

## ***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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Received and published: 16 January 2010

Response to the comments of the H. Van Diest's referee:

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 is certainly a nice piece of research work with useful data, reporting about the exchange of COS between soils from different provinces of China and the atmosphere. Data was acquired both from laboratory and field measurements showing a general uptake of COS for agricultural soils and forest soils, as already investigated by Van Diest and Kesselmeier [2008] for some agricultural and

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forest soils. In addition, an emission of COS was measured for two paddy soils. Furthermore, the authors emphasize the importance of ambient COS concentration, temperature and soil water content. Also the compensation points for some soils were compared at 17\_C and 25\_C, which showed an increase of the compensation point at increasing temperature. Answer: We highly appreciate your general comments. The questions you mentioned here are answered specifically as follows.

Important comments:

Question 1: Some of the comments are already mentioned by referee #1: e.g. the unclear description of the flux chambers on page 10562 line 11; the meaning of “certain sulfurproducing bacteria”; what is S(effect)? Answer: These questions are replied in the answer for referee#1. The description of the flux chambers on page 10562, line 11 was revised as: “Four Teflon tubes were connected to the four inlets at the outside of the chamber, and the other ends of the four tubes rose to 50 cm above ground.” To our knowledge, there is still no report about COS-producing bacteria in soils. Therefore, it is difficult for us to specify the bacteria which are far from our research scope. The sentence could be deleted due to meaningless. Soil available sulfur (Seffect) means the sulfur in the soil can be used for crops assimilation, including soluble sulfur and part of the adsorption sulfur and organic sulfur. Soil available sulfur was measured by turbidimetry method after extraction from soils with 0.5 mol L<sup>-1</sup> NaHCO<sub>3</sub>. The definition and measurement of Seffect were noted in Table 1 (P. 10575) (attached in the supplement file).

Question 2: On page 10561, line 6, you wrote “COS concentrations within the desired range were obtained by mixing compressed air (50ppt COS) with high-concentration COS gas (500ppb COS)”. It would be helpful to give more details about the mixing and how you preserve a constant COS concentration of e.g. only 500ppt in the cuvettes. Answer: To give more details about the mixing procedure, the corresponding paragraphs were rephrased as following: The investigated soil was put into a glass dish (1D, 15 cm) at the bottom of the enclosure. Soil temperature was controlled by putting the

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enclosure in a super-constant-temperature water boiler (CS501, Chongqing Testing Equipment Corporation, Chongqing, China). COS concentrations within the desired range for flushing the enclosure were obtained by mixing a purified compressed air (50 ppt COS) with high-concentration COS gas (5-50 ppb COS) from a glass flask (10 L). The flow rates of the purified compressed air and the high-concentration COS gas was controlled by two mass flow meters (SY-9506, Beijing Shengye Technologic Development Corporation, Beijing, China) with ranges of 0-5 L/min and 0-100 mL/min, respectively. Before being introduced into the enclosure, the mixed air was humidified by a water bubbler which was also placed inside the water boiler to prevent the soil samples from drying during the experiments. COS concentration from the exhaust of the water bubbler was analyzed by the GC-FPD every 10 min, could achieve steady value after 30 min. The total air-flow rate through the enclosure was normally kept at 0.7-0.8 L min<sup>-1</sup>.

Question 3: Kesselmeier et al. (1999) found a linear correlation of COS exchange and soil mass up to 100g soil per cuvette, which shifted to a saturation-like exchange behavior with increasing soil masses between 200g and 400g. In this study (page 10561 lines 23-26) you observed a saturation-like exchange behavior with increased soil mass already between 100g and 200g. Did you measure this behavior for all your soils? Answer: The saturation-like exchange behavior with increased soil mass was only investigated by three types of soils, two soils of lawn and winter wheat from Beijing, and one paddy soil from Jiaxing.

Question 4: Page 10562, line 16: "After flushing the chamber for 30min with ambient air, : : ." Please make clear if this air was taken from the ambient outside the cuvettes (in the field) or if the cuvette was flushed with air with an ambient COS concentration of ca. 500ppt? Was the actual ambient COS-concentration measured during the field experiments? Answer: The air was taken from the ambient outside the cuvettes in the field and COS concentrations from the outlet of the reference chamber were considered as the actual ambient COS-concentrations as listed in Table 4 (Page 10578). The

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description of these contents was not clear in our original manuscript, and revised as following: To verify our laboratory simulation for paddy field soil, we carried out a brief set of field measurements in Jiaxing, Zhejiang province, the collection site for our paddy soil sample. Two dynamic chambers were adopted for exchange rate measurements. Each dynamic chamber consists of a Polyvinylchlorid tube (30 cm (H) ×20 cm (ID)) that has an inner surface covered by Teflon film (0.1 mm). Four inlets of Teflon tubes were evenly connected to each chamber at the outside with heights of 5 cm above the bottom, and the other ends of the four tubes rose to 50 cm above ground. A mini-pump connected with an outlet at the top of the chamber was used to drive ambient air into the chamber. The flow rate was kept at 3.27 L min<sup>-1</sup>. During COS exchange rate measurements, one chamber was mounted on a pedestal (15 cm (H) ×20 cm (ID)) with bottom open, the other one was also mounted on the same pedestal, but with bottom covered by Teflon film. The pedestal had a gutter around the outside of its upper rim that could be filled with water to make an airtight seal with the chamber. The pedestals for the chambers other than the reference one was inserted 10 cm into the investigated soil for one day before the exchange rate measurements. After flushing the chamber for 30 minutes with outside ambient air, air samples were collected into 2-L Teflon bags (0.1 mm film) and analyzed within 3 days after collection.

Question 5: Page 10564, lines 11-13: If the actual ambient concentration was measured and if this was lower than the compensation point (supposing that the cuvette was always flushed with 500ppt COS), is there an emission of COS possible? Answer: The actual ambient concentrations during field measurement in Jiaxing were significantly larger than the compensation points obtained by our laboratory simulation flushing with ~500ppt COS, only with exception for the waterlogged plot, while other plots acted as sources for COS even under ambient COS concentration of 1800 ppt. The possible reason is that the paddy soils were strongly disturbed by sampling and treatments, and the redox potentials of the paddy soils for simulation might increase significantly, and resulted in lower compensation points. For the details, please consult our answers for the questions raised by the reviewer 2.

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Question 6: Another question about the compensation point (page 10564, lines 24-26): What do you expect when the compensation point was measured at more than two temperatures? Is there a linear correlation between temperature and compensation point? It would be worthwhile for these soils to see what happens with the compensation point at a temperature less than 15\_C. A linear correlation would suggest an increase of emission or a decrease of deposition with increasing temperature (and a constant ambient COS-concentration). But I would assume, according to the optimum deposition velocity you found at temperatures between 15 and 20\_C for W1, W2 and F (page 10565, lines 8-10), you should find a higher compensation point at temperatures lower than 15\_C (compared to the compensation point at 17\_C). Answer: Thanks for your valuable suggestions! Yes, we totally agree with your assumption, it is impossible for a linear correlation between temperature and compensation point. Anyway, we would like to conduct such an interesting experiment in the near future.

Question 7: Page 10565, line 7 and page 10566 line 9: I suggest adding the error (e.g.  $\pm 80$  ppt as in line 7 of page 10563). Answer: According to your suggestion, we added the error in the revised manuscript.

Question 8: Page 10568, line 25-27: please explain: "the optimal soil WFPS for COS uptake from the investigated boreal soils in this study must be greater than 19%, especially for the soil from the forest". For further investigations it would be nice to see if there is a correlation between the bulk density of the Chinese soils and the deposition velocity, as earlier found by Van Diest and Kesselmeier (2008) for the 4 arable and forest soils from Germany, Finland, Siberia and China. But I understood, as you already mentioned (authors reply on referee #1), you didn't measure the bulk density for the soils in this study. Answer: Thanks for your valuable suggestion! Assuming the bulk density of the investigated soils were about  $1\text{ g cm}^{-3}$ , WFPS can be calculated according to the general particle density using the formula used by Van Diest and Kesselmeier (2008). The calculated WFPS value of optimal COS uptake for W1 soil was 21.5% which is coincident with that of Van Diest and Kesselmeier (2008).

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However, the values for W2 (36.9%) and F (93.6%) soils were much higher than 19%.

Question 9: Figure 3 and 4: Some points have no error bars, does it mean that the error bars are smaller than the symbol? See e.g. figure 3 for soil F (also after correction referee #1). If so, please add the e.g. the following sentence: "Some error bars are smaller than the symbol." Answer: We improved the figures and the error bars were much clearer (Figure 4 and 5 attached in the supplement file).

Question 10: Table 3: please add that the water content of the soil is the original as found in the field. Answer: According to your suggestion, we noted that "the water content of the soil is the original as found in the field" in Table 3 (attached in the supplement file).

Question 11: Please change "concentration" into "concentration" as found on page 10561 line 10, on page 10563 line 20, on page 10564 line 12 and on page 10565 line 7. Question 12: Please change "higher" on page 10566 line 12 into "higher". Answer: Sorry for these types of mistakes! They are corrected.

Please also note the supplement to this comment:  
<http://www.biogeosciences-discuss.net/6/C3984/2010/bgd-6-C3984-2010-supplement.pdf>

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

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