

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.

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We thank referee 2 for helpful comments and suggestions!

In the following are the replies to general comments:

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 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 ambient air surrounding the

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observed leaves or plants (and thus relevant for gas exchange calculations) is that in the sample chamber. Using reference concentrations instead leads to systematic biases. For example, stomatal conductance will be underestimated when based on reference cell humidity because leaf transpiration increases the humidity in the air surrounding the leaves (in the sample chamber) with respect to the reference cell. Similarly, $v_{\text{COS}}/v_{\text{CO}_2}$ ratios will be underestimated because the COS drawdown in the sample chamber is greater than the CO₂ drawdown. I have tried to better explain this in the text and Table 2 caption.

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. > Good point ... The (newer) direct measurements have not confirmed the emissions reported in older papers. The non-zero intercepts were derived by extrapolation, and may have been experimental artifacts or normalization issues (for example, plotting uptake rates against the higher reference cell concentrations would shift the regression line to a negative intercept). No emissions were found in the later experiments, even at low (or zero) ambient COS concentrations.

It appears that two different global mean $V_{\text{COS}}/V_{\text{CO}_2}$ 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 ratios in Table 2 are based on direct COS and CO₂ measurements. This is the most relevant data for $v_{\text{COS}}/v_{\text{CO}_2}$ ratios, but there is not a lot of direct data available yet. Carbon isotope data provides a much better coverage of the different ecosystem types at the global scale.

The usefulness of COS on broader scales to derive information related to GPP requires

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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). > added to sentence

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. > changed

Below are the replies to specific comments:

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. . . > added to sentence

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. > We did not include stomatal conductance data in Figure 2 because it is available in Sandoval-Soto et al 2005.

Line 14: it is not clear at this point that the deposition velocity ratio is $V_{\text{COS}}/V_{\text{CO}_2}$ and not its inverse. . . > added to sentence

Section 2, p. 9283. It is proposed in their treatment of conductance that $g_{i,\text{COS}}$ is assumed to be a small fraction of g_s or that the ratio $g_{i,\text{COS}}/g_{s,\text{COS}}$ 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? > I agree - in most cases, it is more appropriate to use a constant internal conductance rather than a constant ratio. The constant ratio approach is probably okay at stable stomatal conductance, or for mean values. I have changed the sentence. I have also

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added an appendix where internal conductance is explicitly included in all equations.

Line 25 of this section: it would help the reader to indicate that calculated and empirically-derived estimates of $R_w\text{-COS}$, though unavailable previously, are provided in what follows. > added

Section 3: Line 1: clearer as "the relationships between stomatal conductances for two different gases correspond..." > changed

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? > The word binary is just to express that the gases diffuse in air, but this is also stated explicitly in the text. I have deleted this word now.

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). > All estimates were derived for a temperature of 23C corresponding to the average air temperature during the chamber experiments. The temperature effect on the ratios of diffusivities is small, and can probably be neglected for plants under natural conditions. I have added a note to the table.

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., $\text{Flux} = \Delta C \cdot \text{conductance}$. My concern: does the extent of reaction influence the derived flux and does this vary for these different gases? What was the ΔC for COS in these measurements? Is it 10-15% as suggested by the potential errors suggested for uncorrected data in Table 2? > The flux is calculated from the measured concentration difference as: $\text{Flux} = \Delta C \cdot \text{flowrate} / \text{leaf area}$. The flowrate is usually set high enough to avoid large changes in the sample chamber air (COS and CO₂ concentration, humidity), and thus minimise the influence of the reaction on the flux

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rate. For example, for the *Fagus* experiments, the COS in the sample chamber was 340 ppt, and the drawdown from the reference cell was 110 ppt. The uncertainty estimates were derived from the errors associated with the concentration measurements in the reference and sample chambers. The experiments are described in much greater detail in the respective original papers.

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? > added: no significant differences between sample and reference mole fractions.

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 (±5%) rather than in the determination of conductance? > Live oak is the common name of the species. The uncertainties in the COS measurements are indeed the largest factor in the overall uncertainties.

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. > changed to "estimate ... consistent with CO₂ and water data"

Line 17-20, Comparing the uptake flux of 10 from Xu to measures of VCOS/VCO₂ is a comparison between apples and oranges. It cannot be done without considering 'ambient' concentrations of these gases. . . > For the comparison, I have now recalculated the appropriate normalized uptake ratio from atmospheric COS and CO₂ concentrations.

p. 9289, line 1-3, clarify specifically which "relationships developed here should also hold for C₄ plants." Do you mean VCOS/VCO₂ or other things? > yes - added to sentence

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