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Precipitation Input and Antecedent Soil Moisture Effects on Mercury Mobility in Soil – Laboratory Experiments with an Enriched Stable Isotope Tracer

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***Running Title*:** Hydrological Impacts on Mercury Mobility

Abstract

Terrestrial soils are net mercury (Hg) sinks, but leaching of Hg from upland environments constitutes an important source to downstream wetlands and water bodies. Broadly, hydrology is instrumental in facilitating Hg transport within, and export from watersheds but the relative influences of specific hydrological factors such as antecedent soil moisture and precipitation in controlling the transport of Hg through upland soils are not well understood. The purpose of this research was to elucidate the relative controls of these hydrological factors using a full factorial laboratory experiment involving the application of an enriched stable Hg isotope tracer to intact soil cores. Antecedent soil moisture and precipitation input depth were statistically significant, mutually exclusive controls on tracer Hg mobility. Neither factor however had a strongly significant influence on the mobility of ambient Hg. Tracer Hg mobility was enhanced with larger precipitation events as well as from initially drier soils and appeared to move via simple piston flow. The majority (>99.5%) of added tracer Hg was sorbed to soil organic matter in the surface 3 cm, regardless of the hydrological treatment combinations. Overall, these results suggest that tracer and ambient Hg are differentially controlled by hydrological conditions. Changes in hydrology may have little impact on ambient Hg mobilization in sandy loam soils. If tracer Hg is broadly representative of contemporary soil Hg stocks, extreme precipitation events among otherwise drier conditions could enhance the export of contemporary Hg from upland systems.

Keywords: mercury; stable isotope tracer; soils; transport; soil moisture; total organic carbon

1 Introduction

Soils store an enormous pool of mercury (Hg), containing approximately 1,000,000 Mg of the global stock (Sunderland and Mason, 2007). In most regions atmospheric deposition is the principal process delivering Hg from local, regional and global sources (Driscoll *et al.*, 2007; Fitzgerald *et al.*, 1998). Although soils are large net sinks for atmospherically-deposited Hg (Gabriel and Williamson, 2004; Grigal, 2003), the accumulated Hg also slowly leaches from soils and moves via runoff to aquatic ecosystems where its toxic and organic form, methylmercury (MeHg), may be produced (Branfireun *et al.*, 1996; Harris *et al.*, 2007). High-flow events such as spring snowmelt appear to amplify the export of both inorganic and organic Hg species from soils and watersheds, although the mechanisms for increased fluxes vary (Bishop *et al.*, 1995; Demers *et al.*, 2010; Haynes and Mitchell, 2012; Mitchell *et al.*, 2008a). Given the toxicological threats of Hg to human and wildlife populations (Mergler *et al.*, 2007; Scheuhammer *et al.*, 2007), it is important to understand how mercury mobility may be affected under different and/or changing hydrological conditions through time.

In field studies it is difficult to discern the relative control of individual hydrological properties, such as the antecedent soil moisture condition, on Hg transport due to confounding effects from precipitation inputs and subsequent runoff production as well as groundwater contributions. At the hillslope scale, Haynes and Mitchell (2012) observed that Hg yield from sandy loam soils with a shallow surficial O-horizon was flow-driven; increasing proportionally with snowmelt runoff with no conclusive evidence that antecedent soil moisture was an important control on the magnitude of runoff Hg fluxes. Previous research in upland environments (e.g. Bushey *et al.* 2008; Dittman *et al.* 2010) has suggested that high-flow event runoff enhances Hg mobility. However, few studies consider the potential influence of

antecedent soil moisture conditions in controlling Hg fluxes through terrestrial environments. A recent study by Oswald and Branfireun (2014) illustrated that antecedent soil moisture conditions aid in accounting for differences observed in the Hg concentration-discharge relationships that occur following the wet snowmelt period as compared to the dry late summer period. Higher THg and soil water dissolved organic carbon concentrations were observed following warmer, drier periods in the boreal Shield watershed (Oswald and Branfireun 2014). These studies suggest that a systematic and controlled testing of the relative controls of antecedent soil moisture and the magnitude of precipitation inputs on Hg mobility is required.

Due to the myriad variables influencing natural systems it is often difficult to accurately identify individual hydrological controls on contaminant mobility. Microcosm-scale laboratory studies reduce the natural variability inherent in field-scale studies and allow for the controlled manipulation of hydrological variables. Experiments of this nature commonly have been used to investigate the role of different hydrological factors such as rainfall intensity or soil moisture on nutrient and pesticide leaching and transport in soil (Phillips, 2001; Phillips and Burton, 2005; Sigua *et al.*, 1993; Vendelboe *et al.*, 2011). In a recent study Reinmann *et al.* (2012) simulated soil frost development and spring snowmelt conditions using intact soil columns to determine the potential effects of frost on carbon and nitrogen losses from forested upland soils. Undisturbed soil columns have also been used to study the leaching of heavy metals such as lead, copper and cadmium under different rainfall intensities (Kim *et al.*, 2008). Only a limited number of studies (e.g. Schlüter *et al.*, 1995; Schlüter 1996) have employed the use of intact soil columns to investigate the impact of hydrological factors on Hg mobility, despite numerous advances in Hg analytical techniques including the increasing use of stable isotopes as environmental tracers (Björn *et al.*, 2007).

Given that Hg in the environment is transported in a highly non-conservative manner, the use of stable isotopes as tracers is an invaluable tool yielding information not only about the transport of Hg but also its speciation under various conditions. The METAALICUS study applied multiple stable Hg isotopes at the landscape scale in order to investigate the potential impacts of altering the atmospheric deposition of Hg and the subsequent downstream effects on Hg bioaccumulation in fish (Harris *et al.*, 2007). A pilot study under the METAALICUS project added an enriched stable Hg isotope to a small, zero-order forested subcatchment as a means of assessing the reactivity and mobility dynamics of newly-deposited Hg as opposed to the large legacy soil pools of Hg at the plot scale (Hintelmann *et al.*, 2002). This field study found that less than 1% of the added Hg appeared in runoff, suggesting that the majority of newly-deposited Hg is incorporated into the organic matter-bound Hg pool in soil and vegetation. Oswald *et al.* (2014) also traced the applied isotope in the watershed upland to assess its distribution (vertical and spatial) and transport, as well as that of ambient Hg through the soil one year following the end of application; with approximately 22% of the spike mass remaining in the upper 15 cm of mineral soil. Despite the increasing application of isotope tracers in field settings, minimal research has been conducted using Hg isotopes in small-scale laboratory experiments to investigate Hg mobility throughout the soil profile. Semu *et al.* (1985) used the radioisotope ^{203}Hg in soil column experiments to investigate the potential for groundwater contamination by Hg leaching through the soil, observing that minimal vertical translocation of Hg occurred with the majority of added Hg being immobilized in the surface soil horizons. Schlüter (1996) similarly used ^{203}Hg to assess the translocation of Hg through soil using small-scale column experiments in order to address the fate of Hg in soils under different rainfall intensities and volumes; concluding that practically all of the added ^{203}Hg is sorbed in the upper organic soil

horizons and that the small amount of Hg translocation is facilitated by complexation with dissolved organic matter. Some more recent work has used column experiments to examine applied non-labelled Hg sorption in soils (e.g. Miretzky *et al.* 2005; Yin *et al.* 1997; Zhu *et al.* 2014). However, such studies did not use intact, undisturbed soil cores working rather with re-packed soil columns (Miretzky *et al.* 2005; Zhu *et al.* 2014) or soil suspensions (Yin *et al.* 1997).

Our work builds on these previous studies by adding antecedent moisture as an experimental variable possibly affecting the mobility and transport of Hg throughout the undisturbed soil profile, and by using new core encasing methods to avoid wall effects and pore blockage that often result from polyvinyl chloride- (PVC) (e.g. Bagarello *et al.*, 2006; Bagarello and Sgroi 2008), resin-encased (e.g. Vanderborght *et al.* 2002) or wax-encased cores.

The overall objective of this study was to determine the relative influences of both antecedent soil moisture and precipitation on the mobility and transport of Hg throughout the soil profile. In a full factorial design we applied an enriched, stable Hg isotope to intact, foam-encased soil cores that had been altered for soil moisture and to which variable amounts of precipitation were added. The experiment was conducted to simulate the broad range in real soil moisture and precipitation input conditions observed in previous field research (Haynes and Mitchell, 2012). A pilot study, described in the Supplementary Information, was also conducted in order to ensure the feasibility of using polyurethane expandable spray foam as a soil-encasing material (e.g., Bagarello and Sgroi 2008) for the purpose of performing Hg leaching experiments while minimizing wall effects.

2 Materials and Methods

2.1 Field Sampling

Eighteen intact soil cores were collected with a 15 cm deep and 10 cm internal diameter stainless steel soil corer in the forested upland of the S7 watershed in the Marcell Experimental Forest (MEF) in north-central Minnesota. The soil corer is equipped with a lever mechanism which allows for extrusion of the soil core from the base of the corer tube without disturbing the soil structure. Characteristic of watersheds in this area, the upper sandy loam soils of the watershed's hillslope are underlain by a low-permeability B-horizon, which acts as a confining layer, directing subsurface runoff as shallow interflow during high-flow events with minimal seepage loss to groundwater (Kolka *et al.*, 2011; Timmons *et al.*, 1977). The soil profile above the clay-rich B-horizon consists of a shallow O-horizon below which there is a well-defined sandy loam A-horizon (mean depth to base of A-horizon 50 ± 27 cm). Hydraulic conductivities in the sandy loam of this area range from 4×10^{-5} to 4×10^{-6} m s^{-1} (Mitchell *et al.* 2009). The surface 15 cm of soil in this hillslope have a mean bulk density of 1.2 g cm^{-3} and mean porosity of approximately 37%. The upland overstory vegetation in the S7 watershed is predominately comprised of sugar maple (*Acer saccharum*), quaking aspen (*Populus tremuloides*) and balsam poplar (*Populus balsamifera*). We sampled only the upper sandy loam horizon that also included a shallow (< 3 cm) organic horizon. Soil cores were collected from outside of experimental hillslope plots previously described in Haynes and Mitchell (2012), all within a 5 m^2 area in order to minimize variability among cores and to allow for the most accurate assessment of the influences of only the two hydrological factors in question (antecedent soil moisture and depth of precipitation input). Each core was extruded in the field onto a flat wooden board. We noted no significant compaction or destruction of the soil cores during the collection and extrusion of each

core. In comparing core depth to the cavity from which it was extracted, approximately 2% (0.3 cm) to a maximum of 5% (< 1 cm) compaction was observed. With the core upright on the wooden board, a 20 cm long cardboard mold was placed around it and the cavity between the soil and mold was filled with low-expansion polyurethane spray foam insulation (MONO brand); similar to the methods of Bagarello and Sgroi (2008). A second board was then placed on top of each filled mold to contain the expansion of the foam. The foam was allowed to cure overnight. Once fully cured, each foam-encased core was removed from the wood base and the exposed bottom of each core was also covered with spray foam insulation. No compaction of any soil core was observed as a result of the expansion of the spray foam. The purpose of this elaborate core encasing methodology was to hypothetically remove much of the wall effect, smear and other issues affecting water movement that often occur in intact core studies conducted in rigid tubes and other encasing materials (e.g. Cameron *et al.*, 1990; Hoag and Price, 1997; Bagarello *et al.*, 2006). With other encasing methods, preferential flow directed along the point of contact between the soil and surrounding casing often occurs rather than flow through the soil matrix. A separate study was conducted in order to test the feasibility of using foam-encased soil cores for the study of hydrological and Hg biogeochemical processes. This is detailed in the Supplementary Information.

2.2 Experimental Design

The soil core experiments were conducted in a full factorial design in which the two manipulated variables (antecedent soil moisture and precipitation input depth) incorporated both a low and high treatment level with three replicate cores per treatment combination (see Table 1). High and low treatment levels were quantified based on field data from the study area. For

precipitation input, the low and high levels were 50 mm and 100 mm, respectively. These values were selected in order to mimic the variability in snowpack snow water equivalent (SWE) levels observed in a previous study (Haynes and Mitchell, 2012). The low antecedent soil moisture treatment level was designed to simulate the 65 mm of available soil water in the surface 45 cm of soil recorded in fall 2009 prior to the 2010 winter in the study area. The high antecedent soil moisture treatment level was represented by field capacity as a means of presenting a distinct contrast to the low moisture treatment. All experiments were conducted at room temperature.

To adjust moisture levels in the low antecedent soil moisture treatments, a known volume of tap water (determined based on the volume of the soil column and the physical characteristics of the soil to achieve the target low moisture level) was slowly added to the top of relatively dry cores over the course of approximately one hour with no ponding. For the high antecedent moisture treatments, cores were placed in a basin of tap water overnight to saturate the soil from the base of each core and then drained by gravity the following day; effectively reaching field capacity. To prevent loss of soil during the wetting process, Nytex mesh (50 µm) was secured around the base of each foam-encased soil core prior to manipulation. Once the moisture manipulations were complete, 90 µg of enriched stable ^{199}Hg isotope (approximately three times ambient soil Hg mass per core) was applied evenly to the top of each core in a 10 mL solution of $^{199}HgCl$ (91.09% ^{199}Hg) via a hydrochloric acid (HCl)-washed Teflon sieve (mean blank ^{199}Hg concentration between uses = 0.6 ± 0.5 ng L^{-1}; see Figure 1a). The Teflon sieve was used to ensure uniform application of the isotopic solution across the top of each soil core. A 5 mL water rinse of the Teflon sieve followed the isotope addition to ensure complete delivery of the isotope application. Although significantly greater than natural rates of atmospheric deposition at the Marcell Experimental Forest (2004-2013 mean annual deposition of 6.8 ± 1.4 µg m^{-2};

National Atmospheric Deposition Program Mercury Deposition Network, 2014), this high level of tracer addition was necessary in order to ensure that the isotope could be analytically detected in the collected outflow waters given the working hypothesis that the majority of the applied tracer would be sorbed in the soil. Given the laboratory setup of this experiment, it would not be feasible to apply the tracer to each of the soil cores at natural deposition rates over the course of multiple years to achieve detectable isotope levels in the core outflow. Immediately following the tracer addition each core was secured to a ring stand balanced on top of a wire mesh above an HCl-washed glass funnel (see Figure 1b). Once secured (approximately five minutes following tracer addition), a rainfall simulator delivered the prescribed level of precipitation input via a metered peristaltic pump. The rainfall simulator was modelled after that used by Weed *et al.* (1998); an evenly-distributed array of hypodermic needles secured through a piece of acrylic tightly bolted to a second piece of acrylic (fitted with a water inlet nut) with a water-tight gasket between the two sheets of acrylic providing a water reservoir. The two levels of precipitation input (low = 50 mm, high = 100 mm) were comprised of tap water (to minimize ionic imbalances), acidified with trace metal grade nitric acid to simulate the pH of natural precipitation (pH~5-6). This simulated precipitation was delivered to each core at a rate of approximately 30-40 mm per hour. The low input experiments were completed over approximately 1.5 hours per core, while the high input experiments took approximately 3 hours to complete. Although designed to simulate two contrasting snowmelt events, the selected levels of input could also be representative of large rain storm events in the study area. There is recent precedent for this intensity of precipitation in the area of north-central Minnesota given the large, record-breaking rainstorms of June 19-20, 2012, in which approximately 185 mm of precipitation (with up to 250 mm reported locally) fell onto already saturated ground and from

which severe flooding resulted; particularly in the Duluth area. Instantaneous rainfall intensities for this storm were observed to be as high as 50-100 mm per hour during the evening of June 19, 2012 (Czuba *et al.*, 2012). In the context of the present study, the timing of the outflow from each of the soil cores may be different than would be observed in the natural environment as a result of the applied precipitation intensity. For each antecedent moisture treatment level a control experiment, in which no further precipitation input was added to each core following isotope addition, was performed to determine the level to which the isotope was transported as a baseline prior to simulated meltwater addition.

Outflow from each core was collected in 50 mL intervals in new polyethylene terephthalate glycol (PETG) bottles. A sub-sample for total organic carbon (TOC) analysis was transferred into a 20 mL high density polyethylene (HDPE) scintillation vial and refrigerated in darkness until analysis (approximately 2-3 weeks following collection). Comparisons of filtered and unfiltered samples were analyzed for TOC to determine if filtration significantly alters TOC concentrations. No significant difference was observed between the filtered and unfiltered samples, most likely due to the Nytex mesh acting to filter particulates from the collected outflow. Therefore, outflow samples were not filtered. Outflow samples for Hg analysis were preserved with 0.5% trace metal grade HCl, stored in darkness and refrigerated until analysis, which was within one month of collection. Once outflow from the core had ceased, each core was cut vertically into two equal parts and the soil from each half was sampled in five 3 cm depth intervals (0-3, 3-6, 6-9, 9-12, 12-15 cm). Soil samples were immediately frozen and then lyophilized prior to analysis.

2.3 Analytical Methods

Unfiltered total Hg (for both tracer ^{199}Hg and ambient Hg analysis) water samples were oxidized by the addition of concentrated bromine monochloride (BrCl) and concentrations were determined following stannous chloride reduction and dual gold-trap amalgamation using a Tekran model 2600 total mercury analyzer that was hyphenated to an Agilent 7700 Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) for mercury isotope detection. The freeze-dried soil samples were nitric acid-digested using a microwave digestor and diluted prior to THg analysis as for waters. The ^{199}Hg concentrations of the added tracer in both the water and soil samples were determined as the excess total ^{199}Hg concentrations above the naturally-occurring ^{199}Hg concentrations as measured by the ICP-MS. These excess total ^{199}Hg concentrations were calculated based on the magnitude of change from the natural ratio of ^{199}Hg above that of ambient ^{202}Hg ($^{199}Hg/^{202}Hg$ = 0.569 in nature) as a result of the addition of the labelled ^{199}Hg tracer (Hintelmann and Ogrinc, 2003). Excess total ^{199}Hg will be herein referred to as 'tracer Hg'. For water samples, recovery of an ambient total mercury spike was 97 ± 9 % (average ± standard deviation, n = 11), replication of duplicates was 6.6 ± 6.8% (n = 10), and the detection limit, calculated as three standard deviations of matrix water blanks, was 0.04 ng L^{-1} (n = 32). Replication of ^{199}Hg duplicates in water samples was 6.3 ± 6.9% (n = 10) and the ^{199}Hg detection limit was 0.007 ng L^{-1} (n = 32). For digested soil samples, replication of ambient THg duplicates was 5.4 ± 4.0% (n = 11), recovery of an ambient THg spike was 101 ± 5% (n = 11) and the ambient THg detection limit was calculated to be 0.09 ng g^{-1}. Replication of ^{199}Hg duplicates of digested soil samples was 9 ± 8% (n = 9) and the ^{199}Hg detection limit was 0.08 ng g^{-1}. Recovery of standard reference material of known ambient Hg concentration, digested and analyzed with the soil samples, was 97 ± 4% (n = 12). Total organic carbon (TOC) was analyzed using a

Shimadzu TOC-V_{CSH} Total Organic Carbon analyzer with an in-line total nitrogen unit (TNM-1) and a high sensitivity combustion catalyst (720°C). Ultraviolet absorbance of the outflow samples was measured at both 254 and 365 nm using matched quartz cuvettes on a Spectronic Genesys 5 UV-VIS Spectrophotometer. We used these two absorbance values measured at these wavelengths to calculate the ratio A254/A365, where the ratio serves as a proxy for dissolved organic carbon quality because of its negative relationship with molecular weight of dissolved organic substances (Berggren *et al.*, 2007). Specific UV absorbance (SUVA) at 254 nm was also calculated to assess aromaticity of dissolved organic substances in outflow samples by dividing the absorbance at 254 nm by the TOC concentration while taking into account the cuvette path length (Weishaar *et al.*, 2003). Loss on ignition (LOI, 550°C for 4 hours) was performed on the soil samples to determine organic matter content.

2.4 Statistical Analyses

Prior to all parametric statistical analyses, data were tested for normality (Shapiro-Wilk *W* test) and heteroscedasticity and were successfully log-transformed or inverse-transformed to achieve normality when parametric assumptions were not met. All statistical tests were performed using SAS Version 9.2 with $\alpha < 0.05$.

A two-way analysis of variance (ANOVA) was performed to determine any significant influences of, and any significant interaction between both hydrological variables (antecedent soil moisture and precipitation input depth) on both tracer Hg and ambient THg outflow loads as well as the proportion of tracer Hg in relation to ambient THg. A one-way ANOVA (with post-hoc analysis using the Tukey adjustment) was conducted on the overall tracer Hg and ambient THg outflow loads to assess significant differences among treatment combinations. A one-way

ANOVA with post-hoc Tukey test was performed in order to determine any significant differences in soil tracer ^{199}Hg concentrations among treatments (including controls) for each of the five depths. Correlation matrices were created using Pearson correlation coefficients in order to assess any significant relationships between the measured outflow variables, as well as between soil tracer Hg concentrations and organic matter. The data for one replicate core in the low moisture-high input treatment and one replicate core in the low moisture-low input treatment were omitted from correlation matrices due to exceedingly high organic matter content in the surface layers resulting from an abundance of decomposing woody debris that could not be seen until cores were sectioned at the end of the study. One replicate core in the high moisture-low input treatment was omitted from all analyses due to a lack of outflow production (from a blockage as a result of a large rock within the core).

3 Results

3.1 Tracer ^{199}Hg and Ambient Hg Outflow Loads by Treatment Combinations

Overall, less than 0.5% (range of 0.03 – 0.38%) of the added 90 µg of the ^{199}Hg tracer was present in the total outflow collected across all treatments combinations. The highest tracer Hg outflow load occurred in the low soil moisture – high precipitation input experiments (mean total load = 341 ng; Table 2). The low moisture-high precipitation outflow tracer Hg load was significantly greater than that of any of the other treatment combinations. The second largest tracer Hg outflow load was observed in the low moisture-low precipitation experiments. There was not a statistically significant difference between the tracer outflow loads resulting from the two high soil moisture treatments (high moisture-high precipitation and high moisture-low precipitation). Both of these treatments were significantly less in outflow tracer Hg than those

resulting from the low moisture treatments ($p < 0.0001$) regardless of the level of precipitation input (Table 2). Similarly, the outflow tracer Hg loads resulting from the high input treatment significantly exceeded the corresponding low input treatment at each level of soil moisture ($p = 0.001$). The total ambient THg loads followed the same general pattern by treatment as the tracer Hg loads (Table 2). However, the statistical significance of the outflow ambient THg differences among the treatment combinations was marginal ($p = 0.07$).

According to the two-way ANOVA results, both antecedent soil moisture ($p < 0.0001$) and precipitation input depth ($p = 0.001$) were significant controls on tracer Hg transport and mobility through soil. The lack of interaction ($p = 0.16$) between these hydrological variables suggested that these controls on tracer Hg mobility acted independent of one another. Precipitation input depth did not exert a strong influence ($p = 0.18$) on the mobility of ambient THg. The influence of antecedent soil moisture was marginal (close to statistical significance at $p = 0.06$).

The time course plots in Figure 2 present the data for a single representative core in each of the experimental combinations. An average could not be adequately depicted due to slight differences in the timing of the outflow for each core, which temporally staggered the data, but the overall pattern in outflow was similar between replicates despite differences in the timing. The time course plots of the tracer Hg and ambient THg concentrations for each of the treatment combinations (Figure 2) illustrated a slight delay in the tracer Hg peak for the high soil moisture treatments (Figure 2*b* and 2*d* each showing one replicate per treatment), with tracer Hg concentrations peaking during the second to fourth 50 mL-interval outflow sample (15-45 minutes lag) at a mean maximum concentration of 106 ± 27 ng L^{-1} (average ± standard deviation). However, for the low moisture treatments, tracer Hg concentrations were highest in

the first collected 50 mL outflow sample (mean maximum ^{199}Hg concentration = 939 ± 664 ng L^{-1}), decreasing with subsequent samples regardless of the precipitation depth (Figure 2*a* and 2*c* each showing one replicate per treatment). Tracer isotope concentrations in outflow were considerably higher for the low moisture treatments than the high moisture treatments.

The first 50 mL sample was collected after 10 ± 3 minutes (average ± standard deviation) on average from the high antecedent moisture experiments and after 17 ± 13 minutes for the low moisture experiments. The rate of outflow was relatively consistent throughout the course of the experiments, with an average overall outflow rate of 5.6 ± 1.0 mL min^{-1} for the high moisture soils and 5.0 ± 1.1 mL min^{-1} for the low moisture soils (Figure 2). Overall, of the 393 mL of added precipitation for the low input treatments, 380 ± 39 mL for the low moisture-low precipitation experiments and 404 ± 23 mL for high moisture-low precipitation was recovered in outflow. For the high input treatments, 745 ± 23 mL for the low moisture-high precipitation treatment and 787 ± 16 mL for high moisture-high precipitation of the 785 mL added as precipitation were collected.

3.2 Proportion of Ambient vs. Tracer Hg in Outflow

Average ratios of tracer Hg to ambient THg outflow loads for each of the treatment combinations were calculated to assess the proportion of tracer Hg vs. ambient THg in outflow. All ratios were greater than one with the mean tracer Hg/ambient THg ratios for both the high moisture-high precipitation and high moisture-low precipitation treatments approximately 4 ± 1 and 4 ± 0.2, respectively. The ratio for low moisture-low precipitation was approximately 9 ± 4 and the low moisture-high precipitation treatment had the highest ratio at 16 ± 6. The tracer Hg/ambient THg ratio for the low moisture-high precipitation treatment was significantly greater

(p = 0.0069) than both of the high moisture treatments (high moisture-low precipitation and high moisture- high precipitation). However, the ratio for this treatment was not statistically different from the low moisture-low precipitation ratio.

A two-way ANOVA of the tracer Hg/ambient THg ratio across treatment combinations revealed soil moisture to be a significant control on the proportion of tracer Hg mobilized expressed as a ratio over ambient Hg (p = 0.002). Precipitation input depth exerted no significant influence (p = 0.26) on the proportion of tracer Hg present in the outflow runoff.

3.3 Tracer and Ambient Hg Loads by Hydrological Factor

Under high soil moisture conditions the amount of both tracer and ambient Hg flushed from the soil was nearly doubled (~1.7 – 1.8X) however, only marginally significant for tracer Hg (p = 0.06) when the precipitation depth was doubled (Table 2). With low moisture conditions nearly three times (~2.7X, $p < 0.01$) as much tracer Hg was mobilized in runoff with two times as much precipitation input whereas the amount of liberated ambient Hg remained nearly unchanged (~1.3X increase, p = 0.35).

With the high level of precipitation input, significantly more tracer Hg (~6X, $p < 0.01$) and approximately 1.5 times as much ambient Hg (p = 0.02) were flushed from the low moisture soil as compared to the soil with high antecedent moisture (Table 2). Low soil moisture soil cores subjected to low levels of precipitation input mobilized significantly more tracer Hg (~4X, $p < 0.001$) and highly variable, but on average twice as much ambient Hg (p = 0.25) as compared to those under high antecedent moisture conditions.

3.4 Relationships among Outflow Solutes – Tracer ^{199}Hg, Ambient Hg, TOC

A significant correlation ($p < 0.0001$) existed between the tracer Hg and ambient THg outflow concentrations with all samples included from all replicates within all experimental combinations (Figure 3*a*). However, only the low soil moisture treatments, low moisture-low precipitation and low moisture-high precipitation, displayed significant correlations ($p < 0.01$ and 0.0001, respectively) individually between the tracer Hg and ambient THg outflow concentrations (Figure 3*b*). Neither of the high moisture treatments exhibited significant relationships between these two variables.

A similar trend was observed for the relationship between tracer Hg and TOC concentrations in outflow. A significant, but weak correlation ($p < 0.0001$, $R^2 = 0.11$) existed between these variables when considering all outflow samples across all treatments (Figure 3*c*). The strength of the relationships improved for each of the low moisture treatments individually ($p < 0.01$ for both low moisture-high precipitation ($R^2 = 0.23$) and low moisture-low precipitation ($R^2 = 0.34$)) (Figure 3*d*). No significant relationship existed however between tracer Hg and TOC for either of the high soil moisture treatments. For all treatments (overall (Figure 3*e*) and individually (Figure3*f*)), significant correlations were observed between the outflow concentrations of ambient THg and TOC (all $p \leq 0.01$; see Figure 3 for Pearson correlation coefficients).

Significant positive relationships ($p < 0.0001$) between the ratio of A254/A365 and both the outflow ambient THg concentrations and tracer Hg concentrations were observed when considering all treatment combinations (Supplementary Figure A-4). However, only the high moisture-high input treatment exhibited a significant correlation individually. A significant correlation between tracer Hg and A254/A365 was also observed for the high moisture-low input

treatment, but not for ambient THg and A254/A365. No significant correlations were observed between either of the tracer or ambient Hg concentrations and SUVA at 254 nm.

3.5 Soil Depth Profiles

The majority of the added tracer Hg was sorbed within the surface 0-3 cm sections of soil across all experimental combinations. A similar trend in tracer Hg concentrations was observed across all treatments (Figure 4). There were no significant differences in tracer Hg concentrations when comparing the same soil depths (0-3, 3-6, 6-9, 9-12 and 12-15 cm) across all treatments including controls. The soil tracer Hg concentrations were significantly positively correlated ($p < 0.0001$; $R^2 = 0.53$) with the percentage of organic matter in the soil, as determined by loss on ignition.

4 Discussion

4.1 Hydrological Controls on Soil Mercury Mobility

Antecedent soil moisture and precipitation input depth were both instrumental in controlling tracer Hg mobility within the soil columns. As there was no observed interaction between these factors, it can be concluded that these hydrological variables act independently of one another. Ambient Hg was not significantly influenced by precipitation input. However, soil moisture did play a marginally statistically significant role; one that we expect may be strengthened with further experimental replication. The mobility of tracer Hg through soil and its presence in outflow was greatly enhanced by the depth of precipitation applied to the soil due to greater flushing. Field studies investigating hydrological transport of Hg at the watershed and hillslope scales have similarly observed increased Hg fluxes as a result of high-flow rain events

and spring snowmelt but differences in Hg concentrations have often been small (e.g. Bishop *et al.*, 1995; Haynes and Mitchell, 2012; Lee *et al.*, 2000; Scherbatskoy *et al.*, 1998). Given the observation of flow-controlled Hg export from terrestrial environments, we investigated only the influence of the amount of precipitation a soil is subjected to rather than the intensity with which precipitation is delivered. The effect of precipitation intensity on both tracer and ambient Hg mobility would be an important avenue for further study.

Although the use of intact soil cores allowed for the investigation of only vertical translocation of Hg through the soil profile, the results may also be used to infer hydrological controls on lateral transport of Hg for the study region. The upland environment in the area is underlain by a low permeability B horizon which acts as a confining layer by directing subsurface runoff as shallow interflow, effectively creating a perched water table (Mitchell *et al.* 2009). During precipitation events, vertical infiltration to the perched water table is the first step in the process of runoff generation before subsurface flow is directed downslope by the confining layer. Therefore, vertical translocation of Hg upon wetting up of the soil profile is important when considering Hg fluxes from upland environments to downstream systems.

The observed timing of tracer and ambient Hg release from these sandy loam soils is likely the result of simple piston flow (Rawlins *et al.* 1997). The chemistry at the onset of outflow from the higher moisture soils would most likely be proportionally dominated by the movement of stored moisture and then replaced proportionally by the tracer added above it over time as the wetting front progressed downward through the core. The fact that outflow ambient THg concentrations were highest initially and subsequently decreased upon further input and that outflow tracer THg concentrations were initially suppressed (Figure 2) support this. Since soil moisture was already low in the low-moisture treatments, the movement of the wetting front

through the core length and the chemistry of its outflow were dominated by the tracer. Additionally, lag times between inputs and outflow were approximately twice as long for low moisture treatments but much more variable than for the higher moisture treatments. Due to this higher variability in lag time and early timing in the tracer Hg outflow peak it is possible that preferential flowpaths directed the applied tracer through the soil core in some of our replicates. When sampling the soil of the low moisture treatments, preferential flow pathways (e.g., cracks) were observed based on the wetting patterns through the low moisture soil cores. The observed piston flow mechanism responsible for the mobility of Hg through these sandy loam soil columns may not be the governing mechanism of Hg mobility in other soil types such as predominantly clay soil. This may influence the manner and rate by which Hg is flushed through different soil types as preferential transport may be the more dominant mechanism in fine textured soils (Weiler and Naef 2003), for example, particularly under low moisture conditions when they are more prone to cracking.

The influence of antecedent soil moisture on the amount of ^{199}Hg tracer present in outflow does not appear to be the result of dilution. Of the low input treatments, the low moisture-low precipitation experiments yielded approximately four times as much ^{199}Hg tracer in outflow than the high moisture-low precipitation experiments while for the high input treatments approximately six times as much tracer Hg was flushed from the low moisture-high precipitation than the high moisture-high precipitation experimental soils (Table 2). Considering that the volume of water in the high moisture soils was approximately 1.8 times greater than that of the low moisture soils, there is no evidence that the tracer was diluted by soil water.

Given the caveat that the one-time ^{199}Hg application in this experiment was much greater than natural rates of atmospheric deposition, the applied tracer in this experiment may broadly

represent contemporary Hg stocks deposited in soil or potentially a point source spill or leak from a concentrated source. The measured ambient soil and outflow water Hg may comparably be indicative of legacy Hg stocks. If the applied tracer is representative of contemporary Hg, our results may suggest that together antecedent soil moisture and precipitation, whether it is rain or snowmelt, may be instrumental in controlling the provision of newly-deposited Hg to downstream wetlands and water bodies; known to be sites of Hg methylation (Mitchell *et al.*, 2008b). Research under the METAALICUS project suggested that newly-deposited Hg was more readily volatilized and methylated than old, legacy Hg as well as initially more mobile following deposition (Hintelmann *et al.*, 2002). In the present study the proportion of tracer Hg as compared to ambient THg present in outflow runoff was significantly affected by soil moisture with more tracer Hg being flushed from low moisture soils. However, precipitation input depth had no significant effect on the proportion of tracer vs. ambient Hg in runoff. Hydrological conditions such as antecedent soil moisture content are key to controlling the magnitude of tracer Hg in runoff, which if representative of contemporary Hg, may be more bioavailable for uptake by aquatic organisms. Therefore, alterations to these hydrological factors may have deleterious downstream consequences on MeHg production and biotic uptake under potential climatic and other environmental changes.

Increased frequency of water table fluctuations may affect Hg mobility and transport by both hydrological and biogeochemical processes. Our results suggest that greater flushing of soil pores by high-flow events, particularly following periods of water table drawdown, may liberate more Hg to downstream environments. The antecedent moisture condition of the soil may affect the partitioning of the Hg between the colloidal and dissolved fractions (although not explicitly investigated in this study) and therefore impact the phase of Hg mobilized following dry periods

as opposed to predominantly wet periods (Babiarz *et al.* 2003; Zhu *et al.* 2014). We recognize that the amount of tracer Hg liberated may be minute in the field as compared to the amount of ambient Hg mobilized given our results following the addition of a high concentration of ^{199}Hg stable isotope to the soil cores. However, given the result of significant precipitation and particularly soil moisture controls on the mobility of tracer Hg, as well as marginally for ambient Hg, changes in hydrological conditions causing drier soils may have implications for the enhanced mobilization and transport of Hg to downstream aquatic ecosystems. One potential limitation of the high level of tracer addition in this study may involve the exceedance of typical binding sites in the soil organic matter. Reduced sulphur binding sites are the dominant sites of Hg sorption in organic matter and typically far exceed the amount of Hg available in natural systems (Ravichandran 2004). These sites may have been exceeded, although the concentration of high quality binding sites in these soils is not known, due to the high concentration of tracer Hg applied to each core and therefore may have affected the phase partitioning of the mobilized Hg.

4.2 Total Organic Carbon and Mercury Transport

Numerous field studies have observed Hg transport associated with that of dissolved organic carbon (e.g. Bishop *et al.*, 1995; Dittman *et al.*, 2010; Schuster *et al.*, 2008). The tendency of Hg to form complexes with organic matter (Driscoll *et al.*, 1995; Schuster, 1991) may act in facilitating the preferential mobilization of Hg during high-flow events as a result of phase partitioning of the Hg into a more-readily mobilized phase. The outflow concentrations of ambient THg were significantly correlated to those of TOC for all four experimental combinations; both individually and collectively. Ambient Hg which has been in the soil for a

longer duration than the applied ^{199}Hg tracer may have equilibrated with the dissolved organic matter over this period. Through the formation of complexes with TOC, the mobility of ambient Hg may be enhanced regardless of the hydrological conditions of the soil. The formation of TOC-Hg complexes may account for the similarity in the ambient THg-TOC relationships as well as the overall ambient Hg outflow loads across the four experimental combinations.

Complexation with TOC in soil may also be important when considering the mobility of newly-applied, tracer Hg. Hintelmann *et al.* (2002) proposed that the initial mobile fraction of newly-deposited Hg flushed from the system during rain events was bound to DOC. Similar laboratory studies have also found that the mobility of added Hg is facilitated by the complexation of Hg with dissolved organic matter (Schlüter, 1996). In the present study we observed the outflow concentrations of tracer Hg to be significantly, albeit weakly, correlated to those of TOC and ambient THg only under low moisture conditions (Figure 3). These observations suggest that tracer Hg is being mobilized from drier soils in a similar manner to that of ambient Hg. Therefore tracer Hg may be mobilized as a result of complex formation with TOC. The drier conditions of the low moisture soils may allow for more of the tracer to interact with the surface area of the organic matter, thereby facilitating greater TOC-tracer Hg complex formation. The relationship between tracer Hg and TOC in outflow runoff may also account for the greater proportion of tracer Hg being mobilized under low moisture conditions as more tracer ^{199}Hg may be partitioned into the mobile, TOC-bound phase. However, there was no significant relationship between tracer Hg and either of ambient THg or TOC for the soils under high moisture conditions. Both high soil moisture experiments (high moisture-low precipitation and high moisture-high precipitation) exhibited significant positive correlations between the tracer Hg concentrations and the absorbance ratios (A254/A365), from which it can be inferred that the

tracer Hg was potentially associated with TOC of lower molecular weight. It is therefore possible that the tracer Hg being flushed from wet soils may be in a different form than that from dry soils. The tracer Hg mobilized from low moisture soil may be found in the colloidal phase bound to TOC while that from high moisture soils may instead be in the true dissolved fraction. A study by Babiarz *et al.* (2003) provides evidence to suggest that the phase in which newly deposited Hg as compared to ambient Hg is transported may differ due to the quality of the carbon and its associated ligands. This differential phase partitioning according to carbon quality in the colloidal and dissolved fractions may account for the observed differences in tracer and ambient Hg mobility. Further study is required for a more detailed assessment of the molecular makeup of the carbon present in the dissolved and colloidal fractions of outflow (as no distinction between phases was made in this study) and its potential influences on the phase partitioning of mobilized Hg. Future research could also focus upon the role of organic matter decomposition on the mobility of tracer and ambient Hg as this may also influence the partitioning of Hg into the mobile phase and the mobility of Hg through the soil profile as well as laterally to downstream ecosystems.

4.3 Distribution of ^{199}Hg Tracer in Soil Column

Overall, across all treatments, less than 0.5% of the added Hg tracer was observed in runoff with the majority being retained in the surface 3 cm section of soil. This result is similar to that of the field study by Hintelmann *et al.* (2002), in which less than 1% of the added tracer appeared in runoff over the course of one season. A significant portion of the newly-deposited Hg was rapidly immobilized by equilibrating with the native pool in both soil and vegetation (Hintelmann *et al.*, 2002). Following six years of tracer application at the same site as

Hintelmann *et al.* (2002) and one year after loading was ended, Oswald *et al.* (2014) were still able to observe approximately 22% of the mass of applied tracer in the top 15 cm of mineral soil, where concentrations decreased with increasing soil depth. Similarly, in the present study, the vast majority of the ^{199}Hg tracer was immobilized in the surface, organic horizons of the soil regardless of both the soil moisture and precipitation conditions. The tracer Hg concentrations decreased rapidly downward with only negligible ^{199}Hg tracer reaching the lower 9 cm of soil across all treatments. The pattern of tracer Hg distribution throughout the soil profiles may be attributed to sorption to soil organic matter as these variables were significantly correlated. Similar soil column studies using an applied Hg tracer concluded that the majority of the added Hg was sorbed near the soil surface with no considerable vertical translocation through the soil (Schlüter, 1996; Semu *et al.*, 1985). It has been proposed that a large proportion of newly-deposited Hg is not immediately mobile rather being initially bound to soil and vegetation (Hintelmann *et al.*, 2002). However, upon repeated flushing with multiple precipitation events following deposition, it is possible that the mobility of this new Hg pool may be altered as the hydrological conditions of the soil change. A similar field investigation by Munthe *et al.* (2001) using an applied ^{199}Hg tracer at the plot scale observed the isotope ratio of ^{202}Hg/^{199}Hg stabilized after a period of approximately three months. During an initial rainstorm following the application of the tracer, Hintelmann *et al.* (2002) observed a significant decrease in runoff tracer concentrations which was not observed for native Hg and was sustained throughout the rest of the season. Future research could focus on the potential effects of repeated precipitation events of varying magnitudes over soils of different antecedent moisture in a controlled manner in order to assess the mobility of an applied Hg tracer to such changes in soil hydrological conditions

over time. The role of temperature in influencing the mobility and cycling of Hg is also an important factor to consider in future study.

4.4 Conclusions and Implications

Both the antecedent moisture condition of the soil and the precipitation input depth are important controls on tracer Hg mobility in upland ecosystems. Soil moisture exerts significant influence on the proportion of tracer Hg mobilized. Overall, mercury mobility is enhanced as a result of high-flow events and from soils with low initial moisture content. Piston flow appears to be the dominant process governing the mobilization of both tracer and ambient Hg through these upland sandy loam soil cores. Preferential transport flowpaths and complex formation with solutes such as TOC may also be important in controlling Hg fluxes, particularly when these soils are dry. Despite significant differences in Hg mobility according to hydrological treatments, the majority of added Hg was sorbed in the surface 3 cm of this sandy loam soil with less than 0.5% of ^{199}Hg tracer appearing in runoff. Given that this result was observed following the addition of a large amount of ^{199}Hg tracer, we acknowledge that the potential magnitude of contemporary Hg mobilized in the field may be minimal given natural rates of atmospheric deposition. However, this study does broaden our understanding of the influence of hydrological conditions; particularly soil moisture on Hg mobility.

The dependence of Hg transport on hydrological factors may be important when considering natural variability in hydrological processes (particularly during high-flow precipitation and spring snowmelt events) as well as the potential impacts of climate change on these processes. Further research on Hg mobility and transport in upland ecosystems is warranted given the potential manifestation of changes in upland Hg export on downstream

processes such as Hg methylation in wetlands (Mitchell *et al.*, 2009) and subsequent biotic uptake of MeHg; particularly during times of greatest Hg export such as spring snowmelt (Bishop *et al.*, 1995; Lee *et al.*, 2000; Mitchell *et al.*, 2008a).

Performing studies of this nature at the scale of a soil column is an invaluable tool given the level of control and manipulation of key hydrological variables afforded by such a technique. The use of expandable spray foam insulation to encase intact soil cores allows for the preservation of soil structure without introducing wall effects or blockage of soil pores for hydrological purposes while also acting as a suitable material for use with an applied Hg tracer. Studies involving the use of undisturbed, intact soil cores also provide a more realistic and natural medium for investigation as opposed to an artificial or repacked soil. Scaling results from the level of a soil core to that of a hillslope or watershed presents limitations and may provide an oversimplification of the processes that could potentially influence Hg mobility in natural systems. However, studies at small scales such as this study provide valuable information and an important first step to a greater understanding of the processes involved at the hillslope or watershed scale. Given the level of heterogeneity at the landscape scale, investigations such as this study at smaller scales facilitate the determination of the relative controls of hydrological processes on contaminant transport in the environment, and broaden our understanding of the level of small-scale spatial variability therein.

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6 Supporting Information

An overview of a separate study that was conducted in order to test the feasibility of using foam-encased soil cores for the study of hydrological and mercury (Hg) biogeochemical processes is described in the Supplementary Information.

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Table 1 Full factorial design with snowmelt input and antecedent soil moisture as the experimental variables; 3 replicate soil cores per treatment combination. Low and high treatment levels are summarized below.

		SNOWMELT INPUT		
		LOW	**HIGH**	**NO INPUT/CONTROL**
ANTECEDENT SOIL MOISTURE	**LOW**	n = 3	n = 3	n = 3
	HIGH	n = 3	n = 3	n = 3

Antecedent Soil Moisture:

Low: similar to 65 mm available soil water in surface 45 cm soil, observed prior to winter 2010

High: field capacity

Snowmelt Input:

Low: 50 mm (spring 2010 snowpack SWE)

High: 100 mm (spring 2011 snowpack SWE)

Table 2 Tracer total ^{199}Hg and ambient THg outflow loads (ng) for all hydrological treatment combinations. Lower-case letter superscripts represent significant differences for tracer (total ^{199}Hg).

Treatment	Tracer THg Load (ng)	Ambient THg Load (ng) *
Low Moisture – Low Input	127 ± 12 [a]	17 ± 11
High Moisture – Low Input	31 ± 0.8 [b]	7.9 ± 0.5
High Moisture – High Input	55 ± 14 [b]	14 ± 1
Low Moisture – High Input	341 ± 100 [c]	22 ± 4

[a,b,c] denote significant differences in tracer THg outflow loads among treatments
* No significant differences in ambient THg outflow loads among treatments

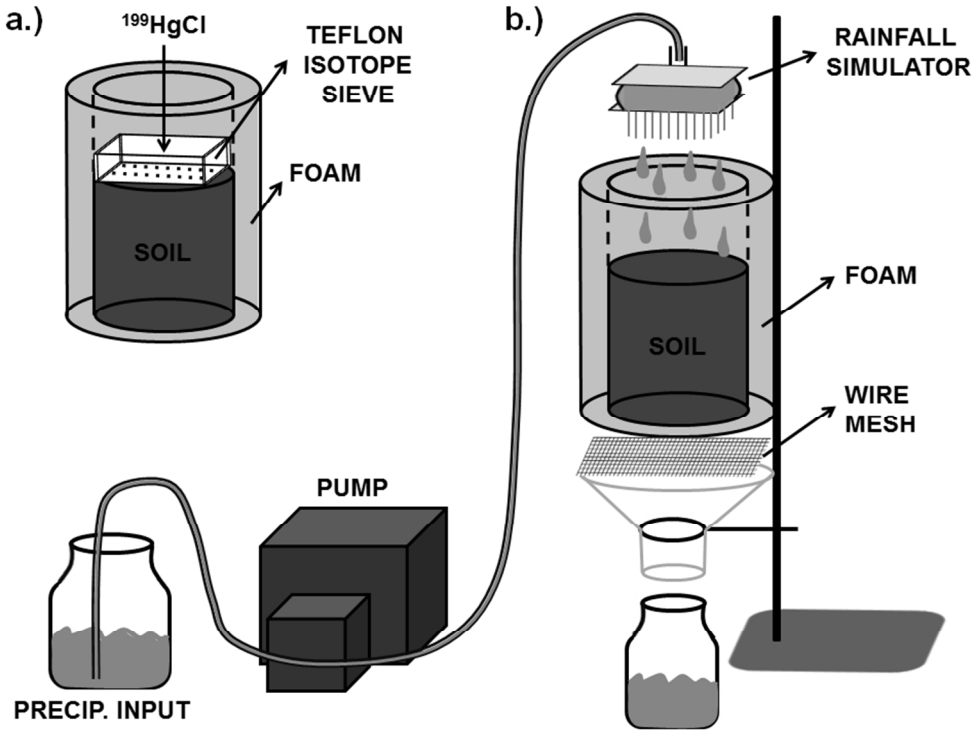

Figure 1 Depiction of procedure for experiments: a.) Following alteration of soil moisture, ^{199}Hg isotope (as ^{199}HgCl) applied to soil surface with Teflon sieve. b.) Immediately after isotope addition, foam-encased core secured to ring stand above acid-washed glass funnel. Precipitation input delivered to soil surface via peristaltic pump and rainfall simulator.
343x258mm (72 x 72 DPI)

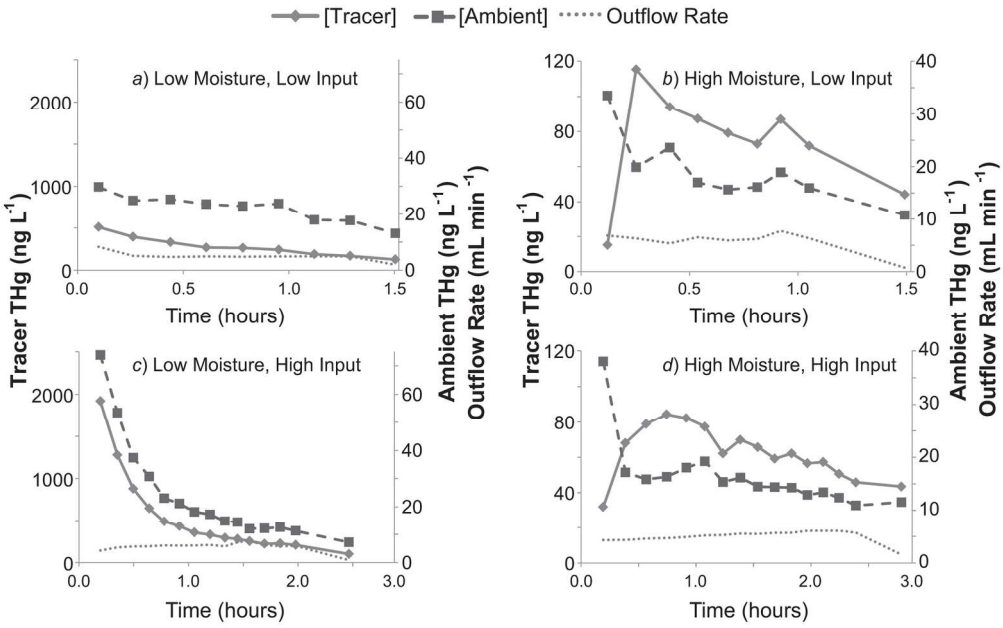

Figure 2 Time course plots of tracer Hg and ambient THg concentrations as well as outflow rates for each of the four treatment combinations. One replicate, representative core was selected from each treatment.
167x103mm (300 x 300 DPI)

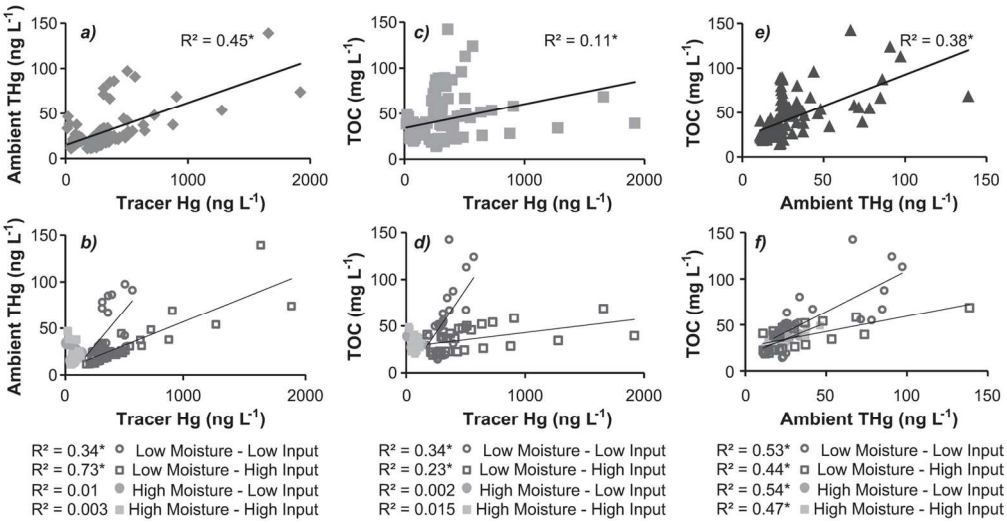

Figure 3 Scatterplots of correlations between outflow variables: a) tracer (total ^{199}Hg) concentrations vs. ambient THg concentrations including all treatments, b) tracer Hg vs. ambient with treatments designated, c) tracer Hg concentrations vs. DOC concentrations including all treatments, d) tracer Hg vs. DOC with treatments designated, e) ambient THg concentrations vs. DOC concentrations including all treatments, and f) ambient THg vs. DOC with treatments designated. *denote significant correlations.
144x74mm (300 x 300 DPI)

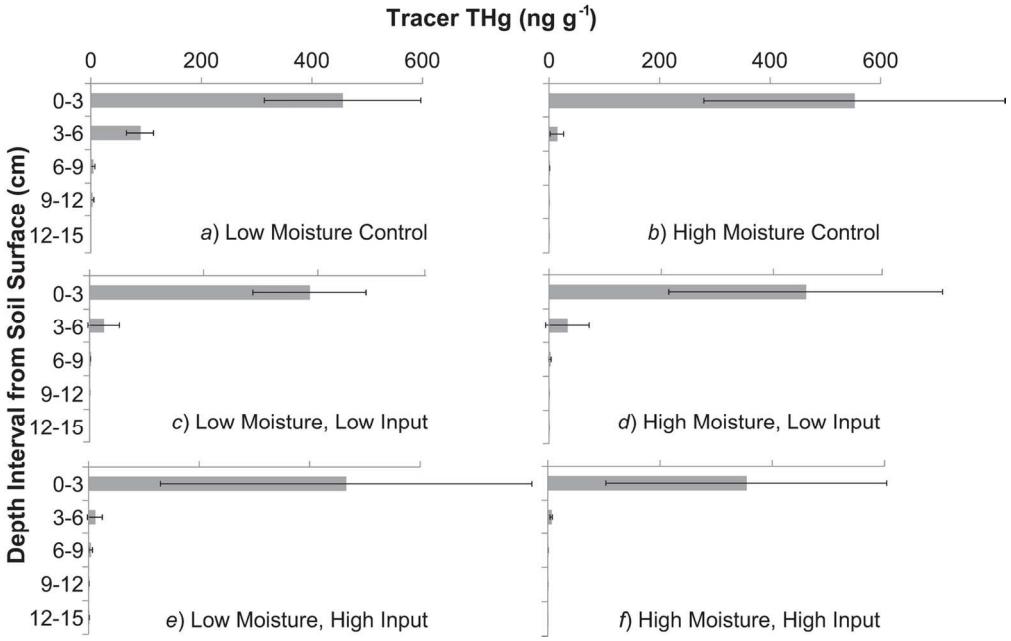

Figure 4 Soil depth profiles of tracer (total ^{199}Hg) concentrations (ng g^{-1}) for all treatment combinations including moisture controls: a) Low Moisture Control, b) High Moisture Control, c) Low Moisture Low Input, d) High Moisture Low Input, e) Low Moisture High Input, and f) High Moisture High Input. Error bars represent standard deviation of the three replicates per treatment.
133x84mm (300 x 300 DPI)