

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/260134375>

Elemental mercury evasion from a boreal peatland suppressed by long-term sulfate addition

CONFERENCE PAPER · JULY 2011

READS

45

7 AUTHORS, INCLUDING:



Christine Alewell

University of Basel

187 PUBLICATIONS 2,992 CITATIONS

SEE PROFILE



Kevin Bishop

Swedish University of Agricultural Sciences

246 PUBLICATIONS 5,891 CITATIONS

SEE PROFILE



Staffan Åkerblom

Swedish University of Agricultural Sciences

19 PUBLICATIONS 151 CITATIONS

SEE PROFILE

Evasion of Elemental Mercury from a Boreal Peatland Suppressed by Long-Term Sulfate Addition

Johannes Fritsche,[†] Stefan Osterwalder,^{*,‡} Mats B. Nilsson,[§] Jörgen Sagerfors,^{||} Staffan Åkerblom,[⊥] Kevin Bishop,^{⊥,#} and Christine Alewell[‡]

[†]Meteotest, CH-3012 Bern, Switzerland

[‡]Department of Environmental Sciences, University of Basel, CH-4056 Basel, Switzerland

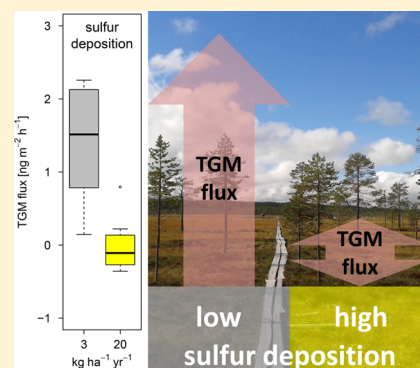
[§]Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, SE-901 83 Umeå, Sweden

^{||}Unit for field-based forest research, Swedish University of Agricultural Sciences, Svartberget Forest Research Station, SE-922 91 Vindeln, Sweden

[⊥]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, SE-75236 Uppsala, Sweden

[#]Department of Earth Sciences, University of Uppsala, SE-75236 Uppsala, Sweden

ABSTRACT: We investigated the evasion of TGM (total gaseous mercury) from experimental plots on a boreal peatland that had been exposed for 15 years to different combinations of atmospheric sulfur (S) and nitrogen (N) deposition as well as greenhouse treatments simulating climate change. Shaded dynamic flux chamber measurements during the summer in 2009 showed emission of TGM to the atmosphere from most of the treated plots ($0.7 \pm 0.94 \text{ ng m}^{-2} \text{ h}^{-1}$). However, TGM exchange rates were significantly lower, occasionally indicating Hg uptake, on plots subjected to S addition at rates of $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Enhanced nitrogen deposition and greenhouse treatment had no significant effect on TGM fluxes. We hypothesize that the lower Hg evasion from the sulfur-treated plots is related to either earlier Hg evasion or Hg binding to S in organic matter, making Hg less susceptible to volatilization and more prone to transport in runoff.



INTRODUCTION

Mercury (Hg) pollution is a major concern, with Hg concentrations in freshwater fish often exceeding acceptable levels, especially in high-latitude regions where peatlands are a common landscape element. Peatlands, with their low redox status and high carbon content, provide favorable conditions for formation of the more bioavailable methylmercury (MeHg)^{1,2} and are thus considered to be a major mediator for the increased levels of Hg in freshwater fish.

Methylation of inorganic Hg to MeHg is strongly enhanced under anaerobic conditions and conducted by Hg-methylating bacteria from several microbial genera but mainly sulfate-reducing bacteria (SRB) when sulfate is in surplus compared to other electron acceptors.^{3–5} The reduction of sulfate (SO_4) to H_2S provides an important binding ligand for inorganic Hg,^{6–8} and as a byproduct, most likely through cometabolism, MeHg is formed in quantities dependent on the prevailing level of sulfide.^{9–11} Application of sulfate to wetlands in field and laboratory experiments has verified the linkage between enhanced sulfate deposition and MeHg production.^{12–19}

However, sulfur also affects other processes within the Hg cycle. The reduction of Hg^{2+} to Hg^0 , which evades to the atmosphere, is connected to relatively high redox potentials (redox equilibria at 659 mV^{20}). This suggests that Hg^{2+} reduction is not rivaled by sulfate reducers that are bound to much lower redox potentials ($E_h < -221 \text{ mV}$ at pH 7 and 25

$^{\circ}\text{C}$). However, reduced sulfur species, and especially sulfides, effectively bind Hg^{2+} by forming stable HgS complexes, thus decreasing the size of the Hg^{2+} pool available for reduction. Following this line of reasoning, we would expect more Hg complexation in soils that have been exposed to elevated levels of S deposition. In contrast, Åkerblom et al.¹⁵ have shown that the total Hg stored in the peat layer of experimental plots from the surface down to 40 cm significantly declined in response to elevated levels of sulfur deposition compared to that in neighboring control plots after 12 years (Table 1).

A variety of factors have been found to influence the emission of Hg from soils such as soil and atmospheric Hg concentrations,^{21,22} soil and air temperature,^{23–25} soil moisture,^{25,26} and incident solar radiation.²⁷ Several recent studies have determined TGM (total gaseous mercury, which primarily consists of Hg^0)²⁸ fluxes from wetlands. Most of these studies have employed dynamic flux chambers (DFCs) with a focus on key factors influencing Hg emission (refs 29 and 30 and other references listed in ref 31). However, the comparison of fluxes from different studies is often challenging because of the different designs and varying operating procedures.³²

Received: April 3, 2014

Revised: August 21, 2014

Accepted: August 25, 2014

Table 1. Means and Standard Deviation of TGM Flux and Inlet Air Hg Concentrations (TGM inlet) Detected on the HighS and LowS Plots^a

site	TGM flux (ng m ⁻² h ⁻¹)	TGM inlet (ng m ⁻³)	Hg _{tot} (ng g ⁻¹)	Hg _{inorg} (ng g ⁻¹)	S _{tot} (μg dm ⁻³)	DFC T (°C)	air T (°C)	RH (%)	pH
HighS (<i>n</i> = 16)	-0.01 ± 0.4	1.48 ± 0.16	45.9 ± 12	43.5 ± 11.5	10.3 ± 2.7	20.3 ± 4	20 ± 4.1	65.4 ± 11	4
LowS (<i>n</i> = 16)	1.40 ± 0.8	1.63 ± 0.14	53.1 ± 11	51 ± 11.2	8.3 ± 2.1	22.3 ± 4	20.2 ± 4.5	52.6 ± 8.5	4
S-only (<i>n</i> = 4)	-0.19 ± 0.8	1.51 ± 0.12	38.1 ± 4.1	34.8 ± 3.1	11.7 ± 0.9	16.7 ± 0.8	17.2 ± 1	50.3 ± 3.4	4
control (<i>n</i> = 4)	1.39 ± 2.3	1.7 ± 0.11	57.3 ± 6	56.3 ± 6.1	7.2 ± 2.7	21.6 ± 1.4	18.7 ± 2.5	79.2 ± 6.4	3.9

^aData for the S-only treatment and control plot (without combinations) are given separately. Air temperatures inside the flux chamber (DFC T), ambient air temperatures (air T), and relative humidity (RH) were measured simultaneously. Total Hg (Hg_{tot}), inorganic Hg (Hg_{inorg}), and total sulfur (S_{tot}) concentrations in the soil (depth of 0–40 cm) were determined by Åkerblom et al.¹⁵ in 2007. The pore water pH was published by Bergman et al.¹⁶ in 2012 and determined in August 1999.

To investigate the hypothesis that TGM evasion is affected by sulfate deposition, we measured TGM flux with a shaded DFC on experimental plots exposed to increased levels of sulfur separately and in combination with two other simulated anthropogenic influences, increased nitrogen deposition rates and a greenhouse treatment to increase soil and air temperatures.

MATERIALS AND METHODS

The mixed acid peatland of Degerö Stormyr, which covers an area of ~6.5 km² and is located ~60 km north of Umeå, Sweden, was our study site. The evasion of TGM was measured on 2 m × 2 m plots, arranged in a random, duplicate 2³-factorial design with ambient and elevated levels of sulfur (S) and nitrogen (N) as well as ambient and elevated temperatures simulated using a greenhouse cover (GH). This has been in operation since 1995 to study the effects of S and N deposition as well as temperature on the emission of methane. See ref 33 for a detailed description of the experimental setup. The lower levels of S and N correspond to ambient deposition rates at the site (3 and 2 kg ha⁻¹ year⁻¹, respectively), while the high levels of 20 kg of S ha⁻¹ year⁻¹ and 30 kg of N ha⁻¹ year⁻¹ correspond to maximal deposition levels in southern Sweden during the 1980s. N as ammonium nitrate (NH₄NO₃) and S as sodium sulfate (Na₂SO₄) are dissolved in 10 L of surface mire water and evenly distributed over the plots with a watering can. Each year, one-third is applied directly after snowmelt and the rest is divided into four doses applied at the beginning of every month from June to September. The temperature was increased by covering the plots with perforated plastic sheets during the snow-free period, resulting in a mean increase in daily air temperatures 25 cm above the vegetation surface of 3.6 °C and significant soil heating (~2 °C) over ambient conditions between May and September.³³

Differences in TGM fluxes among the three main treatments and their two-way and three-way interactions were evaluated by analysis of variance (ANOVA) using R version 2.15.1.³⁴ The level of significance was taken as *p* < 0.05.

Between August 14 and 26, 2009, the emission of TGM was measured two times on each plot with a dynamic flux chamber made of polycarbonate [0.367 m (length) × 0.267 m (width) × 0.195 m (height)]. The DFC was shaded to exclude the effect of direct sunlight on TGM emissions. Although sunlight is a major driver of evasion of TGM from soils,³⁵ we minimized the effect of this factor to reveal the influences and interactions of S, N, and GH on the exchange of TGM. Ambient air was circulated through the chamber at a flow rate of 11 L min⁻¹. At the inlet and outlet, a substream of air was diverted and drawn over a pair of gold cartridges at a rate of 0.5 L min⁻¹ for 30 min.

The Hg on the gold cartridges was then thermally desorbed and analyzed with a Tekran 2537A mercury vapor analyzer. Fluxes were then derived from eq 1

$$F_{\text{TGM}} = \frac{(C_{\text{out}} - C_{\text{in}}) \cdot Q}{A} \quad (1)$$

where *C*_{out} and *C*_{in} designate the inlet and outlet concentrations of TGM, respectively, *Q* is the air flow rate, and *A* is the surface area covered by the DFC. The sampling lines to the gold cartridges were heated to avoid water condensation and loss of Hg. Passivation of the gold cartridges was checked repeatedly by adding TGM-saturated air from a temperature-controlled permeation source (Tekran 2505 calibration unit) to the sampled air stream. The recovery rate of these standard additions reached 98.3 and 99.7%. Thus, it was assured that instrumental artifacts did not affect our measurements. Chamber blanks were performed in the field with the flux chamber placed on an acid-cleaned PTFE sheet and measured three times for 1.5 h before and after and two times in the middle of the campaign (*n* = 8). The blanks averaged zero and were not subtracted upon calculation of soil fluxes. The air temperature and relative humidity inside and outside the chamber were determined simultaneously with the flux measurements using EL-USB-2 Humidity, Temperature and Dew Point Data Loggers (DataQ Instruments, Akron, OH).

RESULTS AND DISCUSSION

The emission of TGM from the peatland surface was generally low at all plots [mean of 0.7 ng m⁻² h⁻¹; standard deviation (SD) = 0.94; *n* = 16] compared to previously published results, most likely because we minimized photoreduction processes by shading the chamber. Other published TGM flux rates measured over nonpolluted wetland sites remote from major Hg pollution sources (soils with <0.1 mg of Hg kg⁻¹) using enclosure methods without shading range from -1.5 and 7.1 ng m⁻² h⁻¹.^{30,36–39}

Just a few chamber studies have been published using shaded chambers⁴⁰ or comparing day and night fluxes.^{41–43} Ericksen et al.⁴³ measured TGM fluxes over 46 background soils, including agricultural, grassland, desert, and mixed and pine forest ecosystems, across the United States and reported significantly elevated TGM emissions in the light compared to dark for all sites except grassland sites. Most of the dark fluxes ranged from -0.1 to 2.7 ng m⁻² h⁻¹ and are thus similar in magnitude to the TGM exchange rates at Degerö Stormyr.

A significant (*p* < 0.001, via ANOVA) reduction in the rate of evasion of TGM from the HighS plots was observed (Figure 1). While the average flux from the LowS plots was 1.40 ± 0.78 ng m⁻² h⁻¹, it was -0.01 ± 0.38 ng m⁻² h⁻¹ from the HighS plots.

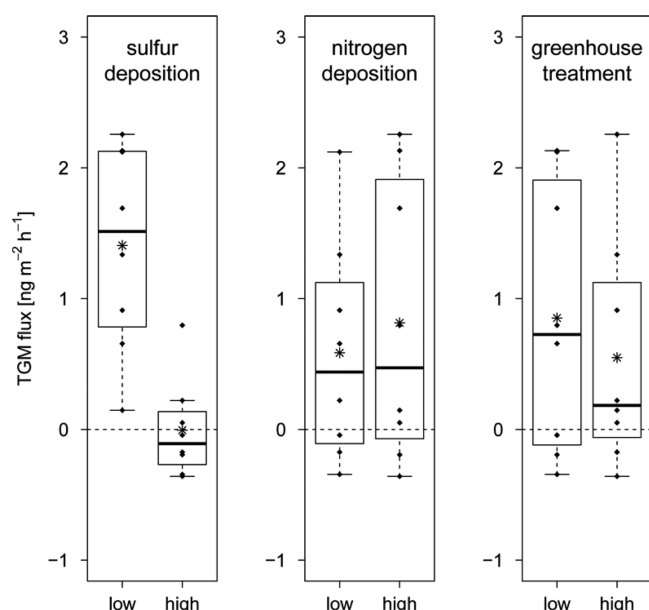


Figure 1. Effect of S, N, and GH treatments on TGM flux at Degerö Stormyr. Low levels of sulfur and nitrogen deposition of 3 kg of S ha⁻¹ year⁻¹ and 2 kg of N ha⁻¹ year⁻¹, respectively. High levels of sulfur and nitrogen deposition of 20 kg of S ha⁻¹ year⁻¹ and 30 kg of N ha⁻¹ year⁻¹, respectively. $n = 8$ for each boxplot; data averaged for each of the runs (one run includes 16 measurements). The upper edge of the box indicates the 75th percentile and the lower edge the 25th percentile. Whiskers indicate the 90th and 10th percentiles, while the line within the box marks the median. Asterisks denote means.

Using a conventionally calculated method detection limit [e.g., $3 \times \text{SD}$ (see ref 32)], the flux values reported here are technically below the detection limit. However, a clear and highly significant HighS treatment effect is revealed by the factorial design. Regardless, absolute flux values presented here should be viewed with caution.

No main treatment effects of N and GH and no two-way or three-way interactions of all three factors were observed. The redox status of the peatland was not monitored during this study. However, at pH 4, the odor of H₂S being emitted from the HighS plots was clearly perceptible, confirming the presence of reduced sulfur species.

It is tempting to suggest that the observed suppression of the TGM evasion may be entirely attributed to elevated levels of S in the peatland and its ability to form stable mercury complexes that reduce the bioavailability of mercury and prevent evasion of Hg⁰ to the atmosphere. However, Åkerblom et al.¹⁵ reported that the total Hg content in the soil (Hg_{tot} and Hg_{inorg} as the mass of Hg per unit dry mass of peat) decreased significantly by 34% in the S-only plots compared to the control plots and by 14% in the HighS plots compared to the LowS plots after enhanced S deposition for 12 years (Table 1). TGM flux and Hg_{tot} in the peat correlate weakly for all plots ($r_{\text{Spearman}} = 0.24$). The amount of S is also larger in the peat of the HighS plots and highest in the S-only plots.

This indicates that since the experiment began, more Hg_{tot} was lost from the HighS plots, while more S accumulated in these plots. One possibility is that the loss of Hg_{tot} resulted from higher rates of evasion of Hg⁰ from the HighS compared to the LowS plots earlier in the experiment when evasion measurements were not being made. This could have lowered the amount of Hg in the peat and contributed to the lower rate

of evasion observed in the experiment over a decade after the addition of S began.

A second possible pathway through which Hg could leave the plots is lateral loss via overland flow bound to the S in organic material. We suggest that elevated rates of sulfur deposition increased the number of available Hg-binding sites in peat organic matter because of the increased availability of thiols and polysulfides as has been shown by Skjellberg.⁴⁴ This favored the export of complexed Hg species via runoff while also hindering TGM evasion. Additionally, changes in methylation rates of inorganic Hg within the experimental plots could have fundamentally altered its mobility and bioavailability, thereby influencing TGM evasion rates.^{45,46}

Besides solar radiation, air temperature is important and also positively correlated to mercury evasion,²⁴ whereas relative humidity is usually negatively correlated to TGM fluxes.⁴⁷ Fluxes from the HighS and LowS plots showed weak (r_{Spearman} range from -0.38 to 0.21) and insignificant correlations with meteorological parameters and inlet air Hg concentrations (Table 1). Compared to ambient values, relative humidity inside the chamber was elevated by 11% on average, but no condensation was observed. We conclude that our comparison study was not biased because of changes in weather conditions and that the shading of the chamber minimized warming of the air inside the chamber.

This study demonstrates that the long-term addition of S to the peatland surface has significantly reduced the rate of evasion of TGM. This result, together with those of Åkerblom et al.¹⁵ who showed a reduced store of Hg in the upper 40 cm of the peat (and an increase in the level of S), suggests that the reducing HighS peatland environment not only favors the formation of MeHg but also alters the long-term balance of Hg inputs and outputs.

Until now, two mechanisms that link the sulfur and Hg cycles had been identified in previous studies. First, the increased bioavailability of HgS species enhances the uptake of Hg²⁺ by sulfate-reducing bacteria,¹⁴ and second, an increased level of sulfate reduction promotes methylation of Hg²⁺.⁴⁸ Our study revealed that after enhanced S deposition for 15 years, the rate of TGM evasion is significantly lower likely due to a combination of direct (suppressed evasion) and indirect (loss of Hg from peat) effects, although this experiment cannot offer a definitive mechanistic explanation. To fully understand the net effects of changes in anthropogenic sulfur deposition on the Hg exchange between the atmosphere and wetlands, this single measurement campaign should be complemented by longer-term observations of exchange dynamics from daily to decadal scales. Such observations will be a useful basis for developing a better process understanding of the specific mechanisms that drive these dynamics of which our study has provided a glimpse.

AUTHOR INFORMATION

Corresponding Author

*E-mail: stefan.osterwalder@unibas.ch.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Swedish Research Council (2009-15586-68819-37).

■ REFERENCES

- (1) Selvendiran, P.; Driscoll, C. T.; Montesdeoca, M. R.; Bushey, J. T. Inputs, storage, and transport of total and methyl mercury in two temperate forest wetlands. *J. Geophys. Res.* **2008**, *113*, G00C01.
- (2) St Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Beaty, K. G.; Bloom, N. S.; Flett, R. J. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *J. Fish. Aquat. Sci.* **1994**, *51*, 1065–1076.
- (3) Yu, R.-Q.; Flanders, J. R.; Mack, E. E.; Turner, R.; Mirza, M. B.; Barkay, T. Contribution of coexisting sulfate and iron reducing bacteria to methylmercury. Production in freshwater river sediments. *Environ. Sci. Technol.* **2012**, *46*, 2684–2691.
- (4) Shao, D.; Kang, Y.; Wu, S.; Wong, M. H. Effects of sulfate reducing bacteria and sulfate concentrations on mercury methylation in freshwater sediments. *Sci. Total Environ.* **2012**, *1*, 331–336.
- (5) Gilmour, C.; Podar, M.; Bullock, A. L.; Graham, A. M.; Brown, S. D.; Somenahally, A. C.; Johs, A.; Hurt, R. A.; Bailey, K. L.; Elias, D. A. Mercury methylation by novel microorganisms from new environments. *Environ. Sci. Technol.* **2013**, *47*, 11810–11820.
- (6) Skjölberg, U.; Qian, J.; Frech, W.; Xia, K.; Bleam, W. F. Distribution of mercury, methyl mercury and organic sulphur species in soil, soil solution and stream of a boreal forest catchment. *Biogeochemistry* **2003**, *64*, 53–76.
- (7) Harmon, R.; King, J.; Gladden, J. B.; Chandler, G.; Newman, L. Methylmercury formation in a wetland mesocosm amended with sulfate. *Environ. Sci. Technol.* **2004**, *38*, 650–656.
- (8) Gabriel, M. C.; Williamson, D. G. Principal biogeochemical factors affecting the speciation and transport of mercury through the terrestrial environment. *Environ. Geochem. Health* **2004**, *26*, 421–434.
- (9) Benoit, J. M.; Gilmour, C. C.; Mason, R. P.; Heyes, A. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol.* **1999**, *33*, 951–957.
- (10) Pedrero, Z.; Bridou, R.; Mounicou, S.; Guyoneaud, R.; Monperrus, M.; Amouroux, D. Transformation, localization, and biomolecular binding of Hg species at subcellular level in methylating and nonmethylating sulfate-reducing bacteria. *Environ. Sci. Technol.* **2012**, *46*, 11744–11751.
- (11) Truong, H.-Y. T.; Chen, Y.-W.; Belzile, N. Effect of sulfide, selenite and mercuric mercury on the growth and methylation capacity of the sulfate reducing bacterium *Desulfovibrio desulfuricans*. *Sci. Total Environ.* **2013**, *449*, 373–384.
- (12) Branfireun, B. A.; Roulet, N. T.; Kelly, C. A.; Rudd, J. W. M. In situ sulfate stimulation of mercury methylation in a boreal peatland: Toward a link between acid rain and methylmercury contamination in remote environments. *Global Biogeochem. Cycles* **1999**, *13*, 743–750.
- (13) Branfireun, B. A.; Bishop, K.; Roulet, N. T.; Granberg, G.; Nilsson, M. Mercury cycling in boreal ecosystems: The long-term effect of acid rain constituents on peatland pore water methylmercury concentrations. *Geophys. Res. Lett.* **2001**, *28*, 1227–1230.
- (14) Gilmour, C. C.; Henry, E. A.; Mitchell, R. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* **1992**, *26*, 2281–2287.
- (15) Åkerblom, S.; Bishop, K.; Björn, E.; Lambertsson, L.; Eriksson, T.; Nilsson, M. Significant interaction effects from sulfate deposition and climate on sulfur concentrations constitute major controls on methylmercury production in peatlands. *Geochim. Cosmochim. Acta* **2013**, *102*, 1–11.
- (16) Bergman, I.; Bishop, K.; Tu, Q.; Frech, W.; Åkerblom, S.; Nilsson, M. The Influence of Sulfate Deposition on the Seasonal Variation of Peat Pore Water Methyl Hg in a Boreal Mire. *PLoS One* **2012**, *7*, e45547.
- (17) Jeremiasen, J. D.; Engström, D. R.; Swain, E. B.; Nater, E. A.; Johnson, B. M.; Almendinger, J. E.; Monson, B. A.; Kolka, R. K. Sulfate addition increases methylmercury production in an experimental wetland. *Environ. Sci. Technol.* **2006**, *40*, 3800–3806.
- (18) Galloway, M.; Branfireun, B. Mercury dynamics of a temperate forested wetland. *Sci. Total Environ.* **2004**, *325*, 239–254.
- (19) King, J. K.; Harmon, S. M.; Fu, T. T.; Gladden, J. B. Mercury removal, methylmercury formation, and sulfate-reducing bacteria profiles in wetland mesocosms. *Chemosphere* **2002**, *46*, 859–870.
- (20) Bisogni, J. J. Using mercury volatility to measure redox potential in oxic aqueous systems. *Environ. Sci. Technol.* **1989**, *23*, 828–831.
- (21) Miller, M. B.; Gustin, M. S.; Eckley, C. S. Measurement and scaling of air-surface mercury exchange from substrates in the vicinity of two Nevada gold mines. *Sci. Total Environ.* **2011**, *409*, 3879–3886.
- (22) Kuiken, T.; Zhang, H.; Gustin, M.; Lindberg, S. Mercury emission from terrestrial background surfaces in the eastern USA. Part I: Air/surface exchange of mercury within a southeastern deciduous forest (Tennessee) over one year. *Appl. Geochem.* **2008**, *23*, 345–355.
- (23) Moore, C. W.; Castro, M. S. Investigation of factors affecting gaseous mercury concentrations in soils. *Sci. Total Environ.* **2012**, *419*, 136–143.
- (24) Kim, K.-H.; Yoon, H.-O.; Jung, M.-C.; Oh, J.-M.; Brown, R. J. C. A Simple Approach for Measuring Emission Patterns of Vapor Phase Mercury under Temperature-Controlled Conditions from Soil. *Sci. World J.* **2012**, 940413.
- (25) Rinklebe, J.; During, A.; Overesch, M.; Du Laing, G.; Wennrich, R.; Staerk, H.-J.; Mothes, S. Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. *Environ. Pollut.* **2010**, *158*, 308–318.
- (26) Xin, M.; Gustin, M.; Johnson, D. Laboratory investigation of the potential for re-emission of atmospherically derived Hg from soils. *Environ. Sci. Technol.* **2007**, *41*, 4946–4951.
- (27) Moore, C.; Carpi, A. Mechanisms of the emission of mercury from soil: Role of UV radiation. *J. Geophys. Res.: Atmos.* **2005**, *110*, D24302.
- (28) Munthe, J.; Wängberg, I.; Pirrone, N.; Iverfeldt, A.; Ferrara, R.; Ebinghaus, R.; Feng, X.; Gardfeldt, K.; Keeler, G.; Lanzillotta, E.; Lindberg, S. E.; Lu, J.; Mamane, Y.; Prestbo, E.; Schmolke, S.; Schroeder, W. H.; Sommar, J.; Sprovieri, F.; Stevens, R. K.; Stratton, W.; Tuncel, G.; Urba, A. Intercomparison of methods for sampling and analysis of atmospheric mercury species. *Atmos. Environ.* **2001**, *35*, 3007–3017.
- (29) During, A.; Rinklebe, J.; Boehme, F.; Wennrich, R.; Staerk, H.-J.; Mothes, S.; Du Laing, G.; Schulz, E.; Neue, H.-U. Mercury Volatilization from Three Floodplain Soils at the Central Elbe River, Germany. *Soil Sediment Contam.* **2009**, *18*, 429–444.
- (30) Kyllönen, K.; Hakola, H.; Hellen, H.; Korhonen, M.; Verta, M. Atmospheric Mercury Fluxes in a Southern Boreal Forest and Wetland. *Water, Air, Soil Pollut.* **2012**, *223*, 1171–1182.
- (31) Sommar, J.; Zhu, W.; Lin, C.-J.; Feng, X. Field Approaches to Measure Hg Exchange between Natural Surfaces and the Atmosphere: A Review. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 1657–1739.
- (32) Eckley, C. S.; Gustin, M.; Lin, C. J.; Li, X.; Miller, M. B. The influence of dynamic chamber design and operating parameters on calculated surface-to-air mercury fluxes. *Atmos. Environ.* **2010**, *44*, 194–203.
- (33) Granberg, G.; Sundh, I.; Svensson, B. H.; Nilsson, M. Effects of temperature, and nitrogen and sulfur deposition, on methane emission from a boreal mire. *Ecology* **2001**, *82*, 1982–1998.
- (34) R Core Team. R: A language and environment for statistical computing; R Foundation for Statistical Computing: Vienna, 2012.
- (35) Carpi, A.; Frei, A.; Cocris, D.; McCloskey, R.; Contreras, E.; Ferguson, K. Analytical artifacts produced by a polycarbonate chamber compared to a Teflon chamber for measuring surface mercury fluxes. *Anal. Bioanal. Chem.* **2007**, *388*, 361–365.
- (36) Marsik, F. J.; Keeler, G. J.; Lindberg, S. E.; Zhang, H. Air-surface exchange of gaseous mercury over a mixed sawgrass-cattail stand within the Florida Everglades. *Environ. Sci. Technol.* **2005**, *39*, 4739–4746.
- (37) Poissant, L.; Pilote, M.; Constant, P.; Beauvais, C.; Zhang, H. H.; Xu, X. H. Mercury gas exchanges over selected bare soil and flooded sites in the bay St. Francois wetlands (Quebec, Canada). *Atmos. Environ.* **2004**, *38*, 4205–4214.
- (38) Lindberg, S. E.; Zhang, H. Air/water exchange of mercury in the Everglades II: Measuring and modeling evasion of mercury from

surface waters in the Everglades Nutrient Removal Project. *Sci. Total Environ.* **2000**, 259, 135–143.

(39) Zhang, H.; Poissant, L.; Xu, X.; Pilote, M.; Beauvais, C.; Amyot, M.; Garcia, E.; Laroulandie, J. Air-water gas exchange of mercury in the Bay Saint Francois wetlands: Observation and model parameterization. *J. Geophys. Res.: Atmos.* **2006**, 111, D17307.

(40) Carpi, A.; Lindberg, S. E. Application of a Teflon (TM) dynamic flux chamber for quantifying soil mercury flux: Tests and results over background soil. *Atmos. Environ.* **1998**, 32, 873–882.

(41) Kuiken, T.; Gustin, M.; Zhang, H.; Lindberg, S.; Sedinger, B. Mercury emission from terrestrial background surfaces in the eastern USA. II: Air/surface exchange of mercury within forests from South Carolina to New England. *Appl. Geochem.* **2008**, 23, 356–368.

(42) Magarelli, G.; Fostier, A. H. Influence of deforestation on the mercury air/soil exchange in the Negro River Basin, Amazon. *Atmos. Environ.* **2005**, 39, 7518–7528.

(43) Ericksen, J. A.; Gustin, M. S.; Xin, M.; Weisberg, P. J.; Fernandez, G. C. J. Air-soil exchange of mercury from background soils in the United States. *Sci. Total Environ.* **2006**, 366, 851–863.

(44) Skyllberg, U. Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and implications for MeHg net production. *J. Geophys. Res.: Biogeosci.* **2008**, 113, G00C03.

(45) Frohne, T.; Rinklebe, J.; Langer, U.; Du Laing, G.; Mothes, S.; Wennrich, R. Biogeochemical factors affecting mercury methylation rate in two contaminated floodplain soils. *Biogeosciences* **2012**, 9, 493–507.

(46) Boening, D. W. Ecological effects, transport, and fate of mercury: A general review. *Chemosphere* **2000**, 40, 1335–1351.

(47) Poissant, L.; Casimir, A. Water-air and soil-air exchange rate of total gaseous mercury measured at background sites. *Atmos. Environ.* **1998**, 32, 883–893.

(48) Ranchou-Peyruse, M.; Monperrus, M.; Bridou, R.; Duran, R.; Amouroux, D.; Salvado, J. C.; Guyoneaud, R. Overview of mercury methylation capacities among anaerobic bacteria including representatives of the sulphate-reducers: Implications for environmental studies. *Geomicrobiol. J.* **2009**, 26, 1–8.