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> Interactive Comment

# *Interactive comment on* "Carbonyl sulfide exchange in soils for better estimates of ecosystem carbon uptake" by M. E. Whelan et al.

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#### **General Comments**

The goal of this paper is to contribute to a discussion around the role of soils within the exchange of carbonyl sulfide (COS) between a forest ecotype and the atmosphere. The net signal of the COS exchange is a significant matter of discussion for estimating Gross primary Productivity (GPP) independently from the complex practice taking into account net carbon exchange corrected by hetero- and autotrophic respiration. However, in order to exploit the gross uptake of COS, a significant contribution by soils must be excluded. Therefore, the authors investigated soils from 5 different sites and came to the conclusion that soil interaction by uptake and/or emission is not negligi-





ble as compared to plant uptake and may interfere with GPP estimation. However, uncertainty of GPP can be regarded to be much larger.

This paper deserves publication in ACP after some revision. Data, discussion and conclusion are principally convincing and may help to find a general approach to determine GPP in future. However, the model still deserves some improvements to match observations under natural conditions. There may be missing links. A profound discussion of the lack of matching observed data would be helpful. One important issue for example is not discussed at all in the paper. We know from several studies that uptake fluxes of COS are linearly depending on atmospheric COS concentrations. How will such fluctuations, which may be considerable, be included? Furthermore, the current measurements as described by the authors are performed under "ambient" COS concentrations. But no concentration data are given. It would be of high interest for the reader to get information about concentrations and eventual fluctuations of atmospheric COS concentrations during the measurements. Such data would allow estimating deposition velocities which are easier to compare with other reports. Furthermore, some variabilities, such as in figure 6 might be caused by fluctuations of atmospheric concentrations? Understanding will be improved by presenting data on COS concentrations. This issue should be carefully discussed if it cannot be taken into account.

#### **Specific Comments**

1. Introduction, page 21097, line 2-6: Citation of the first report on the close relationship between COS uptake and GPP as derived from deposition velocity corrected COS/CO2 uptake by branch level measurements might be nice. Sandoval-Soto et al (2005) were the first to demonstrate that the COS/CO2 uptake ratios corrected against atmospheric ratios and deposition velocities indicate the potential for GPP estimation. This paper initiated the current COS-related GPP discussions for ecosystems.

2. Introduction, page 21097, line 9-13: Enzymatic consumption of COS has not only been demonstrated with the isolated enzyme carbonic anhydrase (CA),

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but also with Ribulose-1,5-bisphosphate-carboxylase/-oxygenase (RuBisCO) and Phosphoenolpyruvate-Carboxylase (PEP-CO). The cooperation of these three enzymes has already been reported in 1992 (Protoschill-Krebs, G. and Kesselmeier, J., Enzymatic pathways for the consumption of carbonyl sulphide (COS) by higher plants. Botanica Acta 105, 206-212, 1992). Furthermore, cooperation of CA with other enzymes was further discussed for soil microorganisms by Wingate et al. (2008). When investigating the function of soils, we should not concentrate only on CA, though it may be the key enzyme, but also mention the potential of other enzymes. In view of the complex "soil organism" our views should not focus too much. Otherwise, we might easily oversee important details.

3. Methods, page 21099, lines 26-28: The authors state that by keeping soils whole (unsieved), this reduced the influence of sample processing artifacts on lab-based flux observations. That sounds too optimistic. It helps to hopefully stay a bit closer to natural conditions. However, sieving helps to reach a highly reproducible material to be analyzed and is used in most cases of soil exchange measurements. Skipping this step can lead to unreproducible soil sample mixtures, which may also create problems. Rewriting this statement in order to give both views a right to exist would be appropriate.

4. Methods, page 21100, lines 8 and following: It is always helpful to give units for formula components. This helps the reader to reproduce calculations. Within line 29 and 31, the two different terms "mixing ratio" and "concentration" are used with the same sense. The use should be harmonized.

5. Methods, page 21100, lines 15-16: What do the authors want to describe with "uninterpretable because of variations in ambient CO2 concentrations, Ci"? Was the CO2 concentration in the incoming air highly fluctuating? Were the measurement performed by switching between in- and outlet or were they performed simultaneously? A little bit more information about measurement procedures would be helpful to understand the authors' concerns.

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6. Results, chapter 3.1.: The authors give the amount of water in soils as volumetric water content %. That is fine. But it might be helpful for readers to compare to other units. Why not giving also weight%?

7. Results, page 21109, line 25-27: The authors cite van Diest and Kesselmeier (2008) and Kesselmeier et al. (1999) and mention that all soils measured within this work were sandy soils. A little bit more information was available and given in these papers. Maybe the authors can also add some more information to their table 1 including some characteristics such as maximum soil water content and calculated water filled pore space.

8. Chapter 4.2., page 21110, line 20-21: The authors cite Whelan and Rew (2015) who autoclaved agricultural soils and found only COS production left. I think this is a questionable prove. Autoclaving cooks the biological material and kills microbes, but what about all the organic stuff, which is still available, may be decomposing now and may be in a very volatile condition. Hence, autoclaving may induce a production and release and may cover any uptake process.

9. Information about calibration, accuracy and precision of the gas analyzers is missing throughout the paper. Within this context, error bars within the figures (5-8) would be of great help.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 21095, 2015.

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