed understanding of how different atmospheric deposition processes are affected by biotic and abiotic landscape factors. Miller et al.[9] developed a Hg-specific model for both wet and dry deposition that estimated Hg deposition rates of ∼5 to >30 μg m^{-2} y^{-1} across rural watersheds in the northeastern United States. Later, Weathers et al.[10] modeled wet and dry deposition of nitrogen and sulfur across two national parks on scales of 100−2000 km^{2}. Both of these models rely on empirical relationships among precipitation, dry deposition, elevation, and vegetation to predict atmospheric deposition across relatively large regions.

Considerable uncertainties in our understanding of dry deposition rates for different chemical species, and limited measurements, especially for RGM and particulate-bound metals, have undermined the accuracy and resolution with which we can predict contaminant fluxes to landscapes.[9−11] The U.S. Hg Deposition Network currently monitors fluxes from precipitation only, which is probably one-third to one-half

Received: November 23, 2011
Revised: May 30, 2012
Accepted: July 3, 2012
Published: July 3, 2012

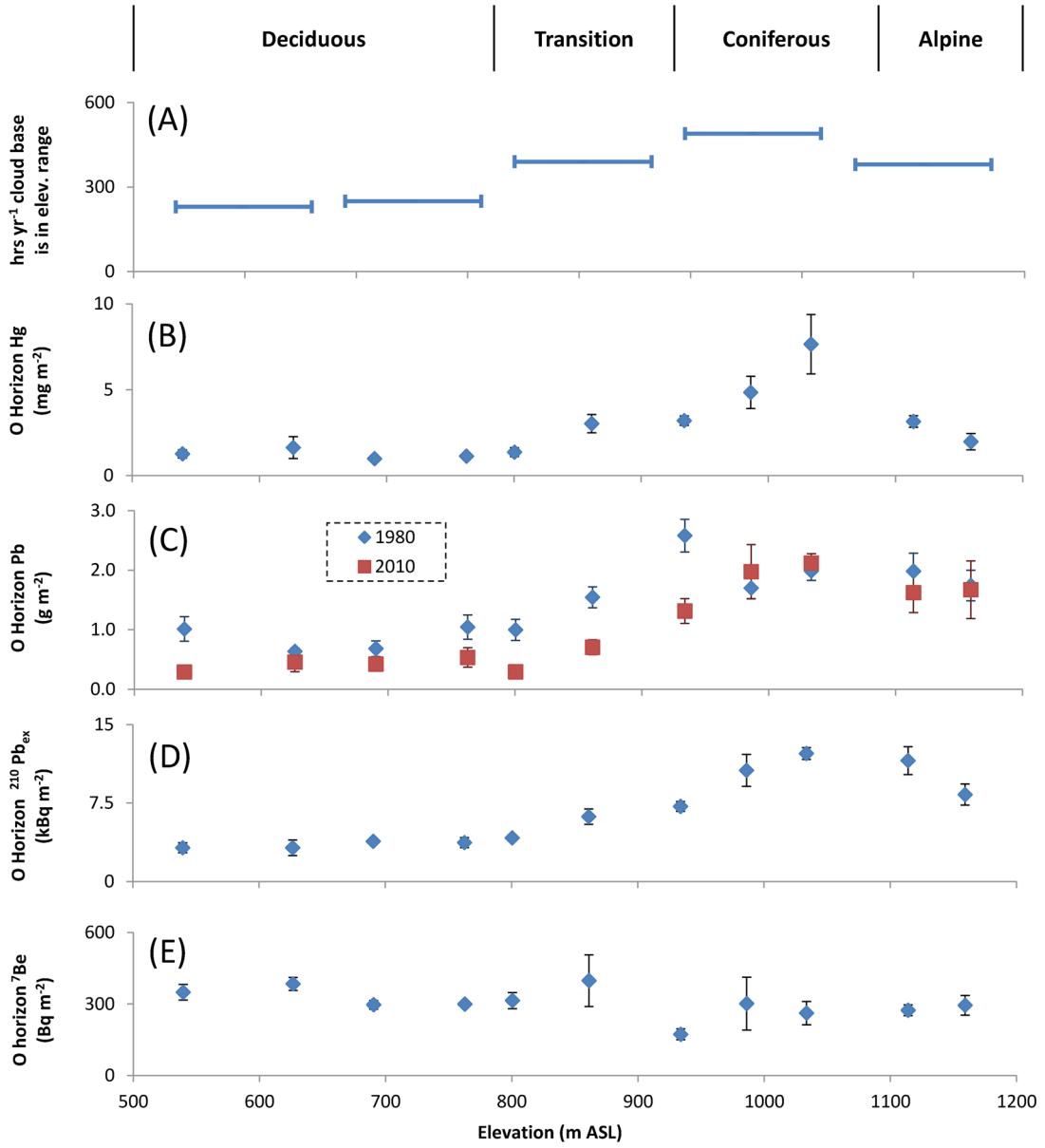


Figure 1. Atmospherically deposited elements in organic horizon soil along the elevation transect. Vegetation zones and cloudbase height data (A) are from Siccama.[26] Cloudbase height units are the number of hours per year that cloudbase was within the 122 m elevation interval represented by the bars. All metal and isotopic pool data are averages of samples collected within a forest stand along the transect; error bars give one standard error of the mean of these measurements. Except for the 1980 Pb data set,[20] all measurements are from samples collected in 2010.

of the total Hg deposition to forested regions,[9] and possibly an even smaller fraction of the total contaminant flux to montane environments. In a high-elevation spruce-fir forest in northern Vermont, direct collection of mercury deposition from cloudwater from August through October was measured to be 7.4 μg m^{-2}. This was about twice the Hg deposition from precipitation over that time period, and GEM uptake by the forest was not even measured.[4] Even with direct atmospheric collections, it is difficult to extrapolate meaningful fluxes, as the ratio of wet to dry deposited mercury can vary by a factor of 80 at a single site over the course of a few years.[12] Moreover, direct measurements of Hg in dry deposition and snowfall may not reflect the quantities that enter the soil reservoir, because substantial amounts may be reduced and re-emitted to the atmosphere as vapor or lost in the initial snowmelt pulse.[13,14]

Deposition patterns can vary widely within small areas, especially in montane environments, further increasing model uncertainties.[10] In some cases, soils can be treated as semiquantitative repositories of atmospheric deposition, which can be useful for calibrating deposition models and inferring processes.[15−19] This method can work if (i) the residence time of the element in soils is long enough to integrate several decades of deposition, and (ii) the element has an atmospheric source term that is significantly larger than (or resolvable from) any geogenic source term. Measurements of Pb in organic soils and mosses have been used for decades to infer atmospheric deposition[20] because the atmospheric flux from pollution was very large during the 20th century.[2] Radioactive fallout from cosmogenic processes or radon decay also provides unique tracers of atmospheric deposition, as specific isotopes that come exclusively from different parts of the atmosphere can be

identified in soils.[15] Because soil elemental pools can reflect decades to centuries of wet and dry deposition,[16,21] and direct atmospheric collections of these processes are technically challenging and resource intensive,[14] soil contaminant pools can be useful for characterizing atmospheric deposition on meaningful spatial and temporal scales.[16−18]

High-elevation landscapes receive significantly greater atmospheric deposition because of both orographic effects and enhanced cloudwater and dry deposition, but the specific relationship between metal deposition and elevation is not well-defined.[5,17,22,23] The most recent spatial study of Hg in soils identified latitude, precipitation, and carbon content as the best predictors of soil Hg burdens across 14 forests in the United States.[24] While elevation was tested as a potential predictor of soil Hg content, correlations between elevation and Hg were inconsistent, perhaps because of confounding factors across the diverse study sites.[24] Here, we measure pools of Hg, Pb, radon-derived ^{210}Pb ($T_{1/2}$ = 22.3 years), and cosmogenic ^{7}Be ($T_{1/2}$ = 53 days) in soils and vegetation along an elevational gradient on Camels Hump Mountain, Vermont, which has been a study site for vegetation, trace metal levels, and atmospheric deposition for nearly 30 years.[19,20,25,26] We make a novel collection of soil measurements at the landform scale, where cloudbase elevations and forest canopy changes have been documented,[26,27] providing a much higher-resolution examination of deposition patterns than would be logistically possible using direct collectors. Atmospheric ^{210}Pb is sourced from the diffusion of ^{222}Rn from land, making ^{210}Pb strongly enriched in cloudwater and aerosols in the lower troposphere,[15] whereas ^{7}Be is derived from cosmogenic processes occurring primarily above 5 km altitude.[28] Dry deposition of ^{7}Be is thus minimal compared with wet deposition, and atmospheric fluxes scale with rainfall rates.[29,30] Thus, soil ^{210}Pb traces cloudwater impaction, dry deposition, and orographic effects on a mountain, but ^{7}Be soil inventories reflect orographic effects only. Our analysis is based exclusively on measured soil inventories of these elements in the landscape, rather than the modeling of complex chemical and physical atmospheric parameters. By measuring tropospherically and stratospherically sourced tracers—^{210}Pb and ^{7}Be, respectively—in soil and live vegetation, our data show the relative significance of different depositional processes in delivering Hg and Pb across a single landform. Furthermore, we compare our measured O horizon metal pools to atmospheric fluxes calculated by others to evaluate O horizon residence times for these metals.

MATERIALS AND METHODS

Site Description and Sample Collection. Camels Hump, Vermont, USA (summit elevation 1244 m at 44°19′12″ N; 72°53′10″ W) is part of the main range of the Green Mountains. The mountain is on state-owned land and managed as an undeveloped park, so the soils and vegetation are relatively undisturbed. Soils are mostly sandy loam podzols developed on glacial till, with O horizons typically ranging in thickness from 4 cm at the lower elevations to 12 cm or more at higher elevations.[19,26] There is a well documented shift in forest canopy species from deciduous to coniferous with elevation on Camels Hump,[26] and we quantitatively collected five 225 cm^2 samples of the entire O horizon at 11 different forest stands across the ∼620 m elevation gradient on the western face of Camels Hump in August 2010 (Figure 1).

Our four lowest elevation stands (540−763 m) are in the deciduous forest zone, which is dominated by sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), and lesser amounts of yellow birch (*Betula alleghaniensis* Britt.). Sugar maple begins to drop rapidly with elevation above 775 m as yellow birch rises in abundance and mixes with red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*) in the transition forest. Transition zones have the highest species diversity,[26] and we sample two stands here, at 801 and 861 m in elevation. Above 900 m, balsam fir is the dominant canopy species (>50%), mixing with spruce and mountain paper birch (*Betula cordifolia*) in approximately equal parts in the coniferous zone. Above 1100 m is the alpine zone, where we maintain our highest two stands in a fir-dominated canopy (>80%).

Each of the 11 sampling sites was identified using a Garmin Colorado 400t hand-held GPS, and coordinates were transferred to ArcGIS to determine elevation (in meters above sea level) on a 1/3 arc second digital elevation model from the USGS Seamless Server. Mineral soil horizons, when present under organic horizons, were sampled in each main vegetation zone. A plastic core tube was used to collect samples of the upper 8−16 cm of mineral soil. Deciduous vegetation was sampled at 690 m, transition vegetation (deciduous and spruce) was sampled at 861 m, and coniferous vegetation was sampled at 934, 986, and 1034 m using a pole pruner. Vegetation samples for different tree species were taken by clipping 6−10 branches from the upper part of the canopy. Siccama and others determined the modal elevations of cloud base height and the dominant vegetation and precipitation patterns on Camels Hump, which we use here (Figure 1).[26,27] Other studies describe the soils at the site and atmospheric Pb pools in the same forest stands that we sampled which have been monitored for over 3 decades.[19−21,25]

Measurements of Hg, Pb, and Fallout Radionuclides in Soils and Vegetation. Soil and vegetation samples were air-dried in a low humidity environment for 2 weeks to prevent evaporative loss of Hg and then weighed to determine mass. Each of the five O horizon samples from each site and vegetation clippings from each species were homogenized separately in a Thomas-Wiley Mill to pass a 1-mm mesh. Total Hg analyses were done with Milestone Direct Mercury Analyzers (DMA-80) calibrated with solutions of Hg in nitric acid. Twenty mg portions of soil samples from each site and 80 mg portions of each vegetation sample were analyzed in duplicate pairs. A standard lake sediment reference material certified by the National Water Research Institute, Environment Canada (WQB-3), was used to check calibrations and was run in duplicate after every six sample analyses and in triplicate at the beginning and end of each sample set. Precision on replicate Hg measurements was typically <3%, and WQB-3 Hg analyses were always within the 95% confidence interval range certified for the material. For total Pb determination, 2 g of ground, oven-dried soil from each soil sample was ashed at 475 °C for 8 h. The ash residue was digested in 10 mL of a 1:1 by volume solution of nitric acid, filtered, and diluted to 60 mL with deionized water. Aliquots of each diluted digestion were analyzed for Pb content using plasma emission spectroscopy.[21] We used a certified pine needle reference material (High Purity Standards) to establish that recovery of Pb was always greater than 90%.

We measured ^{7}Be, ^{210}Pb, and ^{226}Ra in soil and vegetation samples by low-background gamma counting with shielded high-purity intrinsic germanium detectors. Samples were packed into 75 mL plastic containers and counted for 24−48 h to accumulate photopeaks at 46 keV (kilo electronvolts) for

^{210}Pb, 352 keV (^{214}Pb), and 477 keV (^{7}Be). Self-attenuation of the 46 keV photon was corrected using the point source transmission method.[31] We calculated atmospheric ^{210}Pb ($^{210}Pb_{ex}$, "in excess" of that supported by in situ production by ^{222}Rn) by subtracting the ^{226}Ra activity from ^{210}Pb. This correction is minimal since the ratio of total ^{210}Pb to ^{226}Ra in O horizon is usually greater than 100.[32] We calculated metal or radionuclide O horizon pools (amount per area) by multiplying the concentration of the measured analyte (in mg kg^{-1} or Bq kg^{-1}) by the mass of the O horizon (kg m^{-2}). Statistical evaluation of our metal and radionuclide pool data was performed using the Windows-based JMP Statistics program (SAS Institute Inc.). Our metal and radionuclide pool data failed (α = 0.05) a Shapiro–Wilk test for a normal distribution within each vegetation zone. All Tukey–Kramer analysis of variance (ANOVA) tests were thus performed on the log-transformed data (which passed the Shapiro–Wilk test) using a significance level of 0.05.

RESULTS AND DISCUSSION

O Horizon Metal Pools along an Elevational Gradient. Average O horizon Hg pools at each site range from a low of 0.99 mg m^{-2} in the deciduous zone to 7.65 mg m^{-2} at 1034 m elevation, just below the alpine vegetation zone (Figure 1). Within-site relative standard errors (n = 3 to n = 5) were typically 9–24%. Mercury pools are statistically indistinguishable using ANOVA across the four low-elevation deciduous zone sites; site averages here ranged from 0.99 to 1.64 mg m^{-2}. Between 801 and 861 m, Hg pools increase by a factor of over 2, from 1.37 to 3.03 mg m^{-2} where vegetation transitions from a deciduous dominated (maple–birch) canopy to a mix of conifer and deciduous species (fir–spruce–birch). Mercury pools continue to increase within the coniferous zone; we measured a 2.4-fold increase between 934 and 1034 m. The highest elevation site (1160 m) in the alpine zone had lower O horizon Hg pools than sites immediately below it (Figure 1).

Organic horizon Pb has a pattern similar to the Hg distribution (Figure 1). Again, the lowest elevation sites have nearly constant Pb amounts, and then increase by a factor of ~2 from 801 to 861 m in the transition forest zone. The sites at 986 and 1034 m in the coniferous forest have the highest Pb amounts measured in 2010, at 1.97 and 2.12 g m^{-2}. Because most of the lead deposition to soils in the northeast U.S. occurred during the 1960s and 1970s,[33] we present data here that document the distribution of Pb on Camels Hump in 1980[20] to give perspective on how soil lead changes across an elevation transect over 30 years in the absence of significant deposition. Lead pools measured in 1980, from samples collected and analyzed in an identical manner, were indistinguishable from those measured in 2010 using ANOVA of the four highest elevation sites. However, lower elevation sites had larger Pb pools in 1980 than in 2010 (>95% confidence in ANOVA). Other more detailed studies show that greater decomposition rates in the deciduous zone cause more leaching losses to the mineral soil below, which probably accounts for the lower-elevation differences seen from 1980 to 2010.[19,25] Despite the differences in the deciduous zone O horizon Pb amounts, the general pattern of Pb pools measured on Camels Hump in 1980 and 2010 are comparable (Figure 1).

Pools of $^{210}Pb_{ex}$ in O horizons have a pattern similar to both Hg and total Pb along this elevation gradient. The first four sites in the deciduous zone, ranging from 540 to 763 m elevation, have indistinguishable $^{210}Pb_{ex}$ pools. From 801 to 861 m, $^{210}Pb_{ex}$ increases by a factor of ~1.5, from 4170 to 6200 Bq m^{-2} as more conifer species mix with deciduous species in the transition zone. Similar to total Pb and Hg, the largest pool of $^{210}Pb_{ex}$ was found in the coniferous zone at 1034 m (12 200 Bq m^{-2}), nearly doubling from the transition zone, and we measured slight decreases in the highest elevation alpine soils (Figure 1). Unlike Hg, total Pb, and $^{210}Pb_{ex}$, cosmogenic ^{7}Be displays no pattern along the elevation transect and has no correlation with elevation; sites range from just 172 to 398 Bq ^{7}Be m^{-2}. Concentrations of Hg and Pb in the O horizon show a similar pattern of elevation responses (Supporting Information table) as the metal pool data plotted in Figure 1.

Atmospheric Deposition Thresholds and Processes. Mercury and Pb can be introduced to O horizons from either above (atmospheric source) or below (plant uptake from soil and subsequent deposition). Natural cycling processes can concentrate metals from mineral soils into vegetation, which eventually becomes litterfall, resulting in larger O horizon metal contents.[34] However, we are confident that the O horizon Hg and Pb pools that we measured at Camels Hump are primarily controlled by wet and dry deposition rather than below ground biological circulation or other natural processes for several reasons. First, detailed Pb isotopic ($^{207/206}$Pb) study at Camels Hump shows that O horizon Pb has a composition that reflects gasoline-derived Pb rather than natural sources,[25] and other studies have demonstrated that plants accumulate Hg mainly from the atmosphere and not from soils.[7] Moreover, the Hg and Pb pools that we measure in the O horizon are consistent with late-20th century deposition projected for the region,[19,33,35] and a large number of studies show that when landforms such as Camels Hump are in the presence of local upwind sources, atmospheric deposition is the dominant source of Hg and Pb to O horizons.[36−38]

We interpret our data set to primarily represent the coupled processes of cloudwater deposition and vegetation scavenging that magnify deposition of critical elements along an elevation gradient with threshold responses. We define threshold responses as a statistically significant (ANOVA) increase in the metal or radionuclide pool of a site from the sites below it. We use O horizon fallout radionuclide pools to evaluate and trace the contribution of lower tropospheric processes depositing pollutant Hg and Pb with increasing elevation (Figure 1). Soil ^{210}Pb serves as a tracer of cloudwater and aerosol deposition to forest canopies and orographic enhancements.[15] In contrast, because of its upper atmospheric source and short half-life, soil ^{7}Be inventories largely reflect changes in wet deposition along the transect.[29,30]

Soil inventories of $^{210}Pb_{ex}$ show two threshold increases on Camels Hump: one above 800 m, and a larger one above 934 m. These threshold responses correspond to the two most frequent cloud base elevations and the two most significant forest canopy changes on Camels Hump (Figure 1). Cloudwater formation concentrates aerosols containing contaminants,[22] and ^{210}Pb is highly enriched on 0.1–0.5 μm size aerosols in the lower troposphere.[39] Coniferous foliage has a higher leaf surface area and canopy density, and therefore more exposure to cloudwater when compared with deciduous trees, which lack foliage in the fall and winter months.[10,23] The discrete elevations where the cloud base intersects the land more frequently coincides with forest transitions from deciduous to coniferous species (Figure 1). This causes a magnification of metal deposition from the combined effect of

Table 1. Concentrations of Hg, $^{210}Pb_{ex}$, and ^{7}Be Measured in the Different Forest Canopy Species at Different Elevations on Camels Hump[a]

vegetation zone	number of samples	species	elevation (m)	Hg (ng g^{-1})	$^{210}Pb_{ex}$ (Bq kg^{-1})	^{7}Be (Bq kg^{-1})
deciduous	2	*Betula*	690	8.60	82.6	214
		Acer		13.9	83.5	135
transition	3	*Betula*	861	12.3	53.9	137
		Picea		17.3	63.7	164
		Picea	934	23.5	124	202
coniferous	2	*Picea*	986	20.1	225	219
		Picea	1034	20.4	159	213

[a]Each sample represents 6−10 branches that were clipped from the upper canopy and homogenized. Typical measurement errors are ≤5% or less for the Hg and ^{210}Pb, and ≤10% for ^{7}Be.

more cloudwater deposition and enhanced scavenging of gases and aerosols by the coniferous species.

Different tree species absorb GEM from the atmosphere at different rates,[6] which could affect soil Hg pools that we measured across the elevation gradient, but there is no direct evidence to support this process at Camels Hump. One study reported that deciduous trees have higher GEM uptake than coniferous trees,[40] which would cause the opposite pattern of O horizon Hg from what we observed here (Figure 1). Instead, we suggest that the effect of the forest canopy shift to a more conifer-rich composition with elevation serves to enhance the scavenging of RGM, cloudwater enriched in metals, and/or aerosol-bound metals. Larger concentrations and fluxes of Hg are typically measured from coniferous throughfall compared with deciduous throughfall or open collectors (under no canopy), which is attributed to the wash off of dry deposited Hg, probably as RGM.[38,41]

The concept that landscape position, which controls both vegetation structure and cloudwater contact time (Figure 1), drives a deposition gradient for both Hg and Pb is supported by our observation that the threshold responses of Hg, ^{210}Pb, and total Pb are found at identical elevations and the magnitudes of the responses are similar. Across the entire elevation gradient, there is a significant correlation between O horizon Hg and ^{210}Pb amounts (r^2 = 0.50; p < 0.001), and, interestingly, the correlation is strongest in the transition stands (n = 10, r^2 = 0.96). The transition forest zone is the section of the mountain with the highest tree species diversity,[26] where there would be localized patches of coniferous trees that magnify deposition of both ^{210}Pb and Hg to soils, but other factors (e.g., O horizon thickness, composition) remain similar. It is also possible that ^{210}Pb and Pb are both proxies for aerosols that facilitate the conversion of GEM to RGM, or serve to scavenge RGM from the atmosphere. This mechanism could be responsible for the correlations that we document in soils here and previously documented correlations between Hg and ^{210}Pb measured in rainfall in remote locations.[42]

Regarding the potential contribution of orographic processes to soil metal burdens, Siccama[26] found that precipitation on Camels Hump increases linearly with elevation at a rate of 2.9 cm per 100 m. Because this increase is linear, it cannot explain the abrupt increases in soil Hg that we measured above 801 and 934 m, nor the drop in soil Hg below 1034 m. A linear function cannot explain our Pb and ^{210}Pb distributions (Figure 1). The ^{7}Be data further indicate that orographic effects on metal pools in the soils are minimal across the landform, because there are no differences in the soil inventories of ^{7}Be between the low and high elevation sites. While our data indicate that the orographic effects are small, it is possible that increasing precipitation rates contribute to a slight and gradual overall increase in Hg and Pb deposition with elevation. However, upper tropospheric and lower stratospheric processes, such as strongly convective storm systems, do not appear to be the main processes influencing the pattern of soil metal pools on Camels Hump because soil Hg and Pb are correlated with soil ^{210}Pb, not with soil ^{7}Be.

Our approach of utilizing elemental pools in soil to trace deposition mechanisms is particularly useful for understanding subtle changes in contaminant loading to a landform. Most notably, we document a decrease in Hg deposition in the alpine zone that is evident at the 1114 and 1159 m sites. This decrease from the coniferous vegetation zone was significant for Hg, but not Pb (ANOVA). We theorize the decrease is due to lower forest biomass in the subalpine region, leading to less Hg scavenging by vegetation and thus less Hg input to the forest floor. Alternatively, high velocity airflow near the summit has been shown to cause a drop in precipitation in certain cases, which could cause a drop in total atmospheric deposition locally.[43] A large fraction of Hg deposition in snowfall (which would be highest near the summit) is lost as the gaseous species before it is absorbed by soils,[13] which is another possible explanation for the decrease we observe at the two highest elevation sites.

While cloudwater has been documented to contain high concentrations of acidic aerosols and metals,[4,22,23,44] our work is the first to show the relative importance of enhanced cloudwater and dry deposition in controlling the accumulation of Hg and Pb in soils at different landscape positions. This finding is especially valuable given the large degree of uncertainty associated with projecting total Hg fluxes to vegetated surfaces.[9,11,45] Measurements of atmospheric elements in canopy vegetation provide valuable supporting data for our conclusions (Table 1). From these data, it is evident that $^{210}Pb_{ex}$ and Hg concentrations in vegetation follow roughly the same pattern as the pools of these elements in organic horizon soils. Concentrations of these elements in live vegetation record metal transfers from the atmosphere by wet, dry, or passive accumulation on the canopy.[46] In many cases, the O horizons that we measured here represent the total soil metal and radionuclide pools, because the O horizons commonly lie directly on blocks of glacial till, bedrock ledges, or large roots. However, by considering the limited mineral soil pools of $^{210}Pb_{ex}$ and Hg we measured in the context of the larger O horizon pools for each metal (Tables 2 and 3), the total pools (O horizon + mineral soil) are largest in the upper reaches of the transition forest and the coniferous zone. At the higher elevations, it appears that the greater O horizon thicknesses (O horizon mass data in Supporting Information)

Table 2. Pools of Atmospheric Elements of Hg and $^{210}Pb_{ex}$ Measured in Upper Mineral Soil Cores Collected at Camels Hump

vegetation zone	mean Hg (mg Hg m^{-2})	Hg standard error	mean $^{210}Pb_{ex}$ (Bq m^{-2})	$^{210}Pb_{ex}$ standard error
deciduous (n = 2)	5.84	1.50	520	31.1
transition (n = 2)	10.4	3.25	2460	1240
coniferous (n = 2 for Hg; n = 3 for $^{210}Pb_{ex}$)	5.66	3.39	1890	1460

relative to lower elevation sites may have inhibited leaching of Hg from the O horizon to mineral soils, a phenomenon for Pb discussed in Kaste et al.[25]

Residence Times of Hg and Pb in O Horizons. Upland soils are a potential source of metals to aquatic ecosystems, so it is critical to understand the residence times of Hg and Pb in O horizons in order to predict the ultimate fate and potential effects of these toxins in ecosystems. Furthermore, an understanding of residence times is essential to effectively relate O horizon metal burdens to historical atmospheric fluxes. The increasing Hg and Pb pools that we quantify with elevation are probably caused by a combination of magnified atmospheric inputs and differences in O horizon retention times, as loss rates of Pb and Hg by leaching and volatile losses of Hg could be different along the transect.

Organic horizons underlying coniferous stands at Camels Hump are large (up to 20 cm in some cases; mass data available in Supporting Information), so one could argue that the increasing metal pools are simply caused by increasing O horizon size with elevation. However, the magnitude of the O horizon mass change is less than half of the metal pool increase on the transect (Supporting Information table). Metal pools in high-elevation coniferous O horizons are greater than the deciduous O horizon metal pools on average by more than 4-fold (Table 3), yet coniferous zone O horizons are on average larger by less than a factor of 2 (Supporting Information table). Moreover, O horizon Hg and Pb concentrations, which would be unaffected by thickness or mass, show the same increasing patterns (Supporting Information table) with elevation as the metal pools. We acknowledge that there have likely been more leaching losses from the thinner lower elevation O horizons, a process that may cause a fraction of the metal pool gradients we show. However, the 1980 Pb data reflect less postdeposition leaching, because those measurements were made closer to the peak atmospheric deposition.[19,33] We note that the ratio of the 1980 coniferous O horizon Pb to deciduous O horizon Pb is approximately 2.5 (Table 3), which nearly matches the ^{210}Pb ratio between the vegetation zones measured in the entire soil profile (2.6) by a previous study[25] and is thus arguably more representative of the atmospheric deposition gradient with elevation.

We also acknowledge the potential for O horizon Hg loss due to leaching or re-emission from soil or vegetation, the potential for which is demonstrated in Lindberg et al.[47] and Ericksen and Gustin,[7] among others. However, the O horizon Hg pools we report here appear to reflect at least several decades of deposition. Perry et al.[35] estimated Hg deposition for northern Vermont using lake sediment records, carefully correcting for variation in sedimentation rates and other factors. Deposition rates in Lake Wheeler and Lake Carmi, Vermont—the two sites closest to Camels Hump—have been between 5 and 20 μg m^{-2} yr^{-1} from 1975 to 1990. These values likely represent wet deposition only, and we would expect forests to receive higher fluxes than a lake because of dry deposition. Assuming that wet deposition represents one-third of the Hg flux,[9] and adopting a conservative wet flux of 12.5 μg Hg m^{-2} yr^{-1} to Northern Vermont over the past 30 years,[35] we would expect a total (wet + dry) accumulated Hg pool of 1.13 mg Hg m^{-2}. This value is lower than the average O horizon pool of Hg we measured in the deciduous zone, and barely 20% of the average Hg pool in coniferous zone O horizons on Camels Hump (Table 3). While we cannot calculate precise residence times for Hg in soils, we argue that our measured pools reflect a relatively long period (>3 decades) of atmospheric deposition. Re-emission or leaching of Hg from organic soils on Camels Hump Mountain are not likely to affect the interpretations that we make here relating soil pools to atmospheric deposition thresholds, perhaps because upland soils have a relatively small fraction of Hg loss by volatilization each year.[48]

We have a more precise understanding of historical Pb deposition and Pb residence times in O horizons at Camels Hump: the average Pb pool that we measured in 2010 in the high elevation coniferous zone was 1.76 g m^{-2}, which is about half of the 3.5 g m^{-2} of industrial era (1800–1990) Pb deposition that Miller et al. projected for high elevation Camels Hump.[19] We observed no significant change in soil Pb pools at high elevation between 1980 and 2010. Taken together, these data are broadly consistent with the 150-year forest floor Pb response time (number of years needed for an e-fold reduction) calculated using ^{210}Pb transport modeling.[25] In the deciduous zone, however, we measured a reduction in O horizon Pb of 50% between 1980 and 2010 (Table 3), indicating a first order loss rate (k) of 0.017 y^{-1}, yielding a forest floor Pb response time ($1/k$) of 59 years, which matches previous model estimates.[25] We would thus expect O horizon Pb pools to be larger by a factor of 2.5 in the higher elevation coniferous zone from solely residence time effects given steady-state conditions,[25] but if inputs are greater than losses, the retention time effect factor on O horizon pools would decrease. Studies in New England have shown that the transport of Hg and Pb in watersheds may be limited by the movement of particulate

Table 3. Mean (± Standard Error) O Horizon Pb Measured in 1980 and 2010, and O Horizon Hg Measured in 2010 in the Deciduous and Coniferous Zones on Camels Hump[a]

vegetation zone (elevation)	1980 Pb (g m^{-2})	2010 Pb (g m^{-2})	2010 Hg (mg m^{-2})
deciduous (540–763 m)	0.843 ± 0.083 n = 20	0.422 ± 0.059 n = 18	1.26 ± 0.16 n = 13
coniferous (934–1034 m)	2.09 ± 0.15 n = 15	1.80 ± 0.19 n = 15	5.38 ± 0.82 n = 14
coniferous/deciduous	2.47	4.27	4.27

[a]Standard errors (1 SE) are given. The last row gives the ratio of the coniferous zone metal pools to the deciduous zone pools in 1980 (Pb only) and 2010 (Hg and Pb).

organic matter,[19,32,49] and if similar processes regulate losses of both metals from the O horizon, then we would expect a similar scaling factor (2.5) of O horizon pools between the forest zones from retention time effects only. However, because O horizons at Camels Hump are probably gaining Hg more rapidly than losing it,[49] retention time effects would be even smaller. The O horizon mass data are further evidence that retention effects are likely to explain at most half of the increasing metal pools with elevation (Figure 1, Table 3) and cannot be solely responsible for the magnitude of the metal pool thresholds. Taken together, our analysis indicates that enhanced cloudwater deposition and vegetation scavenging of aerosols and reactive gases, which is controlled by landscape position, magnify metal deposition by a factor of approximately 2, but further work is needed to quantify the various accumulation pathways.

While Hg has a wider range of chemical species present in both the atmosphere and soils than Pb does, bulk O horizon Hg and Pb pools are regulated by related depositional processes and similar retention time scales across the elevation gradient. There is mounting evidence that both Pb and ^{210}Pb are effective at tracing a scavenging process related to the removal of gaseous Hg from the atmosphere,[42] a process that may in part cause the similar distributions we document here. In the presence of local upwind sources, O horizon metal burdens exhibit threshold increases where the land surface intersects the two modal cloud base elevations. Threshold responses evident in the Hg and Pb pools are caused by more focused tropospheric deposition as cloudwater and dry deposition become more prevalent and efficient with the shift from deciduous broad leaf species to coniferous species. Over time, differences in O horizon contaminant pools between low elevation and high elevation sites are magnified because of the more rapid O horizon losses in the low elevation deciduous zone.

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental data table. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jmkaste@wm.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Ellen Stofan Fund and the Mercury Sustained Global Inquiry Group at the College of William & Mary, The Jeffress Memorial Trust, and instrumentation provided by NSF EAR-0650533 to J.M.K. We thank Paul Zietz, Dartmouth Environmental Studies, for assistance with the laboratory analysis, and Daniel Cristol, College of William and Mary, and Mike Newman, Virginia Institute of Marine Science, for providing access to the DMA instruments. Justin Richardson commented on an earlier version of this manuscript, and The Vermont Agency of Natural Resources granted a sampling permit for Camels Hump.

■ REFERENCES

(1) Streets, D. G.; Devane, M. K.; Lu, Z. F.; Bond, T. C.; Sunderland, E. M.; Jacob, D. J. All-Time Releases of Mercury to the Atmosphere from Human Activities. *Environ. Sci. Technol.* **2011**, *45*, 10485−10491.

(2) Galloway, J. N.; Thornton, J. D.; Norton, S. A.; Volchok, H. L.; McLean, R. A. N. Trace-metals in atmospheric deposition - A review and assessment. *Atmos. Environ.* **1982**, *16*, 1677−1700.

(3) Guentzel, J. L.; Landing, W. M.; Gill, G. A.; Pollman, C. D. Processes influencing rainfall deposition of mercury in Florida. *Environ. Sci. Technol.* **2001**, *35*, 863−873.

(4) Lawson, S. T.; Scherbatskoy, T. D.; Malcolm, E. G.; Keeler, G. J. Cloud water and throughfall deposition of mercury and trace elements in a high elevation spruce-fir forest at Mt. Mansfield, Vermont. *J. Environ. Monit.* **2003**, *5*, 578−583.

(5) Reiners, W. A.; Marks, R. H.; Vitousek, P. M. Heavy metals in subalpine and alpine soils of New Hampshire. *Oikos* **1975**, *26*, 264−275.

(6) Stamenkovic, J.; Gustin, M. S. Nonstomatal versus Stomatal Uptake of Atmospheric Mercury. *Environ. Sci. Technol.* **2009**, *43*, 1367−1372.

(7) Ericksen, J. A.; Gustin, M. S.; Schorran, D. E.; Johnson, D. W.; Lindberg, S. E.; Coleman, J. S. Accumulation of atmospheric mercury in forest foliage. *Atmos. Environ.* **2003**, *37*, 1613−1622.

(8) St Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Hall, B. D.; Rolfhus, K. R.; Scott, K. J.; Lindberg, S. E.; Dong, W. Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. *Environ. Sci. Technol.* **2001**, *35*, 3089−3098.

(9) Miller, E. K.; Vanarsdale, A.; Keeler, G. J.; Chalmers, A.; Poissant, L.; Kamman, N. C.; Brulotte, R. Estimation and mapping of wet and dry mercury deposition across northeastern North America. *Ecotoxicology* **2005**, *14*, 53−70.

(10) Weathers, K. C.; Simkin, S. M.; Lovett, G. M.; Lindberg, S. E. Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecol. Appl.* **2006**, *16*, 1590−1607.

(11) Lin, C. J.; Pongprueksa, P.; Lindberg, S. E.; Pehkonen, S. O.; Byun, D.; Jang, C. Scientific uncertainties in atmospheric mercury models I: Model science evaluation. *Atmos. Environ.* **2006**, *40*, 2911−2928.

(12) Lombard, M. A. S.; Bryce, J. G.; Mao, H.; Talbot, R. Mercury deposition in Southern New Hampshire, 2006−2009. *Atmos. Chem. Phys.* **2011**, *11*, 7657−7668.

(13) Fain, X.; Grangeon, S.; Bahlmann, E.; Fritsche, J.; Obrist, D.; Dommergue, A.; Ferrari, C. P.; Cairns, W.; Ebinghaus, R.; Barbante, C.; Cescon, P.; Boutron, C. Diurnal production of gaseous mercury in the alpine snowpack before snowmelt. *J. Geophys. Res.-Atmos.* **2007**, *112*.

(14) Graydon, J. A.; St Louis, V. L.; Lindberg, S. E.; Hintelmann, H.; Krabbenhoft, D. P. Investigation of mercury exchange between forest canopy vegetation and the atmosphere using a new dynamic chamber. *Environ. Sci. Technol.* **2006**, *40*, 4680−4688.

(15) Graustein, W. C.; Turekian, K. K. The effects of forests and topography on the deposition of sub-micrometer aerosols measured by Pb-210 and Cesium-137 in soils. *Agric. For. Meteorol.* **1989**, *47*, 199−220.

(16) Klaminder, J.; Bindler, R.; Rydberg, J.; Renberg, I. Is there a chronological record of atmospheric mercury and lead deposition preserved in the mor layer (O-horizon) of boreal forest soils? *Geochim. Cosmochim. Acta* **2008**, *72*, 703−712.

(17) Liptzin, D.; Seastedt, T. R. Regional and local patterns of soil nutrients at Rocky Mountain treelines. *Geoderma* **2010**, *160*, 208−217.

(18) Weathers, K. C.; Lovett, G. M.; Likens, G. E. Cloud deposition to a Spruce Forest edge. *Atmos. Environ.* **1995**, *29*, 665−672.

(19) Miller, E. K.; Friedland, A. J. Lead migration in forest soils - repsonse to changing atmospheric inputs. *Environ. Sci. Technol.* **1994**, *28*, 662−669.

(20) Friedland, A. J.; Johnson, A. H.; Siccama, T. G. Trace metal content of the forest floor in the Green Mountains of Vermont. *Water, Air, Soil Pollut.* **1984**, *21*, 161−170.

(21) Kaste, J. M.; Bostick, B. C.; Friedland, A. J.; Schroth, A. W.; Siccama, T. G. Fate and speciation of gasoline-derived lead in organic horizons of the northeastern USA. *Soil Sci. Soc. Am. J.* **2006**, *70*, 1688−1698.
(22) Miller, E. K.; Friedland, A. J.; Arons, E. A.; Mohnen, V. A.; Battles, J. J.; Panek, J. A.; Kadlecek, J.; Johnson, A. H. Atmospheric deposition to forests along an elevational gradient at Whiteface Mountain, NY, USA. *Atmos. Environ., Part A* **1993**, *27*, 2121−2136.
(23) Lovett, G. M.; Kinsman, J. D. Atmospheric pollutant deposition to high-elevation ecosystems. *Atmos. Environ., Part A* **1990**, *24*, 2767−2786.
(24) Obrist, D.; Johnson, D. W.; Lindberg, S. E.; Luo, Y.; Hararuk, O.; Bracho, R.; Battles, J. J.; Dail, D. B.; Edmonds, R. L.; Monson, R. K.; Ollinger, S. V.; Pallardy, S. G.; Pregitzer, K. S.; Todd, D. E. Mercury Distribution Across 14 US Forests. Part I: Spatial Patterns of Concentrations in Biomass, Litter, and Soils. *Environ. Sci. Technol.* **2011**, *45*, 3974−3981.
(25) Kaste, J. M.; Friedland, A. J.; Sturup, S. Using stable and radioactive isotopes to trace atmospherically deposited Pb in montane forest soils. *Environ. Sci. Technol.* **2003**, *37*, 3560−3567.
(26) Siccama, T. G. Vegetation, soil, and climate on the Green Mountains of Vermont. *Ecol. Monogr.* **1974**, *44*, 325−349.
(27) Richardson, A. D.; Denny, E. G.; Siccama, T. G.; Lee, X. Evidence for a rising cloud ceiling in eastern North America. *J. Clim.* **2003**, *16*, 2093−2098.
(28) Lal, D.; Peters, B., Cosmic Ray Produced Radioactivity on the Earth. In *Handbuch Physik 2*, 1967; Vol. *46*, pp 551−601.
(29) Wallbrink, P. J.; Murray, A. S. Distribution and variability of Be-7 in soils under different surface cover conditions and its potential for describing soil redistribution processes. *Water Resour. Res.* **1996**, *32*, 467−476.
(30) Whiting, P. J.; Matisoff, G.; Fornes, W. Suspended sediment sources and transport distances in the Yellowstone River basin. *Geol. Soc. Am. Bull.* **2005**, *117*, 515−529.
(31) Cutshall, N. H.; Larsen, I. L.; Olsen, C. R. Direct analysis of Pb-210 in sediment samples - self absorption corrections. *Nucl. Instrum. Methods Phys. Res.* **1983**, *206*, 309−312.
(32) Kaste, J. M.; Bostick, B. C.; Heimsath, A. M.; Steinnes, E.; Friedland, A. J. Using atmospheric fallout to date organic horizon layers and quantify metal dynamics during decomposition. *Geochim. Cosmochim. Acta* **2011**, *75*, 1642−1661.
(33) Johnson, C. E.; Siccama, T. G.; Driscoll, C. T.; Likens, G. E.; Moeller, R. E. Changes in lead biogeochemistry in response to decreasing atmospheric inputs. *Ecol. Appl.* **1995**, *5*, 813−822.
(34) Reimann, C.; Arnoldussen, A.; Englmaier, P.; Filzmoser, P.; Finne, T. E.; Garrett, R. G.; Koller, F.; Nordgulen, O. Element concentrations and variations along a 120-km transect in southern Norway - Anthropogenic vs. geogenic vs. biogenic element sources and cycles. *Appl. Geochem.* **2007**, *22*, 851−871.
(35) Perry, E.; Norton, S. A.; Kamman, N. C.; Lorey, P. M.; Driscoll, C. T. Deconstruction of historic mercury accumulation in lake sediments, northeastern United States. *Ecotoxicology* **2005**, *14*, 85−99.
(36) Klaminder, J.; Farmer, J. G.; MacKenzie, A. B. The origin of lead in the organic horizon of tundra soils: Atmospheric deposition, plant translocation from the mineral soil or soil mineral mixing? *Sci. Total Environ.* **2011**, *409*, 4344−4350.
(37) Klaminder, J.; Bindler, R.; Emteryd, O.; Renberg, I. Uptake and recycling of lead by boreal forest plants: Quantitative estimates from a site in northern Sweden. *Geochim. Cosmochim. Acta* **2005**, *69*, 2485−2496.
(38) Witt, E. L.; Kolka, R. K.; Nater, E. A.; Wickman, T. R. Influence of the Forest Canopy on Total and Methyl Mercury Deposition in the Boreal Forest. *Water, Air, Soil Pollut.* **2009**, *199*, 3−11.
(39) Sanak, J.; Gaudry, A.; Lambert, G. Size distribution of Pb-210 aerosols over oceans. *Geophys. Res. Lett.* **1981**, *8*, 1067−1069.
(40) Millhollen, A. G.; Gustin, M. S.; Obrist, D. Foliar mercury accumulation and exchange for three tree species. *Environ. Sci. Technol.* **2006**, *40*, 6001−6006.
(41) Rea, A. W.; Lindberg, S. E.; Keeler, G. J. Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall. *Atmos. Environ.* **2001**, *35*, 3453−3462.
(42) Lamborg, C. H.; Fitzgerald, W. F.; Graustein, W. C.; Turekian, K. K. An examination of the atmospheric chemistry of mercury using Pb-210 and Be-7. *J. Atmos. Chem.* **2000**, *36*, 325−338.
(43) Schlesinger, W. H.; Reiners, W. A.; Knopman, D. S. Heavy metal concentrations and deposition in bulk precipitation in montane ecosystems in New Hampshire, U.S.A. *Environ. Pollut.* **1974**, *6*, 39−47.
(44) Lovett, G. M.; Reiners, W. A.; Olson, R. K. Cloud droplet deposition in subalpine balsam fir forests - hydrological and chemical inputs. *Science* **1982**, *218*, 1303−1304.
(45) Zhang, L. M.; Wright, L. P.; Blanchard, P. A review of current knowledge concerning dry deposition of atmospheric mercury. *Atmos. Environ.* **2009**, *43*, 5853−5864.
(46) Russell, I. J.; Choquette, C. E.; Fang, S. L.; Dundulis, W. P.; Pao, A. A.; Pszenny, A. A. P. Forest vegetation as a sink for atmospheric particulates - quantitative studies in rain and dry deposition. *J. Geophys. Res.* **1981**, *86*, 5247−5363.
(47) Lindberg, S. E.; Meyers, T. P.; Taylor, G. E.; Turner, R. R.; Schroeder, W. H. Atmosphere-surface exchange of mercury in a forest - results of modeling and gradient approaches. *J. Geophys. Res.-Atmos.* **1992**, *97*, 2519−2528.
(48) Graydon, J. A.; Louis, V. L. S.; Hintelmann, H.; Lindberg, S. E.; Sandilands, K. A.; Rudd, J. W. M.; Kelly, C. A.; Hall, B. D.; Mowat, L. D. Long-Term Wet and Dry Deposition of Total and Methyl Mercury in the Remote Boreal Ecoregion of Canada. *Environ. Sci. Technol.* **2008**, *42*, 8345−8351.
(49) Scherbatskoy, T.; Shanley, J. B.; Keeler, G. J. Factors controlling mercury transport in an upland forested catchment. *Water, Air, Soil Pollut.* **1998**, *105*, 427−438.

Supplementary Information Stankwitz et al

Stand I.D.	Elevation m asl	O horizon Mass oven dry kg/m2	Mass Standard Error oven dry kg/m2	Hg Concentration mg/kg	Hg Standard Error mg/kg	Pb Concentration mg/kg	Pb Standard Error mg/kg
CH7	540	5.92	0.94	0.197	0.015	46.9	7.2
CH8	627	10.23	2.05	0.149	0.025	40.9	9.1
CH9	690	7.20	1.05	0.142	0.021	56.0	8.5
CH10	763	7.61	1.26	0.168	0.003	65.4	8.1
CH11	801	6.17	0.87	0.220	0.019	46.1	6.5
CH12	861	11.85	2.24	0.245	0.010	61.1	3.8
CH13	934	9.55	0.80	0.355	0.039	138.1	23.1
CH14	986	14.17	1.31	0.347	0.051	136.1	23.2
CH15	1034	19.48	3.87	0.386	0.018	124.4	19.6
CH16	1114	9.98	0.56	0.293	0.020	159.6	18.7
CH17	1159	7.27	2.05	0.272	0.045	229.7	64.0

O horizon masses are oven-dried (105 degrees Celsius for 2 days)

Hg and Pb concentrations are mg of metal per kg (oven-dried) O horizon

m asl meters above sea-level

All data were collected in August 2010