Susceptibility of Soil Bound Mercury to Gaseous Emission As a Function of Source Depth: An Enriched Isotope Tracer Investigation

Maxwell E.E. Mazur, Chris S. Eckley, Carl P.J. Mitchell

Version Post-print/ Accepted manuscript

Citation Mazur, M. E. E.; Eckley, C. S.; Mitchell, C. P. J. *Environmental Science & Technology* **2015**, *49* (15), 9143–9149.
(published version)

Publisher's statement This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Environmental Science & Technology*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see [DOI: 10.1021/acs.est.5b01747](https://doi.org/10.1021/acs.est.5b01747).

How to cite TSpace items

Always cite the published version, so the author(s) will receive recognition through services that track citation counts, e.g. Scopus. If you need to cite the page number of the TSpace version (original manuscript or accepted manuscript) because you cannot access the published version, then cite the TSpace version **in addition to** the published version using the permanent URI (handle) found on the record page.

1 **Susceptibility of soil bound mercury to**
2 **gaseous emission as a function of source**
3 **depth: an enriched isotope tracer**
4 **investigation**

5 Maxwell E.E. Mazur^{a#}, Chris S. Eckley^b, Carl P.J. Mitchell^{*a}

6

7

8

9 *Corresponding Author: carl.mitchell@utoronto.ca; tel: (416) 208-2744; fax: (416) 287-
10 7279

11 a. University of Toronto Scarborough, Department of Physical and Environmental

12 Sciences, 1265 Military Trail, Toronto, ON, M1C 1A4, Canada

13 b. U.S. Environmental Protection Agency, Region 10, 1200 Sixth Avenue, Seattle, WA,

14 98101, United States

15 #. Current address: Alberta Environment and Parks, 111 Twin Atria Building, 4999 – 98

16 Avenue, Edmonton, AB, T6B 2X3, Canada

Abstract

Soil mercury (Hg) emissions are an important component of the global Hg cycle. Sunlight induced photo-reduction of oxidized Hg to gaseous elemental Hg is an important mechanism controlling emissions from the soil surface, however we currently understand little about how subsurface Hg stores participate in gaseous Hg cycling. Our study objective was to investigate the ability of Hg at deeper soil depths to participate in emissions. Soil fluxes were measured under controlled laboratory conditions utilizing an enriched stable Hg isotope tracer buried at 0, 1, 2 and 5 cm below the surface. Under dry and low-light conditions, the Hg isotope tracer buried at the different depths participated similarly in surface emissions (median flux: $7.5 \text{ ng m}^{-2} \text{ h}^{-1}$). When the soils were wetted, Hg isotope tracer emissions increased significantly (up to $285 \text{ ng m}^{-2} \text{ h}^{-1}$), with the highest fluxes (76% of emissions) originating from the surface 1-cm amended soils and decreasing with depth. Mercury associated with sandy soil up to 6 cm below the surface can be emitted, clearly demonstrating that volatilization can occur via processes unrelated to sunlight. These results have important implications for considering how long older, legacy soil Hg contamination continues to cycle between soil and atmosphere.

1. INTRODUCTION

The flux of gaseous elemental mercury (Hg) from soils to the atmosphere is an important component of the global mercury cycle, and acts as a control on the accumulation of Hg in soils.¹ Soil Hg is typically oxidized (e.g. Hg^{2+}) and bound to organic matter with emissions being a function of reduction to Hg^0 and its transport and flux from the soil.² The magnitude of surface-air fluxes is often significantly correlated with several physical and chemical variables, including: incident solar radiation, soil Hg concentration, temperature, soil moisture, soil disturbance, soil texture, mineralogy, air Hg and oxidant concentrations, and atmospheric turbulence.³⁻⁷

Mercury emissions are typically higher during the daytime than at night and are usually strongly correlated with variations in meteorological factors.⁸ Controlled laboratory experiments have confirmed the importance of solar radiation (particularly in the UV range 410-700 nm) in promoting the photo-reduction of Hg^{2+} to Hg^0 and subsequent emission.^{7,9-11} During night/dark conditions, some studies have shown that Hg emissions cease or change direction toward net deposition.^{4,8} While nighttime fluxes are usually lower than daytime, significant Hg emissions can occur during dark/low-light conditions and be an important contributor to the overall magnitude of diel emissions.⁹ Mercury fluxes from forested soils during the growing season mostly occur during low-light conditions because closed canopies provide significant shading and very limited solar radiation reaches the surface.¹²

Given that solar radiation cannot penetrate beyond the surface, possibly only the very top of the soil column can supply Hg for emission via photo-reduction.^{10,13,14} To

sustain emissions over time for radiation-driven fluxes, the surface layer must be replenished from above (e.g. wet/dry deposition) and/or below the soil interface. The potential for sub-surface transport and subsequent emission is not well understood, but has important implications for the mobility of the large pool of terrestrial Hg that occurs below fresh/partially decomposed litter.¹⁵ Recent studies have suggested that sub-surface Hg transport contributes to surface emissions; however there remain important questions regarding the depth over which these processes operate and the variables controlling their release.^{16,17}

In field and laboratory studies, soil Hg emissions often increase in response to rain events/surface wetting.^{6,18-20} Possible mechanisms for this phenomenon include physical displacement of Hg in interstitial soil air, Hg release from soil due to competition for binding sites by polar water molecules, and preferential photo-reduction of soluble pore water Hg^{2+} to Hg^0 .²⁰⁻²³ Mercury dissolved in soil water may also be transported vertically toward the surface via capillary forces, particularly as the soils dry.^{7,17,19,20} The extent over which vertical Hg transport may occur and then participate in soil Hg fluxes could be better elucidated through tracer experiments, but no such research has yet been undertaken.

In this study, we used an enriched stable Hg isotope tracer in laboratory experiments to identify the susceptibility of soil Hg to emission in relation to the depth of the Hg source in the soil column. This objective was investigated under both dry and wet soil conditions. Understanding the extent to which soil Hg at different depths is able to participate in surface emissions and continue to actively cycle environmentally, versus being strongly sequestered by soil burial, is important for predicting ecosystem response

times to changes in anthropogenic Hg emissions. Our use of an enriched stable isotope Hg tracer provides a powerful tool that allows the direct observation of Hg flux dynamics originating from specific soil depths. Such direct measurements are important in supporting/rejecting existing theories regarding surface Hg emissions based on field and laboratory observations of ambient Hg. We hypothesized that deeper soil layers contribute to Hg emissions and that episodes of soil wetting promote subsurface Hg transport and increase the potential for Hg in deeper layers to be released via surface emission.

2. EXPERIMENTAL

2.1. Experimental design

Controlled laboratory experiments to measure gaseous Hg fluxes from soil were conducted, mimicking conditions observed at the forest floor during summer leaf-out in a deciduous forest, similar to the setting in recent field research.²⁴ This included constant low-light ($18 \pm 5 \text{ W m}^{-2}$) irradiance supplied by two fluorescent tubes with relatively stable air ($24 \pm 1 \text{ }^{\circ}\text{C}$) and soil temperatures ($22 \pm 2 \text{ }^{\circ}\text{C}$). The low-light conditions contrast with other experimental work intended to mimic a desert setting (e.g., Ericksen et al.²⁵), but are representative of the $\sim 20 \text{ W m}^{-2}$ average irradiance observed during the breadth of overcast to full-sun conditions at the deciduous forest floor during summer.¹²

In each experiment, we laid 1-cm deep layers of sandy soil labeled with an enriched stable Hg isotope tracer (91.09% abundance ^{199}Hg amended as HgCl_2) at

different depths (surface, -1 cm, -2 cm, and -5 cm, plus a control without a tracer-amended soil layer) in experimental mesocosms, and measured gaseous Hg fluxes to the atmosphere using dynamic flux chambers and gold traps (measurements detailed in section 2.1.2). Experimental mesocosms consisted of a polycarbonate container (length 42 cm, width 33 cm, height 17 cm) with a perforated bottom to allow drainage during wetting of the soil (Figure 1). Experiments were conducted in random order, one replicate at a time using 10% nitric acid washed mesocosm containers. Apart from the depth at which the labeled soil was laid down, each experiment was conducted exactly the same with respect to soil handling and timing. Soil was left to sit in tubs for one week prior to being used in each experimental replicate. Each of the five different experimental treatments (labeled soil at surface, -1 cm, -2 cm, -5 cm and an unlabeled control) was conducted in triplicate for a total of 15 separate, multi-day experiments. For each experiment, unamended soil (without the Hg tracer) was carefully added into the container, the depth depending on the experimental treatment. Soil amended with ^{199}Hg tracer was then carefully placed as a 1-cm deep layer at the experimental depth, defined as the top of the amended soil layer. Except for experiments with amended soil at the surface, unamended soil was then added to ensure each experiment had a total soil depth of 8 cm.

Figure 1: Diagram of the experimental apparatus. This example is for an experiment with ¹⁹⁹Hg amended soil at 2-cm depth.

In each experiment, a series of Hg flux measurements were conducted over a period of approximately one day on each mesocosm when soils were dry (n=3-4 for each experimental replicate). Soils were then wetted to approximate field capacity by slowly adding deionized water until droplets of water formed along the perforations on the bottom of the soil mesocosm. Water was added over a perforated lid secured to the top of the mesocosm container to simulate rainfall, although our rate of addition (a total of 2.5 l; equivalent to 180 mm hr⁻¹) was much higher than usually observed. A piece of nytex mesh was placed directly onto the surface of the soil to reduce the velocity of water droplets and to better disperse droplets such that wetting was even and imparted as little physical disturbance to the soil surface as possible.²⁸ Following soil wetting, mercury flux measurements (n=9-12 for each experimental replicate) continued for approximately 3 days.

2.1.1. Preparation of labelled soil

To ensure consistency, soil was prepared in large batches in the lab by combining sand with high organic content soil, to a final organic matter content of $5 \pm 1\%$ by mass. A sandy soil with organic matter content of $\sim 5\%$ was chosen as it is representative of surface upland forest soils in the western Great Lakes region of North America.^{24,26} When packed in the experimental mesocosms, mean bulk density of the soil was 1.14 g cm^{-3} , which is similar to unimpacted sandy loam surface soils (mean of 1.05 g cm^{-3} in Stone and Elioff²⁹) within the northern Minnesota region on which this lab study was based. Field capacity was estimated from the continuous soil moisture data measured in the experiments (i.e., where soil moisture content begins to stabilize post-wetting) as 0.28 ± 0.03 (mean $\pm$ standard deviation).

Ambient Hg concentrations in the soils were very low, ranging from 0.6-4.2 ng Hg g⁻¹ dry weight, with a median concentration of 1.4 ng Hg g⁻¹. Isotope amended soil layers were created by mixing dry soil with an enriched ¹⁹⁹Hg tracer solution (made from a stock batch of enriched, 91.09% abundance ¹⁹⁹HgCl₂) to a target final soil concentration of 100 ng ¹⁹⁹Hg g⁻¹. This concentration is representative of background soil concentrations where point sources of Hg pollution do not exist.²⁷ Each amended soil batch was allowed to air-dry completely (1-2 days) before incorporation into each mesocosm. Soil then settled in mesocosms for 7 days before starting experiments, effectively allowing for complete incorporation of the added isotope tracer into the solid soil matrix.

2.1.2. Measurement details

Gaseous Hg emissions were measured using a cylindrical Teflon dynamic flux chamber (0.036 m² footprint, 6.5 cm height, 2.0 litre volume, with 1 cm diameter inlet holes every 2.5 cm around the perimeter and a 5 cm wide bottom flange)⁵ placed directly on the surface of the soil mesocosms. Gold traps, utilizing gold-coated silica beads, were used to accumulate Hg in air. We simultaneously sampled air from two locations using two different gold traps: immediately adjacent to one of the flux chamber's perforated side inlets (using a retort stand to hold the inlet line in place) and from the outlet port at the top of the flux chamber (Figure 1).¹³ Air sampling pumps were utilized to draw air through the gold traps at a rate of 1.5 l min⁻¹. A bubble flow calibrator was used to verify this flow rate before and after every measurement. The Hg flux was calculated as:

$$F = Q * (C_0 - C_i) / A \quad (1)$$

where F is the Hg flux (ng m⁻² h⁻¹), Q is the chamber flushing flow rate (m³ h⁻¹), C₀ is the air Hg concentration measured at the outlet (ng m⁻³), C_i is the Hg concentration measured at the inlet, representing the amount of Hg flowing into the chamber's inlet holes, and A is the footprint area of the chamber (m²).

Measurement durations ranged from 30-120 minutes; shorter durations were used to rapidly collect several flux measurements under stable conditions (i.e. blanks, dry fluxes) while longer durations were used to characterize flux response to wetting. Chamber blank measurements were made prior to each experiment to verify the cleanliness of the flux chamber (the flux chamber was soaked in 10% nitric acid and

rinsed thoroughly following each experiment). Chamber blank measurements were made over clean polycarbonate film laid on top of the experimental soil. Similar to other studies, chamber blank fluxes were low ($0.6 \pm 1.2 \text{ ng}^{199}\text{Hg m}^{-2} \text{ h}^{-1}$) indicating no influence on the observed fluxes due to the chamber itself.^{5,13} Physical environmental variables, including air temperature (Campbell Scientific CR1000 internal temperature sensor), soil temperature (BetaTherm 100K6A1B thermistor), soil moisture content (Decagon Devices EC-5 soil moisture sensor) at 1-cm depth, and incident solar radiation (Kipp & Zonen SP-LITE2 Silicon Pyranometer) were logged at 1 minute intervals using a Campbell Scientific CR1000 data logger throughout each experiment.

2.2. Analytical methods

Desorption of gaseous Hg adsorbed to the gold traps was carried out on a Tekran 2600 mercury analyzer, using the US EPA Compendium Method IO-5 for sampling vapour phase Hg in ambient air.³⁰ Mercury isotopes were detected by directly hyphenating the Tekran desorption system to an Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Agilent Model 7700x). In brief, the sample gold trap was thermally desorbed in a stream of Hg-free argon and collected onto a second pure gold trap. The second trap was thermally desorbed and introduced directly into the torch of the ICP-MS, which was programmed to detect Hg isotopes, specifically ^{199}Hg (the dominant isotope in the Hg tracer) and ^{202}Hg (the most naturally abundant Hg isotope). We used a 5-point calibration curve ($r^2 > 0.99$) before each analysis using manual injections of known quantities of gaseous Hg dispensed from a Tekran 2505 calibration unit. Periodically during analysis

(every 10 samples) ICP-MS detector stability was verified and drift was monitored with manually injected Hg samples. Gold traps were tested after each use to ensure desorption efficiency using manual injections of known quantities of Hg and were removed from use if the desorbed Hg quantity differed by >10%. The mass of Hg desorbed from each trap that was attributed to excess ^{199}Hg mercury isotope content (henceforth: tracer Hg) as well as the ambient Hg naturally present (measured using the most naturally abundant stable isotope, ^{202}Hg ; henceforth: ambient Hg) was calculated using the matrix calculations described in Hintelmann and Evans³¹, which take into account the certified isotope abundances of the ^{199}Hg tracer and natural Hg isotope abundances. The detection limit for ^{199}Hg fluxes was $3.4 \text{ ng m}^{-2} \text{ h}^{-1}$. Analytical precision, calculated as the relative standard deviation of $^{199}\text{Hg}/^{202}\text{Hg}$ ratios from known, natural abundance Hg^0 injections was 1.6%.

At the end of each experiment the soil mesocosm was carefully sectioned into samples of 1-cm thickness (~10 g each). These samples were analysed simultaneously both for excess tracer Hg concentration and ambient Hg concentration. Each sample was digested according to US EPA Method 3051A using concentrated nitric acid in a microwave digester.³² The digestate was diluted with deionized water, oxidized by adding 1% by volume BrCl , and analysed using a Tekran 2600 automated mercury system, for desorption via US EPA method 1631,³³ directly hyphenated to our ICP-MS. Briefly, this system automatically mixes SnCl_2 with each sample digestate to reduce the Hg^{2+} in the sample to Hg^0 , which is stripped from the aqueous mixture by passing Hg-free argon across a glass rod phase separator, and then dual amalgamating the vapour onto gold traps. The gold traps are thermally desorbed in succession and the Hg vapour is

passed directly into the ICP-MS for detection of the specific Hg isotopes. Our QA/QC procedures included random inclusion of blanks, duplicates, spikes, and certified reference materials (MESS-3). The detection limit for soils, calculated as three standard deviations of digestion blanks was $0.03 \text{ ng } ^{199}\text{Hg g}^{-1}$. Duplicate relative standard deviations were on average 4.3% for ^{199}Hg , spike (ambient) recoveries were $96 \pm 3\%$, and the recovery of standard reference material was $95 \pm 4\%$.

2.3. Statistical methods

Where analyzed samples from the gold traps and soil sections (for ambient and tracer Hg) were below the practical detection limit of the analysis methodology, a value of zero was assigned. Statistical tests were carried out using the RStudio package.³⁴ Non-parametric statistical methods were used throughout the paper because the data were not normally distributed (Shapiro-Wilk test, $p < 0.05$). The Wilcoxon-Mann-Whitney test was utilized ($\alpha = 0.05$) to make comparisons between wet and dry fluxes measured from each tracer-depth experiment. Correlations among measured variables were analyzed using Spearman's rank order correlation coefficient ($\alpha = 0.05$).

3. RESULTS AND DISCUSSION

3.1. Mercury fluxes from subsurface sources under dry, low light conditions

The ambient Hg fluxes were similar and relatively low throughout the experiments (median ambient flux: $0.2 \text{ ng m}^{-2} \text{ h}^{-1}$, range: -9.5 to $+19.1 \text{ ng m}^{-2} \text{ h}^{-1}$, $n=36$, $p = 0.21$), likely as a result of the low ambient Hg concentrations in the soils and indicating that the conditions promoting Hg fluxes were consistent between experimental treatments (Figure 2A). The results of the tracer Hg depth experiments showed that the emission of tracer Hg under dry, low-light conditions was similar regardless of tracer depth (median tracer flux from all depths: $7.5 \text{ ng Hg}^{199} \text{ m}^{-2} \text{ h}^{-1}$, range: 0 to $68 \text{ ng Hg}^{199} \text{ m}^{-2} \text{ h}^{-1}$, $n=36$, $p=0.19$, Figure 2B). These tracer Hg fluxes were significantly greater than observed in control experiments where ^{199}Hg was not added ($p<0.0001$). As such, our results clearly indicate the ability for subsurface Hg pools to participate in surface emissions, even in the absence of significant soil moisture. In addition, this demonstrates the potential for surface Hg emissions to occur under low-light conditions presumably through processes other than photo-reduction. As indicated by other studies, we expect that emissions from the surface amended soil layer would have been much larger than subsurface emissions if our mesocosms were exposed to higher levels of solar radiation.^{13,19,35,36}

Figure 2: Box plots of: **A)** ambient Hg fluxes, **B)** tracer Hg fluxes in relation to depth of the enriched stable Hg isotope tracer amended 1-cm soil layer. Boxes correspond to range between 25th and 75th percentiles, with medians marked. Where data available, 5th and

95th percentiles represented by whiskers. The ambient Hg fluxes were measured at the same time as the tracer Hg fluxes; however the soil depth where the ambient flux originated should not be inferred from the data. Instead, the ambient data represents the variability in flux measurements that occurred throughout the experiment that is unrelated to the tracer Hg addition to the soil. Overall, the ambient data showed that conditions were relatively stable throughout the experiment.

Since we maintained low-light conditions throughout our study, and observed Hg emissions from sources at depths much greater than light penetration (up to 5 cm below the surface), it is likely that a non-light related mechanism was occurring. These results differ from Quinones and Carpi (2011)¹⁶ which focused on much shallower soil depths and higher light conditions and concluded the light may continue to drive emissions to a depth of 0.4 cm below the surface. While the exact oxidation state of the amended Hg tracer was not tracked in our mesocosms, similar experiments using Hg²⁺ amended soils indicate that amended Hg tracers are entirely bound to soil particles as Hg²⁺ with no detectable fraction of Hg⁰.³⁷ Therefore in order to observe emission of Hg from our experimental mesocosms, reduction of Hg²⁺ to Hg⁰ had to occur in dark and low-light conditions. Other studies that observed Hg emissions in the absence of radiative sources identified elevated soil temperature as a significant correlate, however the exact mechanisms remains poorly substantiated due to the relatively low magnitude of observed emissions.^{9,13,14,36,38} Both Xin et al.¹⁴ and Kim et al.³⁶ identified temperature as an important variable associated with the release of soil bound Hg⁰, exhibiting sufficiently low activation energy to occur at environmental soil temperatures, however reduction would still need to occur for the creation of soil bound Hg⁰. In light of findings

from other studies, we propose two probable mechanisms resulting in the emission of Hg from soils not exposed to light. The bulk of associative evidence linking soil temperature to Hg emissions in dark conditions suggests a mechanistic link, potentially as a form of thermal reduction whereby elevated soil temperatures provide substantial energy to reduce soil bound Hg^{2+} to Hg^0 . Alternatively, though most likely in tandem with a thermal mechanism, chemical reduction of Hg^{2+} via abiotic reactions with humic matter or other chemical reductants may also contribute to the Hg emissions observed under dark conditions.³⁹ Biotic reduction⁴⁰ is another possibility that can potentially have significant impacts on Hg reduction in this system and more likely real world systems, but investigating the impact of this specific factor is outside the scope of this study. Our experimental design involving the amendment of soil with Hg^{2+} allowed us to identify that a reduction process occurs in the absence of light and can produce a constant source of Hg^0 . While we can only speculate on the mechanism facilitating reduction it is clear that under dry, low light conditions Hg fluxes can originate from sources at least as deep as 5 cm at significant, albeit relatively low magnitudes.

3.2. Mercury fluxes following wetting of dry soil

In our wet soil experiments, fluxes of ambient Hg following wetting showed no distinct trends associated with the depth of tracer Hg amended soil ($p = 0.141$, Figure 2A). Tracer Hg fluxes were similar across experiments prior to wetting, but fluxes increased substantially when soils were wetted to field capacity, with the largest fluxes observed post-wetting, when soils began to dry (Figure 2B, 3). Peak shape and timing agree well

with observations from other studies investigating ambient Hg fluxes.^{7,17,19,25} Our observations of peak Hg fluxes at soil moisture contents of 22-31% during drying suggests that emissions are likely favored at soil moisture contents slightly less than field capacity (mean of 28% in this study). These patterns were particularly evident for the 0 cm and 1 cm amended experiments, which showed similar timing responses to one another although the magnitude of the flux was considerably less for the 1 cm amended experiments. For the surface soil amended experiments, the maximum post-wetting Hg fluxes were up to 285 ng m⁻² h⁻¹ whereas for the 1 cm tracer amended experiments, the maximum post-wetting Hg fluxes were up to 126 ng m⁻² h⁻¹. When the tracer Hg amended soil was deeper in the mesocosm (i.e. 2 cm and 5 cm), emissions were less than those observed for near-surface tracer applications, but mostly still detectable (maximum flux up to 14 ng Hg¹⁹⁹ m⁻² h⁻¹ at 2cm and 12 ng Hg¹⁹⁹ m⁻² h⁻¹ at 5 cm; Figure 2B, 3).

Figure 3: Tracer ¹⁹⁹Hg fluxes of triplicate experiments by tracer amended depth in relation to median volumetric soil moisture content from all experiments. Measurements corresponding to negative time since wetting represent dry soil fluxes. Flux measurement values indicate means $\pm$ standard error with measurements grouped in half-day time intervals.

Tracer Hg fluxes were significantly and negatively related to the depth of the tracer amended soil layer ($\rho=-0.862$; $p<0.0001$; Figure 4), indicating that fluxes increased when the tracer amended soil layer was closer to the surface. The correlation suggests that Hg emissions approach the magnitude of our control fluxes when the Hg source depth reaches 6.4 cm beneath the soil surface. The incorporation of a tracer in our experiment shows that 76% of the tracer fluxes originated from the top 1 cm of the soil, 16% originated from the 1-2 cm layer, and 8% overall from soil between 2 cm and 6 cm depth. Transport processes in sandy soils similar to those used in the mesocosms are therefore capable of acting over a somewhat broader range than previously suspected, but as previously inferred are indeed dominated by processes within the first 2 cm of the surface.^{10,13,14}

Figure 4: Spearman correlation between tracer Hg amended soil layer depth and tracer Hg flux, under wet soil conditions.

Though soil moisture content and tracer Hg fluxes generally followed one another, especially for tracer Hg amended soils at 0 cm and 1 cm depths, temporal lags were apparent and so there was not a direct correlation between % soil moisture and Hg emissions (e.g. 0 cm: $\rho=-0.2581$, $p=0.1764$). Any correlation between soil moisture and

Hg emissions is likely dependent on the degree to which the soil moisture is increased. For example, studies with relatively low soil moisture contents (<20%) have shown strong correlations with emissions;¹⁹ whereas studies in wetter soils such as ours do not show this correlation, due to flux suppression at the highest moisture levels.¹⁷ Flux suppression at saturated soil contents is thought to occur due to water filling the soil pore spaces and reducing gas exchange with the atmosphere^{19,41}. It is clear from our data and others that a singular relationship between a particular soil moisture content and Hg flux does not exist. Rather, the increase in flux is related to a particular change in soil moisture (i.e., drying out), and thus potentially either to changes in soil water tension or evaporation. This is somewhat in line with a hypothesis forwarded by Bahlmann et al.⁴¹ who suggested that maximal Hg fluxes are supported at a particular soil moisture content but that Hg fluxes would decline if this optimal soil moisture were exceeded. However, our findings align better with the conceptual model recently put forward by Briggs and Gustin¹⁷ that Hg flux is strongly controlled by the evaporative stage of soil moisture and work by Gustin and Stamenkovic¹⁹ that upward transport and subsequent deposition of Hg nearer the soil surface may occur, facilitating continued fluxes as soils dry. If Hg transport were facilitated by soil water tension at the surface during soil drying, one might expect that the depth of Hg sources that could participate in emissions could be even deeper in fine-grained soils such as silts and clays because of stronger capillary forces. Alternatively, Hg transport facilitated by the opening of pore spaces during soil drying, allowing deeper participation of evaporative losses, may be less sensitive to soil properties. While the work of Briggs and Gustin¹⁷ suggests the latter, additional

experimental work is needed to verify the mechanisms and thus the potential depths of Hg sources for emission in different soil types.

Measurements of tracer Hg in soil after the moisture experiments showed that there was no significant migration above or below the layer where it was placed (Figure 5). The relatively small and highly variable pools found in the layers immediately above our 2-cm and 5-cm experiments most likely represent inadvertent mixing of layers when sampling. We caution that our use of deionized water as input to the experiments differs from natural rainwater, and that this may affect the dissolution and transport of subsurface Hg though it is likely that a percolating soil solution would quickly gather ligands from the soil matrix. Still, it is important to note that outside of the surface tracer experiment, we observed no accumulation of tracer at the surface from any of the other, more deeply applied tracer experiments. Therefore our results do not show that Hg is transported from deeper in the soil profile and accumulated at the surface to fuel longer-term reduction and emissions, but rather that the transport mechanism occurs over a short time period and without re-oxidation of Hg^0 . Such findings are unique and indicate that a relatively direct connection between subsurface Hg pools and the atmosphere can exist.

Figure 5: Median soil concentration of tracer ^{199}Hg after conclusion of wet flux measurements, grouped by depth of the ^{199}Hg amended layer. Error bars represent range of observations from triplicate experiments.

While this tracer experiment demonstrates that subsurface Hg sources (≥ 5 cm depth) participate in surface Hg emissions, these fluxes are clearly dominated by nearer surface sources (0-2 cm depth), especially when soils are moist. We observed that 0.4% of the amended tracer Hg at 0 cm was emitted from the soil over the course of the post wetting flux peak which lasted ~ 3 days. Similar results from studies using stable isotope tracers have observed 0.1-3% re-emission of tracer Hg over the period immediately following wetting.²⁵ There is some uncertainty as to the susceptibility of recently deposited versus legacy pools of Hg for emission, with as much as 10% of Hg isotope tracer re-emitted on a seasonal basis.⁴² While the reactivity of native pools of older Hg found at deeper depths requires further research, our findings suggest that subsurface Hg pools may not be entirely sequestered and have the potential to participate in surface emissions. These results have important implications for the ability of Hg pollution to continue to actively cycle between soil and the atmosphere long after initial deposition has occurred.

ACKNOWLEDGEMENTS

Haiyong (Planck) Huang gratefully provided assistance with laboratory analysis. Funding for this research was provided by a Natural Sciences and Engineering Research Council Discovery Grant to CPJM.

4. References

1. Poissant, L.; Casimir, A. Water-air and soil-air exchange rate of total gaseous mercury measured at background sites. *Atmos. Environ.* **1998**, *32*, 883-893.
2. Grigal, D.F. Inputs and outputs of mercury from terrestrial watersheds: A review. *Environ. Rev.* **2002**, *10*, 1-39.
3. Bahlmann, E.; Ebinghaus, R.; Ruck, W. Development and application of a laboratory flux measurement system (LFMS) for the investigation of the kinetics of mercury emissions from soils. *J. Environ. Manage.* **2006**, *81*, 114-125.
4. Gustin, M.S.; Engle, M.; Ericksen, J.; Lyman, S.; Stamenkovic, J.; Xin, M. Mercury exchange between the atmosphere and low mercury containing substrates. *Appl. Geochem.* **2006**, *21*, 1913-1923.
5. Eckley, C.S.; Gustin, M.; Lin, C.-J.; Li, X.; Miller, M.B. The influence of dynamic chamber design on operating parameters on calculated surface-to-air mercury fluxes. *Atmos. Environ.* **2010**, *44*, 194-203.
6. Eckley, C.S.; Gustin, M.; Marsik, F.; Miller, M.B. Measurement of surface mercury fluxes at active industrial gold mines in Nevada (USA). *Sci. Total Environ.* **2011**, *409*, 514-522.
7. Lin, C.J.; Gustin, M.S.; Singhasuk, P.; Eckley, C.; Miller, M. Empirical models for estimating mercury flux from soils. *Environ. Sci. Technol.* **2010**, *44*, 8522-8528.
8. Kim, K.H.; Lindberg, S.E.; Meyers, T.P. Micrometeorological measurements of mercury-vapor fluxes over background soils in eastern Tennessee. *Atmos. Environ.* **1995**, *29*, 267-282.

- 425 9. Zhang, H.; Lindberg, S.E.; Marsik, F.J.; Keeler, G.J. 2001. Mercury air/surface
426 exchange kinetics of background soils of the Tahquamenon river watershed in the
427 Michigan Upper Peninsula. *Water Air Soil Pollut.* **2001**, *126*, 151-169.
- 428 10. Gustin, M.S.; Biester, H.; Kim, C.S. Investigation of light-enhanced emission of
429 mercury from enriched substrates. *Atmos. Environ.* **2002**, *36*, 3241-3254.
- 430 11. Moore, C.; Carpi, A. Mechanisms of the emission of mercury from soil: Role of
431 UV radiation. *J. Geophys. Res.* **2005**, *110*, D24302.
- 432 12. Hutchison, B.A.; Matt, D.R. The distribution of solar radiation within a deciduous
433 forest. *Ecol. Monogr.* **1977**, *47*, 185-207.
- 434 13. Carpi, A.; Lindberg, S.E. Sunlight-mediated emission of elemental mercury from
435 soil amended with municipal sewage sludge. *Environ. Sci. Technol.* **1997**, *31*, 2085-
436 2091.
- 437 14. Xin, M.; Gustin, M.; Johnson, D. Laboratory investigation of the potential for re-
438 emission of atmospherically derived Hg from soils. *Environ. Sci. Technol.* **2007**, *41*,
439 4946-4951.
- 440 15. Obrist, D. Mercury distribution across 14 U.S. forests. Part II: Patterns of methyl
441 mercury concentrations and areal mass of total and methyl mercury. *Environ. Sci.*
442 *Technol.* **2012**, *46*, 5921-5930.
- 443 16. Quinones, J.L.; Carpi, A. An investigation of the kinetic processes influencing
444 mercury emissions from sand and soil samples of varying thickness. *J. Environ. Qual.*
445 **2011**, *40*, 647-652.

- 446 17. Briggs, C.; Gustin, M.S. Building upon the conceptual model for soil mercury
447 flux: Evidence of a link between moisture evaporation and Hg evasion. *Water Air Soil*
448 *Pollut.* **2013**, *224*, 1744.
- 449 18. Engle, M.A.; Gustin, M.S.; Zhang, H. Quantifying natural source emissions from
450 the Ivanhoe Mining District, north-central Nevada, USA. *Atmos. Environ.* **2001**, *25*,
451 3987-3997.
- 452 19. Gustin, M.S.; Stamenkovic, J. Effect of watering and soil moisture on mercury
453 emission from soils. *Biogeochemistry*, **2005**, *76*, 215-232.
- 454 20. Song, X.X.; Van Heyst, B. Volatilization of mercury from soils in response to
455 simulated precipitation. *Atmos. Environ.* **2005**, *39*, 7494-7505.
- 456 21. Lindberg, S.E.; Zhang, H.; Gustin, M.; Vette, A.; Marsik, F.; Owens, J.; Casimir,
457 A.; Ebinghaus, R.; Edwards, G.; Fitzgerald, C.; Kemp, J.; Kock, H.H.; London, J.;
458 Majewski, M.; Poissant, L.; Pilote, M.; Rasmussen, P.; Schaedlich, F.; Schneeberger,
459 D.; Sommar, J.; Turner, R.; D. Wallschlager; Z. Xiao. Increases in mercury emissions
460 from desert soils in response to rainfall and irrigation. *J. Geophys. Res.-Atmos.* **1999**,
461 *104*, 21879-21888.
- 462 22. Wang, S.F.; Feng, X.B.; Qiu, G.L.; Wei, Z.Q.; Xiao, T.F. Mercury emission to
463 atmosphere from Lanmuchang Hg-Tl mining area, Southwestern Guizhou, China.
464 *Atmos. Environ.* **2005**, *39*, 7459-7473.
- 465 23. Kocman, D.; Horvat, M. A laboratory based experimental study of mercury
466 emission from contaminated soils in the River Idrijca catchment. *Atmos. Chem. Phys.*
467 **2010**, *10*, 1417-1426.

- 468 24. Mazur, M.; Mitchell, C.P.J.; Eckley, C.S.; Eggert, S.L.; Kolka, R.K.; Sebestyen,
469 S.D.; Swain, E.B. Gaseous mercury fluxes from soils in response to forest harvesting
470 intensity: A field manipulation experiment. *Sci. Total Environ.* **2014**, *496*, 678-687.
- 471 25. Ericksen, J.A.; Gustin, M.S.; Lindberg, S.E.; Olund, S.D.; Krabbenhoft, D.P.
472 Assessing the potential for re-emission of mercury deposited in precipitation from arid
473 soils using a stable isotope. *Environ. Sci. Technol.* **2005**, *39*, 8001-8007.
- 474 26. Haynes, K.M.; Mitchell, C.P.J. Inter-annual and spatial variability in hillslope
475 runoff and mercury flux during spring snowmelt. *J. Environ. Monitor.* **2012**, *14*, 2083-
476 2091.
- 477 27. Grigal, D.F. Mercury sequestration in forests and peatlands: a review. *J. Environ.*
478 *Qual.* **2003**, *32*, 393-405.
- 479 28. Vaze, J.; Chiew, F.H.S. Study of pollutant washoff from small impervious
480 experimental plots. *Water Resour. Res.* **2003**, *39*, 1160.
- 481 29. Stone, D.M.; Elioff, J.D. Soil properties and aspen development five years after
482 compaction and forest floor removal. *Can. J. Soil Sci.* **1998**, *78*, 51-58.
- 483 30. U.S. Environmental Protection Agency. *Compendium method IO-5: Sampling and*
484 *analysis for vapor and particle phase mercury in ambient air utilizing cold vapor*
485 *atomic fluorescence spectrometry (CVAFS)*. Center for Environmental Research
486 Information, Office of Research and Development, Cincinnati, OH, **1999**.
- 487 31. Hintelmann, H.; Evans, R.D. Application of stable isotopes in environmental
488 tracer studies - Measurement of monomethylmercury (CH_3Hg^+) by isotope dilution
489 ICP-MS and detection of species transformation. *Fresen. J. Anal. Chem.* **1997**, *358*,
490 378-385.

- 491 32. U.S. Environmental Protection Agency. *Method 3051A: Microwave assisted acid*
492 *digestion of sediments, sludges, soils and oils*. Office of Solid Waste; Economic,
493 Methods, and Risk Analysis Division, Washington, DC, **2007**.
- 494 33. U.S. Environmental Protection Agency. *Method 1631, Revision E: Mercury in*
495 *water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry*.
496 US EPA Statistics and Analytical Support Branch, Washington, DC, **2002**.
- 497 34. RStudio. RStudio: Integrated development environment for R (Version
498 0.98.1091) [Computer software]. Boston, MA. Retrieved November 27, **2014**.
499 Available from <http://www.rstudio.org/>
- 500 35. Zhang, H.; Lindberg, S.E.; Kuiken, T. Mysterious diel cycles of mercury
501 emission from soils held in the dark at constant temperature. *Atmos. Environ.* **2008**,
502 *42*, 5424-5433.
- 503 36. Kim, K.H.; Yoon, H.O.; Jung, M.C.; Oh, J.M.; Brown, R.J.C. A simple approach
504 for measuring emission patterns of vapor phase mercury under temperature-controlled
505 condition from soil. *Sci. World J.* **2012**, 940413.
- 506 37. Mauclair, C.; Layshock, J.; Carpi, A. Quantifying the effect of humic matter on
507 the emissions of mercury from artificial soil surfaces. *Appl. Geochem.* **2008**, *23*, 594-
508 601.
- 509 38. Moore, C.W.; Castro, M.S. Investigation of factors affecting gaseous mercury
510 concentrations in soils. *Sci. Total Environ.* **2012**, *419*, 136-143.
- 511 39. Schluter, K. Review: evaporation of mercury from soils. An integration and
512 synthesis of current knowledge. *Environ. Geol.* **2000**, *39*, 249-271.

- 513 40. Barkay, T.; Miller, S.M.; Summers, A.O. Bacterial mercury resistance from
514 atoms to ecosystems. *FEMS Microbiol. Rev.* **2003**, *27*, 355-384.
- 515 41. Bahlmann, E.; Ebinghaus, R.; Ruck, W. The effect of soil moisture on the
516 emission of mercury from soils. *Mater. Geoenviron.* **2004**, *51*, 791-794.
- 517 42. Hintelmann, H.; Harris, R.; Heyes, A.; Hurley, J.P.; Kelly, C.A.; Krabbenhoft,
518 D.P.; Lindberg, S.; Rudd, J.W.M.; Scott, K.J.; St. Louis, V.L. Reactivity and mobility
519 of new and old mercury in a boreal forest ecosystem during the first year of the
520 METAALICUS study. *Environ. Sci. Technol.* **2002**, *36*, 5034-5040.

521

Figure Captions

Figure 1: Diagram of the experimental apparatus. This example is for an experiment with ^{199}Hg amended soil at 2-cm depth.

Figure 2: Box plots of: **A)** ambient Hg fluxes, **B)** tracer Hg fluxes in relation to depth of the enriched stable Hg isotope tracer amended 1-cm soil layer. Boxes correspond to range between 25th and 75th percentiles, with medians marked. Where data available, 5th and 95th percentiles represented by whiskers. The ambient Hg fluxes were measured at the same time as the tracer Hg fluxes; however the soil depth where the ambient flux originated should not be inferred from the data. Instead, the ambient data represents the variability in flux measurements that occurred through the experiment that is un-related to the tracer Hg addition to the soil. Overall, the ambient data showed that conditions were relatively stable throughout the experiment.

Figure 3: Tracer ^{199}Hg fluxes of triplicate experiments by tracer amended depth in relation to median volumetric soil moisture content from all experiments. Measurements corresponding to negative time since wetting represent dry soil fluxes. Flux measurement values indicate means $\pm$ standard error with measurements grouped in half-day time intervals.

Figure 4: Spearman correlation between tracer Hg amended soil layer depth and tracer Hg flux, under wet soil conditions.

541 **Figure 5:** Median soil concentration of tracer ^{199}Hg after conclusion of wet flux
542 measurements, grouped by depth of the ^{199}Hg amended layer. Error bars represent range
543 of observations from triplicate experiments.