RE: A point-to-point response to the reviewer's comments

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Title: "Reaction kinetics and multi-sulfur products formation of sulfur-containing volatile organic compounds with OH radicals"

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Dear Prof. Jason Surratt,

Thank you very much for providing us with the opportunity to revise our manuscript. We sincerely appreciate the reviewers' careful evaluation and constructive comments, which have been very helpful for improving the scientific rigor, clarity, and presentation of our work.

In this study, we investigated the •OH-initiated oxidation kinetics and product formation of a series of sulfur-containing volatile organic compounds (sulfur-VOCs) with different functional groups using chamber simulations coupled with Vocus-PTR-LToF-MS and nitrate-CI-LToF-MS. Our results provide kinetic information for several sulfur-VOCs and reveal the formation of multi-sulfur products through bimolecular reactions of sulfur-containing RO_2• under low-NO_x conditions. In addition, sulfur-VOCs emitted from freshwater algae samples were characterized, providing environmental relevance for the investigated sulfur-VOCs and their atmospheric oxidation pathways in our work.

In response to the reviewers' comments, we have conducted additional experiments to accurately obtain OH reaction constants of sulfur-VOCs using other reference species (i.e., isoprene) and carefully revised our manuscript and Supporting Information. The revisions focus on the main issues raised by the reviewers, including the estimation and uncertainty of •OH concentration, the fate of RO_2• under low-NO_x

conditions, the potential influence of PTR-MS fragmentation and semi-quantitative analysis, the incomplete sulfur mass balance associated with the yields of multi-sulfur products, and the atmospheric relevance of the observed low-volatility multi-sulfur products. We have further refined the interpretation of sulfur-VOCs emitted by freshwater algae and revised multiple figures including their corresponding captions to enhance the clarity, accuracy, and scientific rigor of data presentation.

In the point-by-point response below, we address all reviewers' comments in detail, specifying the corresponding revisions implemented in the manuscript and SI. The reviewers' comments appear in *italics*; our responses are in normal font; and all changes introduced in the revised manuscript and SI are highlighted in blue. Line numbers correspond to the clean version of the revised manuscript.

We thank you again for your time and consideration!

Yours sincerely,

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Reviewer #1：

Q0. This manuscript describes a set of experiments exploring the OH oxidation of various sulfur compounds with ranging functionality. The researchers present OH rate constants for a handful of compounds as well as exploring the potential for these sulfur species to form low volatility multi-sulfur compounds. Lastly, the work explores the emission of sulfur compounds from an algae-rich freshwater lake. The authors identify the potential of sulfur compounds to form low volatility multi-sulfur compounds under OH oxidation pointing to a potentially important source of SOA. The work presented investigates an important area of research with findings useful to the community.

In the work's current state, I personally believe the experiment design and parameters are not sufficiently outlined in the main text or SI. More descriptions and experimental information need to be presented for better replication of work and understanding. Conclusions about the multi-sulfur products provide an important finding but need further exploration of the experimental parameters and their comparison to the oxidative environment in which the explored sulfur compounds are emitted. Lastly, the methodology for OH rate constants have some large assumptions that need further exploration. I cannot recommend this publication in its current form. I would request significant revisions before publication.

Response:

We sincerely appreciate Reviewer *#1'*s positive assessment of the importance of this work and the constructive comments and suggestions. We have conducted additional experiments and revised our manuscript and Supporting Information to address the raised concerns, which are experimental design descriptions, atmospheric relevance of multi-sulfur products, and uncertainty in the •OH rate-constant determination method.

First, we expanded the detailed descriptions of the chamber setup and experimental conditions, •OH generation, instrumental operation, calibration procedures, wall/dilution loss correction, and kinetic analysis in the Methods section and Supporting Information to improve reproducibility of our work and understanding.

Second, we sincerely appreciate the reviewer's recognition of our finding regarding

multi-sulfur products—as noted in the comment, "Conclusions about the multi-sulfur products provide an important finding." We have revised the discussion of multi-sulfur products to more clearly define the experimental conditions and the limitations of this finding for atmospheric applications. The revised manuscript now emphasizes that the NO_x-free experiments represent an idealized low-NO_x conditions, and the reported yields are partial gas-phase yields of nitrate-CI-LToF-MS-detected multi-sulfur products rather than total sulfur-containing product yields. Sulfur mass closure cannot be estimated in our experiments.

Third, in light of the assumptions underlying the original rate-constant determination method, we conducted additional relative-rate experiments using isoprene as the reference compound for selected representative sulfur-VOCs covering major functional groups. These new experiments provide a more direct constraint on the •OH reaction rate constants, because they do not rely on applying a single DMS-derived •OH exposure to all sulfur-VOCs. The new reaction rate constants obtained from additional relative-rate experiments for sulfur-VOC species with available literature data, including ethanethiol, DMS, and DMDS, agree well with previous ones, supporting the reliability of our chamber experiments. The comparison between the original DMS-constrained estimates and the new relative-rate results indicates that the DMS-based approach can introduce species-dependent deviations in sulfur-VOC rate constants, especially for compounds with significantly different •OH reactivities. Therefore, in the revised manuscript, the rate constants of some of sulfur-VOCs have been updated by new ones obtained from additional relative-rate experiments.

Major comments:

Q1a. Multiple rate constants are presented in the work, but I have some questions about the OH value calculation and its usage throughout the work. The OH concentration within the chamber is approximated using the decay of DMS. While this is an appropriate application, I don't believe that the calculated OH can be utilized for all other sulfur compounds. The steady-state or experimental OH will depend on multiple factors (in your experiment) including the O_3, RH and OH reactivity. While the OH

production could be relatively consistent given similar O_3 and RH, the order of magnitude difference in OH reactivity of DMS compared to some faster sulfur compounds (DMDS) will lead to a different apparent OH concentration. To account for this, most laboratory experiments investigating rate constants include a reference species with a well-known OH rate constant (e.g. propane, 1,2,4-trimethylbenzene). For this reason, I would encourage more discussion on the uncertainty of the rate constants. If experiments cannot be redone, I would encourage more investigation into the box modeling utilized on DMS to better approximate observations from the chamber.

Response:

We thank the reviewer for this insightful comment regarding the applicability of the DMS-derived •OH concentration. We agree that the •OH concentration inferred from DMS decay represents an effective bulk constraint on chamber •OH exposure (or production) under the experimental conditions, but it may not be universally applicable to all sulfur-VOCs.

To address this concern, we have conducted additional relative-rate experiments using isoprene as the reference compound for selected representative sulfur-VOCs covering major functional groups, including monothiol, dithiol, acyclic sulfide, cyclic sulfide, and disulfide. Isoprene was selected because its •OH reaction rate constant at room temperature is well established. In this work, the •OH reaction rate constant of isoprene was taken as 10.00×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K, consistent with previous kinetic studies (Iida et al., 2002; Medeiros et al., 2018). In these experiments, each selected sulfur-VOC was introduced simultaneously with isoprene into the chamber, and the relative rate constants were derived according to:

$$ln\left(\frac{[sulfur-VOC]_0}{[sulfur-VOC]_t}\right) = \frac{k_{sulfur-VOC}}{k_{isoprene}} ln\left(\frac{[isoprene]_0}{[isoprene]_t}\right)$$

where sulfur-VOC denotes the compound under investigation and isoprene was used as the reference compound. The measured concentrations of sulfur-VOCs and isoprene were corrected by dilution and wall loss. Each relative-rate experiment was conducted in triplicate, and the uncertainties are reported as the standard deviations of the derived

rate constants from the replicate measurements.

A representative time series of DMDS in the additional relative-rate experiments is now provided as Figure R1. In each experiment, the sulfur-VOC and isoprene were introduced simultaneously into the chamber, followed by wall and dilution loss stage prior to UV irradiation.

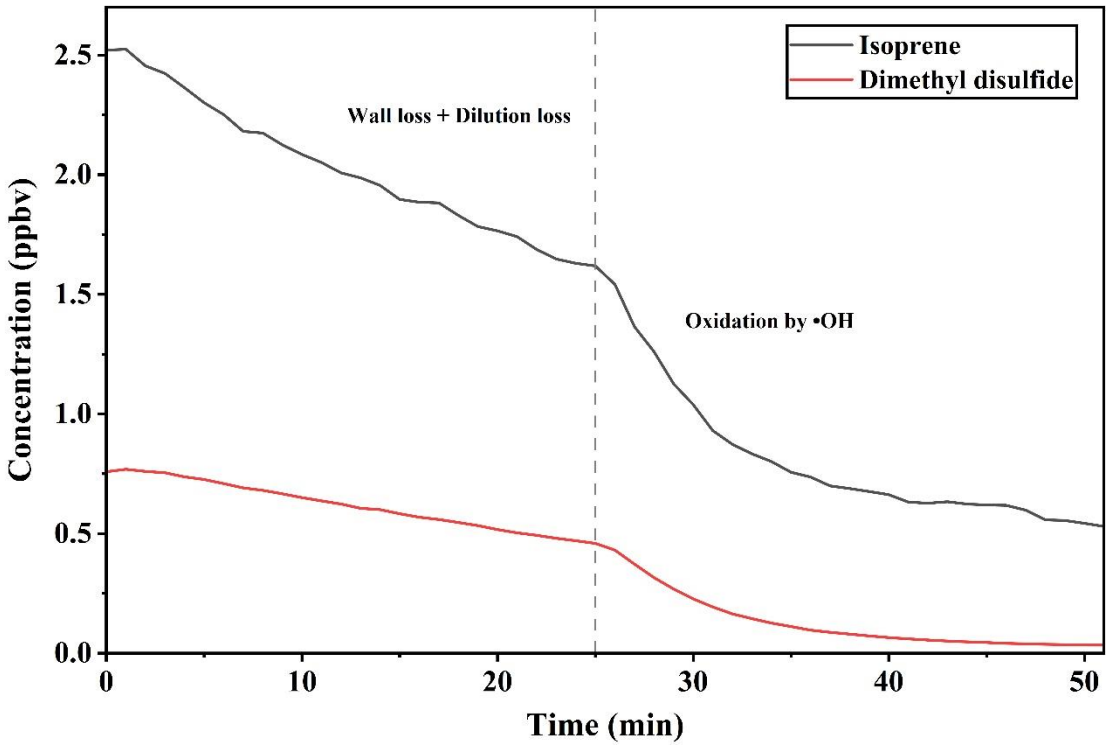


Figure R1 (Figure S4 in our revised SI). Representative time series of isoprene and dimethyl disulfide during an additional relative-rate experiment.

The new results from the additional relative-rate experiments were summarized in Table R1 (Table 2 in our revised manuscript).

Table R1 (Table 2 in our revised manuscript). The •OH reaction rate constants of selected sulfur-VOCs determined by the relative-rate method using isoprene as a reference species at 298 ± 2 K.

Species	sulfur-VOCs	Formulae	$k \times 10^{11}$ (cm^3 $molecule^{-1}$ s^{-1})	T (K)	p (Pa)	Buffer gas	Technique [a]	References
Monothiol	ethanethiol	CH_3CH_2SH	3.89 ± 0.57	298	1.01×10^5	air	CP-GC	Wang et al., 2008
			4.50 ± 0.50	300	1.01×10^5	N_2	CP-GC	Barnes et al., 1986
			4.21 ± 0.32	298	1.0×10^4	Ar	FP-RF	Wine et al., 1984
			4.51 ± 0.32	298±2	1.01×10^5	air	Vocus-PTR	This work
Dithiol	1,2-ethanedithiol	$HS(CH_2)_2SH$	14.36 ± 0.26	298±2	1.01×10^5	air	Vocus-PTR	This work
Acyclic sulfide	dimethyl sulfide	CH_3SCH_3	0.87 ± 0.03	298	1.01×10^5	air	CP-GC	Wang et al., 2008
			0.78 ± 0.18	299	1.01×10^5	air	CP-FTIR	Albu et al., 2005
			0.80 ± 0.05	298±3	1.01×10^5	air	CP-GC	Barnes et al., 1988
			0.83 ± 0.08	298±2	1.01×10^5	air	Vocus-PTR	This work
	bis(methylthio)methane	$CH_3SCH_2SCH_3$	3.50 ± 0.09	298±2	1.01×10^5	air	Vocus-PTR	This work
Cyclic sulfide	trimethylene sulfide	C_3H_6S	26.99 ± 1.04	298±2	1.01×10^5	air	Vocus-PTR	This work
	1,3-dithiolane	$C_3H_6S_2$	0.95 ± 0.05	298±2	1.01×10^5	air	Vocus-PTR	This work
Disulfide	dimethyl disulfide	$CH_3S_2CH_3$	23.90 ± 3.00	297	1466	N_2	HPF-LIF	Abbatt et al., 1992
			19.80 ± 1.80	298	6666-26664	Ar	FP-RF	Wine et al., 1981
			22.30 ± 8.00	298	1.01×10^5	air	CP-GC	Cox and Sheppard, 1980
			20.18 ± 1.53	298±2	1.01×10^5	air	Vocus-PTR	This work

Note: The •OH reaction rate constant of isoprene was taken as 10.00×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Iida et al., 2002; Medeiros et al., 2018). The uncertainties of rate constants represent the standard deviations of triplicate measurements.

[a] CP: continuous photolysis; GC: gas chromatography; FTIR: Fourier transform infrared spectroscopy; FP: flash photolysis; RF: resonance fluorescence; HPF: high-pressure fast flow; LIF: laser-induced fluorescence.

The relative-rate-derived rate constants for species with available agree well with previous literature data under 298 ± 2 K. For example, the rate constants obtained for ethanethiol, DMS, and DMDS are 4.51 ± 0.32, 0.83 ± 0.08, and 20.18 ± 1.53 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively, which are consistent with the corresponding literature values at the similar temperature. In particular, the relative-rate-derived value for DMDS agrees much better with previous measurements than the original DMS-constrained estimate, indicating that the DMS-constrained •OH exposure approach can introduce species-dependent deviations for highly reactive sulfur-VOCs.

These results demonstrate that the relative-rate method provides a more direct and robust determination of •OH reaction rate constants because it does not rely on an external •OH concentration estimated from a single sulfur-VOC compound. Accordingly, in the revised manuscript, the reaction rate constants of the selected sulfur-VOCs have been updated by the new ones obtained from the additional relative-rate experiments (Table R1). We have also revised the Methods and Discussion sections to clarify the relative-rate methodology, the wall/dilution loss correction, and the limitations of using DMS-derived •OH exposure for compounds with different reactivities.

Q1b. I believe more discussion is needed with respect to the potential H-migration and its role in the formation and/or competition with the RO_2+RO_2 reactions. As per Figure S7, the HO_2 and RO_2 in the chamber are modeled to be very low (<50 ppt). This would allow for very long RO_2 lifetimes and thus increased potential for isomerization reactions. Using 0.1 s^{-1} for the DMS RO_2 isomerization, 90% of this RO_2 should isomerize and form HPMTF. I encourage building upon the recent work that has extensively explored the autoxidation of DMS and DMDS. This literature can help inform and constrain the RO_2, then explore other sulfur compounds.

Response:

We agree that H-migration can become highly competitive under the modeled low HO_2• and RO_2• conditions. To address this issue quantitatively, the H-shift isomerization of the initially formed DMS-derived RO_2• (i.e., CH_3SCH_2OO•), was

explicitly represented in the box-model analysis using a first-order rate coefficient of 0.1 s^{-1}. This value is consistent with recent room-temperature DMS oxidation studies reporting $CH_3SCH_2OO•$ isomerization rate coefficients on the order of 0.1 s^{-1} and the formation pathway of hydroperoxymethyl thioformate (HPMTF) (Berndt et al., 2019; Jernigan et al., 2022; Ye et al., 2022).

The revised model results support the reviewer's estimate that the initially formed DMS-derived $RO_2•$ is expected to isomerize efficiently. In the simplified box-model analysis, H-shift accounts for 92.7% of the initial fate of RO_2-MSP ($CH_3SCH_2OO•$) on average during 1-6 min, whereas direct RO_2-MSP + $RO_2•$ and RO_2-MSP + $HO_2•$ reactions account for 3.8% and 3.6%, respectively. This result indicates that H-migration is a dominant competing pathway for the initially formed DMS-derived $RO_2•$ under our chamber conditions, and that direct bimolecular reactions of this initial $RO_2•$ radical are expected to be minor. This interpretation is also consistent with the relatively low apparent yields of DMS-derived multi-sulfur products observed in this study. Therefore, the efficient H-shift isomerization of the initially formed DMS-derived $RO_2•$ can restrain the formation of multi-sulfur products, but a minor fraction of sulfur-containing $RO_2•$ still can proceed through bimolecular pathways to form multi-sulfur products under the present NO_x-free conditions. This result has been added to Text S6 and is shown in Figure R2.

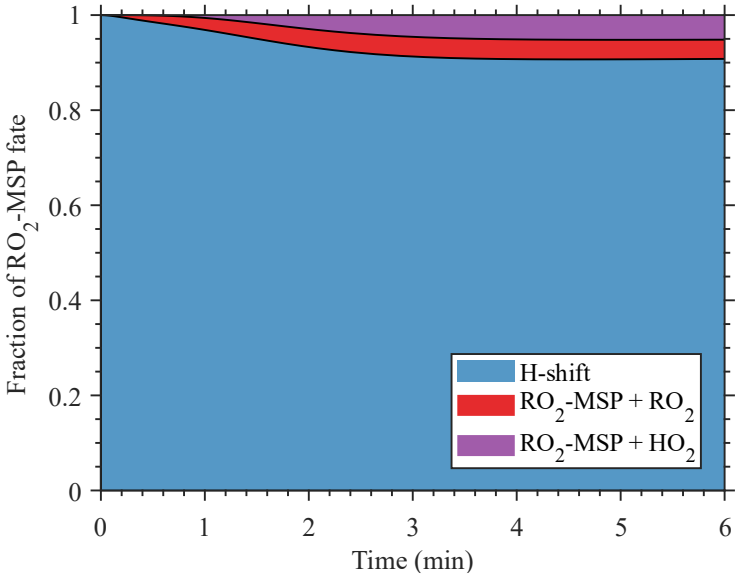


Figure R2 (Figure S7 in our revised SI). Simulated initial fate of the DMS-derived RO_2-MSP radical during DMS oxidation under NO_x-free conditions (Exp. 10 in Table 1). The pathways include intramolecular H-shift, RO_2-MSP + RO_2•, and RO_2-MSP + HO_2• reactions. H-shift was represented using a first-order rate coefficient of 0.1 s^{-1}. The results show that H-shift dominates the initial fate of RO_2-MSP under the present chamber conditions.

Based on this analysis, we revised the interpretation of multi-sulfur product formation in the DMS oxidation system. The observed multi-sulfur products from DMS oxidation are no longer described as products formed solely or directly from reactions of the initially formed DMS-derived RO_2•. Instead, we now state more cautiously that H-migration competes strongly with direct bimolecular loss of the initial DMS-derived RO_2•, and that the detected DMS-derived multi-sulfur products should be interpreted as evidence for potential bimolecular reactions involving sulfur-containing RO_2• under NOx-free conditions.

It should be noted that the explicit H-shift analysis was conducted only for the initially formed DMS-derived RO_2-MSP (CH_3SCH_2OO•), because relatively well-constrained H-shift rate information is available for this RO_2• from recent DMS oxidation studies associated with HPMTF formation. For the other sulfur-VOCs investigated in this work, analogous RO_2• H-migration rate coefficients are not

available, and their multi-sulfur products were therefore not interpreted using the same quantitative H-shift competition framework. Instead, these products are discussed qualitatively as potential products from sulfur-containing RO_2• + $R'O_2$• bimolecular chemistry under NO_x-free conditions.

Accordingly, the previous discussion of the competition between RO_2• + RO_2• and RO_2• + HO_2• reactions within the total sulfur-containing RO_2• pool has been removed, because such partitioning represents only the simplified bimolecular loss channels considered in the DMS model and should not be interpreted as a complete RO_2• fate budget or as a quantitative constraint on multi-sulfur product yields.

Representative revision in the manuscript, Lines 275-284:

"Notably, under NO_x-free conditions, sulfur-containing RO_2• are not efficiently removed by NO, and their subsequent fate is expected to involve the competition among unimolecular isomerization via H-migration, and bimolecular reactions of RO_2• + HO_2• and RO_2• + $R'O_2$• (Jenkin et al., 2003; Orlando and Tyndall, 2012). Recent studies of DMS oxidation have shown that H-shift isomerization of CH_3SCH_2OO• can be an important pathway associated with hydroperoxymethyl thioformate (HPMTF) formation (Berndt et al., 2019; Jernigan et al., 2022; Ye et al., 2022). In the box-model analysis of DMS oxidation by •OH, this H-shift process was included to evaluate its competition with bimolecular reactions of RO_2• (Text S6; Figure S7). The model results indicate that H-shift dominates the initial fate of CH_3SCH_2OO• under the present chamber conditions."

Q1c. Overall, there seems to be a lack of citations or validation for some of the comments made throughout the work. Comprehensive citations referencing mechanisms, techniques and analysis used and previous sulfur work is missing. Additionally, work on sulfur oxidation and emissions have been studied over the past 4 decades and none of that original work seems to be acknowledged in this work.

Response:

We thank the reviewer for this valuable and constructive suggestion. We agree that the original manuscript did not sufficiently cite and acknowledge previous studies on

sulfur emissions, oxidation mechanisms, measurement techniques, and analytical methods used in this work. In the revised manuscript and Supporting Information, we have substantially expanded the citation framework and linked the added references to specific scientific statements and comments. In total, 26 new references were added to the revised manuscript and Supporting Information.

First, we added foundational studies on atmospheric sulfur emissions, DMS/DMSP cycling, and the climatic relevance of natural sulfur sources to better acknowledge previous sulfur work over the past several decades. Newly added references include Andreae and Raemdonck (1983), Charlson et al. (1987), Bates et al. (1992), Andreae and Crutzen (1997), Kettle et al. (1999), Kiene and Linn (2000), and Stefels et al. (2007) together with related recent studies on sulfur-derived aerosol formation and marine biogenic sulfur emissions, such as Fiddes et al. (2021), Jokinen et al. (2022), Revell et al. (2024), Novak et al. (2022), Zhao et al. (2021), Mynard et al. (2025), and Rocco et al. (2025). These references were added mainly to the section of Introduction to support the discussion of DMS as a major biogenic sulfur compound, its biological production through the DMSP pathway, and its role in atmospheric sulfur cycling and aerosol-climate interactions.

Representative revision in the manuscript, Lines 44-50:

"These compounds play a key role in the global atmospheric sulfur cycle, and their atmospheric oxidation products such as sulfuric acid (H_2SO_4) and methanesulfonic acid (CH_3SO_3H) are able to combine with basic species (e.g., NH_3 and amines) to form new particles and particulate sulfate, which can contribute to the formation of cloud condensation nuclei (CCN) and then have an effect on regional and global climate (Bates et al., 1992; Charlson et al., 1987; Fiddes et al., 2021; Jokinen et al., 2022; Revell et al., 2024; Wang et al., 2023a)."

Second, we strengthened the citations of previous studies to support atmospheric oxidation kinetics and mechanisms of sulfur-VOCs. Newly added or retained references include Cox and Sheppard (1980), Wine et al. (1981, 1984), Barnes et al. (1986, 2006), Atkinson (1990), Abbatt et al. (1992), Atkinson and Arey (2003), Atkinson et al. (2004),

and Cruz-Torres and Galano (2007). These references now support the statements that sulfur-VOCs can be oxidized by multiple atmospheric oxidants, including •OH, NO_3•, and O_3, and their •OH reactivity depends strongly on their molecular structures.

Representative revision in the manuscript, Lines 81-84:

"Once released into the atmosphere, sulfur-VOCs can undergo oxidation by multiple atmospheric oxidants, including hydroxyl radicals (•OH), nitrate radicals (NO_3•), and ozone (O_3), with •OH typically acting as the dominant daytime oxidant and NO_3• becoming important during nighttime (Atkinson and Arey, 2003; Barnes et al., 2006; Du et al., 2007; Stark et al., 2007)."

Third, we incorporated recent mechanistic studies on sulfur-containing RO_2 radicals, including H-migration, autoxidation, and HPMTF-related reaction pathways to improve the interpretation of sulfur-RO_2• chemistry and multi-sulfur product formation. Newly added references include Berndt et al. (2019, 2023, 2024), Jernigan et al. (2022), Shen et al. (2022), Ye et al. (2022), Goss and Kroll (2023), and Chen et al. (2023), and related RO_2• chemistry studies such as Jenkin et al. (2003, 2015), Orlando and Tyndall (2012), Cho et al. (2023), and Nozière (2025). These references were cited to support the discussion of the reactions of RO_2• + HO_2• and RO_2• + $R'O_2$•, H-migration, and potential bimolecular sulfur-RO_2• chemistry under low-NO_x conditions.

Fourth, we added relevant references to better support the measurement techniques and semi-quantitative analyses used in this study. References on the working principles and quantification uncertainties of PTR-ToF-MS, including Hansel et al. (1995), Krechmer et al. (2018), and Yuan et al. (2017) were added to support the discussion of molecular assignment, compound-dependent sensitivities, and semi-quantitative uncertainty. Additionally, some references on nitrate-CIMS detection and semi-quantification of sulfuric acid and highly oxygenated organic molecules, including Jokinen et al. (2012), Ehn et al. (2014), Hyttinen et al. (2015), Bianchi et al. (2019), and Tiusanen et al. (2023), were also added to support the detection and semi-quantification of formed multi-sulfur products.

Representative revision in the manuscript, Lines 361-368:

"It should be noted that the semi-quantification of these multi-sulfur products is based on the calibration factor of gaseous sulfuric acid (H_2SO_4) (Text S2), a common approach in nitrate-CIMS measurements due to the lack of authentic standards for highly oxygenated organic compounds (Ehn et al., 2014; Jokinen et al., 2012). It was assumed that the ionization efficiency of multi-sulfur products towards the reagent ions ($(HNO_3)_n \cdot NO_3^-$, n=0, 1 and 2) is the same as that of H_2SO_4. As a result, the reported yields may have an additional uncertainty because of ionization efficiency difference between H_2SO_4 and multi-sulfur products towards the reagent ions, as discussed in previous studies (Ehn et al., 2014; Hyttinen et al., 2015)."

In summary, these newly added references together with original references provide a more complete and better-supported literature framework for sulfur-VOC emissions, atmospheric sulfur cycling, atmospheric oxidation mechanisms of sulfur-VOCs, analytical techniques, and semi-quantitative uncertainty analysis, while explicitly acknowledging foundational studies on sulfur oxidation and emissions over the past several decades.

Minor comments:

Q2. Line 54: Ronald P. Kiene performed a lot of good work exploring DMSP and its transformation in the marine system. This and subsequent work should be acknowledged.

Response:

We thank the reviewer for this valuable suggestion. The discussion of DMSP transformation in marine systems has been revised to explicitly acknowledge foundational works by Ronald P. Kiene and subsequent related studies. In particular, we added the references to illustrate that DMSP can undergo microbial cleavage and demethylation in marine systems, producing reduced sulfur compounds such as DMS and methanethiol. These references include the early work on DMSP demethylation and thiol production in anoxic marine sediments (Kiene and Taylor, 1988), methanethiol production from DMSP in marine surface waters (Kiene, 1996), tracer-based studies on the fate of dissolved DMSP in seawater (Kiene et al., 2000), and related

studies on DMSP microbial transformation pathways (Kiene and Service, 1991; Visscher et al., 1994; Yoch, 2002). These references have been incorporated into the section of Introduction to better recognize the established DMSP literature and to provide clearer background for the biogenic origin of sulfur-VOCs.

Representative revision in the manuscript, Lines 54-58:

"Foundational studies by Kiene and co-workers demonstrated that DMSP can be transformed in marine systems through microbial cleavage and demethylation pathways, leading to the formation of reduced sulfur compounds such as DMS and methanethiol (Kiene, 1996; Kiene et al., 2000; Kiene and Taylor, 1988; Kiene and Service, 1991; Visscher et al., 1994; Yoch, 2002)."

Q3. Line 77: OH is not the only oxidant of DMS and sulfur compounds, but it is the dominant during the day.

Response:

The statement has been revised to avoid implying that •OH is the only atmospheric oxidant of DMS and other sulfur-VOCs. The revised text now explicitly mentions that sulfur-VOCs can also be oxidized by •OH, NO_3• and O_3, while clarifying that •OH is typically the dominant oxidant during daytime and NO_3• can become important during nighttime. Additional references have been added to support this statement, including Atkinson and Arey (2003), Barnes et al. (2006), Du et al. (2007), and Stark et al. (2007).

Q4. Line 80: Rate constants are temperature dependent when presented should have the temperature at which it is calculated. There are multiple instances throughout the piece where a temperature of the rate constant should be present.

Response:

The reported kinetic parameters have been revised to include the corresponding temperatures. Owing to the rate constants reported in this work were derived under the temperature of 298 ± 2 K, this temperature has been specified when presenting our measured values. For cited rate constants from previous studies for inter-comparison, the corresponding temperatures have also been listed in Table 2.

Q5. Line 108: A description of the mass spectrometers needs to also be in the methods and should have more description of operation.

Response:

A comprehensive description of the operational principles—including reagent ions, ion–molecule reaction pathways, and sample introduction protocols—for both mass spectrometers employed in this study (i.e., Vocus-PTR-LToF-MS and nitrate-CI-LToF-MS), has been incorporated into the section of Methods. For the Vocus-PTR-LToF-MS, the text now specifies that hydronium ions and their water-cluster ions, including H_3O^+, $(H_2O)_2 \cdot H^+$, and $(H_2O)_3 \cdot H^+$ were adopted to detect sulfur-VOCs via proton transfer reactions. For the nitrate-CI-LToF-MS, the text now describes the nitrate reagent ions, including NO_3^-, $HNO_3 \cdot NO_3^-$, and $(HNO_3)_2 \cdot NO_3^-$, and clarifies that sulfuric acid and highly oxygenated organic oxidation products are detected mainly through nitrate-adduct cluster formation. Additional operational details, including mass resolution, mass calibration, and calibration procedures, are provided in Text S1.

Representative revision in the manuscript, Lines 146-152:

"The Vocus-PTR-LToF-MS detects sulfur-VOCs mainly through proton-transfer reactions between reagent ions (i.e., hydronium ions (H_3O^+) and their water-cluster ions ($(H_2O)_2 \cdot H^+$, and $(H_2O)_3 \cdot H^+$)) and sulfur-VOCs with proton affinities higher than that of water. The nitrate-CI-LToF-MS employs nitrate reagent ions, including NO_3^-, $HNO_3 \cdot NO_3^-$, and $(HNO_3)_2 \cdot NO_3^-$, to detect sulfuric acid and highly oxygenated organic oxidation products mainly through nitrate-adduct cluster formation. Additionally, a more detailed description of instrument operation, mass calibration, and calibration procedures is provided in Text S1."

Q6. Line 167: There is a tilda (~) as well as error constraints on the OH concentration. This is confusing as tilda points to approximate, but you give tight constraints. This is contradictory. I also strongly encourage the removal of tildas throughout the piece especially when values were calculated and closely measured.

Response:

We thank the reviewer for this suggestion. The use of the tilde symbol has been

removed throughout the whole manuscript and Supporting Information.

Q7. Line 174: Rate constants need the temperatures at which they were calculated.

Response:

The corresponding sentences in the whole manuscript and Supporting Information have been revised to explicitly state that the reported rate constants were obtained at the experimental temperature of 298 ± 2 K. Besides, the temperature information for the cited rate constants have also added.

Q8. Line 182: What is the "current value" of the DMDS rate constant? Please add citations.

Response:

The ambiguous phrase "the current value" has been removed and replaced with the explicitly determined DMDS + •OH reaction rate constant from the additional isoprene relative-rate experiments. In the revised manuscript, the DMDS + •OH rate constant obtained in this work is reported as $20.18 \pm 1.53 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 ± 2 K. This value is compared with previously reported room-temperature literature values, including $23.90 \pm 3.00 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 297 K from Abbatt et al. (1992), $19.80 \pm 1.80 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K from Wine et al. (1981), and $22.30 \pm 8.00 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K from Cox and Sheppard (1980). These citations have been added in the revised Table 2 and the corresponding discussion.

Q9. Figure 1: Please add error bars to the data points as I assume the 1 min data points are 1 min averages.

Response:

In the original submission, Figure 1 showed the temporal decay of sulfur-VOCs based on 1 min averaged signals. As discussed in response to Q1a, we have conducted additional relative-rate experiments using isoprene as the reference compound, which provide more direct constraints on the •OH reaction rate constants. Therefore, in the revised manuscript, the original time-dependent decay plots have been replaced by relative-rate plots derived from the new experiments (Figure R3).

In Figure R3, each data point represents the paired loss-corrected logarithmic depletion of a sulfur-VOC and isoprene measured under the same chamber conditions. The uncertainties in the derived rate constants are reported in Table R1 as the standard deviations from triplicate relative-rate experiments.

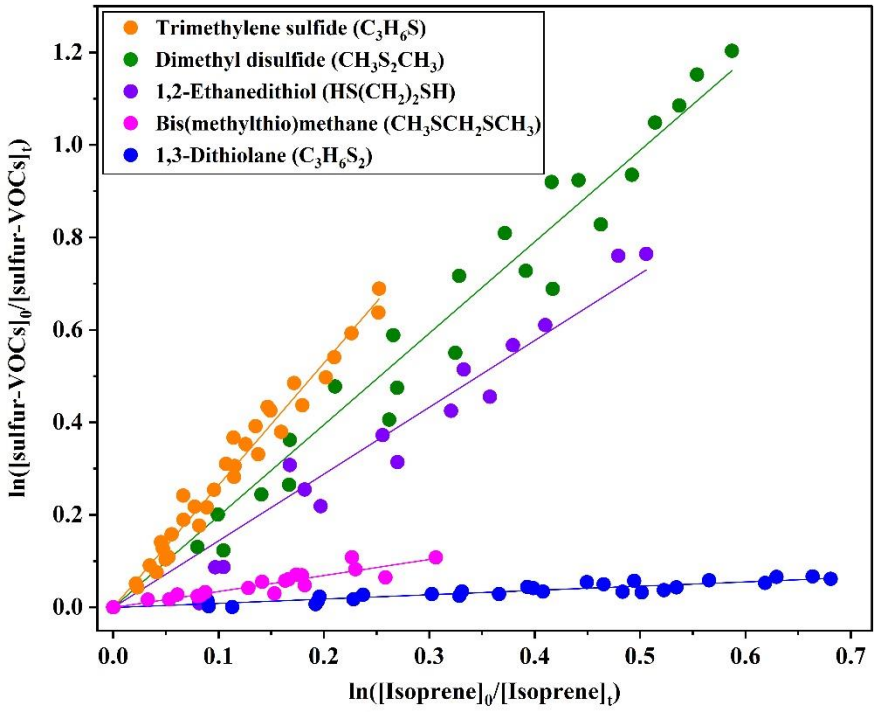


Figure R3 (Figure 1 in our revised manuscript). Relative-rate plots for selected sulfur-VOCs using isoprene as the reference compound. The loss-corrected logarithmic depletion of each sulfur-VOC is plotted against that of isoprene. Different colors indicate different sulfur-VOCs, and solid lines denote linear regressions used to derive the •OH reaction rate constants.

Q10. Table 2: The JPL Publication 19-5 indicates that some of the sulfur compounds reported have temperature dependent rate constants, I would recommend calculating them at 291K to better compare your derived value.

Response:

In our revised manuscript, the original kinetic results in Table 2 have been updated by the newly determined rate constants obtained from the additional relative-rate experiments using isoprene as the reference compound at 298 ± 2 K, as described in response to Q1a. Literature values are also listed together with their reported experimental temperatures, and most available comparison values for the selected

sulfur-VOCs were measured near room temperature (297-300 K), making them directly comparable to our relative-rate results.

For compounds with evaluated temperature-dependent recommendations available in JPL Publication 19-5 or IUPAC, these evaluations were considered where applicable to ensure that the comparison was temperature-consistent.

Q11. Line 203: Acyclic sulfur compounds and well as cyclic should and can undergo OH-addition reactions, which are enhanced under cooler temperatures. This is mostly omitted for discussions about H abstraction. I encourage more discussion here.

Response:

The discussion of structure-dependent reactivity has been revised to include both H-abstraction and •OH-addition pathways. The original text emphasized H-abstraction from α-C-H bonds for acyclic sulfides and did not sufficiently acknowledge that •OH-addition to the sulfur atom can also contribute, particularly at lower temperatures. The revised text now states that acyclic sulfides and cyclic sulfides can react with •OH through both H-abstraction and •OH-addition pathways. We also clarify that the rate constants determined in this study represent overall precursor decay rate constants; therefore, the relative importance of different initiation channels is discussed based on literature mechanisms rather than directly quantified as separate branching ratios in the present experiments.

Representative revision in the manuscript, Lines 249-257:

"Acyclic and cyclic sulfides can react with •OH through both H-abstraction from α-C-H bonds and •OH-addition to the sulfur atom. Previous studies have shown that the •OH-addition pathway can become more competitive under lower-temperature conditions (Barnes et al., 2006; Ye et al., 2022). Because the rate constants reported here are derived from overall precursor decay, the observed values represent the combined contribution of possible initiation pathways, and the relative branching between H-abstraction and •OH-addition cannot be directly separated in the present experiments. Overall, the kinetic results demonstrate that the •OH reaction rate constants of sulfur-VOCs depend on molecular features, such as reactive S-H groups,

sulfur functionality, α-C-H sites and ring strain."

Q12. Line 245-262: A significant portion of this section discusses the RO_2-RO_2 combinations and the potential to for "multi-sulfur" species. How does the eventual yields of these compounds compare when these compounds are oxidized in the atmosphere? I would expect CH_3O_2 and $CH_3C(O)OO$ would be dominant in the atmosphere. I encourage discussion of how the findings here will translate to the remote atmosphere. Additionally, I encourage discussion about carbonyls and hydroxyls that can for from RO_2 + RO_2 reactions.

Response:

This section has been revised to clarify the atmospheric interpretation of the multi-sulfur product yields. The chamber experiments were conducted under NO_x-free conditions with precursor concentrations higher than those typically found in the remote atmosphere. These conditions favor longer sulfur-containing RO_2• lifetimes and enhance the probability of sulfur-RO_2• + sulfur-R'O_2• reactions. Therefore, the product yields reported in this study should be interpreted as chamber-based yields under idealized low-NO_x conditions, rather than as direct atmospheric yields.

In the ambient atmosphere, HO_2•, NO, and organic peroxy radicals, including CH_3O_2• and $CH_3C(O)OO$•, can compete with sulfur-RO_2• + sulfur-R'O_2• reactions and thereby suppress the formation of multi-sulfur products. We have therefore revised the discussion to state more cautiously that the observed multi-sulfur products represent a potential formation pathway favored under low-NO_x conditions with sufficient sulfur-containing RO_2• abundance. The main purpose of reporting these yields is to demonstrate the formation and detection of low-volatility multi-sulfur products from sulfur-VOC oxidation, rather than to provide direct atmospheric product yields applicable to all environments.

We also expanded the discussion of RO_2• + R'O_2• chemistry to acknowledge that these reactions do not exclusively produce accretion/peroxide-type products. Depending on the reaction channel, RO_2• + R'O_2• reactions can also produce carbonyl- and hydroxyl-containing products, including alcohol-type products, through radical

termination pathways.

Q13. Line 339: Molecular formulas (e.g CH_2S, C_2H_6S) are given mixing ratios with little discussion of how and what absolute sensitivity was used to calculate. Without knowledge of the compound how was the sensitivity to that compound applied? I would encourage adding uncertainty or clarification on how this was calculated as DMS and EtSH are isobaric but can have different calibration factors.

Response:

The quantification method for algae-emitted sulfur-containing formula-level signals has been clarified in both the main text and Text S4 in SI. The reported apparent mixing ratios were calculated based on calibrated Vocus-PTR-LToF-MS signals using selected sulfur-VOC standards. As shown in Figure S13, calibration curves were obtained for methanethiol, DMS, ethyl methyl sulfide, and DMDS, with sensitivities of 0.61, 0.92, 0.57, and 0.82 cps $pptv^{-1}$, respectively. To make the calibration strategy clearer, Table S5 has been revised to include the sensitivity assignment for each detected sulfur-VOCs (Table R2).

For sulfur-VOCs without compound-specific standards, proxy sensitivities were assigned according to the number of sulfur atoms in the assigned molecular formula: the DMS sensitivity was used for mono-sulfur organic signals, whereas the DMDS sensitivity was used for multi-sulfur organic signals.

Table R2 (Table S5 in our revised SI). Molecular formulas, molecular masses, sulfur atom numbers, semi-quantitative apparent mixing ratios, and sensitivity assignments of sulfur-VOCs detected from freshwater algae emissions by Vocus-PTR-LToF-MS.

Molecular formula	Molecular mass	Number of sulfur atoms	Apparent mixing ratio (ppbv)	Sensitivity (cps $pptv^{-1}$)
CH_2S	45.9877	1	4.09	0.92
CH_4S	48.0033	1	11.77	0.61
C_2H_4S	60.0033	1	3.57	0.92
C_2H_6S	62.0190	1	8.60	0.92
C_3H_6S	74.0190	1	0.69	0.92
C_3H_8S	76.0346	1	1.19	0.57
CH_2S_2	77.9597	2	0.08	0.82
CH_4S_2	79.9754	2	0.04	0.82
$C_2H_4S_2$	91.9754	2	0.19	0.82
$C_2H_6S_2$	93.9910	2	0.32	0.82
$C_3H_4S_2$	103.9754	2	0.25	0.82
$C_3H_6S_2$	105.9910	2	0.69	0.82
$C_3H_8S_2$	108.0067	2	0.31	0.82
$C_5H_8S_2$	132.0067	2	0.06	0.82
$C_6H_{14}S_2$	150.0536	2	0.78	0.82
$C_2H_6S_3$	125.9631	3	0.07	0.82
$C_3H_6S_3$	137.9631	3	0.06	0.82
$C_4H_{10}S_3$	153.9944	3	0.50	0.82
$C_2H_6S_4$	157.9352	4	0.01	0.82
$C_3H_6S_4$	169.9352	4	0.01	0.82

Note: The selected calibration standards included methanethiol, DMS, ethyl methyl sulfide, and DMDS, with sensitivities of 0.61, 0.92, 0.57, and 0.82 cps $pptv^{-1}$, respectively. For sulfur-VOCs without compound-specific standards, DMS and DMDS sensitivities were used as proxies for mono-sulfur and multi-sulfur species, respectively. The listed mixing ratios represent semi-quantitative apparent rather than unambiguous isomer-specific concentrations.

The reviewer is correct that Vocus-PTR-LToF-MS cannot distinguish isomeric species with the same molecular formula, such as DMS and ethanethiol (C_2H_6S), solely

by exact mass. These isomeric species may have different PTR-MS sensitivities due to differences in proton-transfer kinetics. Therefore, the revised manuscript explicitly states that the reported mixing ratios represent formula-level apparent values and may include additional uncertainty associated with proxy-sensitivity assignment and possible isomeric contributions.

Representative revision in the manuscript, Lines 404-408:

"Because Vocus-PTR-LToF-MS measurements constrain molecular formulas rather than isomer-specific structures, isomeric species (e.g., DMS and ethanethiol, C_2H_6S) cannot be distinguished solely by their exact mass and may have different sensitivities. Therefore, the reported mixing ratios should be interpreted as semi-quantitative apparent ones rather than definitive isomer-specific concentrations."

Q14. Line 340: PTR-MS have been shown to produce fragmentation and artifacts generated within the drift /ionization region. During your single component calibrations was there any evidence of fragmentation and if so where fragments accounted for in the concentration calculations as well as the mass defect plots (i.e. Figure 4a)?

Response:

Fragment-like ions were checked based on single-component calibration experiments of representative sulfur-VOC standards, including ethanethiol, 1,2-ethanedithiol, DMS, trimethylene sulfide, and DMDS. Several low-abundance fragment-like ions were observed to vary synchronously with the corresponding parent ions during standard-gas introduction, suggesting possible PTR ionization-related fragmentation. However, because trace impurities or other ionization-related artifacts cannot be completely excluded, these ions are conservatively referred to as "fragment-like ions" rather than definitive fragments.

To document this evaluation, we added new figures showing the time series of selected parent ions and fragment-like ions during single-component calibrations (Figure R4) and a new table summarizing the signal ratios of fragment-like ions to their parent ions calculated from stable calibration plateaus (Table R3). Fragment-like ions

were identified based on their synchronous temporal variation with the parent ions during standard-gas introduction. The observed fragment-like ion signals were generally small, with fragment-to-parent ratios ranging from 2.0 % to 10.0 % for the representative standards examined. These evidences suggest that the effect from fragment-like ions on our calibrations was minor. Therefore, these fragment-like ions were not taken into account for the calibrations of sulfur-VOCs.

Besides, to eliminate the potential influence of fragment-like ions, they have been removed from Figure 4a (Figure R3).

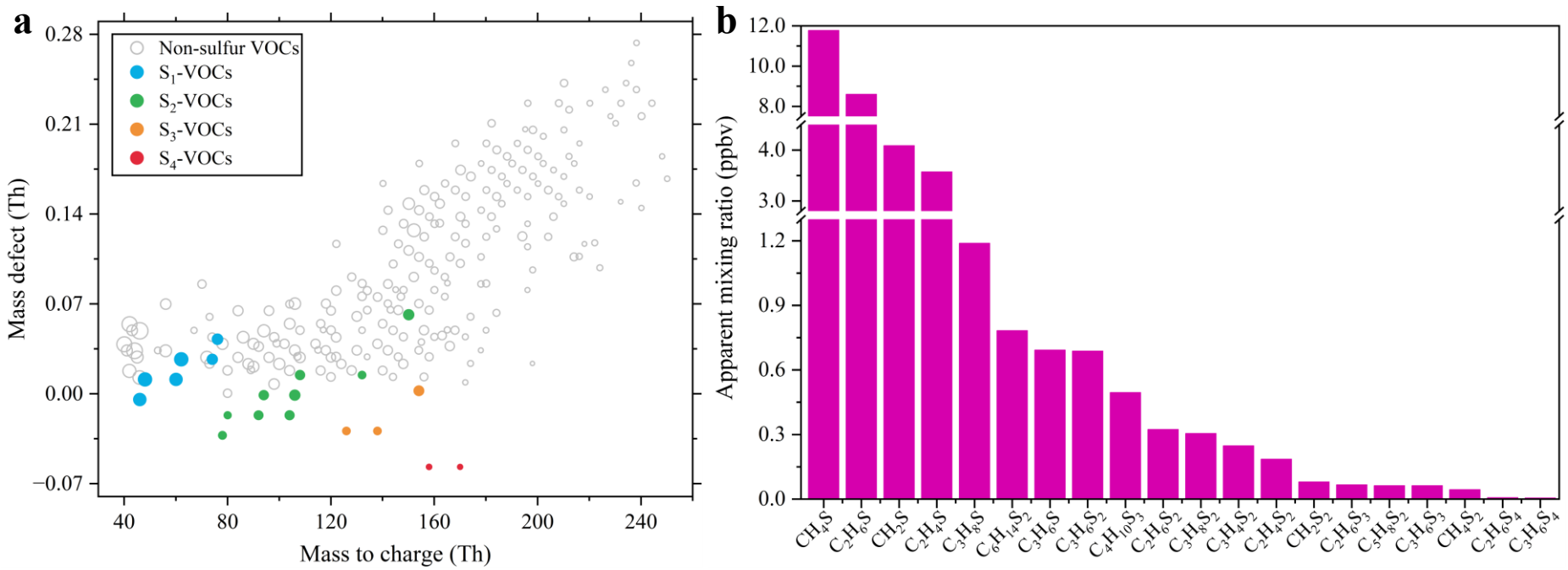
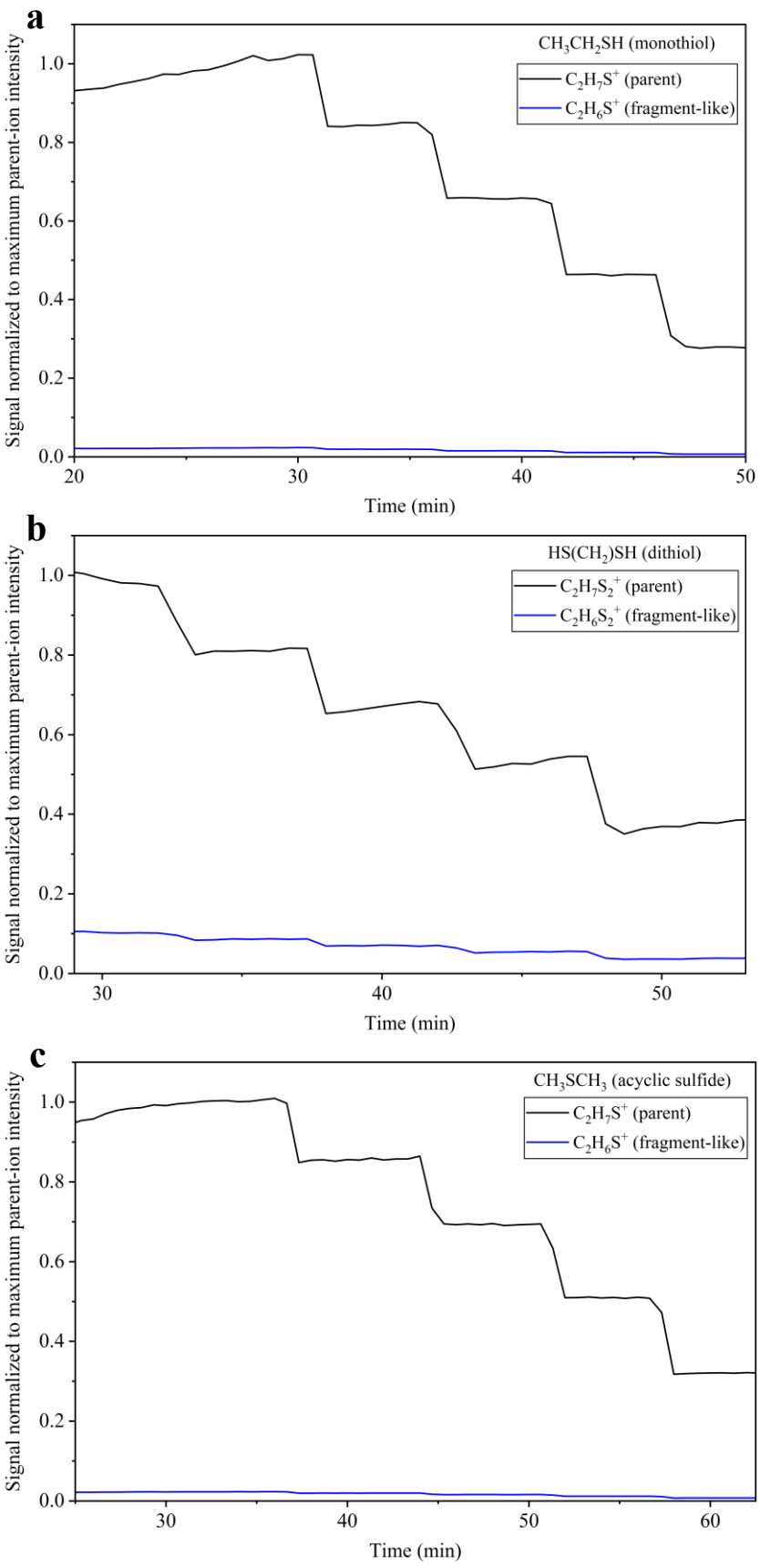


Figure R4 (Figure 4 in our revised manuscript). (a) Mass-defect plot of VOCs detected by Vocus-PTR-LToF-MS before oxidation. The 20 sulfur-VOCs are highlighted and grouped according to the number of sulfur atoms in their assigned molecular formulas, while non-sulfur VOCs are shown in gray. Marker size represents normalized PTR-MS signal intensity rather than calibrated concentration. (b) Semi-quantitative mixing ratios of the 20 sulfur-VOCs detected from the algal emissions.


a
CH3CH2SH (monothiol)
C2H7S+ (parent)
C2H6S+ (fragment-like)
Signal normalized to maximum parent-ion intensity
Time (min)
b
HS(CH2)SH (dithiol)
C2H7S2+ (parent)
C2H6S2+ (fragment-like)
Signal normalized to maximum parent-ion intensity
Time (min)
c
CH3SCH3 (acyclic sulfide)
C2H7S+ (parent)
C2H6S+ (fragment-like)
Signal normalized to maximum parent-ion intensity
Time (min)

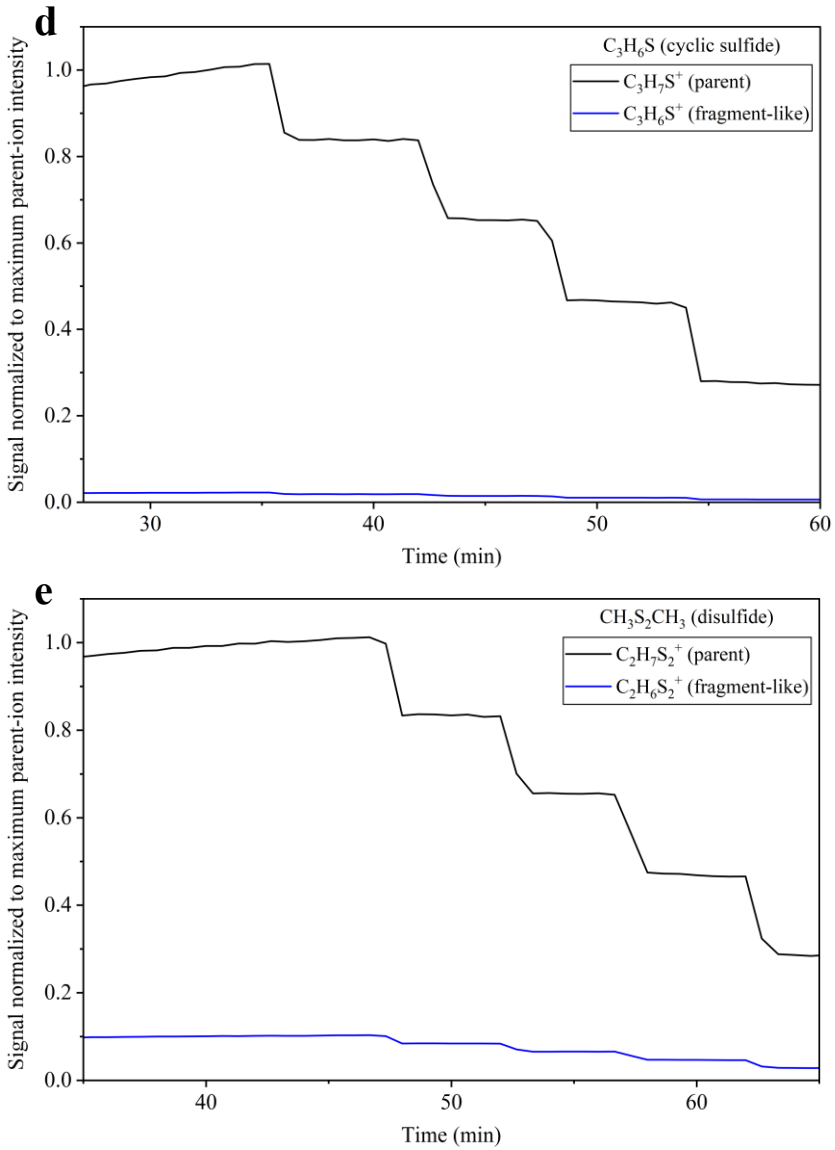


Figure R5 (Figure S14 in our revised SI). Time series of selected parent ions and fragment-like ions observed during single-component calibration experiments of representative sulfur-VOCs by Vocus-PTR-LToF-MS. The representative sulfur-VOCs compounds include (a) ethanethiol (CH_3CH_2SH), representing monothiols; (b) 1,2-ethanedithiol ($HS(CH_2)_2SH$), representing dithiols; (c) dimethyl sulfide (DMS, CH_3SCH_3), representing acyclic sulfides; (d) trimethylene sulfide (C_3H_6S), representing cyclic sulfides; and (e) dimethyl disulfide (DMDS, $CH_3S_2CH_3$), representing disulfides. Signals in each panel were normalized to the maximum parent-ion intensity of the corresponding precursor during the calibration sequence.

Table R3 (Table S4 in our revised SI). Fragment-to-parent signal ratios for representative sulfur-VOC standards during single-component calibrations.

Sulfur-VOC standards	Formulas	Parent ion	Fragment-like ion	Fragment-to-parent ratio (%)
Monothiol	CH_3CH_2SH	$C_2H_7S^+$	$C_2H_6S^+$	2.0
Dithiol	$HS(CH_2)_2SH$	$C_2H_7S_2^+$	$C_2H_6S_2^+$	10.0
Acyclic sulfide	CH_3SCH_3	$C_2H_7S^+$	$C_2H_6S^+$	2.0
Cyclic sulfide	C_3H_6S	$C_3H_7S^+$	$C_3H_6S^+$	2.0
Disulfide	$CH_3S_2CH_3$	$C_2H_7S_2^+$	$C_2H_6S_2^+$	10.0

Note: Fragment-to-parent ratios were calculated from stable calibration plateaus during single-component Vocus-PTR-LToF-MS calibrations. Fragment-like ions were identified based on their synchronous temporal variation with the corresponding parent ions, as shown in Figure S14.

Q15. Line 346: What was the filter size and information? The formation of sulfur compounds is also dependent on the aquatic biota. Bacteria can break down and convert DMSP and other dissolved sulfur. Post filtration how can you discern the effect of algae vs that of additional biological processing independent of algae?

Response:

The algae-containing freshwater sample was filtered using three stacked layers of ordinary qualitative laboratory filter paper. Such qualitative filter papers are generally used for clarification of suspensions and have nominal particle-retention sizes on the order of several to tens of micrometers. The filtration procedure was repeated three times to enhance the removal of visible algal particles and particulate biological material. Therefore, this treatment should be interpreted as removal of visible particulate biomass rather than size-resolved membrane filtration.

To better document the filtration control experiment, we have added a new section in the Supporting Information (Text S7) and included photographs showing the filtration process and the visual appearance of the sample before and after repeated filtration (Figure S16). After three rounds of filtration, the green algal suspension became nearly clear, indicating effective removal of most visible algal biomass (Figure

R6). The comparison of the signals of sulfur-VOCs before and after filtration is now shown in Figure R7.

We agree that this filtration experiment cannot distinguish direct algal emissions from sulfur transformation mediated by algae-associated bacteria or other biological processing. Therefore, the decrease in the signals of sulfur-VOCs after filtration is now interpreted as evidence that these signals were mainly associated with algae-related biological processes.

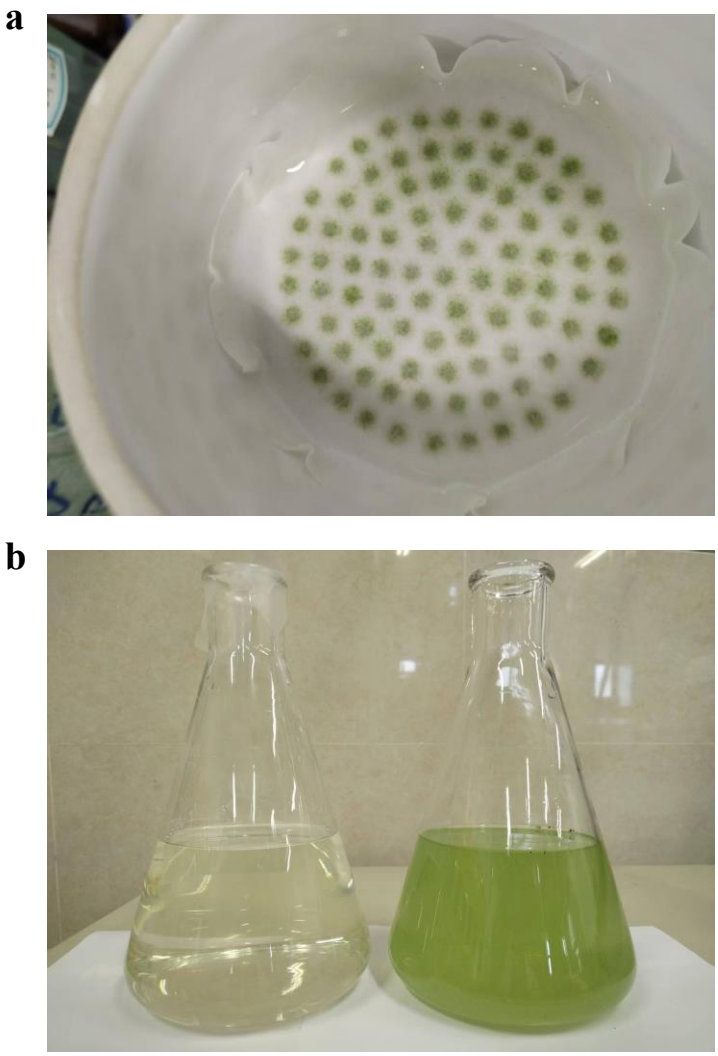


Figure R6 (Figure S16 in our revised SI). Photographs of the filtration control experiment for freshwater algae samples. (a) Algal particles retained on stacked laboratory filter papers after repeated filtration. (b) Visual comparison between the sample after three rounds of filtration (left) and the original algae-containing freshwater sample (right).

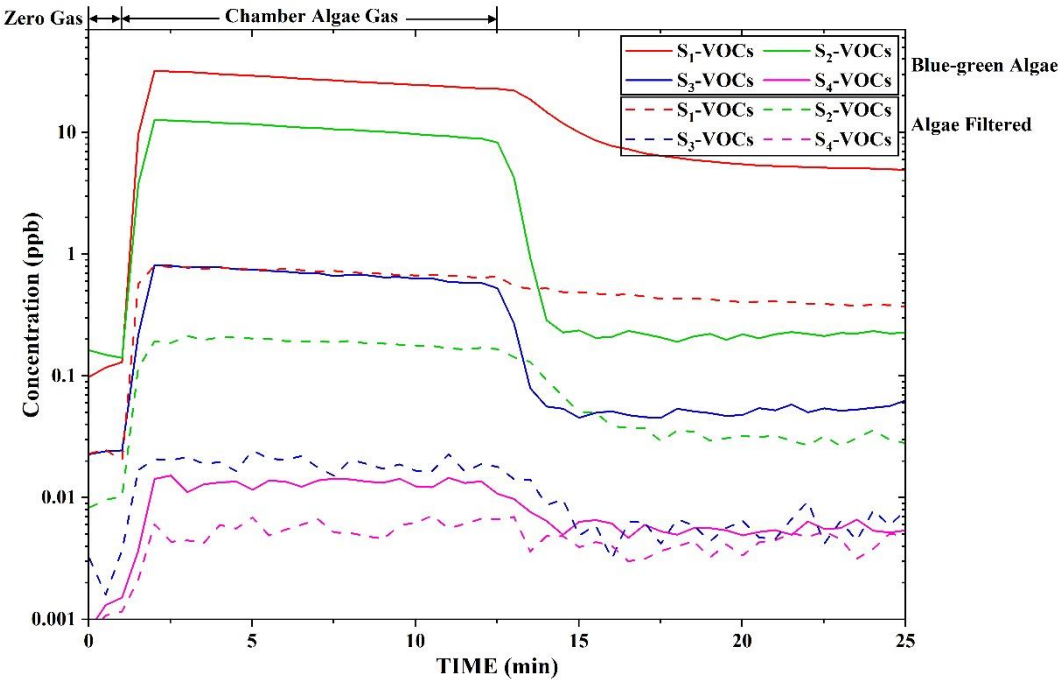


Figure R7 (Figure S17 in our revised SI). Comparison of semi-quantitative mixing ratios of sulfur-VOCs measured before and after repeated filtrations of freshwater algae samples. The sulfur-containing signals are classified into four groups (S_1 to S_4) according to the number of sulfur atoms in their assigned molecular formulas.

Representative revision in the manuscript, Lines 409-418:

"Photographs taken before and after repeated filtrations show that the green algal suspension became nearly clear, indicating effective removal of most visible algal biomass (Figure S16). Consistently, removal of algal biomass by repeated filtration through stacked qualitative filter papers led to a remarkable decrease in the abundance of sulfur-VOCs (Figure S17), suggesting that the emissions of sulfur-VOCs were closely associated with the algal biological processes. Although only molecular formulas rather than structures could be assigned, the results still provide a comprehensive inventory of freshwater algae-emitted sulfur-VOCs. However, because the freshwater lake samples contained natural microbial communities and the filtration procedure was not designed to sterilize the samples or fully remove bacteria, this experiment cannot distinguish direct algal emissions or other biological processing."

Q16. Figure 4a: Could you describe what this figure is telling us? I understand that it gives a general display of the complex mixture, but its showing more CHO that CHS.

Also, can you compare that to a post-OH experiment to highlight the formation of more sulfur compounds?

Response:

Figure 4a provides an overview of the primary VOC emissions from freshwater algae before oxidation, as measured by Vocus-PTR-LToF-MS. As shown in Figure R3 (Figure 4 in the revised manuscript; see response to Q13), among these emitted VOC formulas, CHO species were more abundant than sulfur-containing formulas. Figure 4a is not intended to show that sulfur-containing compounds dominate the total emitted VOC mixture. Instead, it shows that sulfur-containing formula-level signals represent a smaller but chemically important subset within the complex algae-emitted VOC mixture. The figure caption and related text have also been revised to clarify that marker size represents normalized PTR-MS signal intensity rather than calibrated concentration.

A direct signal-based comparison between Figure 4a and the post-•OH oxidation products would not be quantitatively meaningful because the primary emissions and oxidation products were characterized by different instruments with different ionization mechanisms and detection selectivity. Vocus-PTR-LToF-MS was mainly used to characterize primary VOC emissions and relatively less oxidized VOCs, whereas nitrate-CI-LToF-MS is more sensitive to sulfuric acid, sulfuric acid clusters, and highly oxygenated or low-volatility oxidation products. Therefore, instead of combining the two datasets into a single signal-based mass-defect plot, we compare the results qualitatively in terms of detected sulfur-containing formula classes and product types.

The post-•OH oxidation products are presented separately in Figure R8 (Figure 5 in the revised manuscript) and Table S8. Compared with the 20 sulfur-containing formula-level signals detected before oxidation by Vocus-PTR-LToF-MS, approximately 110 oxidation-product formulas were identified after •OH exposure using nitrate-CI-LToF-MS, including dozens of mono-sulfur organic products, inorganic sulfur-containing species such as H_2SO_4 and its clusters, and 11 multi-sulfur products. Thus, the comparison between Figure 4a and Figure 5 demonstrates the transition from primary

algae-emitted sulfur-containing formula-level signals to a broader suite of more oxidized sulfur-containing products after •OH oxidation. Because mono-sulfur and inorganic sulfur-containing oxidation products are also formed but are not the central focus of this work, the revised discussion emphasizes that our study focuses particularly on the detection and potential formation pathways of low-volatility multi-sulfur products rather than attempting a complete product inventory or direct quantitative intercomparison between the two instruments.

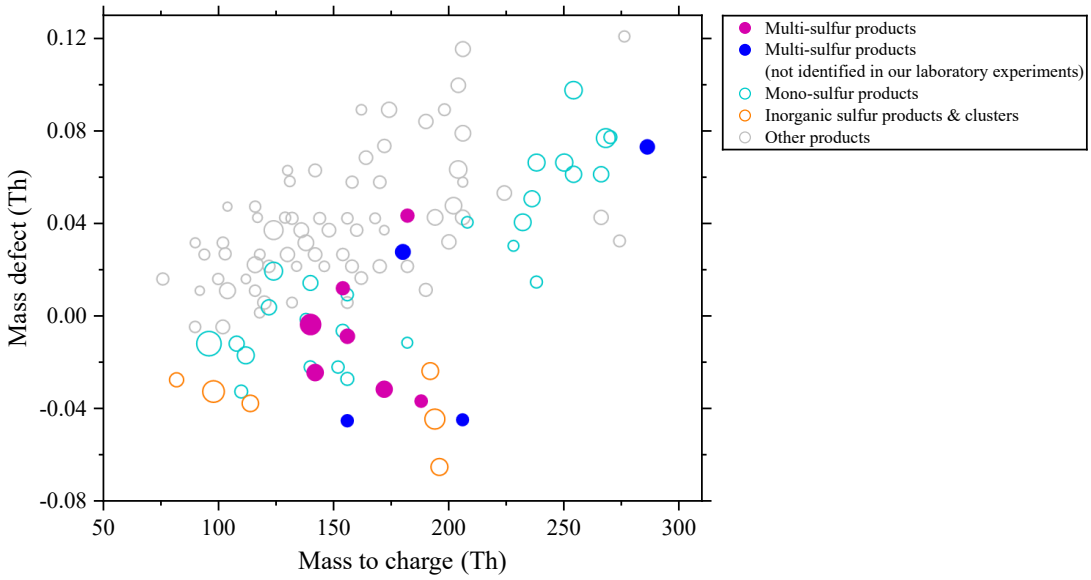


Figure R8 (Figure 5 in the revised manuscript). Mass defect plot of oxidation products detected by nitrate-CI-LToF-MS duringthe •OH-initiated oxidation of algae-emitted VOCs. Multi-sulfur products shown in deep purple represent species whose molecular formulas were also identified in our chamber simulation experiments of the selected sulfur-VOCs, whereas those shown in dark blue represent multi-sulfur products whose corresponding molecular formulas were not identified in our chamber experiments. Marker size is proportional to the corresponding signal intensity.

Q17. Line 409: Please add citations for the declining SO_2.

Q18. Line 411: I would also include passive SO_2 and H_2S, both of which will form H_2SO_4 and would also become very important under this lowering Anthropogenic SO_2 world.

Response:

The citations Crippa et al., 2016; Fioletov et al., 2022; Smith et al., 2011; Zheng et al., 2018 have been added to support the decline trend in anthropogenic SO_2 emissions over recent decades, including studies on long-term global and regional anthropogenic SO_2 emission trends.

In addition to anthropogenic SO_2, we now explicitly mention H_2S, DMS-derived SO_2, and naturally emitted SO_2, including passive volcanic SO_2 emissions, as relevant sulfur sources in the atmosphere. These additions integrate biogenic sulfur-VOCs into the broader atmospheric sulfur cycle and indicate that their relative contribution to total sulfur cycling may increase as anthropogenic SO_2 emissions continue to decline.

Representative revision in the manuscript, Lines 486-494:

"In addition to anthropogenic SO_2, natural sulfur sources such as H_2S, DMS-derived SO_2, and naturally emitted SO_2, including passive volcanic SO_2 emissions, can also contribute to gaseous H_2SO_4 and particulate sulfate formation (Bates et al., 1992; Faloona, 2009; Yvon and Saltzman, 1996). In this evolving context, the relative contribution of biogenic sulfur-VOCs become increasingly important, particularly in low-NO_x environments. Our results demonstrate that, in addition to conventional oxidation pathways, sulfur-containing RO_2• bimolecular reactions can lead to the formation of low-volatility multi-sulfur products, providing an additional pathway linking sulfur-VOCs to secondary aerosol formation."

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Reviewer #2:

Q0. In this manuscript the authors describe an experimental study of the kinetics of the reactions of a selection of sulfur-containing volatile organic compounds with OH radicals and the products formed in the absence of NOx. Experiments were conducted in a small Teflon chamber, and the decay of the reactant was monitored with a PTR-MS and the products with a nitrate-CIMS. Rate constants measured using relative rate kinetics and product yields were estimated using sulfuric acid as a calibration standard. Samples of algae were also collected from a freshwater lake, and their emissions of sulfur-containing VOCs were compared with compounds identified here.

The experiments and data analysis were well done, and the interpretation of the results, including the proposed reaction mechanisms, are reasonable. The authors make good use of the literature, and the manuscript is clearly written. The study provides useful new results on the kinetics and products of atmospheric reactions of an important class of understudied compounds. I recommend publication in ACP and have only a few minor comments.

Response:

We sincerely appreciate *Reviewer #2*'s positive assessment of our work and the thorough evaluation of the experimental design, data analysis, and mechanistic interpretation. In response to the reviewer's comments, we have clarified the uncertainty and limitations associated with product-yield estimation, sulfur-containing product interpretation, and the atmospheric relevance of the NO_x-free chamber experiments. Corresponding revisions have been made in the manuscript and Supporting Information.

Q1. The product yields are very low, with totals typically less than about 10%? Where does all the mass go? This is a tiny reactor, so I assume much is lost to the chamber walls. Have the authors estimated gas-wall partitioning of products? Do they know how much aerosol is formed?

Response:

We agree that the yields of the detected multi-sulfur products are low in most reaction

systems. We have therefore clarified that these values should not be treated as total oxidation product yields and sulfur mass closure cannot be reached based on these yields. Instead, they only represent gas-phase partial yields of the semi-quantified multi-sulfur products detected by nitrate-CI-LToF-MS.

The unaccounted sulfur mass is expected to be distributed among several other product classes and loss pathways. First, a substantial fraction of sulfur may be converted to inorganic sulfur products and mono-sulfur oxidation products, including SO_2, H_2SO_4, sulfoxides, sulfones, methanesulfonic-acid-related products, and other mono-sulfur oxygenated compounds. These species were not included in the reported multi-sulfur product yields. Second, nitrate-CI-LToF-MS preferentially detects highly oxygenated and low-volatility compounds, so more volatile or less oxygenated sulfur-containing products may be underrepresented. Third, gas-wall partitioning of newly formed low-volatility products may reduce the observed gas-phase concentrations of multi-sulfur products.

Regarding wall losses, product wall loss or gas-wall partitioning of newly formed low-volatility oxidation products was not directly quantified in this study. To reduce the influence of cumulative product wall loss, the reported product yields were derived from the maximum observed gas-phase concentrations of the detected multi-sulfur products. Nevertheless, product wall loss may still contribute to the low apparent gas-phase yields, and the reported multi-sulfur product yields should therefore be regarded as lower-limit gas-phase estimates for multi-sulfur products.

Regarding aerosol formation and possible particle-phase losses, particle number concentration, size distribution, particle-phase chemical composition, and aerosol mass yields were not measured in these chamber experiments. Therefore, particle formation and aerosol mass yields were not directly quantified. However, no amines were introduced into the chamber. Thus, sulfuric-acid-related nucleation under our experimental conditions is expected to be closer to the H_2SO_4-H_2O binary nucleation pathway rather than the highly efficient H_2SO_4-amine nucleation pathway. As shown in Figure R9, literature results indicate that the H_2SO_4-H_2O binary nucleation pathway

produces much lower particle formation rates than amine-assisted sulfuric-acid nucleation at comparable sulfuric acid concentrations (Yao et al., 2018). In our chamber experiments, the average of the peak H_2SO_4 concentrations across multiple experiments was approximately 3.8×10^8 cm^{-3}. Based on this comparison, new particle formation under our chamber conditions was not expected to be sufficiently strong to dominate the loss of gas-phase multi-sulfur products during the short experiments.

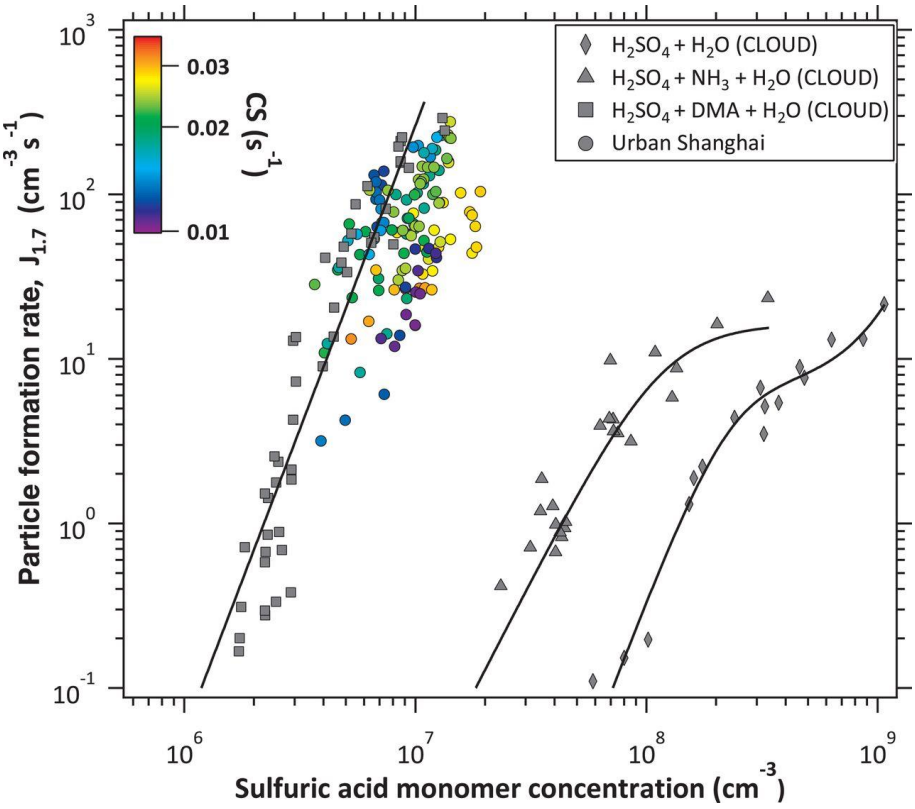

Figure R9. Literature-reported particle formation rates as a function of sulfuric acid monomer concentration for different sulfuric-acid-based nucleation systems. The figure shows particle formation rates for H_2SO_4-H_2O, H_2SO_4-NH_3-H_2O, and H_2SO_4-DMA-H_2O nucleation systems, as well as observations from urban Shanghai. The comparison illustrates that amine-assisted sulfuric-acid nucleation can produce much higher particle formation rates than binary H_2SO_4-H_2O nucleation at comparable sulfuric acid concentrations. Reproduced from Yao et al. (2018).

Representative revision in the manuscript, Lines 369-379:

"Although the formation yields of many detected multi-sulfur products are relatively low, their low volatility indicates SOA forming potential. The reported yields represent

only the gas-phase multi-sulfur products detected by nitrate-CI-LToF-MS and should not be interpreted as total oxidation product yields. A substantial fraction of sulfur may be converted to inorganic sulfur products and mono-sulfur oxidation products, such as SO_2, H_2SO_4, sulfoxides, sulfones, methanesulfonic acid, and other mono-sulfur oxygenated compounds, which are not included in the reported multi-sulfur product yields. In addition, nitrate-CI-LToF-MS preferentially detects highly oxygenated and low-volatility compounds, while more volatile or less oxygenated sulfur-containing products may be underrepresented. Product wall loss and possible particle-phase transfer may further reduce the observed gas-phase concentrations of multi-sulfur products. Therefore, the reported yields should be treated as lower-limit gas-phase yields of multi-sulfur products."

Q2. Are emissions of sulfur-containing VOCs sufficient that these low product yields can matter for the atmosphere?

Response:

The present study does not claim that the detected multi-sulfur products make a quantified contribution to SOA mass or new particle formation. Rather, the atmospheric relevance of the formation of multi-sulfur products is discussed in terms of the occurrence of sulfur-VOC emissions and the potential particle-phase relevance of these low-volatility oxidation products.

Sulfur-containing VOCs, including DMS, methanethiol, DMDS, and related reduced sulfur compounds, have been widely reported in marine and freshwater-influenced environments. In eutrophic freshwater systems and algal-bloom-affected regions, biological and microbial sulfur-transformation processes can release abundant sulfur-VOCs. Therefore, even low-yield multi-sulfur product channels may be chemically relevant under favorable conditions, particularly in sulfur-VOC-rich and low-NOx environments where sulfur-containing RO_2• lifetimes are extended and bimolecular reactions of RO_2• become more competitive.

At the same time, the interpretation has been limited to avoid overstating the atmospheric impact of multi-sulfur products. As discussed in response to *Q1*, the

reported yields are gas-phase partial yields of nitrate-CI-LToF-MS-detected multi-sulfur products rather than total oxidation yields. Therefore, the role of these multi-sulfur products is described as a potential particle-phase relevance inferred from their low volatility, rather than as a quantified contribution to SOA mass or new particle formation.

Representative revision in the manuscript, Lines 436-445:

"These experimental results not only provide evidence that multi-sulfur products can be formed from bimolecular reactions of sulfur-containing RO_2• under low-NO_x conditions, but also improve our understanding of the atmospheric oxidation chemistry of algae-emitted sulfur-VOCs in ambient air (especially in low NO_x environments). Notably, the detection of H_2SO_4 and its clusters, which are well-established precursors for atmospheric new particle formation, suggests that the oxidation of algae-emitted sulfur-VOCs may contribute to secondary particle formation (Jokinen et al., 2012; Lee et al., 2019; Yao et al., 2018). These findings expand the current understanding of the atmospheric processing of biogenic sulfur-VOCs released from freshwater algae and suggest that their chemical complexity may have broader implications for sulfur transformation and secondary aerosol formation."

Q3. What areas in China are these NOx-free conditions appropriate for?

Response:

Truly NO_x-free environments are uncommon in the real atmosphere, especially in populated or industrial regions of China. The purpose of using NO_x-free conditions in this study was to suppress RO_2• + NO reactions and to facilitate bimolecular radical chemistry, including RO_2• + HO_2• and RO_2• + $R'O_2$• pathways, which can become more important when RO_2• termination by NO is less competitive.

The results are most applicable to sulfur-VOC-rich environments with relatively low NO_x levels and strong biogenic emissions, such as remote marine boundary layers, polar regions, inland eutrophic lakes, and rural/background areas with limited anthropogenic influence. In China, although strictly NO_x-free environments are unlikely, certain inland freshwater systems and rural and remote areas may partially

resemble lower-NO_x regimes compared with polluted urban air. These environments should therefore be regarded as partial analogues for the low-NO_x chemistry investigated here.

The manuscript has been revised to better define this limitation and to avoid overgeneralizing the experimental conditions to ambient environments. We now state that the present results demonstrate a potential multi-sulfur product formation pathway favored under sulfur-VOC-rich and low-NO_x conditions.

Q4. The quantities reported here are reaction rate constants or rate coefficients, not reaction rates, which is the term used throughout the text.

Response:

The terminology has been checked and modified throughout the whole manuscript and Supporting Information.

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