Reply to RC1 from referee #3

Blue: Referee comments
Black: Our comments
Red: The sentences in our manuscript

The reviewed manuscript presents a method for collection and concentrating OCS (the most abundant atmospheric sulfur species) from air. The concentrated OCS sulfur isotopes are then measured by IRMS. Having such measurement method is an important contribution. The results seems robust, and the manuscript is usually well written.

Reply: Thank you very much for your comments.

The main problem I see regarding the suitability of this method for atmospheric sampling is related to samples preservation. So far, it is shown only for 7 days, which is not always enough to get a sample (i.e. from ship cruise or remote location) back to the lab and to analyze it. Also, no tests were done for preservation effect on isotopes. The authors themselves recognized this point as missing and wrote that "Further investigation of preservation of OCS concentrations and isotopic integrity during the storage of the adsorption tubes with respect to storage temperature and materials of the adsorption tube are currently underway. I recommend that the results from these investigations will be included as part of this paper.

Reply: We agree that the preservation period of OCS in adsorption tubes is important. During the process of the review, we investigated preservation of OCS in adsorption tubes at 25 °C, 4 °C, −20 °C, and −80 °C. At −80 °C, we found that the $\delta^{34}S(OCS)$ value is not changed at least up to 14 days. The OCS concentrations are preserved up to 90 days. Therefore, we added data reflecting these experimental results to our manuscript.

Detailed comments:

Page 1 (abstract), Line 17 – "7 inch tubes (1 cm^{-3})" – better to give both dimensions in cm.

Reply: We apologize for inappropriate expressions because it is difficult to identify what 7 inches was referring to. We replaced "inch" units with "cm".

Action: We described the sentence in page 1 line 18 as follows: adsorption tubes (1/4 inch (0.64 cm) outer diameter, 17.5 cm length, approx. 1.4 cm^3 volume).

Page 1 (abstract), Line 17 "preserving samples" – need to add "up to 7 days", or to whatever the new investigations show.

Reply: As we replied above, we have confirmed the preservation of OCS amount and its $\delta^{34}S(OCS)$ values in Sulfinert-treated adsorption tubes at −80 °C up to 90 days and 14 days, respectively.

Action: We added "the OCS amount and $\delta^{34}S(OCS)$ values at −80 °C, respectively, for up to 90 days and 14 days," here.

Page 1 (abstract), line 20 – should be "lack of diurnal variations".

Reply: We replaced "No significant diurnal variation" with "lack of diurnal variation" here.

Page 1 (abstract) line 20 and Page 11 line 6 – It appears here as this method enables measurements also of ^{33}S in air samples. In fact, this has worked out only for standards, and an interference prevented measuring this in air. Please correct.

Reply: As you have pointed out, the ^{33}S for atmospheric OCS was not measured. Therefore, we deleted the precision of $\delta^{33}S$ and $\Delta^{33}S$ values for atmospheric OCS in the *Abstract* and *Conclusion* (summary).

Page 1 (abstract) – Portability is reported here based on the sample tubes. But the size and weight of the sampling system is also a main issue. Please report this, at least in the method section.

Reply: The sampling system size and weight are 50 cm × 50 cm × 50 cm (width × height × depth), and 4 kg except for a dewar (37 cm outer diameter, 66 cm height and 11 kg weight). For the field campaign, the system was disassembled. We carried the parts of the system in two containers 40 cm × 30 cm × 20 cm (width × height × depth) except for the dewar. Then, we were able to assemble the sampling system on site and use the system. Therefore, we can carry our sampling system to field campaigns. We added this information to our manuscript.

Action: We added sampling system size and weight information and handles for the field campaign to our revised manuscript on 1st paragraph of section 2.2.

Page 3, line 30 – Please explain the need for both glass-beads, Tenax TA, and Porapak N. On which of those is the OCS trapped? All of them?

Reply: We are sorry that we did not specify the necessity of each adsorbent in the sampling tubes. The sampling tube design is based upon the description by Bahlmann et al. (2011). According to Bahlman et al. (2011), glass beads trap the remaining water vapor from the sampled air and prevent adsorption of the water vapor on the Tenax TA and Porapak N and increase the temperature exchange between walls of the cryotrap and the sampled air. The Tenax TA and Porapak N can be used for trapping volatile organic compounds. We assume that OCS as our purpose is supposed to be sampled on the Tenax TA and/or Porapak N, but most of OCS might be trapped Tenax TA. Although some components might not be necessary for OCS collections, it works well for OCS sampling. Therefore, we do not plan to modify these in this system.
Action: In the revised manuscript, we described the following on 2nd paragraph of section 2.2: "We developed this sampling tube according to Bahlmann et al. (2011). Detailed functions of respective components are described therein. Briefly, the glass bead traps the remaining water vapor from the sampled air and prevents water vapor adsorption on the Tenax TA and Porapak N. The glass bead further increases the temperature exchange between the cryotrap walls and the sampled air. The Tenax TA and Porapak N can be used for trapping volatile organic compounds. We assume that OCS is sampled on the Tenax TA and Porapak N, but most of OCS might be trapped on Tenax TA. Although some components might not be necessary for OCS collections, up to this point, it is working well for OCS sampling.".

Page 4, line 7 – "less than -110C". Can you be more specific? It can be important for someone trying to use this method. Also, if you get as low as liquid N_2 temperature, than some O_2 (having higher boiling point) will be liquefied.
Reply: We are sorry for the ambiguous sentence. Although it is difficult to keep the temperature constant using vapor of liquid N_2, we confirmed that the temperature in the dewar was at least −140 °C to −110 °C for 3 hr. Because the sampling tube temperature is over −140 °C, O_2 is not trapped in the sampling tube during sampling.
Action: We added the temperature during sampling 4th paragraph of section 2.2 (page 5 line 7) as follows: at temperatures of −140 to −110 °C.

Page 6, line 5 – Rephrase. It should be explained in a different sentence that standard A is not pure OCS because of ...
Reply: Thank you for your comments.
Action: We separated the sentence in 1st paragraph of section 2.5 as follows: Reference OCS of sample A was purified with liquid N_2 (−196 °C) and then introduced via a conventional dual inlet system. Pure OCS is not commercially available in Japan because of its toxicity (Hattori et al. 2015).

Page 7, line 11 – Refer to figure 3a.
Reply: Corrected accordingly.

Page 7, line 23-24 – Not clear. Please rewrite.
Reply: We apologize for the unclear sentence.
Action: We rewrote the text to clarify the sentences (1st paragraph at section 3.2) as follows: 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 8, Line 16. This is only true if the blanks always have atmospheric values. Please consider how it will affect the unceraintty in atmospheric measurements, if the blanks are in the expected range of OCS sources.
Reply: Thank you for your suggestion. We estimated the contamination effect for accuracy and precision of $\delta^{34}S(OCS)$ values when the 5 % of contaminated OCS ranging $\delta^{34}S(OCS)$ value from 3 to 18 ‰ as follows. 5 % of OCS contamination change the accuracy of $\delta^{34}S(OCS)$ value with ± 0.3 ‰. The precision of our repeated measurement is ± 0.2 ‰. Then the overall precision of measurement is ± 0.4 ‰. Additionally, the standard deviation of four atmospheric samples we observed are ± 0.2 ‰. Therefore, the $\delta^{34}S(OCS)$ value for atmospheric OCS at Suzukakedai campus was (10.5 ± 0.4) ‰. We modified precision and Figure 6 in our manuscript.
Action: We added some text to 2nd paragraph of section 3.2 as follows: When considering (0.30 ± 0.16) nmol OCS (i.e. approx. 4 % for 8 nmol OCS samples) with $\delta^{34}S$ of 3–18 ‰ covering reported $\delta^{34}S$ range of OCS sources (Newman et al., 1990), the accuracy of the $\delta^{34}S(OCS)$ can be shifted −0.3 to +0.3 ‰. Because the precision of 1σ uncertainty is 0.2 ‰, the overall precision values (1σ) for $\delta^{34}S$ of this sampling/purification system were estimated as 0.4 ‰. Additionally, we modified the error in Figure 6.

Page 9, line 3 – The variability in concertation reported by Montzka (2007) is seasonal, not diurnal. Any possible explanation for the diurnal variability, and how it is related to what reported for other sites?

Reply: As you have pointed out, Montzka et al. (2007) did not observe diurnal variation of OCS concentration. For the diurnal variation of OCS concentration, we expected that the OCS concentrations are low at 12:00 compared to 00:00 because of plant uptake in our observation. However, we did not observe the trend. Berkelhammer et al. (2014) reported diurnal variation for OCS concentrations in USA with the lowest at 8:00 and the highest at 16:00 with 80 pmol mol^{-1} changes in a day. The differences of OCS concentrations for four atmospheric samples were smaller than 80 pmol mol^{-1}. The observed δ^{34}S(OCS) values of four atmospheric samples were in the range of 10.4–10.7 ‰ (Figure 6b) and averaged (10.5 ± 0.4) ‰, and δ^{34}S(OCS) values also showed no clear diurnal difference (*p*-value = 0.29) (Figure 6b). Given the diurnal OCS variations, future study is clearly necessary to test whether or not δ^{34}S(OCS) values have diurnal variations by comparing δ^{34}S(OCS) values for the highest OCS concentration at 8:00 and the lowest OCS concentration at 16:00. We added related discussion of the matter to the revised manuscript (3rd paragraph of section 3.3).

Reference

Berkelhammer, M., Asaf, D. Still, C., Montzka, S., Noone, D., Gupta, M., Provencal, R., Chen, H. and Yakir, D.: Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide, Global Biogeochem. Cycles, 28, 161–179, 2014. doi:10.1002/2013GB004644.

Page 9, line 12 – Is this 1 permil change (not this small) is also accompanied by a change in concertation? Can this be related to the blank problem? Please explain in the text.

Reply: Yes, the 1 ‰ change might be caused by both isotopic fractionation for OCS decomposition and blank effect. When the contaminated OCS with δ^{34}S(OCS) value of over 17 ‰ are considered, the δ^{34}S(OCS) value can be increased by 1.2 ‰ in sample G. However, such a high δ^{34}S(OCS) value in the blank is not reasonable because the contaminated OCS coming only from the ocean is not likely. Indeed, because the atmospheric δ^{34}S(OCS) value observed in this study was 10.5 ‰, and OCS concentration in sample G was lower than atmospheric OCS concentration, the increased δ^{34}S(OCS) value is expected to be affected by isotopic fractionation during OCS degradation in the cylinder.

Action: We added some text to the revised manuscript as follows: It is possible to explain this 1.2 ‰ increase for δ^{34}S(OCS) value for a case in which the contaminated OCS has δ^{34}S(OCS) value with over 17 ‰. However, such a high δ^{34}S(OCS) value from contamination requires a situation in which the contaminated OCS come only from the ocean, which is not likely. Because the atmospheric δ^{34}S(OCS) values in this study were (10.5 ± 0.4) ‰ and higher than that for sample G, the increased δ^{34}S(OCS) values are expected to be affected by isotopic fractionation during OCS degradation in the cylinder and not by contamination.

Page 9, line 19 – What do you mean by "reasonable signals"

Reply: We apologize for the lack of clarity. We intended the words "reasonable signals" as a representative value when compared to δ^{34}S(OCS) value of (4.9 ± 0.3) ‰ reported in Hattori et al. (2015) because the atmospheric δ^{34}S(OCS) value of 10.5 ‰ is close to 11 ‰ as estimated based on the mass balance of OCS source from land and oceans. Additionally, because the OCS of compressed air in the cylinder can be decomposed and the δ^{34}S(OCS) value may be changed in the cylinder, we do not know if the OCS in the cylinder represents atmospheric OCS. If we consider the δ^{34}S(OCS) value of 13‰ in Israel and Canary Islands reported by Angert et al. (2018) during process of review, the δ^{34}S(OCS) values might not be homogeneous in the world.

Action: We deleted these words from our manuscript.

Page 9, line 20 – "We earlier discussed", where? In previous papers by the same group? I tried to read this in Hattori et al. (2015), but it is not clear to me. Please explain in more detail here how this isotopic balance was done. Also, if both the earlier value and the new value agree with the SSA value, then this is not a strong constraint for atmospheric OCS δ^{34}S.

Reply: We are sorry for an inadequate explanation. First, "We earlier discussed" refers to the discussion described in Hattori et al. (2015) and by Leung et al. (2002). As you have pointed out, both δ^{34}S(OCS) value of (4.9 ± 0.3) ‰ and (10.5 ± 0.4) ‰ agree with the δ^{34}S(OCS) value of SSA value, indicating that it is not a strong constraint of δ^{34}S(OCS) value for atmospheric OCS. However, we earlier hypothesized the δ^{34}S(OCS) value of (4.9 ± 0.3) ‰ reported by Hattori et al. (2015) as a global signal, but it would be not correct. Therefore, we inferred the importance of showing that the new observed δ^{34}S(OCS) value is suitable as a sulfur source of SSA, but it is still similar to a discussion put forth by Schmidt et al. (2013), who hypothesized a δ^{34}S(OCS) value of 11 ‰ according to Newman et al. (1990). Because the discussion has already been reported and because the δ^{34}S(OCS) value is close to 11 ‰, we deleted these discussions and instead used a more detailed description in the revised manuscript.

Action: We delete these discussions in favor of more detailed description in the revised manuscript.

Page 10, Line 3 – Please report the magnitude of these effects, and estimate how this should influence the atmospheric OCS.

Reply: First, sulfur isotopic fractionations of OCS for the troposphere was estimated as −5 to 0 ‰ for reaction with OH radical (Schmidt et al., 2012), −2 to −4 ‰ for decomposition by soil microorganisms (Kamezaki et al., 2016; Ogawa et al., 2017) and −5.3 ‰ for plant uptake (Angert et al., 2018). We added these values to our manuscript. We added Angert et al. (2018) as a new reference.

Secondly, we discussed how isotopic fractionation influences δ^{34}S(OCS) values for atmospheric OCS as follows: all isotopic fractionation constants by OCS degradation are negative, indicating that the δ^{34}S(OCS) values can be increased by OCS degradation in the troposphere. Because the main OCS sink is photosynthesis by plants, the δ^{34}S(OCS) values in the atmosphere might be increased during the growing season in April. However, because of the long lifetime of OCS, the changes in δ^{34}S(OCS) values might not be detected with a seasonal pattern. Future studies must be conducted for determination of isotopic fractionation constant and observation of δ^{34}S(OCS) values to estimate the dynamics of atmospheric δ^{34}S(OCS) values in troposphere.

Action: We added isotopic fractionation constants for OCS degradation process in our revised manuscript and discussed the matter in the revised manuscript (1st and 2nd paragraph at section 3.5).

References:

Angert, A., Said-Ahmad, W., Davidson, C., and Amrani A.: Sulfur isotopes ratio of atmospheric carbonyl sulfide constrains its sources, Scientific Reports, 9(741), 1-8, 2018.

Page 10, line 29 – These “further investigations” seem critical to establish the method. Are there new results since the manuscript was first submitted?

Reply: Yes, we conducted further OCS preservation testing and added the results to section 3.4 in the revised manuscript. We added the results as follows: A rapid OCS decomposition of approximately 20 % during 7 days of storage was observed for the stainless steel adsorption tubes stored at 25 °C. A similar pronounced loss was observed for the Sulfinert-treated adsorption tubes stored at 4 °C but at a storage temperature of −20 °C. The OCS was stable for 30 days at −20 °C, and for at least 90 days at −80 °C within 1σ uncertainty of 6 % (Figure 8a). Furthermore, we found that the δ^{34}S(OCS) values showed no significant change during storage for at least 14 days at −80 °C (Figure 8b). These results demonstrate that it is possible to apply this method for field campaigns by storing the adsorption tube at −80 °C after sampling.

Page 11, line 26 – Please be more specific. Instead of “some shortcomings in terms of sample amount” write down the ratio of sample amounts in the two methods.

Reply: We apologize for an ambiguous sentence.

Action: We added “IR-MS method requires a 300 times larger sample OCS than GC/MC-ICP-MS method.” to section 3.6.

Page 11 - The conclusion section mentions for the first time another method (by Said-Ahmad, 2017). The mentioning of other existing methods should be done in the introduction, and comparison with other methods should be in the discussion, and include advantages and disadvantages. Similarly, writing in the last lines of the paper that the current method has the advantage of enabling carbon and oxygen isotopes measurements seems out of place, since this is not demonstrated in the current manuscript. However, this can be mentioned in the discussion.

Reply: We agree with your suggestion.

Action: We added the GC/MC-ICP-MS method to the *Introduction* section. We made section 3.6 to present a comparison between IR-MS method and MC-ICP-MS method. Although our IR-MS method has shortcomings related to the sample size, we emphasize that this IRMS method can potentially be updated to multiple isotope measurement with carbon and oxygen isotopes. Also, we deleted the discussion related to carbon and oxygen isotope of OCS from the *Conclusion* section.

The discussion should also refer to the new paper by Angert et al., mentioned in the online discussion. Are the atmospheric values reported by the two papers identical, considering all experimental uncertainties? If not, is this a methods issue, or a real geographic effect?

Reply: As you have recommended, we cited Angert et al. (2018) in the revised manuscript. The δ^{34}S(OCS) values of 13 ‰ reported by them are not the same as ours. Because our data are calibrated with the IAEA standard with to obtain δ value with VCDT scale via chemical conversion from OCS to SF_6, we do not expect that a 3 ‰ difference originates from some method-related difficulties in our system. To clarify whether or not we have method-related problems, inter-laboratory calibration is expected to be helpful for future studies.

Additionally, the geographic effect might induce differences of the δ^{34}S(OCS) value between the two studies. In the revised manuscript, we discussed geographic effects that can be considered for explanation of the variations in δ^{34}S(OCS) values. To discuss geographic effects, we added this discussion at 4th paragraph in section 3.5 and added a new citation as a relevant reference: Zumkehr et al. (2018).

Reference

Zumkehr, A., Hilton, T. W., Whelan, M., Smith, S., Kuai, L., Worden, J., Campbell, J. E.: Global gridded anthropogenic emissions inventory of carbonyl sulfide, Atmos. Environ., 183, 11-19, 2018.

Figure 3a – Maybe better to show versus sampling time (and not run number). Also the 10min is black in the legend and gray in the figure.

Reply: Thank you for your suggestion. We believe that the combination of Figure 3a and 3b nicely presents that there was no memory effect, and the relation between sampling time and OCS amount collected. Therefore, we retain this in the revised manuscript, but we changed the legend color from black to gray in the legend of Figure 3.

Action: We changed the legend color from black to gray in the legend of Figure 3.

Figure 8 – Better to start the y-axis at 80%. Also, need to show longer preservation periods.

Reply: Thank you for your suggestion. We did not start at 80 % on the y-axis because we added the OCS preservation results. We added results of longer preservation tests of OCS storage in adsorption tubes.

Thank you for reviewing our manuscript.

Shohei Hattori on behalf of co-authors.