

I believe this manuscript effectively demonstrates the efficacy of the AIRCORE sampling technique for characterizing stratospheric Carbonyl Sulfide (OCS) through offline analysis using a Quantum Cascade Laser Spectrometer (QCLS). The authors successfully build upon the work of Kryzstofiak et al. (Kryzstofiak et al., 2015) by comparing balloon-borne OCS profiles with the sparse ACE-FTS satellite dataset. They are also able to compare the AIRCORE profiles with earlier measurements from the SPIRALE instrument. Their results provide additional evidence supporting the reliability of the ACE-FTS remote retrievals, consistent with more recent airborne observations from the 2023 SABRE campaign (Gurganus et al., n.d.).

The manuscript also makes a valuable contribution by addressing long-standing concerns about potential OCS depletion when co-sampling with ozone, as reported three decades ago (Engel & Schmidt, 1994). Both in-situ stratospheric data and supporting laboratory experiments presented here indicate that this loss process is not evident. Indeed, the JPL Chemical Kinetics and Photochemical Data Evaluation includes no direct OCS + O₃ reaction, and to my knowledge, no subsequent studies have reproduced such a mechanism. The results therefore suggest that any previously reported depletion was likely specific to cryogenic whole-air sampling with uncoated stainless-steel canisters—a limitation not relevant to AIRCORE, which employs inert internal coatings.

These main points in this manuscript are clearly supported by the data and analysis presented and represent important advances in improving our understanding of the stratospheric sulfur budget. Accordingly, I find the manuscript well-suited for publication. My main concern, however, is the extensive use of quantitative comparisons among highly sparse datasets spanning more than a decade. Given the substantial natural variability in the stratosphere, such comparisons should be interpreted with caution, and I encourage the authors to temper the quantitative emphasis or further justify the robustness of these cross-temporal comparisons.

The authors have made a good effort to address the minor points from the first round of review so here I will only detail the three broader concerns that I hope the authors can address before final publication.

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Main Points:

1. The background motivation for OCS depletion by co-sampled O₃ is not well supported by the references provided. Of the 4 references provided only one (Engel & Schmidt, 1994) actually mentions OCS loss resulting from co-sampling of ozone. The others discuss DMS depletion when co-sampled with Ozone which would produce excess OCS in line with the results reported here in the Appendix. I would ask the authors to revise the text to avoid conflating Ozone reaction with OCS and sulfur compounds more broadly (including H₂S, CS₂, DMS).
 - Line 62: Possible impacts of stratospheric ozone (O₃) (Engel and Schmidt, 1994) as well as pollution-induced tropospheric O₃ (Andreae et al., 1990, 1993; Hofmann et al., 1992; Persson and Leck, 1994) on collected air samples for COS observations have been reported in previous studies.
 - Line 740: “This is in contrast with the O₃-induced COS loss reported in previous studies (Andreae et al., 1990; Engel and Schmidt, 1994; Hofmann et al., 1992; Persson and Leck, 1994).”

Quotes from the references listed in the manuscript:

(Andreae et al., 1993) Incorrectly cited as 1990 in this manuscript

“A cotton scrubber was found to be effective in removing oxidants from air samples collected for DMS analysis. It performed better than the Na₂CO₃/Anakrom scrubber under the most challenging sampling conditions (e.g., high O₃ and low DMS concentrations).”

(Engel & Schmidt, 1994) Cryo-Trap w/ Electro-Polished Stainless Steel containers

“Laboratory tests showed that COS is decomposed during sampling in the presence of ozone. To avoid this COS destruction, a catalyst was developed that decomposes ozone prior to sampling. The catalyst consisted of manganese dioxide (MnO₂) supported on silanized glass wool. The COS recovery rates, relative to the inert CF₂Cl₂ (F12) used as an internal standard, are shown in Figure 1 for three different cases: sampling without ozone, with ozone, and with ozone plus the catalyst. The COS loss when using the catalyst was less than 10%, even when ozone mixing ratios of up to 10 ppmv were applied. The sample stability in the containers was also good, with a maximum observed decrease of COS of about 5% per month for the stratospheric samples.” See Figure #1

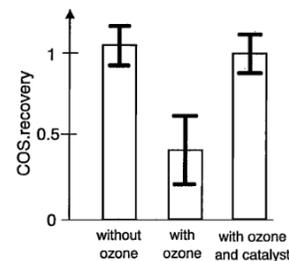


Figure 1. COS recovery relative to F12 for samples collected without ozone, with ozone and with ozone and catalyst. The error bars represent 1σ standard deviations.

(Hofmann et al., 1992) Cryo-Trap w/ Salinized Glass

“The results clearly show that the Nafion drier in combination with cotton wadding as an oxidant scavenger is suitable for sampling reduced volatile sulfur compounds. Labile compounds such as H₂S and especially DMS may be protected from being destructed. COS and CS₂ are hardly affected.” See Figure #5:

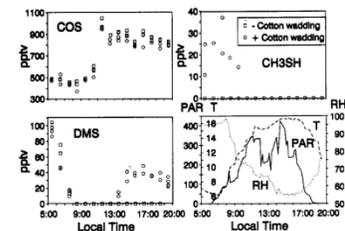


Fig. 5. Diurnal patterns of reduced sulfur compounds and climatic data measured at the botanical garden at the University of Mainz (21 March 1990). Open circles: use of a cotton scrubber as an oxidant scavenger in front of the Nafion drier. Open boxes: use of the Nafion drier without an oxidant scavenger. PAR (solid line): photosynthetic active radiation ($\mu\text{mol photons m}^{-2} \text{s}^{-1}$); T (broken line): temperature ($^{\circ}\text{C}$); RH (dashed line): relative humidity (%). Ozone data: half hourly means obtained through the “Landesamt für Umweltschutz und Gewerbeaufsicht, Rheinland-Pfalz”

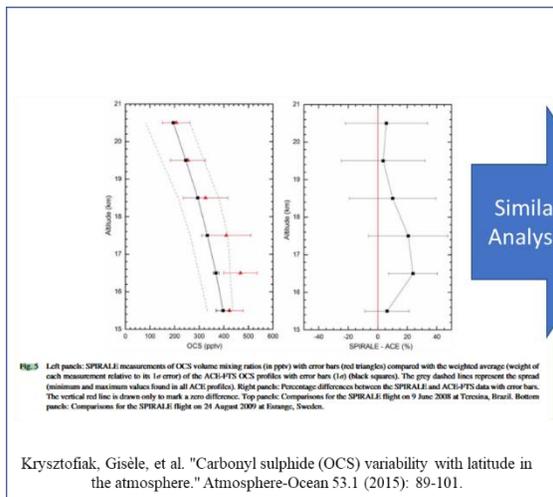
(Persson & Leck, 1994) Gas Chromatography with Flame Photometric Detection

“The described method has a potential for future development. The system could be converted for analyses of COS. COS was detected in every ambient air sample from the Arctic. However, quantification was not possible, due to quenching with carbon dioxide in the FPD.”

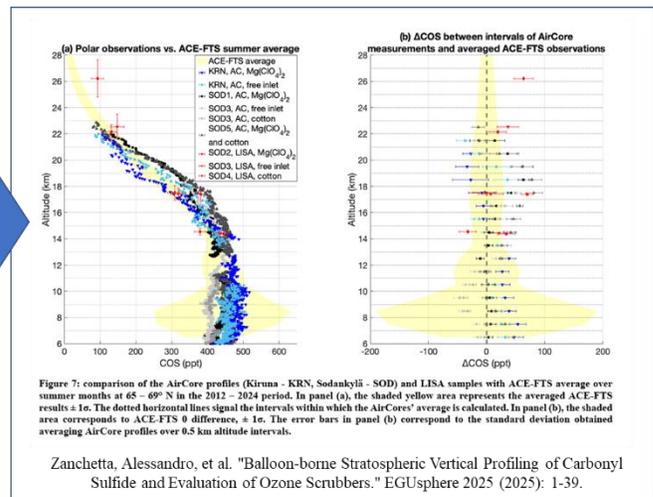
- The authors present reasonable qualitative evidence that the AirCore profiles show good agreement with ACE-FTS satellite and SPIRALE balloon observations (Figures 3, 4, 6, and 7), consistent with the results of Krysztofiak et al. (2015) (see comparison of figures below). However, the detailed quantitative statistical and regression analyses shown in Figures 5 and 8 and Tables 4 and 5 are not appropriate in this context. The authors cannot adequately account for temporal variability in stratospheric OCS abundance—arising from factors such as sudden stratospheric warming events, PyroCb injections, or other transient perturbations—given the many years separating these datasets, which span 15 years.

Datasets Compared (2009-2024):

- SPIRALE: 2009 & 2011
- ACE-FTS: 2012-2024
- TRN: 2019
- KRN: 2021
- SOD: 2023



Similar Analysis



- The inclusion of LISA (Big and Small) data in this manuscript appears inappropriate, as the authors are compelled to arbitrarily exclude certain datasets despite the existence of a mitigation strategy specifically designed and implemented for these measurements (see examples below). This selective omission raises concerns about the reliability and reproducibility of the sample bag technique for quantifying OCS in the stratosphere.

- LISA (Line 158): “The leftover volume of one of these samples was insufficient for analysis (SOD3– L4), while two others showed unusually high mole fractions for several of the analysed gas species (SOD2 – L4, SOD5 – 160 L3), in spite of the pre-conditioning of these bags before flight. These three samples were labelled as outliers and will not be presented in this work.
- BigLISA (Line 201): “Similarly to LISA, samples labelled as outliers due to unusually high mole fractions of multiple tracers (KRN - BL7, BL10, BL11 and BL12) will not be presented in this text.”

References:

- Andreae, T. W., Andreae, M. O., Bingemer, H. G., & Leck, C. (1993). Measurements of dimethyl sulfide and H₂S over the western North Atlantic and the tropical Atlantic. *Journal of Geophysical Research: Atmospheres*, 98(D12), 23389–23396. <https://doi.org/10.1029/91JD03016>
- Engel, A., & Schmidt, U. (1994). Vertical profile measurements of carbonylsulfide in the stratosphere. *Geophysical Research Letters*, 21(20), 2219–2222. <https://doi.org/10.1029/94GL01461>
- Gurganus, C., Bednarz, E. M., Rollins, A. W., Waxman, E., Ray, E. A., Hints, E. J., et al. (n.d.). Constraining the Stratospheric Sulfate Budget in Global Models: Insights from In-Situ OCS Measurements during 2023 SABRE and Comparison with Satellite, Balloon and Surface Data. Retrieved from <https://www.authorea.com/doi/full/10.22541/au.174923128.88516613?commit=5f0b422b86690bc6f443801462c6ddf39dd9c571>
- Hofmann, U., Hofmann, R., & Kesselmeier, J. (1992). Cryogenic trapping of reduced sulfur compounds using a nafion drier and cotton wadding as an oxidant scavenger. *Atmospheric Environment. Part A. General Topics*, 26(13), 2445–2449. [https://doi.org/10.1016/0960-1686\(92\)90374-T](https://doi.org/10.1016/0960-1686(92)90374-T)
- Kryzstofiak, G., Té, Y. V., Catoire, V., Berthet, G., Toon, G. C., Jégou, F., et al. (2015). Carbonyl Sulphide (OCS) Variability with Latitude in the Atmosphere. *Atmosphere-Ocean*, 53(1), 89–101. <https://doi.org/10.1080/07055900.2013.876609>
- Persson, Cecilia., & Leck, Caroline. (1994). Determination of Reduced Sulfur Compounds in the Atmosphere Using a Cotton Scrubber for Oxidant Removal and Gas Chromatography with Flame Photometric Detection. *Analytical Chemistry*, 66(7), 983–987. <https://doi.org/10.1021/ac00079a009>