

***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.***

**P. Harley (Referee)**

harley@ucar.edu

Received and published: 11 November 2009

It is a pleasure to review a paper of considerable scientific significance, and one which is so well-written, clear and concise. The coupling between COS and CO<sub>2</sub> uptake has been recognized for many years, and has formed the basis for a number of estimates of the global COS sink. This attempt to invert the process, and constrain global estimates of the terrestrial CO<sub>2</sub> sink using COS deposition measurements is novel and potentially quite significant. The authors develop the theory in a straightforward and concise manner (although I suggest a few slight changes below), and convincingly describe the link between the ratio of CO<sub>2</sub> and COS deposition velocities and the Ci/Ca

C2978

ratio. The observational evidence they present is generally convincing, as Ci/Ca ratios predicted using COS deposition generally fall within the range one might expect. The authors are certainly correct in concluding that additional work is necessary to evaluate many of the assumptions underlying their model (although in general, they seem pretty robust to me, or at least the model is not terribly sensitive to variation in the input parameters over a reasonable range), and to improve the analytical precision of COS measurements. Nevertheless, this is an excellent start, and provides a clear framework on which to build.

I'm hard pressed to offer much constructive criticism. It seems the analysis rests on the implicit assumption that all deposition of both CO<sub>2</sub> and COS occurs through the stomata. If a significant fraction of COS deposition is to soils or other non-vegetated surfaces, does this significantly compromise the technique? Or does stomatal deposition overwhelmingly dominate the overall downward flux? Although I'm convinced that COS measurements can serve as a proxy for Ci/Ca, the utility of such a tool at global or regional scales escapes me, perhaps because I rarely work at those scales. Perhaps the authors could elaborate further on the potential applications of their results. Although the focus is clearly on the relationship between CO<sub>2</sub> and COS, I wonder if COS deposition rates can be used to somehow constrain or better understand other bi-directional fluxes from forest ecosystems at local scales (e.g., organic acids, aldehydes, etc.).

A number of small, largely editorial, suggestions follow:

p. 9282, l. 21 Although you go into detail in Section 3 about the nature of R, it might be well to define it here as 'the ratio of diffusivities'

p. 9283, l. 8 You introduce the term  $g_{i,COS}$  here and say it accounts for the 'transfer of COS into the mesophyll'. Is it strictly speaking a true diffusion resistance or does it also incorporate biochemistry and the presumed rapid reaction with CA?

p. 9285, l. 11 I don't understand the need to 'calculate' values of ambient w, CO<sub>2</sub> and COS. Aren't they measured directly in the sample chamber?

C2979

p. 9286, l. 10 by 'vapour fluxes' do you mean water vapour fluxes, and if so, why are they highly uncertain? Analytical constraints for COS lead to considerably uncertainty, but water vapour?

p. 9286, l. 13 In my experience, deposition velocities are generally expressed as  $\text{m s}^{-1}$  (including Sandoval-Soto, 2005). You choose to normalize the fluxes by mole fraction, rather than concentration, resulting in units of  $\text{mol m}^{-2} \text{s}^{-1}$ . Is there any advantage to this?

p. 9287, l. 3 I found all the algebraic manipulations in the derivation straightforward until I reached the derivation of Eq (8); i.e., the step from the first to the second equality in Eq (8) requires a leap of faith. I finally convinced myself it was valid, but it would be a lot easier for the reader if they had a little help. That is, in order to get from the first to the second equality in Eq (8), one needs to use (1) the fact that  $R_{c-COS}$  is equal to  $g_{sc}/g_{s,COS}$  which, although obvious, is not explicitly stated in the text until the following paragraph, and (2) the fact that  $g_{COS}=(1/g_{s,COS}+1/g_{i,COS})^{-1}$  which is buried in the text on l. 9, page 9283.

p. 9288, l. 10 ratio given in Table 2 is 2.6, rather than 2.4

p. 9288, l. 23 doesn't Eq (4) imply an internal COS concentration of zero (as opposed to small)?

p. 9289, l. 5 Please elaborate as to why  $C_i/C_a$  estimates at high humidities are less reliable

p. 9289, l. 6 'calculated'

p. 9290, l. 12 Rather than 'taking into account possible variations', aren't you assuming a ratio of 0.1 in order to come up with your GPP weighted global mean?

Fig. 3 caption: In the text, you use  $R_{c-COS}$ , not  $R_{CO_2-COS}$ ; suggest 'neglecting this component (i.e., assigning a value of 0.001). . .'

Table 2 caption: Is it accurate to say (final line) that values could exceed (rather than simply differ from) those in the table by 10-15%? i.e., is there a systematic underestimation?

---

C2980

Interactive comment on Biogeosciences Discuss., 6, 9279, 2009.

C2981