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Investigation of factors affecting mercury emission from subtropical forest soil: A field controlled study in southwestern China

Jun Zhou [a,b], Zhangwei Wang [a,*], Xiaoshan Zhang [a], Ting Sun [a,b]

[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Recent studies demonstrated that subtropical forest in China was considered as a large pool of atmospheric mercury and soils of forested watershed is a large reservoir of atmospherically deposited mercury. However, forest ecosystems not only act as sinks but also as sources of previously deposited mercury emitted back to the atmosphere. In this study a field controlled method was performed in Tieshanping National Forest Park (TNFP) to identify the effects of the most important parameters that controlled mercury emissions from soil surfaces, including chamber flushing flow turnover times (TOTs), soil water content and watering, total gaseous mercury (TGM) in air and understory. Flushing flow rates significantly affected the calculation of mercury flux and the optimal TOTs were 0.94 min in the forest. TGM in atmosphere was significantly inhibited mercury emission from soils, and the deposited mercury was not absorbed firmly by the soils in a short time and emitted back to atmosphere rapidly when TGM concentration decreased. Higher soil moisture reduced the emission of mercury and initial watering produces a spike in the mercury emissions due to the interstitial soil gas mercury displaced by infiltrating water physically. However, subsequent watering was reducing the fluxes, because surface soil was saturated and soil pores were blocked by water film and inhibited the soil mercury emission. Soils under the understory had a higher mercury concentrations and deep organic layers. However, the fluxes of soil under the understory significantly were inhibited in daytime because solar radiation was blocked by the understory and the higher litter layer.

1. Introduction

Mercury is a highly toxic heavy metal and is well-known global contaminant that can continuously go through the deposition to terrestrial and aquatic ecosystems and re-emission back to atmosphere by natural sources (Poissant et al., 2000; Chung and Chon, 2014). Natural sources generally include the emissions from natural reservoirs (e.g., volcanic activity and forest fires) and the re-emission of mercury deposited previously from anthropogenic and natural sources (Zhang et al., 2014). Some recent studies and models of its cycle in the environment suggested that mercury emissions and re-emissions from soil and vegetation were estimated up to 5500–8900 tons, accounting for 19–51% of the current release to the atmosphere from all sources (UNEP, 2013). Furthermore, studies have also reported that mercury evasion from forest and grassland was an important source of total gaseous mercury (TGM) in the atmosphere in the background area (Zhou et al., 2015; Ericksen et al., 2006; Choi and Holsen, 2009a; Almeida et al., 2009). Therefore, soil/air exchange flux is an important component of the mercury global biogeochemical cycle. Management of this environmental contaminant necessitates the accurate measurement of the exchange flux between earth surfaces and the atmosphere (Eckley et al., 2010).

However, unlike the measurement of mercury release from anthropogenic point sources, characterization of emissions from natural sources is difficult, especially from soil, because spatial and temporal variability of mercury emission is controlled by multiple interacting factors, such as experimental methods, substrate mercury content and fractions (Eckley et al., 2010; Liu et al., 2014), soil physical–chemical factors (soil temperature and humidity, soil gas mercury, soil total organic matters (TOM), pH, etc.) (Choi and Holsen, 2009b; Yang et al., 2007) and meteorological parameters (e.g. UV radiation, air temperature, rainfall) (Gabriela et al., 2011; Almeida et al., 2009). However, results of how these factors influence the mercury emissions are often inconsistent and even contradictory (Park et al., 2014). Thus regional field and simulation studies of soil/air flux appear to be particularly important.

Numerous researches have used dynamic flux chambers (DFCs) to measure mercury fluxes from a large assortment of surfaces around the globe (Bash et al., 2007). But it should be noted that short-term variability in Hg^0 concentration made contributions to the uncertainty level in DFC-derived flux significantly and relative bias for DFC-derived fluxes was estimated to be ~10%, and for ~85%

* Corresponding author.
E-mail address: wangzhw@rcees.ac.cn (Z. Wang).

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of the measurement (Zhu et al., 2015). Moreover, Lin et al. (2012) demonstrated that flux measured by conventional DFC may be underestimated at low flushing flow rate (≤5 L min^{-1}) compared to the new DFC, because the direct air flow reduced surface shear in conventional DFC. The difference in chamber volume and flushing flow rate used by researchers has varied by over an order of magnitude and the resulting chamber turnover times (TOTs) have varied by over 2-orders of magnitude, which results in fluxes variation in by order of magnitude (Eckley et al., 2010). However, flushing flow rate or TOTs differ world-widely in measuring fluxes of forest soil, therefore, optimal TOTs are required. In addition, flux between soil and air is the relationship of dynamic diffusion between mercury concentrations of soil gas in soil column underneath the soil surface layer (0–5 cm, our unpublished data) and TGM in atmosphere, indicating that mercury concentrations variation in atmosphere or soil gas seriously influences the flux (Zhang et al., 2002). Subtropical forest in China is considered as a large pool of atmospheric mercury (Zhou et al., 2013, 2015; Wang et al., 2009), while soils of forested watershed is a large reservoir of atmospherically deposited mercury, accounting for up to 90% of mercury in forests (Grigal, 2003). Forest ecosystems not only act as sinks but also as sources of previously deposited mercury emitted back to the atmosphere. Previous researches focused mostly on mercury deposition to forest, while the influence factors and process of mercury evasion from forest soil were not studied in detail and the process was not clear. Furthermore, at present, no studies are conducted to explore the influence of TGM in atmosphere and understory on the exchange flux between soil and air. In the current study, a field control experiment is conducted (1) to study the optimal flushing flow rate and TOTs, (2) to isolate the effects of moisture and watering on the emission of mercury from the soil surface, (3) to characterize the influence of TGM in atmosphere and (4) understory (e.g., shrub and fern) on the exchange flux in a subtropical forest in southwestern China.

2. Materials and methods

2.1. Sites description

This work was conducted at Tieshanping National Forest Park (TNFP) (29°38′N, 104°41′E), one of the Sino-Norwegian multidisciplinary Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems (IMPACTS) project monitoring sites, is located on a sandstone ridge, 20 km in the northeast of the metropolitan Chongqing City. The forest stand in TNFP is a Masson Pine dominated, coniferous-broad leave mixed subtropical forest and trees were planted in the 1960s. The soil is typically mountain yellow earth and its texture is haplic acrisol/alisol, which is severely acidified with an acidic pH 3.79 and TOM 12.7% in the organic horizon (Zhou et al., 2015). Based on our precious study, atmospheric deposition and soil pools of mercury were significantly elevated in TNFP area, which was several or even dozens of times compared to estimates obtained in North America and Europe (Wang et al., 2009; Zhou et al., 2015).

2.2. Soil properties

Soil profiles were collected at two locations which were under the understory (ferns) and under the forest canopy without ferns. The two locations were distanced no more than 1 m and corresponded to the substrates of Experiment 4 in Section 2.4. Soil samples were collected in polyethylene bags and air-dried in a clean environment in our laboratory. Subsequently the air-dried soil samples were homogenized to a size of 150 meshes per inch with a mortar before chemical analysis. For mercury analysis in soil samples, a DMA–80 direct mercury analyzer (Milestone Ltd., Italy) was used. TOM content in forest soils and litter was determined by using the sequential loss on ignition (LOI) (Zhou et al., 2013).

2.3. Flux measurement

The soil/air mercury fluxes from forest soil were conducted in the field of TFNP and determined by using a coupling method of DFCs and manual pure gold quartz trap (Fig. 1). A semi-cylindrical quartz glass and open-bottom DFCs (4.71 L) were used throughout the sampling campaign. The square of the DFCs covering over the soil surface was 20 × 30 cm with six inlet holes (1 cm diameter) and a detailed description can be found in Fu et al. (2008). At the outlet of the chamber, an orifice was connected to two exits, one was connected in a regulated suction pump with a flow rate of 5 L min^{-1}, whereas the other exit was connected to a gold trap for trapping outlet TGM. On the two opposite sections of the chamber, the other gold trap was placed to trap inlet TGM in the outside air. Sampling flow rate was maintained 0.3–0.4 L min^{-1} by rotameter and the air volume passing through each trap was accurately measured by an integrating volume flow meter. The mercury flux was calculated using the following equation:

$$F = (C_0 - C_i) \times Q/A \quad . \tag{1}$$

Where F is the mercury flux (ng m^{-2} h^{-1}); C_o and C_i are the steady state mercury concentration (ng m^{-3}) of the outlet and inlet air stream, respectively; A is the surface area enclosed by the chamber; and Q is the flushing flow rate. All the gold traps which measured inlet and outlet air TGM concentrations in every 20-min interval, were brought back to TNFP Forestry Station for mercury quantification by CVAFS detector (Brooks Rand III, US EPA, Method 1631, 1999) using dual gold trap amalgamation procedure after every sampling.

For all mercury analysis, quality assurance and quality control measures included all gold traps' recovery, collection efficiency, and the system blanks. All the gold traps' recovery were calibrated by injecting a volume of mercury saturated air with known concentration. The recoveries before and after all experiments were in the range of 97.4–102.9% and 97.3–103.5% by using dual gold trap amalgamation procedure and the standard deviation of parallelism was <2.6%. To detect the collection efficiency of our gold quartz traps before sampling in field, two traps were connected in sequence and collected the ambient lab air for 1 h. For all the traps, there was an extra-low concentration beyond the detection limit of the CVAFS on the second traps, which can be ignored. The blanks of the flux sampling system were routinely measured by placing the chamber on a quartz glass surface and the averaged blank was 0.13 ± 0.21 ng m^{-2} h^{-1} ($n = 10$). The r^2 of the calibration curve had to be greater than 0.99 before the sample analysis could proceed.

Meteorological parameters were collected and averaged over 5-min intervals. Percent moisture was monitored with Time Domain Reflectometry (TDR) Hydra Probe II (SDI-12/RS485) and a Stevenswater cable tester (USA). Air temperature and solar radiation were monitored by TP 101 digital thermometer and GLZ-C photosynthetically radiometer (TOP Ltd., China), respectively.

2.4. Experimental approach

Four experiments were performed from September to October in TNFP as follows. For purposes of comparison, mercury fluxes were measured by two chambers side by side simultaneously. The experiments were designed such that the measurement varied one parameter in one chamber, the other one can easily observed the variation of this parameter effect on the mercury flux. Dynamic flux chambers were moved from subsample locations to another one to avoid disturbance from previous experiments. The setup of the dynamic flux chamber for measuring soil/air mercury flux was showed in Fig. 1.

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