

## ***Interactive comment on “Exchange of carbonyl sulfide (COS) between the atmosphere and various soils in China” by J. Liu et al.***

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Response to the comments of the anonymous referee#2:

We are grateful for spending your valuable time on our manuscript, and for your constructive suggestions! We have revised our manuscript carefully according to your suggestions. The following is the responses to your comments.

General comments: This manuscript reports exchange rates of COS by different soil types, measured both in the lab and in the field, and respective dependencies of the exchange on the COS ambient concentrations, temperature, and soil water content. Data presentation and discussion is pretty much straight forward. The work is a valuable add to the small pool of available soil COS exchange data. The generalization of

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dependencies which were yet measured only for a few soil types represents the largest source of uncertainty in global COS budget exercises (Kettle et al. 2002). Answer: We highly appreciate your general comments. The questions you mentioned here are answered specifically as follows.

Specific comments: Question 1: In general, I would suggest to omit the term “flux” in conjunction with enclosure measurements, as it is rather used in terms of micrometeorological measurements (eddy covariance, aerodynamic gradient etc.). Hence replace “flux” and “exchange flux” by “exchange” and “exchange rates” in the whole manuscript (likewise, omit “flux enclosure”). Answer: According to your suggestion, “flux” and “exchange flux” in the manuscript were replaced by “exchange” and “exchange rate”.

Question 2: I would suggest showing the data of COS exchange as a function of COS concentration in an individual diagram, like the authors did for the dependencies on soil water content and temperature. And/or show in Table 3 the intercept of the y-axis (extrapolation of the linear regression to zero COS concentration, with appropriate units), as an estimate for the COS emission/production potential (compare e.g.: Kesselmeier et al. 1999). Add the correlation coefficients of the linear correlation analysis. Also in this context: the flush rate of the enclosure was relatively small; hence the expected concentration differences at the inlet versus the outlet of the enclosure were probably high: please indicate whether the inlet or the outlet concentration was used to calculate deposition velocities (I do assume the latter). Answer: According to your suggestion, the data of COS exchange as a function of COS concentration was shown in an individual diagram (Figure 3), and the ordinate intercepts, the slopes and the correlation coefficients of the regression lines were also added in Table 3. Just as you expected, the concentration differences at the inlet versus the outlet of the enclosure were large especially under the case when the exchange rate was high. The deposition velocities were re-calculated based on the outlet concentration of COS (Table 2).

Question 3: One main open question: what made the difference between the setup and/or soils sample investigated by Yi et al. (2008; reporting uptake of COS by dry

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paddy soils in the field and emission of COS only by waterlogged, non-planted paddy soils) and the field results presented in this manuscript. With a compensation point concentration of 765 ppt found in the laboratory for the paddy soil from Jiaxing, a deposition of COS would have to be assumed when the soil faces the extremely high ambient concentrations observed at the field site, which would be in accordance with the findings of Yi et al. (2008). This was not the case for the field data presented in here, and even at concentrations above 1500 ppt emission was observed. Obviously at the field site the conditions for COS ambient concentration, temperature or soil moisture all greatly varied in concert for the different patches shown in Table 4, hence it is hard to what are the determining variables. Devai and DeLaune (1995) found that the (potential) COS production rate generally depends on the redox potential of the soil. At negative values (under reducing conditions) the emission increases, whereas at positive redox potentials, it decreases. Waterlogged soils are anoxic and usually have low redox potential. COS production is assumed to be considerably enhanced in such soils, leading to an increased compensation point, as was found for paddy soils by the authors. Do the authors have an idea on the redox status of the paddy soils that emitted COS? I would assume that the difference in soil water content, as investigated in the laboratory (decreased emission with increasing water content), might rather be a short-term effect of the higher gas diffusion resistance within the soil column due to the higher water content (for P1 the steady state exchange at high water contents was zero). Only within a longer timescale the higher resistances will have an effect on the composition of the microbial community (hence COS production), as might have been the case at the field site (also relevant for the zero exchange at waterlogged conditions). Answer: Yes, we totally agree with you. The laboratory simulation can only qualitatively reveal the character of COS exchange between soils and the atmosphere, but it is difficult for exactly quantifying the actual exchange rates, because the soil samples were strongly disturbed by sampling and treatments, e.g., the soils would become loose after sieving, and the redox potential of the soils would become higher due to the increasing probability of the air contacting with the soils. The influence of treatments

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on the investigated paddy soils may be more serious than the wheat soils, because the field paddy soils are always under anoxic condition. The increasing redox potential of the paddy soils would result in less COS production rate and lower compensation points, and the compensation points for the two paddy soils obtained by this study only represented their lower limits. Yang et al. (1998) found that COS mainly exhibited emission (only sometimes with uptake) from a paddy field (including rice plant) in Nanjing. Kanda et al. (1992) also observed net COS emission from a paddy field in Japan after harvest when the paddy soil was dry. The preliminary field measurement in this study supported their findings, because strong COS emission potential of the paddy soils during non-waterlogged period. The results of laboratory simulation in this study indicated that COS emission potential (the compensation points and the emission rates under various conditions) of the paddy soil from Guangzhou was much higher than the paddy soil from Jiaxing, however, Yi et al. (2008) observed net sink of COS from the paddy soil of Guangzhou during non-waterlogged period, which was inconsistent with our field measurement and those investigated by Kanda et al. (1992) and Yang et al. (1998). As for waterlogged soils, the laboratory simulation in this study may underestimate COS emission strength due to short time incubation as you mentioned. However, the field measurement for the waterlogged paddy soil (it was under waterlogged status for at least one month) in Jiaxing was in good agreement with the laboratory simulation. The results of this study for the waterlogged soil were inconsistent with previous studies both on field measurements (Yi et al., 2008; Kanda et al., 1992) and laboratory simulation (Devai and DeLaune, 1995). In addition to the short time incubation for laboratory simulation, the dynamic chamber setup used in this study was responsible for underestimation of COS emission from the waterlogged soil. Gas exchange between the air and water surface mainly depends on the degree of turbulence in the fluids (Liss and Slater, 1974). Compared with those of static chambers using fans for mixing the air (Yi et al., 2008; Kanda et al., 1992) and that using purge method (Devai and DeLaune, 1995), the turbulence of the interface between the air and water under the steady and slow air flow rate in the dynamic chambers might be negligible.

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Minor comments, corrections:

Question 4: The diagrams in the revised version (supplement) are now much better. I would suggest to add an x-axis at  $y=0$  (like in the original version), to be able to better differentiate between emission and deposition. Answer: An x-axis at  $y=0$  was added in Figure 4 and Figure 5.

Question 5: Check the whole manuscript (several instances) for the typo “concentration” Answer: Sorry for the mistake! The whole manuscript was carefully re-checked and these mistakes were corrected.

Question 6: Page 10558, line 10: rephrase “For the : : COS emission increased exponentially with increasing soil temperature : : and COS emission decreased with increased soil water content.” Answer: This sentence was rephrased as follow: “COS emission rates from the two paddy soils increased exponentially with increment of the soil temperature, and decreased with increasing the soil water content.” (Page 10558, Line 10)

Question 7: Page 10561, line 7: As the humidification of air by the water bubbler was done after addition of high-concentration COS gas: did that setup actually have an effect on the COS concentration (by solution of COS)? Answer: Because the mixed air was equilibrated with the water in the bubbler for at least 30 min, and COS concentration at the outlet of the bubbler was very stable, the effect of COS solution was negligible for COS exchange.

Question 8: Page 10566, line 12: replace “hifger” by “higher” Answer: Thanks! The mistake was corrected in our revised manuscript.

Question 9: Page 10567, line 12: Why should the negative pressure within the enclosure favour COS emission? A mass transfer of air from the soil to the atmosphere (induced by un- derpressure in the enclosure) would enhance the apparent (measured) emission rates in case when there is an production of COS by the soil (i.e., sucking

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COS enriched air into the enclosure); but would enhance the apparent (measured) deposition rates in case when there is an uptake of COS by the soil (i.e., sucking COS-depleted air into the enclosure). So, I do agree that an artificial underpressure enhances the measured exchange rates, but this can hardly be assigned for a change of the sign of exchange (inhere from deposition expected by the lab measurements, to emission observed in the field). For an alternative reasoning: do you have an idea of the redox potential of the individual samples paddy soils in the field, and their (water-logged) history, respectively? Answer: Yes, the influence of negative pressure within the enclosure on COS exchange depends on cases. As your suggestion, the difference of COS exchange for the paddy soil in Jiaying between the laboratory simulation and field measurement wasn't ascribed to the artificial pressure variation in the enclosure, was probably due to the variation of the soil's redox potentials. As our answers for your question 3, the soil samples were strongly disturbed by sampling and treatments, especially for the paddy soils. The changes of the redox potentials of the soils during treatments were probably responsible for the difference between laboratory simulation and field measurement. Regrettably, the redox potentials of the soils were not measured by this study. The duration of the waterlogged field soil in Jiaying was at least one month.

Question 10: Page 10567, line 17: As some of your paddy soil patches in the field strongly emitted COS event at ambient concentrations above 1500 ppt, I would expect that the high ambient concentrations might stem from COS emissions by the soil. Answer: According to your valuable suggestion, the corresponding sentence was rephrased as “The high COS concentration in the field may be ascribed to the emission by the soil and the direct sources from a power plant about 1 kilometer away and a pig factory nearby the field.” (Page 10567, line 17).

Question 11: Page 10567, line 25: “: : might be useful in quantitatively predicting: : :” Answer: This sentence was meaningless, and deleted in the revised manuscript.

Question 12: Additionally to the global budget of Watts (2000), please check the

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work done by Kettle et al.: Global Budget of Atmospheric Carbonyl Sulfide: Temporal and Spatial Variation of the Dominant Sources and Sinks. *Journal of Geophysical Research*, 107 (D22), 2002. According to your suggestion, the reference of Kettle et al. (2002) was added in the revised manuscript (Page 10558, Line 25; Page 10559, Line 5; Page 10571, Line 33).

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/6/C3977/2010/bgd-6-C3977-2010-supplement.pdf>

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Interactive comment on *Biogeosciences Discuss.*, 6, 10557, 2009.

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