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Interactive comment on “A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation” by U. Seibt et al.

Anonymous Referee #2

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This is a nice paper that adds clarity to the relationship between COS and CO₂ by applying a conceptual model to interpreting older measurement data collected by some of the co-authors. My comments relate primarily to improving clarification of the points and methods used in the analysis.

In that regard, one point worth elucidation further in the text relates to using Ca in sample rather than reference cell in calculating different parameters such as fluxes and deposition velocities. In previous papers by these authors they used a different normalization concentration - yet here a broad statement is made that sample cell concentrations should be used, and that "often the first need to be calculated from

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reference chamber values and flux rates." (p. 9285, lines 8 - 11). Please clarify this here and elsewhere (p. 9288, Table 2) so it is clear why different concentrations should be used. Currently, the text is not clear in explaining this change in approach.

The authors find that the assumption that C_i, COS is likely negligible with respect to C_a, COS as it provides reasonably good approximations of observational data. Why do older Kesselmeier/Merk papers sometimes show evidence for non-zero intercepts (emissive flux) for sub-ambient COS concentrations? Does this also relate to normalization issues, problems in older analyses, etc.? Please explain.

It appears that two different global mean VCOS/VCO_2 ratios are discussed - one from updated or reanalyzed data presented in Table 2 and another from the consideration of Carbon isotopes in section 6. Yet only the isotopes ratio is applied to GPP to derive a global COS uptake flux to vegetation. Some indication as why this estimate is more reliable is needed.

The usefulness of COS on broader scales to derive information related to GPP requires this vegetative flux to dominate others, or for those other fluxes to be well characterized. It would seem that some mention of this point is necessary in the conclusion (lines 9-16 on p. 9291). Also in lines 5-8 - this general point has been proposed previously by others. Perhaps this manuscript is more precisely described as providing a framework for understanding of COS fluxes that should improve the usefulness of this approach to derive information regarding GPP.

Other issues for improving clarity and accuracy: Abstract: Line 9, the change: "realistic COS fluxes to leaves...from field and laboratory leaf and branch chambers" would reinforce the notion that the paper is about leaf, not ecosystem fluxes. . .

Line 10, "We confirm that COS uptake...is directly linked to stomatal conductance" is implicit from the agreement between observed and calculated COS fluxes. This point would be reinforced if data for stomatal conductance (or transpiration) were included in Figure 2, for example.

Line 14: it is not clear at this point that the deposition velocity ratio is V_{CO_2}/V_{CO} and not its inverse. . .

Section 2, p. 9283. It is proposed in their treatment of conductance that g_{i,CO_2} is assumed to be a small fraction of g_s or that the ratio $g_{i,CO_2}/g_s$ might be constant. Is this second assumption perhaps less appropriate under conditions under which leaf conductance might change dramatically owing to light changes or variations in ambient humidity? Does the available data and agreement allow some comment on this point?

Line 25 of this section: it would help the reader to indicate that calculated and empirically-derived estimates of R_w-CO_2 , though unavailable previously, are provided in what follows.

Section 3: Line 1: clearer as "the relationships between stomatal conductances for two different gases correspond..." Page 9284, Line 5 and line 13. Given that this analysis requires only relative diffusivities, it is a bit confusing when the derivation of a molecular diffusivity is called "binary diffusion"... is this necessary?

Table 1: the temperature at which the calculations were performed needs indicating. Is this the same temperature as used in Massman (1998)? Indicate as a note to the table, perhaps, which parameters given in the table were from Bird (2007).

Section 4: p. 9285, Following up on the first point of the review, the description of how fluxes were measured might be improved and briefly elaborated upon... essentially fluxes are derived from measured concentration differences in sample and reference chambers, i.e., $\text{Flux} = \Delta C \times \text{conductance}$. My concern: does the extent of reaction influence the derived flux and does this vary for these different gases? What was the ΔC for CO_2 in these measurements? Is it 10-15% as suggested by the potential errors suggested for uncorrected data in Table 2?

Line 20, state this point more clearly-is it that the fluxes derived in the absence of light were smaller than the uncertainties in the analysis?

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Line 22, were these enclosures around live whole branches of oak that were studied? And are the uncertainties (Figure 2) primarily the result of imprecision in the COS measurement ($\sim 5\%$) rather than in the determination of conductance?

Section 5: P. 9287, line 12: It is not clear from discussion in section 4 that $g_s, \text{COS} / g_i, \text{COS} = 0.1$ was actually derived as a best estimate, perhaps label it as something different here. Line 17-20, Comparing the uptake flux of 10 from Xu to measures of $\text{VCOS} / \text{VCO}_2$ is a comparison between apples and oranges. It cannot be done without considering 'ambient' concentrations of these gases. . . p. 9289, line 1-3, clarify specifically which "relationships developed here should also hold for C4 plants." Do you mean $\text{VCOS} / \text{VCO}_2$ or other things?

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