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Mercury flux from naturally enriched bare soils during simulated cold weather cycling

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HIGHLIGHTS

- Hg flux during cold temperature cycling was observed at varying moisture contents.
- During freeze-thaw events, flux levels correlated with energy inputs and outputs.
- During sub-zero events, flux spikes correlated with air temperature minimums.
- Mechanisms are proposed to account for the Hg flux levels and spikes.

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ABSTRACT

Elemental mercury flux released from terrestrial surfaces is a critical area of research due to mercury's potent toxicity and persistency on a global scale. However, there is significant uncertainty surrounding mercury flux in colder environments. The objective of this research was to investigate and identify the potential mechanisms responsible for the release of elemental mercury flux from bare soils in cold weather temperature cycling under simulated laboratory conditions. Seasonal cycling scenarios, including freeze-thaw and sub-zero, were utilized to simulate Fall, Winter, and Spring. The results for both freeze-thaw and sub-zero cycles indicated that there are separate and distinct mechanisms present that promote elemental mercury flux at temperatures below 0°C. During the freeze-thaw cycles, the amount of flux released was linked to the amount of energy leaving and entering the system, respectively. During the sub-zero cycles, flux spikes were produced by the thin surface layer of soil and corresponded to air temperature minimums rather than soil temperature minimums. This rapid drop in temperature was speculated to force mercury from the ice structure, due to further freezing of the liquid water content, increasing the mercury concentration within the remaining water and creating a pathway that encourages volatilization to the atmosphere. This was not observed in the thin layer clean soil trials. Additionally, as the soil water content approached a field capacity of approximately 20%, the flux pattern was suppressed during freeze-thaw cycles, as the number of available interstitial pore spaces decreased. However, this pattern was not observed during sub-zero cycling, as the largest response was triggered with the highest water content.

1. Introduction

Elemental mercury (Hg^0) has an atmospheric residence time of up to two years and can be readily deposited and re-emitted from terrestrial surfaces, allowing both anthropogenic and naturally emitted mercury to cycle on a global scale (Schroeder and Munthe, 1998; Pirrone et al., 2010). Adverse environmental and health effects have been observed in areas directly impacted by major point sources as well as remote locations far removed from emissions. Enhanced Hg accumulation occurs in polar regions due to long range transport and global circulation (Pirrone et al., 2010). This global distillation results in the Arctic being a sink for environmental mercury, due to its colder temperatures where indigenous populations are at risk from Hg bioaccumulation and biomagnification in the Arctic food chain.

Global and regional scale Hg modelling involves a large number of inputs, transformation processes, and depositions, making

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models, which attempt to account for all relevant reactions, very complex. In cold environments, one method used to simplify the models is to remove terrestrial emissions from soils when they are at or below the freezing point (Gbor et al., 2007). However, recent studies over bare soils have provided evidence that this assumption may be inaccurate since Hg^0 flux spiking events have occurred in sub-zero soil temperatures in both laboratory and field studies (Corbett-Hains et al., 2012; Cobbett, 2007). Frozen soils with snow cover have been shown to suppress Hg flux, although bare soils are governed by different influencing variables, similar to those for unfrozen soils.

Soil moisture content (SWC), soil temperature, air temperature, solar radiation, and precipitation have all been shown to strongly influence Hg^0 flux from soils subject to above 0°C conditions (Gustin and Stamenkovic, 2005; Lin et al., 2010; Boudala et al., 2000). Relative humidity (Kim and Kim, 2001), biological activity, and oxidizing agents (Choi and Holsen, 2009) have also been investigated as important factors, although their influence is less defined. In general, many environmentally relevant variables are interrelated, making it difficult to isolate their individual effects during field studies.

Soil moisture, however, is one influencing variable which has been well isolated and characterized. A study by Gustin and Stamenkovic (2005) showed increasing SWC caused Hg^0 flux to rise until the soil neared saturation and the interstitial pore air spaces became disconnected. This has been confirmed in subsequent studies (Bahlmann et al., 2006; Choi and Holsen, 2009; Corbett-Hains et al., 2012) by using optimal moisture contents to promote flux below the soil's field capacity. The effect of temperature has also been suitably described with an Arrhenius relationship evident for both soil and air temperature (Kim et al., 2012). After applying a logarithmic transformation, increasing temperatures produced a linear relationship with increasing Hg flux, although only under unfrozen conditions.

The objective of the current experiments was to investigate and characterize the mechanism(s) responsible for Hg^0 flux from bare soils in sub-zero conditions. A laboratory scale dynamic flux chamber (DFC) study was conducted, which used simulated seasonal temperature cycling to analyse both freeze-thaw and sub-zero temperature cycles relevant to cold environments. Fall and Spring cycles incorporated phase changes within the soil matrix through freeze-thaw while Winter cycles were limited to sub-zero soil temperature cycles. A naturally enriched soil, containing high concentrations of Hg, was used for the trials to facilitate response detection and better mechanism observation.

2. Materials & methods

The experimental set-up was adapted from the laboratory scale study conducted by Corbett-Hains et al. (2012). Specific modifications from the previous experiment have been generally described here.

2.1. Experimental set-up

A laboratory scale polycarbonate acrylic DFC was used in conjunction with a polycarbonate soil column casing, both shown in Fig. 1. The two parts were sealed together with Hg resistant epoxy and placed inside a scientific grade freezer (Marvel 17CAF). A 5 cm layer of expanded polystyrene foam insulation (R value of 8.08 (Solutions, 2011)) was added to the sides and bottom of the column to facilitate one dimensional freezing from the soil surface. Unidirectional freeze thaw from the top down is more representative of natural conditions compared to omnidirectional freeze thaw that present in previous experiment conducted by Corbett-Hains et al. (2012). Type T thermocouples were used to monitor soil temperatures at depths of 2, 5, and 15 cm, as well as air temperatures in the DFC headspace, freezer, and ambient air.

Outdoor air, drawn into the system at 12.5 L/min, was conditioned using a knock-out column to remove air moisture prior to entering the freezer. This flow rate was large enough to maintain an approximate flow rate of 10 L/min across the DFC. Air supply lines were open to the freezer to allow for further moisture removal and equilibration before entering the DFC inlet. Using a Campbell Scientific CR23X datalogger and a solid state relay, the freezer's compressor was manipulated to allow for precise control of the air and soil temperature. Therefore, temperature cycles could be carefully selected and evaluated with repeatable cycle profiles.

The soil column was produced artificially prior to each trial using a naturally Hg enriched soil collected near Clyde Forks, Ontario. The soil was air dried and sifted to a 1 mm particle size with water added prior to each trial to reach the appropriate SWC. Physical properties of the experimental soil used are presented in Table 1. It should be noted that the Hg concentration of the soil is highly elevated compared to background soils or other enriched soils studied. This specific soil was selected to provide an easily detectable response when soil temperatures are very low, a condition often assumed to completely suppress Hg^0 flux. Therefore, the flux measurements reported in this paper are not environmentally relevant in magnitude, but are used to characterize the mechanisms which promote flux during cold environment temperature cycles.

The Hg concentrations emitted from the soil surface were measured using a Tekran 2537A Mercury Vapour Analyzer (2537A). The 2537A was programmed using a standard method, requiring a flow rate of 1.5 L/min on a 5 min cycle for each the alternating sample cartridges. Internal calibrations for the machine were completed every 25 h using the internal permeation source to minimize the potential for diurnal patterns. The Tekran 1100 Zero Air Generator was used in conjunction with the 2537A during calibration, to provide an air stream free of contamination.

To prevent cartridge bias, Hg concentrations present in the ambient and DFC air were measured by both Cartridge A and B. However, when alternating between sources the sample lines may contain residual mercury, influencing the following measurement. To maintain accuracy, the first and last sample measured after alternating flow paths was discarded. Therefore, using a 5 min cycle, a total time of 20 min was required for both ambient and DFC air to be measured in both cartridges, and a 40 min cycle was required to determine the flux.

2.2. Methodology

2.2.1. Seasonal cycling

To simulate soil temperature cycles environmentally relevant soil and air temperature cycles were produced, including realistic freezing and thawing temperature gradients. This was accomplished by designing three temperature profiles (Fall, Winter, and Spring) that could be cycled sequentially at any given SWC. Fig. 2 provides an overview of the seasonal cycles used.

2.2.2. Capping of soil column with a thin layer of clean soil

To evaluate the contribution of the surface soil layer, one seasonal cycling trial was conducted using a 1 cm layer of clean soil (1.4 μg/g Hg) as the surface layer above the Hg enriched soil column at the same SWC. This isolated the Hg^0 flux from the top layer while allowing the column to act as one thermodynamic mass through which air and water vapour could transfer freely.