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Short communication

Warming increases methylmercury production in an Arctic soil☆

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ABSTRACT

Rapid temperature rise in Arctic permafrost impacts not only the degradation of stored soil organic carbon (SOC) and climate feedback, but also the production and bioaccumulation of methylmercury (MeHg) toxin that can endanger humans, as well as wildlife in terrestrial and aquatic ecosystems. Currently little is known concerning the effects of rapid permafrost thaw on microbial methylation and how SOC degradation is coupled to MeHg biosynthesis. Here we describe the effects of warming on MeHg production in an Arctic soil during an 8-month anoxic incubation experiment. Net MeHg production increased >10 fold in both organic- and mineral-rich soil layers at warmer (8 °C) than colder (−2 °C) temperatures. The type and availability of labile SOC, such as reducing sugars and ethanol, were particularly important in fueling the rapid initial biosynthesis of MeHg. Freshly amended mercury was more readily methylated than preexisting mercury in the soil. Additionally, positive correlations between mercury methylation and methane and ferrous ion production indicate linkages between SOC degradation and MeHg production. These results show that climate warming and permafrost thaw could potentially enhance MeHg production by an order of magnitude, impacting Arctic terrestrial and aquatic ecosystems by increased exposure to mercury through bioaccumulation and biomagnification in the food web.

1. Introduction

Mercury (Hg) is a global pollutant that can be transported long distances in its gaseous elemental form [Hg(0)] and, following oxidation, large amounts of atmospheric Hg have been deposited in polar regions since the Industrial Revolution (Cooke et al., 2009; Kirk et al., 2012; Macdonald, 2005). A large portion of this Hg is associated with soil minerals and organic matter due to their high binding affinities (Kirk et al., 2012; Rydberg et al., 2010). Climate change models predict a 13%–28% decrease in Arctic permafrost by 2050 (Schuur et al., 2015; Tarnocai et al., 2009), and thawing permafrost is expected to be a significant source of Hg to Arctic freshwater and marine ecosystems (Kirk et al., 2012; Macdonald, 2005; Rydberg et al., 2010; Schartup et al., 2015a; Soerensen et al., 2016; Sonke and Heimburger, 2012; Stern et al., 2012). An additional risk of Hg release from permafrost is concurrent release of labile SOC, which can provide an important substrate to fuel microbial conversion of inorganic Hg to methylmercury (MeHg) (Barkay et al., 2011; MacMillan et al., 2015). Human consumption of MeHg accumulated and biomagnified in fish and whales can cause neurological damage (Dietz et al., 2009; Kirk et al., 2012; Soerensen et al., 2016).

MeHg concentrations in Arctic seawater and marine biotas are known to be elevated compared to lower latitude oceans, but the sources of seawater MeHg remain poorly understood (Schartup et al., 2015a; Soerensen et al., 2016). Mercury mass balance calculations suggest large freshwater inputs to the Arctic Ocean (Soerensen et al., 2016), possibly originating from runoff following Hg methylation in Arctic soils (Dietz et al., 2009; Kirk et al., 2012). MeHg production in Canadian Arctic thaw ponds and marine sediments has been reported (Kirk et al., 2012; Lehnherr et al., 2011,

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2012; MacMillan et al., 2015; St Pierre et al., 2014), but only a few studies have examined the effects of warming on Hg methylation in Arctic soils (Loseto et al., 2004; Oiffer and Siciliano, 2009). The rates and mechanisms that link SOC degradation in permafrost soils to an increase in Hg methylation remain uncertain, hindering development of predictive models of Hg transport and fate in a warming climate. The present study was undertaken to focus on the impact of temperature rise on MeHg production and its coupling with SOC degradation for up to 8 months in microcosms of thawed active layer soil from a continuous permafrost region.

2. Materials and methods

2.1. Soil samples and microcosm setup

Two frozen soil cores (8.3 cm diameter × 91 cm length) were collected in April 2012 from the trough area of a high-center polygon (N 71°16.757' W 156 °36.274) at the Barrow Environmental Observatory (BEO), Barrow, Alaska, USA (Fig. S1). The cores were sealed inside PVC liners and kept frozen during transport and stored at −20 °C until use in December 2014. They were sectioned into organic- (8–20 cm depth from the land surface) and mineral-rich layers (20–45 cm depth) based on soil color and carbon content (Roy Chowdhury et al., 2015; Yang et al., 2016). The top layer (0–8 cm), consisting mostly of plant roots, and the lower layer of ground ice (below 45 cm) were excluded from the study. The organic- and mineral-layer soils were homogenized by stirring with a spatula in a N_2-filled anoxic glove chamber, and analyzed for basic geochemical characteristics (Table S1). Additional site descriptions and geochemical information can be found elsewhere (Herndon et al., 2015a; Roy Chowdhury et al., 2015; Yang et al., 2016). Anoxic microcosms for both organic- and mineral-layer soils were constructed to mimic water-logged active layers due to poor drainage in permafrost. Homogenized wet soils (150 g thawed soil) were placed in 600-mL sterile bottles, sealed with thick butyl rubber stoppers, and kept inside the glove chamber. They were incubated in the dark at −2 °C and 8 °C to simulate near-freezing and warmest month temperatures, respectively, at the BEO field site (Roy Chowdhury et al., 2015). The 600-mL incubation permitted periodic soil sampling at selected time intervals, and the headspace was flushed with ultra-pure N_2 for 2 min after each sampling event. Three replicates per temperature per soil layer were conducted.

To assess the effects of labile soil organic carbon and freshly added Hg on net MeHg production, we added glucose and isotope-labeled Hg as follows. On day 145, when the reducing sugars reached a steady state, D-(+)-glucose, used as an analog for labile organic substrate, was added to soil incubations at 8 °C to examine its effects on Hg methylation. A small volume (1 mL) of glucose was introduced and well mixed in the soil, so that soil water content and chemistry were minimally affected. The total amounts of glucose added to the organic and mineral soils were 6.0 ± 1.0 and 0.5 ± 0.1 μmol of glucose C g^{-1} dwt. soil, respectively. On day 189, when net MeHg production reached a steady state, stable ^{201}Hg isotope [as dissolved $^{201}HgCl_2$] was added to the 8 °C incubations of the organic and mineral soils at 14 ± 1 and 22 ± 1 ng ^{201}Hg g^{-1} dwt. soil, respectively. Glucose or ^{201}Hg isotope was added only once in the course of the study.

2.2. Chemical analysis

At pre-determined time intervals, headspace CO_2 and CH_4 were analyzed with a gas chromatograph equipped with a methanizer and a flame ionization detector (Roy Chowdhury et al., 2015; Yang et al., 2016). Aliquots of wet soil samples (1–2 g) were collected and equilibrated with 10–20 mL of either 0.1 M KCl (pH ~ 5.0) or 10 mM NH_4HCO_3 (pH ~ 7.3) solution. The NH_4HCO_3 extraction was subsequently used to determine soluble soil organic compounds (e.g., total dissolved organic carbon, reducing sugars, and ethanol), and the KCl extraction was used to determine exchangeable and dissolved inorganic species including Fe(II), Fe(III), major anions and cations, as described in detail elsewhere (Herndon et al., 2015b; Yang et al., 2016). Sulfate concentration was below the detection limit (0.01 μmol g^{-1} dwt., Table S1). Except for Hg analysis, samples were centrifuged for 15 min at 6,500*g*, and the supernatants were collected and filtered through 0.45-μm membrane filters before analysis. Fe(II) concentrations were quantified using the HACH Ferrous method 8146 on a HACH DR 900 colorimeter, whereas total dissolved iron concentrations were determined using the HACH FerroVer method 8008.

Procedures for determining total extractable Hg and MeHg in soils were similar to those described previously (Bloom et al., 1997). In brief, the soil slurry (1 mL) was transferred into a 50-mL conical centrifuge tube and digested with 9 mL of 1.1 M $CuSO_4$, 8 M H_2SO_4 and 4 M KCl. Isotope-labeled $CH_3^{200}Hg$ was added as an internal standard so that any potential loss during extraction could be accurately determined. The whole mixture was shaken for 1 h. Half of the well-mixed sample slurry was used for total Hg analysis after oxidation with 5% (v/v) BrCl overnight at 4 °C. Excess amounts of $SnCl_2$ were then added to convert Hg(II) to Hg(0), which was quantified via cold-vapor atomic fluorescence spectrometry (CVAFS) with an automated Brooks Rand MERX (Model III) analytical system. For total MeHg analysis, the remaining soil slurry was extracted with 10 mL methylene chloride (99.99%, Fisher Scientific) following EPA Method 1630. After extraction, the methylene chloride fraction was transferred into a separate centrifuge tube filled with deionized water, where MeHg was transferred into the aqueous layer by evaporating methylene chloride with N_2 purging. The MeHg-containing water was then combined with a citrate buffer and an ethylating reagent in an amber glass vial before injection into the MERX system, connected to an inductively coupled plasma mass spectrometer (Elan-DRCe, PerkinElmer) to determine Hg isotopes (Hu et al., 2013; Lin et al., 2014). The detection limit for total Hg and MeHg was about 6 pg.

3. Results and discussion

A survey of an area of continuous permafrost and interstitial tundra at BEO, Barrow, Alaska, showed MeHg concentrations ranging 0.3–2.3 ng L^{-1} in ponded surface water and active layer soil pore waters (Table S2), which is more than 10 times higher than those typically found in uncontaminated soils and sediments at lower latitudes (Gray et al., 2014). The respective total Hg and MeHg concentrations per gram dry weight soil in the core sample before incubation were 55.2 ± 1.3 and 0.08 ± 0.01 ng in the organic layer, and 54.0 ± 1.2 and 0.07 ± 0.01 ng in the mineral layer. Following incubation at 8 °C, net MeHg production increased about 35 fold to 2.8 ± 0.2 ng g^{-1} (~5.1% of total Hg) in the organic soil after 100 days, and >5-fold to 0.35 ± 0.02 ng g^{-1} (~0.7% of total Hg) in the mineral soil after 60 days (Fig. 1). On a dry weight basis, organic soil produced nearly 10 times more MeHg than mineral soil (Fig. 1a,b). Even at −2 °C, net MeHg concentrations increased slowly but consistently, and accumulated a total of 100 and 90 pg g^{-1} in the organic and mineral layers, respectively (Fig. 1). The estimated methylation rate at −2 °C was similar in both soils at about 0.2 pg g^{-1} dry soil day^{-1}. These results indicate that warming can accelerate net MeHg production in Arctic soil.

However, contrasting temporal patterns of MeHg production and accumulation at 8 °C were observed between the two soil layers (Fig. 1). In the organic layer, MeHg production showed three