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Significant interaction effects from sulfate deposition and climate on sulfur concentrations constitute major controls on methylmercury production in peatlands

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Abstract

Transformation of inorganic mercury (Hg) to methyl mercury (MeHg) in peatlands is a key process in making boreal catchments a source of MeHg to freshwater ecosystems. Due to the importance of sulfur-reducing bacteria (SRB) for this process, past atmospheric deposition of sulfate (SO_4^{2-}) may have increased net terrestrial Hg methylation. A long-term (14-year) factorial design field experiment was used to investigate the effect of enhanced SO_4^{2-} deposition and raised temperature using a greenhouse (GH) treatment (air temperature~+4 °C; soil temperature 20 cm below mire surface ~+2 °C) on sulfur (S) turnover, net Hg methylation, MeHg and total Hg concentrations in a boreal mire in northern Sweden. Of the SO_4^{2-}–S added during 14 years, 50% was retained in the plots without GH treatment while the combination of SO_4^{2-} addition and GH treatment resulted in 15% S retention. The addition of SO_4^{2-} (7-fold ambient SO_4^{2-}-deposition) increased ($p < 0.05$) the net Hg methylation (200%) as well as the store of S (150%) and MeHg (120%) in the peat. A combination of enhanced SO_4^{2-} deposition and GH treatment decreased both the net Hg methylation rate constant ($0.018 \pm 0.006\ d^{-1}$) and MeHg content (1.2 ± 0.2 ng g^{-1} dry weight (dw)) relative to the sites with enhanced SO_4^{2-} deposition without GH treatment ($0.065 \pm 0.013\ d^{-1}$ and 3.7 ± 0.6 ng g^{-1} dw, respectively). The concentration of Hg in the peat declined ($p < 0.05$) in response to experimental addition of SO_4^{2-}. Despite the decrease in Hg in response to SO_4^{2-} deposition, these plots had the highest amounts of MeHg as well as the highest Hg methylation rate constants. This indicates that the concentration of S is more important than the concentration of Hg for the production of MeHg in this boreal landscape. These results also show that long-term chronic SO_4^{2-} deposition at rates similar to those found in polluted areas of Europe and North America increase the capacity of wetlands to methylate Hg and store MeHg, which can ultimately be released to streams and lakes. This study also, for the first time, indicates that the enhancing effect of SO_4^{2-} on the production of MeHg might be counteracted by increased temperature.

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1. INTRODUCTION

Concern about mercury (Hg) concentrations in freshwater fish and wildlife exceeding environmental and human health advisory levels has raised questions about the factors controlling the availability of methylated Hg to freshwater foodwebs (Johansson et al., 2001; Kamman et al., 2005; Driscoll et al., 2007). Over 90% of the Hg found in freshwater predatory animals appears as methyl mercury (MeHg), while inorganic Hg dominates atmospheric deposition and terrestrial pools (Munthe et al., 2007). This indicates the importance of net Hg methylation. Mires are particularly suitable for Hg methylation processes (Grigal, 2003; Mitchell et al., 2008b). Their hydrological connectivity to streams and lakes also makes mires potential sources of MeHg to freshwater ecosystems (Richardson et al., 2007).

The runoff of Hg and MeHg, as well as the levels found in fish can vary considerably between different catchments despite similar levels of atmospheric Hg deposition (Lee et al., 1998), suggesting that MeHg species are produced within the catchments (Branfireun et al., 1999). While mires are potentially important hotspots for MeHg production and accumulation, there is considerable variability in the strength of these hotspots across the landscape (Richardson et al., 2007; Tjerngren et al., 2011, 2012). Some of this variability relates to sulfur (S) availability in soils and it is also supposed that the distribution of S ultimately determines the fate of MeHg in a watershed (Skyllberg et al., 2003).

Water saturation of boreal mires promotes microbial dissimilatory reduction of SO_4^{2-} by sulfate-reducing bacteria (SRB). The importance of SRB for methylation of Hg^{2+} is well-documented (Compeau and Bartha, 1985; Ranchou-Peyruse et al., 2009), although iron-reducing bacteria can also contribute to Hg methylation (Kerin et al., 2006). Some recent findings indicate that the availability of SO_4^{2-} for SRB and the bioavailability of inorganic neutral Hg-sulfides, determined by competition between thiols, inorganic sulfides and polysulfides (Skyllberg, 2008), are major factors regulating the concentration of MeHg in mire porewater. S addition experiments to mires have also shown a positive response in net Hg methylation (Branfireun et al., 2001; Jeremiason et al., 2006; Bergman et al., 2012). However, the persistence of the influence of S addition is not well-documented and is important to investigate since other factors are also important for the regulation of SO_4^{2-} reduction, and hence any sustained effect of SO_4^{2-} on net Hg methylation.

Anthropogenic S and Hg deposition at rates several-fold higher than natural deposition have increased soil concentrations of S (Eriksson et al., 1992) and Hg (Steinnes and Friedland, 2006) above their natural background levels in many regions. Increased SO_4^{2-} deposition has been blamed for enhanced methylation of Hg in lake and terrestrial ecosystems (Gilmour and Henry, 1991; Branfireun et al., 2001; Orem et al., 2011). Anthropogenic influences on the climate are also likely to influence S and Hg cycling. The redox conditions around or just below the average water table position in boreal peatlands are favorable for SO_4^{2-} reduction (Thompson et al., 2009; Eriksson et al., 2010b). Global climate change influences microbially mediated processes such as SO_4^{2-} reduction, organic matter mineralization and losses of gaseous S compounds (Conrad, 1996). The soil storage of Hg is partly controlled by evolution of gaseous compounds, predominantly elemental Hg (Hg^0) (Schroeder and Munthe, 1998), a process that might also be controlled by microbial reduction processes (Fritsche et al., 2008). Jokic et al. (2003) suggest that a potential drying of wetlands in response to climate change may increase the degradation of organic matter and the relative quantity of oxidized S compounds, thus eventually increasing the capacity of wetlands to release heavy metals and their organic species. The degree to which prolonged anthropogenic SO_4^{2-} deposition and/or increased temperature due to climate change will alter net methylation of Hg and the MeHg concentration in boreal mires is thus of major concern.

This study examined the influence of sulfate (SO_4^{2-}) deposition on MeHg production and accumulation in a boreal minerogenic mire (fen) in northern Sweden. The overall objective was to assess the effects of experimentally enhanced SO_4^{2-} deposition in combination with greenhouse (GH) induced increases air and soil temperature on S and Hg stores, net Hg methylation and MeHg accumulation in boreal peatlands. Our starting hypothesis was that enhanced SO_4^{2-} deposition would result in more S in the peat, a higher net Hg methylation rate, and more MeHg storage in the soil. GH treatment to increase temperature was predicted to increase reduction of SO_4^{2-} and gaseous S evasion from boreal mires and decrease the S content in the upper part of the peat. This decrease in S content would in turn decrease Hg methylation rates and MeHg concentration. To evaluate these hypotheses, peat soil material from a long-term field experiment at Degerö Stormyr with combinations of enhanced SO_4^{2-} deposition and GH treatment in a factorial design was analyzed for total content of S, Hg, and MeHg as well as for Hg methylation rate constants. The Hg methylation rate constant was determined by laboratory incubations using stable Hg-isotope additions.

2. MATERIALS AND METHODS

2.1. Field site

The field site was Degerö Stormyr (Lat. 64°09′N, Long. 20°22′E, altitude 270 m a.s.l) within the Kulbäcksliden Research Park of the Vindeln Experimental Forests, 70 km from the coast of the Gulf of Bothnia, Sweden. Details of mire vegetation, the climate regime at the site, and the experimental design can be found in Granberg et al. (2001) and Wiedermann et al. (2007). The climate at the site is classified as cold temperate humid. Based on records from the closest national meteorological station (Kulbäcksliden: 64°12′N, 19°34′E, altitude 200 m a.s.l.), the long-term (1961–1990) mean annual total precipitation is 523 mm, mean annual temperature +1.2 °C, July temperature 14.7 °C, and January temperature −2.4 °C (Alexandersson et al., 1991).

The ongoing field experiment was established in 1995 (Granberg et al., 2001) as a fully factorial design (Fisher,