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 Krysztofiak et al. (Krysztofiak 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 + O_3 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.

Authors' response (AR): *the authors would like to thank the Referee for the positive comments and the generous effort made to provide this detailed feedback. Our responses will be organized point-by-point in paragraphs formatted similarly to the present one.* ***Major modifications*** *in the preprint will be presented as* ***italic bold text*** *together with their respective page and line numbers, when applicable.*

Contents

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 produces 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)."

<u>Quotes from the references listed in the manuscript:</u>

(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 Na_2CO_3/Anakrom scrubber under the most challenging sampling conditions (e.g., high O_3 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 (MnO_2) supported on silanized glass wool. The COS recovery rates, relative to the inert CF_2Cl_2 (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

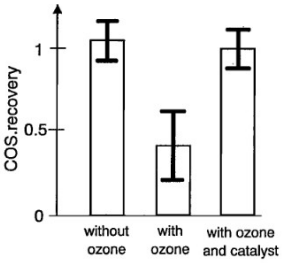


Figure 1. COS recovery relative to F12 for samples collected without ozone, with ozone and with ozone and catalyst. The error bars represent 1σ-standard deviations.

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

"The results clearly show that the Nation 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:

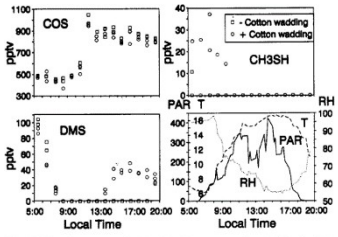


Fig. 5. Diurnal patterns of reduced sulfur compounds and climatic data measured at the botanical garden at the University of Mainz (21 March 1990). Open circles: use of a cotton scrubber as an oxidant scavenger in front of the Nafion drier. Open boxes: use of the Nafion drier without an oxidant scavenger. PAR (solid line): photosynthetic active radiation (μmol photons $m^{-2} s^{-1}$); T (broken line); temperature (°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."

Authors' response (AR): *the authors would like to thank the Referee for suggesting the implementation of a better description of the reasons supporting the investigation of O_3 influence on COS sampling, as well as for pointing out the typo about Andreae et al. (1993) paper citation. Most studies cited to justify the study of O_3 influence on COS sampling cover indeed other sulfur compounds and not COS specifically. To avoid confusion, the following modifications have been implemented:*

Lines 61 – 74:

Possible impacts of stratospheric ozone (O_3) ***on collected air samples for COS observations have been reported in previous studies (Engel and Schmidt, 1994) as well as pollution-induced tropospheric O_3 on other reduced sulfur compounds, such as dymethyl sulfide (DMS) or carbon disulfide (CS_2) (Andreae et al., 1993; Hofmann et al., 1992; Persson and Leck, 1994), known precursors of atmospheric COS (Whelan et al., 2018).*** *O_3, a strong oxidant, may in fact react with reduced sulfur compounds causing a variable, yet possibly significant reduction in their abundance* ***(Andreae et al., 1993; Engel and Schmidt, 1994; Hofmann et al., 1992; Persson and Leck, 1994). Recent tests with a detection limit of around 50 ppt, however, reported no influence of O_3 on neither DMS, nor CS_2, but found positive interference on measurements of Volatile Organic Compounds (VOCs) containing carbonyl compounds (Ernle et al., 2023).***

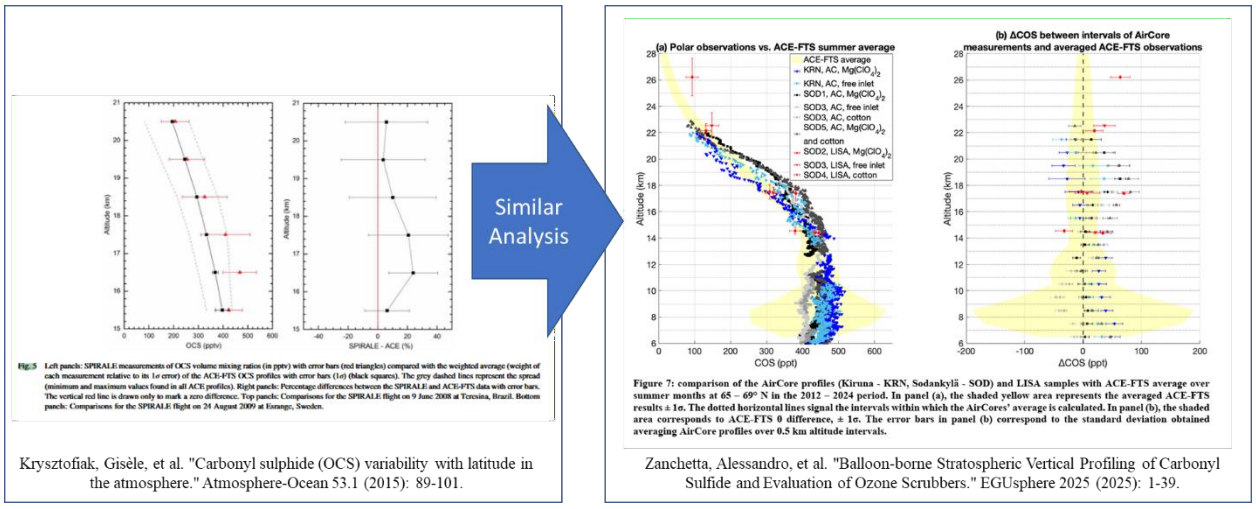
Lines 1243 – 1246:

As shown in Fig. 3, COS mole fraction was found significantly higher than the bypass channel when O_3 was generated for both with and without the squalene scrubber. ***This is in contrast with the O_3-induced COS loss reported in previous studies (Engel and Schmidt, 1994) and resembles the positive interference on carbonyl-bearing VOCs measurements reported by Ernle et al. (2023).***

2. 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



Krysztofiak, Gisèle, et al. "Carbonyl sulphide (OCS) variability with latitude in the atmosphere." Atmosphere-Ocean 53.1 (2015): 89-101.

Zanchetta, Alessandro, et al. "Balloon-borne Stratospheric Vertical Profiling of Carbonyl Sulfide and Evaluation of Ozone Scrubbers." EGUsphere 2025 (2025): 1-39.

Authors' response (AR): *the authors thank the Referee for pointing out the critical points of this analysis. To address this, we have removed the Figures and Tables reporting the linear regression analyses between our datasets and ACE-FTS or SPIRALE observations, leaving space to the qualitative comparisons resembling the one presented by Krysztofiak et al. (2015). Accordingly, paragraphs 4.2 and 4.3 have been adapted, removing descriptions and references to these linear regressions.*

3. 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."

Authors' response (AR): *the authors thank the Referee for underlining these aspects of the (Big)LISA analysis. Indeed, it's likely that some LISA (Big and Small) samples were contaminated. However, we were able to filter out these data based on independent information or identify them as clear outliers. Furthermore, as a novel method for sampling air for COS measurements, the provided information about (Big)LISA is valuable for future studies, particularly regarding the sampling procedure – e.g., the "pre-treatment" introduced during the SOD campaign. To better clarify this aspect, the following changes have been implemented in the text:*

Lines 161 – 164:
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 – L3), in spite of the pre-conditioning of these bags before flight, ***most likely due to contamination with tropospheric air during sampling and/or while transferring the samples****. These three samples were labelled as outliers and will not be presented in this work.*

Lines 468 – 480:
As described in Sect. 2.1.2, during the SOD campaign we introduced a pre-treatment technique that has mitigated this issue for COS, based on previous laboratory tests. Filling and vacuuming the bags with a stratospheric-mimicking gas seemed to have reduced the contamination significantly for most LISA samples, as previously reported in Fig. 2 and Table 2. However, in some cases and in particular for smaller samples collected at higher altitudes (SOD2 – L4, SOD5 – L3), this pre-conditioning was not sufficient to prevent biases that are likely ascribable to the bags employed during the campaign ***or may be due to contamination during sampling or during the transferring procedure of the samples in glass flasks****. For the remaining samples, when LISA flew on the same balloon as one of our AirCores (e.g. SOD1, SOD3), the largest average difference of 31 ± 15 ppt was found when both instruments were flown with a free inlet. Although*

some variability can be observed between different LISA samples at similar altitudes, their COS mole fraction falls well within the range of the AirCore profiles (see Sect. 4.1.3, 4.2 and 4.3). ***Overall, LISA samples may need further improvement regarding the sampling and measurement protocols. However, the results presented in this study suggest that this technique should be suitable to obtain reliable COS measurements and that the pre-treatment of MLF bags prevents, or at least reduces, COS contamination due to outgassing from the inner layers of these sample containers.***

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., Hintsa, 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

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Krysztofiak, 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