ATMOSPHERIC DEPOSITION AND RE-EMISSION OF MERCURY ESTIMATED IN A PRESCRIBED FOREST-FIRE EXPERIMENT IN FLORIDA, USA

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Abstract. Prescribed fires are likely to re-emit atmospherically deposited mercury (Hg), and comparison of soil Hg storage in areas affected by prescribed fire to that in similar unburned areas may provide cross-validating estimates of atmospheric Hg deposition. Prescribed fires are common in the southeastern United States (US), a region of relatively high Hg deposition compared to the rest of the US, and are thus a potentially significant source of re-emitted atmospheric Hg. Accordingly, Hg was determined in soil layers of a prescribed fire experiment in a Florida longleaf pine forest. The Hg deficit in the annually burned forest floor relative to the forest floor unburned for 46 years (0.180 g ha^{-1} yr^{-1}) agreed to within 5% of an independent estimate of Hg deposition for this site based on a regional monitoring network and computer model (0.171 g ha^{-1} yr^{-1}). Consideration of other potential inputs and outputs of Hg suggested that atmospheric deposition was the primary input of Hg to the site. If extrapolated, these results suggest that prescribed fires in the southeastern US mainly re-emit atmospherically deposited Hg and that this re-emission is less than 1% of total US anthropogenic emissions. However, emissions at other sites may vary due to the possible presence of Hg in underlying geological strata and differences in fire regime and levels of atmospheric Hg deposition.

Keywords: forest soil, mercury deposition, mercury emission, podzol, prescribed fire, spodosol

1. Introduction

Elevated Hg levels in surface soils of remote areas have been ascribed to atmospheric deposition of mercury (Hg) from industrial sources (Nater and Grigal, 1992; Bringmark, 1997). Fates of soil Hg include long-term storage, transport to aquatic systems (where methylation may occur), and re-emission to the atmosphere (Grigal, 2002; Mason *et al.*, 2005). Fire is likely a significant pathway of re-emission in some ecosystems, but only limited information is available on the extent and significance of this process.

Prescribed fires of low to moderate intensity are a key forest management practice in the southeastern United States (US). These fires serve to reduce wildfire risk, prepare sites for planting or seeding, and promote fire-dependent species (Stanturf *et al.*, 2002), and occur on 900,000–1,700,000 hectares yr^{-1} (Southern Area Coordinating Group, 2003; Haines *et al.*, 2001).[1] Given this extensive burning, and the relatively high inputs of atmospheric Hg to this region compared to other parts of the US (see maps by National Atmospheric Deposition Program (NADP), 2005),

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prescribed burning in this region represents a potentially significant but unknown input (or return) of Hg to the atmosphere. Data from other regions of the US indicate that forest fires may emit significant amounts of Hg to the atmosphere, with emission estimates ranging from 3–14% (data from Friedli *et al.*, 2003a; W. Cannon, personal communication) of US anthropogenic emissions (144 Mg yr^{-1}, US Environmental Protection Agency, 1997). However, these estimates rely heavily on data extrapolated from the western and north-central US. The southeastern US merits special attention in Hg cycling studies as it has fire regimes, climate, and ecosystems that are distinct from other areas of the US.

Comparison of Hg storage in surface soils of prescription-burned forests with similar unburned soils can provide an estimate of the Hg emissions resulting from prescribed fire. Further, such comparison may provide estimates of atmospheric Hg deposition independent of those derived from regional monitoring networks and computer models. Such independent deposition estimates could be used for verification, or for identification of knowledge gaps in our understanding of the global Hg cycle.

The main objectives of this study were (1) to obtain a preliminary estimate of Hg emissions due to prescribed burning in the southeastern US, and (2) to derive an independent estimate of atmospheric Hg deposition by comparing Hg storage in surface soils of unburned and frequently burned forest plots. A secondary objective was to assess the effect of prescribed fire on the vertical distribution of Hg in a highly leached sandy soil (podzol or Spodosol). The soil was used as a record of ecosystem Hg dynamics because the vast majority of Hg in forest ecosystems resides in soil (Grigal, 2003).

2. Materials and Methods

2.1. Site description and prescribed burning treatments

The study site was on a tract of land (approximate dimensions 386 m × 488m) in the Osceola National Forest, Florida (82° 24′39″ W, 30° 14′13″ N), which lies in the Coastal Plain region of the southeastern US (Figure 1). The site lies in the humid subtropical climate zone (Henry *et al.*, 1994), has mean annual temperature and precipitation of 20°C and 136 cm, respectively (NOAA, 2002), and has slopes in the range zero to two percent (Watts, 1996). Soils are mapped as Sapelo fine sand, which includes the Sapelo series (sandy, siliceous, thermic Ultic Alaquods; Spodosols or Podzols) and similar soils (Watts, 1996; Soil Survey Staff, 2004). These marine-deposited soils are generally poorly drained (Watts, 1996), sandy, and rock-free. From the surface downward, they are characterized by a layer of fresh and partially decomposed litter, an A horizon with "salt-and-pepper" appearance due to the presence of both quartz sand and organic matter, a sandy, light-colored nutrient-poor E horizon, and a spodic (podzolic) B horizon enriched in clay, sesquioxides,

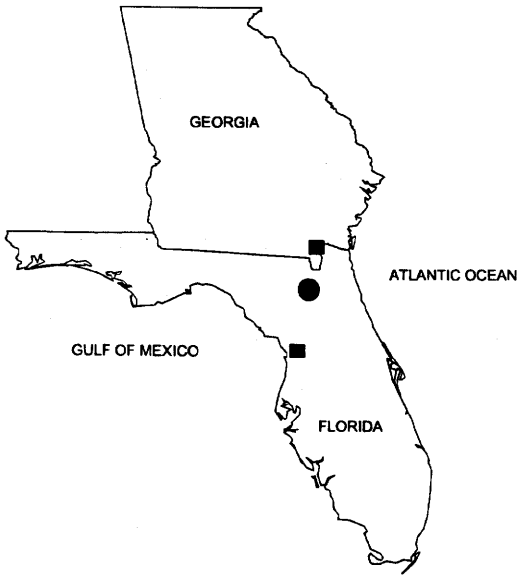

Figure 1. Map showing study site location (•), and monitoring stations (■, NADP, 2005) used for calculation of wet deposition.

and organic matter. Average horizon boundaries occur at depths of 10 cm (A-E) and 33 cm (E-B) below the surface of the mineral soil. Stream inputs are negligible to this site (K. Outcalt, personal communication). Surface runoff is likely to occur during rainy periods but the erosive potential of this runoff is low owing to the flat topography and relatively dense vegetation. The overstory vegetation consists of longleaf pine (*Pinus palustris* Mill.) which ranges from approximately 50-80 years old at present (K. Outcalt, personal communication). The understory vegetation includes shrubs such as saw palmetto (*Serenoa repens* Bartr.) and gallberry (*Ilex glabra* [L.] Gray), along with a diverse assemblage of herbaceous plants.

In 1958 a prescribed burning study was initiated by burning the entire site, subdividing the entire site into parallel rectangular blocks with somewhat different soil moisture patterns, and randomly assigning 0.8 ha plots within each block to different fire regimes (Outcalt *et al.*, 2002; D. Wade, personal communication). The fire regimes studied here were (1) unburned since 1958, (2) annually burned since 1964, and (3) burned every four years since 1958. Plots were burned during or close to the dormant season, which occurs from December to March (K. Outcalt, personal communication). The fires primarily consumed surface fuels with only limited damage to pine trees. On the annual plots, this burning consumed mostly needlefall from the previous year, as longleaf and other pines of this region have two periods of peak needlefall: a small summer peak (July) and a larger autumn peak (October) (Gresham, 1982; Williams, 1995).

Presently, the plots have a basal area of pine trees ranging (in all fire treatments) from 16–20 m^2 ha^{-1} (K. Outcalt, unpublished data). Percent canopy cover is almost identical among the treatments, ranging from 58 to 61% (J. O'Brien, unpublished data). The primary difference among fire treatments is a shift from woody to herbaceous understory vegetation with increasing fire frequency, and an approximate four-fold decrease in understory live plant biomass from the unburned (727 g m^{-2}) to the annually burned (170 g m^{-2}) plots (Glitzenstein *et al.*, 2003; Hanula and Wade, 2003).

2.2. Soil sampling and processing

Soils were collected from four blocks (four plots per treatment) of the above-described experiment during July 2004, based on a systematic grid with five sample locations per plot. At the time of sampling, 160 days had elapsed since the last prescribed fires on the annually and quadrennially burned plots. Samples were composited by horizon within each plot, giving a total of 48 samples (3 fire frequencies × 4 blocks × 4 horizons). The compositing scheme reflected that each plot constituted an experimental unit (i.e., replicate); spatial variability of Hg within plots was not examined in this study. Forest floor (O horizon) samples were obtained with a square metal cutting device (100 cm^2), and the A, E, and B horizons (distinguished at each sampling location by color and texture) were collected by means of a slotted metal soil probe (cross-sectional area = 2.39 cm^2); only the top 10 cm of the B horizon was sampled. Sampling in this manner permitted the calculation of areal amounts of Hg, C, and N by horizon without directly measuring soil bulk density. In the field, samples were initially placed in plastic bags. After completing a given plot, soils in the bags were mixed (either by stirring with a clean spoon or shaking) and a subsample for Hg analysis (about 30 g) was transferred to a new, pre-tared, glass environmental sampling jar (certified clean for Hg; Chase Scientific Glass, Tennessee, USA). All samples were stored on ice until return to the laboratory – thereafter they were stored at 7 °C. The main samples (for C and N analysis) were oven-dried (40°C), weighed, crushed with a wooden rolling pin, and sieved (2 mm); subsamples of the sieved soils were ball-milled and analyzed for C and N. The Hg subsamples were brought out of cold storage, equilibrated to ambient temperature, weighed without opening jars, and, in the case of the A, E, and B horizons, returned to cold storage (without further processing) until Hg analysis.

The Hg subsamples from the O horizons were not immediately returned to cold storage after weighing, but were uncapped and oven-dried to constant mass (approximately 10 d at 40 °C) in a gravity convection oven. The oven contained an open beaker of powdered activated C to lower the levels of gas-phase Hg contamination. Once dry, the O horizons were ground in a rotating-blade mill and returned to cold storage until Hg analysis. Subsequent to the oven-drying of

the O horizon Hg subsamples, powdered apple leaves (US National Institute of Standards and Technology Standard (NIST) Reference Material No. 1515, certified concentration = 44 ng Hg g^{-1}) were dried in like manner and analyzed for Hg. This test served to assess the possibility of Hg loss or contamination during oven-drying.

2.3. Chemical analyses

Because Hg is closely linked with soil organic matter, total C and N were determined on all samples (automated dry combustion, Perkin Elmer Series II 2400 CHNSO Analyzer). Carbon and nitrogen are expected to be almost completely in organic form at this highly leached, unfertilized site, and thus serve as indices of soil organic matter.

Mercury was determined at the University of Georgia Laboratory for Environmental Analysis on either unsieved, unground, field-moist samples (mineral soils) or dried and ground samples (O horizons). First, samples were digested per the US Environmental Protection Agency Method 3051 (USEPA, 1994) within 53–64 days of sample collection. A CEM 81D microwave was used with sealed Teflon containers containing 5 mL concentrated trace-metal grade nitric acid and either 0.2 g of O horizon sample or 0.6 g (dry equivalent) mineral soil. The containers were irradiated in the microwave for 40 minutes (modified from the standard 10 minutes in USEPA 3051) in order to achieve complete recovery of Hg (other than Hg occurring as a component of soil minerals). Moisture content of mineral soils was determined in order to correct final data to a dry mass basis. With each 12 samples, one standard reference material (SRM) from the US National Institute of Standards and Technology (SRM 1547, peach leaves, certified concentration = 31 ng Hg g^{-1}) and three blanks were digested. Following digestion, extracts were centrifuged and the liquid portion analyzed for Hg by inductively coupled plasma mass spectrometry. The mean ratio of Hg in blanks to Hg in samples was 0.13 (standard deviation 0.11) and all results were blank-corrected. Recovery of Hg in the SRM ranged from 93 to 102%, excluding one sample which was not analyzed due to a digestion error.

Analysis of Hg in samples remote from point sources of Hg is difficult because of low concentrations and ease of contamination. Accordingly, some samples were digested and analyzed more than once. E horizon samples were run in duplicate or triplicate (according to reproducibility), yielding average coefficients of variations (CV) (of replicate analyses) of 19 and 63%, respectively. Means were used as final data for the duplicate analyses and medians were used for the triplicate analyses. Half of the A horizon samples from each combination of block and treatment were run in duplicate, yielding an average CV of 15%. Means were used as final data for these samples. The B and O horizons typically underwent only one analysis per sample because of the relatively high Hg concentrations in these samples.

2.4. Data analysis

Data from the A, E, and B horizons were omitted from one unburned plot in all analyses, due to a previous unknown disturbance which had virtually destroyed the soil horizonation. The randomized complete block experiment was analyzed by a repeated-measures mixed models procedure (MIXED procedure; SAS Institute, 1999–2000). This analysis allowed fire frequency and soil horizon to be modeled as fixed factors, while block was modeled as a random factor. Repeated measures were specified in the analysis to reflect that the soil horizons in each plot were correlated in space. In order to make the most appropriate statistical inferences, the data were modeled with five common covariance structures in preliminary analyses as per Littell *et al.* (1996). The five structures were (1) unstructured, (2) compound symmetry, (3) variance components, (4) autoregressive first-order, and (5) Huynh-Feldt (Littell *et al.*, 1996; SAS Institute, 2000; Schabenberger and Pierce, 2002). The best covariance structure for the data was identified as that yielding the lowest value of Akaike's corrected information criterion (SAS Institute, 1999–2000) and was subsequently used for the final analysis. This procedure was applied separately for each response variable of interest (areal carbon concentration, areal nitrogen concentration, mercury per mass of soil, and areal mercury concentration).

Using the above procedures, F-values were generated for each soil horizon and served to test *simple main effects* (fire's effect on Hg in each horizon) as per Schabenberger and Pierce (2002). Probability values (p) were multiplied by 0.5 if differences occurred in a pre-hypothesized one-tail direction. P-values were increased using Bonferroni's correction (Milliken and Johnson, 1992) within horizons that did not exhibit significant F-values ($p = 0.1$). Treatment differences with p-values of 0.1 or less were taken as significant, as has been suggested for studies with few replicates (Steel and Torrie, 1980).

Linear regressions of Hg versus total C or total N (by horizon) were run in Microsoft® Excel. Simple linear regressions were chosen because multiple regression of a dependent variable (Hg) against two highly correlated "independent" variables (C and N) can lead to problems of collinearity (SAS Institute, 2000).

2.5. Independent estimate of Hg deposition to the study site

An independent estimate of Hg deposition aided in the interpretation of Hg cycling at the site. Wet deposition to the study site was based on the two nearest sites in the US National Atmospheric Deposition Program's Mercury Deposition Network (NADP, 2005), Okefenokee National Wildlife Refuge, Georgia (82° 7′43″ W, 30° 44′25″ N), and Chassahowitzka National Wildlife Refuge, Florida (82° 33′15″ W, 28° 44′58″ N). These monitoring sites are approximately collinear with the study site (Figure 1) and wet deposition at the study site was computed as the distance-weighted mean of the values at the two monitoring sites. These means were computed for each year of data availability (1998–2003) and averaged across

years, yielding a figure of 0.136 g Hg ha^{-1} yr^{-1}. Dry deposition was estimated as 0.035 g Hg ha^{-1} yr^{-1}, based on a national-scale map of dry deposition presented by Seigneur *et al.* (2004). The sum of wet and dry deposition, 0.171 g Hg ha^{-1} yr^{-1}, was taken as the total deposition to the site. For simplicity and due to lack of further data, the total wet plus dry deposition was assumed to be constant over the 46-year period of the prescribed burn study.

3. Results and Discussion

3.1. Soil carbon and nitrogen

Soil C and N data are presented in Figure 2. Amounts of these elements decreased with increasing fire frequency in the O horizon, whereas the opposite trend was observed in the A horizon. These data suggest a fire-related redistribution of these

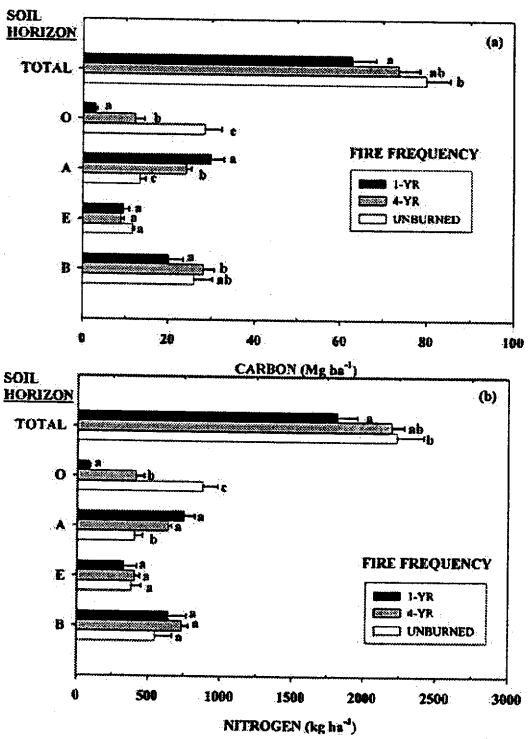

Figure 2. Carbon (a) and nitrogen (b) areal concentrations in soil at the Osceola National Forest. Different letters indicate significant differences within a horizon at the $p = 0.1$ level. Average horizon boundaries were at 10 (A-E) and 33 cm depths (E-B). Error bars represent standard errors of the mean.

elements from the forest floor to the mineral soil. The secondary accumulation of C and N in the B horizon (all treatments) is characteristic of podzolic soils. Fire frequency had a significant effect on C amount in the B horizon, but the explanation of this effect is beyond the scope of this paper.

3.2. Effect of oven-drying treatment on Hg levels in the forest floor samples

The drying treatment (40 °C, 10 d) caused an increase from 1 to 24 ng g^{-1} in Hg concentration in the NIST Standard Reference Material (powdered apple leaves). These results indicate that the O horizon samples may have taken up some Hg from the laboratory atmosphere during oven-drying. However, this potential contamination likely would have only a small impact on the results of this study because the calculation of Hg emissions from prescribed fire is based upon differences in Hg concentration across fire treatments, rather than upon absolute Hg concentrations. Furthermore, the Hg levels of the relatively unhumified O horizon of the annually burned plots (fresh litter plus a small amount of humus), 34–44 ng g^{-1} (Figure 3b), are reasonably close to pine needle litter Hg levels previously measured at this study site (27 ng g^{-1}) and another site in the southeastern US (26 ng g^{-1}; Savannah River Site, Aiken, South Carolina) (Friedli *et al.*, 2003b). The higher Hg levels in the (entire) O horizon of the annually burned plots relative to the litter (Oi horizon only) of Friedli *et al.* (2003b) probably result from C being mineralized more rapidly than Hg during decomposition, as suggested by Grigal (2003).

3.3. Concentrations and emissions of soil Hg

Soil Hg concentrations per area and per mass are shown in Figures 3a and 3b, respectively. Mercury concentrations were significantly affected by fire only in the O horizon; areal concentrations consistently decreased with fire frequency and the per mass concentration was lowest in the annually burned treatment. However, the 4-year treatment had a higher Hg per mass concentration than the unburned treatment (Figure 3b). A possible explanation is that Hg deposition has increased over the 46-year experimental period. Such a trend is consistent with certain North American sites (Florida Everglades, Rood *et al.*, 1995; Upper Fremont Glacier, Schuster *et al.*, 2002; Western Minnesota lakes, Engstrom and Swain, 1997) but inconsistent with others (Savannas Marsh, Florida, Rood *et al.*, 1995; Eastern Minnesota lakes, Engstrom and Swain, 1997). None of the above sites are likely to be fully reflective of the conditions at the Osceola National Forest, and the long-term deposition chronology at the study site remains a topic for future research. The high levels of Hg in the B horizon suggest downward movement from the surface regardless of fire frequency (Figures 3a and 3b).

Correlation results between Hg and (C or N) are shown in Table I. The O and A horizons exhibited no statistically significant correlations between Hg and (C or N).

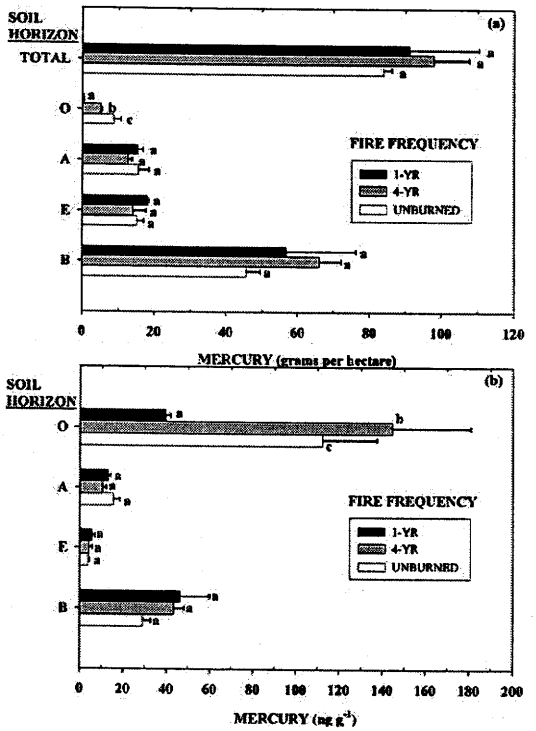

Figure 3. Mercury concentrations per area (a) and per mass (b) in soil at the Osceola National Forest. Different letters indicate significant differences within a horizon at the $p = 0.1$ level. Average horizon boundaries were at 10 (A-E) and 33 cm depths (E-B). Error bars represent standard errors of the mean.

In the O horizon, the lack of correlation may simply be a result of a narrow relative range of C contents among the samples (260 to 380 g C kg^{-1} in the O horizon). The lack of Hg-organic matter correlations in the A horizon (with a broader *relative* range of C contents, 10 to 32 g C kg^{-1}) suggest an input of O horizon material and perhaps a decoupling of Hg and C mineralization (Grigal, 2003).

Significant correlations between Hg and (C or N) arise in the E and B horizons ($R^2 = 0.34 - 0.59$, $p = 0.01 - 0.06$, Table I)[2]. These correlations suggest that Hg in the A horizon is transported through the E horizon by mobile organic matter and is subsequently deposited in the B horizon. Indeed, the downward movement of organo-metal compounds with accumulation in the B horizon is a dominant process in podzolic soils (Buol *et al.*, 2003). This is evident in the vertical distributions of Hg, C, and N as measured in this study (Figures 2 and 3).

Assuming that the atmosphere is the primary source of Hg to the soils at this site (an assertion supported in Section 3.4), the correlations of Table I support

TABLE I

Correlation results for Hg versus (C or N)[a,b].

		carbon			nitrogen		
horizon	n[c]	R^2	p[d]	slope (μg Hg g^{-1} C)	R^2	p[d]	slope (μg Hg g^{-1} N)
O	12	0.00	NS	–	0.18	NS	–
A	11	0.01	NS	–	0.00	NS	–
E	11	0.53	0.01	1.38	0.35	0.06	24.0
B	11	0.34	0.06	2.54	0.59	0.01	128

[a] Hg taken as dependent variable, C or N taken as independent variables. Correlations run separately for C and N. Data were pooled by horizon due to low number of replicates (4) in each combination of fire frequency and horizon.

[b] Input data were concentrations on a per mass basis.

[c] Data from the A, E, and B horizons were omitted from one unburned plot due to a previous unknown disturbance which virtually destroyed the horizonation.

[d] NS: $p > 0.10$

the following general cycle of Hg at the study site: Hg reaches the O horizon via litterfall and throughfall (Grigal, 2002), is eventually incorporated into the A horizon, is transported out of the A and through the E horizon by mobile organic matter, and is subsequently deposited in the B horizon.

Assuming that the areal Hg concentration differences in the burned versus unburned O horizons (Figure 3) are due only to Hg loss during fire (as gas and/or smoke) and that these differences developed during the 46-year old experiment, the four- and one-year burn cycles emit 0.0769 and 0.180 g Hg ha^{-1} yr^{-1}, respectively (emission = [$Hg_{UNBURNED}$ - Hg_{BURNED}] / 46 yr). Some uncertainty in Hg_{BURNED} arises due to the timing of soil sampling with respect to the prescribed burn cycle and can be approximated as (annual Hg deposition rate) × (time between fires). This uncertainty is calculated to result in errors of 19 and 2% for emission from the four- and one-year burn cycles, respectively.

If the above emissions are extrapolated to the maximum 1,700,000 hectares per year burned in the southeastern US, the four- and one-year burn cycles emit approximately 0.128 and 0.299 Mg of Hg per year, respectively. These emissions correspond to 0.09–0.2 % of the 144 metric tons emitted annually in the US (USEPA, 1997), but are highly uncertain as they are based on only one site. Emissions at other sites may vary due to the possible presence of Hg in underlying geological strata and differences in fire regime and levels of atmospheric Hg deposition.

3.4. Plots of known fire history may provide an independent estimate of Hg emissions

Overall, data from these plots of known fire history may provide an independent measure of atmospheric Hg deposition and suggest that the atmosphere is the

primary source of the Hg input at this site. This assertion is based on the close agreement between the estimated emission of Hg from the annually burned plots, 0.180 g ha^{-1} yr^{-1} (Section 3.3), and the deposition to this site as estimated from independent data generated from a regional monitoring network and computer model, 0.171 g ha^{-1} yr^{-1} (Section 2.5). The resulting interpretation is that all inputs of soil Hg are emitted each year from the O horizon of the annually burned plots, whereas nearly all Hg inputs have been retained in the O horizon of the unburned plots over the 46-yr study period. Requisite assumptions are that (1) there is not significantly different mercury deposition to plots with different fire regimes, (2) the O horizons of the site can sequester Hg for decades in the absence of fire, and (3) non-atmospheric inputs and outputs of Hg to the O horizons are small. These assumptions appear to be satisfied at this site, as discussed below.

The assumption of no significant differences in the Hg deposition to plots with different fire regimes requires that the vegetation in each treatment have a similar ability to intercept gaseous and particulate Hg in the absence of rainfall. Working in an area of Minnesota with diverse forest cover types, Kolka *et al.* (1999) demonstrated that mercury deposition was correlated to percent canopy cover for a given ecosystem. Percent canopy cover for the plots of the present study was essentially invariant, ranging from 58–61% among the different fire treatments (J. O'Brien, unpublished data).

The assumption of long-term retention of Hg in the unburned O horizon requires that any Hg reaching this horizon be tenaciously bound and that the O horizon have a slow turnover time. The binding of Hg in the O horizon is supported by the lack of a significant increase in the areal Hg concentrations of the unburned A horizons relative to the burned A horizons (Figure 3). Further, the ability of the O horizon to retain Hg is suggested by the data of Schwesig *et al.* (1999). These authors studied acid forest soils in an area of Germany impacted by high deposition of air pollutants and found that only negligible amounts of Hg in the humified O horizons were extractable by water or ammonium acetate. The previously discussed downward movement of Hg into the A, E, and B horizons (Section 3.3) does not contradict the above arguments concerning the binding of Hg in the O horizon in the last half-century; over longer time scales (e.g. centuries) appreciable amounts of Hg probably reach the mineral soil horizons (Aastrup *et al.*, 1991).

The longevity of the unburned O horizon itself at the study site is a reasonable assumption. Data from a 1978 sampling of these plots (McKee, 1982) in conjunction with the present data indicate that forest floor C has accumulated in a linear fashion in the unburned treatment from 1958 to 2004 (unpublished observation of the authors). Moreover, Gholz and Fisher (1982) report linear accumulation of forest floor material for at least 34 years at a site with similar soils and vegetation in Bradford County, Florida (approximately 40 km from the present site).

The assumption of relatively low non-atmospheric inputs and outputs of Hg to the O horizon requires that the Hg fluxes associated with runoff, erosion, evaporation, geological degassing, and translocation to foliage due to root uptake at depth

be small. Surface runoff is likely during rainy periods and may result in losses of Hg bound to dissolved or particulate organic carbon (Grigal, 2002). However, such losses are probably limited by the relatively flat topography (0–2% slope; Watts, 1996) and dense vegetation of this site. Erosive gains or losses are minimal, as the soil erodibility factor (K) for Sapelo fine sand surface material is low (K = 0.10; Watts, 1996). Evaporation of Hg has considerable uncertainty (Grigal, 2002). However, the unburned O horizon at the site studied here (a critical layer in the Hg budget of this study) is likely to lose Hg to the atmosphere by evaporation and capture Hg vaporized from the underlying A horizon (Schlüter, 2000); these simultaneous processes lessen the probability of significant *net* evaporative loss from the unburned O horizon. Geological degassing from the subsurface (Rasmussen, 1994a) is likely low as this area is not in the mercuriferous zones identified by Jonasson and Boyle (1972). Further, the parent material of the soil is likely marine-deposited quartz sand (Watts, 1996), whereas geological mercury is typically associated with sulfur-bearing minerals (Jonasson and Boyle, 1972). Root uptake of Hg at depth followed by translocation to foliage is unlikely because vascular plants, especially trees, are not expected to translocate Hg from roots to foliage except under conditions of gross contamination (Rasmussen, 1994b; Godbold, 1994).

4. Synthesis and Conclusion

The validity of an estimate of Hg deposition for this site based on a regional monitoring network and computer model (0.171 g ha^{-1} yr^{-1}), is suggested by the close agreement (to within 5%) of the estimate to the annualized Hg deficit of the O horizon of the annually burned plots (0.180 g ha^{-1} yr^{-1}). Offsetting errors, such as the underestimation of both dry deposition and leaching in the O horizon might be cited as the reason for the agreement; however, data from both the present study and the literature suggest that confounding inputs and outputs are limited.

Two cautions are noted in interpreting this study. First, the nature of Hg fluxes at other sites may cause fire-related emissions to differ from atmospheric deposition. For example, runoff and erosion may be more important at sites that have sloping terrain or have been denuded by wildfires. Second, the results presented here point to the atmosphere as the primary Hg input to the study site but do not provide information on whether the atmospherically deposited Hg comes from natural or anthropogenic sources. The results of this study suggest that prescribed fires in the southeastern US mainly re-emit atmospherically deposited Hg and that such re-emission is small relative to the USEPA (1997) inventory of US anthropogenic emissions (estimated prescribed fire re-emission in southeastern US = 0.09–0.2% of US anthropogenic emissions). This suggestion is further supported by the fact that most forests are subjected to low severity burns in which the O horizon is only partially consumed (Metz *et al.*, 1961; Schoch and Binkley, 1986). However, Hg emissions undoubtedly vary according to local conditions (e.g. fire regime, levels

of atmospheric Hg deposition, the possible presence of Hg in underlying geological strata) and may be relatively high where fire is reintroduced after a lengthy period of fire suppression.

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