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Dimethyl Sulfide Emissions From a Peatland Result More From Organic Matter Degradation Than Sulfate Reduction

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Abstract Volatile sulfur compounds (VSCs) contribute to acid rain, cloud formation, and albedo, and thus influence the climate. Their global emissions are quite uncertain, especially contributions from freshwater wetlands. We investigated the processes leading to hydrogen sulfide (H_2S), methanethiol (MeSH), and dimethyl sulfide (Me_2S) emissions in a slightly acidic peatland and found multiple indications that organic matter degradation rather than sulfate reduction is the main driver for Me_2S emissions in this system. Evidence includes: the lack of labeled $Me_2{}^{34}S$ production after addition of $Na_2{}^{34}SO_4$ despite high emissions of $Me^{34}SH$ and $H_2{}^{34}S$, and increased emission rates when soils were amended with organic substrates containing thiol groups (H_2S emissions), methylthiols (MeSH), and dimethyl sulfonio groups (Me_2S). VSC precursors were identified from an *Untargeted Metabolomics* data set from the same soil. The abundance of sulfur cycling microbes like *Acidobacteria* SD 1 and *Desulfosporosinus* correlated with VSC emissions. We conclude that organic matter degradation is more important than sulfate reduction as a source of Me_2S in our peatland system, and potentially also in other organic and wetland soils.

Plain Language Summary Sulfur gases influence acid rain and the way clouds form. In peats and swamps, there are two mechanisms to form sulfur gases. First, when the soils are flooded soil microbes use sulfate for respiration as an alternative to oxygen for the degradation of organic matter. During this process, microbes can convert sulfate to the sulfur gases hydrogen sulfide and methanethiol. In some wetland soils, methanethiol can then be converted to dimethyl sulfide, but we found that this only happens very slowly in our peatland soil. Second, soil microbes degrade organic sulfur compounds and produce sulfur gases as waste even in conditions where O_2 is present. Which sulfur gas is produced depends on the structure of the organic sulfur compound that serves as a substrate. Compounds with a free -S-H group form hydrogen sulfide (H-S-H), compounds with a -S-CH_3 group form methanethiol (CH_3-S-H), compounds with a -S(-CH_3)$_2$ group form dimethyl sulfide (H_3C-S-CH_3), while compounds without those groups do not produce sulfur gases. We also found microbes that could be feeding on these VSC precursors. This means that emissions of sulfur gases from wetlands are caused not just by the reduction of sulfate under anoxic conditions, but directly from the degradation of organic matter, even in oxic soils outside of wetlands.

Key Points:

- Organic matter decomposition is a main source of volatile sulfur compound (VSC) emitted from organic soils and wetlands
- Sulfate reduction is also an important source of methanethiol and hydrogen sulfide but not dimethyl sulfide
- Interconversion of volatile sulfur compounds is slower than formation and emission

Supporting Information:

Supporting Information may be found in the online version of this article.

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1. Introduction

Oceans and wetlands are major sources of reduced volatile sulfur compounds (VSCs), including hydrogen sulfide (H_2S), methanethiol (MeSH), and dimethyl sulfide (Me_2S) (Aneja & Cooper, 1989). These compounds are oxidized to SO_x in the atmosphere. In contact with water, SO_x forms H_3O^+ and $SO_4{}^{2-}$. As shown following high industrial SO_2 and SO_3 emissions in the last century, H_3O^+ can cause acid rain. Further, $SO_4{}^{2-}$ can act as cloud condensation nuclei. Thus, the distribution of VSCs influences local patterns of cloud formation, rainfall and sunlight reflection by cloud albedo (Berglen et al., 2004). Enhanced VSC emissions have also been discussed as a negative climate feedback: As increased temperatures enhance biogenic activity and thus VSC emissions, the increased sulfur burden in the atmosphere will increase cloud formation and stabilize the climate (Charlson et al., 1987). Yet, there are large uncertainties about the magnitude of and factors controlling VSC emissions, particularly on the contribution of freshwater wetlands and other terrestrial ecosystems (Watts, 2000).

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In terrestrial and freshwater ecosystems, several mechanisms for release of volatile sulfur species exist (Figure 1): First, MeSH and Me_2S emissions can be related to organic matter degradation, as amending soil with the amino acids cysteine, methionine, and S-methyl methionine has led to increased VSC emissions (Banwart & Bremner, 1975; Segal & Starkey, 1969). One of the identified involved enzymes is methionine-γ-lyase (Carrión et al., 2015, 2017). Methylthio groups from amino acids can be cleaved to MeSH, and dimethyl sulfonio groups from amino acids to Me_2S (Dahl, 2020; Schäfer & Eyice, 2019). Second, H_2S can be generated by sulfate reduction (Lin et al., 2010; Stets et al., 2004). This usually occurs at a pH-dependent redox potential between −100 and −200 mV (Kirchman, 2012). Acetogenic bacteria can methylate H_2S to form MeSH and Me_2S via methylthiol transferases (Drotar et al., 1987). The methyl group can originate from methoxyaromatic compounds, for example, lignin degradation products (Bak et al., 1992; Finster et al., 1990). Third, Me_2S formation from dimethylsulfoxide (Me_2SO) and MeSH formation from dimethyl disulfide have been observed (Kiene & Capone, 1988). Together with methanogenesis, sulfate reduction is considered a main pathway of VSC formation in anoxic lake sediments, with VSCs being degraded when passing through the water column (Lomans, Op den Camp, Pol, & Vogels, 1999). However, the potential for formation of VSCs during organic matter degradation was never explicitly investigated, so emissions could occur at a broader range of environmental conditions than previously thought. Here, we investigated the mechanisms of VSC production in detail, to better understand the underlying processes and the potential importance of VSC formation from organic matter degradation.

In this study, we investigated how sulfate reduction and organic matter degradation lead to VSC emissions in a peat soil known for its active sulfur cycling and frequent fluctuations in redox potential (Hausmann et al., 2016; Küsel et al., 2008; Loy et al., 2004; Paul et al., 2006). Our first hypothesis was that VSC arise from sulfate degradation. To test this, we added isotopically labeled $Na_2{}^{34}SO_4$ to the soil and measured subsequent appearance of the label in H_2S, MeSH, and Me_2S emissions in a dynamic chamber setup via Selective Ion Flow Tube Mass Spectrometry (SIFT-MS). A dynamic chamber as defined in this paper is a soil incubation chamber that is continuously flushed with pure gas, in our case nitrogen.

The second hypothesis was that degradation of organic sulfur compounds can lead to VSCs, and that this is a more general mechanism that works with not just amino acids, but also other organic sulfur compounds as precursors. We investigated potential precursors for organic matter degradation by correlating sulfur compounds in organic matter extracts of the soil with VSC concentrations in the headspace after a prolonged soil incubation. The potency of these organic sulfur precursors was tested by adding them to soil and observing subsequent VSC emission profiles. Soil microbial community composition was also investigated to evaluate their contribution to VSC production.

Our third hypothesis was that VSCs can be converted into each other (Figure 1). To separate VSC (de)-methylation reactions from the initial production of the VSCs, we combined dynamic and static chamber approaches. In the dynamic chambers, the headspace was continuously flushed with nitrogen, whereas in static chambers, the chamber was purged multiple times with argon/nitrogen in the beginning, but then closed off and left as a closed system to incubate until samples were taken. We show that H_2S and MeSH emissions mainly originate from sulfate reduction, whereas Me_2S originates from organic matter degradation. As a general rule for organic matter degradation, thiols can cleave to H_2S, methylthiols to MeSH, and dimethylsulfonio groups can cleave to Me_2S. In an equilibrated, stable headspace, all VSCs can be interconverted such that Me_2S emissions remain the highest, followed by MeSH and then H_2S emissions.

2. Materials and Methods

2.1. Site Description

For detailed investigations of the role of moisture, redox potential and substrate addition on VSC fluxes, we used peat soil sampled from the well characterized Schlöppnerbrunnen fen, in central Germany. This is a minerotrophic peatland fed by mineral-rich surface water in the Lehstenbach catchment in the Fichtel Mountains (50°07′54.2″N, 11°52′51.4″E) (Hausmann et al., 2016; Küsel et al., 2008; Loy et al., 2004; Paul et al., 2006). The exact sampling locations were the same as in Kügler et al. (2019). At the sampled site, a fibric histosol layer covers a Gleysol formed on the granite bedrock found at 70–90 cm depth (Paul et al., 2006; Reiche et al., 2008). The vegetation is mainly the grass *Molinia caerula*. The water table depth varies seasonally between 0.13 and 0.76 m (Paul et al., 2006). High concentrations of total Fe (200–900 μmol/g_{dw} in top 5 cm, 2007), Fe(II) (mean

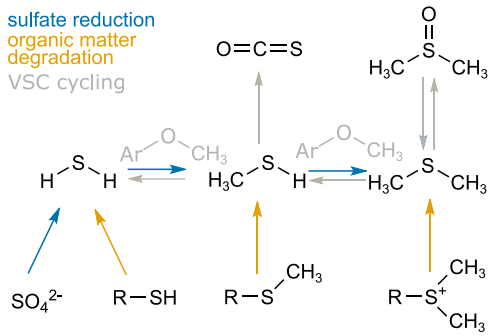

Figure 1. Scheme of known volatile sulfur compound (VSC) production pathways and subsequent reactions (interconversions) affecting the profile of emitted S gases. The most important mechanisms involve sulfate reduction to H_2S (hydrogen sulfide) and then methylation to MeSH (methane thiol) and Me_2S (dimethyl sulfide). From amino acids, the thiol in cysteine can be cleaved to H_2S, methyl thiols from methionine to MeSH, and dimethyl sulfonio groups from *S*-methyl methionine to Me_2S as a form of organic matter degradation. Degradation of Me_2S to MeSH to H_2S is known in the presence of aryl methoxy (Ar-O-) groups. Additionally, MeSH can be oxidized to carbonyl sulfide, and dimethyl sulfide to dimethyl sulfoxide. This paper investigates the processes linked to production of different VSC and subsequent reactions that may change the net emissions of VSC and contribute to the sulfur flux to the atmosphere from freshwater wetlands.

of quarterly sampling 2001–2004 = 0.3 mmol L^{-1}), dissolved organic carbon (DOC, mean of quarterly sampling 2001–2004 = 5.1 mmol L^{-1}), solid organic carbon (C_{org}, mean of quarterly sampling 2001–2004 = 37%), and total reduced inorganic sulfur (8–25 µmol/g_{dw}) have been reported previously (Küsel et al., 2008; Reiche et al., 2008).

The site was sampled in June 2019 and September 2019 for both the long-term incubation and the dry-out and rewetting experiments and again in July 2020 for the manipulation and labeling experiments. The water table depth was approximately 50 cm below the surface for 06/2019 and 07/2020 and at 20 cm below the surface for 09/2020. Soil cores were taken with a Pürckhauer corer. After removal of the plant cover with a shovel, the cores were separated into depth intervals of 0–10 cm and 10–20 cm for the rewetting experiment, and pooled at 0–20 cm depth for the other experiments. Cores were stored at 4°C in polyethylene ziplock bags from which the air was removed. Peat water was collected with a syringe and a ¼" silicone tube directly from the water table in the holes the Pürckhauer corer left and stored in completely filled (bubble free) 2 L Schott bottles at 4°C.

2.2. Analytical Methods

We measured VSCs with SIFT-MS, dissolved organic analytes with Ultra High Precision Liquid Chromatography-Orbitrap Mass Spectrometry, microbial community composition using 16S rRNA gene amplicon sequencing, CO_2, CH_4, and N_2O with Gas Chromatography-Barrier Ion Discharge Ionization (GC-BID), and total C, organic C, total N, total S using combustion analysis. We also continuously monitored pore fluid pH and redox potential using in situ sensors and analyzed extractable NO_2^-/NO_3^-, and SO_4^{2-} at the end of the experiment. Details on the analytical methods can be found in the Supporting Information S1.

2.3. Incubation Experiments

With these analytical methods, a range of different incubation experiments was conducted, Table 1. All results and raw data can be found in Lehnert et al. (2021).

2.3.1. $^{34}SO_4^{2-}$ Labeling for Investigation of Sulfate Reduction Mechanism and Addition of Unlabeled Organic Substances

We used isotopically labeled sulfate (90 atom % ^{34}S, 98% (CP)) to trace the degree to which sulfate reduction produced measured VSCs. For this, we incubated 100 g field-moist pooled peat soil from 07/2020 under constant flushing with nitrogen (200 mL/min) for two days. Then, water was added through the gas outlet to reach the original water content. For each of the four replicates, 60 mg $Na_2{}^{34}SO_4$ dissolved in 10 mL freshly deionized water were added to four of the chambers. 60 mg Na_2SO_4 with natural isotope abundance (95% ^{32}S, 5% ^{34}S) in 10 mL deionized water were added to a fifth chamber, and 10 mL deionized water without any sulfate salt was added to a sixth chamber. The gas emissions of the samples were measured continuously with SIFT-MS. After one week, we added the same amount (41 mmol) of sulfur/organic analyte to these samples, but this time contained in non-labeled organic substances to detect whether this moves VSC production from sulfate reduction to another pathway. The following organic substances were dissolved in 10 mL fresh deionized water and added to chambers 1–3: (1) cysteine, (2) a 1:1 mixture of methionine and S-methyl methionine, and (3) a 1:1 mixture of syringic acid and 1,3,5-trimethoxybenzoate. The experiment was continued for another 4 days with continuous VSC-measurements of the gas exiting the dynamic chamber.

2.3.2. Long-Term Anoxic Incubation in Static Chambers Under Argon

We also performed long-term anoxic incubations with larger amounts of soil to track changes in VSC emissions and the microbial community over time. To accomplish this, 120 g of the pooled peat soil cores from 09/2020 were submerged in 100 mL peat water in 250 mL Schott bottles with 2 cm thick butyl rubber plugs. The mixture was supplemented with 60 µL solution of 1 M glucose, 1 M lactate, and 1 M acetate, to a final concentration of

Table 1
Overview Over the Experiments Discussed in the Manuscript, and Which Section to Find Them in

Experiment	Chamber type	Measurements	Timeframe
Dryout (SI)	Dynamic chamber, N_2	SIFT-MS: continuous, other: beginning versus end 3 replicates, 2 controls	~21days until dry, measurement every 1.5 hr
Rewetting (SI)	Incubation open, then dynamic chamber (N_2)	4 humidities, 2 replicates + 1 control each	Incubated for 12 hr, each replicate measured once
$^{34}SO_4^{2-}$ Labeling (Section 2.3.1)	Dynamic chamber, N_2	4 replicates with $Na_2{}^{34}SO_4$, 1 control with normal Na_2SO_4, 1 unspiked control. Of the 4 spiked replicates, 3 were spiked with 1) cysteine, 2) methionine/S-methyl methionine, 3) syringate/gallate	0–7 days: only $^{34}SO_4^{2-}$ spiking, 8–10 days: addition of other compounds. Measurement every 1.5 hr
Long-term anoxic incubation (2.3.2)	Incubation: static, Ar SIFT-MS measurement: dynamic, N_2, after 30 min equilibration	5 replicates + 1 autoclaved control/time point	4 weeks, destructive sampling 1x/w
Substrate manipulation—dynamic (2.3.3)	Dynamic chamber, N_2	1 replicate/substance	4 days, measurement every 1.5 hr
Substrate manipulation—static (2.3.4.)	Static chamber, N_2	3 replicates/substance	6 days, measurement 1x/d
Antibiotics treatment (2.3.5)	Static chamber, N_2	3 replicates/substance	6 days, measurement 1x/d

Note. SI: Supplementary information.

$2.73 \cdot 10^{-7}$ mol/g peat/pore water mixture. During the month-long incubation, the bottles were kept under a static atmosphere of Argon: The bottles were flushed with Argon for 1 hr and then incubated at 13°C in the dark for up to 4 weeks. Five bottles were autoclaved twice at 120°C for 20 min before incubation. The next morning and then every week, five bottles plus one autoclaved bottle were sampled destructively. First, VSC emission measurements were done, followed by greenhouse gas (GHG) emission measurements (CO_2, CH_4, N_2O) and then extraction of organic matter, nutrients, and DNA. Since SIFT-MS quantification is not well established in Argon atmospheres, the Argon atmosphere in the bottles was replaced by nitrogen for the measurement. Thus, for analysis, the bottles were flushed with 400 mL/min nitrogen for 30 min followed by a SIFT-MS measurement of the VOC emissions in the gas stream exiting the bottle. 11 scans were done per measurement. Scan time per ion was 500 ms for most ions, 1 s for the reagent ion m/z = 19, 30, and 32 u, and 5 s for dimethyl sulfide (H_3O^+/63 u and O_2^+/62 u), methanethiol (H_3O^+/49 u) and carbonyl sulfide (O_2^+/60 u).

Then, headspace samples for the GHG emission measurements (CO_2, CH_4, N_2O) were taken 5, 20, and 35 min after chambers were flushed and reclosed. Using a syringe, 3 × 20 mL chamber headspace were inserted into a previously evacuated 20 mL vial and measured for CO_2, CH_4, and N_2O concentration using GC-BID.

After GHG sampling, aliquots of the soil were frozen to −80°C for subsequent soil Metabolomics and 16S rRNA amplicon sequencing (for methods see SI), the nitrite content and pH were measured from the fresh soil, and another aliquot was dried at 40°C and then used for the geochemical analyses (Figure S3 in Supporting Information S1).

2.3.3. Substrate Manipulation in Dynamic Chambers to Check Validity of VSC Precursors

A more expanded experiment to link different organic substrates to VSC emissions tested a total of 24 different organic substrates (see SI for analytical methods): methionine, cysteine, *S*-methyl-methionine, *S*-methyl cysteine, cystine, *N*-acetyl methionine, *N*-formyl methionine, methionine *S*-oxide, cysteic acid, taurine, thiophene-3-carboxylic acid, sulfosuccinate, 3-(methylthio)-propionic acid, gonyol, dimethylsulfonio acetate, sodium sulfate, sodium sulfide, sodium methiolate, dimethyl sulfide, dimethyl sulfoxide, (coenzyme M), 2-mercaptoethane sulfonate, syringic acid, and 1,3,5-trimethoxybenzoid acid. For each added substrate, 100 g field-moist pooled peat soil from 11/2019 was incubated under 200 mL/min nitrogen (i.e., anaerobically) at room temperature. The chamber was continuously flushed such that the headspace was replaced after 1–2 min. Note that most of the air was released to the atmosphere directly, so in theory it is possible for VSCs to diffuse back into the chamber. However, we never detected any VSCs in the lab air, so the concentration gradient was from the chamber to the lab.

To achieve anoxic conditions, the soil was preincubated for 2 days before the measurements started. After measuring the initial soil emissions, 1.29 mmol of the substance was dissolved in 10 mL distilled water was added through the outlet of the Teflon chamber using a syringe. This amount equals the total amount of sulfur observed in the soils based on the element analysis (0.36% *m S/m dry soil*), and was chosen as a balance between being high enough to create enough signal to detect VSC level changes with the SIFT-MS and being low enough to not completely disturb the peat ecosystem. For every six substances, one control with only distilled water was measured. The VSC emissions were tracked for 4 days immediately following addition. Every time each of the seven chambers incubated in parallel was measured, a one-point calibration at 1 ppb VSC-standard was made to account for changes in the instrument performance. Remaining soil moisture, sulfate and nitrite/nitrate content were measured after each incubation.

2.3.4. Sulfur Substrate Addition in Static Chambers to Simulate Conversions in Pore Space

For a more robust link between organic sulfur compound additions and VSC emissions without the influence of changing humidity, and for checking further conversions of VSCs when they build up, like in a soil pore space, we repeated the experiment from Section 2.3.3 in static chambers with more replicates. Field-moist pooled peat soil from 07/2020 (8 g) was incubated under nitrogen in 120 mL glass bottles with a butyl rubber septum. The soil was flushed with nitrogen for 1 hr. After 24 hr, 103 µmol of different sulfur substances dissolved in 3 mL distilled water were added to the bottles with a syringe, leading to a final concentration of 1,288 µmol/g wet soil. Triplicates were analyzed for each treatment, as well as six control samples where only water was added. Immediately after the substrate addition, and then daily, VSC emissions were measured via a needle connected to the SIFT-MS via a short tube. A 60 s Selected Ion Mode (SIM) scan with 1 s scan time per ion and a count limit of 100,000 counts was done for measuring VSCs.

The headspace air that was withdrawn for the measurement was replaced by N_2 via a second needle leading to a tube continuously flushed with N_2. This way, the headspace was not completely exchanged, but kept as stable as possible.

In comparison to the dynamic chambers, the headspace should be stable throughout the incubation. Although we cannot rule out the diffusion of VSCs through the rubber septum completely, these chambers were much more gas-tight than the dynamic chambers, and we introduced a slight overpressure in the chambers to avoid gas flow into the static chambers in case of small leaks.

2.3.5. Inhibition Treatments in Static Chambers

To gain insight into whether sulfate reducers, methanogens, or methylotrophs are involved in generating and degrading VSCs, or whether this might even be an abiotic process, we incubated the soil in static chambers with inhibitors. Like described by Kiene & Hines (1995); Visscher et al. (1995), glutaraldehyde and chloramphenicol were used to reduce general microbial activity, bromoethanesulfonate (BES) to inhibit methanogens, tungstate to inhibit sulfate reducers, and chloroform to inhibit methyl transfer reactions. The experimental setup is the same as in Section 2.3.4 except for the spiked substance. Each soil was treated with one inhibitor, and triplicates of each treatment were conducted. Glutaraldehyde, tungstate and BES were added to a final concentration of 2 mM, chloramphenicol to 25 mM, and chloroform to 1 mM. These conditions match the conditions from Kiene and Hines (1995); Visscher et al. (1995). Like above, VSC emissions were tracked right after the spiking and then daily.

3. Results

Preliminary dryout experiments of peatland soils under anoxic conditions demonstrated that H_2S emissions declined, but Me_2S emissions increased as the soil dried and redox potentials increased, while MeSH showed intermediate behavior (Figure S3 in Supporting Information S1). Even though the exact emission profiles were not reproducible for one of the three replicates (Figure S3 in Supporting Information S1), these preliminary experiments gave a first clue that these three VSCs might be produced via different mechanisms. The different release rate profiles at different humidities persisted in rewetting experiments over a range of different soils (Figures S4 and S5 in Supporting Information S1). Especially, H_2S and Me_2S showed very different profiles, indicating that they might be caused by different soil processes. We tested this hypothesis with the following experiments.

3.1. VSCs From Sulfate Reduction—Labeling With $Na_2{}^{34}SO_4$ and Unlabeled Organic Substances

First, we investigated which sulfur gas emissions arise from sulfate reduction by labeling soils with $^{34}SO_4{}^{2-}$. Addition of ^{34}S labeled sulfate in amounts that doubled the initial sulfate concentrations led to increasing emissions of labeled $H_2{}^{34}S$ and $Me^{34}SH$ over time, Figure 2. By the end of the experiment, $H_2{}^{34}S$ and $Me^{34}SH$ emissions were as high as the $H_2{}^{32}S$ and $Me^{32}SH$ emissions in the same sample. Since we added as much $^{34}SO_4{}^{2-}$ as $^{32}SO_4{}^{2-}$ already present in the soil, these two VSCs must arise mostly from sulfate reduction (Figure 2, S6).

In contrast, emissions of labeled $Me_2{}^{34}S$ were close to the detection limit and not significantly different from the control, whereas non-labeled $Me_2{}^{32}S$ emissions remained constant at a relatively high level throughout the

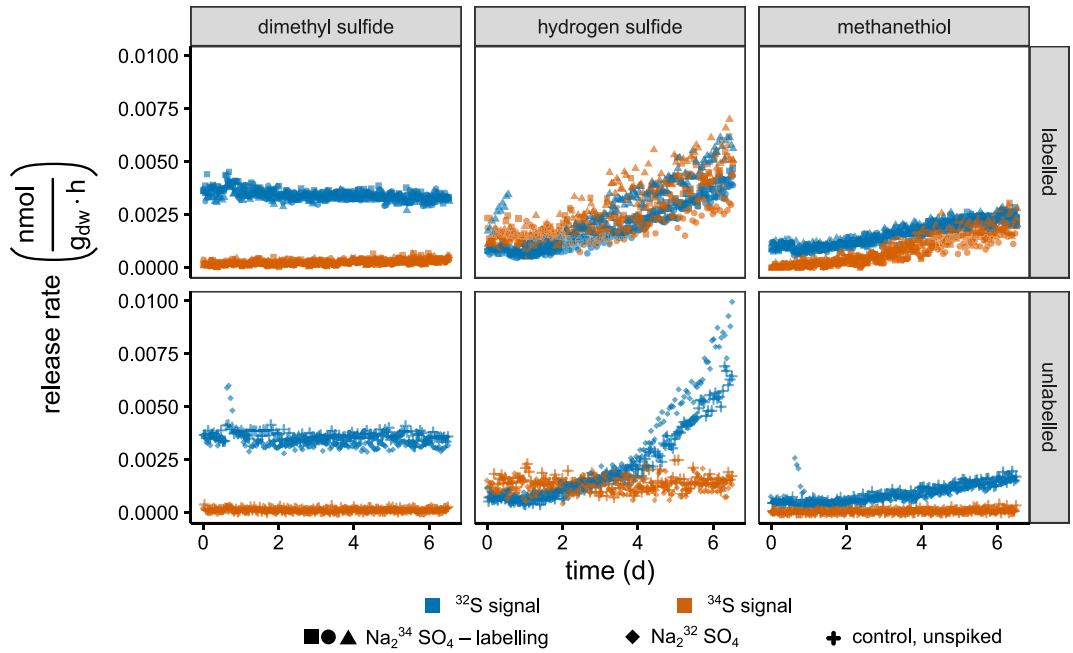

Figure 2. Release rates of unlabeled (blue) and labeled (orange) hydrogen sulfide, methanethiol, and dimethyl sulfide when spiking with $Na_2{}^{34}SO_4$ ($n = 3$, upper plots, different point shapes represent the different chambers) with a natural abundance Na_2SO_4 control (~95% ^{32}S, 5% ^{34}S) and a control without any increase in Na_2SO_4 concentration (both $n = 1$, lower plots).

experiment. These differences indicate not only that Me_2S is not derived directly from sulfate reduction, but that while the conversion of H_2S into MeSH was active, the conversion of MeSH to Me_2S was very limited (Figure 2).

The incorporation of the sulfate label was also rather low—accumulated over the time of the experiment, we found 18 ± 3 ppm ^{34}S incorporated into H_2S, 5 ± 3 ppm into MeSH, and undetectable amounts converted to Me_2S since it was not significantly different from the control.

In a second step, we added organic, non-labeled molecules to check their influence on VSC production. We added cysteine with normal isotopic ratios to the soils labeled with $Na_2{}^{34}SO_4$. Cysteine can be an organic thiol H_2S source (Morra & Dick, 1991), and we wanted to check how it impacts ^{34}S-VSC formation. However, its addition decreased H_2S formation (for both labeled and unlabeled $SO_4{}^{2-}$) and decreased the amount of labeled MeSH by a factor of three (Figures S8–S10 in Supporting Information S1). Further literature research found similar effects at the experiments of Dalby et al. (2018), where they just attributed it to a culture crash, but Kredich (2008) states that cysteine can inhibit assimilatory sulfate reduction if enough sulfur is present in the cells. This could be a potential explanation for the dramatic reduction in VSC emissions.

As direct MeSH and Me_2S precursors, we added a mixture of methionine and *S*-methyl methionine in the same manner as cysteine. This had no influence on H_2S emissions, but non-labeled MeSH and Me_2S emissions increased by 2–3 orders of magnitude (Figures S7–S9 in Supporting Information S1).

To test whether we could enhance the conversion of H_2S to MeSH and MeSH to Me_2S by adding methyl group donors, we added syringate and trimethoxybenzoic acid like done by Lomans et al. (2001, 2002). This increased the emission of $H_2{}^{32}S$ and $Me^{32}SH$ by a factor of 10, but did not have an influence on $H_2{}^{34}S$, $Me^{34}SH$, $Me_2{}^{32}S$ and $Me_2{}^{34}S$ (Figures S7–S9 in Supporting Information S1).

3.2. Long-Term Anoxic Incubation, Correlation of VSCs and Organic Matter

Our second hypothesis was that organic matter degradation can lead to VSC formation, so we designed an *Untargeted Metabolomics* experiment to identify possible precursor products. In a broad sampling approach, we measured VSCs, CO_2, CH_4, N_2O, nutrients, extractable organic matter, and changes in microbial community composition during a 4-week-long closed-chamber incubation under Argon, Figure 3.

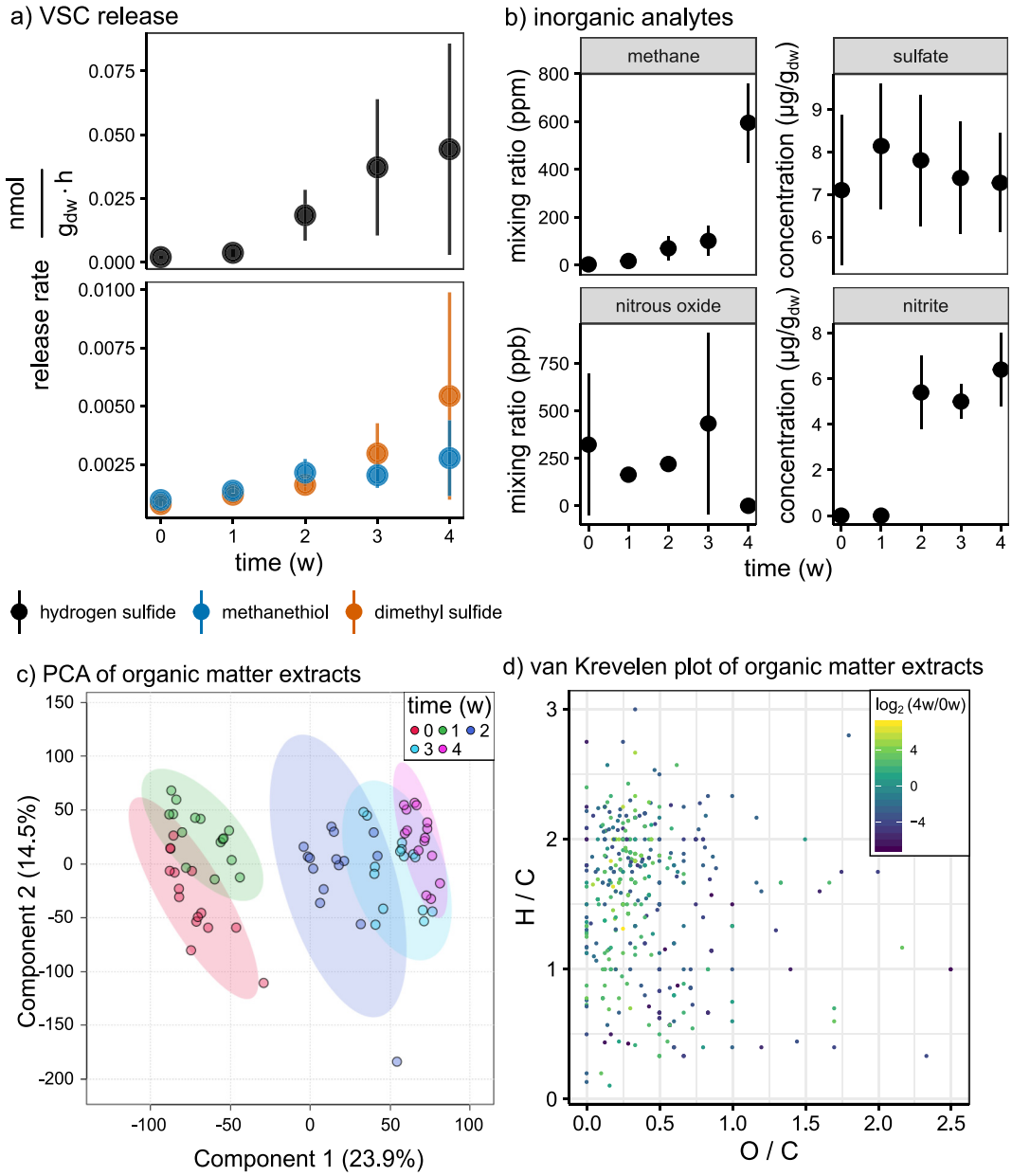

Figure 3. Long-term incubation over 4 weeks. (a) Release rates (±95% confidence interval (CI), $n_{soil} = 5$ at each time point) of the reduced sulfur compounds hydrogen sulfide, methanethiol, and dimethyl sulfide. Emission rates of the three compounds are significantly different ($p < 0.05$ for repeated measures Analysis of Variance (ANOVA)). (b) Mixing ratios of methane, and nitrous oxide in the flasks (±95% CI, $n_{soil} = 5$ at each time point) and sulfate and nitrite concentration in the slurry (±95% CI, $n_{soil} = 5$ at each time point). (c) Principal least squares discriminant analysis (PLS-DA) scores plot of the non-volatile organic matter extracts measured with Ultra High Precision Liquid Chromatography-Orbitrap Mass Spectrometry (UHPLC-Orbitrap-MS) in positive polarity. Obtained from MetaboanalystR after log-transformation and Pareto-Scaling of the data. The five replicates analyzed each week were measured three times each ($n_{total} = 15$). The ellipses represent the 95% CI of each time point. (d) Van Krevelen Diagram of significantly changing non-volatile organic substances, as detected via (UHPLC-MS) in positive polarity. Substances are filtered to be up-/downregulated by at least a factor of 3.

The transition from nitrate reduction in the first 2 weeks to sulfate reduction and methanogenesis in the last 2 weeks of the incubation was observed in the changing makeup of peat waters and methane emissions (Figure 3b). Parallel activities of sulfate reduction and methanogenesis in the Schlöppnerbrunnen fen, which is characterized as a low-sulfate habitat, were shown previously (Küsel et al., 2008). The decrease in sulfate correlated with an increase in H_2S and Me_2S levels, whereas MeSH first increased and then remained constant in the second half of

the experiment (Figure 3a). Repeated Measures Analysis of Variance (ANOVA) showed a significant difference between the three gases at 95% confidence level.

Non-volatile organic sulfur species were measured in water and acetonitrile extracts of organic matter using UHPLC-Orbitrap MS. Principal component analyses of the resulting metabolome indicated alteration of the organic matter over time (Figure 3c and Figure S11 in Supporting Information S1), with a general decrease of H/C and O/C Figure 3d, Figure S13 in Supporting Information S1), but not S/C ratios of sulfur compounds (Figures S12 and S14 in Supporting Information S1). Looking at all compounds weighted by their peak area, we visually observe a decrease of S/C ratios over time for incubated samples and not for autoclaved controls, yet this is not significant ($p = 0.95$, Neumann trend test).

We then tried to identify organic precursors by their change in concentration over time. Our logic was as follows: If a sulfur compound is degraded over time (i.e., its concentration correlates negatively with time), it is consumed by microbes and thus could be a precursor for MeSH or Me_2S. If a sulfur compound increases over time (positive correlation with time), it could (a) be produced from H_2S produced by sulfate reduction or (b) be produced from other inorganic and organic sulfur compounds by other microbes. A fraction of its concentration could again be degraded by other microbes to form MeSH and Me_2S. We could putatively identify 29 organic sulfur compounds correlating positively with time and 60 organic compounds correlating negatively with time based on a matching isotope pattern for S, a Variable Importance in the Projection (VIP) score of the Principal Least Squares Discriminant Analysis (PLS-DA) > 1, a change in concentration of at least a factor of 5, and at least 2x higher concentrations as in the autoclaved control samples (Table S2, Figure S15 and S16 in Supporting Information S1). This matches a Level 4–3 identification acc. Schrimpe-Rutledge et al. (2016). Of the 89 detected tentative compounds, 11 could be identified by MS^2-experiments (Level 2 identification), and of these 11, five could be confirmed by co-injection of standards (Level 1 identification). These five Level 1-identified compounds are *N*-acetyl-methionine, taurine, thiophene-3-carboxylate, *N*-formyl-methionine, 2-sulfosuccinic acid. They were then tested in the spiking experiments.

Quantification of the compounds showed that their concentrations were between 0.004 and 0.1 $nmol/g_{soil\ dry\ weight}$. Relative to the soil's sulfur content, between 1 in 10^6–10^9 S atoms were extracted as these organic sulfur compounds, and approximately 2% of all S atoms could be extracted as sulfate—in other words, 98% of the sulfur could not be attributed to any compound class by these extractions (Table S2 in Supporting Information S1) and was likely not in soluble form.

3.3. Organic Matter Sulfur Compound Precursors—Immediate Response of VSC Emission

To test whether organic sulfur compounds could be precursors for VSC emissions from soils, we spiked soils with the compounds identified in the Metabolomics experiment as well as analogs of literature-identified VSC precursors, and measured the immediate VSC response in dynamic chamber incubations under N_2 (Figure 4, Table S3 in Supporting Information S1). Our hypothesis was that dimethylsulfonio groups should be cleaved to Me_2S, methyl thiol groups to MeSH, and thiol groups to H_2S by a substitution reaction with OH^- (Bentley & Chasteen, 2004; Cooper, 1996; Sawamura et al., 1978) or potentially also by an elimination reaction analogous to the dimethylsulfonio propionate (DMSP)-lyase mediated cleavage (Chasteen & Bentley, 2004). The addition of substances with oxidized or aromatic sulfur atoms like cysteic acid or thiophene carboxylate should not lead to enhanced VSC emissions, as they cannot be converted to VSCs directly. Our results mostly confirmed our hypotheses—addition of cystine, sodium sulfate, and sodium mercaptoethane sulfonate/coenzyme M lead to increased H_2S emissions, while methionine, *S*-methyl cysteine, and *N*-formyl methionine led to increased MeSH emissions. *S*-methyl methionine, dimethylsulfonio acetate, and gonyol were cleaved to form Me_2S, while addition of cysteic acid and thiophene carboxylate did not increase Me_2S emissions. Methionine *S*-oxide also enhanced MeSH emissions, which might reflect quick reduction to methionine before it is cleaved.

However, some compounds did not behave as expected: Cysteine led to MeSH emissions, addition of N-acetyl methionine and 3-(methylthio)-propionic acid led to substantial amounts of Me_2S, but hardly any MeSH emissions. We conclude these compounds were methylated before cleavage, as we did also not observe the methylation of MeSH.

3.4. Conversions of VSCs in the Chamber Headspace

After using dynamic chambers to analyze the immediate VSC emission response to adding organic sulfur compounds to the soil, we tested whether VSC mixing ratios reflect other reactions when they are allowed to

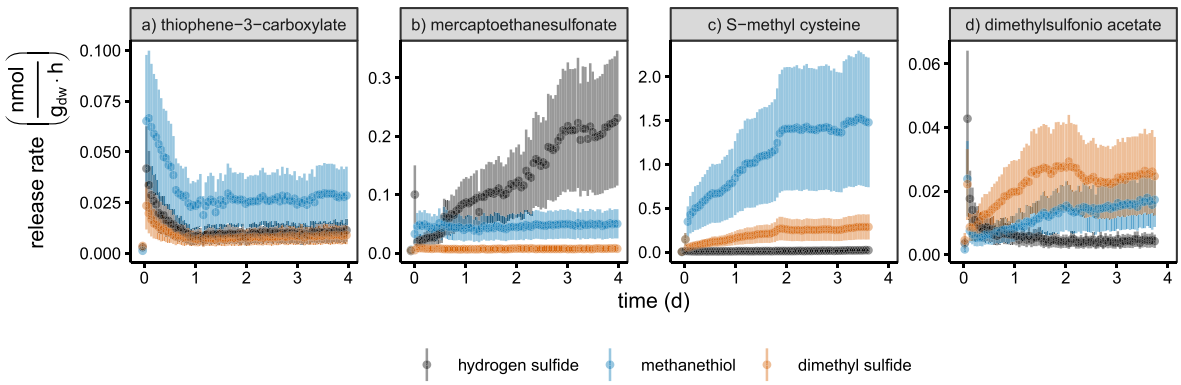

Figure 4. Effect of thiophene-3-carboxylate, mercaptoethane sulfonate (coenzyme M), *S*-methyl cysteine, and dimethylsulfonio acetate addition to peat soil incubated in continuously N_2-flushed dynamic chambers. Release rates ±95% CI. $n_{soil} = 1$ per substance, 5 scans per timepoint. These analytes are examples of the behavior we consistently found: R-SH like in mercaptoethane sulfonate cleaves to H_2S, R-SMe like in S-methyl cysteine cleaves to MeSH, R-SMe_2^+ like in dimethylsulfonio acetate cleaves to Me_2S, and sulfur bound to the molecule like in thiophene-3-carboxylate does not cleave.

build up in the chamber headspace, as they would in soil pores. Therefore, we incubated peat soil with the same added substrates in static chambers with a stable N_2 headspace. In both cases, we generally see an increase in release rate (dynamic chambers) and in headspace mixing ratio (static chambers), Figure S17 in Supporting Information S1. For most spiked substances, we observe higher net Me_2S production rates during incubation in static chambers than in dynamic chambers, Figure 5. Even for substances that mainly produce H_2S or MeSH in the dynamic chambers, Me_2S is the major component in the headspace when incubating in static chambers with an up to 10-fold excess of Me_2S over MeSH and H_2S. We thus conclude that cycling between the different VSCs determines VSC mixing ratios when their residence time in the pore space is high enough.

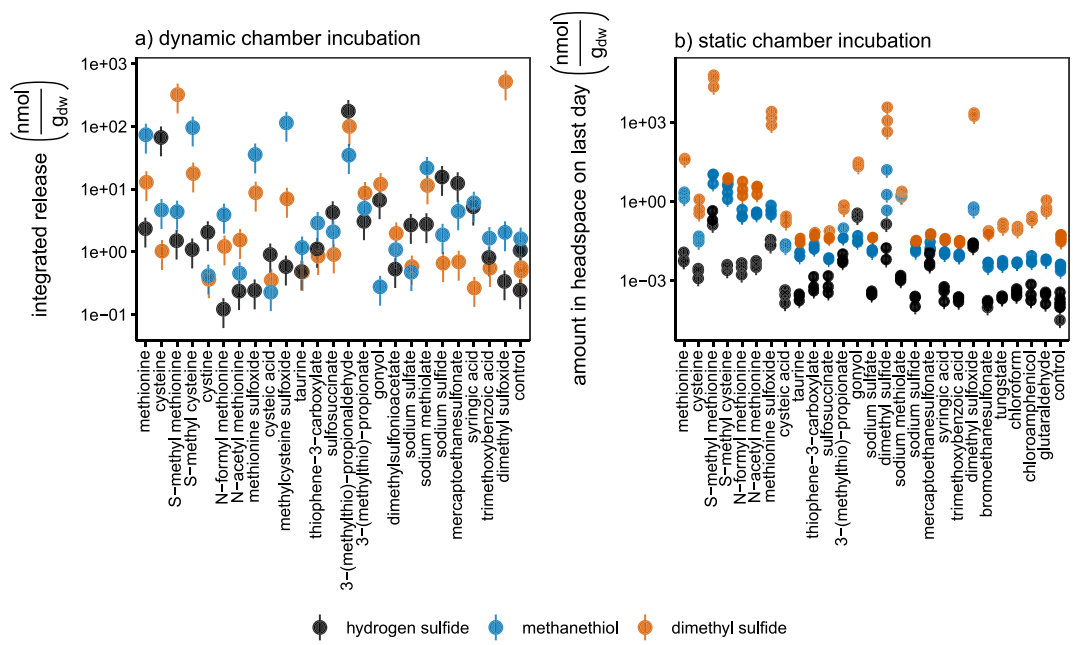

Figure 5. Volatile sulfur compound (VSC) emissions when incubating soil spiked with a variety of different substances in dynamic and static chambers. (a) the integrated release rate of VSC emissions over time in the dynamic chambers, as a measure of total emissions from the soils in these chambers, normalized to soil dry weight. Release ±95% CI. $n_{soil} = 1$ per substance, 5 scans per timepoint, measurement every 15 min over the course of 3 days. (b) the molar amount of VSC in the headspace of the chamber on the last day of incubation (day 6), normalized to the soil dry weight. Headspace mixing ratio normalized to soil amount ±95% CI, 5 scans per time point and substance, $n_{soil} = 3$.

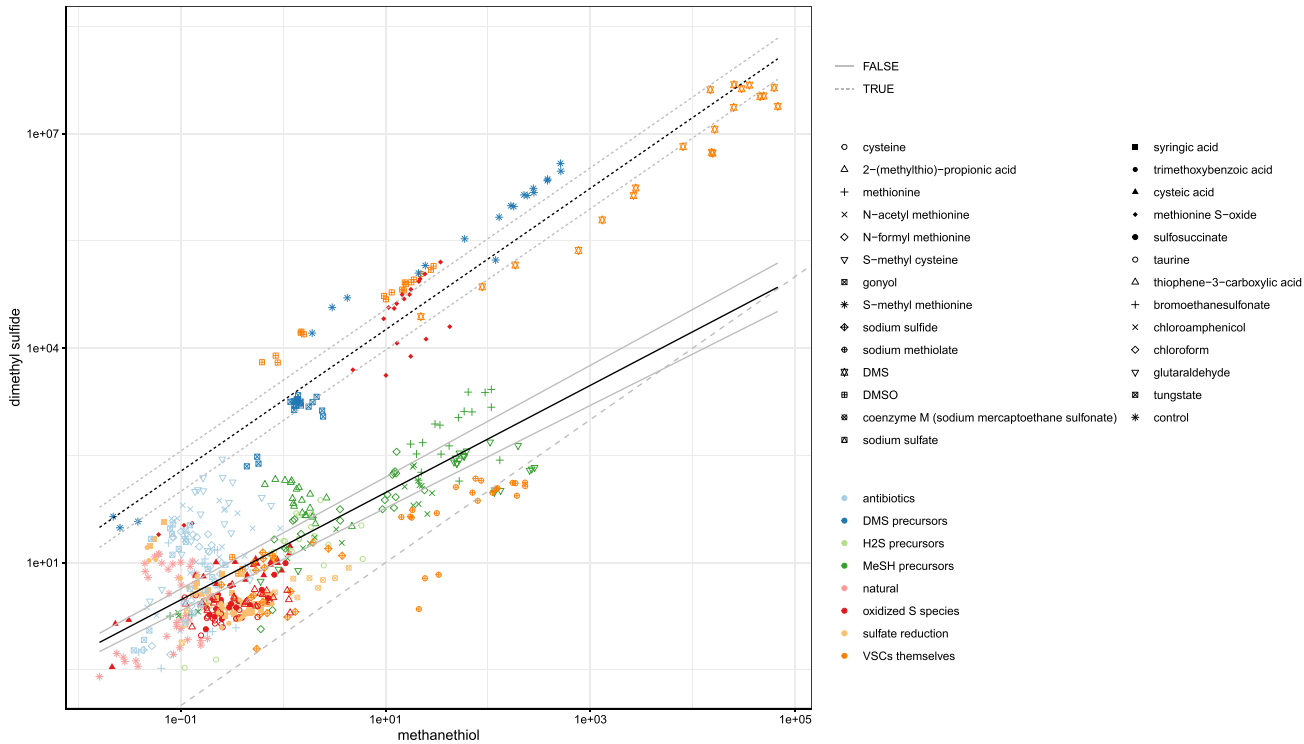

Figure 6. Relation of Me_2S and MeSH release rates when spiking with precursor substances (colored by substance class) in a dynamic chamber incubation. Every point is a measurement in time. Separate regression curves for Me_2S precursors (dotted lines, mean ±95% CI) and other substances that do not contain dimethyl sulfonio groups (solid lines, mean ±95% CI). Gray dashed line: 1:1 line.

The total fraction of sulfur emitted to the chamber headspace from the spiked substances is in the range of 1%–5% for the dynamic chamber systems. On the final day of incubation in static chambers, the amount of sulfur in the headspace is <1% of the added sulfur except for the compounds with dimethylsulfonio groups: here, the amount of sulfur in the headspace reaches up to 6%. It is likely that microbes utilize the sulfur themselves and only emit a small fraction of it, and that other microbes take up sulfur from these VSCs when they reach the compensation concentration.

To see whether the ratio of Me_2S:MeSH reaches an equilibrium, we plotted all the measurements of the static chamber substance additions in one graph (Figure 6). We could still distinguish Me_2S precursor compounds from MeSH precursors, as the ratio of Me_2S to MeSH was much higher (100–1,000:1 vs. 1–10:1) and had a higher slope than for all other samples. Since we can distinguish between situations where Me_2S was emitted initially and where H_2S or MeSH were emitted initially, MeSH conversion to Me_2S is more prominent than Me_2S conversion to MeSH.

3.5. Effect of Inhibitors on VSC Cycling

To assess which microbial process might be involved in VSC formation and cycling, we repeated the anoxic static chamber incubations with inhibitors for specific pathways. We used BES for inhibition of coenzyme M in methanogens, tungstate to inhibit sulfate reducers, chloroform to inhibit methyl transfer reactions, and glutaraldehyde and chloramphenicol for a general microbial inhibition, like Kiene and Hines (1995), and Visscher et al. (1995) (Figure 5b). Bromoethanesulfonate and tungstate should thus block methylation of H_2S and MeSH by Me_2S producers, chloroform should block demethylation by Me_2S degraders, and the others should reduce biotic processes.

Regardless of the inhibitor added, Me_2S was increased compared to a control without inhibitors (Figure 5b), which either means Me_2S is formed abiotically or that the activity of Me_2S degraders was inhibited more strongly than the activity of Me_2S producers.

MeSH emission increased in treatments with glutaraldehyde, chloramphenicol, and chloroform (Figure 5b), which supports the hypothesis that VSC degraders were inhibited more strongly than VSC producers. Tungstate and BES showed no significant effect on MeSH and H_2S levels; suggesting that methanogens and sulfate reducers were not involved in MeSH/Me_2S formation using the known methylation processes. If they were involved, we would expect a decrease in Me_2S levels and an increase in H_2S/MeSH levels. Since we observe the opposite, we conclude that methanogens and sulfate reducers are not converting H_2S/MeSH to Me_2S in our experiments.

H_2S emissions decreased with all inhibitors except when adding BES (Figure 5b). Perhaps the inhibition of methanogens increased the amount of substrate available for sulfate reducing bacteria, which in turn were more active in reducing sulfate to sulfide.

3.6. Microbial Community Composition Changes Correlating to VSC Emissions

Additionally, we tracked the microbial community composition during the long-term anoxic incubation (Section 3.2). During the entire 4 weeks of incubation, microbial communities were dominated by Acidobacteria, Proteobacteria, Firmicutes, Verrucomicrobia, and Actinobacteria, that together accounted for up to 87% of the sequence reads in the samples. All these genera have members associated with dissimilatory S cycling processes (sulfate/sulfite reduction and sulfur oxidation). Overall, the microbial community composition on the phylum level remained stable throughout the course of the incubation period (Figure 7), with exception of Firmicutes, which increased from 0.13% ($n = 1$) at T0 to 12% ($n = 4$) after 3 weeks (Figure S17A in Supporting Information S1). A pronounced shift in the microbial community composition was not expected, as fen microbes should be adapted to water table fluctuations inducing redox fluctuations.

On the genus level, we found 33 genera linked to sulfur cycling based on previous literature (Figure 6d, Figure S17b in Supporting Information S1). *Acidobacteria* SD 1 ($r = 0.71$), *Desulfosporosinus* ($r = 0.72$), and *Pseudomonas* ($r = 0.50$) correlated positively with time and VSC emissions, *Desulfobacca* ($r = -0.63$), uncultured *Desulfobulbaceae* ($r = -0.55$), *Synthrophobacter* ($r = -0.68$), and uncultured *Thermodesulfovibrio* ($r = -0.57$) correlated negatively. The expression of acidobacterial sulfur-metabolism genes and their upregulation under anoxic conditions during incubation experiments of peat soil obtained from the Schlöppnerbrunnen fen was shown by Hausmann et al. (2018).

4. Discussion

4.1. Organic Matter Degradation, Rather Than Sulfate Reduction Is an Important Source of Me_2S From the Peat Soils Investigated

Taken together, our experiments demonstrate the importance of organic matter degradation rather than sulfate reduction as a source of Me_2S emissions. The evidence that sulfate reduction alone was not responsible for producing the measured VSCs comes from tracing the isotopic label of added $Na_2{}^{34}SO_4$ in our peatland soils. Appearance of the label in $H_2{}^{34}S$ and $Me^{34}SH$ emissions are in accord with other labeling studies (Dalby et al., 2018). As we could not detect $Me_2{}^{34}S$, we conclude that the methylation of MeSH to Me_2S is less favorable or slower than the methylation of H_2S to MeSH. We observed that $Me^{34}SH$ release rates were of the same order of magnitude as $H_2{}^{34}S$, whereas $Me_2{}^{34}S$ was not detected (Figure 2). This is in contrast to the studies claiming a high thiol methylation potential and thiol methyltransferase activity in soil (Carrión et al., 2015, 2017; Drotar et al., 1987), and studies with MeSH present only in trace concentrations (Bak et al., 1992; Finster et al., 1990).

Precursor organic compounds were present in the pore waters of the Schlöppnerbrunnen (Section 3.6) that over the long-term incubation varied in concentration in ways consistent with VSC fluxes. When representative compounds were added to short-term incubations, VSC fluxes responded in expected ways: thiols like 2-mercaptoethane sulfonate (coenzyme M) are cleaved to H_2S, methylthiols like *S*-methyl cysteine are cleaved to MeSH, and dimethyl sulfonio groups like in dimethylsulfonio acetate are cleaved to Me_2S. However, the precursors previously reported in the literature, including cysteine, methionine, and *S*-methyl methionine, exhibit the highest VSC release rates—possibly indicating that they provide a favored substrate for the enzymes responsible for the cleavage of S-moieties from these molecules.

The individual concentrations of the identified organic compounds were rather small; only 10^{-6}–10^{-9} mol/mol S were found for the quantified organic compounds. Since both the organic sulfur compound and the sulfate

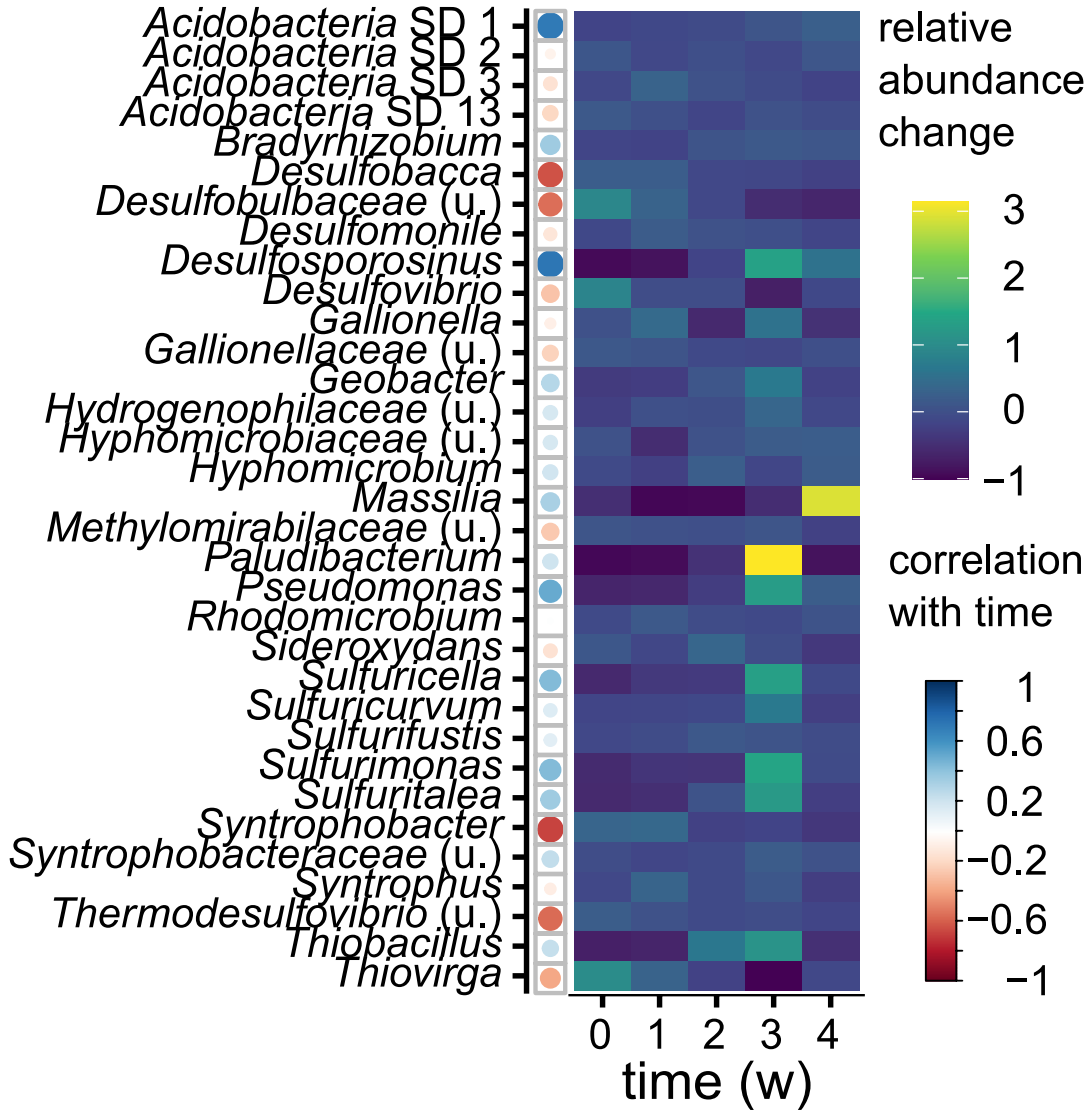

Figure 7. Relative 16S rRNA gene abundance of genera associated with dissimilatory S cycling (sulfate/sulfite reduction and S oxidation). Red and blue circles: Pearson's correlation between relative 16S rRNA gene abundance and time. Purple/yellow heatmap: Change of the average relative abundance ($n = 5$) per time point, centered and scaled by the average abundance of this species, rel.A.change(T_1) = $\left(A(T_1) - \overline{A}\right)/\overline{A}$. Note, at $t = 4$ w, only 4 replicates are shown due to a failed library preparation for this sample prior to amplicon sequencing.

analyses were only performed on extracts of the soils and this only accounts for ~2% of the total sulfur, the actual concentrations of the different sulfur compounds in the soil remain unknown. In a survey of 30 different soils by Meredith et al. (2018) only 1%–25% of the total sulfur was sulfate, but 20%–55% was organic sulfur in the form of R–S–S–R, R–SH, or R–S–R, which could be potential VSC precursors. Similarly, Prietzel et al. (2009) found ~20% of these reduced sulfides at Schlöppnerbrunnen. Thus, it seems highly likely that a high number of very different organic sulfur compounds are present, each individually at a low concentration, but when summed together they can be the most abundant VSC precursor in the soil. Alternatively, it is also possible that the compound concentrations do not provide the best indication of fluxes, since they might be harvested from insoluble organic matter stock, dissolved, and metabolized very quickly.

In contrast to the labeling experiment (see Section 3.1), the ratio of MeSH/H_2S was very low in the long-term incubation experiment. Taken together with the static chamber incubations, we deduce an increase in the activity of sulfate reducers to form H_2S compared to the activity of the H_2S methylators such that the conversion is slower than the production and hence, we observe more H_2S and only some MeSH. Another possibility would be that

during the long-term incubation, the redox potential dropped further than for the dynamic experiments. The time frame was also long enough that microbes could adjust their metabolism to persistently higher concentrations of MeSH such that they could methylate MeSH to Me_2S. Similar lag phases were observed when switching the methyl source from for example, methanol to MeSH for different methylotrophs (Ni & Boone, 1993; Visscher & Taylor, 1993). This could explain why we only saw MeSH methylation to Me_2S in the longer-lasting static experiments.

Inhibition of sulfate reducers and methanogens by BES and tungstate led to an increase in Me_2S formation, had no effect on MeSH formation, and decreased H_2S formation, whereas general microbial inhibitors also inhibited MeSH formation. This contrasts with results from Kiene and Hines (1995), and Visscher et al. (1995), and provides another indication that processes other than sulfate reduction may be involved in VSC production. Potentially, methanogens and sulfate reducers might be stronger involved in Me_2S degradation rather than formation in these soils, even though mechanisms like this have not been identified yet to the knowledge of the authors.

In the context of searching for alternate mechanisms, the microbial community shifts during the long-term incubation provided an additional piece to the puzzle. Some of the *Acidobacteria* are able to liberate sulfite from organosulfonates, which suggests organic sulfur compounds as complementary energy sources that would also affect VSC emissions. Despite its small population size in our incubations *Desulfosporosinus* has been shown to be a keystone species in this fen, where it is responsible for a considerable proportion of sulfate reduction due to its high cell-specific sulfate reduction rates (Pester et al., 2010), demonstrating the importance of rare species for ecosystem activities (Jousset et al., 2017). The other sulfur cycling species had correlation coefficients lower than 0.5. *Thiobacillus* and *Hyphomicrobium*, known for their VSC demethylation (Hayes et al., 2010), only showed a weak correlation with time/VSC emissions ($r = 0.19$ and 0.24, respectively). As outlined above, microbial abundance does not necessarily reflect microbial activity, so also other microbes potentially could have contributed to VSCs cycling as well.

4.2. Comparability of Static and Dynamic Chamber Approaches

Conclusions on the interconversion of the different VSC in the pore space heavily rely on a comparison of static and dynamic chamber approaches. First, while static chambers are a completely closed system, the constant air flow in the dynamic chambers not only flushed out volatiles from the headspace, but also contributed to drying of the sample. Over the course of the week, the samples lost about 30% of its water content, going from a completely submerged sample to a humid, but not submerged sample. This might have an impact on pore air exchange and redox potential that is not seen in static chambers, where the peat stayed submerged.

Second, the redox potential could vary between the two setups. Unfortunately, our chambers with redox electrodes were limited in number and not leak-tight enough for use in static chamber experiments, and our efforts to measure the redox potential at the end of the experiments were unsuccessful, so we do not have insights into changes of redox potential upon substrate addition. We did choose a soil humidity that led to rather stable redox potential that remained in the range of 210–240 mV even in our dry-out experiments, so we assume that the redox potential was similar in other experiments.

Third, the buildup of headspace gases might lead to changes in the microbial community as microbes utilizing H_2S, MeSH, and Me_2S would grow in numbers and/or become more active. This is supported by the fact that the headspace mixing ratios in the static chambers level off—indicating a dynamic equilibrium where formation and consumption of VSCs balance. In our long-term incubation experiment, we did observe a positive correlation of *Acidobacteria* SD 1, *Desulfosporosinus*, and *Pseudomonas* with time and VSC emissions, and a negative correlation of *Desulfobacca*, uncultured *Desulfobulbaceae*, *Synthrophobacter*, and uncultured *Thermodesulfovibrio*, which might explain the changes in the headspace concentration ratios.

4.3. Possible Alternate Mechanisms

MeSH and Me_2S emissions from H_2S involving methoxylated aromatic compounds, observed in anoxic sphagnum peats (Bak et al., 1992; Finster et al., 1990; Kiene & Hines, 1995; Lomans et al., 1997; Stets et al., 2004), likely do not play a big role in other freshwater environments (Lin et al., 2010). MeSH formation from sulfate reduction without involvement of methoxylated aromatic compounds could take place, either directly via thiol

methyltransferases (Dalby et al., 2018; Drotar et al., 1987), or with methane (Lee et al., 2012), CO (Moran et al., 2008) or CO_2/bicarbonate (Lin et al., 2010; Moran et al., 2007) being involved. Me_2S emissions are most likely not by-products of inefficient methanogenesis, as methanogens were not involved (no inhibition by BES) (Lin et al., 2010; Scholten et al., 2003). Alternatively, abiotic VSC formation by FeS in the presence of CO_2 (Heinen & Lauwers, 1996) would be supported by the fact that Me_2S emissions always increased with inhibitors. However, temperatures above 50°C were needed to observe significant abiotic conversions (Heinen & Lauwers, 1996), supporting a biotic source in our soils. Formation of FeS could decrease H_2S emissions, though we think this unlikely because dissolved iron is mostly complexed by dissolved organic matter in this system (Kugler et al., 2019) and FeS has only been observed in very small quantities in previous studies (Alewell & Novak, 2001).

When we allowed the headspace to build up to high VSC mixing ratios, we found that Me_2S mixing ratios were always much higher than MeSH and H_2S emissions. Me_2S might actually be formed to detoxify H_2S and MeSH (Lomans, Op den Camp, Pol, van der Drift, & Vogels, 1999; Lomans, Op den Camp, Pol, & Vogels, 1999; van Leerdam et al., 2009), suggesting a threshold mixing ratio above which the conversion into the less toxic Me_2S occurs. Still, from our data, the most likely mechanism is organic matter degradation, as the mechanisms discussed above rely on sulfate reduction to H_2S, and we found that Me_2S emissions were independent of sulfate reduction.

4.4. Generalizability of Organic Matter Degradation as a Source of VSC

The range of VSC emissions we observed from our peat soil under anoxic conditions was up to 2 ng/(g_{dw} h) H_2S, 1 ng/(g_{dw} h) MeSH, and 1.5 ng/(g_{dw} h) Me_2S. These emissions extrapolate to approx. 40 mg S/(m^2 a) H_2S, 15 mg S/(m^2 a) MeSH, and 20 mg S/(m^2 a) Me_2S. The H_2S emissions are similar to emissions from American histosol peats and bogs measured by Adams et al. (1981), but the Me_2S emissions are a factor 2–5 higher than their reported values. In comparison to different Florida wetlands, our H_2S and Me_2S release rates are well within the reported range of release rates (Cooper et al., 1987). Estimated Me_2S emissions were similar in magnitude to the maximum emissions observed from Canadian Shield lakes (1.5 µmol/(m^2 d) in our study versus a maximum of 1.2 µmol/(m^2 d), Richards et al., 1991). Comparison to other lake studies is difficult, because usually, only the concentration in the water column is reported.

5. Conclusions

We conclude that Me_2S emissions from organic matter as well as H_2S and MeSH emissions from sulfate reduction are immediate processes, whereas VSC interconversion is a slower, more long-term process generating energy and lowering VSC toxicity. This increases the number of VSC-emitting soils greatly, since organic matter degradation not only occurs in wetlands, but also in more well-drained soils. Thus, future field studies to measure VSC emissions from regions with high litter and soil organic matter contents are warranted, to better constrain their role in global sulfur budgeting.

Data Availability Statement

Code and data are available as a data publication (Lehnert et al., 2021). Amplicon sequencing data were deposited at the National Center for Biotechnology Information Sequence Read Archive (NCBI SRA) and are accessible under the following BioProject accession: PRJNA1010022 (https://www.ncbi.nlm.nih.gov/bioproject/PRJNA1010022), last access 05 September 2023.

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