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Formation and mobilization of methylmercury across natural and experimental sulfur deposition gradients[☆]



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ABSTRACT

We investigated the influence of sulfate (SO_4^{2-}) deposition and concentrations on the net formation and solubility of methylmercury (MeHg) in peat soils. We used data from a natural sulfate deposition gradient running 300 km across southern Sweden to test the hypothesis posed by results from an experimental field study in northern Sweden: that increased loading of SO_4^{2-} both increases net MeHg formation and redistributes methylmercury (MeHg) from the peat soil to its porewater. Sulfur concentrations in peat soils correlated positively with MeHg concentrations in peat porewater, along the deposition gradient similar to the response to added SO_4^{2-} in the experimental field study. The combined results from the experimental field study and deposition gradient accentuate the multiple, distinct and interacting roles of SO_4^{2-} deposition in the formation and redistribution of MeHg in the environment.

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1. Introduction

Mercury (Hg) accumulates as methylmercury (MeHg) in aquatic biota to levels that are of concern for wildlife or humans health (Scheuhammer et al., 2007). Decreasing the use and anthropogenic emission of Hg has been the main action to reduce contamination in aquatic and marine ecosystems globally (Selin, 2014; UNEP, 2013) and nationally (EPA, 2011). The bioaccumulation of Hg also depends on the net transformation of inorganic Hg (I-Hg) to methyl-Hg (MeHg) and transportation of MeHg to environments prone to bioaccumulation (Harris et al., 2007; Hsu-Kim et al., 2018).

Deposition of Hg to soil surfaces is an important input and control on the Hg pool that is potentially available for Hg methylation (Driscoll et al., 2007; Driscoll et al., 2013; Hrenchuk et al.,

2012). Experimental additions of I-Hg to mesocosms (Orihel et al., 2007) as well as to whole catchments (Harris et al., 2007) have led to conclusions that decreases of I-Hg deposition effectively decrease accumulation of Hg in aquatic food webs. The addition of S from anthropogenic sources could, however, increase the vulnerability of freshwater ecosystems to Hg bioaccumulation by influencing the formation of MeHg in peatlands and its mobilization.

Formation and mobilization of MeHg from terrestrial catchments is a major contributor to elevated concentrations of Hg present in high-latitude aquatic biota (Morel et al., 1998) with peatlands identified as key landscape elements for net MeHg formation and export to downstream aquatic ecosystems (Dittman and Driscoll, 2009; Kolka et al., 2011; Mitchell et al., 2009; Morrison and Steffen, 2016; Tjerngren et al., 2012).

The importance of sulfur (S) availability for Hg methylation processes has indirectly been demonstrated in peatlands, by observed positive relationships between rates of S deposition and MeHg concentrations (Branfireun et al., 1999; Coleman Wasik et al., 2012; Jeremiason et al., 2006; Johnson et al., 2016; Mitchell et al., 2009; Orem et al., 2011; Åkerblom et al., 2013). There are several

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ways by which S can influence the net formation of MeHg. Sulfate (SO_4^{2-}) acts as an important electron acceptor for anaerobic bacteria known to methylate Hg (Compeau and Bartha, 1985; Muyzer and Stams, 2008). Redox conditions and fluctuation in groundwater level have been shown to be important to predict MeHg in porewaters (Bergman et al., 2012; Du et al., 2019). Sulfur also influences the availability of I–Hg for methylating bacteria and alter the distribution of Hg between the liquid and solid phases (Benoit et al., 1999). Both reduced organic and inorganic S take part in the formation of thermodynamically stable complexes with I–Hg in mineral phases (Jonsson et al., 2014; Jonsson et al., 2012) as well as in porewaters (Benoit et al., 1999; Drott et al., 2007). The multiple roles of S in the control of Hg methylation even makes S availability more important than the total concentration of I–Hg for net MeHg production in aquatic ecosystems (Chen et al., 2012; Kelly et al., 1995). Notably, at the long-term S-manipulation field experiment at Degerö Stormyr enhancement of S deposition resulted in increased MeHg concentrations while the pool of inorganic Hg (I–Hg) in peat soil at the same time decreased (Åkerblom et al., 2013).

The role of S for net methylation of Hg in peatlands has been demonstrated at other experimental sites as well, such as at the Marcell Experimental Forest (Minnesota, USA) where the experimentally enhanced supply of SO_4^{2-} to the mire surface induced an increase in stream MeHg concentration and flux (Jeremiason et al., 2006). The point of conducting such experimental manipulations has been to identify and predict factors controlling net methylation of Hg at the landscape scale. This emphasizes the need to actually test experimental scale findings at the landscape scale under ambient conditions to further elucidate the importance of S influence on the Hg cycle in high-latitude ecosystems. A novel study by Wang et al. (2020) show that higher peat soil MeHg concentrations is found in younger (100–500 yrs) and more mesotrophic peatlands compared to older (2500–3200 yrs) peatlands. Other existing landscape scale studies (e.g. Drevnick et al. (2007); Orem et al. (2011)) are few and often lack information on soils and soil waters that can test hypotheses about biogeochemical mechanisms.

In this study we combined peat soil and peat porewater data from a gradient of atmospheric S deposition along a 300 km, east-west transect crossing southern Sweden with results from a long-term field experiment with enhanced S deposition in northern Sweden (Fig. 1) (Bergman et al., 2012; Branfireun et al., 2001; Osterwalder et al., 2017; Åkerblom et al., 2013). We used the data to analyze the role of S for: i) net Hg methylation, ii) solubility of I–Hg, and iii) solubility of MeHg. Along the gradient, historical deposition rates of Hg and S follows a pronounced gradient from higher peat S values in the west to lower in the east. (Harmens and Norris, 2008; Lövblad et al., 1995; Åkerblom et al., 2008). We hypothesized that the content of S in peat soils: i) enhances the formation of MeHg in peat, and ii) enhances the concentration of MeHg in the peat porewater by altering the distribution of I–Hg and MeHg between solid and liquid phases. Thus, this study aims to fill the knowledge gap between the effects of S-deposition in field experiments and effects of ambient S deposition operating at the landscape scale on peat soil and porewater MeHg.

2. Material and methods

2.1. Field sites

2.1.1. Degerö Stormyr

The field site for the long term experiment was Degerö Stormyr (64°09'N, 20°22'E, altitude 270 m a.s.l) within the Kulbäcksliden Research Park of the Vindeln Experimental Forests, SLU, 70 km from

the coast of the Gulf of Bothnia, Sweden (Fig. 1). The ongoing field experiment was established in 1995 (Granberg et al., 2001) as a fully factorial design (Fisher, 1926) with three experimental factors (S and N deposition and greenhouse (GH) treatments) (Fig. 1). For details on vegetation, climate regime at the site, experimental design and effects therefrom see e.g. Granberg et al. (2001), Eriksson et al. (2010a, 2010b), and Wiedermann et al. (2007). The effects from S deposition on Hg turnover were seen with a doubling in the net Hg methylation and a 20% increase in MeHg concentration in the peat compared to control plots (Åkerblom et al., 2013). A combination of enhanced S deposition and GH treatment decreased both the net Hg methylation rate constant and MeHg content relative to the sites with enhanced S deposition without GH treatment. The concentration of Hg in the peat have also declined in response to experimental addition of S.

2.1.2. South Sweden sulfur deposition gradient

To cover a gradient in S concentrations across southern Sweden, mires were selected along an east-west transect that follows an gradient in atmospheric deposition of pollutants (Fig. 1, Tables S–1). During the 1980s, when anthropogenic S deposition peaked, the annual deposition ranged from over 15 kg S ha⁻¹ yr⁻¹ on the Swedish west coast to 5 kg S ha⁻¹ yr⁻¹ on the eastern end of the transect (Lövblad et al., 1995). A similar geographic gradient in Hg deposition is also reflected in moss surveys (Harmens et al., 2008). The mires were classified as ombrogenic mires and oligotrophic to mesotrophic minerogenic mires. The altitude of the mires varied between 148 and 275 m.a.s.l. Vegetation was dominated by Sphagnum mosses, cotton grass (*Eriophorum vaginatum*), heather (*Calluna vulgaris*), purple moor grass (*Molinia caerulea*), common hair moss (*Polytrichum commune*) with some smaller abundances of pine (*Pinus sylvestris*), birch (*Betula* sp.) and bog rosemary (*Andromeda polifolia*) (Tables S–1).

3. Field sampling and sample preparation

3.1. Peat soil

Data on peat soil chemistry from Degerö Stormyr plots were used from samples taken in September 2008 and previously presented by Åkerblom et al. (2013). Peat soils samples were taken in duplicates at 11–19 and 19–27 cm below the mire surface. Along the deposition transect peat soil cores were taken 5–30 cm below the mire surface between May 15 and June 12 in 2003. In the deposition transect three replicate surface peat cores were taken within each mire. Peat cores were frozen within two days and kept frozen until further preparation. Samples were taken to the laboratory for further analysis of total S, total Hg and MeHg concentrations. At the laboratory the peat soil samples to be analysed for total Hg and S concentration were dried (40 °C for 48 h), cooled and stored in a desiccator and then stored until further analysis (Eriksson et al., 2010b). Concentrations were reported per dry mass of peat, after correction for the water content in the samples.

3.2. Porewater

Water samples were extracted from the peat porewater with a 70 cm long, custom-made, Teflon sampler (Branfireun et al., 2001). Sampling of porewater were done in the same spots as for the peat soil samples taken in 2008 (Åkerblom et al., 2013). The Teflon sampler was connected to sample bottles by Teflon tubing (Length = 0.75 m; Ø = ¼ inch) through Teflon connectors. The sample collector was Durham glass (1 L) along the deposition transect and a 250 mL high density polyethylene (HDPE) bottle at

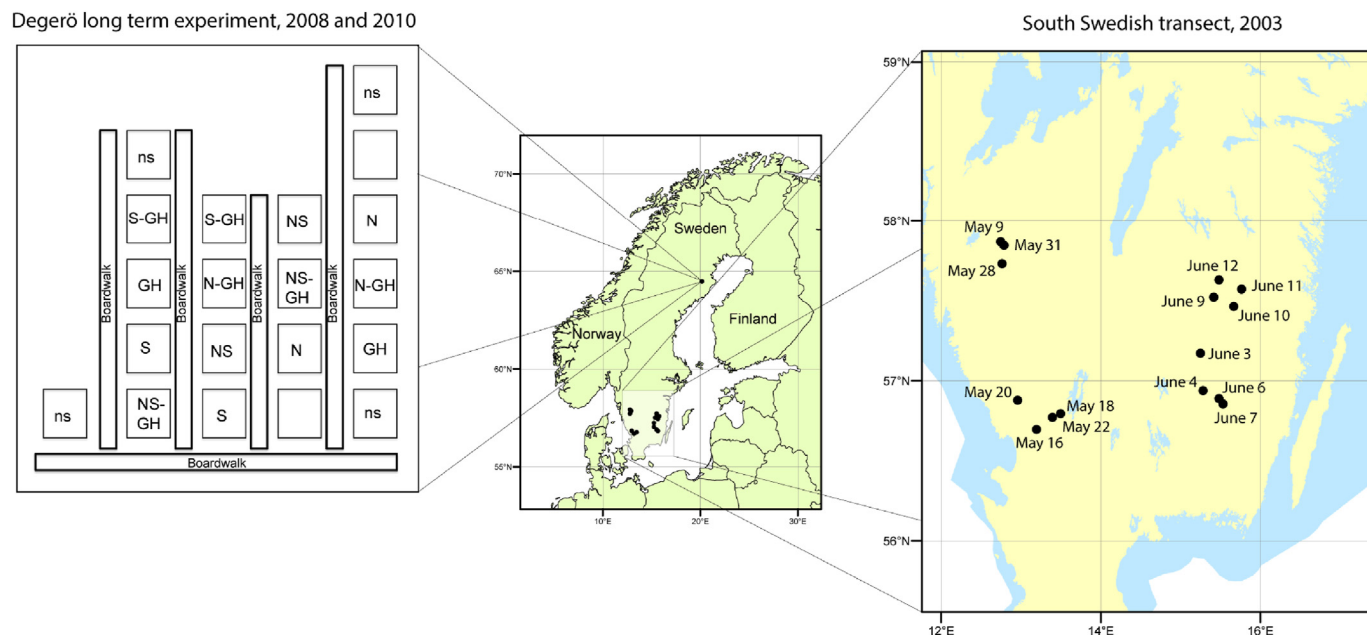


Fig. 1. Mire locations along the south Swedish S deposition transect (right) and the long-term experiment at Degerö Stormyr plots in northern Sweden (left). Peat porewater and soil sampling dates in southern Sweden are indicated for each site. The different experimental treatments (2×2 m plots) at Degerö Stormyr plots are indicated as follows: greenhouse treatment (GH); $30 \text{ kg N ha}^{-1} \text{ y}^{-1}$ (N); $20 \text{ kg S ha}^{-1} \text{ y}^{-1}$ (S); and mid-point plots with nitrogen ($15 \text{ kg N ha}^{-1} \text{ y}^{-1}$) and sulfur ($10 \text{ kg S ha}^{-1} \text{ y}^{-1}$) (ns). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Degerö Stormyr plots. Along the transect soil water subsamples (50–100 mL) were taken from spots ($n = 30$) evenly distributed over each mire at a depth 10–20 cm below the surface. Porewater composite samples were filtered ($0.45 \mu\text{m}$) and samples for Hg analysis were transferred to Teflon bottles (250 mL).

Along the deposition transect porewater was collected and analysed for MeHg and DOC. At Degerö Stormyr plots the collected porewater was analysed for total Hg, MeHg, DOC and pH. Prior to each sampling occasion, all sampling equipment were acid washed with HNO_3 (10% pro analysis in millipore water) overnight and rinsed with Millipore water.

Along the deposition transect porewater samples were collected parallel to peat soil sampling. At Degerö Stormyr plots porewater was collected during 4 sampling occasions in 2008 (June 18, July 8, August 11 and September 7) and 3 occasions in 2010 (July 8 and September 15) (Tables S–2). WTL was estimated at 30 positions close to the site of porewater sampling at each mire in the deposition transect. At Degerö Stormyr plots WTL was measured at 5 positions within each treatment plot in connection with the porewater sampling. Porewater samples were then taken at a depth 10–20 cm below the GWL.

At Degerö Stormyr plots tubes and sample bottles were flushed with N_2 to create anoxic conditions in the sampling device. The porewater was thereafter pumped into the transfer bottle by collecting approximately 50 mL of water from each of 5 evenly distributed spots within each experimental plot to create a pooled sample of 250 mL. The samples were stored in the laboratory at 4°C until analysis within 24 h. All handling of samples from Degerö Stormyr plots was made in a glovebox with an atmosphere of hydrogen/nitrogen mixture (95% N_2 , 5% H_2). The sampled porewaters were filtered ($0.45 \mu\text{m}$), subsampled and stored in bottles separately for analysis of total Hg (Hg) (100 mL HDPE), MeHg (250 mL HDPE), DOC (25 mL Falcon tube), sulfides (4 mL cryovials) and pH (50 mL HDPE). All samples were preserved directly after filtration in the glove box.

4. Chemical analysis

4.1. Peat soil S, Hg and MeHg

Peat soil Hg concentrations in dried peat samples was analysed using a Leco AMA-254 according to EPA method 7473. The concentrations of S was analysed on a NCS 2500 elemental analyzer (CE-Instruments, Italy) through combustion at 1350°C in a pure oxygen atmosphere with the S-oxide content determined by infrared absorption. Peat soil MeHg from the deposition transect was determined by GC-ICP-MS using isotope dilution analysis directly after arrival at laboratory (Lambertsson et al., 2001).

4.2. Porewater total Hg and MeHg

Porewater total Hg concentrations from Degerö Stormyr plots were analysed by the Department of Applied Environmental Science at Stockholm University (Stockholm, Sweden). Nitric acid (65%) was added to filtered samples in order to attain a sample concentration of 0.5% HNO_3 for preservation. Samples were stored (8°C in dark) at SLU (Umeå) before transport and analysis of the samples. Determination of Hg in porewater was done by cold vapour atomic fluorescence spectroscopy (PSA Millennium Mercury Analyzer) after sample oxidation by BrCl (US Environmental Protection Agency standard method 1631). The detection limit was 0.3 ng L^{-1} and the analytical precision was $\pm 3\%$ relative to the standard deviation.

Analysis of MeHg in porewaters from the deposition transect were done according to methods described by Lee et al. (1994). Porewater samples from Degerö Stormyr plots used for MeHg analysis were spiked with an isotope enriched (97.7%) Me^{200}Hg -standard within a day after sampling. Ethylation and derivatization of MeHg in the samples and subsequent determination of MeHg concentrations on GC-ICP-MS were done according to Lambertsson and Björn (2004). The limit of detection, calculated as 3 standard deviation (SD) of blanks, was 0.035 ng L^{-1} and the recovery of

added spikes were equal to incipient analyte.

During the 2008 field sampling at Degerö Stormyr plots blank samples were used to account for potential contamination of Hg or MeHg. The concentrations of both Hg and MeHg were below the detection limit.

4.3. Determination of pH, DOC and sulfur species in Degerö Stormyr porewater

pH of filtered samples were determined in the glove-box using a pH-electrode (InLab®412 coupled to an MA120 ion-meter). Calibration (pH 4 and 7) of the electrode was done during the sample analysis at the beginning and in the middle of the sample sequence. The concentrations of [DOC] was determined (Shimadzu TOC 5000A Analyzer) within a week on samples stored at 8 °C. Within 24 h after filtration the total concentrations of aqueous sulfide (S^{II} , = $[HS^-] + [H_2S]$) was analysed spectrophotometrically (at 670 nm), with correction for blanks following the procedure of Fonselius et al. (1976).

4.4. Mobilization of I-Hg and MeHg

Concentrations of I-Hg in peat soil and porewater samples were estimated by subtraction of MeHg from the total Hg concentration. Mercury solubility was determined as the solid-solution partition coefficient for I-Hg and MeHg ($\log K_d$ I-Hg and $\log K_d$ MeHg, respectively, ($L\ kg^{-1}$)) using Eq. (1) where [peat I-Hg] is the concentration of I-Hg in the peat and [porewater Hg-I] the concentration of I-Hg in the porewater. Data on peat I-Hg and peat MeHg were taken from Åkerblom et al. (2013) and data on porewater I-Hg and porewater MeHg were generated in this study.

$$\log K_d \text{ I-Hg} = \log \left(\frac{[\text{Peat I-Hg}]}{[\text{pore water I-Hg}]} \right) \quad (1)$$

and MeHg:

$$\log K_d \text{ MeHg} = \log \left(\frac{[\text{Peat MeHg}]}{[\text{pore water MeHg}]} \right) \quad (2)$$

We refer to decreased $\log K_d$ as an increase in solubility (redistribution of I-Hg or MeHg from the solid/absorbed to the aqueous phase). Estimations of $\log K_d$ were calculated based on peat I-Hg and MeHg concentrations at a depth close to the groundwater level where porewater were sampled.

4.5. Data handling and statistics

Missing values in the dataset from porewater sampling campaigns at Degerö Stormyr plots were replaced by estimates from imputations (Palarea-Albaladejo and Martin-Fernandez, 2013). The imputation procedure was based on mean differences between sampling campaigns and treatment groups (individual S, N and GH treatments and their 2 and 3-way interactions). During the imputation we assumed equal variance between duplicate treatments in the factorial design. To validate the accuracy in sampling procedures and analytical data were duplicate samples from an experimental plot taken twice during each sampling campaign in 2008. Correlation coefficients and paired *t*-test between duplicate samples were used for the validation procedure. At Degerö Stormyr plots duplicate samples ($n = 5$) with $[S^{II}] > 50$ nM showed a strong correlation ($r = 0.97$) and a comparison (2-sided paired *t*-test) showed no significant difference (t -ratio = 1.11, $p = 0.33$) between the analysed concentrations in duplicate samples (data not shown). The limit of detection for H_2S was thus set to 50 nM. Samples analysed for $[S^{II}] < 50$ nM ($n = 82$) were replaced by randomly

generated data with values between 0 and 50 nM that gave a data set that followed a normal distribution ($\mu = 25$, $\sigma = 11$) (Davison and Hinkly, 2006).

Statistical calculations were performed using JMP software version 13.0.0 (SAS Institute Inc., USA). To test for differences in variables between the deposition transect and Degerö Stormyr plots analysis of variance (ANOVA) was applied. Treatment effects on porewater variables were tested using repeated measures ANOVA (RM-ANOVA) with each sampling occasion as an individual observation. Sphericity was tested for all groups using Mauchly's sphericity test (Mauchly, 1940) and if violated degrees of freedom were corrected using the Greenhouse-Geisser correction term (Greenhouse and Geisser, 1959).

Dependent variables in peat soil (I-Hg and MeHg concentrations and %MeHg) and porewater (MeHg concentrations) from both deposition transect and Degerö Stormyr plots were tested against independent peat soil variables (S, I-Hg and MeHg concentrations) using linear regression models. Covariation between peat soil S and I-Hg concentrations interfere with the description of causality from these independent variables for MeHg concentration. To separate the effects from peat soil S and I-Hg on MeHg concentrations, residuals were used as a dependent variable from regression models between peat soil S and MeHg concentrations as well as between peat soil I-Hg and MeHg concentrations. These residuals were then tested against peat soil I-Hg and S concentrations, respectively. To further describe the causal relationship of S, I-Hg and solubility of MeHg ($\log K_d$ MeHg) on MeHg concentration in peat porewater and peat soil multiple linear regression (MLR) was applied. To find variables that contributed to the best MLR model prediction a forward selection technique with the Bayes information criteria (e.g. Schwarz (1978)) was applied. Log-transformed variables were used for regression analysis and ANOVA to fulfill the requirements of normal distributions according to Shapiro Wilk (Shapiro and Wilk, 1965).

5. Results

5.1. Peat soil and porewater chemistry

Porewater samples from the Degerö Stormyr field experiment ($n = 120$) and the deposition transect ($n = 18$) were available for statistical analysis (Table 1 and Tables S–2). The concentrations of MeHg in the porewater are consistent with those observed at the Degerö experimental field experiment in 1998 (0.17–3.16 $ng\ L^{-1}$) (Branfiren et al., 2001) and 1999 (0.24–3.12 $ng\ L^{-1}$) (Bergman et al., 2012). Along the transect, peat soil concentrations of S, I-Hg and MeHg varied between 0.29%–1.03% DW, 45–155 $ng\ g^{-1}$ and 4.5–25 $ng\ g^{-1}$, respectively (Tables S–3). At the Degerö Stormyr field experiment, the respective ranges of S, I-Hg and MeHg concentrations were between 0.10 and 0.25%, 22–65 $ng\ g^{-1}$, and 0.4–7.0 $ng\ g^{-1}$ (Åkerblom et al., 2013). The $\log K_d$ MeHg range was 3.4–4.7 $L\ kg^{-1}$ along the transect and 2.4–4.7 $L\ kg^{-1}$ at the Degerö Stormyr field experiment. The $\log K_d$ I-Hg was only available at the Degerö Stormyr field experiment, where it varied between 3.4 and 4.8 $L\ kg^{-1}$ (Tables S–2).

Peat soil concentrations of S, I-Hg and MeHg were significantly higher along the deposition transect in southern Sweden (ANOVA with site as factor) as compared to the control plots with ambient S deposition at the Degerö Stormyr field experiment in northern Sweden (F-ratio (degrees of freedom (df)), *p*-value: S = 66 (21), $p < 0.0001$; I-Hg = 10 (21), $p < 0.0045$; MeHg = 35 (21), $p < 0.0001$) (Table 1). Concentrations of MeHg in peat porewater along the transect were also significantly higher relative to the control plots in the Degerö Stormyr field experiment (52 (21), $p < 0.0001$). The

Table 1

Peat chemistry in soil solids and porewater from the experimental site in northern Sweden (Degerö Stormyr) and along the south Swedish deposition transect (Fig. 1).

		Peat chemistry statistics (mean ± SE)						
		deposition transect		Northern Sweden experimental site, Degerö Stormyr: main effects ^a			GH	
			kg S ha ⁻¹ y ⁻¹		kg N ha ⁻¹ y ⁻¹			
Peat variables	Response variables	(n = 16)	3 (n = 8)	20 (n = 8)	2 (n = 8)	30 (n = 8)	No GH (n = 8)	With GH (n = 8)
Peat soil solids ^b	I-Hg (ng g ⁻¹)	86 ± 10	51 ± 3.8	43 ± 4.1	42 ± 3.7	52 ± 3.9	47 ± 2.8	43 ± 2.3
	MeHg (ng g ⁻¹)	11.0 ± 1.45	2.1 ± 0.4	3.7 ± 0.6	1.7 ± 0.7	2.8 ± 0.5	2.5 ± 0.4	1.6 ± 0.3
	S (%)	0.51 ± 0.05	0.15 ± 0.01	0.20 ± 0.01	0.16 ± 0.01	0.19 ± 0.01	0.18 ± 0.01	0.17 ± 0.01
Peat soil porewater (n = 120)	I-Hg (ng L ⁻¹)		2.8 ± 0.2	3.2 ± 0.3	2.7 ± 0.2	3.3 ± 0.2	3.1 ± 0.2	2.7 ± 0.2
	MeHg (ng L ⁻¹)	0.95 ± 0.16	0.19 ± 0.02	1.19 ± 0.14	0.66 ± 0.11	0.73 ± 0.13	0.77 ± 0.10	0.50 ± 0.07
	pH		3.89 ± 0.04	4.07 ± 0.04	3.94 ± 0.04	4.03 ± 0.04	3.99 ± 0.03	3.94 ± 0.04
	DOC (mg L ⁻¹)	36.7 ± 11.6	39.1 ± 1.3	43.3 ± 1.4	39.9 ± 1.2	42.5 ± 1.5	43.0 ± 1.2	39.4 ± 1.2
	Hg/DOC		0.08 ± 0.01	0.11 ± 0.01	0.09 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.09 ± 0.01
	MeHg/DOC	0.04 ± 0.01	0.01 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
	S ^{II} (nM)		123 ± 62	313 ± 95	208 ± 91	228 ± 71	218 ± 63	156 ± 68
	log K _d I-Hg (L kg ⁻¹)		4.25 ± 0.03	4.04 ± 0.03	4.13 ± 0.04	4.16 ± 0.03	4.14 ± 0.03	4.16 ± 0.03
	log K _d MeHg (L kg ⁻¹)	4.05 ± 0.06	4.04 ± 0.05	3.46 ± 0.07	3.66 ± 0.07	3.84 ± 0.07	3.71 ± 0.06	3.74 ± 0.06
	Peat chemistry statistics (mean ± SE)		Northern Sweden experimental site, Degerö Stormyr: 2-way interaction effects ^a					
	Response variables	S*N	S*GH		N*GH			
		kg S and N ha ⁻¹ y ⁻¹	kg S ha ⁻¹ y ⁻¹		kg N ha ⁻¹ y ⁻¹			
		3 and 2 (n = 12)	20 and 30 (n = 4)	3 no GH (n = 16)	20 with GH (n = 4)	2 no GH (n = 16)	30 with GH (n = 4)	
Peat soil solids (5–30 cm) ^b	I-Hg (ng g ⁻¹)	46 ± 3.3	50 ± 6.3	47 ± 3.1	41 ± 3.1	45 ± 3.1	47 ± 4.6	
	MeHg (ng g ⁻¹)	2.1 ± 0.5	2.7 ± 1.1	2.4 ± 0.5	1.2 ± 0.2	2.1 ± 0.5	2.1 ± 0.6	
	S (%)	0.16 ± 0.01	0.22 ± 0.02	0.18 ± 0.01	0.17 ± 0.02	0.17 ± 0.01	0.19 ± 0.01	
Peat soil porewater (n = 120)	I-Hg (ng L ⁻¹)	2.9 ± 0.2	3.3 ± 0.3	3.1 ± 0.2	2.6 ± 0.2	2.9 ± 0.2	3.1 ± 0.3	
	MeHg (ng L ⁻¹)	0.50 ± 0.08	1.26 ± 0.21	0.63 ± 0.08	0.81 ± 0.12	0.68 ± 0.08	0.59 ± 0.12	
	pH	3.93 ± 0.03	4.12 ± 0.06	3.97 ± 0.03	3.98 ± 0.06	3.97 ± 0.03	3.97 ± 0.05	
	DOC (mg L ⁻¹)	39.5 ± 1.0	46.4 ± 2.3	42.0 ± 1.0	39.8 ± 1.5	41.7 ± 1.0	41.2 ± 1.9	
	Hg/DOC	0.09 ± 0.01	0.10 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	
	MeHg/DOC	0.01 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	
	S ^{II} (nM)	161 ± 61	391 ± 134	211 ± 56	124 ± 61	211 ± 56	123 ± 61	
	log K _d I-Hg (L kg ⁻¹)	4.17 ± 0.03	4.08 ± 0.03	4.16 ± 0.03	4.08 ± 0.04	4.15 ± 0.03	4.14 ± 0.04	
	log K _d MeHg (L kg ⁻¹)	3.82 ± 0.06	3.53 ± 0.09	3.77 ± 0.05	3.54 ± 0.09	3.70 ± 0.05	3.81 ± 0.10	

^a Treatment effects for SO₄²⁻ (S) and NH₄NO₃ (N) deposition and GH treatments and 2-way interactions. Details of the experimental setup are presented in Granberg et al. (2001).^b Peat soil data from the Degerö Stormyr experimental site is taken from Åkerblom et al. (2013).

MeHg partitioning coefficient ($\log K_d \text{ MeHg}$), however, did not differ between peat soils along the transect and control plots at Degerö Stormyr (0.001 (21)/0.98).

5.2. Regression analysis between peat soil and porewater variables

Sulfur concentrations in peat soils in the combined dataset of the deposition transect and the Degerö Stormyr field experiment

(control and treatment plots) displayed significant, positive relationships with the concentration of I-Hg in peat soil (F-ratio (df)/p-value: 26 (33)/ $p < 0.0001$, Fig. 2A) as well as with MeHg concentrations in peat soil (70 (33)/ $p < 0.0001$, Fig. 2C) and in the porewater (21 (33)/ $p < 0.0001$, Fig. 2D). For the same dataset, concentrations of S also showed positive relationships with the % MeHg in peat soil (21 (33)/ $p < 0.0001$, Fig. 2B). A separate analysis of the two datasets revealed a significant relationship between peat

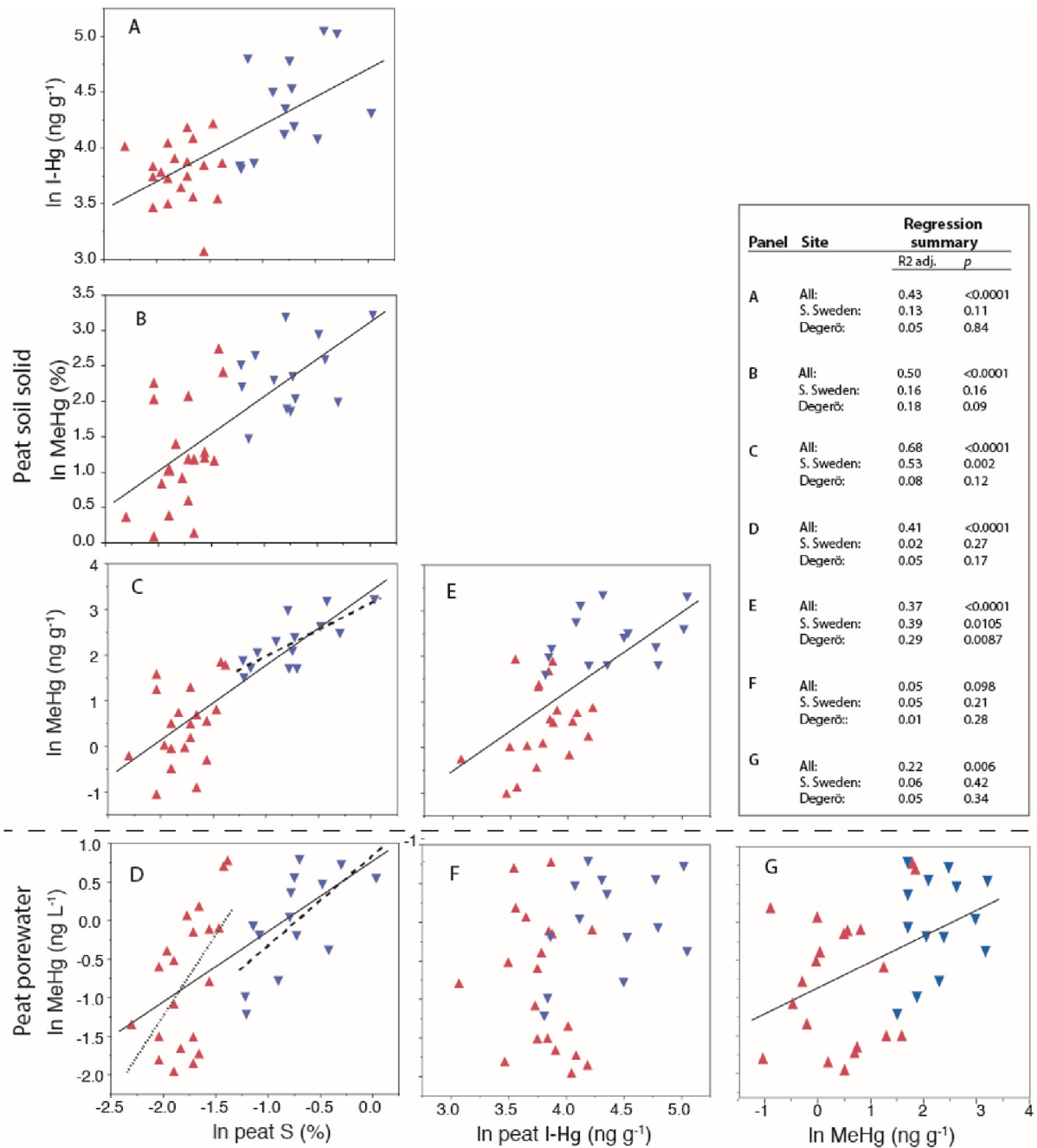


Fig. 2. The left panels displays: A) concentration of inorganic Hg (I-Hg) in the solid peat soil matrix, B) MeHg in the solid peat as a fraction of total Hg (MeHg (%)), C) MeHg in peat soil and D) MeHg in porewater as a function of peat soil S content. The middle panels displays: E) MeHg in peat soil and F) MeHg in porewater as a function of inorganic mercury in the peat soil. The right panel displays MeHg in peat porewater as a function of MeHg in peat soil solid. Data from the South Swedish deposition transect are displayed (blue downward triangles) and data from all Degerö Stormyr plots (control as well as treated plots) (red upward triangles) (Fig. 1). Significant linear regressions for southern (dashed line) and northern (dot-dash line) Swedish data when treated separately are also shown. Regression lines are only shown for $p < 0.05$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

soil S and porewater MeHg concentrations along the transect (9.2 (13)/ $p = 0.0105$) as well as at the Degerö Stormyr field experiment (8.7 (19)/ $p = 0.0087$). Also, peat soil S concentration across the transect demonstrated significant positive relationships with peat soil MeHg concentrations (16 (13)/ $p = 0.0020$), but no such relationship was found at the Degerö Stormyr field experiment (2.7 (19)/ $p = 0.12$, Fig. 2C).

In the combined dataset, concentrations of peat I-Hg correlated positively with peat MeHg (24 (33)/ $p < 0.0001$, Fig. 2E) but not with porewater MeHg (2.9 (33)/ $p =$ not significant (ns), Fig. 2F). Despite a significant correlation between peat soil S content and I-Hg when combining data from the two sets, we could not find any significance when analysing the two sets separately.

Residuals from simple linear regression models that predicted peat MeHg from peat I-Hg concentrations (Fig. 2E) were used as dependent variables and correlated positively with peat S concentrations (11.8 (33)/ $p = 0.0016$, Fig. 3 left panel). Residuals from models that predicted peat MeHg from peat S concentrations (Fig. 2C) did, however, not correlate with I-Hg concentrations (1.0 (33)/ $p =$ ns, Fig. 3 right panel).

The step-wise selection of independent variables for MLR models using porewater MeHg concentrations as the dependent variable resulted in a final model with peat soil S concentration, having a positive coefficient, and $\log K_d$ MeHg, having a negative regression coefficient (adj. $R^2 = 0.73$, $n = 34$) (F-ratio (df) = 9.7 (33), $p = 0.0005$). Notably, the concentration of peat soil I-Hg was not selected in the MLR. A MLR model using peat soil MeHg as the dependent variable was obtained with concentrations of S and I-Hg in peat soil as independent variables with positive coefficients ($R^2 = 0.85$, $n = 34$, F-ratio(df) = 95.1 (33), $p < 0.0001$).

5.3. S deposition effects on I-Hg and MeHg

Experimentally enhanced S deposition at Degerö Stormyr increased peat porewater concentrations of I-Hg, MeHg, S^{II} and increase in pH and the ratios of Hg/DOC and MeHg/DOC relative to control plots (Table 1 and Tables S-5). A combination of enhanced S deposition and green house (GH) treatment decreased the peat

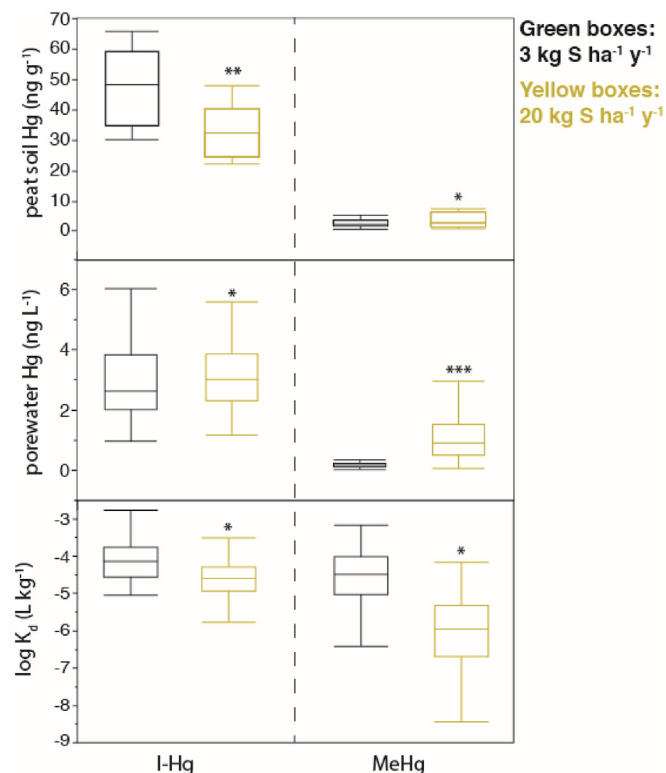


Fig. 4. Concentrations of inorganic Hg (I-Hg) and MeHg respectively in solid phase (top panel) and aqueous phase (middle panel) respectively in response to S deposition rates 3 (ambient) and 20 kg S ha⁻¹ yr⁻¹ at the Degerö Stormyr experimental site. The solid-solution partition coefficients ($\log K_d$ (L kg⁻¹)) are shown in the bottom panel. Box plots (Bars = 10 and 90 percentile; box = 25 and 75 percentile; horizontal line = median). Data for inorganic Hg and MeHg in peat soil solids are from Åkerblom et al., (2013) (Åkerblom et al., 2013). Differences in peat soil I-Hg, MeHg, porewater I-Hg, MeHg, $\log K_d$ I-Hg, $\log K_d$ MeHg, in response to S application rates of 3 and 20 kg S ha⁻¹ yr⁻¹ respectively are all significant (Åkerblom et al., 2013 and Table 2). Significant levels are indicated above boxes with * ($p > 0.05$), ** ($p > 0.01$), and *** ($p > 0.0001$).

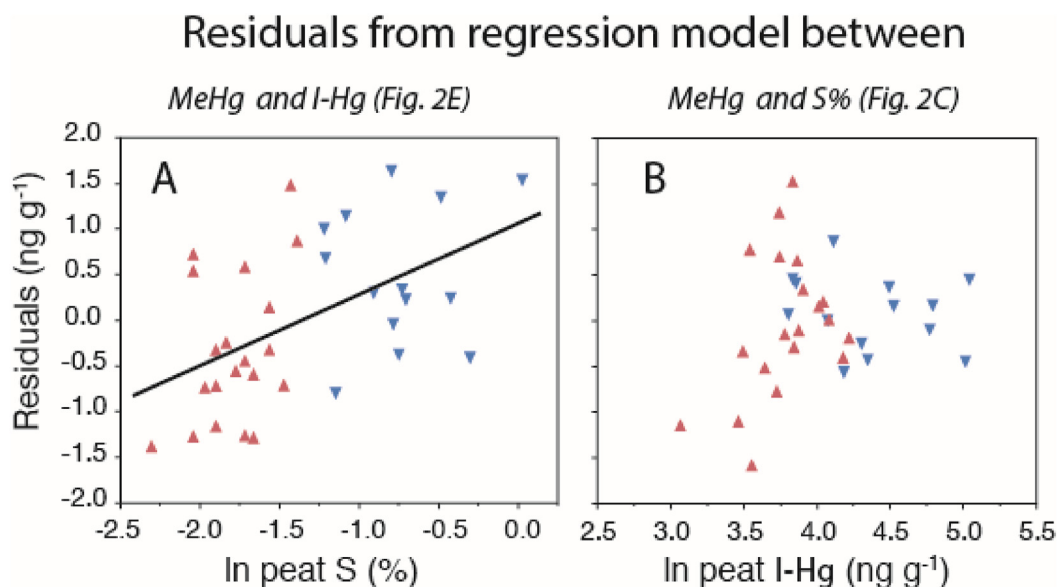


Fig. 3. Linear regression models with the unexplained variation (residuals) in MeHg peat soil concentrations as dependent variables from regression models with I-Hg (Fig. 2E) and S (Fig. 2C) and peat soil concentrations of I-Hg (A) and S (B) as independent variables. Concentrations from the South Swedish deposition transect (blue downward triangles) and from the Degerö Stormyr field experiment (red upward triangles). Significant regression models are indicated by a solid line ($R^2 = 0.27$, $p = 0.0027$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

porewater MeHg and S^{II} concentrations as well as Hg/DOC-ratio relative to plots with only enhanced S deposition. The combination of enhanced S deposition and GH treatments also decreased the amount of MeHg in the solid phase of the peat soil (Fig. 4) (Åkerblom et al., 2013). Within the plots with enhanced S deposition the amount of peat soil I-Hg was lower ($p = 0.014$, $35 \pm 1.6 \text{ ng g}^{-1}$, $n = 4$) compared to those with ambient S deposition ($56 \pm 3.1 \text{ ng g}^{-1}$, $n = 4$, Fig. 4) (Åkerblom et al., 2013).

Sulfur concentrations in peat soils across the combined dataset of the transect and Degerö Stormyr field experiment did not display any significant relationship with $\log K_d \text{ I-Hg}$ or $\log K_d \text{ MeHg}$ (Fig S-2). However, at Degerö Stormyr the S deposition resulted in an increased solubility of both I-Hg and MeHg (decreased $\log K_d \text{ I-Hg}$ or $\log K_d \text{ MeHg}$) (Fig. 4 and Tables S-5). The increased solubility of I-Hg may be interpreted to be directly caused by S, as corroborated by a negative correlation between $\log K_d \text{ I-Hg}$ and measured porewater S^{II} concentrations within plots subject to ambient S deposition ($6.2 (7)/p = 0.048$). This was further strengthened by chemical speciation model calculations, revealing the neutral $\text{Hg}(\text{SH})_2^0$ species (which was the dominant species in porewater of I-Hg) to be positively related to across all experimental treatments at Degerö Stormyr ($7.1 (19)/p = 0.016$) (Table S1, Fig. S-2). Partitioning of MeHg ($\log K_d \text{ MeHg}$) was negatively correlated to the DOC concentration across all sites ($12 (33)/p = 0.002$), but also separately along the transect ($6.4 (13)/p = 0.026$) and at Degerö Stormyr ($4.4 (19)/p = 0.05$) (Fig. S-2).

6. Discussion

Higher concentrations of both S and I-Hg were observed in peat soils along the deposition transect in comparison to the control plots at Degerö Stormyr located in northern Sweden (Fig. 1). During the 1970s, atmospheric deposition of S exceeded $15 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ at the western end of the transect (Lövblad et al., 1995). Those levels were the culmination of several decades of increasing S deposition from anthropogenic sources. Due to subsequent reductions in S emissions to the atmosphere, the bulk S deposition across the deposition transect was lowered, and ranged from $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ on the western end to $3.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ on the eastern end in 1991/92 and even lower ($\approx 2 \text{ kg ha}^{-1} \text{ yr}^{-1}$) in northern inland of Sweden where Degerö is located (Lövblad et al., 1995). The observed concentration gradient in the peat soils of the transect sampled in this study reflect the historical atmospheric deposition rates of S where S is retained in the peat soil over several decades. The gradient in S deposition also coincides with Hg deposition gradients, with higher annual Hg deposition in south western Sweden that decreases towards the east and north of Sweden (Rühling and Tyler, 2001). This is also reflected by the higher Hg content in peat soils along the deposition transect relative to levels found in the control plots of Degerö Stormyr.

6.1. Increased net formation of MeHg

Using data from both the deposition gradient and Degerö Stormyr field experiment, positive relationships were observed between the concentration of MeHg in peat soil and the concentration of S and I-Hg, respectively (Fig. 2). The observed positive correlation between the S and MeHg in soil (Fig. 2B and C), both in the combined data set and in data of the south Swedish S deposition gradient, suggests that S deposition enhances net formation of MeHg. This observation is in line with previous experimental studies (Branfireun et al., 1999; Jeremiason et al., 2006; Johnson et al., 2016; Åkerblom et al., 2013) but such results have in this study also been combined with data derived along a S deposition

gradient.

Given comparatively low rates of atmospheric deposition of MeHg (Munthe et al., 1995), concentrations of MeHg in soils are the net effect of I-Hg methylation and MeHg demethylation processes. The former is controlled by the amount of I-Hg available for Hg methylating bacteria as well as the activity, and the composition, of the Hg-methylating bacterial community (Hsu-Kim et al., 2013). Sulfur is known to influence the activity of some types of Hg-methylating bacteria, but S can also influence the availability of I-Hg to methylating microorganisms, including those that do not use sulfur-reduction in their metabolism (Bravo et al., 2018). As the concentrations of S and I-Hg in the peat soils covary across the entire range of MeHg concentrations in the southern transect data set, it is difficult to separate the effects which S and I-Hg may have on the concentrations of MeHg. A positive relationship between the concentration of S and %MeHg in peat soil (an indicator of net MeHg formation) in the combined data set (Fig. 2B) supports the role of S in promoting net formation of MeHg. To separate the effects peat S and I-Hg on the concentrations of MeHg in peat soil, the residuals of MeHg concentrations from the bivariate regression models (Fig. 2) and the MLR models were evaluated (Table 1, Fig. 3). This demonstrated that there was not a significant influence of I-Hg, but the prolonged deposition of S being retained in peat soil had a significant influence on the formation of MeHg in the combined dataset.

Estimates of the amount S added that were retained in the peat during 14 years at Degerö Stormyr varied between 15 and 55% (Åkerblom et al., 2013). Retention of S within a mesocosm experiment using peat cores sampled across eastern Canada showed retention in peat and vegetation between 21 and 97% (Moore et al., 2005), even though large spatial variation in S cycling is expected across a peat catchment (Mandernack et al., 2000). It follows from this that the prolonged S deposition to the peat surface for decades during the epoch of industrialization has increased the amount of S retained in peat soils and thus enhanced net MeHg formation. Retained S in peat soils are available for microbial reduction and at favorable redox conditions an increase in sulfide is expected (Knorr and Blodau, 2009). While S initially may enhance bacterial methylation, subsequent formation of reduced sulfur species may also effect methylation by altering the solubility of I-Hg and increasing the availability of the porewater pool of I-Hg for Hg methylating bacteria (Drott and Skyllberg, 2007). Partitioning of I-Hg into porewater has been shown to increase in systems in which the formation of HS^- is enhanced (Miller et al., 2007), as was also the case at the Degerö Stormyr field experiment (Fig. S-2).

These mechanisms can explain why deposition of S has repeatedly been shown to correlate to enhanced MeHg production in different peat soils (Branfireun et al., 1999; Jeremiason et al., 2006; Johnson et al., 2016; Åkerblom et al., 2013). Reduction of SO_4^{2-} to S^{II} was manifested at Degerö Stormyr plots by a positive effect of enhanced S deposition on the concentration of S^{II} in porewaters. Higher dissolved sulfide concentrations also result in the formation of neutrally charged inorganic sulfide complexes ($\text{Hg}(\text{HS})_2^0(\text{aq})$), as shown for the porewater at the Degerö Stormyr field experiment (Fig. S-1B), a form of I-Hg presumed bioavailable for Hg methylating microbes (Benoit et al., 1999; Drott et al., 2007). It should be noted that enhanced concentrations of sulfides also can inhibit the availability of I-Hg by precipitation of $\text{HgS}(\text{s})$. However, an increased porewater concentrations of I-Hg available for Hg methylating bacteria have been verified in Hg contaminated paddy soils (Li et al., 2019) and therefore support the mechanism of an increased net methylation in the experimental plots with increased S deposition.

In our study however, peat soil S concentration did not show any

correlation to the solubility of I-Hg ($\log K_D \text{ I-Hg}$) at the Degerö Stormyr field experiment. While sulfides are important ligands for the complexation of Hg^{II} , they also function as an important intermediate for the formation of organic thiols and polysulfides, as demonstrated in karst aquifers in southern Germany (Einsiedl et al., 2007). The formation of reduced organic S species was also demonstrated in estuarine sediments where humic substances can be a large sink for reduced S that is formed during SO_4^{2-} reduction (Brüchert and Pratt, 1996). The role of S for the solubility of I-Hg was corroborated by a linear relationship between those two parameters in sediments of estuaries in Long Island Sound, USA ($r^2 = 0.70$, $p < 0.0001$) (Schartup et al., 2014). Deposition of S may thus both enhance the activity of Hg methylating sulfate reducing bacteria, as well as increase the formation of reduced organic S species, which increases the potential for Hg^{II} uptake by Hg-methylating bacteria in peatlands (Skylberg, 2008) even if the $\log K_D \text{ I-Hg}$ does not change.

6.2. Hg and MeHg solubility

The solubility of I-Hg and MeHg were both enhanced by the experimental addition of S deposition. This can be explained by an increased formation of inorganic and organic reduced S ligands. The combined effects of increased net MeHg formation and solubility led to the high levels of MeHg in peat porewater. Adsorption kinetic studies have shown that the partitioning (K_d) of MeHg newly added to soil stabilizes within hours to a day (Hintelmann and Harris, 2004). Higher concentrations of MeHg in the porewater would therefore be expected in systems with higher concentrations of I-Hg available for Hg methylating bacteria and in systems where net methylation is enhanced. This is in line with our observed relationship between concentrations of S in peat and concentrations of MeHg in porewater and soil in the combined data set as well as along the transect (Fig. 2). We also observed a significant relationship between concentrations of S in peat and concentrations of MeHg in porewater at Degerö Stormyr even though there was not a significant relationship between peat soil concentrations of S and MeHg. A relationship was also observed in the combined dataset between the concentrations of MeHg in soil and porewater, supporting the concept that concentrations of MeHg in the solid phase control concentrations of MeHg in the porewater.

Higher concentrations of MeHg in porewater would also be expected in systems with higher MeHg solubility which is controlled by the chemical composition of the porewater and the solid material. The $\log K_d \text{ (L kg}^{-1}\text{)}$ for MeHg decreased significantly with S addition at Degerö Stormyr, suggesting S also has an effect on MeHg solubility (Fig. 4). No difference in $K_d \text{ MeHg}$ was however observed between the field experimental control treatments and the southern transect and no relationship was observed between the %S and $\log K_d \text{ MeHg}$ in any of the tested datasets. This suggests that other factors are of larger importance across landscapes or in experimental systems where also other factors are introduced (e.g. green house treatment).

Enhanced S deposition at the Degerö Stormyr field experiment led to an increase in the Hg/DOC-ratio and could partly explain the observed enhanced solubility of I-Hg (decreased $\log K_D \text{ I-Hg}$) (Tables S–5, Fig. 4) and the decrease of I-Hg concentrations in the peat soil. A strong association between organic matter and I-Hg is expected and factors that enhance the Hg/DOC-ratio would also be expected to influence the concentration of Hg in the solid phase (Åkerblom et al., 2008). An increase in Hg/DOC-ratio was one component that increased the solubility of I-Hg at the Degerö Stormyr field experiment even though experimental treatments

had no influence on the variation in DOC concentration.

Variation in the partitioning of I-Hg between aqueous and solid/adsorbed phases ($\log K_d \text{ I-Hg}$, Eq. (1)), can be explained by the variability in reduced S ligands (inorganic and organic) associated with particles and in solution (Miller et al., 2009). In this study we did not measure the concentration of low molecular mass (LMM) thiols, which limits our modelling approach. However, the high molecular mass (HMM) thiols, associated with DOC, were estimated based on the RS/C ratios reported for terrestrial DOC in previous studies (Skylberg, 2008). Even if the concentrations of LMM would reach to the order of 100 nM, as observed in wetlands in southern Sweden (Liem-Nguyen et al., 2014), we would expect HMM thiols associated with DOM to be in large excess. Hence, since our thermodynamic modelling show that the competition between HMM thiols and porewater sulfides was in favor of $\text{Hg}(\text{SH})_2^0$, we can conclude that although Hg^{II} complexes with LMM thiols, which have been shown to be bioavailable (Schaefer et al., 2011), $\text{Hg}(\text{SH})_2^0$ likely was the dominant form present for uptake by methylating bacteria in our studied soils (Benoit et al., 1999; Drott et al., 2007; Jonsson et al., 2014; Jonsson et al., 2012). At the relatively low pH values of our studied soils, polysulfides are not competitive to change the chemical speciation (e.g. Skylberg (2008); Skylberg et al. (2000)), and they could therefore be excluded in the calculations.

The variation in DOC concentrations could not be explained by any of the experimental treatments at Degerö. However, we did observe a negative relationship between the concentrations of DOC and $\log K_d \text{ MeHg}$ in both the combined dataset as well as along the southern transect and at the Degerö field experiment. Although concentrations of S could not explain variations in DOC concentrations at the different sites, data may suggest that the absolute concentrations of DOC are of importance for the solubility of MeHg.

The significant relationships obtained between concentrations of S in peat and MeHg in the associated porewater, for each of the two data sets separately and in the combined data set (Fig. 2D), could be interpreted as an indirect effect caused by the S-induced net MeHg formation. However, the previously reported observation (Fig. 4) that $\log K_d \text{ MeHg}$ decreased significantly with S deposition at Degerö Stormyr suggests S also has a direct effect on MeHg solubility.

An estimate of the relative contribution of newly methylated MeHg and release of sorbed MeHg was not feasible in this study, but in a previous study on enhanced MeHg concentrations in streams after forest clearcut it was estimated that 1/6 of the MeHg mobilized from the catchment was attributed to the altered solubility of MeHg and 5/6 was caused by increased methylation of I-Hg (Skylberg et al., 2009).

Because regression equations successfully model the data from the experimental plot at Degerö Stormyr field Experiment, together with data collected in peatlands along the S-deposition gradient located over 1000 km further south, we suggest the underlying processes are the same in both systems. A strong dependence on S-deposition for the net formation and redistribution of MeHg into peat porewater in boreal peatlands was thereby manifested. The combined observation that MeHg concentration in peat porewater strongly correlates to peat soil S concentration and a lack of correlation to peat soil I-Hg supports our hypothesis that increased S availability contributes to changes in MeHg formation by increasing the solubility and speciation of I-Hg.

7. Conclusion

This study demonstrates that the direct and indirect influences of S deposition on the conversion of I-Hg to MeHg and subsequent

dissolution of MeHg at the experimental-scale were also operating at the landscape scale, which helped to explain the landscape scale patterns. Increasing SO_4^{2-} deposition will increase both the formation of I–Hg–DOC complexes as well the bioavailability of I–Hg for methylating bacteria from the formation of neutral Hg-sulfides. With increasing S deposition the capacity of DOC to carry I–Hg will increase and potentially decrease pools of I–Hg in the peat. It is important to follow how changes in DOC properties is affected by S deposition to better predict the magnitude of MeHg loads from peatlands.

Covariation in the spatial distribution of S and Hg deposition across Scandinavia confounds the interpretation of what influences Hg bioaccumulation in natural ecosystems. In contrast to the strong relationship observed between peat soil S concentration and porewater MeHg concentration, peat soil I–Hg concentrations were not correlated to either the extent to which Hg dissolves (as represented by $\log K_d \text{ I-Hg}$) or to the concentration of MeHg in peat porewater.

Thus, we conclude that the effect of S deposition is particularly important in peatland dominated catchments. The results of the current study thus support the view that S is relatively more important than I–Hg in determining MeHg concentrations and exposure in peatland dominated catchments. Such effects needs to be taken into account when evaluating the effectiveness of measures taken to decrease I–Hg loads to aquatic ecosystems (Gustin et al., 2016).

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Staffan Åkerblom: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing - original draft, Writing - review & editing, Project administration. **Mats B. Nilsson:** Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Funding acquisition. **Ulf Skjällberg:** Resources, Writing - original draft, Writing - review & editing. **Erik Björn:** Resources, Validation, Writing - original draft. **Sofi Jonsson:** Validation, Writing - original draft. **Bo Ranney:** Validation, Formal analysis. **Kevin Bishop:** Investigation, Writing - original draft, Funding acquisition.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.114398>.

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