

## Commentary

# Bi-directional COS exchange in bryophytes challenges its use as a tracer for gross primary productivity

In this issue of *New Phytologist*, Gimeno *et al.* (pp. 965–976) report results that challenge the main assumption underlying the concept of inferring plant gross primary productivity (GPP) from the uptake of carbonyl sulphide (abbreviated alternately as COS or OCS) by plants (Campbell *et al.*, 2008; Wohlfahrt *et al.*, 2012). Using two astomatous bryophyte species, Gimeno *et al.* quantified the concurrent CO<sub>2</sub> and COS gas exchange at different levels of hydration, light intensity, temperature and ambient COS mole fraction. In contrast to their hypotheses, they found (1) the largest COS uptake to occur during darkness and cooler conditions, and (2) lower COS uptake and, under low hydration levels, even release of COS during warmer daylight conditions.

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Plant COS uptake during darkness is consistent with the view that the enzyme catalysing the irreversible hydration of COS, carbonic anhydrase (CA), is light-independent (Protoschill-Krebs *et al.*, 1996). Previous studies on COS uptake by vascular plants during darkness at leaf- (Stimler *et al.*, 2011) and ecosystem-scale (Wehr *et al.*, 2017), however, reported uptake rates to be quite small compared with daytime conditions. This is due to near-complete stomatal closure in darkness, which imposes a major resistance to the uptake. Using astomatous model organisms, Gimeno *et al.* were able to elegantly demonstrate that the COS uptake may be significant during darkness, if not curbed by diffusive limitations. While COS uptake during darkness is not new, the comparably smaller uptake, or even release of COS, during daylight conditions in the presence of active photosynthesis contradicts our present understanding of the coupled CO<sub>2</sub> and COS uptake by plants (Seibt *et al.*, 2010). Using a combination of COS, temperature and light response curves, Gimeno *et al.* were able to show that (1) concurrent production and consumption of COS must be at work inside the

investigated bryophytes, causing a nonzero COS compensation point (i.e. the ambient COS concentration at which the COS exchange equals zero), and that (2) the invoked COS production term was highly temperature-dependent. The lower COS uptake during light, compared with dark conditions, could thus be explained by the associated higher temperatures when the light was on, which increased production of COS more than consumption, and thus lowered the net uptake and eventually caused it to switch sign. Even though the authors were not able to unambiguously identify the production process, they hypothesized that COS may have been produced from sulphur-containing amino acids, which are expected to have degraded during desiccation as diagnosed from the observed reduction in protein and nonstructural carbon contents.

The existence of a COS compensation point is at odds with most of the previous literature, which suggests that leaf COS exchange is unidirectional, with a near-zero compensation point, due to the strong affinity of CA to COS (Protoschill-Krebs *et al.*, 1996). Gimeno *et al.* determined a compensation point of 345 pmol mol<sup>-1</sup> in the light, which is lower than the global average COS mole fraction of *c.* 500 pmol mol<sup>-1</sup>, but which may be reached close to and within plant canopies during active leaf gas exchange (Blonquist *et al.*, 2011) and thus cause the COS exchange to cease or switch sign. The assumption of a unidirectional COS flux underlies the rationale of using COS as a tracer for GPP, which at the ecosystem scale is impossible to directly quantify. With a near-zero compensation point, the COS exchange must be directed into the leaf, driven by the ambient COS mole fraction and the series of resistances from the ambient air to the site of hydrolysis by CA. As the exchange of CO<sub>2</sub>, even though it exhibits a nonzero compensation point, shares most of the resistances with COS (up to the hydrolysis by CA), measurements of the leaf COS uptake have been suggested to allow inference of GPP, which otherwise is confounded by concurrent respiration processes.

To this end a metric coined the leaf relative uptake (LRU) rate has been instrumental. The LRU represents the ratio of the leaf COS to CO<sub>2</sub> uptake rates normalized by the respective ambient concentrations and, collectively, data from the literature suggest it to converge to a value of *c.* 1.7 during high radiation, and in the absence of stress (Berkelhammer *et al.*, 2014). With a known LRU and data on the COS flux and the COS and CO<sub>2</sub> mole fractions at hand, GPP can be inferred (Asaf *et al.*, 2013). Previous criticism of the constant LRU concept focussed mainly on the fact that it does not account for changes in the internal to ambient CO<sub>2</sub> mole fraction ( $C_i : C_a$ ) ratio (Wohlfahrt *et al.*, 2012), which, for example, has been shown to cause the LRU (Stimler *et al.*, 2011) or its ecosystem-scale analogue (ecosystem relative uptake (ERU); Wehr *et al.*, 2017) to deviate from its background value at low light.

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This article is a Commentary on Gimeno *et al.*, 215: 965–976.

If, on top of this, the COS exchange was, as Gimeno *et al.* demonstrate for bryophytes, dependent on a variable compensation point, the LRU concept would be rendered questionable and the usefulness of COS as a proxy for GPP (and stomatal conductance; Wehr *et al.*, 2017) would be at stake. The key question in this context is whether the leaf internal production of COS (and thus a nonzero compensation point) is specific to bryophytes or whether this is a process that also occurs in vascular plants and, if so, how important it is? Bryophytes are characterized by a specialized physiology and are well adapted to rapid and recurring drying/rehydration cycles, which Gimeno *et al.* hypothesize to underlie the invoked COS production term. Stress-related protein turnover, which may cause COS to escape from sulphur-containing compounds, is however common in vascular plants as well, begging the question as to why available vascular plant LRU rates converge to such a narrow range (Berkelhammer *et al.*, 2014) and hardly any reports of leaf COS emission exist (but see Maseyk *et al.*, 2014). Partially, the answer may lie in the fact that up-to-date leaf COS gas exchange data have been collected with an emphasis on understanding the basic principles and exploring the variability between species (e.g.  $C_3$  vs  $C_4$  photosynthetic pathways), and thus has mostly investigated experimental plants under near-optimal growth conditions. Possibly, there also might be a publication bias; results not conforming to the established LRU concept being less likely to be published. In other words – to date, we simply may lack the data to answer this question and thus targeted experiments exposing vascular plants to specific stressors are urgently needed. At present, it is also unclear whether stomatal closure in stressed vascular plants curtails any COS emissions, causing internally produced COS to be hydrolysed by CA. As suggested by Gimeno *et al.*, experiments with mutants that lack stomatal control would be a promising pathway to pursue to this end. Testing the stress-response of COS exchange will also be beneficial for narrowing down the range of conditions under which the LRU may be treated as a constant.

Even though the findings of Gimeno *et al.* challenge the major assumption underlying the LRU, personally I am nevertheless confident that COS will develop into a sensible and useful constraint of ecosystem scale GPP (and stomatal conductance). Too convincing is the convergence of LRU across different vascular plant species (under high light and unstressed conditions; Berkelhammer *et al.*, 2014), the clear uptake of COS observed by the (few) available ecosystem-scale flux measurements (e.g. Asaf *et al.*, 2013; Commane *et al.*, 2015), and the strong seasonal covariance between atmospheric COS and  $CO_2$  across latitudes (Montzka *et al.*, 2007). However, it also has become clear during the past few years that COS will not be the ‘silver bullet’, as a scientist recently put it in a COS meeting. On theoretical grounds, the LRU cannot be expected to be constant under all conditions (Wohlfahrt *et al.*, 2012) and nonleaf, in particular soil (Whelan *et al.*, 2015; Kitz *et al.*, 2017) sinks and sources of COS complicate the attribution of the leaf sink, an issue to which the findings of Gimeno *et al.* contribute. The ‘new window into the carbon cycle’ (Berry *et al.*, 2013), may thus not be transparent everywhere and all the time, but in a multiple-constraints approach in concert with flux partitioning based on  $CO_2$  (Lasslop *et al.*, 2010), the stable isotopes of  $CO_2$

(Wehr *et al.*, 2016), and proximal sensing-based light-use efficiency approaches (Migliavacca *et al.*, 2017), I still expect COS to make an important future contribution to disentangling the ecosystem-scale  $CO_2$  flux components.

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