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Comment on acp-2022-215

Anonymous Referee #1

Referee comment on "Constraining the budget of atmospheric carbonyl sulfide using a 3-D chemical transport model" by Michael P. Cartwright et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-215-RC1>, 2022

Michael P. Cartwright and coauthors present an evaluation of two OCS flux inventories using OCS concentration observations from 14 NOAA towers and from the ACE-FTS satellite instrument. The first inventory is mainly based on Kettle et al. (2002) and is used as a control for the second inventory. The authors define this second inventory using the LRU approach to compute vegetation OCS fluxes, then scaling the other OCS flux components to obtain a balanced global OCS budget. The OCS fluxes from both inventories are transported with the TOMCAT atmospheric transport model. Finally, the surface OCS flux components are evaluated by comparing the seasonal cycles of the simulated OCS concentrations to NOAA flask measurements. The vertical profiles of the simulated OCS concentrations are also evaluated against ACE-FTS OCS concentration profiles between 5 and 30 km. The authors conclude on a better performance of the new balanced OCS flux inventory compared to the control simulation in terms of seasonal cycle representation. The strength of this work is to make use of ACE-FTS observations to evaluate the simulated OCS concentration vertical profiles. However, major revisions should be considered before publication.

General comments:

1. This work makes insufficient use of OCS state-of-the-art. References to recent studies are missing in the introduction. For example, when describing atmospheric OCS trend, Hannigan et al. (2022) should be mentioned as they found positive trends in the troposphere and in the stratosphere between 2008 and 2016 at most of the studied sites. The reference of the study by Glatthor et al. (2017) should also be contrasted with the increasing trend found by Hannigan et al. (2022) in the free troposphere at the Jungfraujoch site between 2008 and 2016, followed by a decreasing trend since

2016–2017. Ma et al. (2021) should be presented as an inversion study and completed with Remaud et al. (2022) that also conclude to a missing source in the tropics. The underestimated OCS anthropogenic source suggested by Zumkehr et al. (2018) was also supported by Aydin et al. (2020).

Using the inventory of Kettle et al. (2002) is also a major weakness as many studies have provided new OCS flux estimates since. Therefore, the conclusion that TOMCATocs gives better results than TOMCATcon does not seem relevant when TOMCATcon is based on out-of-date estimates (except for the anthropogenic emissions from Zumkehr et al., 2018). Many limitations that were highlighted in OCS literature arise from using the inventory from Kettle et al. (2002). For example, oxic soil contribution considers a constant atmospheric OCS concentration while recent studies have shown the importance of considering variable atmospheric concentrations for both soil and vegetation OCS fluxes (Kooijmans et al., 2021, Maignan et al., 2021, Abadie et al., 2022). Important processes are also not included in the control inventory. Indeed, oxic soils can not only take up OCS but also produce OCS, and it has recently been shown that anoxic soils cannot be neglected at the global scale (Abadie et al., 2022).

In Section 3.3, why choosing to use a single constant LRU value while several studies provide PFT-dependent LRU values? For example, these sets of LRU per PFT can be found in Seibt et al. (2010), Whelan et al. (2018), Maignan et al. (2021). Moreover, as JULES land surface model distinguishes several PFT categories, it would be possible to use PFT-dependent LRU values.

In Section 3.4, the OCS fluxes that were adjusted to obtain a balanced budget should be contrasted with more recent estimates. For example, choosing to scale CS₂ oceanic emissions to 439 GgS/y is not supported by Lennartz et al. (2020) who estimated a total source of 70 GgS/y from CS₂. An oxic soil budget of 322 GgS/y is also not in line with the recent estimates of Kooijmans et al. (2021) and Abadie et al. (2022) based on the mechanistic soil model of Ogée et al. (2016).

More recent studies should be added in Table 2 to compare to the OCS budget from this work, such as Maignan et al. (2021), Kooijmans et al. (2021), Remaud et al. (2022).

2. The scaling of OCS fluxes to better match estimates made after Kettle et al. (2002) and to obtain a balanced OCS budget seems quite arbitrary. Such adjustments should be made using an inversion framework as done in Ma et al. (2021) or in Remaud et al. (2022). Without an analytical inverse system that optimizes the fluxes, why aiming at a balanced COS budget? A balanced OCS budget is also not required if analyzing the detrended OCS concentrations.

Moreover, this scaling assumes that the OCS flux spatial distribution of each component is not modified compared to the control inventory, which might not agree with flux distribution obtained in more recent studies.

3. Not considering interannual variations is a strong assumption that should at least be better justified. The study from Chen et al. (2017) does not conclude that interannual variability in GPP amplitude can be neglected. GPP interannual variability could easily be included in this work as GPP is modeled by JULES. Considering only the year 2010 does not reflect the yearly increase in atmospheric CO₂ concentration and the fertilization effect.

Otherwise, could the impact of not considering OCS flux interannual variability be quantified? For example, OCS vegetation uptake could be defined as a first order relationship with OCS mixing ratio. Therefore, inter-annual variations in OCS vegetation flux might have a strong impact on the simulated atmospheric OCS concentrations.

4. It is not clear what the goal of this study is, and the title is confusing. It is mentioned that this work evaluates the suitability of gross primary productivity to estimate the OCS vegetative uptake. However, doing so by comparing a vegetation OCS uptake based on GPP to a vegetation OCS uptake based on NPP and NDVI seems outdated (Sandoval-Soto and Stanimirov, 2005). Moreover, the modification of several OCS flux components with the rescaling makes it difficult to compare seasonal cycles of TOMCATcon and TOMCATocs regarding vegetation OCS fluxes. Please specify clearly what are the main goals of this study.

Should this work focus more on the advantage of using ACE-FTS compared to other available OCS concentration observations? Or on the information that can be retrieved from ACE-FTS about the modelling of OCS atmospheric sinks?

Specific comments:

Abstract:

L25: "At the surface, the model captures background concentrations at most of the surface sites to within the maximum and minimum of the seasonal measurements". It does not seem to be a strong condition to satisfy. It might be better to highlight results on the seasonal cycle amplitude or the phase.

1. Introduction:

L49: "The main source of atmospheric OCS is oceanic emission". This could be replaced by "one of the main sources" as anthropogenic emissions are also a major source of OCS. For example, Zumkher et al. (2018) estimated an anthropogenic OCS source of about 400 GgS/y. Aydin et al. (2020) suggested that this estimate could be underestimated with an anthropogenic OCS source of about 600 GgS/y.

L57: "with estimates ranging from 210 to 2400 Gg S yr⁻¹ (Kettle et al., 2002; Sandoval-Soto and Stanimirov, 2005; Suntharalingam et al., 2008; Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2015; Launois et al., 2015b; Ma et al., 2021)". Add references to more recent studies such as Maignan et al. (2021), Kooijmans et al. (2021), Remaud et al. (2022) for vegetation OCS uptake estimates.

L61: "OCS hydrolysis also occurs in soil, again catalysed by carbonic anhydrase". Note that OCS can also be consumed by other enzymes in soils, such as nitrogenase, CO dehydrogenase, or CS₂ hydrolase (Smith and Ferry, 2000; Masaki et al., 2021).

L63: "with an estimated annual loss of 127-355 Gg S (Kettle et al., 2002; Montzka et al., 2007; Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2015)". More recent studies should be mentioned, such as Kooijmans et al. (2021) and Abadie et al. (2022) that lead to smaller soil OCS budgets.

L65: "Soil has also been observed to act as an emitter of OCS in warm conditions (Maseyk et al., 2014)". This was not observed only for warm conditions. OCS emissions have also been related to soil types (Whelan et al., 2013), nitrogen content, light radiations reaching the soil surface (Spielmann et al., 2019; Kitz et al., 2020).

L69: "the latter of which has been used as a benchmark for more recent studies". Please add the references of the studies.

2. Observations:

Section 2.1: Please provide and detail the uncertainties associated with ACE-FTS retrievals.

3. Chemical transport modelling of OCS:

Section 3.1: What is the timestep used to run the TOMCAT model?

L139 to L224: Please make it clearer which fluxes have been used for TOMCATcon and which one have been used for TOMCATocs.

L153: "The three sink terms are an oceanic sink, soil uptake and a vegetative sink". OCS photolysis in the stratosphere and OCS oxidation by OH radical in the troposphere should also be included in OCS sinks, as atmospheric OCS reactions are not explained before in section 3.1.

Equation 1: Precise the unit for each term of this equation. What is used for OCS background concentration?

L173: Please replace "LRU is the normalised ratio of OCS assimilation rates to CO₂ at the leaf-scale. This is then normalized by background concentrations of the two gases" by "LRU is the ratio of OCS assimilation rates to CO₂ at the leaf-scale, both normalized by their respective concentration".

L180: "but is slightly under half that of the largest estimation of 1115 Gg S in Table 2 from Montzka et al. (2007)". Launois et al. (2015) estimated a larger plant OCS uptake than Montzka et al. (2007) for the ORCHIDEE land surface model.

L204: "at Northern Hemisphere (NH) NOAA-ESRL sites". Please precise which sites and whether they receive air masses mainly coming from the ocean.

Table 2: Why were more recent studies not included in this table for comparison? Such as Maignan et al. (2021), Kooijmans et al. (2021), Remaud et al. (2022).

4. Results:

L243 to L245: "TOMCATCON was initialised using OCS values in each grid box from TOMCATOCS, after 10 years (1994 – 2003) spin-up. Only 2004 monthly mean mixing ratios from TOMCATCON have been included, as this flux inventory has a 245 net negative budget and therefore a negative trend over longer periods". Should this be in Section 3 as it is related to the method?

L244: "Only 2004 monthly mean mixing ratios from TOMCATCON have been included, as this flux inventory has a net negative budget and therefore a negative trend over longer periods". Please precise the net negative budget. The trend in atmospheric COS concentrations should not be an issue if you remove the trend and compare the detrended atmospheric concentrations.

L249: "Error bars associated with the observations represent the maximum and minimum values for each month at every site". Representing the standard deviation would be a better indication of the uncertainty of the mean value.

L253: "Comparisons between TOMCATocs and TOMCATcon are shown here to emphasise the improvements made by the flux inventory developed in this study". 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)?

L254: "The root mean square error (RMSE) for the entire period is shown for each site, alongside the seasonal cycle amplitude (SCA)". Precise that in the following you also compare the phases of observed and simulated seasonal cycles.

L255: "Generally, there is an improvement in RMSE across all the sites, but in some cases, there is a degradation, which is mostly attributed to background concentration, rather than the model's ability to capture a suitable seasonal cycle, hence both are shown." By "background concentration", do you mean the average concentration? If so, could you please show that the degradation in RMSE is due to the average concentration?

L264: "This seasonal cycle resembles that of CO₂, hence GPP is a suitable proxy for calculating OCS uptake". Please rephrase as similar seasonal cycle is not reason enough to use GPP as a proxy of vegetation OCS uptake.

L275: "Here we show realistic amplitudes in the seasonal cycle from TOMCATOCS, 76 ppt at LEF and 71 ppt at HFM, compared to observed values of 123 ppt and 128 ppt, respectively". Please rephrase as the SCA at these two sites are still largely underestimated.

L279 to 282: The constant LRU value used in this study could be compared to other LRU estimates for the same vegetation types found at LEF and HFM to see if it could be underestimated. If a constant OCS mixing ratio was used to compute OCS vegetation uptake, this could also affect the SCA.

L329: "OCS values decline above and below the UTLS due to removal by photosynthesis at the surface". Soils can also absorb OCS at the surface.

L345: "potentially attributed to slower surface OCS uptake". It could also be due to an underestimated surface OCS uptake.

Figure 2: What could explain the net distinction between higher mixing ratios in NH compared to SH found in TOMCAT in JJA and SON?

L364: "this suggests the upper atmospheric sinks are modelled well by TOMCATocs". Isn't it in contradiction with the steeper gradient of TOMCATocs in the stratosphere mentioned above?

Section 4.2 attributes model-observation mismatches to OCS sources or sinks, what about the potential mismatches from TOMCAT transport?

5. Discussion:

L376: "the TOMCATocs simulations of atmospheric OCS concentrations and the vegetative flux, which are dependent on one another in the model". The simulated OCS concentrations are dependent on vegetation OCS fluxes that were transported, but it is not said which OCS concentrations are used to compute the vegetation OCS fluxes.

L385: "inverse modelling of OCS fluxes shows that some combination of a larger tropical oceanic source and vegetative sink resolves the budget". Kooijmans et al. (2021) also show that considering a variable atmospheric OCS concentration reduces the vegetation sink in the tropics, meaning that a smaller tropical OCS source would be needed to close the budget.

L392: "such as calculating OCS uptake using a constant LRU value of 1.6 is not representative of reality". It could be interesting to give the range of values proposed for LRU in the literature, to illustrate how LRU values can vary.

L394: "Our estimation of vegetative uptake in this work does not replicate OCS uptake universally and it is unclear if this is due to localised differences in LRU or on the GPP fields themselves". Could you provide a global map of vegetation OCS uptake obtained with your approach using a constant LRU value and compare it to similar maps found in the literature (Berry et al., 2013; Kooijmans et al., 2021; Maignan et al., 2021) to analyse the spatial distribution of the fluxes? Could you also provide a map of TOMCAT simulated atmospheric CO₂ concentrations used to compute vegetation OCS uptake?

L396: "the distribution is based on work by Kettle et al. (2002) and has since been updated, for example by Ogée et al. (2016)". It has also been updated by Sun et al. (2015). It could be interesting to compare the spatial distribution of your soil OCS fluxes to other maps based on the mechanistic approach from Ogée et al. (2016) (Kooijmans et al., 2021; Abadie et al., 2022).

6. Conclusion:

L453: "Therefore, further study following on from this work will be to derive an a posteriori set of fluxes using an inversion scheme based on an up-to-date prior, and surface observations and a dataset containing vertical information near the surface". Important drawbacks are acknowledged by the authors as this work does not rely on an optimization framework and uses out-of-date OCS fluxes. These drawbacks should explicitly appear in the abstract.

Minor comments:

L19: "To compensate for this larger vegetative sink". I would not use "larger" here as it has not been explained yet that it is larger than the vegetation OCS uptake from Kettle et al. (2022).

L30: Is this really "Hawaiin" and not "Hawaiian" (replace everywhere if needed)?

L56: Please replace "Vegetative uptake is the most important atmospheric sink of OCS" by "Vegetative uptake is the most important sink of atmospheric OCS".

L107: Please develop the abbreviation HITRAN.

Table 1: Please replace "Barrow" by "Utqiagvik (formerly Barrow)" and "Cape Grim" by "Kennaook / Cape Grim". For PSA and SPO stations, please precise "Antarctica (United States)".

L135: Should "surface emission fields" be replaced by "surface flux fields" as surface OCS fluxes are not only sources?

L136: Please replace "six sources and three sinks" by "six net sources and three net sinks" as soils can be both a sink or a source of OCS for example. Please also name the sinks and sources here.

L147: Remove "an" in this sentence "Eleven anthropogenic sources of OCS were an quantified by Zumkehr et al. (2018)".

L175: Please develop the abbreviation WATCH.

L235: "so we only compare the main simulations". Please precise that it is TOMCATocs.

L301: Please remove "Gg" in the following "from 17.7 Gg ppt to 3.4 ppt".

Figure1: Please improve the resolution of the figure to be able to read the RMSE scores.