Gaseous mercury in background forest soil in the northeastern United States

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[1] Although the soil gaseous mercury (Hg) reservoir is an important component of the soil Hg emission process, little is known of the behavior of gaseous Hg in soil pores and the processes governing the ultimate evasion of Hg from soil surfaces. In this study, gaseous Hg in background forest soil in the northeastern United States was examined during 2003 and 2004 using a novel flask sampling technique. This represents the first detailed study of gaseous Hg concentration within the soil profile. Soil gaseous Hg varied seasonally with soil temperature, and highest concentrations consistently occurred in the O- and upper A-horizons. The study revealed clear gradients in gaseous Hg concentrations, which bore striking resemblance to gradients in bound Hg. In addition, measurements of soil Hg flux were correlated with soil gaseous Hg concentrations at 2 cm depth. These results indicate that the upper soil layers, rich in bound Hg, act as a source of gaseous Hg that may ultimately be emitted to the atmosphere. Large changes in soil gaseous Hg over shallow layers underscore the importance of fine vertical resolution of measurements, and therefore the utility of flask sampling.

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1. Introduction

[2] The total atmospheric load of mercury (Hg) consists of both anthropogenic and natural sources. Natural source contributions are not known with great certainty. Although anthropogenic sources have been thought to contribute the most to the global Hg cycle [e.g., *Fitzgerald*, 1989; *Schroeder and Munthe*, 1998], natural sources may be more important than previously believed, and possibly of equal importance to anthropogenic sources [*Fitzgerald*, 1995; *Gustin et al.*, 1999]. Research during the past decade has established the importance of soils in environmental Hg cycling, showing that emission from soils, especially naturally enriched substrates, may contribute substantially to the global atmospheric load of Hg [*Gustin et al.*, 1996; *Zhang and Lindberg*, 1999; *Gustin and Lindberg*, 2000; *Engle et al.*, 2001; *Engle and Gustin*, 2002; *Coolbaugh et al.*, 2002].

[3] Understanding and quantifying the mechanisms controlling the exchange of Hg between terrestrial surfaces and the atmosphere is therefore critical toward overall comprehension of the global Hg cycle. However, achievement of this goal is hindered by lack of direct experimental data. Fluxes of Hg from soil and vegetation are influenced by soil temperature, radiation and other meteorological variables [*Lindberg et al.*, 1992; *Kim et al.*, 1995; *Lindberg et al.*, 1998; *Poissant and Casimir*, 1998], and therefore long-term, interseasonal studies may be required to accurately quantify these emissions.

[4] Forest soils receive Hg inputs from throughfall, litter and dry deposition. However, recent studies suggest that Hg emission from forest soil is comparable to or greater than depositional inputs [*Kim et al.*, 1995]. Although net emission from soil is a small percentage of total canopy emission [*Lindberg et al.*, 1998], the development of global and regional Hg budgets and models is incomplete without a better understanding of Hg exchange over terrestrial surfaces. Knowledge of Hg cycling in and emission from background forest soils (i.e., soils subject to minimal influence from pollution), particularly in the United States, is limited, as few direct experiments have been performed. *Zhang et al.* [2001] measured Hg fluxes over background forest soil in the Michigan Upper Peninsula that were comparable to those measured over forest soils in Canada [*Poissant and Casimir*, 1998] and Sweden [*Schroeder et al.*, 1989; *Xiao et al.*, 1991]. Slightly higher fluxes observed over temperate forest soils in the United States [*Lindberg et al.*, 1995] may reflect the influence of Hg deposition from local emission sources. These studies represent our limited body of knowledge of the magnitude of Hg emission from forest soils.

[5] A more detailed knowledge of not only the magnitude of background forest soil emissions and the environmental variables that influence them, but of the physical and chemical behavior of Hg within soils in general is essential to a full understanding of regional and global Hg budgets. Relatively little experimental evidence exists to confirm modes of Hg transport within and evasion from soil or the

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exact desorption sites of oxidized Hg. It is known that oxidized forms of Hg are more prevalent and persistent in soils with high organic matter content [*Yin et al.*, 1997]. Although data are limited, field studies have shown that bound Hg is concentrated in the upper, organic matter-rich soil layers (O- and A-horizons) where it is deposited after long-range atmospheric transport and forms stable complexes with humic compounds [*Schlüter*, 2000; *Amirbahman et al.*, 2004; *Tyler*, 2004].

[6] Mercury vapor exists in the gases that occupy soil pore space, primarily as elemental Hg (Hg^0), and has been observed in background soils in concentrations ranging from 1 to 53 ng m^{-3} [*Johnson and Lindberg*, 1995]. This gaseous Hg exists in kinetic steady state with Hg in soil solution and its partitioning into the gas phase has been described as a function of the temperature-dependent Henry's Law coefficient [*Scholtz et al.*, 2003].

[7] Although recent experimental evidence suggests that the ultimate release of Hg from soil may not be diffusion-controlled and therefore not purely a function of gaseous Hg concentrations within the soil [*Johnson et al.*, 2003], gaseous Hg is transported over small distances within soil matrices by diffusion, and may be sorbed by the organic matter in the upper soil layers [*Schlüter*, 2000]. Most of the Hg that is ultimately emitted from soil is likely from those layers where the highest concentrations of bound Hg are found, under conditions favoring the formation of volatile, gaseous Hg^0 and where little binding to overlying soil layers will occur, i.e., the O- and A-horizons [*Schlüter*, 2000]. In those layers, Hg may be desorbed by surface processes such as increases in soil temperature, exchange of Hg sorbed onto soil particles with water molecules, or sunlight-enhanced reactions by which Hg(II) is reduced by humic substances [*Pehkonen and Lin*, 1998; *Lindberg et al.*, 1999; *Scholtz et al.*, 2003], thereby increasing the pool of gaseous Hg^0 available for emission. In addition, it has been hypothesized that Hg^0 transpired from forest canopies may originate from gaseous Hg^0 in soil pores, which provides another impetus for quantifying this parameter.

[8] The soil gaseous Hg reservoir is therefore undoubtedly an important component in the soil Hg emission process. Direct measurements of soil gaseous Hg profiles may be useful toward identifying sites of Hg desorption, or soil layers that act as active sources or sinks of Hg and therefore influence if not govern the ultimate evasion of Hg from soil. However, few field measurements of this kind have been made, owing primarily to the lack of a widely accepted measurement method.

[9] The primary objective of this study was to determine typical gaseous Hg concentrations within background forest soil in the northeast United States. This is intended to be the first detailed study of gaseous Hg in soil. Field data were collected using a novel flask sampling technique (see Appendix A) and examined for seasonal variation in soil gaseous Hg concentration and the relationships between soil gaseous Hg and environmental variables. Also, the existence of vertical gradients of gaseous Hg within the soil profile, the sites or layers of active sorption of gaseous Hg within the soil, and the possible relationship of those sites to the ultimate flux of gaseous Hg from the soil surface were investigated.

2. Methods

2.1. Site Description and Hg Profile Measurements

[10] Measurements of soil gaseous Hg were taken at a forested site in Coventry, Connecticut, United States (41°47″N, 72°21″W) during separate field campaigns in 2003 (July–November) and 2004 (May–October). The site, managed by the University of Connecticut (UCONN) Department of Natural Resources Management and Engineering, is a mixed-species forest (primarily red maple, white pine and oak) near an agricultural field. The site is less than 1 km from a heavily traveled road and within 40 km of Hartford, Connecticut, and could therefore be subject to local pollution sources. However, mean soil Hg content in the upper 5 cm is 0.24 ± 0.21 μg g^{-1} (soil samples were collected and analyzed for Hg content (cold vapor atomic absorption spectroscopy) by the UCONN Environmental Research Institute). Though somewhat higher than background forest soils in Michigan [*Zhang et al.*, 2001], this is comparable to other background sites [*Lindquist et al.*, 1991; *Kim et al.*, 1995; *Alriksson*, 2001; *Johansson et al.*, 2001; *Grigal*, 2003] and lower than U.S. forest soils impacted by local pollution sources [*Lindberg et al.*, 1998]. The site can therefore be considered a background site with total soil Hg < 0.5 μg g^{-1} [*Lindberg et al.*, 1999].

[11] Soil gaseous Hg was measured using a mercury vapor analyzer (model 2537A, Tekran, Inc., Toronto, Canada), which produces 5-min averages of total gaseous mercury (TGM). TGM includes elemental Hg (Hg^0), reactive gaseous mercury (RGM) and particulate Hg. However, soils emit predominantly Hg^0 [*Kim et al.*, 1995]. The analyzer was housed in a small shed located on site. Soil air samples were collected and ultimately analyzed using a flask sampling technique, which has been successfully used to determine carbon dioxide (CO_2) concentrations in both air [*Ehleringer and Cook*, 1998] and at depth in soil [*de Jong and Schappert*, 1972; *Cerling et al.*, 1991; *Hersterberg and Seigenthaler*, 1991; *Wood et al.*, 1993; *Fang and Moncrieff*, 1998], but is unexplored as a means of determining soil gaseous Hg concentrations. A detailed description of the development, testing and field application of this system is provided in Appendix A.

[12] Soil TGM measurements were taken in three separate plots with slightly different elevations and soil characteristics. The plots were laid out along a slope (~33%) with a westerly aspect, and are referred to simply as "west," "central" and "east." The west plot was situated on flat ground (~145 m in elevation) and the east plot farthest upslope (~160 m). All plots lay below thick canopy cover and were therefore primarily shaded and subject to constantly changing light regimes and sun fleck activity.

[13] The plots were characterized by a thin O-horizon (~5 cm for the west plot, 3 cm for the east and central plots). Each O-horizon contained moderately to highly decomposed, amorphous organic matter topped by a thin (~1 cm) layer of slightly decomposed leaf litter. This litter layer was of similar composition for all plots (white pine, red maple, yellow birch and oak). Both the central and west

plots contained some small patches of exposed organic matter, while the east plot was completely covered with litter. Each plot contained similar hardwood understory growth, primarily red maple and yellow birch. The east and west plots contained 3–5 seedlings each (≤50 cm in height) and few vascular plants. The central plot was richer in both understory growth (~10 small seedlings) and vascular plants (e.g., oak fern).

[14] In the central and west plots, the O-horizon was underlain by an A-horizon (8 cm) of partially decomposed organic matter and sandy material. The west plot A-horizon was darker and richer in organic matter which was also somewhat more fibrous and less decomposed than the material in the central plot. The west plot also tended to be wettest, as the water table was close (at times within 70 cm) to the surface. Each of these plots was underlain by B-horizons of approximately 8 cm, and a deep C-horizon composed of sand and some organic matter.

[15] In the east plot, the O-horizon was thinner (3 cm) and underlain by a shallow (1 cm) A-horizon and a sandy B-horizon of greater than 20 cm. Both of these horizons were of lighter color than the central and west plots. Although organic matter content was not measured, visual inspection and measurements of percentage of solid matter suggest that organic matter content throughout the profile depth was lowest at the east plot, and highest at the west (Jesse Bash, UCONN ERI, personal communication, 2004).

[16] During the 2003 field campaign, soil TGM was measured at 5 cm depth at each plot, approximately once per week from early July through September, and sporadically during October and November. A deeper profile was measured at the central plot, with funnels installed at 20 and 50 cm. In this case, funnels were placed 10–15 cm apart laterally in order to avoid disturbance during installation. Typically, samples from different depths were measured in sequence from 5 cm to 50 cm. Profile measurements were performed once per week from mid-July through mid-September.

[17] Surface and profile measurements of soil TGM were repeated in 2004, although the experiment was expanded in several important ways. To better assess TGM gradients within the soil, sampling funnels were installed at 2 cm depth, which is essentially the interface between the litter layer and the upper organic soil layer, at each plot. To better understand vertical and horizontal variability in soil TGM, full profile measurements were taken at all plots, so that each of the three plots had sampling funnels installed at 2, 5, 20 and 50 cm depth. A full profile at one plot was measured per site visit, and two visits per week were made from late May through September of 2004, with several additional visits in October (the full profiles were not installed at each plot until early June).

2.2. Flux Chamber Measurement

[18] To better understand relationships between soil TGM concentrations and evasion of mercury from forest soil, a dynamic flux chamber was used during the 2004 campaign to measure TGM flux from each soil plot during flask collection periods. This is the same chamber used by *Gillis and Miller* [2000a, 2000b], and a full description of its operation can be found in those papers. Briefly, the chamber is a 30 × 60 × 30-cm opaque Teflon box with nine 2.5-cm diameter holes cut into the front. Air was drawn through the chamber by a Teflon tube (OD 0.64 cm) attached to the exhaust side of the chamber. This tube was connected via T-junction to a pump and a three-way solenoid valve controlled by a CR10X data logger (Campbell Scientific Inc., Logan, Utah). A flow meter was used to restrict the flow rate through the chamber to 11.5 L min^{-1}. Uncertainties caused by pressurization effects within flux chambers due to changes in flow rate are well documented [e.g., *Lund et al.*, 1999; *Wallschläger et al.*, 1999; *Lindberg et al.*, 2002]. This flow rate was chosen to be consistent with that of *Gillis and Miller* [2000a, 2000b] and other studies [*Carpi and Lindberg*, 1998; *Poissant and Casimir*, 1998].

[19] The solenoid valve was also attached to the analyzer sampling line, and another Teflon tube led from the valve to the chamber inlet. The TGM concentration was measured at the chamber inlet and outlet using the same 25-m Teflon line. A 45-s time lag between the data logger and the Hg analyzer was introduced to ensure that the sampling line would be clear of inlet air before the valve switched to outlet sampling (or vice versa). To account for variation in ambient TGM concentration and cartridge bias, fluxes were typically calculated as the average of four inlet samples and two outlet samples (therefore over a span of 30 min). The difference in concentration between inlet and outlet samples (ΔC, n g m^{-3}) was used to determine soil TGM flux (F) as

$$F = \mathrm{R}[\Delta C]A^{-1},$$

where R is the air volume flow rate through the chamber (L min^{-1}) and A is the area of the exposed soil within the chamber (0.18 m^2). Laboratory blanks indicated slight absorption but were not significantly different from zero (-0.1 ± 0.13 ng m^{-2} hr^{-1}, n = 8). Fluxes measured in the field were therefore not corrected for blank values. During each site visit, fluxes were measured concurrently with and in the same plot as soil TGM profile sampling. Typically, 8–10 hourly flux observations were made per site visit.

2.3. Supporting Measurements

[20] During the flask collection period, the analyzer continuously measured ambient TGM at 40 cm above the soil. Additionally, soil temperature was measured every hour using a hand-held digital thermometer at funnel depth for the 2- and 5-cm measurements, and at 5 cm during the 20- and 50-cm measurements. Soil moisture was measured at 10, 20, 30 and 40 cm using a portable soil moisture probe (PR1, Dynamax, Inc., Houston, Texas). Soil moisture data were lacking for most of August 2003 owing to a malfunction of this instrument. Incident solar radiation was measured using a homemade solarimeter placed on top of the chamber.

3. Results and Discussion

3.1. Soil Gaseous Mercury and Environmental Variables

[21] Soil TGM concentrations measured at Coventry during both field campaigns varied from below the detection limit of the system (0.75 ng m^{-3}, assuming an analyzer sampling volume of 7.5 L and analyzer detection limit of 0.1 ng m^{-3}) to 22 ng m^{-3}, but typically ranged from 1 to

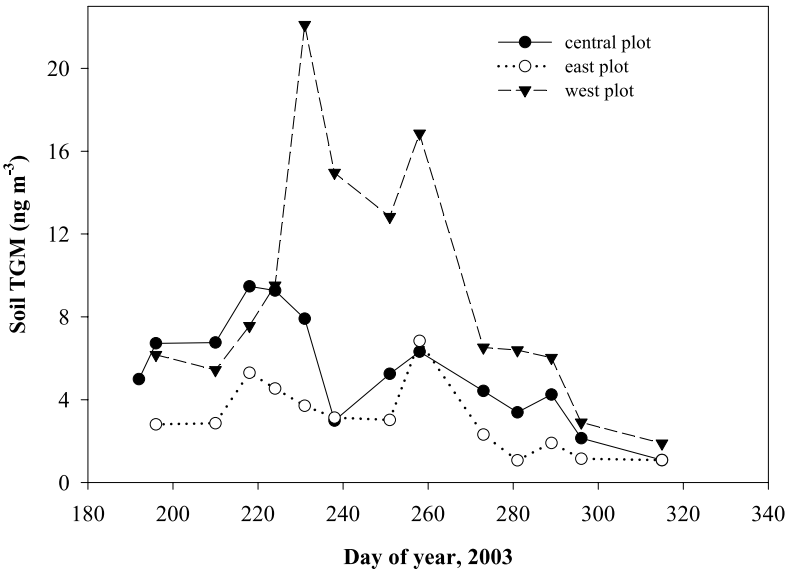

Figure 1. Variation in soil TGM at 5-cm depth at Coventry (Connecticut) forest site, July–November 2003.

4 ng m^{-3}. Mean soil TGM concentrations at 5 cm depth did not vary significantly between field campaigns, with the exception of the west plot. Two important objectives of the field experiment were to examine the data for seasonal variation in soil gaseous Hg concentration and relationships between soil gaseous Hg and environmental variables. Observations during both field campaigns confirmed seasonal variation in soil TGM, especially in the upper soil layers (Figures 1 and 2). Concentrations at 2 and 5 cm were generally higher in mid to late summer and decreased during autumn. Soil TGM was strongly dependent on temperature in the upper soil layer (5 cm depth; Figure 3, Table 1). This relationship is best explained by an exponential function, much like that for Hg vapor pressure and temperature, and also similar to observed relationships between soil TGM flux and soil temperature [e.g., *Carpi and Lindberg*, 1998; *Zhang et al.*, 2001]. This temperature dependence is the primary reason for the observed seasonal variation, as soil temperature is highly dependent on ambient air temperature (note correlation between soil TGM and air temperature, Table 1, which may be a result of covariation of soil and air temperature). Soil TGM at 20 and 50 cm was also correlated with soil temperature, though more weakly than in the upper layers, as the variation in TGM was much smaller.

[22] During the 2003 experiment, soil TGM measurements were negatively correlated with soil moisture, though the relationship was not as strong as with soil temperature (not shown). The correlation is possibly explained by increased sorption of Hg to water molecules [*Fang*, 1981; *Schlüter*, 2000]. However, this relationship was less often observed during the 2004 experiment. This result and the somewhat weak correlation between moisture and soil TGM observed in 2003 may owe to the lack of significant variation in soil moisture (typically less than 10% at any depth) during both field campaigns. More research is therefore needed to confidently understand the relationship of soil TGM with moisture.

[23] A conspicuous spike in TGM (22 ng m^{-3}) at 5 cm was observed at the west plot during August 2003 (Figure 1). Although short-term contamination of the sampling system cannot be ruled out as a possible reason for this spike, no obvious disturbance of the plot or funnel was recorded. Moreover, environmental conditions during this event present a plausible explanation. The spike is at least partially explained by enhanced soil temperature (Figure 3). However, Figure 3 also shows that 5-cm measurements taken at similar soil temperatures in 2004 did not result in the same high concentrations. Accordingly, the west plot linear correlation coefficient for 2003–2004 combined is much lower than that for the east and central plots (the west plot linear correlation coefficient for 2003 data alone is 0.99). Although the concentrations are not as high, the east and central plots showed enhanced 5-cm TGM concentrations at or near the same day of year as the west plot (Figure 1), and all three plots also showed increases in TGM during mid-September (day of year 260 in Figure 1). It is possible that these enhancements are related to both high soil temperature and unusually dry conditions at the site, given that some measurements indicated a negative correlation between soil moisture and TGM, especially during 2003. Although accurate soil moisture measurements were not available during August 2003 owing to equipment malfunction, the Coventry area experienced only a trace of precipitation during the middle 2 weeks of the month, more than 95% below normal. This period was the driest of both field experiments. Similarly, precipitation was 60% below normal during the first half of September 2003.

[24] Although solar radiation does not penetrate the soil, some correlation between soil TGM and radiation in the uppermost soil layers might be possible since Hg(II) may be desorbed from organic matter exposed to sunlight and thereby enhance Hg volatilization from soil [*Senesi and Schnitzer*, 1977], and the 2- and 5-cm measurements were taken near the interface between the soil and litter layers. Soil TGM in the upper soil layers was positively though

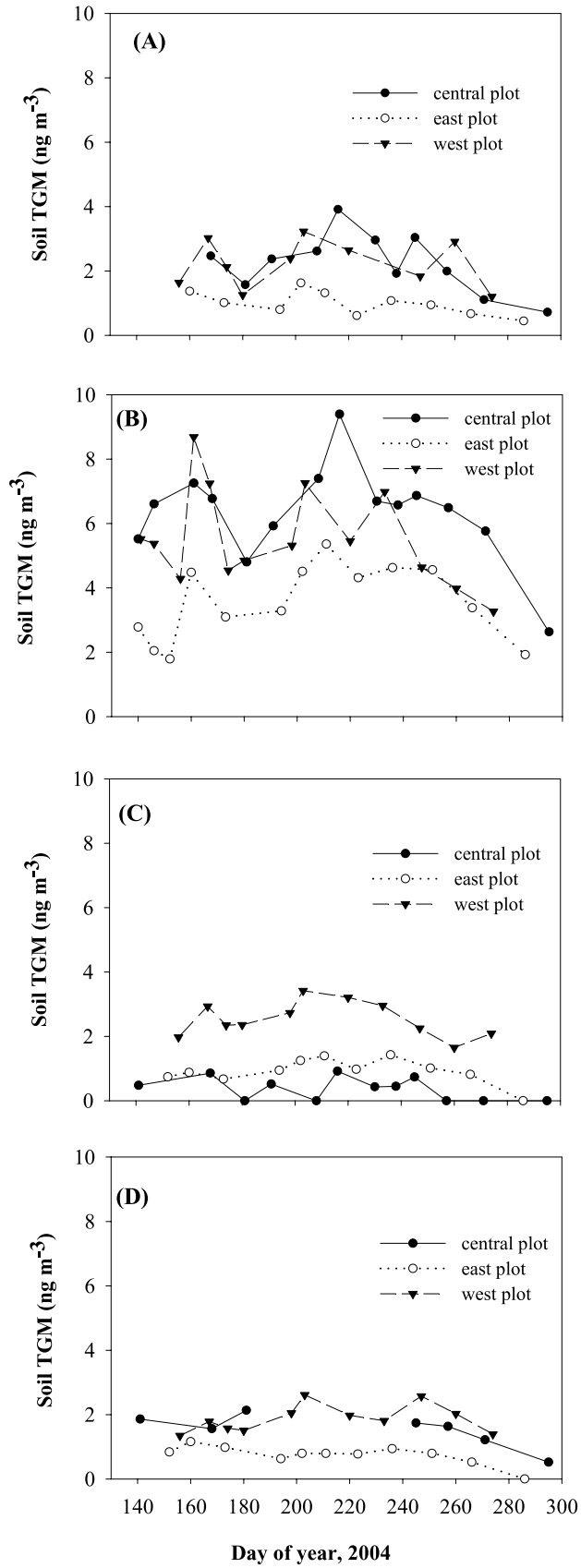

Figure 2. Variation in soil TGM at (a) 2 cm, (b) 5 cm, (c) 20 cm, and (d) 50 cm depth at Coventry forest site, May–October 2004.

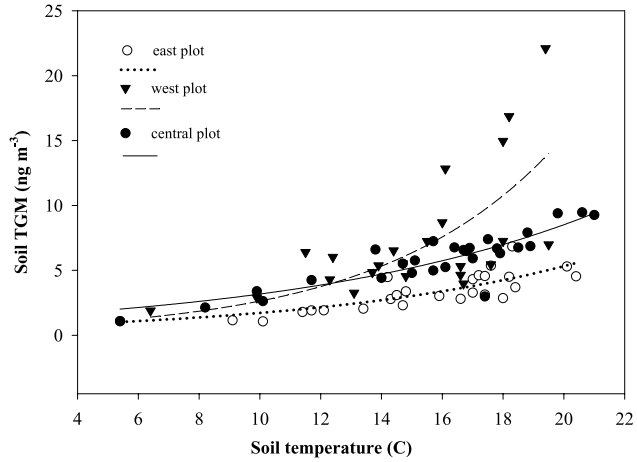

Figure 3. Exponential regressions of soil temperature and soil TGM at 5 cm depth, east ($y = 0.56e^{0.113x}$, $R^2 = 0.65$, n = 26), central ($y = 1.19e^{0.01x}$, $R^2 = 0.77$, n = 28), and west ($y = 0.46e^{0.176x}$, $R^2 = 0.44$, n = 23) plots, Coventry forest site, during 2003–2004 field campaigns.

insignificantly correlated with solar radiation in 2004 (Table 1). However, any possible relationship between soil TGM near the surface and irradiance on exposed leaf litter or organic matter is difficult to gauge in this experiment because air samples were collected over 4-hour periods, while radiation at the forest floor fluctuated constantly and varied spatially owing to gaps in the canopy. Furthermore, the solarimeter was placed on or near the flux chamber, which was positioned up to 1 m away from the funnel inlets to minimize disturbance, and the correlations shown in Table 1 are based on relatively few observations. Also, the correlation may merely be a result of covariance between solar radiation and soil temperature.

3.2. Soil TGM Profiles

[25] Mean soil TGM profiles during 2003 (central plot only) and 2004 are shown in Figure 4. The profiles were similar at each plot (Figure 4a). The remarkable consistency of the profile shapes from week to week in addition to the relationship of measured soil TGM with soil temperature (Figure 3) suggests that the flask sampling technique is a robust methodology.

[26] The data reveal the existence of gradients in gaseous Hg in background soils. Clear gradients in TGM were consistently observed, especially above 20 cm depth (Figure 4). With the exception of the east plot, TGM concentrations at 2 cm were slightly higher than ambient. In all cases, TGM was highest at 5 cm and showed marked decreases above and below that depth. Both slight increases (central plot, both years) and decreases (east and west plots, 2004) in TGM between 20 and 50 cm were observed. However, concentrations at these depths were typically small, and often below the detection limit of the flask sampling system at 20 and 50 cm depths at the east plot, and at 20 cm at the central plot in both field campaigns.

[27] A significant increase ($p < 0.001$) in TGM was observed between 20 and 50 cm at the central plot in both field campaigns. Possible funnel contamination was ruled out when samples collected using fresh Teflon tubing

Table 1. Linear Correlation Coefficients (r) for Soil TGM and Environmental Variables, Coventry Forest Site

	Soil temperature	Air temperature	Radiation	Soil moisture	Ambient TGM
TGM, 2 cm					
East plot	0.66 (10)[a]	0.74 (10)[a]	0.35 (7)	−0.32 (10)	0.71 (10)[a]
West plot	0.82 (10)[b]	0.82 (10)[b]	0.37 (5)	−0.17 (10)	0.67 (10)[a]
Central plot	0.89 (11)[b]	0.81 (11)[b]	0.37 (9)	0.10 (11)	0.32 (11)
TGM, 5 cm					
East plot	0.81 (26)[b]	0.83 (24)[b]	0.09 (8)	−0.09 (21)	0.32 (26)
West plot	0.60 (27)[b]	0.84 (25)[b]	0.56 (7)	−0.63 (23)[b]	−0.08 (26)
Central plot	0.88 (28)[b]	0.71 (25)[b]	0.08 (9)	−0.32 (23)	0.16 (28)
TGM, 20 cm					
East plot	0.71 (9)[a]	0.67 (9)[a]	0.32 (8)	−0.02 (9)	0.15 (8)
West plot	0.55 (11)	0.53 (11)	0.40 (5)	−0.20 (11)	0.30 (7)
Central plot	0.45 (20)	0.28 (20)	0.47 (8)	0.20 (17)	0.04 (18)
TGM, 50 cm					
East plot	0.32 (11)	0.63 (11)[a]	0.47 (6)	0.14 (11)	0.30 (9)
West plot	0.71 (11)[a]	0.77 (11)[b]	0.10 (5)	−0.35 (9)	−0.24 (9)
Central plot	0.45 (15)	0.55 (12)	0.48 (4)	0.13 (7)	0.31 (14)

Data are for 2003–2004 campaigns combined, except radiation and 2-cm TGM data, which were only collected during 2004. Soil moisture at 10-cm depth was used for 2- and 5-cm TGM correlation, and at 20 and 40 cm, respectively, for 20- and 50-cm TGM correlation.
[a]Significant at $p < 0.05$.
[b]Significant at $p < 0.01$.

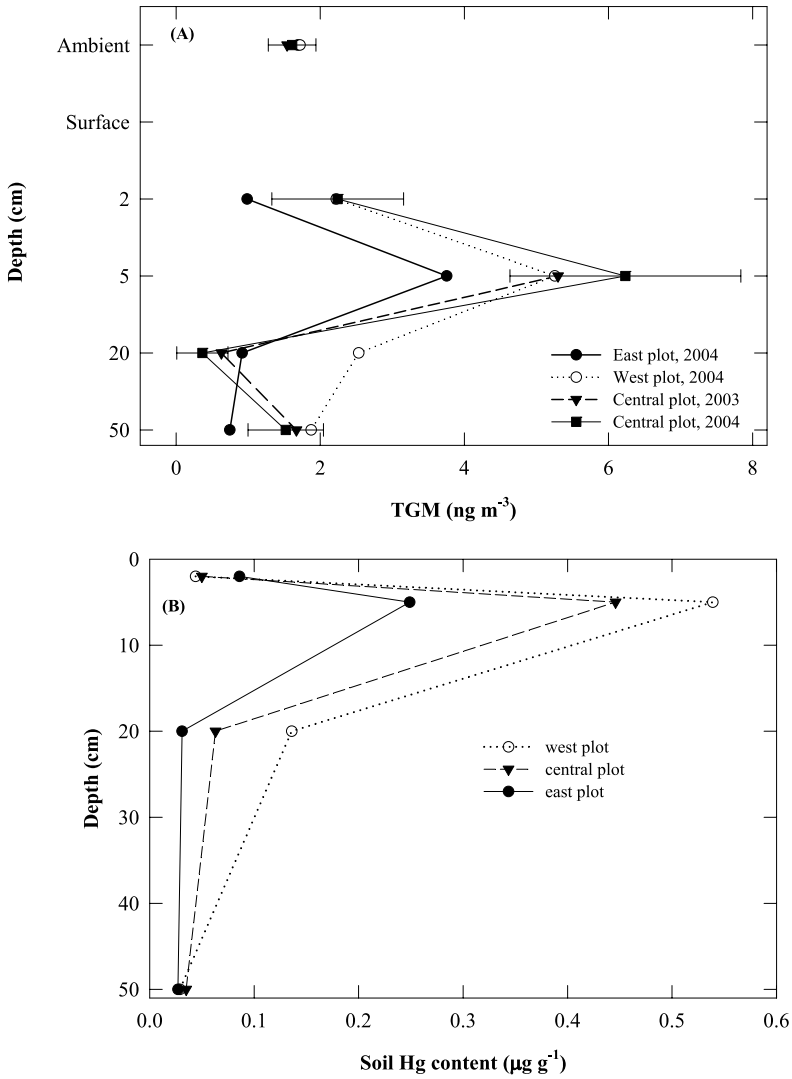

Figure 4. (a) Mean soil TGM profiles at Coventry forest, 2003 and 2004. Standard deviations for central plot (2004) measurements are shown. Ambient measurements (40 cm above surface) represent averages during flask collection periods. (b) Profile of soil Hg content at each plot, September 2004.

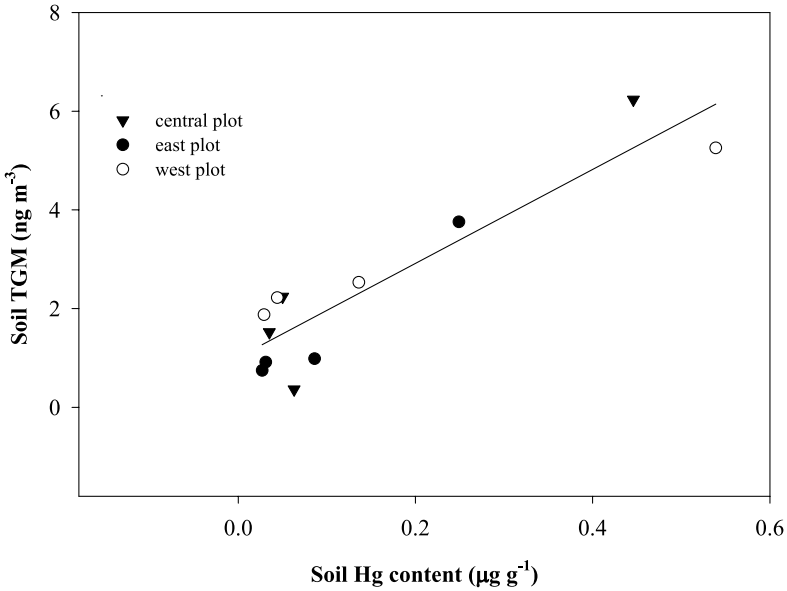

Figure 5. Linear regression of soil TGM observations (mean of all values at each plot and depth, May–October 2004) and soil Hg content (September 2004) at Coventry forest (y = 9.52x + 1.01; r = 0.91, n = 12).

inserted to the same depths without funnels yielded concentrations within the standard deviation of the other measurements (0.4 ng m^{-3} at 20 cm, 1.3 ng m^{-3} at 50 cm (central plot)). This observation as well as the larger 20-cm concentration observed at the west plot in 2004 (Figure 4) indicates fine spatial variability in soil TGM profiles, possibly dependent on local differences in porosity, organic matter and Hg content.

[28] The consistent observations of soil TGM gradients in both field campaigns are notable as they are in contrast to other studies [e.g., *Johnson et al.*, 2003] which, as in this study, found no vertical TGM gradients in soil between 20 and 40 cm, but did not examine TGM concentrations above 20 cm depth. These observations may indicate the presence of active zones of release of Hg in the upper soil layers that could contribute to the pool of Hg that is ultimately released by soil.

[29] For further exploration, bound soil Hg content was measured at each sampling depth in each plot. The mean soil TGM profiles measured during the 2004 campaign are compared to the soil Hg content (μg g^{-1}) at each depth in Figure 4b. Both total Hg content and vertical variation were similar to other background soils in the sense that bound Hg content was high in the organic layer (O- and upper A-horizon) and much lower with increasing depth [*Alriksson*, 2001; *Johansson et al.*, 2001; *Grigal*, 2003]. The profile in soil Hg content is strikingly similar to the mean TGM profiles at each site. In particular, maximum TGM concentrations were observed at 5 cm depth, where Hg content is uniformly highest. Between 5 and 20 cm, Hg and TGM decline significantly with depth.

[30] Inter-site comparison of profiles in both TGM and Hg content (Figure 4) reveals a pattern of correlation between these two variables (Figure 5). For example, just as TGM at 20 and 50 cm at the east plot were typically close to or below the detection limit of the flask sampling system, soil Hg content at those locations was close to the instrument detection limit. TGM concentration at 5 cm was high and not significantly different at the central and west plots, but was significantly lower ($p < 0.01$) at the east plot, corresponding to the marked depletion in soil Hg content in the east plot at this depth (Figure 4b). Also, both Hg content and TGM at 20 cm at the west plot are more than twice as high as measurements at the same depths at the other plots. Therefore, there is a strong relationship between the presence of bound Hg and gaseous Hg within the soil profile. If soil Hg content data in the regression shown in Figure 5 are converted to volumetric units (not shown), the slope of the regression line possibly indicates the fraction of bound Hg contributing to gaseous Hg ($y = 0.0057x + 0.66$ (r = 0.91), where y is soil TGM (ng m^{-3}) and x is bound Hg (ng m^{-3}, mass of Hg per unit bulk soil volume)).

[31] There are exceptions to this pattern. For instance, mean TGM at 5 cm was higher at the central plot in 2004 while bound Hg was higher at the west plot. However, mean TGM concentrations at these plots were not significantly different ($p > 0.9$), and the bound Hg concentrations were similar (also, mean TGM concentration at 5 cm was higher at the west plot during the 2003 campaign). The near absence of detectable TGM at 20 cm at the central plot is also notable given that Hg content at that depth was twice that of the east plot. A possible explanation for this discrepancy is that soil samples were not taken from the exact location of the funnel and bound Hg content may not be uniform within the plot.

[32] Figure 4 indicates that the organic layers (O- and upper A-horizons) are the richest zones in both Hg content and gaseous Hg in the soil pore spaces. The soil is depleted in both bound and gaseous Hg below these layers. It is possible that gaseous Hg diffuses upward through the soil and is sorbed, likely by organic matter. These data also suggest that the Hg-rich organic layer is actively desorbing Hg, thereby acting as a source of gaseous Hg in soil pore spaces that may ultimately be emitted to the atmosphere, as

Table 2. Monthly Means and Standard Deviations of Soil TGM Flux (ng m^{-2} hr^{-1}) at Coventry Forest Site, 2004

	Mean flux, central	Mean flux, east	Mean flux, west
May	9.5 (±11.6)	1.9 (±1.2)	2.8 (±1.9)
June	2.7 (±2.7)	2.5 (±2.0)	3.2 (±3.1)
July	1.8 (±2.5)	1.8 (±0.9)	2.0 (±0.8)
August	1.5 (±1.9)	1.0 (±0.4)	1.5 (±0.7)
September	0.9 (±0.8)	1.0 (±0.6)	1.3 (±0.7)
October	3.0 (±2.9)	1.2 (±1.1)	N/A
All data	2.8 (±5.5)	1.6 (±1.2)	2.1 (±1.9)

Hg released in the organic layer may be transported by diffusion toward the litter layer. The strong, positive correlation (r = 0.7–0.9) between TGM observed at 2 and 5 cm at all plots is possible evidence of this process.

[33] Soil organic matter is known to play a central role in the storage and release of Hg in soils [e.g., *Grigal*, 2003]. Organic matter content was not measured in this study. However, even without direct measurements, circumstantial evidence suggests a possible link between bound (and therefore gaseous) Hg and spatial variation in organic matter. For example, measurements of percent solid matter, which are typically inversely related to organic matter content [*Brady and Weil*, 2002], were strongly and negatively correlated with bound Hg (r = −0.7). Also, visual inspection of the soil indicated that the east plot was lighter in color, sandier and therefore lower in organic matter below 3 cm depth than the other plots. At the west and central plots, the 5-cm measurements were made at or near the interface between the O- and A-horizons (see section 2.1), which should be enriched in organic matter. Measurements at this depth also showed high concentrations of TGM and bound Hg. The 5-cm TGM measurements in the east plot, which were always significantly lower than the other plots, were made below the A-horizon and therefore likely in a zone with lower organic content. Conversely, the west plot, richest in bound Hg, was darker than the other plots down to 50 cm which could reflect higher organic matter content. Additionally, a study conducted in Connecticut forests showed vertical enhancement of organic carbon content between the surface and the upper 7.5 cm of soil, and decreased levels below [*Finzi et al.*, 1998]. Other soil studies in forests in Connecticut and Massachusetts have shown declines in organic matter from 0–5 cm to 20 cm depth [*Gulledge et al.*, 2004], or exponential declines in carbon content between 3–6 cm and 50 cm depths [*Kulmatiski et al.*, 2003]. These trends are somewhat similar to the profile in bound and gaseous Hg shown in Figure 4. Although actual measurements of organic matter content are necessary in order to firmly conclude a link between organic matter content and gaseous Hg within the soil profile, spatial variation of organic matter is a possible explanation for the observed horizontal and vertical variability in soil gaseous Hg.

3.3. Soil TGM Flux Measurements

[34] Mean daytime soil TGM fluxes observed at all three plots at the forest during May–October 2004 were 2.2 ± 5.2 ng m^{-2} hr^{-1}. Deposition events (slightly negative flux, −0.5 ng m^{-2} hr^{-1}) were observed on three occasions during the early morning (0600–0800 LST); otherwise, all observations indicated emission (0.1–43 ng m^{-2} hr^{-1}) with maximum fluxes in the afternoon (1400 LST). Mean fluxes were comparable to those observed at other background forest sites [*Schroeder et al.*, 1989; *Poissant and Casimir*, 1998; *Zhang et al.*, 2001]. These relatively low fluxes combined with few deposition events and low bound Hg content in the soil may indicate low Hg loading at the site from deposition or throughfall [*Zhang et al.*, 2001].

[35] On average, fluxes were slightly higher at the central plot, although not significantly different from the west plot ($p > 0.9$). Fluxes at the east plot were significantly lower than west and central ($p \leq 0.06$). As in other studies [e.g., *Zhang et al.*, 2001], this variation is likely explained by lower Hg content and soil TGM in the east plot (Figure 4). When fluxes at each plot were normalized to soil Hg content (5 cm), no significant differences were observed among the plots ($p > 0.2$; not shown).

[36] Similar to soil TGM concentration (Figures 1 and 2), some seasonal variation in soil TGM flux was observed (Table 2). However, it should be emphasized that monthly observations presented in Table 2 are typically based on only 2–3 days of observation per plot. Unlike soil TGM, seasonal variation appears to be more strongly related to changes in solar radiation levels than temperature, as fluxes were actually highest in May and early June before maximum foliage levels, and increased during October when canopy foliage had thinned considerably.

[37] On a diurnal basis, hourly fluxes were correlated with both air temperature (mean daily r-value of 0.62) and, more weakly, soil temperature (mean daily r-value of 0.52) at each plot. This is consistent with other measurements of soil Hg flux at a variety of sites, although many studies have shown fluxes to be more strongly correlated with these variables, especially soil temperature [*Carpi and Lindberg*, 1998; *Poissant and Casimir*, 1998; *Lindberg et al.*, 1999; *Zhang et al.*, 2001]. The weaker correlation observed in this study was possibly related to the lack of high-resolution measurements of soil temperature, which was measured on average once per hour. Also, soil temperature typically varied by no more than 1.5°C for the duration of each site visit.

[38] Poor correlation between soil TGM flux and soil moisture was observed. This is not surprising as moisture did not change diurnally in the absence of rain, and varied little throughout the experiments. Also, fluxes were not measured during rain events, which are known to lead to increases in soil Hg emissions. The poor correlation between soil TGM flux and moisture observed here may reinforce the notion that the response of soil Hg emissions to rainfall is short-term (12–24 hours) [*Lindberg et al.*, 1999].

[39] Correlation between soil TGM flux and solar radiation was observed at all plots (mean daily r-value of 0.73, eight hourly observations per visit) throughout the 2004 campaign. This correlation, illustrated in Figure 6 and similar to other studies which showed correlation between flux and radiation [e.g., *Carpi and Lindberg*, 1998; *Poissant and Casimir*, 1998; *Zhang et al.*, 2001], was typically stronger than that observed between flux and soil or air temperature. The linear correlation coefficient (r) between hourly fluxes and solar radiation was less than 0.6 on only

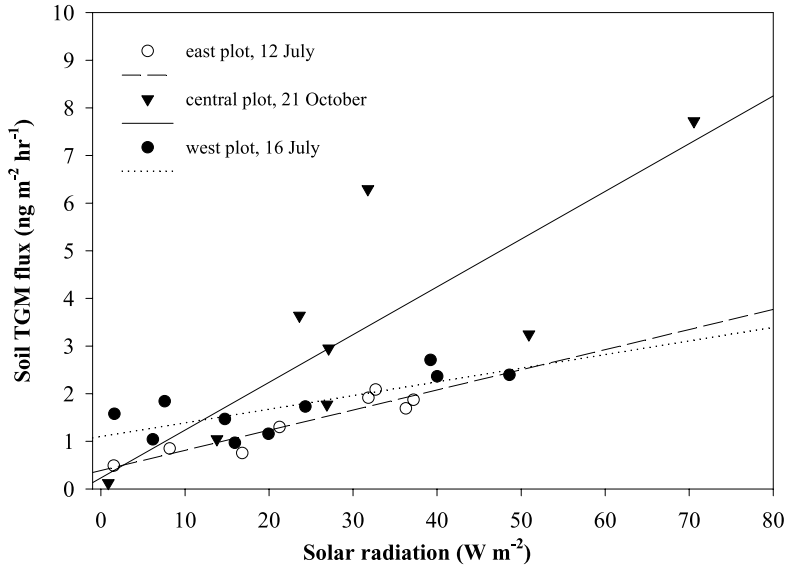

Figure 6. Linear regression of soil TGM flux and solar radiation at central plot, 21 October 2004 (r = 0.85), east plot, 12 July 2004 (r = 0.93), and west plot, 16 July 2004 (r = 0.76), Coventry forest site. Data represent hourly averages.

three site visits, and above 0.7 on more than half of the visits.

[40] This correlation was recorded despite the seeming paradox that the chamber was not transparent. Six observations of fluxes >10 ng m^{-2} hr^{-1} were recorded, all during late May to mid-June. Although radiation data were not collected when these observations were made, they occurred during periods when a high percentage of the plot was illuminated by direct sunlight. Synchronous with these episodes, the time series of ambient TGM concentration outside of the chamber showed sudden 3–6 ng m^{-3} enhancements to levels much higher than normal ambient concentration (~1.6 ng m^{-3}). These high fluxes were therefore probably not a chamber artifact. These observations are similar to those from other field experiments using opaque chambers and may show that TGM freely circulates laterally within soil pores independent of chamber placement [*Poissant and Casimir*, 1998].

[41] Results of other field studies suggest that radiation, not increase in temperature, is the dominant mechanism for enhanced soil Hg fluxes [*Carpi and Lindberg*, 1998; *Engle et al.*, 2001; *Zhang et al.*, 2001], as strong correlation between solar radiation and soil Hg flux has been observed even when soil temperature is held constant [e.g., *Zhang et al.*, 2001]. The strength of the observed correlation between soil TGM flux and radiation exemplified in Figure 6 supports this notion. Although partially explained by differences in soil Hg content among plots (see section 3.4), the observation of significantly higher fluxes at the central and west plots compared to the east could also support the hypothesis of Hg desorption from small patches of organic matter exposed to radiation, which were present only in the central and west plots (see section 2.1). However, no controlled experiments were performed during the field study. Therefore the possibility that the correlations illustrated in Figure 6 is the result of covariance between solar radiation and soil temperature (and ultimately heating rather than photochemistry) cannot be ruled out, especially since the solarimeter was placed on top of the opaque chamber. The interrelations between these environmental parameters makes quantitative determination of the underlying mechanisms controlling soil Hg flux difficult in this particular study.

[42] The highest mean (Table 2) and instantaneous soil Hg fluxes (>40 ng m^{-2} hr^{-1}) were measured at the central plot. This plot also consistently showed the steepest response curve to solar radiation (Figure 6) and although radiation levels at each plot were not significantly different throughout the 2004 experiment ($p > 0.2$), experienced the highest instantaneous radiation levels (70–80 W m^{-2}, 1200–1400 LST). The presence of small pockets of organic matter exposed to higher instantaneous radiation levels than what was observed in the west plot is a possible explanation in support of the notion that photochemistry is the dominant mechanism. However, it is notable that the central plot possessed somewhat different understory characteristics than the east and west plots. Although leaf litter composition and exposed organic matter were similar to the west plot, more seedlings and vascular plant species were present (see section 2.1). It is possible that the difference in emission recorded at the central plot is in part explained by biotic factors (e.g., soil-root interaction or enhanced transpiration) related to the somewhat denser surface vegetation.

3.4. Relationship of Soil Hg Flux and Soil TGM Concentrations

[43] A major purpose of this study was to investigate the relationship of the soil gaseous Hg profile, and therefore the role of different soil layers, with the ultimate effusion of gaseous Hg from the soil surface. Therefore flux measurements were compared with soil TGM measurements. When

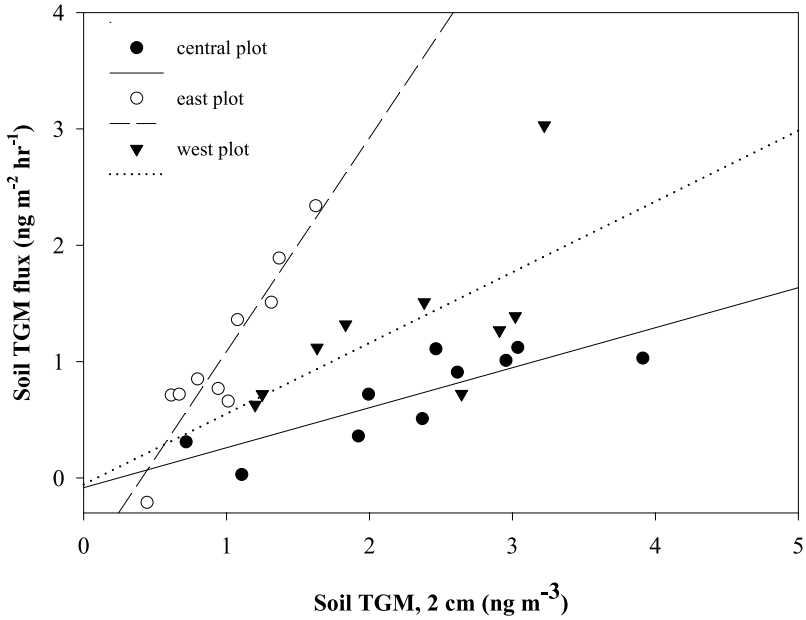

Figure 7. Linear regression of soil TGM at 2 cm depth and soil TGM flux at central (r = 0.84), east (r = 0.94), and west (r = 0.65) plots, Coventry forest site, May–October 2004. The linear correlation coefficient for all data combined is 0.37.

averaged over the duration of each soil gas collection period, no correlation was found between soil TGM flux and soil TGM at 5, 20 or 50 cm. However, flux was strongly correlated with gaseous Hg concentrations at 2 cm (Figure 7). This suggests that the points of desorption and ultimate release of Hg from the soil are within the upper 5 cm and is consistent with studies showing correlation between soil CO_2 flux and CO_2 concentrations at shallow (1 cm) depths in background forest soils [*Risk et al.*, 2002; *Oishi and Lee*, 2002]. If this pattern holds in other surfaces, any measurements of TGM concentrations or gradients deeper in the soil will show little relation to flux.

[44] The relationships depicted in Figures 3, 6 and 7 show considerable variation among plots. To explore a possible reason for this variation, soil TGM measurements were normalized to soil Hg content at 5 cm. This depth was chosen because Hg content was highest and varied more significantly among plots than the 2-cm measurement. Normalizing by Hg content reduces the spread of the data shown in Figure 7, and increases the overall linear correlation coefficient from 0.37 to 0.5. Similar results occur when soil TGM concentrations or fluxes in Figures 3 and 6 are normalized to Hg content. Therefore variations in the individual regression lines shown in Figures 3, 6 and 7 are at least in part due to differences in soil Hg content among the plots (Figure 4b).

4. Conclusions

[45] The observed correlation between soil flux and TGM at 2 cm depth (Figure 7) and the large gradients in soil TGM observed over relatively small depths (e.g., 2–5 cm, 5–20 cm; Figure 4) are notable. Previous studies of this kind revealed no gradients in soil TGM over larger depths (20–40 cm) and found no correlation between flux and gaseous Hg within the soil. This may be due to a lack of soil TGM measurements above 20 cm depth [*Johnson et al.*, 2003].

[46] Soil TGM measurements at 5 cm depth suggest that the organic layer, which is rich in bound Hg, is also an active source of gaseous Hg which may ultimately be emitted to the atmosphere. The correlation between flux and TGM at 2 cm suggests that the litter layer is the approximate point of release of soil TGM into the air. Lack of correlation between flux and TGM concentration at 5 cm suggests that soil material, possibly organic matter, between the litter layer and the funnel placement at 5 cm is actively sorbing or desorbing Hg. Therefore TGM concentrations are not uniform throughout the organic layer. Changes in soil temperature strongly influences soil TGM concentration at any depth, but temperature profile and changes in bound Hg content should result in vertical variation in TGM concentration, even within a relatively shallow organic layer. The surface processes that result in the emission of Hg into the atmosphere (e.g., photochemical reactions or changes in thermal energy) likely occur within the litter layer or over a small, finite layer at the interface between the O- and A-horizon.

[47] In any case, these results underscore the importance of soil TGM measurements with high spatial resolution within the vertical soil profile and the importance of the upper 5 cm of soil in the soil gaseous Hg pool. Measurements taken below the organic layer will show no relationship between flux and soil TGM concentration, even though such a relationship exists close to the surface. Measurement systems which are subject to contamination from ambient air are limited in their ability to observe fine soil TGM gradients or capture processes within the O- and A-horizons. The flask sampling system developed in this study is therefore valuable as it allows analysis of soil

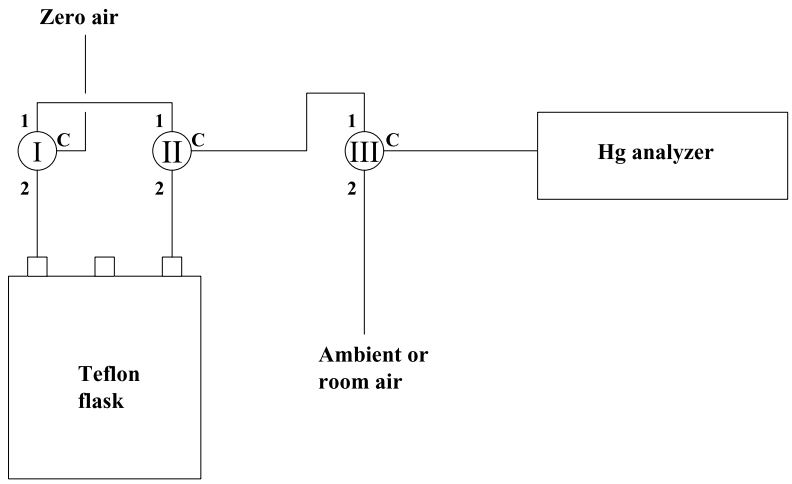

Figure A1. Schematic diagram of valve assembly. Each valve has three ports. In the unenergized mode, port 1 is connected to the common port (labeled as "c"). During the collection period, valve III is energized to allow direct measurement of ambient air near the soil-air interface.

gas samples, even at depths close to the surface, with minimal contamination from ambient air.

Appendix A: Methodology for Soil TGM Measurements

A1. Overview of Flask Sampling System

[48] Existing studies of TGM in soil employed such techniques as inserting Teflon wells to depth and withdrawing air through a syringe [*Johnson et al.*, 2003] or drawing air through Teflon-coated steel tubes directly into an Hg analyzer [*Wallschläger et al.*, 2002]. In the latter study, Hg concentrations were diluted by the intrusion of ambient air due to the high flow rate and sample volume. A robust measurement system should therefore be able to sample known volumes of air with minimal disturbance to the surrounding soil, and promote mass flow into the system without drawing in ambient air from above the surface.

[49] Flask sampling has been successfully used to determine carbon dioxide (CO_2) concentrations in air [*Ehleringer and Cook*, 1998] and at depth in soil [*de Jong and Schappert*, 1972; *Cerling et al.*, 1991; *Hersterberg and Seigenthaler*, 1991; *Wood et al.*, 1993; *Fang and Moncrieff*, 1998] but is unexplored as a means of determining soil TGM concentrations. The flask sampling system developed here, which is intended for easy deployment in the field and general applicability to the study of soil Hg and other trace gases [*Sigler*, 2006], entails collection of soil air in a 1-L Teflon flask equipped with three ports and fitted with a steel pressure fixture. Air is drawn into one port through Teflon tubing (60 cm length, 0.64 cm OD) connected to a Teflon funnel (6.4 cm diameter), which can be placed at varying depths in soil. The funnel is placed aperture-downward in the soil. During field application, soil disturbance during funnel installation could potentially affect vertical variation in soil gaseous Hg. Therefore soil should be carefully removed by layer and then replaced over the funnel in the same sequence, preserving the existing profile as much as possible. Also, displaced soil should be allowed to settle around the funnel for several days before sampling.

[50] Since more than 1 week would be required to reach an equilibrium Hg concentration in the flask by diffusion, the collection period is shortened by attaching a low flow (450 mL min^{-1}) pump (model NMP05 minipump, KNF Inc.) to the second port. The pump flow is split by flowmeters so that the actual flow out of the soil is normally 20 mL min^{-1}. A small flow rate combined with a large funnel aperture should minimize the intrusion of ambient air. A flow rate of 30 mL min^{-1} is sufficient to minimize the dilution effect on soil CO_2 measurements [*Fang and Moncrieff*, 1998]. Also, vertical air speed caused by natural wind pumping in the top 10 cm of the soil is in the range of 10^{-4} to 10^{-2} m s^{-1} [*Farrell et al.*, 1966; *Colbeck*, 1989]. Air speed produced by the flask sampling should be smaller than this to minimize ambient air intrusion. In the system described here, the vertical air speed across the funnel aperture is 9×10^{-5} m s^{-1}, which is lower than that used for soil CO_2 by *Fang and Moncrieff* [1998].

[51] Air is collected over a 4-hour period, and therefore cycled through the flask volume approximately 5 times to ensure thorough flushing. In the field experiment described in this study, the collection period was shortened from 4 to 3 or 3.5 hours during rainy weather or when difficulty was encountered stabilizing the flow rate into the flask below 30 mL min^{-1}. This was a common problem in the field, but is not expected to significantly impact the measurement as multiple (3–4) flushings of the flask and typical values of vertical air speed in soil are maintained. Also, to maximize the number of measurements during particular site visits, the flow rate into the flask can be increased to 50 mL min^{-1} and total sampling time reduced to 90 min for the deeper measurements, as was done for 20- and 50-cm measurements during the 2004 field experiment described in this study. Field tests during the 2003 campaign showed that higher flow rates did not impact measured TGM levels at 20 and 50 cm depth. This is likely due to the fact that soil at these depths is more compact and the intrusion of ambient air is less likely.

[52] Upon completion of soil air collection, the flask is detached from the funnel tubing and connected via a valve assembly (Figure A1) to the Hg analyzer. The assembly

consists of three solenoid valves (Tekran, Inc.), each with three ports. The common ports on each valve, labeled as "c" in Figure A1, connect the analyzer sample stream to a "zero" (or clean, Hg-free) air canister (Tekran, Inc.) by Teflon tubing. In the default mode (valves not energized), the zero air bypasses the flask and enters the analyzer. When valve III is energized, the analyzer samples ambient air near the soil surface. In order to analyze the TGM concentration inside the flask, the flask is first attached to ports 2 on valves I and II, and valve III is deactivated so that ambient air is no longer drawn into the analyzer. Valves I and II are then energized, the flask ports are opened and the flask air is drawn into the analyzer using the zero air as carrier.

[53] While sampling zero air, the analyzer may detect small blank, or baseline, levels of TGM (typically $\leq$0.1 ng m^{-3}). The flask should be flushed for three to four additional 5-min cycles after the soil air sample is released into the analyzer, so that the blank concentration is determined as the average of those additional cycles. By recovering the blank, the sample concentration can be more accurately determined by subtracting the average blank from that of the detected sample concentration. However, in the field, a concentration of zero was typically attained after a single 5-min flushing.

[54] Field testing of the system indicated that a dry flask and zero air stream are desirable. Moist air within the flask or the valve assembly may result in high blanks and an inability to determine a flask TGM concentration above baseline. This problem is minimized by operating in dry conditions and by allowing the incoming air stream to pass through a container of silica gel desiccant before the zero air canister (Figure A1).

A2. Laboratory Test Results

[55] Four laboratory experiments were conducted to test the reliability and accuracy of the flask sampling system. The first involved collection and recovery of zero air. The flask was connected to the valve assembly, flushed with zero air for 10–15 min, sealed with zero air trapped inside and sampled after periods of 2–12 hours. The second experiment involved collection and recovery of room air. The flask lid was opened for a period of 18–24 hours, allowing room air to enter by diffusion, then sealed and sampled. The third experiment involved direct injection of Hg vapor into the flask. A 50-μL syringe was used to draw known volumes (5 to 30 μL) of saturated Hg vapor from a bottle of pure liquid Hg placed in a water bath at a known temperature. The Hg vapor was injected through a septum into the flask. The mass of injected Hg was determined by multiplying the known concentration of the saturated Hg vapor by the syringe volume. For three of the injections, the flask was left sealed and undisturbed for 14, 19 and 24 hours before sampling, in order to test for slow leakage.

[56] In the fourth experiment, the entire system (flask collection setup and valve assembly) was tested in the laboratory. Room air was pumped through the Teflon funnel and into the flask over a 4-hour period. Simultaneously, valve III was energized (Figure A1) and room air was sampled by the analyzer. At the end of the collection period, the analyzer was switched to zero air as the flask was attached. Several 5-min cycles of zero air were obtained both before and after the flask air was sampled. Unless sorption of Hg is occurring within the system, the converted flask concentration should be approximately equal to the average room concentration during the collection period.

[57] Average TGM concentrations recovered from the flask sample in the zero air tests were 0.05 ± 0.02 ng m^{-3}, similar to those in standard, zero air samples, which tend to be <0.1 ng m^{-3} (during the test, standard zero air concentrations were 0.02 ± 0.04 ng m^{-3}). The same was true when the flask was left undisturbed for a 12-hour period. When the same test was performed with ambient air substituted for zero, TGM concentrations in flask air (2.09 ± 0.38 ng m^{-3}) typically agreed with those of ambient air within approximately 3% (2.15 ± 0.37 ng m^{-3}).

[58] The direct injection experiment yielded a significant linear correlation ($y = 0.14+1.02x$, r = 0.98, n = 27, where x is injected Hg and y is measured Hg) between measured and injected TGM concentrations. No significant differences were observed when the flask was allowed to sit for 14–19 hours between injection and sampling. A diluted concentration measured after a 24-hour wait between injection and sampling may indicate some slow leakage from the container over periods longer than 19 hours.

[59] In the ambient air test, good agreement between flask and ambient air was generally achieved ($y = 0.22 + 0.91x$; r = 0.88, n = 7). Over-recovery of TGM during this experiment occurred when an LDPE funnel was used, as a Teflon funnel was unavailable at that time (for all other collections, a Teflon funnel was used). Use of Teflon materials is preferred to avoid contamination.

[60] The combined results of these four experiments support two important conclusions. First, neither the flask collection nor valve assembly experiences significant leakage over periods as long as 12 hours. Leakage in the system would draw in ambient air, resulting in recovered concentrations above baseline in the zero air tests and below the large concentrations considered in the injection experiment (mean ambient TGM concentrations in the laboratory were 1.5–2.0 ng m^{-3}). Second, the system can accurately recover known TGM concentrations at very low levels. Results indicate no contamination within the flask collection setup or valve assembly, or inability of the system to accurately analyze the air trapped within the flask. The system is therefore robust for collecting and analyzing samples in the field, and can be used to collect and transport field samples to a laboratory within a 19-hour timeframe for analysis.

[61] A drawback of the system is the inability to analyze soil air samples with high time resolution. To avoid contamination and disturbance, it is essential to draw in soil air at a low flow rate and over a long sampling period. It is therefore difficult to investigate potential diurnal changes in soil TGM, which may be expected given observed diurnal variation in soil Hg emission, and presents difficulty in examining the impacts of highly variable meteorological parameters such as solar radiation. This drawback could be improved by placing multiple funnels at a common depth within a soil plot and initiating air sampling at staggered starting times using multiple flasks.

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