Constraining the budget of atmospheric carbonyl sulfide using a 3-D chemical transport model

Response to Reviewers' Comments

We thank the reviewers for taking the time to evaluate our manuscript and for their positive and helpful comments. These comments are reproduced below in *italics*, followed by '>>' and our responses.

References to line numbers for new specific sentences based on Reviewer comments refer to the marked-up version of the new manuscript.

Reviewer 1

The authors have made a large effort to answer a majority of the comments; I notably appreciate the addition of Figure 2 representing seasonal anomalies of OCS concentrations at NOAA sites, as well as the various OCS flux maps provided in the Supplementary Material. However, although the manuscript has been improved and is now clearer and easier to follow, not all answers were satisfying and there are still several points that need to be correctly addressed.

General comments

State-of-the-art fluxes

It's a good start to consider state-of-the-art (SOTA) fluxes, but comparing the concentrations derived from the transport of the prior SOTA fluxes to the concentrations derived from the transport of the optimized TOMCAT-OCS fluxes does not make sense. You have to think about the scientific message that you want to convey, which is probably not that you can better match observed concentrations by manually scaling outdated fluxes.

My initial comment was the following one: "How could the improvements obtained with TOMCATocs on atmospheric OCS concentrations be compared to the improvements made when using inversion systems such as in Ma et al. (2021) and Remaud et al. (2022)?"

Indeed, comparing with concentrations computed based on the optimized fluxes from Ma et al. (2021) and/or Remaud et al. (2022) would have been more fruitful.

>> "*You have to think about the scientific message that you want to convey, which is probably not that you can better match observed concentrations by manually scaling outdated fluxes*." – We have considered this point and have included some additional comments in the discussion and conclusion on what the difference between $TOMCAT_{OCS}$ and $TOMCAT_{SOTA}$ means in terms of the fluxes. For example, why is the mechanistic model (the SOTA vegetative flux) not capturing the seasonality adequately? What underlying difference between the two methods is causing a dissimilar seasonality at surface sites?

"*Indeed, comparing with concentrations computed based on the optimized fluxes from Ma et al. (2021) and/or Remaud et al. (2022) would have been more fruitful*." – It is worth noting that while these are optimised fluxes, they do not provide information on bottom-up processes. Hence, we direct the reader to consider the above, i.e., the difference between the LRU method and the mechanistic approach.

New passages can be found in Section 5 around line 620 in the marked-up version of the new manuscript and line around 680 in Section 6.

Comparison with ACE-FTS

In your conclusion you write (L587-589): "Furthermore, we see an excellent comparison with ACE-FTS throughout most of the atmosphere, which suggests the free troposphere and gradient above the UTLS is well represented by $TOMCAT_{OCS}$, and therefore so too are the sources and sinks driving the model. Which shows promise for future OCS work using TOMCAT". I strongly disagree regarding sources and sinks and suggest removing this assertion. It contradicts what you wrote earlier (L351-352): "As ACE measures the upper troposphere and stratosphere primarily, this region is less sensitive to surface processes, so we only compare $TOMCAT_{OCS}$". What you write later (L612-613) is thus more sensible: "While we have shown that $TOMCAT_{OCS}$

compares well with satellite observations, the region between the surface and approximately 6 km, which is not measured by ACE-FTS, could hold a lot of information useful in resolving surface fluxes."

>> "Furthermore, we see an excellent comparison with ACE-FTS throughout most of the atmosphere, which suggests the free troposphere and gradient above the UTLS is well represented by $TOMCAT_{OCS}$, and therefore so too are the sources and sinks driving the model. Which shows promise for future OCS work using TOMCAT." – We agree that parts of this quote required a change and it now reads (line 647):

"Furthermore, we see good comparisons with ACE-FTS throughout most of the atmosphere, which suggests the free troposphere and gradient above the UTLS is well represented by $TOMCAT_{OCS}$. Therefore, there is a suitable balance between model sources and sinks from the surface to simulate atmospheric OCS."

We still assume they are a reasonable set of fluxes, as they are able to model the OCS global spatial distribution in absolute values.

ACE-FTS can test the overall budget in the mid-upper troposphere and give some indication of spatial variations, but it won't discriminate between different processes at the surface. ACE-FTS is an important additional piece of information which can test models, but cannot replace actual surface observations.

Specific comments

L39-40: « This work also shows that the LRU approach is a suitable alternative to mechanistic approaches to quantifying vegetative uptake and will be valuable in using OCS to estimate GPP going forward. » -> It is not clear at all that you made such a demonstration in this study.

>> Agreed. We have amended this statement to read (line 38): "This work also shows that the LRU approach is an adequate representation of the OCS vegetative uptake, but this method could be improved by various means, such as using a higher resolution GPP product or plant-functional-type-dependent LRU."

L145-147: Please quantify the uncertainties associated with ACE-FTS retrievals.

>> The errors in OCS measurements by ACE-FTS are approximately 4% throughout the entire profile, and are approximately 7.2% below 10 km and 3.4% above 20 km. Between these altitudes, the error varies latitudinally and is somewhat dependent on tropopause height but is around 3.8%. An additional sentence has been included at the end of Section 2.1 (line 156):

"The errors in ACE OCS measurements amount to a mean of approximately 3.8% throughout the entire profile globally. In the lower troposphere, below 10 km, errors are larger, approximately 7.2% and above 20 km, are relatively low, at 3.4%."

L170-173: I understand the COS concentration is computed every 6 hours, but the GPP is available on a monthly basis, please state that the OCS vegetation flux is also computed every 6 hours.

>> OCS vegetation flux in $TOMCAT_{OCS}$ is indeed calculated every 6 hours. Additional sentence added (line 184): "In the case of $TOMCAT_{OCS}$, the vegetative flux is also calculated every 6 hours."

Additionally, "Each time-step in the model a new F_{OCS} value is calculated" can be found around Line 230. Which was in the second version of the text.

L204: "Anoxic soil emissions are neglected in this study." -> Justify your choice, their contribution is quantified in Abadie et al. (2022) to help you discuss this matter.

>> Anoxic soil emissions have undergone several improvements in our understanding and their quantification since the initial model runs in this study. The above phrase has been amended to (line 220): "Anoxic soil emissions are neglected in this study but with the availability of new data sets future simulations could include these sources (Abadie et al. 2022; Whelan et al. 2022)."

L229-230: "The use of a constant LRU value has been found to contribute less to error in the calculation of Focs than differences in GPP between models on a continental scale (Hilton et al., 2017)." -> Yes, but you are using a single GPP in this study. Plus Maignan et al. (2021) state the opposite (40% of uncertainty on Focs with different land surface models against 70% of uncertainty with different LRUs).

>> Sentences have been amended to (line 246): "The use of a constant LRU value was found to contribute less to error in the calculation of F_{OCS} than differences in GPP between models on a continental scale by Hilton et al. (2017). However, Maignan et al. (2021) found the opposite, that 70% of uncertainty was attributed to the use of three different LRU datasets and 40% when considering three land surface models. As there are available plant-functional-type-dependent LRU datasets, implementing spatially-varying LRU values will be considered in future work (Seibt et al. 2010; Maignan et al. 2021)."

Ultimately a single LRU was used at the start of the study as no spatially resolved LRU datasets were available at the time, as far as we were aware. However, future TOMCAT studies of OCS can exploit such data sets.

L235-236: "Only monthly data for 2010 was used, as the interannual variability in the amplitude of the GPP cycle is only about 1% (Chen et al., 2017)." -> As already stated in my former review, the study from Chen et al. (2017) does not conclude that interannual variability in GPP amplitude can be neglected, you have to change your argumentation.

>> When this work started, we only had a few years of TOMCAT CO_2 data to help calculate the vegetation flux. However, it made sense to use the TOMCAT CO_2 data since we were using TOMCAT to simulate OCS (e.g. consistent dynamics etc.). As a result, 2010 was chosen as it represented a year approximately in the middle of the study period and would be reasonably representative of the long-term absolute values. Since 2010 was used for the CO_2 fields, we then used 2010 for the GPP fields for consistency. The reviewer is correct that in an optimised setup, CO_2 and GPP would be annually varying across the full study period. Therefore, in future work on OCS using TOMCAT, longer-term CO_2 and GPP data sets can be included.

The following text:

"Only monthly data for 2010 was used, as the interannual variability in the amplitude of the GPP cycle is only about 1% (Chen et al., 2017). Monthly mean gridded CO_2 surface mixing ratios for 2010 from a TOMCAT simulation which assimilated surface flask observations of CO_2 are used for the CO_2 concentration (see Fig. S4 in the supplement) (Gloor et al., 2018). As we compare only monthly means at the surface and seasonal OCS to ACE-FTS, long-term inter-annual variability was not considered in the scope of this work."

Has been amended to (line 254):

"Monthly mean gridded CO_2 surface mixing ratios, used to calculate F_{OCS}, came from a TOMCAT simulation which assimilated surface flask concentrations for 2010 (see Fig. S4 in the supplement) (Gloor et al., 2018). Given that 2010 is situated approximately in the middle of the study period, it should be a reasonable estimate of the long-term average. Therefore, the GPP data used was also for 2010, given its relatively small inter-annual variability (Chen et al., 2017). As we compare only monthly means at the surface and seasonal OCS to ACE-FTS, long-term inter-annual variability was not considered in the scope of this work. However, future work using TOMCAT can exploit longer-term records of surface CO_2 mixing ratios and GPP."

L242-243: "is slightly under half that of the largest estimation of 1115 Gg S" -> 629 is larger than 557.

>> under -> over

L243: "over half that estimated by Launois et al. (2015b), 1335 Gg S" -> 629 is lower than 667.

>> over -> under

L246: The title of this section « Balancing the OCS Budget » should be « Manual scaling of the prior fluxes to balance the OCS budget and improve the agreement with the NOAA sites », given lines 277-280 are a bit hidden but justify the notion of « constraint » in your updated title.

>> The section title has been renamed: 'Scaling of OCS Prior Fluxes to Balance OCS Budget'.

L323: « which calculates uptake based on leaf surface area, saturation and air pressure » -> The Berry et al. (2013) model uses the atmospheric OCS concentration and a series of conductances.

>> We have amended the first few sentences of this paragraph having re-read the methodology presented by Berry et al. (2013) (line 347):

"The sink due to vegetation was derived by implementing the OCS vegetative uptake model from Berry et al. (2013) into the land surface model ORCHIDEE, undertaken and explained in detail by Maignan et al. (2021). Berry et al. (2013) calculate OCS uptake using a series of mechanistically and empirically derived conductances that quantify diffusion of OCS from the boundary layer to leaf stomata, where it is eventually hydrolysed by CA in the leaf cell."

L325: "in the LMDz6 CTM" -> LMDz6 is an Atmospheric Transport Model (no chemistry here).

>> Done. We have amended this overall sentence to:

"Additionally, Maignan et al. (2021) compare the mechanistic model to the LRU-GPP approach, used in the calculation of OCS in Section 3.3.1, by running the two in the LMDz6 atmospheric transport model."

L326-327: "it is not adequate for global estimation, unlike the LRU-GPP approach." -> That's a gross misunderstanding, please read what is written in their abstract: "Although the mechanistic approach was more appropriate when comparing to high-temporal-resolution COS flux measurements, both approaches gave similar results when transporting with monthly COS fluxes and evaluating COS concentrations at stations."

>> We agree. Having re-read Maignan et al. (2021), we have clearly misinterpreted some of their concluding remarks. The sentence has been rephrased (line 352):

"They found that while the mechanistic approach works better on shorter time and smaller spatial scales, both are suitable for global estimation of vegetative OCS uptake".

L327-330: "Maignan et al. (2021) propose the idea of implementing soil fluxes into the ORCHIDEE land surface model, simultaneously with vegetation, which would be a significant step forward in the capability of constraining and quantifying surface uptake. The reason being: both uptake of OCS by soil and vegetation follows very similar enzymatic pathways, catalysed by carbonic anhydrase (Protoschill-Krebs and Kesselmeier, 1992; Kesselmeier et al., 1999)." -> This is not clear, we need a model for soil exchanges whatever the process, and do not forget about the emission part too, I suggest removing this part.

>> Done. This is not really in the scope of this work, so we agree removing it is reasonable.

L332-333: "Note, the vegetation estimate does not match that of Maignan et al. (2021) (-756 Gg S yr-1)." -> As explained in Abadie et al. (2022), they got a different estimate from Maignan et al. (2021) as they considered spatially and temporally varying atmospheric OCS concentrations.

>> We have removed this sentence and included some additional information in the preceding sentences (line 359):

"Preliminary work on implementing a mechanistic soil uptake model, originating from Ogée et al. (2016), into ORCHIDEE was used as the soil flux in this work (Abadie et al. 2022). Calculation of both vegetation and soil

uptake, using ORCHIDEE, utilise temporally and spatially varying OCS surface mixing ratios (Remaud et al. 2023), obtained from the TM5 atmospheric transport model, driven by posterior fluxes calculated by (Ma et al. 2021)."

L528: 753 – 756 Gg S yr-1 -> Add the revised vegetation estimate by Abadie et al. (2022).

>> The estimate by Abadie et al (2022) is now included (576 Gg S) (line 571):

"By utilizing the LRU-GPP approach, we estimate a mean yearly vegetative OCS uptake of 629 Gg S yr-1, which is within the range and uncertainty of the magnitude of this flux from previous top-down studies (see Table 2). Our estimate is also in the range of recent bottom-up estimates by Kooijmans et al. (2021), Maignan et al. (2021) and Abadie et al. (2022) (576 – 756 Gg S yr-1)."

L571: « by Ogée et al. (2016) » -> Ogée et al. (2016) provides a model, not a distribution of soil fluxes.

>> We have removed Ogee and left just Abadie et al. (2022).

Minor comments

L53: "This trend is matched stronger positive trends"??

>> Resolved. "Stronger positive trends are observed in the stratosphere above all sites for 2009-2016, up to 1.93±0.26% yr^{-1}"

L86: "dependent such components as temperature" -> dependent on?

>> Done.

L94: suggests -> suggest

>> Done.

L186: "our new inventory of fluxes described in Sect. 3.3, TOMCATOCS and to TOMCATSOTA." -> our new inventory of fluxes described in Sect. 3.3, TOMCATOCS and to TOMCATSOTA in Sect 3.4.

>> Done.

L230: plant-function-type -> plant-functional-type

>> Done.

L278: NOAA-ESRL sites; ALT, BRW and MHD -> NOAA-ESRL sites, ALT, BRW and MHD

>> Done.

L283: "to the changes to the vegetative and soil CS2 fluxes."-> OCS fluxes

>> Done.

L373: "The fluxes used to model TOMCATOCS reduces" -> reduce

>> Done.

L304: "The total oceanic emission has been increased 146%" -> by 146%?

>> Done.

L429-430: "The RMSE in Fig. 1 at KUM is reduced by 56.8% and improved SCA compared to TOMCATCON by 81%, from 17.7 ppt to 3.4 ppt. » -> …and the SCA is improved compared…

>> Done.

L577: "fair more" -> far more

>> Done.

L585: "TOMCATOCS is compared ACE-FTS" -> to ACE-FTS

>> Done.

L601: to other work -> to other works

>> Done.

L883: Whelan et al. (2018) is not in discussion anymore.

>> This reference has been updated in all instances, as has the bibliography.

Reviewer 2

The manuscript needs to be read and corrected in detail, also by the co-authors. The revisions are OK, but hardly improved the manuscript, which still adds little to existing knowledge on OCS, except for the comparison to ACE-FTS. I include an annotated pdf with my remarks.

Minor comments – from pdf document

L48-50: "In the stratosphere the OCS mixing ratio declines strongly with increasing altitude and has a longer mean lifetime than the troposphere, of approximately 64 ± 21 years (Barkley et al., 2008), ranging from 54.1 ± 9.7 years in the sub-tropics to 103.4 ± 18.3 years in the Antarctic (Hannigan et al., 2022)." -> here, this is likely global burden over stratospheric loss. As written now, it sounds like OCS "Lives longer in the stratosphere", which I doubt (that would be calculated as stratospheric burden over stratospheric loss...

>> Here we are quoting the partial lifetimes in the troposphere and stratosphere which are indeed estimated from the total atmospheric burden divided by the loss in either region. This is done so that the partial lifetimes can be combined to give a total lifetime (i.e. $1/\tau_{total} = 1/\tau_{trop} + 1/\tau_{strat}$). The larger stratospheric lifetime mainly reflects the much lower burden of OCS compared to the troposphere, as well as the higher OH concentrations.

In the revised text we explain the definition of lifetimes quoted. Which can be found around line 53.

L64: "source" -> sources

>> Done.

L86-L87: "dependent such components as temperature, soil moisture, nitrogen content and incident solar radiation" -> ???

>> Done: "dependent **on** such components as temperature, soil moisture, nitrogen content and incident solar radiation."

L95: "trend" -> up to 2015?

>> This trend is up-to and including 2016. Figure 8-11 in Hannigan et al. (2020). "up to 2016".

L170: "2-3%" -> unclear give OCS loss

>> We have included values of photolysis: "30 – 34 Gg S yr^{-1} (approximately 3%)"

L175-176: "varying inter-annual variability" -> varying variabilit?

>> This has been clarified and made more readable: “Depending on the inventory in use, some vary inter-annually, i.e., vegetative uptake and anthropogenic emission, and the remaining fluxes do not (oceanic emission, soil uptake and biomass burning).”

L180-182: “Monthly mean surface concentrations are calculated from the flask observations made by the NOAA-ESRL network and compared with monthly mean TOMCAT output averaged across the time period, used for each respective setup.” -> would say that co-sampling could be important?

>> In hindsight, co-sampling the model with the surface observations would offer a more like-for-like comparison. Due to the long life-time and the fact OCS is well-mixed, this should only have a small impact on the study.

We have included the following sentence around line 196: “Co-sampling of the model output with NOAA-ESRL measurements would be a more representative comparison, but here we have not subsampled the model on the specific days of NOAA observations.”

L226: “units of ppb” -> ??

>> The inclusion of ppb is from a recommendation on the original manuscript: “*Equation 1: Precise the unit for each term of this equation. What is used for OCS background concentration?*”, from Referee #1. We have specified parts per billion in the text.

L227: “typical for TOMCAT” -> ???

>> Removed this. Unnecessary to include this.

L227: “We then convert to Gg S yr-1 following simulation.” -> ???

>> Removed this. Again, unnecessary to mention this.

L238: “concentration” -> concentration or mixing ratio

>> Mixing ratio. This has been changed here and in other sentences around this highlighted phrase.

L244-245: “The spatial distribution of F_{OCS} for the months of January, April, July and October, in 2010 only, is presented in the supplement: Fig. S5.” -> here I am a bit sceptical, because you can only calculate this flux if you have a full simulation that is providing the OCS mixing ratios. So, the OCS flux can only be given after a simulation that compares well to surface observations. Also, since OCS is changing from year to year, fluxes should also change...

>> “*here I am a bit sceptical, because you can only calculate this flux if you have a full simulation that is providing the OCS mixing ratios.”* - The vegetative flux is calculated in the first model time-step using an initial value of 500 ppt of OCS. Each successive time-step the flux is calculated using the OCS concentration from the previous one. Therefore a ‘full’ simulation is not necessary.

“*So, the OCS flux can only be given after a simulation that compares well to surface observations.*” – This is true to an extent. A lot of preliminary testing went into the scaling of fluxes that would yield both a balanced budget and a suitable estimate of the vegetative flux. This is justified in the text by comparing the scaled flux magnitudes to the literature.

“Also, since OCS is changing from year to year, fluxes should also change...” – The flux does change. We picked 2010 for simplicity, as the inter-annual variability is not too large. Also, as the photochemistry experiment(s) were executed for 2010 only also.

L278-279: “the latter of which receives ocean air masses frequently.” -> is this referring to MHD? Unclear

>> This section was removed. While it is true MHD is susceptible to ocean masses frequently, this didn't seem relevant as ocean emissions in the NH were amended as it was the most sensible to change, rather than anthropogenic emissions for example, which has a better certainty.

L279: "frequently" -> highlighted..

>> See above.

Table 1: "-432" -> unclear??? Sinks (1194) and sources (1187) are in balance: something wrong here..

>> The total source amount in the table was incorrect. This has been amended.

L355: "stratosphere" -> It would be instructive to include these in the table and to provide a net flux.

>> As this is a minor test, we believe the text is sufficiently clear at explaining the reduction in photolysis. It is clear that the largest spatial changes in OCS are contained to the stratosphere and do not influence the troposphere hugely in the 1-year test presented.

L367-368: "is mostly attributed to average concentration." -> ??? unclear

>> We have changed the structure of the paragraph in Section 4.1 around this comment. And justified the above based on difference in RMSE in Figure 2.

L403: "to" -> too

>> Done.

L505: "The intension if this simulation" -> sorry, but does somebody read the manuscript?

>> Amended to 'intention of'.

L528: "Maignan et al., 2021)" -> highlighted

>> Done. Maignan et al., (2021)

L530: "CS_2 emission" -> from the ocean?

>> Done. Amended to: "enlarged oceanic CS_2 emission source"

L582-583: "Where $TOMCAT_{CON}$ uses fluxes estimated by Kettle et al. (2002) and $TOMCAT_{SOTA}$ uses a series of novel fluxes from recent literature" -> does not run

>> We removed the word "where".

L589: "Which shows promise for future OCS work using TOMCAT." -> is no sentence.

>> This sentence has been removed.

L603: "the following changes are necessary in future, such as" -> the following.....such as....bad construct

>> Improved the sentence structure (line 668): "The following changes are necessary in the future to improve the GPP-LRU approach such as: using inter-annually varying GPP and CO_2 mixing ratios, and a temporally and spatially resolved LRU."

L604: "3" -> i count either 4 or 2....

>> Changed the sentence to (line 670): "It is challenging to achieve at a high resolution LRU product on a global scale".