Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: potential and limitations

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BACKGROUND AND OBJECTIVES

Canopy net photosynthesis, transpiration and stomatal conductance are key conceptual terms in most contemporary models of ecosystem carbon and water cycling. While they can be quantified accurately with enclosures at the leaf scale, obtaining reliable estimates at the canopy scale is much more difficult. As a consequence, available estimates of canopy net photosynthesis, transpiration and stomatal conductance are inherently uncertain, which in turn translates into uncertain model parameterisations and predictions. Recently, several authors have advocated measurements of carbonyl sulfide (COS) exchange to provide independent constraints in particular on canopy net photosynthesis, as well as on canopy transpiration and stomatal conductance. The rationale for these proposals derives from both leaf and (very few) ecosystem flux measurements which show a high degree of co-variation between the net exchange rates of CO_2, H_2O and COS. Given the promising possibility of quantifying ecosystem-scale COS exchange by using the eddy covariance method in conjunction with new analytical techniques, the objective of the present paper is: (i) to review the mechanistic link between leaf- and ecosystem scale CO_2, H_2O and COS fluxes, (ii) to critically evaluate the assumptions required for estimating canopy net photosynthesis, transpiration and stomatal conductance from COS exchange measurements, and finally (iii) to indicate areas of future research.

LINKING LEAF CO_2, H_2O and COS EXCHANGE

The diffusive flux of CO_2, H_2O and COS in/out of leaves, as sketched in Fig. 1, can be described by a set of three equations:

$$F_l^C = -\left(\chi_a^C - \chi_i^C\right)\left(\frac{1}{g_b^C} + \frac{1}{g_s^C}\right)^{-1} = -\left(\chi_a^C - \chi_c^C\right)\left(\frac{1}{g_b^C} + \frac{1}{g_s^C} + \frac{1}{g_i^C}\right)^{-1} \quad \text{Eq. (1)}$$

$$F_l^V = \left(\chi_i^V - \chi_a^V\right)\left(\frac{1}{g_b^V} + \frac{1}{g_s^V}\right)^{-1} \quad \text{Eq. (2)}$$

$$F_l^S = -\left(\chi_a^S - \chi_i^S\right)\left(\frac{1}{g_b^S} + \frac{1}{g_s^S}\right)^{-1} \equiv -\chi_a^S\left(\frac{1}{g_b^S} + \frac{1}{g_s^S} + \frac{1}{g_i^S}\right)^{-1} \quad \text{Eq. (3)}$$

It can be seen that the diffusion pathway of COS is not identical to, but more similar for CO_2 than H_2O (Fig. 1). In the following we will discuss the implications of these differences for using COS as a tracer for canopy CO_2 and H_2O exchange. Note that Eqs. (1-2) contain too many unknowns that can not be eliminated with Eq. (3) alone, so that no analytical solution is possible.

THE LEAF CO_2-COS CONNECTION

In order to provide independent estimates of canopy net photosynthesis, the ratio of the COS to CO_2 deposition velocities, referred to as λ^C, needs to be parameterised. After some manipulation of Eqs. (1 and 3) one arrives at the following equation:

$$\lambda^C = \frac{F_l^S}{\chi_a^S} \Big/ \frac{F_l^C}{\chi_a^C} = \left[\left(1 - \frac{\chi_i^C}{\chi_a^C}\right)\beta^C\right]^{-1} \quad \text{Eq. (4)}$$

$$\beta^C = \frac{\left(\frac{1}{g_b^C} + \frac{1}{g_s^C}\right)^{-1}}{\left(\frac{1}{g_b^S} + \frac{1}{g_s^S} + \frac{1}{g_i^S}\right)^{-1}} = \frac{\left(\frac{1}{1.14g_b^S} + \frac{1}{1.21g_s^S}\right)^{-1}}{\left(\frac{1}{g_b^S} + \frac{1}{g_s^S} + \frac{1}{g_i^S}\right)^{-1}} \quad \text{Eq. (5)}$$

Equation (4) functionally relates the deposition velocities for CO_2 and COS and shows that the CO_2 deposition velocity will, for any given COS deposition velocity, vary with four unknowns: the ratio of intercellular to ambient CO_2 mole fraction, g_b^S, g_s^S and g_i^S. Assuming physically/physiologically plausible values for g_b^S, g_s^S, g_i^S and χ_i^C/χ_a^C ratios yields a range of 0.6-4.3 for λ^C, broadly in correspondence with the spread of 0.4-10.3 reported in literature. An example of the actual variability of λ^C as a function of the intercellular to ambient CO_2 concentration and β^C is shown in Figure 2.

Both the variability in λ^C inferred from theoretical considerations and experimental evidence suggest λ^C to differ between plant species and vary dynamically in response to changing environmental conditions. This conclusion seems to be inconsistent with constant λ^C values in the range of 2-3 assumed in previous studies. On the basis of Eqs. (4-5), we suggest λ^C values on the order of 2-3 to reflect similar experimental conditions rather than an underlying universal principle. Most of the studies to date have been performed at leaf-level under laboratory conditions by using enclosures systems and thus tend to be biased towards high boundary layer and relatively low stomatal conductances. If true, the reliability of available λ^C values for estimating canopy net photosynthesis under field conditions may be seriously questioned.

FROM LEAF TO CANOPY SCALE

In order to explore the magnitude and variability of ecosystem-scale λ^C and differences to leaf-scale values, we re-analysed data collected by Xu et al. (2002) over a Norway Spruce forest in Germany. Values of λ^C calculated by considering NEE and GPP averaged 10.3 and 5.8 (Fig. 3), respectively. Considering that GPP overestimates canopy net photosynthesis, λ^C values resulted to be at least by a factor of 2 larger than those reported based on leaf-level laboratory enclosure studies.

Canopy transpiration can be estimated in analogy to Eqs. (4-5), however the ratio of internal to external water vapour mole fraction can be expected to be much more variable, which is confirmed by the ecosystem-scale measurements of λ^V (data not shown). By re arranging Eq. (3) leaf stomatal conductance to COS, may be calculated as:

$$G_s^S \equiv \left(-\frac{\chi_a^S}{F_l^S} - \frac{1}{G_b^S} - \frac{1}{G_i^S}\right)^{-1} \quad \text{Eq. (6)}$$

Eq. (6) differs from the equations developed for canopy net photosynthesis and transpiration in three different aspects: (1) the COS to CO_2 (λ^C) and H_2O (λ^V) deposition velocity ratios are not included; (2) instead Eq. (6) contains two unknowns as absolute numbers – the boundary layer (G_b^S) and the internal conductance for COS (G_i^S); (3) G_b^S and G_i^S represent bulk quantities: G_b^S includes both the aerodynamic and the quasi laminar boundary layer conductance, while G_i^S is the integral of the internal conductance over the canopy leaf area – in order to emphasise this difference to the leaf-scale conductances we have used upper-case letters in Eq. (6). While models for the combined aerodynamic and quasi laminar boundary layer conductance are available, little *a priori* knowledge is usually available on the magnitude of g_i^S, which is *inter alia* why λ^C and λ^V were introduced earlier, prohibiting a reliable up scaling to G_i^S.

CONCLUSIONS

At present we face a serious lack of ecosystem scale field measurements that represent an essential requirement for assessing the practical significance of the limitations highlighted above and whether or not ecosystem COS flux measurements will be able to provide sensible constraints on canopy net CO_2 and H_2O exchanges. Our preliminary theoretical analysis and the re-analysis of the few available ecosystem-scale data suggest COS to represent a better tracer for canopy net photosynthesis than transpiration and to be least useful for estimating the canopy stomatal conductance. Concurrent measurements of the ecosystem-scale COS, CO_2 and H_2O exchange are urgently required.
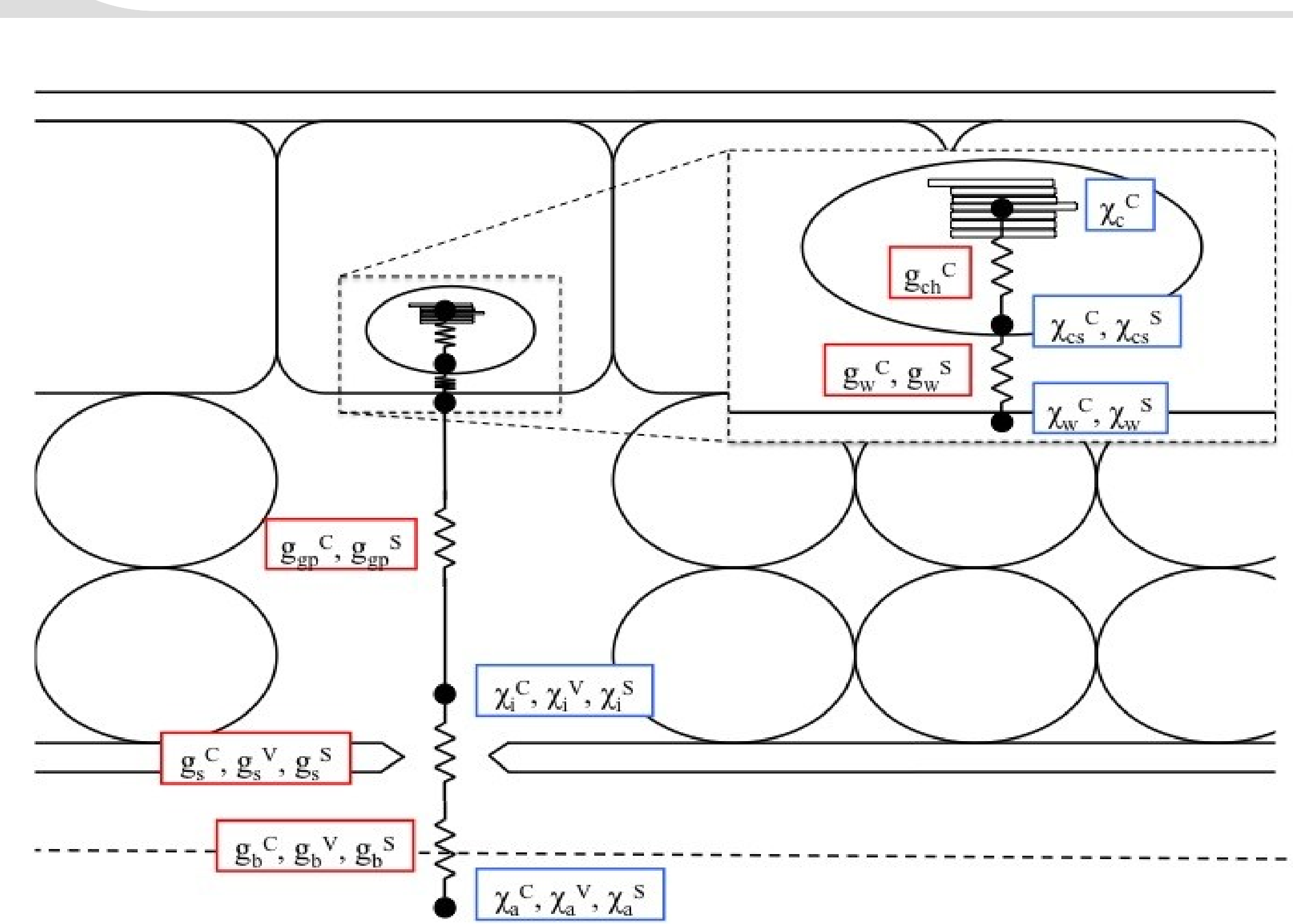
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Stimler et al. (2010) New Phytologist 186, 869-878
Xu et al. (2002) Atmospheric Chemistry and Physics 2, 171-181

Figure 1 Schematic illustration of the diffusion pathways of CO_2, H_2O and COS into/out of a leaf.
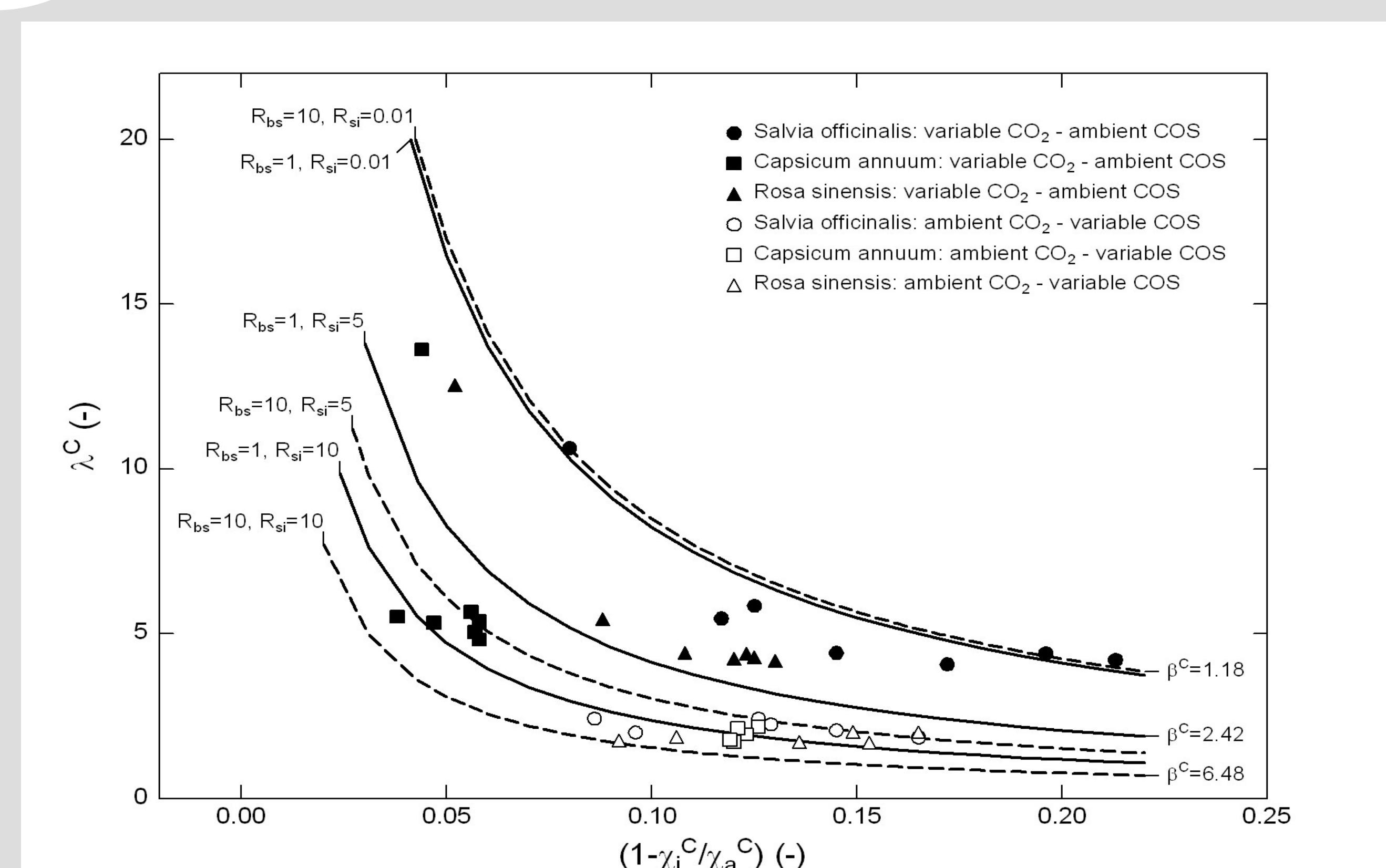

Figure 2 The ratio of COS to CO_2 deposition velocities (λ^C) as a function of the intercellular to ambient CO_2 concentration (data from Fig. 6 of Stimler et al. (2010).
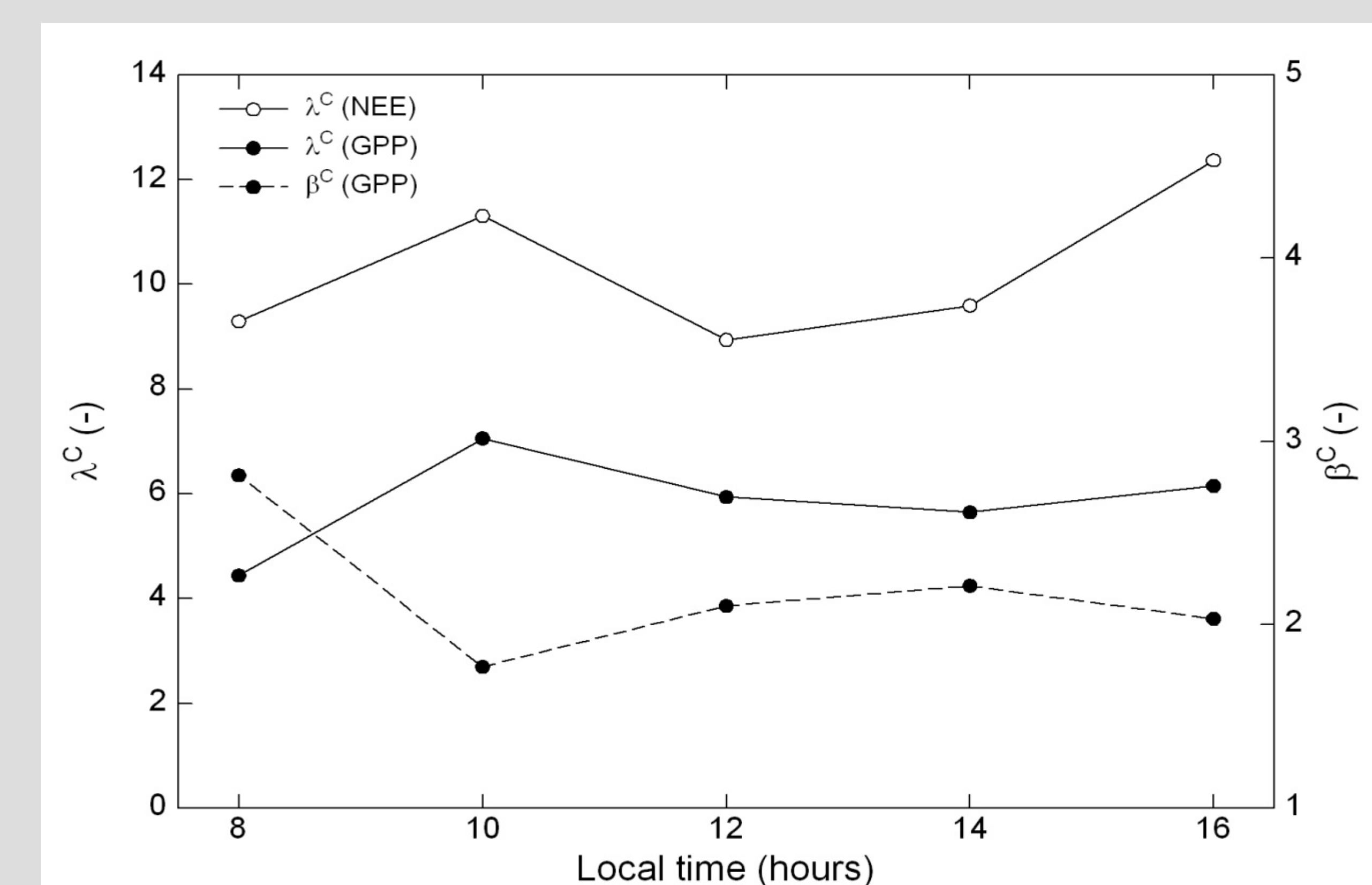

Figure 3 Ecosystem scale λ^C values re-calculated from bin averaged CO_2 and COS flux measurements over Norway Spruce (data from Xu et al., 2002).