Author responses to reviews to EGUSPHERE-2024-549 "Improved understanding of anthropogenic and biogenic carbonyl sulfide (COS) fluxes in Western Europe from long-term continuous mixing ratios measurements"

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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 sections of the manuscript are reproduced in italic blue.

We also provide a track-change manuscript.

1 Report #1 by referee #3: Wu Sun

In this manuscript, Berchet et al. use a five-year record of atmospheric COS concentrations measured at a Paris suburb site to examine anthropogenic and biogenic COS fluxes over Western Europe. Given the sparsity of COS observations globally, it is encouraging to see this work leveraging long-term COS observations at a single site to shed light on regional COS flux components, aided by a Lagrangian transport model. The study shows promise in enhancing the usability of COS as a photosynthetic tracer at regional scales.

While the revised manuscript has been improved in response to prior review comments, I find some remaining issues. I have a few suggestions for improving the robustness and clarity of the findings.

We thank Wu Sun for these comments on our manuscript and we hope we answered all of them in the following.

1.1 Main comments

To alleviate potential bias from nighttime boundary layer parameterization, I suggest running additional tests to re-examine the diagnostics for different flux combinations (Table 2) using only mid-afternoon COS observations. Parameterization of the nighttime boundary layer is notoriously challenging and can lead to transport errors (e.g., Díaz-Isaac et al., 2018; Lopez-Coto et al., 2020; Monteiro et al., 2024). As a result, most Lagrangian inverse modeling studies assimilate only observations during well-mixed afternoon conditions, which both the authors and the reviewer, Dr. Whelan, have acknowledged. Lacking information on how well FLEXPART represents the nighttime boundary layer, I am not confident that bias in simulated nighttime concentrations could be attributed solely to the representation of nighttime stomatal conductance in terrestrial biosphere models (ORCHIDEE and SiB4). While I agree with some of the reasoning in the authors' response, I do not see this issue fully addressed. I reckon that the simplest way to test this issue could be to redo a set of analyses using only mid-afternoon COS observations and see if error diagnostics still follow the patterns in Table 2. As the atmosphere integrates fluxes day and night, afternoon observations should still be sensitive to fluxes in previous nights within the footprint area.

We think there is a misunderstanding: in the Table 2, we actually use observations during the afternoon i.e. 12:00-18:00 UTC, which corresponds in France to 1 p.m.-7 p.m. local time in winter and 2 p.m.-8 p.m. in summer. We have clarified this in the legend of Table 2 - now Table 3: *Statistical indicators of the performances of the model compared to the measurements at GIF for each contribution, based on the daily afternoon (12:00-18:00 UTC) means of simulated and measured mixing ratios; [. . .]* **and have added a general explanation in the text at the beginning of Section 3.1:** *In the following, we use the afternoon (12:00-18:00 UTC) daily averages of measured and simulated mixing ratios because the model is assumed to better represent the vertical mixing in the afternoon so that the comparison to measurements highlights the discrepancies in fluxes compared to the model's errors.* **See also the answer to the next comment.**

On the evaluation of anthropogenic COS flux estimates, because point sources of viscose and coal industries are largely collocated (Fig. 2c), their influences on observed COS concentrations would be highly correlated. Therefore, it seems challenging to evaluate COS fluxes from these two sectors separately. On the other hand, because changes in the wind direction may allow the site to pick up flux signals coming from different regions (Paris/Rouen, Benelux, British Isles, etc.), it would seem more helpful to focus on contributions from different regions rather than different industries that are collocated in space.

We agree that if both sectors were co-located, discriminating their contributions would be impossible. Nevertheless, they are actually not located so close to each other that the station at GIF cannot discriminate. For example, in France, where there is almost no coal industries but three coal power plants on the coasts in the Channel, on the Atlantic ocean and on the Mediterranean sea, the viscose industry is found in areas remote from the coasts i.e. in the North and in the East (see Fig. 2c in the paper and the zoom for France in Figure R1 here). The two activities also differ in their time profile e.g. coal COS emissions have an Inter-Annual Variability (IAV) derived from the IAV of CO_2 emissions due to power plants whereas viscose industry has constant emissions. This is why we chose to assess the emissions both for sectors and for different areas (see Fig. 2d for the areas definitions).

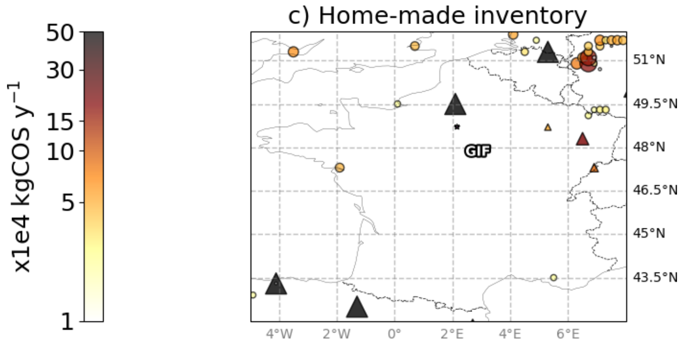

Figure R 1. *Zoom of Fig. 2c over France. Triangle: viscose industry; circle: non-viscose industry i.e. here, coal industry, mainly power plants; amount of emissions shown by diameter and color, according to the scale on the left hand-size. Star: location of GIF station.*

On the evaluation of biogenic COS fluxes, given that the focus is on nighttime bias, presumably resulting from underestimated nighttime stomatal conductance, and on summertime bias caused by potential emissions from certain crops, it may help to further assess bias, RMSE, and correlation (following Table 2) for daytime and nighttime measurements and by season. Model bias in representing nighttime COS uptake has been known since Kooijmans et al. (2017), and it would be better to give quantitative insights beyond reiterating this message. I suggest some simple tests along this line, for example, treating nighttime and daytime ecosystem fluxes as two separate tracers and checking how much nighttime fluxes need to be bumped up in order to match observed COS concentrations. This would provide more detailed insights into model bias and help inform relevant process representations in terrestrial biosphere models.

We agree that the reader may wish to see the whole set of statistics, following Table 2. We added supplementary material in Appendix C, here in Table R1, and refer to it in the main text: *In the following, we use the afternoon (12:00-18:00 UTC) daily averages of measured and simulated mixing ratios because the model is assumed to better represent the vertical mixing in the afternoon so that the comparison to measurements highlights the discrepancies in fluxes compared to the model's errors. More detailed results for the whole day or nighttime and per season are shown in Table C1.*

The idea of using two tracers for nighttime and daytime ecosystem fluxes and to evaluate how much nighttime fluxes must be changed to match the observations may be applied in atmospheric inversion to species such as CO_2 or CH_4 in Europe, where a whole network of measurement sites (e.g., ICOS) is available. With one station only for COS, we lack information for estimating the absolute values of the fluxes: only differences can be quantified. We added a sentence in Section 3.3 to clarify this point: *Disentangling the main contribution of mismatches between observations and simulations is very challenging with one site only. Differences at the synoptic scale, as represented in Figure 1, can originate from erroneous background, transport discrepancies, or from incorrect fluxes. Moreover, with one site only, absolute values of the biogenic fluxes cannot be systematically estimated. We therefore focus on the variations through time, particularly between day and night and seasonally. As represented in the time series in Appendix A, fine scale temporal variability, corresponding to the diurnal cycle, is well reproduced during some periods of the year, especially in Spring. The diurnal cycle is dominated by local* *influences, with remote influence of the background and of distant fluxes transported to GIF filtered out. We therefore focus here on 12-hour day/night differences [. . .]*

Table R 1: *Statistical indicators of the performances of the model compared to the measurements at GIF for each contribution; indicators are either computed over the whole period, i.e., Aug. 2014 - Dec. 2019 (see Section 2.1 , "whole"), separated into four seasons ("winter" = January, February, March; "spring" = April, May, June; "summer" = July, August, September; "fall" = October, November, December) or only over the year 2016 for comparison with the available contribution by the 3-hourly varying vegetation. For each period, the means are during the afternoon (12:00-18:00 UTC, "pm"), the whole day ("day") or nighttime (21:00-02:00 UTC, "night"). Bias = mean difference model minus measurement; RMS = root mean square model minus measurements; corr = Pearson's correlation coefficient between model and measurement time series. HM indicates emissions from our home-made inventory (see Section 2.2.3).*

Contribution	period	bias (ppt)			RMS (ppt)			corr		
		pm	day	night	pm	day	night	pm	day	night
Background	whole	23	26	25	33	34	34	0.76	0.78	0.77
	winter	16	19	19	26	26	26	0.54	0.56	0.55
	spring	23	27	33	32	35	43	0.27	0.26	0.46
	summer	22	22	20	31	30	30	0.72	0.82	0.79
	fall	30	34	31	40	43	42	0.35	0.43	0.42
Background + ocean	whole	23	26	25	33	35	35	0.75	0.78	0.76
	winter	17	19	19	26	26	26	0.53	0.55	0.54
	spring	26	30	30	34	37	38	0.28	0.3	0.23
	summer	22	22	20	31	29	29	0.72	0.83	0.80
	fall	28	32	31	40	42	42	0.3	0.38	0.42
Background + biogenic land	whole	-5	-10	-17	25	28	36	0.73	0.72	0.62
	winter	-1	0	-2	21	19	21	0.43	0.45	0.38
	spring	-14	-24	-34	28	35	48	0.43	0.43	0.31
	summer	-10	-22	-33	24	30	43	0.7	0.79	0.67
	fall	3	3	0	26	23	25	0.45	0.61	0.60
Background + biogenic land	2016	-4	-8	-14	25	28	36	0.72	0.73	0.65
Background + biogenic land with 2016 3-hourly vegetation	2016	-5	-5	-7	26	27	32	0.71	0.73	0.66
Background + ocean + biogenic land	whole	-5	-10	-17	25	27	35	0.74	0.74	0.64
	winter	-1	0	-2	21	19	21	0.44	0.46	0.39

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Table R 1: *Statistical indicators of the performances of the model compared to the measurements at GIF for each contribution (continued)*

Contribution	period	bias (ppt)			RMS (ppt)			corr		
		pm	day	night	pm	day	night	pm	day	night
	spring	-11	-20	-31	27	34	46	0.44	0.44	0.32
	summer	-10	-22	-33	25	30	43	0.71	0.81	0.70
	fall	1	1	-3	27	24	26	0.41	0.57	0.57
Background + ocean + biogenic land	2016	-3	-7	-13	25	27	36	0.73	0.75	0.65
Background + ocean + biogenic land with 2016 3-hourly vegetation	2016	-4	-4	-7	26	26	32	0.72	0.75	0.68
Background + anthro. Zumkehr	whole	100	165	231	151	230	358	0.11	0.02	0.02
	winter	103	144	176	164	214	292	0.1	0.19	0.17
	spring	83	164	264	105	216	384	-0.09	-0.17	-0.13
	summer	78	180	284	96	240	414	0.19	-0.09	-0.07
	fall	131	172	206	203	248	336	0.01	-0.13	-0.15
Background + anthro. Zumkehr w/o Paris/Rouen	whole	58	65	66	87	87	94	0.27	0.3	0.27
	winter	59	64	65	105	93	98	0.15	0.28	0.26
	spring	51	63	68	70	83	97	-0.12	-0.19	-0.14
	summer	46	52	52	60	66	70	0.37	0.36	0.31
	fall	73	77	78	101	99	103	0.01	-0.07	-0.06
Background + coal (HM)	whole	26	29	28	35	37	37	0.73	0.76	0.74
	winter	19	22	22	28	28	28	0.52	0.59	0.54
	spring	25	29	29	34	37	38	0.21	0.19	0.15
	summer	24	24	22	32	32	32	0.71	0.8	0.77
	fall	34	37	36	44	46	46	0.29	0.36	0.39
Background + viscose (HM)	whole	25	28	27	34	36	36	0.74	0.77	0.75
	winter	18	21	21	27	28	27	0.51	0.55	0.55
	spring	24	29	29	33	36	38	0.23	0.2	0.15
	summer	23	24	22	32	32	32	0.71	0.81	0.78
	fall	32	36	36	43	45	45	0.32	0.38	0.41
Background + coal (HM) + viscose (HM)	whole	27	31	30	37	39	39	0.71	0.74	0.72

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Table R 1: *Statistical indicators of the performances of the model compared to the measurements at GIF for each contribution (continued)*

Contribution	period	bias (ppt)			RMS (ppt)			corr		
		pm	day	night	pm	day	night	pm	day	night
	winter	21	24	24	30	30	30	0.47	0.55	0.51
	spring	26	31	32	35	39	40	0.16	0.13	0.09
	summer	25	26	24	34	34	34	0.69	0.79	0.75
	fall	36	39	39	47	49	49	0.25	0.32	0.34
Background + ocean + biogenic land + anthro. Zumkehr	whole	72	129	190	129	198	323	0.14	0.05	0.02
	winter	85	125	155	149	196	274	0.11	0.21	0.17
	spring	49	117	206	71	172	335	0.05	-0.11	-0.10
	summer	46	136	231	67	203	372	0.26	-0.07	-0.06
	fall	102	138	170	179	219	307	0.03	-0.1	-0.13
Background + ocean + biogenic land + anthro. Zumkehr w/o Paris/Rouen	whole	29	29	24	66	59	66	0.33	0.39	0.32
	winter	41	44	44	93	77	82	0.16	0.31	0.28
	spring	17	16	10	39	44	60	0.11	0.04	0.00
	summer	13	8	-1	34	34	41	0.49	0.53	0.41
	fall	43	44	42	76	70	73	0.05	0.04	0.06
Background + ocean + biogenic land + coal HM + viscose HM	whole	-1	-5	-12	25	25	33	0.74	0.74	0.64
	winter	4	5	3	21	18	20	0.49	0.59	0.48
	spring	-8	-16	-26	24	30	41	0.45	0.45	0.32
	summer	-7	-18	-30	23	27	39	0.72	0.82	0.71
	fall	6	6	3	29	26	27	0.36	0.54	0.54

Lastly, the study could give readers a high-level view of whether anthropogenic or biogenic COS fluxes dominate the variability in observed COS drawdown or enhancement (ΔCOS). Comparing Fig. 1d and Fig. 4, it appears the study domain is dominated by biogenic COS fluxes, but I'm not sure. I suspect that many in the carbon cycle research community would care about this question, but I don't see it explicitly answered.

We agree that our text was not explicit enough. We changed the title of Section 3.1 "General performances of the model at GIF", which is now *General patterns of simulated and measured COS concentrations at GIF* **and added a few sentences to clarify the relative weights of the contributions** *At GIF, the seasonal variations of COS mixing ratios are dominated by the contributions of the background and ocean i.e. by large scale fluxes; the variations at shorter time scales (week or day) are driven by the biogenic land contribution (Belviso et al., 2023). Finally, depending on the wind speed and direction, anthropogenic emissions may dominate for short episodes of high concentrations (see section 3.3.2 Selected winter* *episodes in Belviso et al., 2023).* **as well as in the abstract** *At GIF, the seasonal variations of COS mixing ratios are dominated by the contributions of the background and ocean; the weekly to daily variations are driven by the biogenic land contribution; anthropogenic emissions may dominate for short episodes of high concentrations.* **and in the general conclusion** *At GIF, the seasonal variations of COS mixing ratios are dominated by the contributions of the background and ocean; the weekly to daily variations are driven by the biogenic land contribution; anthropogenic emissions may dominate for short episodes of high concentrations (Belviso et al., 2023).*.

1.2 Specific comments

1. L4: "at a better scale than the global scale" –> "at the regional scale"

   OK, changed to *Moreover, COS atmospheric mixing ratio data are still too sparse to evaluate the estimations of these sources and sinks at the regional scale.*

   L13–14: "We find that the net ecosystem COS uptake simulated by both ORCHIDEE and SiB4 is underestimated in winter at night" - As I suggested above, it would be better to redo the evaluation with mid-afternoon COS observations only to confirm if the bias results from nighttime stomatal conductance representation.

   See our answer to the third main comment and the new supplementary Table in Appendix C. The statistical indicators computed with the background plus the ocean plus the biogenic land contribution (Table R1, lines "Background + ocean + biogenic land") confirm that the diurnal cycle of the fluxes plays a role in the poor night-time agreement between the simulations and the measurements. The vegetation uptake is only a small portion of the terrestrial uptake (see Maignan et al. 2021): too weak a soil uptake could explain part of the discrepancy. The remainder of the discrepancies during the night is indeed possibly due the transport. The underestimation of the ecosystem COS uptake by ORCHIDEE and SiB4 in winter at night is next to be precisely quantified, which is not in the scope of this work using only one station.

   L16–17: "In Summer, both models properly represents fluxes, with better agreement from ORCHIDEE in terms of magnitudes." - What about potential COS emission episodes?

   As stated in the main text l.79-80: "Some natural processes emitting COS in the atmosphere are still only suspected, for example in plants used in agriculture (Belviso et al., 2022a; Maseyk et al., 2014; Bloem et al., 2012). Therefore, such emissions are as yet no taken into account in ORCHIDEE, SiB4 nor any other model to our knowledge. Nevertheless, these suspected COS emissions by crops (rapeseed in this case) are very localised in time (at the end of the summer) and are not expected to affect the seasonality. In addition to these possible COS emissions due to crops, soils may emit COS, even though they are overall a net sink of COS. These emissions are taken into account in ORCHIDEE and SiB4 (each model with its own parameterizations) and high-temperature situations may make soils a net source of COS. We modified in the summary *In Summer, both models represent fluxes sufficiently well, with better agreement from ORCHIDEE in terms of magnitudes.*

L24–37: Since this study is not an atmospheric inversion, I don't see a need to introduce it. Consider focusing on the forward model application of linking flux fields to mixing ratios.

We agree that this study is not an atmospheric inversion. Nevertheless, we feel that it is important to keep this study connected to the community of atmospheric inversion. COS has been studied by the CO_2 flux community for estimating CO_2 fluxes linked to photosynthesis by atmospheric inversion. We think it is important to link this work to this community because it may help in assessing the feasibility of using COS measurements for constraining CO_2 fluxes. This is particularly relevant for network planning and funding.

L40–80: This part feels overly detailed as an introduction. I suggest consolidating these bullet points into a coherent paragraph and emphasizing the key uncertainties this study aims to tackle. To tidy it up, it may help to list the magnitudes of different COS flux components in a table.

We agree that the bullet points are each very detailed. This is because this part is aimed at the CO_2 community, which wants to make use of COS but does not have an extended knowledge of COS sources and sinks. We added Table R2 (Table 1 in the new version of the paper) to consolidate the main information.

Table R 2: *COS sources and sinks: global estimates available at the time of this study, from Whelan et al., 2018; Remaud et al., 2023.*

Category	flux component	magnitude ($GgS.y^{-1}$)	references
natural oceanic	source via DMS and CS_2 + emissions	265±210 507	Lennartz et al., 2017, 2021 Remaud et al., 2022 (see Sect. 2.2.1)
anthropogenic viscose industries anthropogenic others	source via CS_2 source via CS_2 + emissions	400±180	Zumkehr et al., 2018
biomass burning	emissions	60±37	Stinecipher et al., 2019
anoxic soils	emissions	96	Abadie et al., 2022
oxic soils	net sink	-126	Abadie et al., 2022
net soils	net sink	-30 -89	Abadie et al., 2022 Kooijmans et al., 2021a
vegetation	uptake	-530 -664	see Section 2.2.2 Kooijmans et al., 2021a
atmospheric oxidation by OH	sink	[-130 , -80]	Whelan et al., 2018
atmospheric photolysis	sink	-50±15	Whelan et al., 2018

L100–L110: This paragraph needs to give a clear roadmap of what the study aims to achieve. Currently, it sounds like this study is picking on the bias in Zumkehr et al. (2018) inventory, but there is more to be said about biogenic COS fluxes and the underlying physiological processes.

It is true that we cannot access the underlying physiological processes in this study, because we use atmospheric data of mixing ratios of COS, which cannot provide information on these. We only aim at assessing the currently available estimates of COS fluxes. We reformulated to make the text clearer: *Therefore, this study aims at quantitatively assessing the anthropogenic and biogenic COS fluxes at the regional scale. It demonstrates that a set-up based on one measurement site in Western Europe, which provides data for over half a decade, makes it possible to:*

- *quantitatively assess the discrepancies in Zumkehr's anthropogenic emission inventory in the footprint of the measurement site*
- *evaluate a new inventory based on industrial emission declaration in the European Union*
- *study the seasonal and diurnal cycles of biogenic fluxes, based on the ORCHIDEE and SiB4 processed-based land surface models, and point to strengths and weaknesses in these two models.*

L121–122: How often was the calibration carried out?

As indicated in Belviso et al. (2020), "Calibration was performed about every three weeks". Information added: *Calibration is carried out every three weeks using 1-ppm primary standard, [. . .]*

L134: Here, it would help to refer to Sect. 2.3 for background calculation (L232–238). Or move that paragraph on background calculation here.

We added a cross-reference to Section 2.3.

L148: "DMS emissions can only be non natural ..." - Wetlands and the ocean do emit DMS. I get the point of this sentence, but the logic does not follow.

This sentence was indeed not clear and also contained typos. It has been rewritten as: *Anthropogenic DMS emissions also exist. However, Sarwar et al. (2023) and von Hobe et al. (2023) have shown that their impact (through oxidation) on simulated COS concentrations is negligible.*

L151: "box models" - I would call them spatially resolved box models to avoid potential confusion.

This was not clear, we modified the sentence: *The emissions of the three species have been computed using coarse-resolution box models calibrated [. . .]*

L165–168: Does this mean that ORCHIDEE and SiB4 COS flux fields used here are optimized posterior estimates?

ORCHIDEE and SiB4 COS fluxes are not optimized posterior estimates. What was meant here is that the atmospheric COS mixing ratio fields at the surface, which are required by ORCHIDEE and SiB4 to compute the COS fluxes from the surface to the atmosphere, are provided from atmospheric inversions assimilating NOAA COS

data, hence representing realistic variability of concentrations. These sentences were confusing and did not bring useful information: they have been removed in the new version of the text.

L172: "In particular, biogenic fluxes exhibit a significant diurnal cycle." - I am confused here. Aren't the posterior fluxes from Remaud et al. (2022) and Ma et al. (2021) monthly?

We agree that the sentence is a bit confusing between model and the real world. Actual biogenic fluxes vary diurnally but modelled fluxes do not. We must therefore assess the impact on the simulated concentrations of not taking into account this diurnal cycle. We have clarified the sentence: *In particular, real-life biogenic fluxes exhibit a significant diurnal cycle (whereas modelled fluxes are constant).*

L175: "We assess the sensitivity of our simulations to daily varying biogenic fluxes by using 3-hourly vegetation uptake as simulated by ORCHIDEE and SiB4 for the year 2016." - Are these posterior flux estimates or unadjusted prior flux estimates?

These are prior flux estimates, see answer to comment on L165-168 above.

L183–184: The components sum to 61.4 GgS per year not 62.1 GgS per year. Are there other minor components not listed here?

Yes, there are: we didn't list the industrial solvents for ≈0.7 GgS nor the paper industry for ≈0.025 GgS, we mention these sub-sectors in the Introduction, in the list of anthropogenic activities, L51seq.

L186: I think you mean "effective" not "efficient".

It's been corrected.

L220: One advantage of a Lagrangian model over an Eulerian model is the flexible resolution at which transport is resolved. As a result, Lagrangian models can use meteorological input at a finer resolution than the resolution at which footprints are aggregated. Is there a reason to run FLEXPART with 1° meteorology input instead of the native resolution (0.25°) of ERA5?

The main reason to use a coarser meteorology is that the simulations with the native resolution require too much computed resources with regards to the aim of the study, especially as we include a large domain beyond continental Europe to cover oceanic contributions.

L243: An RMSE of 35 ppt does not feel like a small error; it seems to be around 1/3 of the seasonal cycle amplitude of COS (Fig. 1b).

We agree, we meant it is small relative to the RMSEs obtained with anthropogenic emissions for example. The sentence has been clarified: *Its contribution at GIF ensures a good simulation of the variability (Table 2: Pearson's correlation ≥ 0.75) and a base-line mean error ≤ 35 ppt over the whole period of interest.*

L246–248: Again, here it is crucial to clarify whether the three-hourly flux estimates are optimized posterior estimates or prior estimates coming out directly from terrestrial biosphere models.

See answer to L165-168 above: we hope it is clear now that they are prior estimates from the biosphere models.

L249: "from 0.74 to 0.72" - The decrease in correlation is a bit surprising because, all else being equal, I would expect the correlation to stay unchanged or increase slightly with the inclusion of diurnal variability. Are these correlation coefficients just for the year 2016 or the entire period?

The computations with the 3-hourly vegetation in 2016 are done only for the year 2016, we added the same computations for comparison (see Table 1 here) and added the information in the legend of the Table: *Statistical indicators of the performances of the model compared to the measurements at GIF for each contribution, based on the daily afternoon (12:00-18:00 UTC) means of simulated and measured mixing ratios; indicators are either computed over the whole period, i.e., Aug. 2014 - Dec. 2019 (see Section 2.1) or only over the year 2016 for comparison with the available contribution by the 3-hourly varying vegetation[. . .]*

L249: "The variability is not better reproduced when adding the natural emissions to the background" - Which component(s) of "natural emissions"?

The "natural emissions" in this sentence are the ocean and biogenic land, we changed the sentence *The variability is not better reproduced when adding the natural emissions from the ocean and the biogenic land emissions from the soils and the vegetation to the background (correlations $\leq$0.75 in all cases), which may be due to a too [. . .]*

L276–291: Unclear from this paragraph how the contributions of biogenic, anthropogenic, and oceanic COS fluxes to observed COS concentrations compare with each other. I suggest adding a table to list their respective contributions to ΔCOS.

To help compare the natural and anthropogenic contributions, we added Figure R2 in Appendix B and added in the text: *At GIF, the seasonal variations of COS mixing ratios are dominated by the contributions of the background and ocean i.e. by large scale fluxes; the variations at shorter time scales (week or day) are driven by the biogenic land contribution (Belviso et al., 2023). Finally, depending on the wind speed and direction, anthropogenic emissions may dominate for short episodes of high concentrations (see section 3.3.2 Selected winter episodes in Belviso et al., 2023). The contributions to COS mixing ratios at GIF due to the ocean, the biogenic land fluxes and the anthropogenic emissions are shown in Figure B1.*

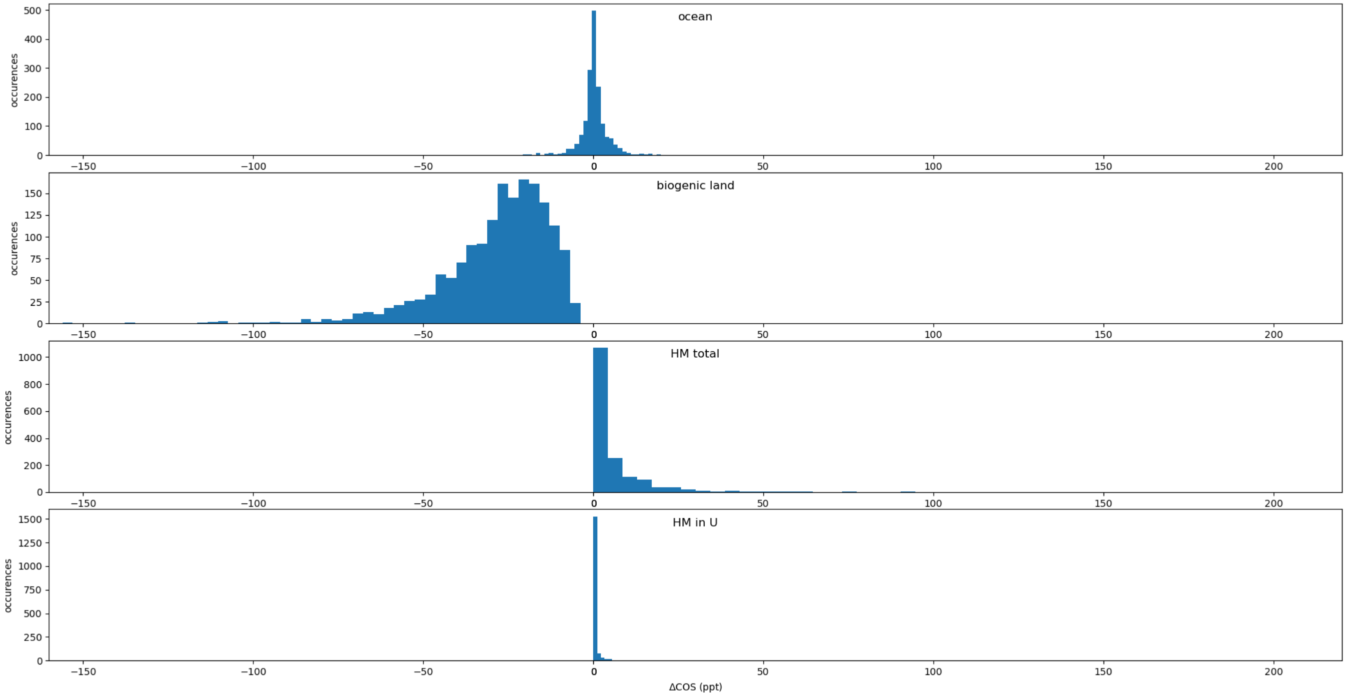

Figure R 2. *Occurrences of contributions (ΔCOS, in ppt) to COS mixing ratios at GIF due to the background, the ocean, the vegetation and soil ("biogenic land") and our home-made anthropogenic emissions (total and only the Paris+Rouen area). Total number of occurrences: 1673 simulated values matching afternoon (12:00-18:00UTC) valid mean observations between 2014 and 2019.*

Fig. 1: In panel a, it's quite challenging to distinguish between GIF (afternoon) from GIF (all). Consider enhancing the color contrast or use different symbols. In the caption, background calculation should refer to Sect. 2.3 not 2.1.

We enhanced the color contrast and increased the size of the figure; the cross-reference has been corrected.

Fig. 2: In panel e, it would be more helpful to show the summed footprint map over the entire study period to check the influence area coverage. Readers may not know if the footprint map for May 2019 is representative of the whole period (2014–2019).

The footprint for May 2019 shown in the Figure is an illustration of the typical size of the area covered by the footprint. We put the footprints summed up over a whole year in the new Figure 2.

Fig. 4: Unclear what "growths" means in the figure legend. For panel c, it would be better to report COS fluxes in pmol m^{-2} s^{-1}.

Figure 4 has been changed accordingly.

2 Report #2 by Anonymous referee #4

3 General comments

This is an interesting paper that performs a detailed analysis of a long time series of COS measurements in GIF, France. Although the wording should be improved (I had difficulties understanding the manuscript at several places), I particularly like the systematic analysis of the impact of different fluxes on the simulated mixing ratios. This allows the authors to draw conclusions about the quality of the anthropogenic emission inventory, and the performance of the biosphere model. Nevertheless, I would like to suggest a couple of checks and/improvements that could further improve the understanding.

(1) CS2 is emitted by industry (VI in their homemade inventory). CS2 is converted in the model to COS with a prescribed timescale. It would be instructive to test (a) the impact of the implied timescale (conversion rate is not very well known and depends on season) (b) the impact of a diurnal variation on the CS2 $\rightarrow$ COS conversion. Since the conversion is performed by the OH radical, these impacts are vital to analyze

We agree that the lifetime of CS_2 is not well known. We tested two of the available values for the kinetics of the oxidation of CS_2 by OH: the conclusions of our study did not change. We added this information in Section 2.3: *Note that a life time of 1.5 day has also been tested (not shown), with almost no changes in the conclusions of this study.*

We agree that a study targeting the diurnal variations would need to take into account the impact of OH diurnal cycle. Since diurnal varying emissions were not available at the time of our study, save for 3-hourly vegetation fluxes for 2016, the impact of chemistry at the hourly resolution is not in the scope of our study. We added this item in the Conclusion: *For anthropogenic and oceanic CS_2 emissions, the kinetics of the conversion of CS_2 into COS through its ts oxidation by OH is not well-known. Moreover, through OH availability and temperature, the lifetime of CS_2 depends on the season and has a diurnal cycle. The impacts of these variations on the chemical source of COS must be assessed, when more relevant information, e.g. varying diurnal emissions are available.*

(2) The model uncertainty is not discussed in any detail. The authors employ a Lagrangian particle model, and it would be instructive to know what is the impact of the number of particles released every six hours, the effect of resolution on the results, etc. Since the analysis is based on only one station, a proper representation of that station in the model is important. How well is the planetary boundary layer height simulated? What about wind validation?

The Lagrangian model used in this study, FLEXPART, plus the meteorological data on which it relies, ECMWF ERA5, are well recognized tools in the atmospheric community. Moreover, the boundary layer height and wind directions are provided by the state-of-the-art ECMWF ERA5 data with very good performances (e.g., Molina et al., 2022). We added more information regarding our choices of configuration in Section 2.3: *The performances of ERA5-provided boundary layer height and wind direction are very good (e.g. Molina et al., 2021).* **and** *FLEXPART and ERA5 meteorological data are well recognized tools in the atmospheric community, the combination of the two being widely used in the atmospheric inversion community (Pisso et al., 2019; Bakels et al., 2024). The choices made for FLEXPART's configuration (number of particles released, frequency of releases, resolution) are consistent with the set ups used for the atmospheric inversions fluxes (e.g., Bergamaschi et al., 2022; Thompson et al., 2021).*

(3) The final analysis of the paper investigates concentration changes between 6 a.m and 6 p.m., and between 6 p.m. and 6 a.m. the next day. In spring the diurnal variation in the biogenic fluxes greatly improves the comparison to simulations. In summer, this is not the case, but this is not analyzed further. My first guess would be that the effects on the diurnal fluxes interfere with the (changing) effect of entrainment from the atmosphere aloft. I would suggest to perform a budget analysis in which the concentration changes are attributed to (1) the effect of the fluxes (2) the effects of vertical transport (i.e. entrainment or detrainment) and (3) advection.

We agree that such a study would be interesting but it would also be very complex and not in the scope of this paper. It is further work required to fully make use of the long COS mixing ratios time series. We added this item as a perpective: *An analysis discriminating between the impacts of i) the fluxes, ii) the chemical source, iii) the vertical transport and iv) the advection on COS mixing ratios could be performed from a set of simulations, with a careful design, computer resources and up-to-date hourly varying fluxes.*

4 Specific comments

Further remarks and suggestions are provided in the annotated pdf.

These remarks are detailed here with our answers.

- 10-13: Too long sentence

  OK *The main limitation of this inventory is the flat temporal variability applied to anthropogenic fluxes due to lack of information on industrial and power-generation activity in viscose factories and in coal-power plants. As a consequence, there are potential mismatches in the simulated plumes emitted from these hot-spots.*

- 27: retrieve: estimate (is better I think)

  OK

- 27,28: in the prior and in the measured: by (or cintained in)

  OK

- 61: 96 GgS: here no uncertainty?

  There is indeed no uncertainty provided by the process-models.

- 94-96->issue: unclear sentence

  We clarified the sentence: *Anthropogenic emissions in the footprint of GIF were proven to be overestimated when analyzing specific events selected in the relatively long continuous time series available. Nevertheless, further characterization was not possible at the time of the study.*

- 112: purposes (or which is the main original purpose)

  OK

- 122: At what mixing ratio level? 1.2% of 1 ppm is not OK!

  Instrument and calibration information are extensively detailed in Belviso et al., 2013 and 2016. Information on calibration was misleading in the previous version of the manuscript. We update it as follows: *Calibration and drift correction is done every three weeks using a calibration gas containing 1.013 ppm of COS in helium, with occasional calibration using a standard of compressed air with 573 ppt of COS, and another standard traceable to NOAA ESRL standard of 448.6 ppt. Calibrations led to a repeatability of 1 % and a precision of 0.2 %.*

- 136: designed -> need specification: was this a global inversion?

  Yes, it was, it has been made clearer: *These global atmospheric inversions were designed to assimilate data from the background NOAA observation sites, such as MHD.*

- 148 DMS emissions: ??? You mean emissions from land? As far as I know ocean emissions are natural.

  This sentence was not clear at all and contained typos. It has been rewritten as: *Anthropogenic DMS emissions also exist. However, Sarwar et al. (2023) and von Hobe et al. (2023) have shown that their impact (through oxidation) on simulated COS concentrations is negligible.*

- 166-168 -> fluxes: Unclear: you use fluxes to compute fluxes? I think you use mixing ratios to compute first order uptake (and not the fixed 500 ppt "placeholder". **What was meant here is that the atmospheric COS mixing ratio fields at the surface, which are required by ORCHIDEE and SiB4 to compute the COS fluxes from the surface to the atmosphere, are provided from atmospheric inversions assimilating NOAA COS data. These sentences were confusing and did not bring useful information: they have been removed in the new version of the text.**

- 176: is: should be are, but maybe assume "performance" instead of performances.

  OK

- 187 no necessarily -> NOT

  OK

- 200: viscose: But how do you account for the indirect nature of CS2 emissions? Oxidation to COS is not instantaneous....

  A cross-reference to the description of how our simulations account for CS_2 oxidization, in Sect.2.3, has been added.

- 213 Beauvais: Why is this relevant? Is there industry there?

  We have made the text clearer: *The closer to GIF (large black triangle in Northern France in Figure 2c) is in the city of Beauvais, which lies about 85 km to the North of GIF, i.e., further than the Paris area.*

- 224: 3 days: OK, maybe mention this earlier in the manuscript somewhere....One more issue on this: CS2 is oxized y OH which has a distinct diurnal cycle: does that matter?

  See answer to L200. For the diurnal cycle, please see the answer to general comment 1.

- 251: what is "coarse variability"?

  Here we mean that the monthly temporal resolution of the oceanic emissions is too low compared to the variability of the transport. This sentence has been modified as: *The variability is not better reproduced when adding the natural emissions from the ocean and the biogenic land emissions from the soils and the vegetation to the background (correlations ≤0.75 in all cases). This may be due to the monthly resolution of the ocean emissions (Section 2.2.1) being too coarse compared to the variability of the transport and to an issue with the variability of the vegetation uptake or the soil exchanges, probably at the seasonal scale, which is assessed in Section 3.3.*

- 270 further invest are -> IS

  OK

- 292 obs sites: here it would also help to analyse stack emissions directly?

  We agree that emission factors used to assess coal-power-plant emissions are very coarse and can vary a lot depending on the power-plant technology, the type, origin and quality of coal used in the plant and other factors. Similarly, we used CS2 emissions as declared and reported by industries, also based on imprecise emission factors. Having extra measurements directly targeted at specific industry would significantly improve our understanding of anthropogenic emissions. In Belviso et al., 2023, we used measurements carried out directly downstream a viscose factory in Rouen to evaluate emissions from this factory. More systematic studies would be needed, although mobile campaigns are complex to operate considering the complexity of COS measurements. We include such short discussion in the text. *Additional continuous observation sites would be needed in different places of Europe to clarify the relevancy of our inventory beyond the Paris area and vicinity. In addition, our inventory is based on coarse emission factors, both for the viscose industry and for coal power plant. Facility-level campaign as carried out around a viscose factory near Rouen in Belviso et al., 2023, would significantly improve our understanding of COS anthropogenic fluxes, thus our inventory.*

- 301: between day D at 6 p.m. and day D at 6 a.m.: strange that you mention the later time first? Maybe swap?; variation: I think "variation" should be better defined. What does it exactly mean?; I guess I get it now (later), but I think "a mean concentration difference between xx and xxx would be much clearer. Variation for me is related to variability. + 307: I must say that variation of variations does not clarifies the situation here? Please define a metric, and give it a name (DV, NV)??? but define properly

  We changed "variation(s)" to "difference(s)" and introduced the notations Δ^{COS}_{day} and Δ^{COS}_{night} where relevant in Section 3.3 and Figure 4.

- 305: have impact on, or impact (without on x2).

  OK

- 322: consistently->consistent

  OK

- 327: uptake: this last addition is unclear....I guess you want to say that plant uptake during night is the cause?
  This sentence was not clear and has been changed to: *This discrepancy suggests a persistent nighttime uptake not adequately represented by ORCHIDEE's diurnal cycle. The ORCHIDEE minimal stomatal conductance at night (see Section 2.2.2) has to be revised.*

- 332: Sib4: . Here, a budget analysis would help. How much of the increments are caused by land-atmosphere exchange, and how much by transport processes mixing the boundary layer (or stabilizing it)? **Such an analysis is beyond the scope of this first study: please see answer to general comment 3.**

- 346, 348, 350: declared -> reported
  OK

- 351: arise -> arises? or limitations arise
  OK

- 360: meteorological: would a "plume" approach help here? Aermod type?
  This study does not treat with scales for which plume based models are relevant. Independently of the quality of the model, a simple shift in the wind direction or speed in the meteorological data leads to high discrepancies in the mixing ratios. Therefore a plume approach would not be less dependent on the transport limitations.

- 367: winter at night: here the question is whether the model is adequately able to represent the stable night-time boundary layers in winter...
  The nighttime BL in winter is probably not very well represented, even though we use state-of-the-art ECMWF data. These uncertainties prevent us from quantifying the under-estimation of the nighttime COS uptake; however, our night-day-based approach confirms qualitatively the existence of this under-estimation. We clarified this in the text *The uncertainties in the modeling of transport at night in winter prevent us from quantifying the under-estimation of the nighttime COS uptake. However, the discrepancies between simulations and observations shown by the nighttime and day differences suggest the existence of such an under-estimation.*