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Supplement of

Stomatal control of leaf fluxes of carbonyl sulfide and CO_2 in a *Typha* freshwater marsh

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S1 Correction of water vapor effects

The effects of water vapor on the spectroscopically retrieved COS and CO_2 dry mixing ratios include a dilution effect and a spectral line broadening effect (Kooijmans et al., 2016). The correction of these effects was done in the TDLWintel data acquisition software on the QCL analyzer (Nelson, 2012), following the equations:

$$[\mathrm{COS}]_{\mathrm{dry}} = \frac{[\mathrm{COS}]_{\mathrm{raw}}}{1 - \gamma_{\mathrm{COS}} \cdot x_{\mathrm{H_2O}}}$$

$$[\mathrm{CO_2}]_{\mathrm{dry}} = \frac{[\mathrm{CO_2}]_{\mathrm{raw}}}{1 - \gamma_{\mathrm{CO_2}} \cdot x_{\mathrm{H_2O}}}$$

where χ_{H_2O} is the mole fraction of water vapor in the air (dimensionless), γ_{COS} and γ_{CO_2} are correction factors for COS and CO_2, respectively. Both correction factors were set to their default values of 1.0 in this campaign, i.e., with only the dilution effect considered, but not accounting for the water vapor broadening of spectral lines. We noted that the preset value of γ_{CO_2} was 2.15 in Kooijmans et al. (2016), for the same make of QCL analyzer; however, they also reported experimentally determined γ_{CO_2} to be lower (1.46 or 1.49 depending on line-fitting settings). The $\gamma_{CO_2} = 2.15$ was hence considered a possible upper bound of the correction factor for CO_2. A mock run of data processing with CO_2 concentration recalculated assuming $\gamma_{CO_2} = 2.15$ was conducted, and the potential bias of CO_2 flux caused by an uncertain γ_{CO_2} was 0.12% (Fig. S1). For COS, the use of a correction factor of 1.0 was acceptable. Thus, the flux uncertainty that might have been introduced by the correction factors of water vapor broadening was insignificant.

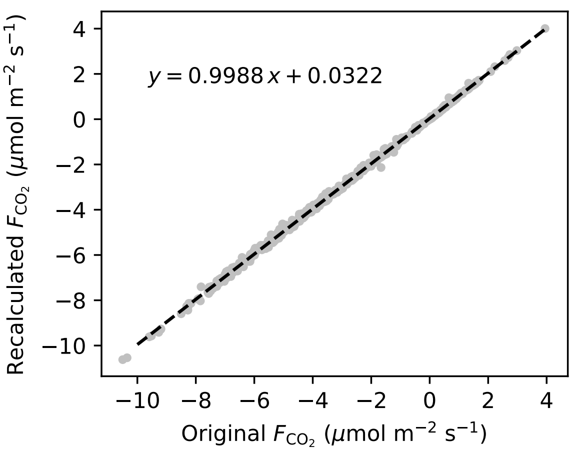

Figure S1. A comparison between the original leaf CO_2 flux (with a water correction factor of 1.0) and the recalculated CO_2 flux assuming a water correction factor of 2.15, which is presumably an upper bound of it.

S2 Blank chamber effects

Blank chamber effects were characterized after the campaign in a different environment, under conditions of temperature between 22 and 28 °C. The blank chamber was made of the same PFA Teflon material and operated in the same flow-through way. The effects are then assumed to be transferable to this campaign. We determined that the fluxes per unit area of the chamber wall material are 0.008 ± 0.045 pmol m^{-2} s^{-1} for COS and 0.003 ± 0.023 µmol m^{-2} s^{-1} for CO_2 (Fig. S2). For this campaign, given that the leaf area was 409.5 cm^2 and the chamber had a surface area of 2658 cm^2, the blank effects translated to a leaf area basis would be 0.05 ± 0.29 pmol m^{-2} s^{-1} for COS and 0.02 ± 0.15 µmol m^{-2} s^{-1} for CO_2. Thus, the blank chamber effects were negligible.

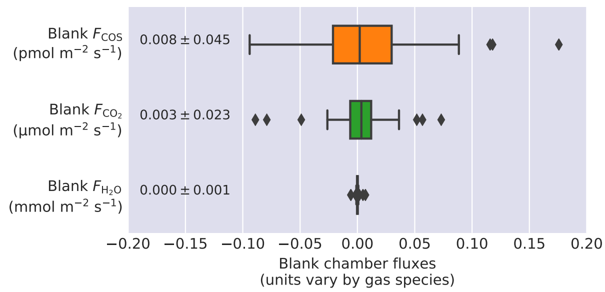

Figure S2. A boxplot of COS, CO_2, and H_2O fluxes from the blank chamber, normalized against the area of the chamber wall material.

S3 Leaf temperature

Leaf temperature was measured using a type T thermocouple attached to the leaf surface with a piece of translucent Scotch® tape. Data are shown in Fig. S3. The difference between leaf temperature and chamber air temperature was mostly less than 2 °C (Fig. S3c). This indicates that the thermocouple tip was properly shielded from solar radiation and the measured leaf temperature was not biased by this. However, the chamber itself had a small artificial heating effect during the 5-minute chamber measurement period (labeled “ch meas” in Fig. 1b in the main text) for both chamber air and leaf temperatures. This was due to reduced sensible heat transfer into and out of the chamber when the ventilation fan was switched off. To avoid the bias from chamber heating, we used leaf temperature in the 2 minutes before the measurement period (“abg” and “ch open” in Fig. 1b). This correction is necessary because the calculated vapor deficit depends on leaf temperature.

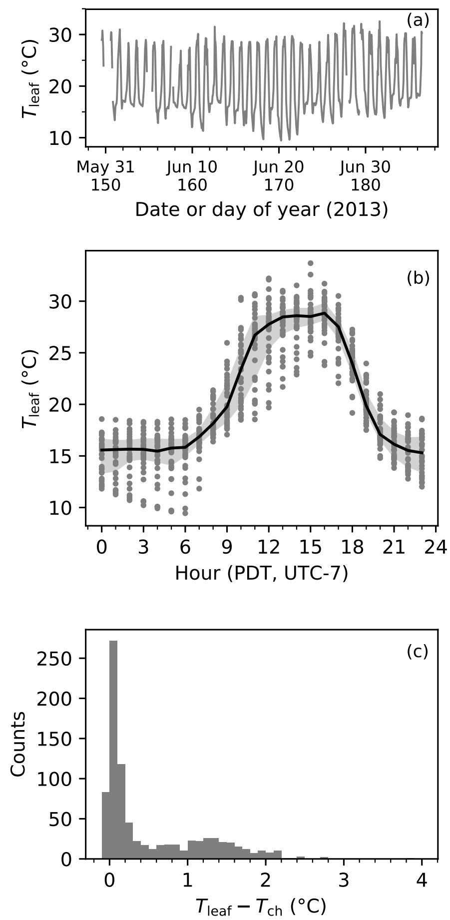

Figure S3. (a) Time series of the leaf temperature. Ticks on *x*-axes indicate the start of the day (0000 h). (b) Diurnal pattern of leaf temperature, with the solid curve indicating the hourly binned medians and the shaded areas indicating the ranges between 25th and 75th percentiles. (c) A histogram of the difference between leaf temperature and chamber air temperature.

S4 An estimate of the nighttime stomatal conductance of COS

From the data of stomatal conductance of H_2O and the total conductance of COS shown in Fig. 6a in the main text, we obtain the daytime averages of them:

$$\overline{g_{s,H_2O}}^{D} = 49.5\ \mathrm{mmol\ m^{-2}\ s^{-1}}$$
$$\overline{g_{tot,COS}}^{D} = 11.7\ \mathrm{mmol\ m^{-2}\ s^{-1}}$$

The daytime average of stomatal conductance of COS, $\overline{g_{s,COS}}^{D} = 24.6$ mmol m^{-2} s^{-1}, after accounting for the diffusivity ratio between H_2O and COS, 2.01 (Seibt et al., 2010). We then obtain the daytime average of internal conductance of COS,

$$\overline{g_{i,COS}}^{D} = \frac{\overline{g_{tot,COS}}^{D} \cdot \overline{g_{s,COS}}^{D}}{\overline{g_{s,COS}}^{D} - \overline{g_{tot,COS}}^{D}} = 22.4\ \mathrm{mmol\ m^{-2}\ s^{-1}}$$

The nighttime average of total conductance of COS is $\overline{g_{tot,COS}}^{N} = 5.0$ mmol m^{-2} s^{-1}. Assuming that the nighttime internal conductance of COS is the same as its daytime average ($\overline{g_{i,COS}}^{N} = \overline{g_{i,COS}}^{D}$), we obtain an estimate of the nighttime stomatal conductance of COS,

$$\overline{g_{s,COS}}^{N} = \frac{\overline{g_{tot,COS}}^{N} \cdot \overline{g_{i,COS}}^{N}}{\overline{g_{i,COS}}^{N} - \overline{g_{tot,COS}}^{N}} = 6.4\ \mathrm{mmol\ m^{-2}\ s^{-1}}$$

This estimate may be a lower bound of the nighttime stomatal conductance of COS, if nighttime internal conductance of COS is lower than its daytime average.

References

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