Author responses to reviews to EGUSPHERE-2024-549 "Can we gain knowledge on COS anthropogenic and biogenic emissions from a single atmospheric mixing ratios measurement site?"

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We thank the referees for their detailed and fruitful comments on our manuscript. We reproduce below their reviews and embed our responses in bold blue text in their comments. Revised section of the manuscript are reproduced in italic blue. We also provide a track-change manuscript at the end of the present document.

1 Referee #1: Mary Whelan

This paper is a good application of the lead author's work making FLEXPART more accessible. The treatment of the CS2 fields here is an improvement for the field, transforming emissions of CS2 to atmospheric COS with a reasonable conversion rate.

I have a few suggestions for making this work more impactful.

1.1 Main comments

1.1.1 Zumkehr inventory

It is unclear why the Zumkehr inventory was used without the improvements suggested by Belviso et al., (2023). Belviso et al., demonstrated the drawbacks to this inventory fairly conclusively! It might make sense to make the necessary changes and move on. Additionally, naming the improved anthropogenic scheme "home-made" is confusing. Zumkehr was also likely working from home. Using the designation "This Study" is clearer.

Belviso et al. (2023) assessed discrepancies between Zumkehr's inventory and measurements at a rather local scale. The objective of the present study is to assess COS fluxes at a regional scale. Thus we chose to re-use Zumkehr as such as a reference inventory, and then we propose an updated inventory based on industrial declarations at the European scale as a new starting point, leading to significant and convincing improvements. We clarify our objectives and rationals in the new manuscript.

We revise the last paragraph of our introduction as follows:

Therefore, the present study aims at building a set-up that makes it possible to quantitatively assess the anthropogenic and biogenic COS fluxes at the regional scale, i.e., in the footprint of one measurement site in Western Europe at a seasonal to diurnal time resolution over a period of half a decade. For this, we use the continuous time series of COS mixing ratios measured in the Paris area from summer 2014 to the end of year 2019, as described in obsgif. We compare them to the concentrations simulated from marine, biogenic and anthropogenic fluxes in the area of interest (detailed in flux) combined to the contribution due to the rest of the world (bckg) by the modeling tool described in model. After an assessment of the general performances of the model (general), we are able to quantitatively evaluate the anthropogenic sources from Western Europe as estimated by Zumkehr et al. (2018) (hereafter referred to as "Zumkehr's inventory") and by our more targeted inventory (anthro), confirming discrepancies from Belviso et al. (2023) in Zumkehr's inventory in France in particular, but also in Western Europe in general. Contrary to Belviso et al. (2023), the present study goes one step further by quantitatively assessing discrepancies in Zumkehr's inventory and by proposing a new inventory based on industrial emission declaration in the European Union. Having more reliable anthropogenic emissions, we can inquire into biogenic emissions, which is one of the main original purpose of studying COS. We study the seasonal and diurnal cycles of biogenic fluxes, based on the ORCHIDEE and SiB4 processed-based land surface models (vegesink); this allows us to point to strengths and weaknesses in the two models.

1.1.2 Land uptake

To improve our understanding of the atmospheric OCS balance, it would make sense to use a different biogenic uptake dataset instead, such as SiB4. Comparing SiB4 to ORCHIDEE in this framework might yield some interesting insights into our treatment of plant uptake.

We recompute our simulations based on SIB4 in complement to ORCHIDEE. We thank the reviewer for this very interesting suggestion that we integrate in the updated manuscript. We updated Sect. 2.2.2 accordingly, adding description of the SiB4 model.

We include results from SiB4 in Fig. 3 and 4 and in Sect. 3.3., as well as in the conclusion.

Overall, SiB4 seems to better reproduce the diurnal cycle of fluxes, especially in Spring, compared to ORCHIDEE. The magnitude of Summer fluxes leads to better agreement with observations when using ORCHIDEE than SiB4.

1.1.3 Temporal coverage of footprints

10, 15-23 and Section 3.3, Figure 4: The footprints used here are calculated throughout the day. In efforts involving WRF-STILT, one recommended approach is to average afternoon tower measurements when the boundary layer is typically well-mixed. As the authors note, it could be that there is variation in the tower concentrations because of shifts in the mixing layer rather than shifts in the plant uptake or ocean background. While OCS is undoubtedly being taken up at night by partially-closed stomata, there is also a dynamic shift in the state of the mixed layer in contact with the tower. How well does FLEXPART treat the boundary layer? Perhaps some explanation needs to be included here on the uncertainty introduced by taking footprints at

different times of day. Alternatively, averaging concentrations when the layer is stable would side-step some of the synoptic-scale complications.

We agree that FLEXPART (and any transport model) is most suitably compared with observations during afternoon time, when the boundary layer is well mixed. This is why general performances and assessment of synoptic scale transport in regards to anthropogenic emissions is done using afternoon data only. This is clarified in the update manuscript.

As there is basically no non-biogenic OCS fluxes in the vicinity of the observation site GIF, we choose to use the diurnal cycle of observations and simulations to deduce variations in the magnitude and sign of local OCS biogenic fluxes. Such an approach relates to a simulation based Radon-method.

Although we are confident in FLEXPART's capability in reproducing well mixed afternoon conditions, there are indeed uncertainties in nighttime simulations, in particular related to the parametrization of PBL mixng, as well as in the value of the PBL height, as provided by ECMWF ERA-5 data at night. Such uncertainties are hard to quantify, but they would only impact the values of our simulations, and not our overall conclusions that stomatae behaviour is not well reproduced in ORCHIDEE and should be further improved. We clarify these points in the updated manuscript in the conclusion and in Sect. 3.3.

1.2 Minor comments

1. The title of the article needs to be revised. "Can we gain knowledge on COS anthropogenic and biogenic emissions from a single atmospheric mixing ratios measurement site?" is a yes or no question. Here we learn that OCS uptake is underestimated at night and that there are limitations in the anthropogenic inventory. Perhaps something like, "improvements to anthropogenic and biogenic fluxes of OCS in Western Europe".

   Thank you for this comment. We update the title to "Improved understanding of anthropogenic and biogenic carbonyl sulfide (COS) fluxes in Western Europe from long-term continuous mixing ratios measurements".

2. Abstract: use of the word "fluxes" versus "emissions" leads to confusing sentence constructions. Page 1, line 3: "Moreover, COS atmospheric mixing ratio data are still too sparse to evaluate the estimations of these sources and sinks." - do you mean on the global scale?

   We clarify the use of emissions/fluxes in the abstract; we rather mention uptake/source. Data are too sparse at the global scale already, despite attempts to do global inversions, but the issue is even more striking for Europe.

3. 4, 25: I don't see the Mace Head data plotted on Figure 1. Is something missing in the pdf?

   NOAA MHD data are depicted as red dots in Fig. 1. We will double check on the final version of the manuscript that these points appear properly.

4. Figure 1. Categories in the legend are missing in the graph in (a) and (b). For (a), it appears that the brown is background and the black dots, which end in 2015, are observations from GIF?

There might be a display bug in some computers. The categories appear on our system. We will double check this on different system during proof-reading.

5. 6, 5-6: There are good reasons to leave out these fluxes. Making the assumptions explicit, e.g. these fluxes do not contribute meaningfully to the observations, would be useful here.

These fluxes are very small in Europe compared to anthropogenic, biogenic and ocean fluxes. They rather play a role at the global scale. We clarify and state explicitly these reasons in the new manuscript.

6. 6, 13: similar results on the global scale?

That is correct. we clarify this point

7. 6, 27: COS uptake is related to stomatal conductance. For C3 and C4 plants, we expect stomatal conductance to increase during the day. Stomatal conductance never quite gets to zero when closed at night or in drought. If the ORCHIDEE plant uptake is based on Berry et al 2013, uptake should vary with stomatal conductance in the model as well as in reality.

The mentioned sentence is indeed misleading. We replace it by:

"In particular, biogenic fluxes exhibit a significant diurnal cycle. Indeed, vegetation COS uptake is regulated by stomatal conductance. There is a residual uptake during nighttime due to incomplete stomatal closure, and a stronger uptake during daytime when stomatal conductance increases."

8. 7, 7-9: It is unclear what this means. Are the national emissions erroneously attributed to urban hot spots? And we know that these hot spots are an artifact? But looking at Figure 2, it appears that Zumkehr spreads national emissions over the entire country, whereas the improved inventory locates emissions in a collection of hotspots.

Zumkehr, when using generic industry proxy, spreads OCS anthropogenic fluxes over the whole country with hotspots around large megalopolises. In our inventory, OCS industrial emissions are indeed limited to a handful of hotspots (with only one coal-power power plant and very few industrial sites, not located near the biggest megalopolises), but not correlated to large urban centers or other proxies. We clarify this sentence.

9. Figure 2. It would be good to have a color bar or similar for the contours in 2(f) so that the figure can be understood without digging into the text.

We agree that more stand-alone information about the contour in the figure is needed. A colorbar is not as informative as expected, regarding the arbitrary units of the sensitivity. We choose to clarify the sub-title for figure 2f

1.3 Concluding remarks

Thanks for the work in interpreting these data. It would be excellent to use this work to initiate a COS observing network analogous to ICOS.

Sincerely,

Mary Whelan

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We thank Mary Whelan for her fruitful comments on our manuscript.

2 Referee #2

2.1 Main remarks

This is an interesting study to gain the knowledge about COS anthropogenic and biogenic emissions from the single atmospheric mixing ratio measurement site at GIF, France. The manuscript is well constructed and well written and the methodology to analyze the emission inventories and comparison with COS measurements is excellent. The study contributes new knowledge to COS measurement and modelling studies; therefore, I recommend publication after minor revision.

Thank you for your fruitful comment. We address them below.

1. How is the measurement error, data quality and quality control of COS at GIF and comparison with COS measurement other locations? Please discuss them in the section of method, and/or in the discussion.

The description of observations and quality control was already detailed in previous publications and we did not want to add too much details in the present study. Still, we agree that we overlooked some key information and we update the manuscript accordingly.

2. The analysis did not consider biomass burning emissions from COS. Why is that?

Biomass burning in Europe, in particular in the vicinity of GIF in France, play a very limited role in OCS concentrations. They would play a role at the global scale, but global scale concentrations from the background already account for biomass burning and long range transport. We clarify this point in the updated manuscript.

3. The authors compared two anthropogenic emission inventories. Is it possible to compare them on the same scale? For example, to compare Fig. 2a and Fig. 2c on the same unit, and estimate the total emissions at the same region.

   It is not possible to use the same scale in Fig 2a and 2c as 2a is built on area sources, whereas 2c is an ensemble of point sources. The total emissions at the European scale are roughly a factor of 6 superior in Zumkehr, compared to our inventory, explaining the large discrepancies in simulations. We highlight this point in the corresponding section describing inventories

4. DMS is also an important precursor of COS. Is there any industrial production of DMS that can explain some of the overestimated COS measurement at GIF?

   To our knowledge DMS rather contributes to COS through oceanic emissions and later oxidation. Oceanic emissions have a very smooth impact on inland GIF concentrations. Thus we do not expect missed observed peaks to be explained by DMS fluxes. We still include some elements on DMS in the updated manuscript.

2.2 Minor comments and technical corrections

1. Page1, Line 3: "Moreover, COS atmospheric mixing ratio data are still too sparse to evaluate the estimations of these sources and sinks." While it is true that the COS mixing ratio data are sparse, but the evaluation of COS sources and sinks are always possible, e.g. using inverse model and satellite data assimilation.

   We agree that our statement is misleading. Observations are very sparse and allow for only rather coarse estimation of fluxes, with regional estimation very challenging.

2. Page 1, Line 4: "in the footprint a measurement site" to "in the footprint of a measurement site".

   We thank the reviewer for this typo

3. Page 1 Line 12: "ORCHIDEE" to "land surface model ORCHIDEE".

   We thank the reviewer.

4. Page 1, Line 17: (Whelan et al., 2018, and references within), this I suggest to cite important papers explicitly.

   We include most important references from Whelan.

5. Page 1 Line 17: "thinking" to "suggestions".

   We agree on the better wording

6. Page 1, Line 20: here the authors introduced inverse method, but there are already a few studies of COS inversions. I recommend proper citations here.

We agree that numerous studies, bottom up and top down have been made since the years 2000, with increased interest in the last 5 years. We include more publications, even though it is hard to include all of them. We are sorry if we overlooked some key publications.

7. Page 3 Line 6: "GgS/y" to "GgS.yr-1" to keep consistency with other units. And elsewhere.

We modified units for consistency

8. Page3 Line 17: "Remaud et al. (2023)" to "Remaud et al. (2023) and Ma et al. (2021)".

We are sorry for not including this citation here, even though it was included elsewhere.

9. Page 3 Line 22: It is suggested to cite Montkza et al. (2007) here.

Thank you for this suggestion

10. Page 6 Line 9: "horizontal resolution" to "horizontal resolution, respectively."

Thank you for this suggestion

11. Page 6 Line 14: "GgS/y" to "GgS/yr". Please fix this unit throughout the text and keep them consistent.

The notation is made consistent throughout the whole manuscript now

12. Page 6 Line 21: "respectively)." to "respectively."

This paragraph has been updated with description of SiB4 and this typo has been fixed as well

13. Page 6 Line 24: "1 degree ×1 degree" to "1o×1o", in order to keep consistent.

Thank you for this correction.

14. Page 6 Line 28: "The difference performance of our model with monthly and 3-hourly fluxes is evaluated in Sect. 3.1.". Maybe refer to "the different performances of our model with monthly and 3-hourly fluxes are evaluated in Sect. 3.1.".

Thank you for this correction.

15. Page 7 Line 4: "GgS", is it "GgS /yr" for the year 2012?

It is indeed per year. It is clarified now.

16. Page 7 Line 22: "in Tab. 2-3 of Belviso" to "in Table 2-3 of Belviso", and elsewhere.

We changed for the proposed notation.

17. Page 8 Line 11: “Barnes et al. (1994)”. This paper discussed DMS conversion rate to COS about 0.7%. It is not about CS2 conversion to COS.

    We agree on the reviewer that Barnes et al. was not well used by Zumkehr et al. We still keep the 87% conversion rate from Zumkehr.

18. Page 8 Line 15: “So called” to “So-called”.

    Thank you for this correction.

19. Page 8 Line 16: “above ground.” to “above ground level.”

    Thank you for this correction.

20. Page 8 Line 19: “(Tab. 1)” to “(Table 1)”.

    Thank you for this correction.

21. Page 10 Line 20: “coarse a variability” to “coarse variability”.

    Thank you for this correction.

22. Page 11 Table 2: “Background + coal (HM) + viscose (HM)” shows slightly larger bias and RMS, and smaller correlation than “Background + coal (HM)” or “Background + viscose (HM)”. Does this indicate the sum of coal and viscose from HM inventory is less accurate than single coal or viscose?

    This table only analyses long term variability. Coal and viscose emissions have impact only as peaks, which are most of the time the same between coal and viscose. With only one site, we cannot dig in systematically on peaks, as their magnitude is difficult to reproduce. The take-home message is that with our inventory, we obtain correct magnitude. We clarify this message.

23. Page 16 Line 2: “Zanchetta et al., 2023” to “Zanchetta et al., (2023)”.

    This reference is already in brackets, hence the year left-out of brackets

24. Page 16 Line 12: “Ramonet et al., 2011” to “Ramonet et al., (2011)”.

    Same as above

25. Page 16 Line 16: “(Remaud et al., 2023)” to “Remaud et al., (2023)”.

    Thank you for this correction.

References

Belviso, S., Pison, I., Petit, J.-E., Berchet, A., Remaud, M., Simon, L., Ramonet, M., Delmotte, M., Kazan, V., Yver-Kwok, C., and Lopez, M.: The Z-2018 emissions inventory of COS in Europe: A semiquantitative multi-data-streams evaluation, Atmospheric Environment, 300, 119 689, https://doi.org/10.1016/j.atmosenv.2023.119689, 2023.

Zumkehr, A., Hilton, T. W., Whelan, M., Smith, S., Kuai, L., Worden, J., and Campbell, J. E.: Global gridded anthropogenic emissions inventory of carbonyl sulfide, Atmospheric Environment, 183, 11–19, https://doi.org/10.1016/j.atmosenv.2018.03.063, 2018.