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Investigation of factors affecting gaseous mercury concentrations in soils

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ABSTRACT

The purpose of this study was to determine the effects of soil temperature, soil moisture, redox potential (Eh) and soil organic matter (SOM) on the total gaseous mercury (TGM) concentrations in background soils. Our measurements were made in a grass field and deciduous forest at the Piney Reservoir Ambient Air Monitoring Station (PRAAMS) in Garrett County, Maryland. Three plots in each area were sampled every third week from July 2009 to June 2010 at the Oe–A soil horizon interface, the A–E soil horizon interface, and 5 and 10 cm into the E soil horizon. The mean soil TGM concentration for all depths in the forest (2.3 ± 2.2 ng m^{-3}) was significantly higher than the mean soil TGM concentration in the grass field (1.5 ± 1.9 ng m^{-3}). Soil TGM at all depths was most strongly and consistently correlated to soil temperature. The soil TGM concentrations were highest and most variable at the forest Oe–A soil horizon interface (4.1 ± 2.0 ng m^{-3}), ranging from 1.5 to 8.4 ng m^{-3}. This soil horizon interface had 11 to 26% more SOM and the soil Eh was 100 to 400 mV lower than the other soil depths. Our results suggest that soil temperature, soil Eh and SOM are significant factors affecting TGM concentrations in forest soils. Future studies of TGM dynamics in background soils may benefit from closely monitoring the organic soil horizon.

1. Introduction

The size and dynamics of the gaseous mercury pool in soils may play an important role in the atmospheric fluxes of mercury (Johnson and Lindberg, 1995; Moore et al., 2011; Sigler and Lee, 2006; Zhang and Lindberg, 1999). Many processes in soils may influence the conversion between Hg(II) and gaseous elemental mercury (GEM), which can be released into the atmosphere (Zhang and Lindberg, 1999). Studying the soil gas mercury pool is different than studying atmospheric fluxes of TGM. For example, soil gas mercury concentrations may change much more slowly and be affected by different environmental parameters than soil TGM fluxes. Unfortunately, however, few studies have examined the factors affecting the gaseous mercury pool in background soils (Johnson et al., 2003; Kromer et al., 1981; Sigler and Lee, 2006; Wallschläger et al., 2002).

GEM is semi-volatile at ambient temperatures and the volatility can be an exponential function of temperature (Sigler and Lee, 2006). Many studies have shown that higher soil temperatures can increase the atmospheric fluxes of TGM (Bahlmann and Ebinghaus, 2003; Carpi and Lindberg, 1998; Choi and Holsen, 2009a; Choi and Holsen, 2009b; Edwards et al., 2001; Ericksen et al., 2006; Gillis and Miller, 2000; Gustin et al., 2004; Gustin et al., 1997; Lin et al., 2010; Obrist et al., 2005; Scholtz et al., 2003; Sigler and Lee, 2006; Tsiros, 2002). However, Sigler and Lee (2006) also showed that higher soil temperatures led to higher TGM concentrations in background soils. These higher soil temperatures may have stimulated microbial activity responsible for the reduction of Hg(II) to GEM (Baldi, 1997; Fritsche et al., 2008; Kritee et al., 2008).

Soil organic matter (SOM) has been shown to provide binding sites for Hg(II) (Meili, 1991; Skyllberg et al., 2006). In forest soils, higher amounts of matrix bound mercury are often associated with higher SOM content (Akerblom et al., 2008; Andersson, 1979; Demers et al., 2007; Gabriel and Williamson, 2004; Grigal, 2003; Johansson et al., 1991; Meili, 1991; Obrist et al., 2009; Obrist et al., 2011; Sigler and Lee, 2006; Yin et al., 1997). The Hg(II) bound to SOM may increase soil TGM concentrations, if reduced to GEM (Gu et al., 2011). Sigler and Lee (2006) speculated that SOM may strongly influence TGM concentrations in soils, but they did not measure SOM in their study.

Soil redox potential (Eh) may affect TGM concentrations in soils by influencing the availability of electrons for oxidation–reduction reactions involving Hg(II) and GEM (Andersson, 1979; Gabriel and Williamson, 2004; Obrist et al., 2009; Schluter, 2000; Schuster, 1991; Zhang and Lindberg, 1999). It was speculated that under low soil Eh conditions, the Hg(II) contained in SOM could be reduced to GEM (Andersson, 1979; Gabriel and Williamson, 2004). This reduction may lead to higher TGM concentrations in soils. At higher Eh, GEM can be oxidized to Hg(II), bound to SOM or lost in soil water export (Andersson, 1979; Gabriel and Williamson, 2004; Schuster, 1991). However, little or no information exists on the effects of soil Eh on the formation of GEM in background soils (Schluter, 2000).

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Increases in soil moisture can affect the movement and formation of TGM in soils (Gustin et al., 2004; Gustin and Stamenkovic, 2005; Lin et al., 2010; Lindberg et al., 1999; Song and Van Heyst, 2005). This effect may be transient, since TGM fluxes have been shown to quickly increase and then decrease in response to precipitation events (Gustin and Stamenkovic, 2005; Lindberg et al., 1999; Song and Van Heyst, 2005). Increases in soil water will often decrease soil Eh, which can increase the reduction of Hg(II) to GEM (Ponnamperum, 1972; Zarate-Valdez et al., 2006). Alternatively, Gustin and Stamenkovic (2005) speculated that more polar water molecule out competes the Hg(II) for binding sites in soils and the Hg(II) is subsequently released from soils into soil water.

Despite the potential importance of the soil TGM pool in the overall cycling of mercury, no studies have simultaneously measured the effects of soil Eh and soil moisture on the TGM concentrations in soils. Also, little information exists on the spatial and temporal variations of the soil TGM pool. Therefore, the purpose of this study was to identify factors that influenced the spatial and temporal patterns of TGM concentrations in background soils.

2. Methods

2.1. Study site

This study was conducted at the Piney Reservoir Ambient Air Monitoring Station (PRAAMS) in Garrett county Maryland (elevation: 781 m) (39° 42′ 21.29″ N, 79° 0′ 43.21″ W). In 2004, the deciduous forest at PRAAMS was selectively harvested in order to establish a large open area for an atmospheric monitoring station. There is currently a suite of atmospheric trace gasses, aerosols, and meteorological parameters measured at PRAAMS. A variety of native grasses, thorns, and flowers now cover the open area, which is mowed when needed. For this study, we established three 3 m by 2 m plots in the open grass field and in the adjacent deciduous forest.

Soils at PRAAMS were Dekalb and Gilpin very stony loams (USDA, 2009). The O horizon was considerably different between the two areas. The forest O horizon extended to a depth of 7 cm and contained more undecomposed organic surface litter (Oi) than the grass field. In the grass field, the O horizon was only 4 cm thick, the Oi layer was very thin (2 mm), and the surface litter consisted of grasses. The A horizons in the two areas were very organic-rich and 6 to 10 cm thick. The E horizons in the two areas started at about 10 cm below the surface. Averaged over all depths, soil pH was significantly lower in the forest (3.99 ± 0.14) than the grass area (4.43 ± 0.17). Soil pH determined with EPA SW-846 Method 9045. In the forest area, the top 25 cm of soil had a mean bulk density of 0.83 g cm^3 (USDA-NRCS, 2011). The mean bulk density for the top 25 cm of soil in the grass area was 1.01 g cm^{-3} (USDA-NRCS, 2011).

2.2. Soil TGM concentrations

Soil TGM concentrations were measured every third week from July 2009 through June 2010 using a new approach described in Moore et al. (2011). Samples were collected twice each day during daylight hours. The measurements represent only the daytime periods and the diurnal variations were not examined. We collected soil gas samples from inverted Pyrex glass funnels installed at the Oe–A soil horizon interface (3–7 cm depth), the A–E soil horizon interface (9–15 cm depth), 5 cm into the E soil horizon (13–20 cm depth), and 10 cm into the E soil horizon (18–25 cm depth) in each plot.

Each sampling period consisted of two consecutive sampling days. On the first day, we randomly sampled one of our sampling areas (grass or forest). The other area was sampled on the second day. These consecutive days were selected to minimize between day differences in precipitation and temperature. On each sampling day, we sampled for 1.5 to 3 h per plot. The 1.5-hour sampling period was only used when we expected significant rainfall because intense rainfall events would flood the shallower funnels. This water would

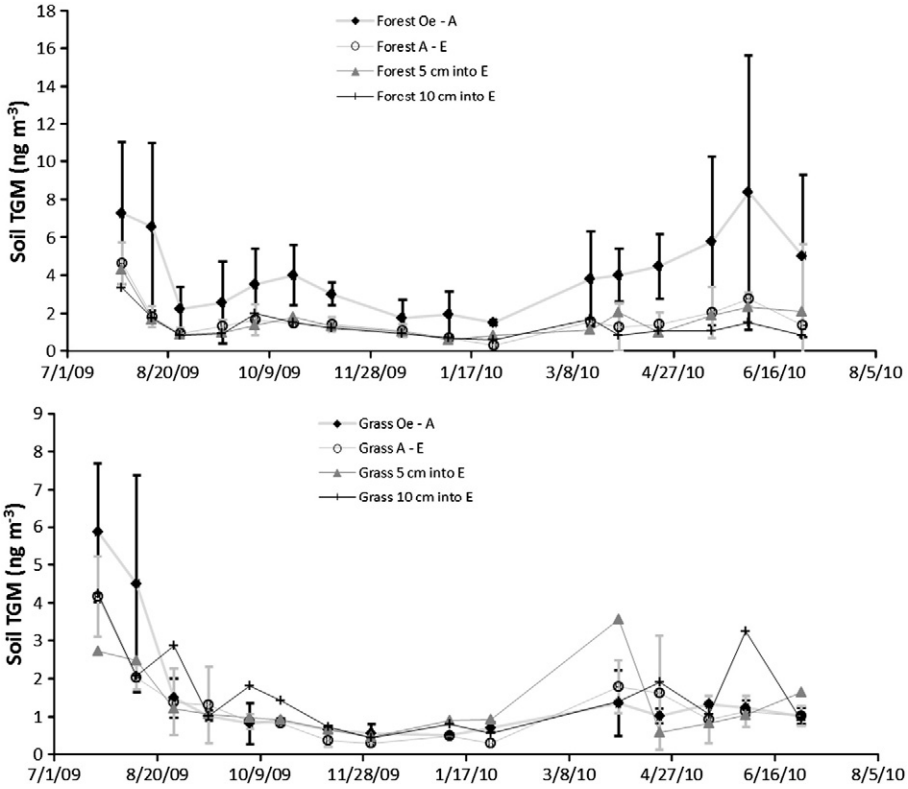

Fig. 1. Mean daily soil gas TGM at all depths in the forest (top) and grass (bottom) areas. Error bars are ±one standard deviation and to simplify the graph error bars are only shown for the Oe–A and A–E soil interface layers (layers with highest standard deviation).