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Abstract

In acid-impacted forests, lime has been applied to neutralize acidity and mitigate acidification of soil and surface waters. However, few studies have evaluated the effects of liming on watershed mercury processes and transport. I investigated the effects of liming on mercury, organic carbon, and sulfur concentrations and stocks in forest soil 19 years after the application of lime to the Woods Lake Watershed, Adirondack Park, New York, USA (42^{0}52’ N, 71^{0}58’ W). The mercury, organic carbon, and sulfur stocks were significantly greater in the forest floor of limed areas (24.5 vs. 11.1 Hg g/ha for Oe and 31.6 vs. 14.6 Hg g/ha for Oa; 36.8 vs. 18.6 OC t/ha for Oe and 33.1 vs. 12.7 OC t/ha for Oa; 0.17 vs. 0.09 S t/ha for Oe and 0.15 vs. 0.06 S t/ha for Oa) than reference areas. My results suggest that the accumulation of mercury stocks in the forest floor of limed areas is a result of enhanced accumulation of organic carbon due to liming. These findings emphasize the importance of understanding of the effects of liming in forest soil, and the long-term impacts of acid deposition on the processing of mercury in forest ecosystems.

The effects of watershed liming on mercury concentrations and stocks in soil of Woods Lake, New York

by

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Introduction

Acid Deposition

Elevated acidic deposition, which is the input of strong acids from the atmosphere to the Earth's surface, has been an environmental problem for decades. It has impacted ecosystems in Asia, Europe and North America. Acidic deposition resulting in the acidification of soil and surface waters, especially in acid-sensitive regions (Greaver et al., 2012). Acidic deposition originates from emissions of nitrogen oxides (NO_x), sulfur dioxide (SO_2), and ammonia (NH_3) (Driscoll et al., 2001). Due to the enactment of the U.S. Clean Air Act (CAA) and subsequent rules established by the U.S. Environmental Protection Agency, emissions of SO_2 and NO_x from electric utilities, and atmospheric sulfate (SO_4^{-2}) and nitrate (NO_3^{-1}) have dramatically decreased in recent decades (Mitchell & Likens, 2011). Although acidic deposition has been partly controlled and some recovery of acid impacted surface water has been evident, soils remain acidified or are continuing to acidify (Warby et al., 2007). As a result, there is interest in accelerating the recovery of acid-impacted ecosystems.

Effects of Acid Deposition

The biological effects of acidification of forest ecosystems are often linked to the mobilization and toxicity of aluminum and depletion of available plant nutrient cations in soil (Greaver et al., 2012; Driscoll et al., 2001). The long-term data from the Hubbard Brook Experimental Forest, New Hampshire indicates that large amounts of Ca^{2+} and Mg^{2+} in soil have been lost from the soil exchange complex due to elevated leaching of strong acid anions associated with acidic deposition (Likens et al., 1996). The mobility of Al is increased by soil acidification and can impair healthy growth and regeneration of forest vegetation, including red spruce and sugar maple (Driscoll et al., 2001). Acidic deposition also impacts surface water quality by decreasing pH, acid neutralizing capacity (ANC) and increasing concentrations of dissolved inorganic Al. These changes in water chemistry have decreased the species richness and impaired the health of aquatic biota (Driscoll et al., 2001; Greaver et al., 2012).

Liming

Liming is defined as the addition of alkaline materials to neutralize acidic conditions and increase ANC. It has been utilized to mitigate acidification of watersheds and surface waters (Olem et al., 1991). A variety of materials have been used for liming applications. Most commonly, calcium carbonate ($CaCO_3$) is applied, but dolomitic limestone, wollastonite and other materials have also been used for some applications. Lime has been applied to mitigate the acidification of watersheds and surface waters in the U.S., Germany, Norway, Sweden, and the United Kingdom (Olem, 1991). During most applications, lime is directly applied to acid-impacted watersheds to increase ANC and pH (Olem, 1991). The addition of lime may cause physical and chemical changes in watersheds, including decreases in transparency, increases in dissolved organic carbon, and color in surface waters (Olem, 1991), and changes in soil (Geary and Driscoll., 1996; Melvin et al., 2013) and plant processes and health (Juice et al., 2006; Battles et al., 2014). However, to my knowledge, there have been no studies investigating the effects of watershed liming on mercury (Hg) dynamics.

Mercury

Mercury (Hg) is a toxic metal that can be released into the environment by natural processes, such as weathering and volcanoes (Driscoll et al., 2007). Substantial emissions of Hg also occur due to human activities, including coal-fired power plants, incinerators, mining, and industrial manufacturing (Driscoll et al., 2013). Finally, Hg emissions include “reemissions” or secondary emissions. Secondary emissions are the release of Hg as elemental Hg that was previously deposited on the Earth’s surface. Three Hg species are emitted to the atmosphere: elemental Hg, gaseous ionic Hg, and particulate Hg (Driscoll et al., 2007). Elemental Hg has a relatively long residence time in the atmosphere (0.5 – 1 year) (Driscoll et al., 2007). In contrast, gaseous ionic Hg and particulate Hg have short atmospheric residence times (i.e. hours – days) (Driscoll et al., 2007). Due to the residence times of these three species, Hg pollution can be a local, regional, or global environmental problem. After Hg is emitted into atmosphere, it is deposited onto vegetation, soil, water and other surfaces by wet or dry deposition. In reducing environments, such as wetlands and sediments, ionic Hg can be converted to methyl Hg by microbiological processes, particularly by sulfate reducing bacteria (Benoit et al., 2003). Methyl Hg is the form that readily bioaccumulates in terrestrial and aquatic food chains resulting in exposure to humans and wildlife.

Effects of Mercury

Mercury is a toxic metal of significant public health concern. It is classified as a persistent bioaccumulative toxin (PBT) (Driscoll et al., 2007; Evers et al., 2011). After the conversion of ionic Hg to methyl Hg, it can be accumulated by organisms and biomagnified in the food chain (Evers et al., 2011). Human and wildlife exposure to Hg largely occur through the consumption of contaminated fish and other organisms (Ever et al., 2011). The effects of methyl Hg exposure can be wide ranging from sublethal to lethal conditions (Evers, 2005). Approximately 8% of U.S. women of child-bearing age have higher blood Hg levels than recommended by the U.S. Environmental Protection Agency (Schober et al., 2003). The health effects of Hg exposure are associated with intelligence quotient (IQ) deficiency and cardiovascular disease (Swain et al., 2007;

Salonen et al., 2000). In response to concerns about Hg exposure, a variety of policies and actions have been proposed and enacted to control Hg pollution (Evers, 2005). The U.S. Environmental Protection Agency has issued a human health criterion of methyl mercury in fish of 0.30 ppm (Schmeltz et al., 2011). In 2011, the U.S. Environmental Protection Agency issued the Mercury and Air Toxics Rule to limit Hg emissions from electric utilities in the U.S. (Schmeltz et al., 2011). In 2013, the United Nations Environment Programme developed the Minamata Convention, an international treaty to limit Hg releases into the environment (Selin, 2014).

Research Question/Hypothesis

In this research, I investigated changes in Hg, organic carbon (OC), and sulfur (S) in forest soil 19 years after a lime application to the Woods Lake Watershed, in the Adirondack Park, New York. In 1989, approximately half of the watershed area in the Woods Lake watershed was treated with lime to mitigate acidification (Driscoll et al., 1996). I hypothesized that the increase in the OC content of the forest floor following liming (Melvin et al., 2013) resulted in an increase in Hg concentrations and pools.

Method

Site Description

This research was conducted in the Woods Lake Watershed, located in the west-central Adirondack Park in New York State, which covers an area of 208 hectares ($42^0$52’ N, $71^0$58’ W; Figure 1). This lake has two major tributary streams, one of which drains a large beaver pond and associated wetlands (Cirmo and Driscoll, 1996). The watershed is forested, mostly with hardwoods. The total wetland area is 11.8 hectares and comprises 5.6% of the watershed (Heinemann et al., 1985). The surficial geology of the Woods Lake Watershed primarily consists of shallow deposits of glacial till, with a large number of small bedrock outcrops of hornblende-rich granitic gneiss (Blette and Newton, 1996). The watershed has been divided into five subcatchments, among which Subcatchments II and IV were treated with lime ($CaCO_3$). Because of their smaller hydrologic contribution to the Woods Lake, Subcatchments III and V were selected as reference watersheds (Driscoll et al., 1996). There are significant differences between soil conditions in the southeast and northwest side of the lake. Subcatchments I, II, and III, in the northwest portion of the watershed, are drier due to the thicker surface material and southern exposure. Subcatchment IV experiences more saturated soil conditions because of the shallow depth to bedrock and northern exposure (Geary and Driscoll, 1996).

Treatment History

Woods Lake is a highly acid-sensitive lake and was investigated as a part of the Integrated Lake-Watershed Acidification Study (ILWAS) (Schofield et al., 1985). This lake was selected as one of three lakes along with Little Simon Pond and Cranberry Pond, for inclusion in the Lake Acidification Mitigation Project (LAMP). The objective of LAMP was to assess the chemical and biological effects of direct of liming to lake ecosystems (Porcella, 1989). The lake itself was initially treated using a 23 Mg dose with a 71% $CaCO_3$ slurry on May 30th and 31st in 1985, which was regarded as "water-column only" manipulation. The duration of the treatment was short-lived, about 15 months. The lake was treated for a second time in September 1986 using a 34.3 Mg dose with a mixture of fine and coarse calcium carbonate particles, which was referred to as "water column/sediment" (wc/s) treatment. The duration of the wc/s treatment was about 20 months (Driscoll et al., 1996). In 1989, the Experimental Watershed Liming Study (EWLS) project was conducted with the application of lime to the Woods Lake watershed (Driscoll et al., 1996). 6.89 Mg of calcium carbonate was applied to the treatment subcatchments using pelletized limestone (1.41 to 4.00 mm in diameter) via helicopter between October 2nd and 19th. The treatment was conducted after leaf-fall to help insure deposition of calcium carbonate to the forest floor (Driscoll et al., 1996).

Soil Measurements

A total of 20 plots were established in the watershed for soil samplings, with each subcatchment containing five 0.04 ha plots. In the summer of 2007, forest floor and mineral soil samples were collected at five locations in each of the 20 plots by researchers at Cornell University (Melvin et al., 2013). The forest floor of Oe and Oa horizons were collected as a single sample, and mineral soils were sampled by depth, including 0-10 cm, 10-20 cm, 20-30 cm, and 30-40 cm. In 2008, additional Oe and Oa horizons and 0-10 cm mineral soil samples were collected at six sampling locations within each plot, by researchers from Syracuse and Cornell Universities. At each of the six sampling locations, duplicate samples of Oe, Oa and 0-10 cm mineral soil were collected. All forest floor chemistry data presented here are from the 2008 sample collection.

The mineral soil samples collected in 2007 at various depths from the 5 locations within a plot were combined into one composite sample per plot at each soil depth for analysis of total Hg, OC, and S. The 0-10 cm mineral soil samples collected in 2008 from each of the 6 locations were combined for each plot into one composite sample per plot for analysis of OC and S. The Oe and Oa horizon samples collected in 2008 from the 6 locations within each plot were combined by plot into one composite sample per plot for each horizon for analysis of OC and S. All samples collected in 2008 from mineral soil layers and forest floor horizons were analyzed for total Hg.

Soil Laboratory Analyses

In the summer of 2012, the forest floor samples collected in 2008 and mineral soil samples collected in 2007 and 2008 were subsampled from Cornell University. The soil samples were sealed in Ziploc bags and brought back to Syracuse University laboratories for analysis. Soil samples were freeze-dried prior to analysis.

Total Hg concentrations were detected via high-temperature combustion using a Milestone Mercury analyzer by thermal decomposition amalgamation and atomic absorption spectrophotometry. The instrument is capable of analyzing 0.001-1.0 g of a sample and the method detection limit (MDL) is 0.031 ng total Hg. Approximately 0.05 g of the forest floor and mineral soil samples was used for each analysis. Each sample was analyzed twice to evaluate analytical precision. Separate spike samples and duplicates (MS/MSD) were prepared and analyzed for each batch of sample analysis. Coal fly ash (1633c), marine sediment reference materials (Mess-3), and San Joaquim Soil (SRM 2709a) were used as soil standards reference materials and carried through the entire preparation and analytical process of each batch for quality control.

Total organic carbon concentration was analyzed by hydrochloric acid digestion followed by detection using a Costech ECS 4010 Elemental Combustion System. Approximately 5 mg of soil were measured and placed in 10mm x 10mm capsules. The samples were wet by adding 3M hydrochloric acid to dissolve any inorganic carbon in the samples. The samples were then placed in an oven at 65℃ for 24 hours before analysis. Apple leaves, atropine and acetanilide were carried through the entire preparation and analytical process as laboratory control samples. Total sulfur concentrations were also analyzed by the Costech ECS 4010 Elemental Combustion System. About 10 ~ 15 mg of forest floor samples and 30 ~ 60 mg of mineral soil samples were measured and prepared for S analysis. Vanadium pentoxide was added into each sample as a catalyst for the reaction. Sulfanilamide, apple leaves, and BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2yl) thiophene) were used as a laboratory control samples and analyzed for each batch of samples.

Quality control procedures were conducted as part of all laboratory work to monitor and evaluate the precision and accuracy of analytical processes. Continuing calibration verifications and continuing calibration blanks were analyzed after every 10 samples. Duplicates, spiked samples, and working standards were routinely analyzed. Percent recoveries in standard reference materials ranged from 90% to 110%, and relative percent difference (RPD) ranged from 90% to 110% for Hg, OC, and S analysis.

Statistical analyses were performed using SigmaPlot 12.0. The subcatchment mean comparisons were made using Tukey's test ($P < 0.05$). The difference in slopes for regressions relationships were carried out using Statgraphics ($P < 0.05$).

Stock Calculations

I used the masses of soil horizons and elemental concentrations to quantify the THg, OC, and S stocks in the forest floor and mineral soil horizons. The calculations are summarized below,

1. THg Stock (g ha^{-1}) = Soil mass (g/cm^2) * THg ng/g (10^{-9}) * 10^8 cm^2/ha
2. OC Stock (t ha^{-1}) = Soil mass (g/cm^2) * OC% * 10^8 cm^2/ha * 10^{-6} t/g
3. S Stock (t ha^{-1}) = Soil mass (g/cm^2) * S% * 10^8 cm^2/ha * 10^{-6} t/g

The soil mass data were obtained from Melvin et al. (2013). The soil mass and concentrations in each subcatchment of each horizon were averaged to determine stock values. The units were converted to g ha^{-1} for THg stock and t ha^{-1} for OC and S stocks.

Results

Soil Response to Liming

Soil Concentrations

The average total Hg concentrations in the Oe and Oa horizons were 287.7 ±77.8 ng g^{-1} (mean ± std. deviation) and 324.3 ±88.4 ng g^{-1} in the limed subcatchments and 260.1 ±81.0 ng g^{-1} and 287.2 ±103.5 ng g^{-1} in the reference subcatchments, respectively (Table 1). The average total Hg concentration in the 0-10 cm mineral soil depth was 103.0 ±119.3 ng g^{-1} in the limed subcatchements and 126.0 ±96.5 ng g^{-1} in the reference subcachments for observations from 2008. The soil profile showed a pattern of increases in Hg from the Oe to the Oa horizon of the forest floor. Concentrations decreased to minimum values in the 0-10 cm mineral soil (61.6 vs. 105.8 ng g^{-1} in the limed and reference), then increased at 10-20 cm (97.2 vs. 152.3 ng g^{-1} in the limed and reference) and decreased at 20-30 cm depths (94.9 vs. 140.7 ng g^{-1} in the limed and reference), and 30-40 cm (76.1 vs. 116.9 ng g^{-1} in the limed and reference, Figure 2A).

Total Hg concentrations in the Oe ($P = 0.094$) and Oa ($P = 0.062$) horizons were greater for the limed than reference soils, but not statistically different (Table 1). A significantly higher total Hg concentration was found in Subcatchment 5 (R2, Reference) for all mineral soil depth increments than the mineral soil concentrations in other subcatchments (Table 1). Because of elevated Hg concentrations in mineral soils for Subcatchment 5 (R2), significantly greater values were observed for the reference than limed soils for all mineral soil depths. When Subcatchment 5 (R2) was excluded from the analysis of liming effect, there was still no significant difference observed both for forest floor and mineral soil horizons ($P > 0.05$ for all horizons).

Like Hg, there were distinct horizonal patterns for OC (Table 1; Figure 2B). Concentrations of OC were elevated in the forest floor, with a slight decrease from the Oe (43.3 vs. 42.9 % in the limed and reference soils) to the Oa horizon (34.2 vs. 22.4 % in the limed and reference soils). Concentrations of OC were much lower in the mineral soil, a pattern that is characteristic of soil development of Spodosols. Concentrations were relatively low at 0-10 cm depth (5.1 vs. 6.3 % in the limed and reference), increased at

10-20 cm depth (5.4 vs. 6.6 % in the limed and reference) and decreased at deeper soil depths (4.4 vs. 5.8 % in the limed and reference of 20-30 cm depth; 3.6 vs. 5.0 % in the limed and reference of 30-40 cm depth; Figure 2B).

Lime treatment had no significant effect on OC in the Oe horizon (P = 0.872, Table 1), but in the Oa horizon OC was significantly elevated in limed plots compared with reference plots (34.2 vs. 22.4%, in the limed and reference, respectively, P = 0.016; Table 1). In the mineral soil, the reference plots had significantly greater OC concentrations at the 0-10 cm depth, but this difference was due to the high OC concentrations evident in the mineral soil in Subcatchment 5 (R2). No significant differences were observed for all mineral soil horizons (P > 0.05 for all mineral soil depths, Table 1). Also if treatment effects are compared only to reference sites in Subcatchment 3, no difference was evident in OC in mineral soil between treatment and reference sites.

The soil profile showed a pattern of decreases in S concentration from the Oe (0.2038 vs. 0.2091 % in the limed and reference soils) to the Oa horizon (0.1591 vs. 0.1198 % in the limed and reference soils) of the forest floor (Figure 2C). Concentrations were much lower in the mineral soil and continued to decrease with increasing soil depths from 0-10 cm depth to 30-40 cm depth (Figure 2C).

Liming had no significant effect on S concentration in the Oe horizon (P = 0.462 for Oe, Table 1), but S concentrations were significantly higher in limed than reference plots for Oa horizon (P = 0.049 for Oa; Table 1). No significant differences were observed for all measured mineral soil depth increments ($P > 0.05$ for all mineral soil depths; Table 1). For all mineral soil depth increments, significantly higher S concentrations were evident in Subcatchment 5 (R2) relative to the other subcatchments (Table 1).

Element Interactions

A positive relationship was observed between THg and OC concentrations in the Oe horizon both in the limed and reference soils. The THg-OC regression relationships explained 36% and 39% of THg variation in the limed and reference soils respectively (Figure 3A). There was no significant difference in slopes of the THg-OC relationship in the Oe horizon of the limed and reference soils ($P = 0.1451$, Figure 3A). For the Oa horizon, a regression relationship with OC explained 78% of THg variation in the reference soils, but a poor relationship was observed for lime treated soils explaining only 23% of THg variation (Figure 3B). The slope of the THg-OC relationship of Oa horizon in the limed soils was negative and significantly different from the positive slope observed in reference soils ($P = 0.0009$, Figure 3B). A positive relationship was observed between THg and OC concentrations in 0-10 cm mineral soil both in the limed ($r^2 = 0.79$) and reference ($r^2 = 0.90$) soils (Figure 3C), with no difference in the slopes of these relationships ($P = 0.9852$). For the lower mineral soils, there were no differences in the relationships between total Hg and OC (Table 2).

A positive relationship was found between THg and S in the Oe horizon both in the limed and reference soils, explaining 15% and 10% of the variation with no difference in slopes between the limed and references (P = 0.6651, Figure 4A). A poor relationship was evident between THg-S in the limed soils of the Oa horizon (R^2 = 0.000040; Figure 4B). In contrast, the THg-S regression relationship explained 65% of THg variation in the reference soils of the Oa horizon (Figure 4B). There was no difference in slope shown in the THg-S relationships in the Oa horizon (P = 0.0590, Figure 4B). A positive relationship was found between THg and S% of 0-10 cm mineral soils in the limed and reference soils (Figure 4C) explaining 95% and 80% of variation, respectively (Figure 4C). Analysis of covariance indicated that the slopes of the THg-S relationships are different between the limed and references of the 0-10 cm mineral soil (P = 0.0004), with a greater slope of the THg-S relationship in the limed soils than the reference soils (Figure 4C).

Positive relationships were found between OC% and S% of the Oe horizon both in the limed and reference soils explaining 6% and 18% of the variation, respectively (Figure 5A). The relationships between OC and S strengthened from the Oe to the Oa and 0-10 cm mineral soil (Figure 5), and were not significantly different between limed and reference soils in Oe and Oa horizons. In the 0-10 cm mineral soils, a significant difference in slopes was observed between limed and reference soils in OC-S relationship (P = 0.0127, Figure 5C).

Total Soil Element Stocks

The average total Hg stock in the Oe and Oa horizons was 24.47±6.59 g ha^{-1} and 31.63±9.04 g ha^{-1} in the limed subcatchments, and 11.08±3.78 g ha^{-1} and 14.57±5.74 g ha^{-1} in the reference subcatchments, respectively (Table 3). The soil profile showed a pattern of increases in Hg stock from the Oe to the Oa horizon of the forest floor. The stock continued to increase to maximum values at a depth of 10-20 cm in the mineral soil, and then decreased at 20-30 cm and 30-40 cm depths (Figure 6A).

Total mercury stocks were significantly higher in the forest floor horizons of limed soils than reference soils ($P < 0.001$ for both Oe and Oa; Figure 7A). Liming had no significant effects on total mercury stock for all measured mineral soil horizons ($P > 0.05$ for all measured depths; Table 3). In all measured depths of mineral soils, a significantly higher total mercury stock was present in Subcachment 5 than the other subcatchments (Table 3). Liming also had no effects on Hg stock of mineral soil horizons after excluding Subcatchment 5 for liming effect analysis ($P > 0.05$ for all measured depths).

Like Hg, I observed decreases in OC stock from the Oe to the Oa horizon (Figure 6B). Liming had a significant effect on OC stocks of the forest floor horizons (Figure 7B). The OC stocks were significantly higher in the limed forest floor horizons than in the reference sites ($P < 0.001$ for both Oe and Oa, Figure 7B). In the mineral soil, no significant differences in OC stock were evident for any of the measured soil depth increments ($P > 0.05$ for all measured depths, Table 3).

Like OC, there was a decrease in S stock from the Oe to the Oa horizon of the forest floor (Figure 6C). A significantly higher S stock was observed in both the Oe and Oa horizons in the limed subcatchments than in the reference subcatchments ($P < 0.001$ for both Oe and Oa; Figure 7C). Liming had no effects on S stocks in the mineral soil increments ($P > 0.05$ for all measured depths, Table 3).

Discussion

Nineteen years after the lime application to Woods Lake Watershed, a larger OC stock was observed in the forest floor of limed than in the reference subcatchments (Melvin et al., 2013). The accumulation of forest floor C was explained as the result of a decrease in decomposition rate of detrital organic matter. This decrease might be due to an alteration of microbial activity, increased production of recalcitrant litter from plants, or physical stabilization via Ca-OM bridging by liming (Melvin et al., 2013). In contrast to the Woods Lake results, some studies have shown increased soil decomposition after liming (Andersson and Valeur, 1994; Baath and Arnebrant, 1994). Because the effects of lime treatment appear to largely occur in the forest floor, I focused my analysis on these horizons.

Consistent with the increase in OC, Woods Lake Watershed showed a large liming effect on forest floor Hg stocks. The Hg stock in the forest floor in the limed subcatchments was over twice the Hg stock in the reference subcatchments. It is well established that soil Hg is closely linked to OC content resulting from the relationship between soil organic matter and Hg (Obrist et al., 2011). Ionic Hg complexes strongly with functional groups of soil organic matter in forest soil (Khwaja et al., 2006; Wu et al., 2013), and the pool of Hg is correlated with soil organic carbon (Yu et al., 2014). Smith-Downey et al. (2010) indicated that soil Hg storage is strongly associated with organic carbon pools, and Hg will be evaded as a by-product of soil organic matter decomposition. At Woods Lake, it appears that the increase in Hg stock may be partially the result of the accumulation of organic matter due to the decrease in decomposition rate in the forest floor horizons in the limed soils. However, note that the relationship between Hg and OC seems to deteriorate in treated soils.

The increase in Hg stocks in forest floor horizons must result from either enhanced inputs or decreases in losses from the limed soils. Total atmospheric Hg deposition in the Woods Lake Watershed can be estimated from Yu et al. (2013). During the period of 19 years after the lime application, the total atmospheric Hg deposition was estimated to be 3.14 g ha^{-1} in the Woods Lake Watershed, which can only account for 17% of the discrepancy in the forest floor stock between the limed and reference soils.

While atmospheric Hg deposition is unlikely to explain the entire observed liming effect, it might contribute partly to the observed discrepancy. The dominant pathway of Hg inputs to deciduous forests is litter Hg inputs (Demers et al., 2007; Yu et al., 2013; Blackwell et al., 2014). Green et al. (2013) reported an increase in transpiration associated with a wollastonite treated watershed at the Hubbard Brook Experimental Forest and speculated this response was due to increases in stomatal conductance resulting from calcium application. An increase in stomatal conductance would also likely increase foliar Hg exchange and this process may be consistent with my observation of higher concentrations of Hg in limed than reference of Oe horizon samples. But this effect is unlikely to explain a large fraction of the treatment effects.

Rather, it seems likely that decreases in mineralization of OC, coupled with decreases in the respiration of soil Hg to Hg^0, are the mechanisms that largely drive the pattern of soil Hg response to liming. Demers et al. (2007) suggested that Hg accumulation in the forest floor is likely an amalgamation of new and old Hg inputs. New Hg has been defined as newly deposited inputs from the atmosphere, whereas old Hg has been deposited and stored in ecosystems for decades (Hintelmann et al., 2002). In the process of respiration, old Hg is reduced to Hg^0, volatilized to the atmosphere, and then can reenter the forest canopy, contributing Hg though litterfall and throughfall (St. Louis et al., 2001). In the Woods Lake Watershed, it seems like the Hg respiration from soil has decreased as a result of the decreased OC mineralization in the limed soils, causing a greater Hg pool in the limed soils than the reference soils.

I expected to see a pH increase following liming might affect the Hg in limed soils. However, no statistical differences in slopes were observed in the THg-pH relationship between limed and reference soils of Oe and Oa horizons (P = 0.0916 for Oe; P = 0.9549 for Oa). However, the pH seemed affected the OC-pH relationship in Oa horizon of the limed soil, which was different than the relationship in reference soils (P = 0.0417). Therefore Liming might influence Hg by affecting the OC content of the forest floor.

Both Hg concentrations and pools were generally higher in the Oa horizon than in the Oe horizon, which is consistent with previous observations in forest soils (Demers et al., 2007; Yu et al., 2014). Another potential explanation for the observed increased Hg stock in the forest floor horizons of the limed soils is that base treatment has altered Hg cycling process in soils. I observed that in the forest floor, both Hg stock and concentration of the limed soils were higher than in the reference soils. Soil Hg is largely stored in the mineral soil horizons both in the limed and reference subcatchments due to the larger mass of mineral soil, although considerable Hg is also present in the forest floor horizons. It is possible that the higher Hg stock in the limed organic soils is derived from the mineral soil horizons and is transferred due to enhanced activity of fungal hyphae or root uptake associated with the liming (Demers et al., 2007). St. Louis et al. (2001) indicated that Hg can be recycled through root uptake of Hg in mineral soils. This pattern is likely due to litter inputs to the Oe horizon, accompanied by an immobilization of inputs of Hg in precipitation and throughfall by the Oa horizon. The reactive Hg at surfaces of the Oe horizon could be reduced and reemitted into the atmosphere and recaptured by the canopy, whereas the organically bound Hg in the Oa horizon is immobilized by microbes (Demers et al., 2007; Smith-Downey et al., 2010).

Higher THg, OC, and S concentrations in the mineral soil were observed in the plots from Subcatchment 5 in the Woods Lake watershed (Table 1). A potential explanation for this pattern is aspect and geological characteristics. Unlike the other subcatchments, the Subcatchment 5 is north facing and therefore cooler. Moreover the surficial deposits are shallower than other subcatchments, and experience greater soil moisture. These differences may contribute to greater soil OC in Subcatchment 5.

Additionally, insight can be obtained by examining changes in Hg stoichiometry. A pattern of increasing Hg/OC ratios with increasing soil depth was observed in both the limed and reference soils, with no significant difference in Hg/OC between the limed and reference soils in the forest floor and deeper mineral soil horizons ($P > 0.05$, Table 2). This horizonal pattern might be explained by either less microbial processing of Hg relative than OC in the forest floor than in mineral soil (Obrist et al., 2011), or that Hg retention is enhanced by binding to mineral surfaces (Yu et al., 2014). The THg-OC relationships were weaker with smaller slopes in the lime-treated Oe and Oa horizons than reference soils. No difference in THg-OC relationship was evident in the mineral soils (10-20, 20-30 cm, and 30-40 cm). This pattern might reflect the condition that the supply of Hg was unable to keep pace with the increases in OC accumulation associated with the lime treatment particularly in the Oa horizon, resulting in deterioration of the stoichiometric pattern.

Atmospheric deposition is the main source of Hg to most watersheds (Fitzgerald et al., 1998). The binding of Hg (II) in soil organic matter plays a key role in the transport and transformations of Hg in the terrestrial ecosystem (Skyllberg, 2010; Skyllberg et al., 2003). Hesterberg et al. (2001) suggested that Hg (II) binds to reduced organic S, rather than to O or N functional groups in soil. In the Woods Lake Watershed, I also observed a higher S stock in the forest floor horizons in the limed subcatchments than in the reference sites. With more S available in the forest floor horizon of the limed soils, this S could contribute to the immobilization of Hg by soil. Mercury in the limed soils could preferably bind to S groups instead of being reduced to Hg^0 and reemitted into the atmosphere. This pattern is consistent with higher Hg stocks in the limed soil than in the reference soils. Note that the OC: S ratios were relatively constant with soil depth and no differences were evident between limed and reference soils (Table 2), suggesting that S is not limiting in its interactions with SOM.

Obrist et al. (2011) proposed that the stoichiometric relationship between Hg/C and C/N could be used to understand the processing of Hg in soil. They suggested that C/N is an indicator of soil decomposition, where high C/N represents less decomposed soil organic matter and low C/N represents more decomposed soil organic matter. Using soil C and N data from Melvin et al. (2013) (Appendix 1), my analysis showed that liming treatment resulted in an increase in OC/N in the Oa and upper mineral soil, indicating of a decrease in soil decomposition and should decrease Hg/OC (Figure 8). Although I did not observe strong patterns, it was evident that increasing in OC/N in the Oa and upper mineral soil coincides with decreases in Hg/OC suggesting a relation with an apparent decrease in decomposition of OC.

Conclusions

In this study, concentrations and stocks of Hg were found to increase in the forest floor of lime-treated soil in comparison to reference soils. This response is consistent with a previous study that reported an increase in the carbon stocks of the forest floor due to a decrease in the decomposition of soil organic matter from lime addition (Melvin et al., 2013). It seems likely that the increase in the forest floor Hg is due to a decrease in Hg losses resulting from liming, possibly due to decreases in the “respiration” of soil Hg to Hg^o.

The mechanism for this pattern and the source of forest floor Hg are not clear. The source of this additional forest floor Hg is probably not enhanced atmospheric deposition but more likely increased supply from the mineral soil. The mechanism driving the increase in forest floor Hg could be increases in soil OC and S which provides binding sites for Hg or decreases in soil respiration of Hg and subsequent Hg loss by evasion associated with decreases in soil forest floor decomposition.

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Table 1. Total Hg, organic carbon, and sulphur concentrations for soil samples of the Woods Lake Watershed

	Sub 3	Sub 5	Sub 2	Sub 4	Lime Effects
THg (ppb)	R1	R2	L1	L2	P value
Oe	282.8±92.8	236.4±59.6	289.5±88.2	285.4±62.2	P = 0.094
Oa	257.2±98.1	331.4±97.4	303.0±79.1	342.5±93.3	P = 0.062
0-10 cm	55.3±17.8	156.3±13.5	40.2±11.7	83.0±27.8	P = 0.029
10-20 cm	96.9±42.1	207.8±37.9	86.0±31.6	108.4±13.8	P = 0.067
20-30 cm	95.3±45.7	186.0±54.3	100.1±34.6	89.8±10.8	P = 0.236
30 - 40 cm	73.5±25.5	160.4±32.9	81.6±27.8	70.6±12.9	P = 0.194
OC (%)					
Oe	43.1±4.3	43.0±2.9	41.8±5.5	44.9±3.0	P = 0.872
Oa	16.1±4.7	28.6±4.2	35.6±7.5	32.8±10.0	P = 0.016
0-10 cm	5.12±1.4	7.5±1.1	4.8±0.6	5.3±1.3	P = 0.168
10-20 cm	5.4±2.6	7.8±2.3	5.5±2.0	5.3±0.4	P = 0.385
20-30 cm	5.1±1.8	6.5±3.1	4.8±2.3	4.0±0.9	P = 0.342
30 - 40 cm	3.7±0.8	6.4±3.4	4.2±1.7	3.0±1.1	P = 0.338
S (%)					
Oe	0.215±0.019	0.203±0.018	0.207±0.022	0.200±0.021	P = 0.462
Oa	0.102±0.052	0.138±0.044	0.153±0.028	0.165±0.057	P = 0.049
0-10 cm	0.020±0.006	0.041±0.003	0.020±0.002	0.025±0.005	P = 0.105
10-20 cm	0.022±0.012	0.045±0.009	0.019±0.005	0.025±0.002	P = 0.109
20-30 cm	0.023±0.005	0.037±0.011	0.022±0.006	0.017±0.009	P = 0.170
30 - 40 cm	0.020±0.006	0.034±0.010	0.018±0.007	0.016±0.005	P = 0.138

*Mean concentrations ± SE for the forest floor and mineral soil horizons within the reference (R1 and R2) and limed (L1 and L2) subcatchments. The soil samples of the Oe and Oa horizons were collected from 2008, and mineral soil samples were collected in 2007. Significant effects of liming are indicated by ($P < 0.05$).

Table 2. Element mass ratios for soil samples for different horizons of the Woods lake Watershed.

	Sub 3	Sub 5	Sub 2	Sub 4	Lime Effects
Hg:OC (ng/mg)					
Oe	69.4±8.3	56.1±5.2	68.3±3.9	64.0±6.1	P = 0.426
Oa	132.8±26.1	118.0±18.2	83.1±20.9	116.2±47.6	P = 0.060
0-10 cm	110.3±29.4	214.4±48.3	92.4±22.7	134.2±49.9	P = 0.025
10-20 cm	165.1±25.3	273.8±38.7	137.1±43.6	204.6±52.1	P = 0.328
20-30 cm	184.3±57.2	320.6±169.4	265.2±131.2	227.8±37.2	P = 0.862
30 - 40 cm	197.0±41.0	298.6±132.4	208.8±56.9	264.3±95.1	P = 0.986
Hg:S (ng/mg)					
Oe	14.0±2.7	11.9±1.8	13.8±1.8	14.7±1.1	P = 0.167
Oa	27.7±9.9	26.1±7.7	19.3±5.6	23.0±3.7	P = 0.105
0-10 cm	27.7±8.0	38.3±5.1	20.2±6.8	34.9±15.7	P = 0.204
10-20 cm	48.4±17.8	46.3±1.8	44.0±12.6	44.2±6.4	P = 0.268
20-30 cm	41.4±15.8	50.6±0.7	47.3±8.4	42.2±2.3	P = 0.993
30 - 40 cm	37.7±7.0	48.6±5.1	45.7±5.5	46.9±12.1	P = 0.485
OC:S					
Oe	2.01±0.16	2.12±0.20	2.02±0.28	2.30±0.26	P = 0.396
Oa	2.07±0.50	2.19±0.45	2.42±0.73	2.07±0.57	P = 0.606
0-10 cm	2.55±0.31	1.82±0.23	2.48±0.17	2.12±0.34	P = 0.871
10-20 cm	2.80±1.68	1.71±0.19	2.70±0.43	2.17±0.27	P = 0.809
20-30 cm	2.21±0.33	1.84±0.74	1.97±0.54	1.99±0.32	P = 0.798
30 - 40 cm	1.95±0.39	1.79±0.59	2.26±0.33	1.93±0.72	P = 0.295

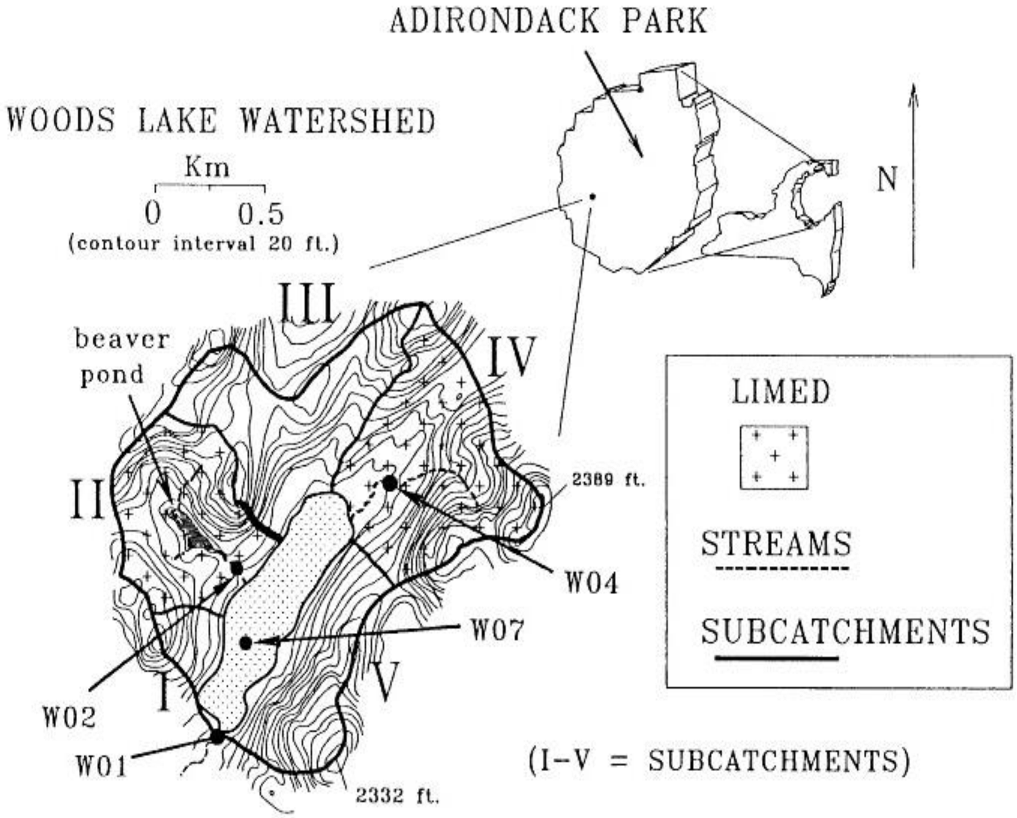
*Mean concentrations ± SE for the forest floor and mineral soil horizons within the reference (R1 and R2) and limed (L1 and L2) subcatchments. The soil samples of the Oe and Oa horizons were collected from 2008, and mineral soil samples were collected in 2007. Significant effects of liming are indicated by ($P < 0.05$).

Table 3. THg, organic carbon, and sulphur stocks for soil samples of the Woods Lake Watershed

	Sub 3	Sub 5	Sub 2	Sub 4	Lime Effects
THg (g ha-1)	R1	R2	L1	L2	P value
Oe	11.7±4.6	10.4±2.6	23.7±7.2	25.4±5.7	$P < 0.001$
Oa	12.1±4.6	18.2±5.36	28.2±7.4	34.6±9.4	$P < 0.001$
0-10 cm	44.0±14.1	104.0±8.9	36.9±10.7	72.9±24.4	$P = 0.071$
10-20 cm	77.3±33.6	139.8±25.5	78.0±28.7	95.6±12.2	$P = 0.210$
20-30 cm	76.1±36.5	127.0±37.1	76.5±14.4	79.9±9.6	$P = 0.260$
30 - 40 cm	59.2±20.6	111.8±22.9	71.5±24.4	63.7±11.6	$P = 0.418$
OC (t ha-1)					
Oe	18.5±1.8	18.8±1.3	34.2±4.5	40.0±2.6	$P < 0.001$
Oa	7.6±2.2	15.7±2.3	33.1±7.0	33.2±10.1	$P < 0.001$
0-10 cm	40.7±11.1	49.6±7.4	44.4±5.4	46.5±11.2	$P = 0.968$
10-20 cm	43.0±20.9	52.5±15.5	50.1±17.9	46.7±3.7	$P = 0.729$
20-30 cm	40.7±14.1	44.6±20.9	42.5±20.4	36.0±7.9	$P = 0.860$
30 - 40 cm	29.6±6.1	44.4±23.6	36.6±14.5	26.7±10.1	$P = 0.688$
S (t ha-1)					
Oe	0.092±0.008	0.089±0.008	0.170±0.018	0.178±0.019	$P < 0.001$
Oa	0.048±0.024	0.076±0.024	0.142±0.026	0.168±0.057	$P < 0.001$
0-10 cm	0.161±0.046	0.273±0.022	0.185±0.018	0.220±0.047	$P = 0.626$
10-20 cm	0.176±0.098	0.303±0.061	0.181±0.050	0.217±0.016	$P = 0.403$
20-30 cm	0.182±0.042	0.251±0.075	0.204±0.054	0.152±0.084	$P = 0.675$
30 - 40 cm	0.157±0.045	0.235±0.068	0.160±0.061	0.145±0.049	$P = 0.339$

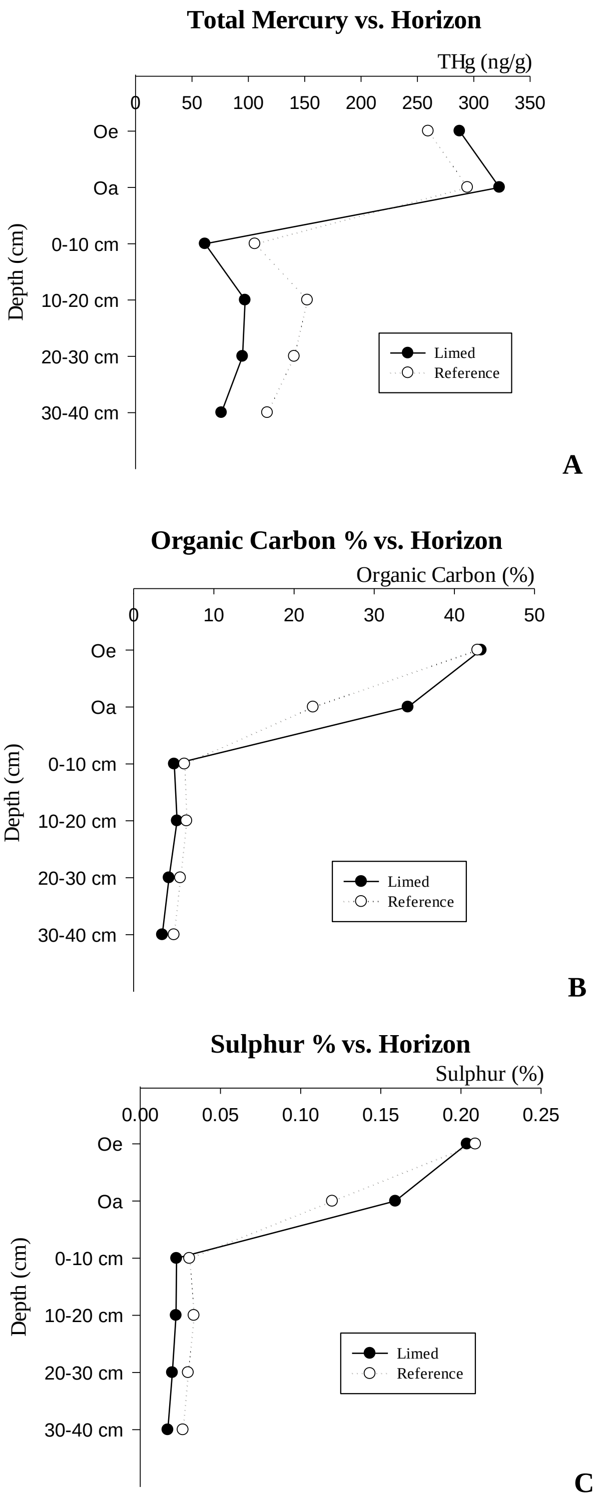
*Mean stocks ±SE for the forest floor and mineral soil horizons within the reference (R1 and R2) and limed (L1 and L2) subcatchments. Significant effects of liming are indicated by ($P < 0.05$).

Figure 1.



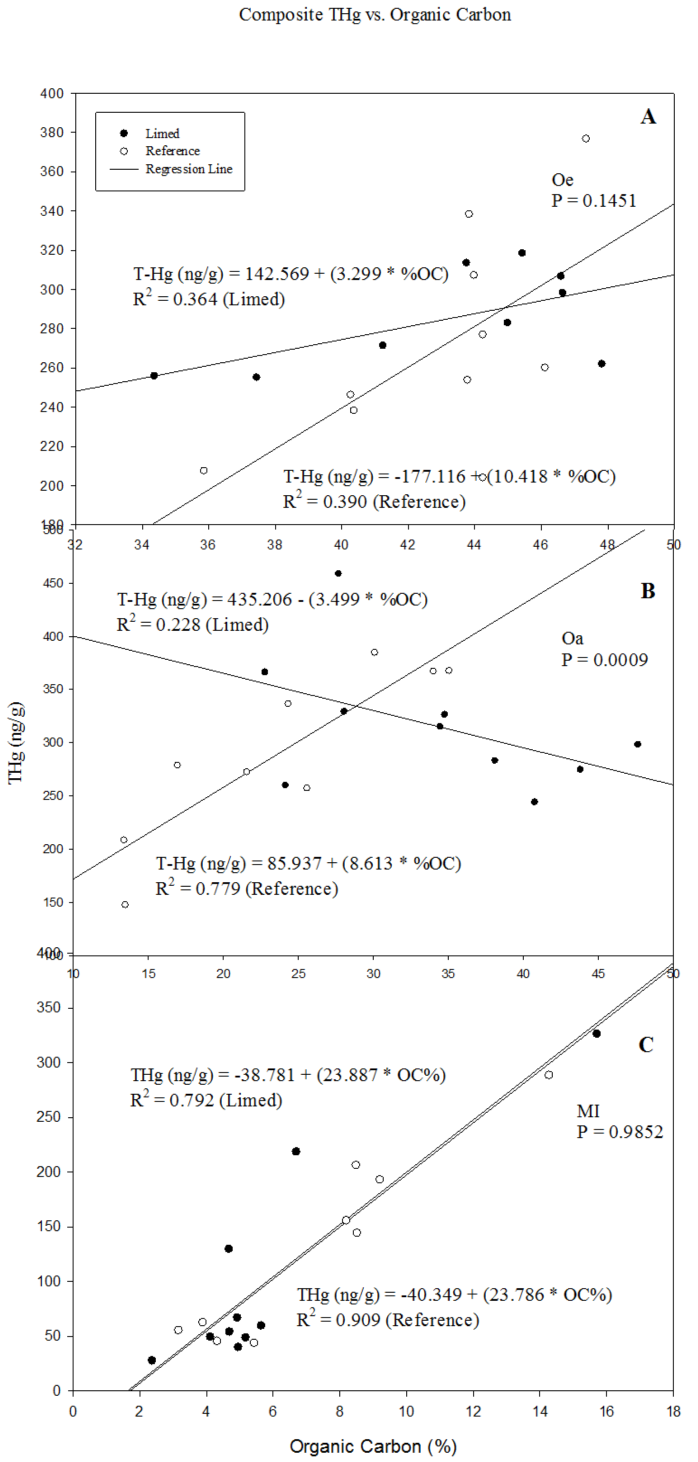
*Map of Woods Lake Watershed. Subcatchment II and IV were treated with lime (Driscoll et at., 1996)

Figure 2.



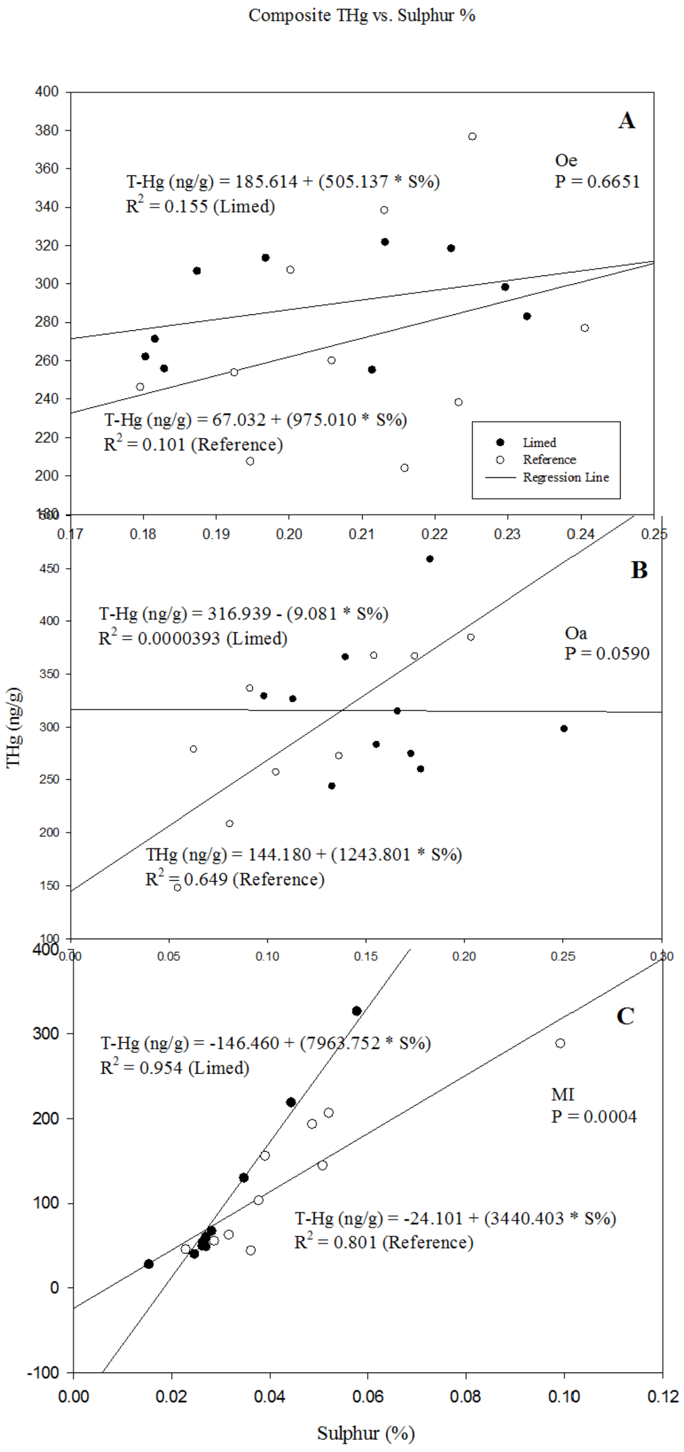
*(A) total mercury concentration, (B) organic carbon concentration and (C) sulphur concentration for all measured forest floor and mineral soil depth increments in reference (R1 and R2) and limed (L1 and L2) subcatchments.

Figure 3.



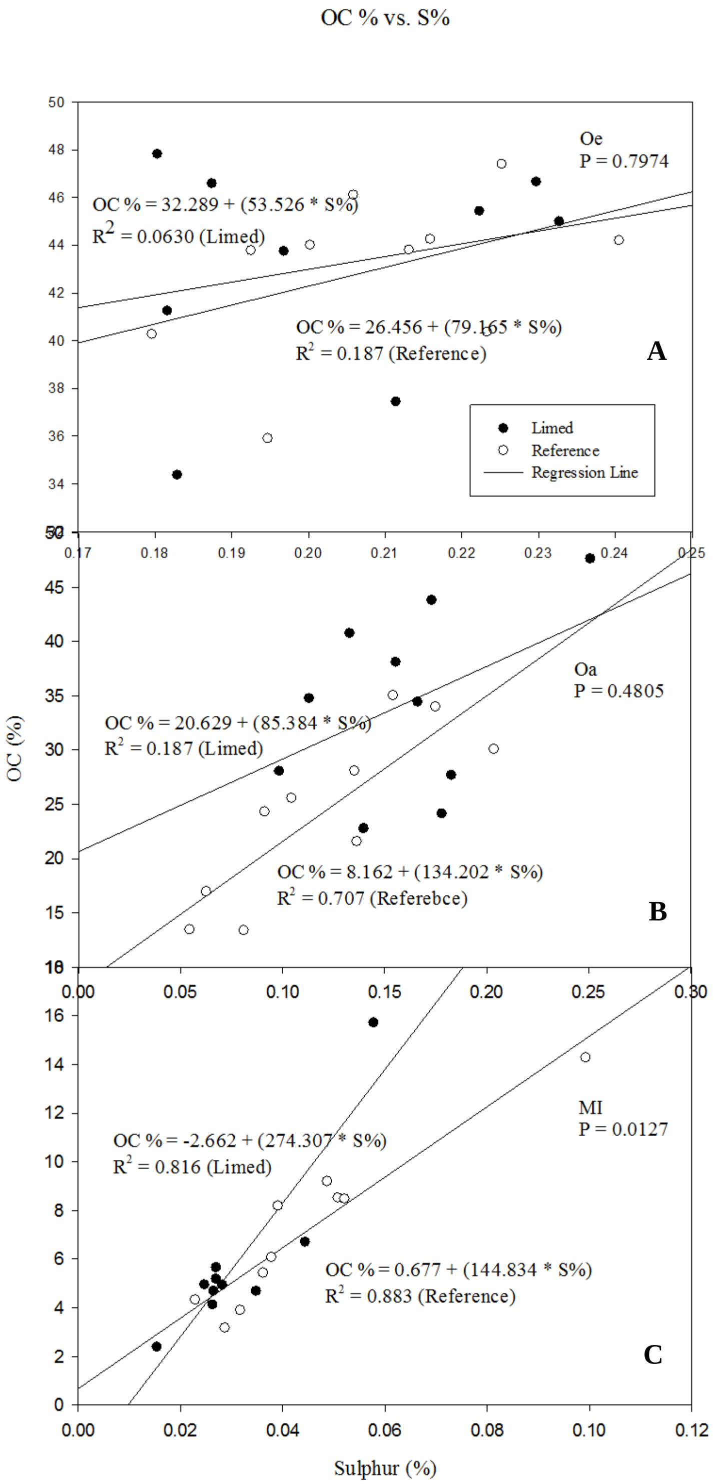
* Total mercury and organic carbon relationship (THg-OC) for (A) Oe, (B) Oa and (C) 0-10 cm mineral soil in reference and limed soils. P values indicate the significant difference between regression relationships in the reference and limed soil ($P < 0.05$).

Figure 4.



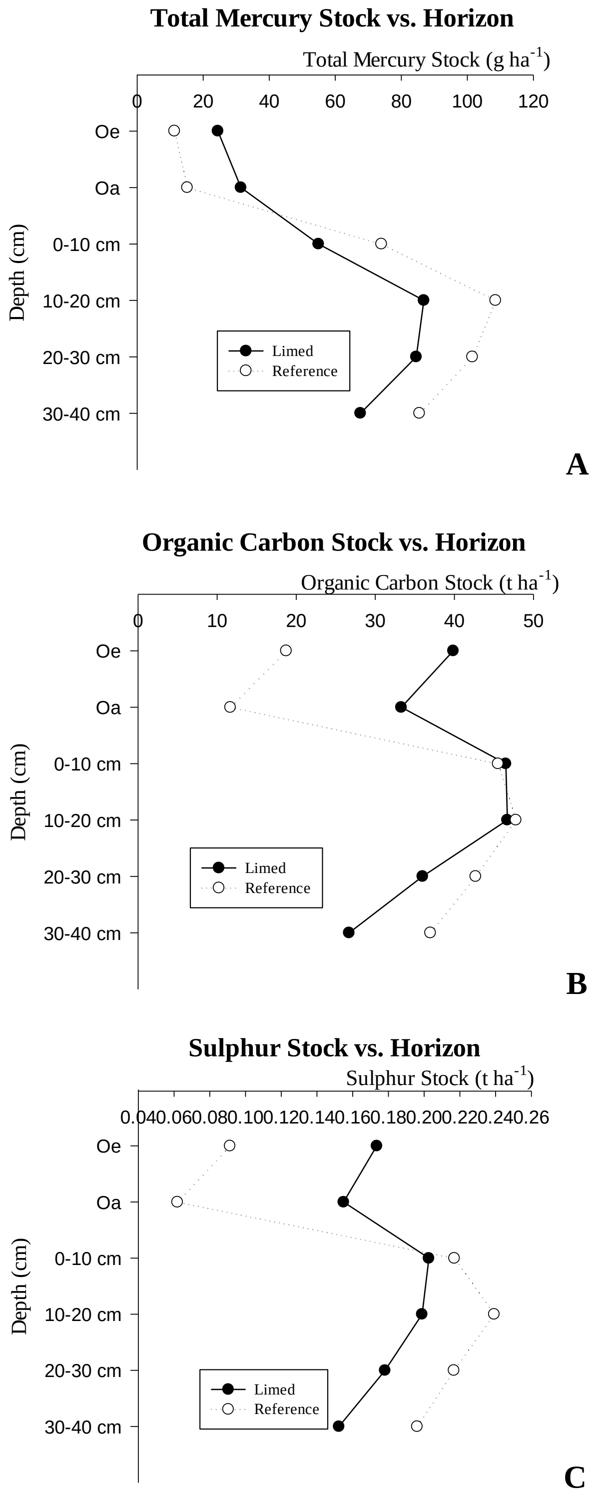
* Total mercury and sulphur relationship (THg-S) for (A) Oe, (B) Oa and (C) 0-10 cm mineral soil in reference and limed soils. P values indicate the significant difference between regression relationships in the reference and limed soil ($P < 0.05$).

Figure 5.



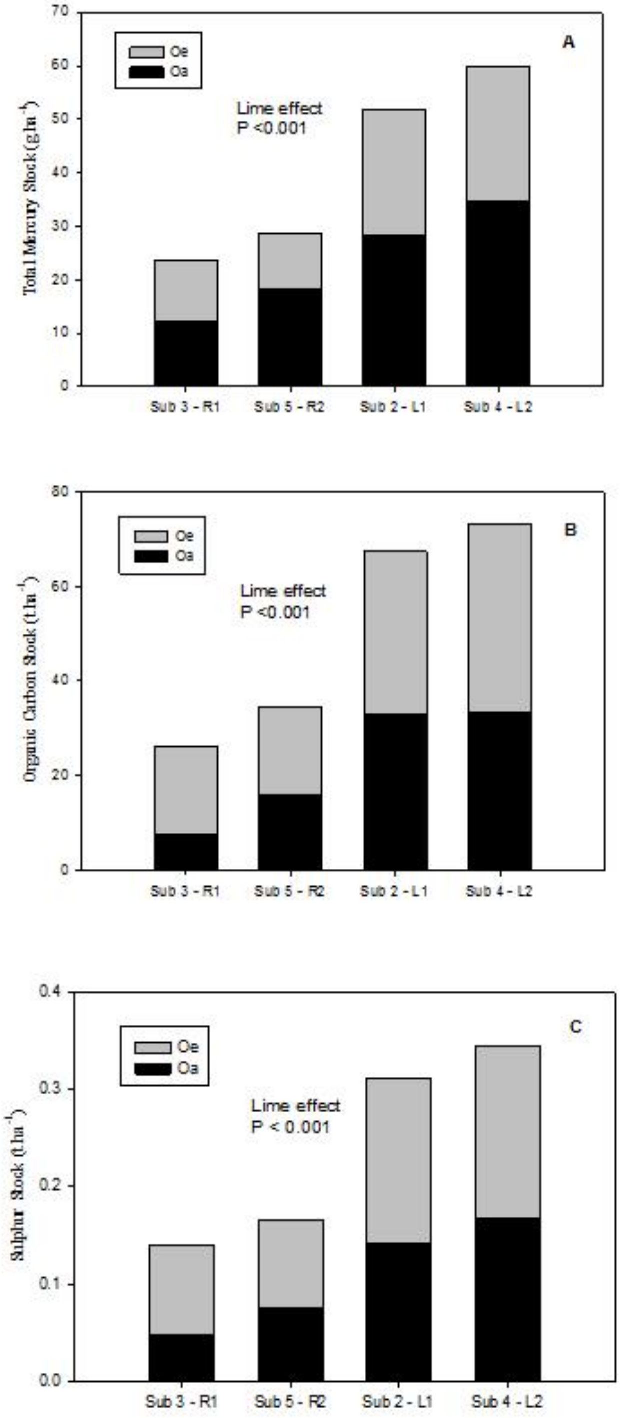
* Organic carbon and sulphur relationship (OC-S) for (A) Oe, (B) Oa and (C) 0-10 cm mineral soil in reference and limed soils. P values indicate the significant difference between regression relationships in the reference and limed soil ($P < 0.05$).

Figure 6.



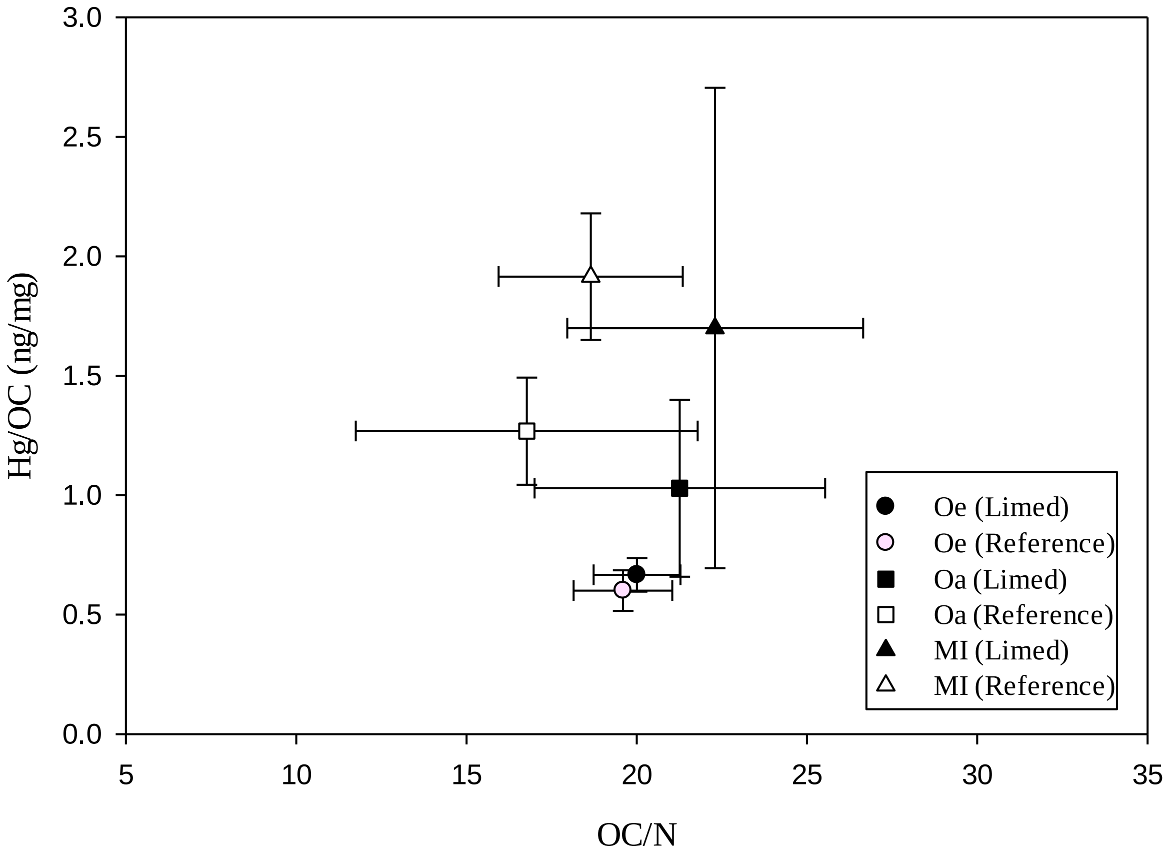
*(A) total mercury stock, (B) organic carbon stock and (C) sulphur stock for all measured forest floor and mineral soil depth increments in reference (R1 and R2) and limed (L1 and L2) subcatchments.

Figure 7.



* Forest floor (A) mercury, (B) organic carbon and (C) sulphur stocks in reference (R1 and R2) and limed (L1 and L2) subcatchments. The forest floor Oe horizon is displayed in gray, and Oa in black. Lime effect indicates the overall response to liming.

Figure 8.



* Relationship of Hg:OC and OC:N mass ratios in soil profile (Oe, Oa and MI) in limed and reference soils.

Appendix 1. Element mass ratios for soil samples of the Woods Lake Watershed

	Sub 3	Sub 5	Sub 2	Sub 4	Lime Effects
Hg:N (ng/g)	R1	R2	L1	L2	
Oe	1.37±0.42	1.14±0.35	1.44±0.53	1.33±0.30	P = 0.167
Oa	1.93±0.63	2.36±0.72	1.71±0.53	2.41±0.60	P = 0.679
0-10 cm	2.49±0.44	3.91±0. 20	2.05±0.77	3.11±0.72	P = 0.070
10-20 cm	4.18±0. 63	5.87±0.22	4.40±1.22	4.84±0.86	P = 0.499
20-30 cm	4.52±1.30	6.07±0.23	6.61±2.83	5.14±0.46	P = 0.436
30 - 40 cm	4.49±0.80	6.95±0.65	5.80±1.87	5.01±1.27	P = 0.814
C:N					
Oe	20.8±1.4	20.5±1.6	21.7±2.4	19.9±1.4	P = 0.679
Oa	20.6±3.5	20.8±2.8	23.3±3.0	22.6±4.3	P = 0.003
0-10 cm	22.1±3.0	21.9±2.3	25.3±2.8	24.1±3.6	P < 0.001
10-20 cm	24.6±2.6	23.6±2.8	28.1±2.6	25.0±2.6	P < 0.001
20-30 cm	25.2±2.8	25.1±3.5	29.2±2.9	25.9±2.1	P < 0.001
30 - 40 cm	24.5±2.6	26.8±4.3	28.4±2.8	26.7±4.1	P = 0.025

*Mean ratios ±SE for the forest floor and mineral soil horizons within the reference (R1 and R2) and limed (L1 and L2) subcatchments. The soil samples of the Oe and Oa horizons were collected from 2008, and mineral soil samples were collected in 2007. Significant effects of liming are indicated by ($P < 0.05$). Carbon and nitrogen data are provided by Melvin, A., 2013.

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