

Reply to RC2 from Referee #2

Blue: Referee comments

Black: Our comments

Red: The sentences in our manuscript

This manuscript attempts to address a current technical challenge within the atmospheric S and to some extent C cycle research community. It is clear that quantifying the movement of sulphur between the ocean, atmosphere and biosphere and detailing potential interactions and transformations is highly desirable but unfortunately it is still an extremely difficult task to conduct. Carbonyl sulphide is the most abundant sulphur containing gas in the atmosphere and currently there is much debate about its current sources and sinks. Within this framework the use of COS isotopic tracers might provide insights on this problem and help close the COS mass budget. As pointed out in the manuscript this not only holds interest for the communities working on the S cycle and its interactions with climate through chemical reactions in the troposphere and stratosphere but also those working on the carbon cycle, as COS is a close analog of CO<sub>2</sub> and as such moves between the atmosphere and the biosphere alongside CO<sub>2</sub> during various steps of the photosynthetic pathway.

**Reply:** Thank you for reviewing our manuscript and for recognizing the importance of this study. We believe that the investigation of isotopic composition for carbonyl sulfide (OCS) can improve understanding of sulfur and carbon cycle.

Consequently, the motivation to study COS isotopes is growing and there is a need to overcome a number of technical challenges that limit the application of these tracers to help address the scientific questions introduced above. The first problem is that COS is a trace gas (atmospheric concentration around 500 parts per trillion) with an extremely low abundance of the rare isotope species thus large sample volumes are required for Isotope Ratio Mass Spectrometry (around 500 L providing ~10nmol of COS, in the case of the present study). Secondly, COS is an extremely reactive gas that can be hydrolyzed and/or produced rapidly from many surfaces and materials commonly used in gas exchange techniques.

**Reply:** As you have pointed out, collection of OCS from air and potential interface from preservation/loss of OCS during sampling are important for isotope analysis of OCS. For this study, we specifically examined how to collect OCS from air. We verified OCS contamination and OCS loss during measurement. This study is expected to be useful for situations in which large amounts of OCS, such as measurement of carbon and oxygen isotopic ratios of OCS, are required in the future, as we have described in our manuscript.

The current study presents a large volume sampling system adapted from a previous system designed for the measurement of volatile halocarbons and hydrocarbons by one of the co-authors of the present study (Bahlmann et al., 2011). This trapping system seems to be capable of tackling the first problem described above by trapping high volumes of air over a relatively short period of time (~100 minutes) and concentrating the air sample in a cryoshipper volume cooled previously with liquid N<sub>2</sub>. Details regarding the temperature of the cryoshipper volume are a little vague stated as less than -110°C. This could be a bit more specific as pointed out by one of the reviewers as other gases may condense at lower temperatures.

**Reply:** We are sorry for the ambiguous sentence. Although it is difficult to keep the temperature constant using vapor of liquid N<sub>2</sub>, we confirmed that the temperature in the dewar was -140 °C to -110 °C for at least 3 h. Because the sampling tube temperature was higher than -140 °C, O<sub>2</sub> is not trapped in the sampling tube during sampling. We increased the temperature during sampling.

**Action:** We added an explanation of the temperature range of the sampling tube to our revised manuscript.

The second problem of sample contamination during sampling and sample storage seems to still be an issue that would prevent the routine use of this sampling approach. For instance the authors purge the sampling tubes with high-purity Helium for 12H before sampling and require high temperatures starting at 160°C and reaching 330°C to condition the material. Can this be done in the lab beforehand on a batch of sampling tubes and does the surface remain inert thereafter, if so for how long? Is this step necessary when switching to Sulfinert valves and tubing? I am also curious to know how long roughly it takes to process one sample from the pre-conditioning stage to the final analysis of the purified sample on the IRMS?

**Reply:** We recognize that OCS contamination can be a serious issue. Indeed, although Tenax TA is suitable for OCS collection because of high-temperature conditioning, several picomoles of OCS are always observed from Tenax TA as blank. As you have pointed out, to reduce OCS blank from adsorbent as much as possible, we conditioned sampling and adsorption tubes for 6 h using pure helium (99.99995 % purity). The conditioning of sampling and adsorption tubes can be prepared in the laboratory before the field observation. We confirmed that the surface was inert for at least three days and the inactive state of the surface of adsorbents in these tubes would be retained under a no leakage condition. However, at present, we recommend conditioning immediately

before use to the greatest degree possible. Note that the conditioning steps would be required if stainless tubes are replaced by Sulfinert-treated tubes/valves, because the aim of conditioning is to include removal of strongly adsorbed volatile organic compounds such as ethanol and acetaldehyde in adsorbents. Given that these stored in the adsorption tube might block OCS collection and react with OCS (Ferm, 1957), we must remove these compounds as much as possible.

Finally, the time span is the following: sampling for 100 min (500 L), transfer for 40 min, pre-concentration for 40 min, and measurement using Q-MS or IR-MS for 20 min.

**Action:** We added information related to conditioning to section 3.3.

It was useful to see the change in COS concentration during the preservation period. However, if I understand correctly this is not the experimental set-up for the rest of the data presented in the paper. Can you also plot the preservation data timeline for the non sulfinert experimental set-up please?

**Reply:** As you have understood, we did not use Sulfinert-treated adsorption tubes for most of the experiments. As we added to Figure 8 in the revised manuscript, the OCS amount in a stainless steel adsorption tube stored at room temperature preserved ( $-6 \pm 6$ ) % of OCS, with no significant changes in  $\delta^{34}\text{S}(\text{OCS})$  values within ( $0.2 \pm 0.4$ ) ‰ after 3 h. All data sets are measurements taken right after the sampling (i.e. shorter than 30 min.). Therefore, we did not expect significant changes in OCS concentrations and the  $\delta^{34}\text{S}(\text{OCS})$  values.

**Action:** We added this information in the revised manuscript in section 3.4.

Reviewing this as a method paper I feel there were a number of details missing or communicated a bit ambiguously. I am not sure it would be so easy to reproduce this methodology as a result. In particular section 2.1 was rather vague in several places, especially when it came to details of the calibration cylinders being used. Nowhere is the material of any of the calibration cylinders stated. This is not trivial as it is well known that COS is highly reactive and the use of stainless steel or aluminium cylinders for storage of COS standards will cause a drift in the COS concentrations over time and I would assume the isotopic composition too. For example, you state that the calibration cylinders F and G are much lower than that of atmosphere (e.g.  $G = 160 \text{ pmol mol}^{-1}$ ), despite being sampled from the atmosphere that should be in the range of  $350\text{--}500 \text{ pmol mol}^{-1}$ . I can only assume that contamination has occurred in the bottles during storage or a scrubber has been used whilst filling the tanks. If I understand these cylinders were filled in 2012 and assumed to represent the global background atmospheric composition. I am keen to know when the calibration curve described in 2.4.1 was actually completed a few days, months or years (2012) before the use of the calibration gases to validate the field measurements for COS concentration and  $\delta^{34}\text{S}$ ? Overall calibration cylinders should be monitored closely over time when filled to see if the cylinder has issues and thereafter regularly checked for drift. It is also recommended to use Sulfinert cylinders or ACULIFE cylinders for COS. Can you confirm whether your calibration cylinders have special wall treatments to minimize contamination of your atmospheric COS gas?

**Reply:** We are sorry that these ambiguous sentences have led to confusion. We found that there are three questions in this comment. First is for the material of cylinder. Second is for how to ensure OCS concentration if the OCS decomposed in cylinder. Third is for trends of OCS decomposition in the cylinder.

First, all cylinders are made of manganese steel without special wall treatments to minimize contamination.

Secondly, as you have expressed, the OCS concentrations and sulfur isotopic compositions for OCS can be changed in some cylinders. This is also a reason why we developed this method. To estimate OCS concentration, the OCS concentrations for sample A and sample B were calibrated using diluted in-house synthesized OCS (i.e. 100 %) to 10 % by high-purity He using a vacuum line. We confirmed that the OCS concentration and isotopic composition for sample B had not changed for four years after we published Hattori et al. (2015). Therefore, the calibration curve was made by using sample B and sample B was used as the daily working standard for sulfur isotopic measurement. The OCS samples in compressed air in the cylinder, on the other hand, were not stable: we found that the OCS concentration in sample H was decomposed to one third within three months. For that reason, we must conduct experiments immediately after we determined OCS concentrations. Therefore, for the example to make Figure 3, OCS in sample F were collected within two days to evaluate collection efficiency, followed by the determined OCS concentration in sample F within a week by calibration with sample B. In a similar manner, the cylinders of sample H, I, J, and K were used for experiment within 2–3 days. Therefore, we do not expect the changes in OCS concentration during the experimental period. Indeed, the effect OCS decomposition was not shown in Figure 3 or Figure 8a. We again emphasize, as you have stated, that the OCS contamination and its sulfur isotopic composition is not likely to be preserved in the cylinder. Also, no scrubber is used when the compressed air was filled in the cylinder.

Thirdly, the OCS concentration in sample B is monitored every time before the experiment. However, we do not monitor the OCS concentration of compressed air in cylinder because we know that the OCS do not preserve the  $\delta^{34}\text{S}(\text{OCS})$  value. As you suggest, we will plan to use a Sulfinert-treated cylinder and ACULIFE for the standard sample. Thank you for informing us.

To the revised manuscript, we added the following information in section 2.1 and 2.4:

- Cylinder Material: “**manganese steel without special wall treatments**”.
- Time span for measurement for sample F, H, I, J and K.
- How we determined OCS concentration in sample A and B: “**The OCS concentrations for samples A and B were determined against to the in-house synthesized OCS (i.e. 100 %) diluted to 10 % using high-purity He (99.99995 % purity; Japan Fine Products Co. Ltd.). It is noteworthy that the OCS concentration in sample B had showed no change at least four years after the publication of Hattori et al. (2015).**”

I also think it would be worth discussing a little the caveats surrounding the fragmentation IRMS approach for example the potential for O<sub>2</sub> contamination and consequences for the  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  analysis/interpretation.

**Reply:** Thank you for your suggestion. However, the caveats of fragmentation IRMS have already been discussed by Hattori et al. (2015). To avoid duplication, we did not add that information to the revised manuscript. As we described in that earlier report by Hattori et al. (2015), the influence by O<sub>2</sub> contamination to  $\delta^{34}\text{S}(\text{OCS})$  value was also discussed; the  $\delta^{34}\text{S}$  value are increased with the OCS amount depleted. The trend can be caused not by O<sub>2</sub> contamination because of natural abundance of rare oxygen isotope (see Hattori et al. (2015) for more detail). Although we must consider isotopic fractionation in ion source in IRMS and its sample size dependency, the effects of size dependence are negligible over 6 nmol of OCS in this study. We added points raised here.

Finally I think section 3.5 breaks the flow of the paper at the end and think it should rather become section 3.3. This would allow the paper to move out of the technical discussion into the scientific discussion and conclude more naturally.

**Reply:** We agree with your suggestion. We moved the results of preservation to section 3.4.

I also feel that the first paragraph of the conclusion is repetition of the results and should be removed.

**Reply:** Thank you for your suggestion. However, the summary of results is important for this method paper. For that reason, we changed the section title from “*Conclusion*” to “*Summary*”.

I also agree with the other reviewer that the last paragraph introducing the carbon and oxygen isotopes should not suddenly appear here a bit out of the blue, their measurement is not trivial.

**Reply:** Agreed. We moved the discussion of carbon and oxygen to the *Discussion*.

Other details

The application of parentheses throughout this paper needs correcting, just because you quote a number does not mean it should be wrapped in brackets especially if it is integral to the sentence structure e.g. Page 1 line 26 and 27 highlights the type of problem that pops up throughout the manuscript. Please double check all parentheses are appropriate.

**Reply:** We checked all parentheses. We corrected parentheses as much as we can.

Page 1 line 26-27 How can you prove which value is correct? They both seem to be within the range of values for S sources. I would also try to clarify this argument/sentence a bit better.

**Reply:** As you have noticed, the both  $\delta^{34}\text{S}(\text{OCS})$  value are in the range of expected  $\delta^{34}\text{S}(\text{OCS})$  source. However,  $\delta^{34}\text{S}(\text{OCS})$  value of 4.9 ‰ for compressed air in cylinder might be affected by decomposition in the cylinder and contamination from the compressor. However,  $\delta^{34}\text{S}(\text{OCS})$  value of 10.5 ‰ is collected atmospheric OCS directly. To clarify this point, we added the “**previous values of  $\delta^{34}\text{S}(\text{OCS}) = (4.9 \pm 0.3)$  ‰ of compressed air in the cylinders were not representative samples for a global signal.**” to the revised text.

Page 2 Line 8 remove “net ecosystem exchange into” from this sentence.

**Reply:** Corrected accordingly.

Page 3 Line 11 state the purity of the Helium in %

**Reply:** We added the text “**99.99995 % purity**” to the revised manuscript.

Page 3 Line 12 can you provide more details of the exact S compounds used

**Reply:** We apologize for the ambiguous information. We used commercial sulfur powders. We added information related to sulfur powders and purity in our manuscript.

Page 3 Line 16 what type of commercial cylinders provide details and how often they were measured.

**Reply:** We used manganese steel cylinders without special wall treatment. The OCS concentration in sample A were measured every month. The OCS concentrations in sample B were measured before every experiment. Other OCS concentrations of compressed air in the cylinder were measured once except for the preservation test.

Can you also provide details of the compressor used to fill the bottles and any filters that were used on the compressor? Was the air dried before filling the cylinders?

**Reply:** We added information related to the compressor in section 2.1. The filter was not used for filling compressed air in a cylinder. The compressed air was not dried.

Page 3 Line 20 this is a super vague statement can you provide details of how you checked for stability.

**Reply:** We are sorry for including this unclear sentence. We deleted the sentence from the revised text because of duplication. Moreover, the method for preservation test was described in section 3.4.

Page 4 Line 3-4 can you explain how the heating was made and where was this step made in the lab or outside?

**Reply:** We conditioned using heating mantles in the laboratory.

**Action:** We added information to 3<sup>rd</sup> paragraph of section 2.2.

Page 4 Line 15 removed using what?

**Reply:** We removed the sampling tube from liquid nitrogen by hand.

**Action:** We added “manually” to this sentence (5<sup>th</sup> paragraph of section 2.2).

Page 4 Line 27-28 is the tubing flexible i.e. in a coil or rigid?

**Reply:** The tubes are made of stainless steel, but we can bend them.

**Action:** We added the U-shaped or coil-shaped before the trap.

Page 4 line 29 how is the heating achieved?

**Reply:** We used heating mantles for heating trap 2.

**Action:** We added information about the heater to 1<sup>st</sup> paragraph of section 2.3.

Page 4 line 30 why use steel and not glass. I guess this was later switched to a sulfinitert tube?

**Reply:** There are three reasons for using stainless steel for traps. Glass also adsorbs OCS, stainless steel is easy to handle compared to glass. Also, the stainless steel has higher thermal conductivity than glass. We will change stainless steel tubes to Sulfinert-treated tubes in future work.

Page 5 line 8 this should be -72°C

**Reply:** Corrected accordingly.

Page 5 Line 11 where did this injected gas come from?

**Reply:** We are sorry for the lack of information.

**Action:** We modified the sentence as follows: The retention times of CO<sub>2</sub> and OCS were initially determined by injecting a mixture of 8 mmol of CO<sub>2</sub> from pure CO<sub>2</sub> in a cylinder (99.995 % purity; Japan Fine Products Co. Ltd.) and 10 nmol of OCS from sample C in 2<sup>nd</sup> paragraph of section 2.3.

Page 5 lines 22-25 not written very clearly please improve

**Reply:** We apologize for this unclear sentence. We think that it is difficult to understand why we made two kinds of calibration curves and how we made calibration curves.

**Action:** We rewrote the information in 2<sup>nd</sup> and 3<sup>rd</sup> paragraph of section 2.4.

Page 5 line 25 how many replicates were analysed to obtain the precision?

**Reply:** We injected sample B in triplicate for each amount of sample size. The precisions were estimated by standard deviation of relative error between measured values and values estimated from calibration curves. The obtained precision was  $\pm 3\%$ .

**Action:** We added “ $n = 3$ ” and “The precision (standard deviation ( $1\sigma$ ) relative to mean) of the OCS amount by a syringe injection was estimated  $\pm 3\%$  by the standard deviation of the relative error between the measured values and the estimated value for calibration curves.” in 2<sup>nd</sup> paragraph of section 2.4.

Page 6 line 11 size of capillary tube?

**Reply:** We added capillary tube size information here.

Page 6 line 9 spec of the diaphragm pump type, flow, pressure?

**Reply:** We used a rotary pump (Pascal 2010; Pfeiffer Vacuum GmbH, Aßlar, Germany). Although we do not know the flow rate and pressure of pumping, we evacuated He gas at approximately 0.3 kPa per second from 30 cm<sup>3</sup> by regulating the seal valve (SS-4TW; Swagelok Co., Ohio, USA).

**Action:** We added the following to our manuscript: **by a rotary pump (Pascal 2010; Pfeiffer Vacuum GmbH, Aßlar, Germany) gently with regulation using a valve.**

Page 6 line 16 tank ID please

**Reply:** The tank is sample B. We added the information to this sentence.

Page 7 line 18-20 this sentence does not make sense to me

**Reply:** We apologize for the unclear text. We thought that it would be difficult to identify the OCS blank.

**Action:** We changed “OCS blank” to “OCS contamination”.

Page 7 line 21-22 ambiguous sentence

**Reply:** We apologize for the unclear sentence.

**Action:** We rephrased the text to the following: **In the developed system, the possibility exists that OCS is lost by passing OCS through GC1. Also, because the flow rate of approx. 50 mL / min was lower than the flow rate of approx. 200 mL / min reported by Hattori et al. (2015), the possibility exists that OCS was lost by Trap 1. Therefore, to assess these possibilities, the following test was conducted. Firstly, 5 nmol of OCS was injected to a system consisting of Trap 2, GC2, and Trap 4 and measured as true value. Then, the same amount of OCS was introduced into the developed purification system and the amount of OCS obtained was compared to true value.**

Page 7 line 26 how? And what does slowly mean?

**Reply:** We conducted the experiment manually. We changed slowly into “over 30 min by syringe” in this part.

**Action:** We added “manually” and “over 30 min by syringe” in our manuscript.

Page 8 line 15 could you explain these OCS blanks please

**Reply:** We used the OCS blank as OCS contamination. Therefore, we changed “OCS blank” into “OCS contamination”

Page 9 line 11 check the units here please and correct

**Reply:** We are sorry for mistakes in the use of units. We changed the “500 nmol mol<sup>-1</sup>” to “500 pmol mol<sup>-1</sup>”.

Page 9 line 14 hydrolysis requires water were your tanks dry?

**Reply:** The compressed air in the cylinder is collected just as air collected by the compressor. For that reason, the air was not dried. Additionally, Kamezaki et al. (2016) reported not hydrolysis but abiotic OCS decomposition.

**Action:** We deleted “OCS is decomposed by hydrolysis, which increases the  $\delta^{34}\text{S}(\text{OCS})$  value.” from our revised manuscript.

Page 9 line 28-30 this sentence needs rewritten as it does not make sense to me

**Reply:** We apologize for the unclear sentence. We thought that we did not show the proportion to what.

**Action:** We changed the sentence in 1<sup>st</sup> paragraph of section 3.5 as follows: **The  $\delta^{34}\text{S}(\text{OCS})$  value of (10.5 ± 0.4) ‰ is generally consistent with earlier estimation by Newman et al. (1991), which expected the  $\delta^{34}\text{S}(\text{OCS})$  values based on the flux of proportional to the organic matter were produced by photosynthesis as 3 ‰ and oceanic emission as 18 ‰ (Newman et al., 1991).**

Page 10 generally there is little statistical testing reported in this paper in general

**Reply:** Thank you for the comment. For statistical analyses, we used *p*-tests. We assumed that the averaged OCS concentrations and  $\delta^{34}\text{S}(\text{OCS})$  values in day and night are not significantly different. The calculated *p*-values are 0.65 and 0.29, for OCS concentrations and  $\delta^{34}\text{S}(\text{OCS})$  value, respectively. These values are over 0.05. Therefore, significant differences are not observed for OCS concentrations and  $\delta^{34}\text{S}(\text{OCS})$  values of day and night. To the revised manuscript, we added *p*-values.

Page 10 this section would really benefit from more results using the sulfinert equipment.

**Reply:** We added all data accumulated from now to Figure 8 in section 3.4.

Thank you for reviewing our manuscript.

Shohei Hattori on behalf of the authors.