

Interactive comment on “Observations of the uptake of carbonyl sulfide (COS) by trees under elevated atmospheric carbon dioxide concentrations” by L. Sandoval-Soto et al.

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Anonymous Referee #2

Authors: We greatly appreciate the extensive effort that referee 2 has spent in reviewing our manuscript and hope that our comments will help to answer all questions.

COMMENT 1 Referee: The paper is appropriate for the journal. The writing could be improved considerably – the paper is hard to follow in many places, and it is easy to get

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lost in all the detail and the nine tables. Writing deficiencies go beyond simple English translation issues.

Authors: We apologize in case things are not perfectly expressed. But none of the authors is a native English speaker. Therefore, we let an American native speaker check and correct the manuscript. We thought that this would be sufficient to publish with an acceptable style. But of course every writer has his own style. We will work on the paper to improve the presentation.

COMMENT 2 Referee: While this is an interesting paper, with potential implications for the amount of COS in the troposphere and the contribution of this COS to the stratospheric sulfate aerosol layer, there are multiple issues that the authors need to address before this paper can be published. Two specific hypotheses put forward by the authors in the introduction warrant further discussion in the introduction, and should be brought up again in the discussion, in relation to the results of the study: P 2126, Lines 5-6 state, “Elevated CO₂ will trigger a decrease of the enzymatic activities which is balanced by a higher CO₂ availability. Thus, the CO₂ uptake will not decline, but a CA acclimation may lead to a reduction of the COS uptake due to a lower metabolic sink as long as the uptake is not also enhanced by higher substrate (COS) concentration.” If carbonic anhydrase activity indeed decreases under future atmospheric CO₂ as the authors suggest, plant COS uptake may not decline in response if atmospheric COS increases, as an increase in atmospheric COS could offset a lowered plant sink. While there is some evidence that global COS sinks and sources are in balance at present (Kettle et al., 2002; Watts et al., 2000), and that atmospheric COS has declined in recent years (Montzka et al., 2004), atmospheric COS has increased significantly since the industrial revolution (Aydin et al., 2008; Montzka et al., 2004), just like CO₂. Thus, there is no guarantee that atmospheric COS will continue to remain constant and/or decline in the future, particularly where some COS sources are anthropogenic and highly uncertain (Watts, 2000). The papers by Aydin et al. (2008) and Montzka et al. (2004) should be cited and the results should be discussed in relation to the higher

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substrate concentration statement made by the authors. The discussion about global relevance in section 3.4 seems overly speculative given these issues.

Authors: There are several papers published describing the acclimation of the carboxylating enzymes. We discussed that issue one page before in line 5-10 "Elevated CO₂ will trigger a decrease of the enzymatic activities which is balanced by a higher CO₂ availability." The referee is right to point out that this may also be valid for COS. We will add a corresponding chapter to the discussion in a revised paper. We further agree that the COS budget is poorly understood. In an earlier paper we reported about significantly increased sink strength of the vegetation (Sandoval et al., 2005) as compared to budget estimations by Watts (2000) or Kettle et al. (2002). Furthermore, we reported about the close relationship of the COS uptake to GPP. These conclusions were adopted by other groups and obviously match comparing observations and modeling (Campbell et al., 2008; Suntharalingam et al., 2008). As a consequence, we may regard the estimation of sources as severely underestimated. Obviously, we do not understand global sources. This conclusion sheds light on the uncertainty of the future development supporting the referee's concern. Yes, we will discuss this issue.

COMMENT 3 Referee: P 2126 line 10: "Furthermore, increased CO₂ without an increase of COS leads to a competitive inhibition of the COS consumption." This is in direct contrast to recent results from Stimler et al. (2010, *New Phytologist*, not cited by the authors), who observed no cross-inhibition effects between COS and CO₂ during leaf uptake by three different species over wide ranges of COS and CO₂. Granted, the measurements by Stimler et al. (2010) were not made on plants exposed to elevated CO₂ for an extended period of time. However, the data from Stimler et al. (2010) indicate that uptake of COS may not be inhibited by competition with CO₂ under conditions of elevated CO₂. Even though the plants used by Stimler et al. (2010) were not exposed to elevated CO₂ before measurements were made, the paper should be cited and the results should be discussed in relation to the competitive inhibition hypothesis proposed by the authors.

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Authors: Well, we had another impression derived from the data presented by Stimler et al. (2010). We are not convinced that there is no competitive inhibition of the COS uptake by high CO₂ concentrations. Regarding the data reported in Figure 6 of the Stimler paper, we agree that increasing COS does not inhibit CO₂ uptake which seems to be reasonable comparing ppm with ppt. But vice versa? Instead, from Fig 6 we got the impression that the increasing CO₂ in all assays led to a slight decrease of the COS uptake already at 450 ppm CO₂. We compare with 800 ppm! The authors themselves state that at high [CO₂], the uptake of CO₂ continued to increase whereas the uptake of COS became saturated. The authors relate this behavior to synchronization with stomatal conductance and conclude that there is no inhibitory effect of CO₂ on COS uptake. The related data sets are not convincing as there is a decrease of COS uptake and we think that a competitive inhibition cannot be excluded. We came to similar conclusions investigating the uptake of COS by decaying leaf litter (no active stomata) with decreasing uptake of COS under high respiration rates (Kesselmeier and Hubert, 2002). Furthermore, studies modeling the consumption of COS by carbonic anhydrase (Schenk et al., 2004; Notni et al., 2007) demonstrate the similarity of the enzymatic handling of COS as compared to CO₂. If we have to assume that CO₂ and COS compete for the same binding site, why do we have to exclude competitive inhibition? By the way, it seems that Stimler et al themselves do not exclude competitive inhibition (see page 876, last sentence of the chapter "Cross-interactions of COS and CO₂").

COMMENT 4 Referee: One of the central arguments that follows from the main conclusion (i.e. COS uptake declines as ambient atmospheric CO₂ increases) is that the tropospheric COS mole fraction should increase, potentially leading to a higher flux of COS to the stratosphere, where COS is thought to be the principal contributor to the stratospheric sulfate aerosol layer during volcanically quiescent periods. The authors indicate that this would lead to increased shortwave radiation reflection by the stratospheric sulfate aerosol layer, thereby counteracting the anthropogenic enhancement of the atmospheric greenhouse effect. However, the authors do not discuss the enhancement of the greenhouse effect that would be caused by an increase in the tropospheric

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mole fraction of COS, as COS is a strong greenhouse gas. This topic is dealt with in a recent paper by Bruhl et al. (2011), cited by the authors (now published in final form, 2012). The relevance of results from Bruhl et al. (2012) in relation to the work being done by the authors should be discussed.

Authors: We discussed this aspect shortly in the introduction “Thus the stratospheric cooling effect by the COS derived sulfate particles can be regarded to approximately cancel the warming tendency as caused by the direct radiative forcing by the trace gas COS within the troposphere (Brühl et al., 2012)” as well as in the discussion “As a consequence, the atmospheric COS level may rise and cause an increase of the direct radiative forcing by this trace gas, which is however counterbalanced by the cooling effect of the COS derived stratospheric sulfate aerosol (Brühl et al. 2012).”

COMMENT 5 Referee: The usefulness of comparisons of measurements from the two different CO₂ treatments are subject to question because the time periods when the measurements were made do not overlap (Table 1), or only overlap for a few days, as was the case for two of the data sets collected for *Quercus ilex*. Thus, there are two variables in the experiment: ambient atmospheric CO₂ and time. What evidence is there to suggest that differences between CO₂ treatments are really a CO₂ effect and not a seasonal effect? Aside from CO₂ deposition velocities following the expected trend of lower deposition velocity under elevated CO₂ (Table 3), it seems there is little evidence to rule out a possible influence of time of year.

Authors: We agree with the referee and we discussed this issue at several points within the paper. We do not rule out seasonal effects. We regard this issue as an important argument to perform future experiments with more samples within shorter time. New COS online measurement techniques will make it possible to shorten the time needed. We regard our paper as a contribution to enhance the discussion around this issue and we think that the results, though preliminary, should be noted.

COMMENT 6 Referee: The conclusions as stated in the final section of the paper are

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much too strong and/or incorrect given the experimental data. The *Fagus sylvatica* COS deposition velocity under elevated CO₂ was not statistically significantly different from the deposition velocity under ambient CO₂ (Table 4). The *Quercus ilex* COS deposition velocity under elevated CO₂ was only statistically significantly different than the deposition velocity under ambient CO₂ for two out three time periods (Table 4). Additionally, there was a statistically significant shift of the *Quercus ilex* compensation point in only two out of three time periods (Table 6), but not the same two time periods as the significant difference in COS deposition velocity. Also, none of the carbonic anhydrase activities, for either species during any of the time periods, were statistically significantly different. Thus, the enzymatic capacity was not decreased, contrary to what is reported in the conclusion section. Additionally, as discussed in section 3.3, the linear regression analysis only indicated acclimation to higher CO₂ in only one case (*Quercus ilex* in 1999), yet acclimation under elevated CO₂ is one of the main topics of discussion in the conclusions section. The conclusions section of this paper should be rewritten to reflect the actual results and corresponding statistics provided in the data tables, and it should be stated that these measured results only weakly support the proposed hypotheses (given in the introduction) for *Quercus ilex*, but not *Fagus sylvatica*.

Authors: The referee is right in pointing out these weaknesses. We fully agree that not all data support the hypothesis we discussed. But we clearly stated in the conclusion section “The data presented in our study support this hypothesis though the data base with two tree species is limited, our study was too short, and was biased by plant development due to the time consuming measurements.” It is a hypothesis, which is supported not by all but by some data of our study. We will make that clearer in a rewritten version.

COMMENT 7 Referee: Given the tenuous results of COS uptake differences under the two different CO₂ treatments, and the fact that the results were from only two tree species, the global impact calculations presented in section 3.4 are little more than

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simulations of a conjecture in relation to the possibility of reduced COS uptake under conditions of elevated atmospheric CO₂.

Authors: Yes, that is true. But let us regard this study to start further investigations with faster instruments. Let me also point out that the uptake and consumption of COS by the biosphere is one of quite well understood examples of exchange of trace gases between biosphere and the atmosphere. Of course we need more experiments with more than two plant species. But as we can generalize the exchange of COS for many biological species from aspects of the atmospheric uptake up to the enzymatic consumption, the two chosen tree species may definitely point into the expected direction. Therefore, we submitted this data to be published. We are ready to see future results supporting or rejecting the hypothesis.

COMMENT 8 Referee: Specific Comments: The word adaption (which implies genetic change) should be changed to acclimation (which implies phenotypical changes within a given genotype) throughout the paper.

Authors: We used both expressions and agree that this should be changed. We will use the term “acclimation” throughout the revised version.

COMMENT 9 Referee: Carbonic anhydrase activity was measured with some sort of pH-based method, as indicated by the heading to Table 5, but no detail for this method was found in the materials and methods section.

Authors: We cited the use of the method as described by Wilbur and Anderson (1948). To our knowledge this technique, based on the drop of pH initiated by CA, is mostly used till today. We will include a short description within the materials and methods section.

COMMENT 10 Referee: Methods section in general – not all equipment detail is provided – some instruments and manufacturers are specified and others are not

Authors: We will carefully check and improve.

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COMMENT 11 Referee: 2125 line27 - 2126 line 2 – these alternative pathways are interesting but their relevance to this manuscript is weak

Authors: Though the relevance to the paper seems weak, these papers demonstrate quite nicely that CA is a ubiquitous enzyme, splitting COS into CO₂ and H₂S.

COMMENT 12 Referee: 2126 line 6: – the enzymatic role is likely not obvious to everyone, reword

Authors: We propose to reword as follows: But on a long term basis this initial stimulation of photosynthesis is often followed by a decline which is obviously caused by a decrease of activities of the carboxylating enzymes Rubisco, PEP-Co and CA.

COMMENT 13 Referee: 2126 line 7: “well-established” is better here than “well-reported”

Authors: accepted

COMMENT 14 Referee: 2126: units of ppm are not concentrations (mole/volume), they are mole fractions (mol/mol)

Authors: We apologize. This is a misuse as often found. We propose to check the whole paper and to use the term “mixing ratio”.

COMMENT 15 Referee: 2128 line 1: “Measurements . . . were”

Authors: accepted

COMMENT 16 Referee: 2128 line 2: “to deal with. . .” – sentence ends in an awkward way

Authors: We propose: Measurements of COS exchange were time consuming and had to be spread over several days up to few weeks.

COMMENT 17 Referee: Table 9 “best estimate” is better than “best guess”

Authors: accepted

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