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Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux

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Limited understanding of carbon dioxide sinks and sources on land is often linked to the inability to distinguish between the carbon dioxide taken up by photosynthesis, and that released by respiration[1,2]. Carbonyl sulphide, a sulphur-containing analogue of carbon dioxide, is also taken up by plants, and could potentially serve as a powerful proxy for photosynthetic carbon dioxide uptake, which cannot be directly measured above the leaf scale. Indeed, variations in atmospheric concentrations of carbonyl sulphide are closely related to those of carbon dioxide at regional, local and leaf scales[3–9]. Here, we use eddy covariance and laser spectroscopy[10] to estimate the net exchange of carbon dioxide and carbonyl sulphide across three pine forests, a cotton field and a wheat field in Israel. We estimate gross primary productivity—a measure of ecosystem photosynthesis—directly from the carbonyl sulphide fluxes, and indirectly from carbon dioxide fluxes. The two estimates agree within an error of ±15%. The ratio of carbonyl sulphide to carbon dioxide flux at the ecosystem scale was consistent with the variability in mixing ratios observed on seasonal timescales in the background atmosphere. We suggest that atmospheric measurements of carbonyl sulphide flux could provide an independent constraint on estimates of gross primary productivity, key to projecting the response of the land biosphere to climate change.

Carbonyl sulphide (COS) is a sulphur-containing analogue of CO_2 with atmospheric mixing ratios of about 500 pmol mol^{-1} and an atmospheric lifetime of 2–4 years. Its main sources are oxidation of CS_2 and dimethyl sulphide, direct emission from the upper ocean, and anthropogenic sources, and its main sinks are uptake by plants and soils, and oxidation in the stratosphere[11–13]. COS and CO_2 flux into leaves and soils are influenced by the same physical, diffusion, pathway followed by hydration reactions catalysed by the enzyme carbonic anhydrase. The hydration reaction (equation (1)) is irreversible for COS (ref. 14) making it essentially a one-way flux into the land biosphere:

$$COS + H_2O \rightarrow H_2S + CO_2 \quad (1)$$

The possibility that COS flux could be used as a proxy for photosynthetic CO_2 uptake is especially attractive because it is impossible to directly measure this CO_2 flux at scales above the leaf. The simultaneous occurrence of respiration from non-photosynthetic parts of plants and soil microorganisms partially offsets the photosynthetic CO_2 uptake in fields and forests. Ecosystem and local eddy covariance studies can therefore only resolve the net ecosystem CO_2 exchange[15] (NEE).

The COS approach relies on a few key assumptions (co-diffusion but no interactions with CO_2; one-way COS flux; and negligible competing fluxes to/from soils[5]) that once met allow a direct estimate of net photosynthetic CO_2 assimilation by leaves, and an approximation (see Supplementary Information) of gross primary productivity (GPP) at the flux tower and larger scales according to[3,5,8]:

$$\frac{GPP}{[CO2]} = \frac{F_{COS}}{[COS]} \times \frac{1}{LRU^*}; \qquad GPP = \frac{F_{COS}}{LRU^*} \times \frac{[CO2]}{[COS]} \quad (2)$$

where F_{COS} is the directly measured flux of COS, [COS] and [CO2] are ambient mixing ratios of COS and CO_2, LRU (estimated at ~1.6; ref. 7) is the leaf-scale normalized ratio of COS to CO_2 assimilation rates, A, ($LRU = (A_{CO2}/[COS])/(A_{CO2}/[CO2])$; refs 3, 6,8) accounting for differences between COS and CO_2 in diffusivity, dissolution and reaction rates, and the asterisk indicates that A_{CO2} was adjusted to GPP (accounting for leaf mitochondrial respiration in the light; see Supplementary Information). Ecosystem-scale relative uptake (ERU; recently estimated to be ~4; ref. 5), which is not required for estimating GPP on the basis of equation (2), provides, nevertheless, a link to atmospheric measurements and can be defined on the basis of net ecosystem exchange of COS (F_{COS}) and CO_2 (F_{CO2}, or NEE), according to:

$$ERU = \frac{F_{COS}}{[COS]} \Big/ \frac{F_{CO2}}{[CO2]}; \qquad ERU = \frac{F_{COS}}{NEE} \times \frac{[CO2]}{[COS]} \quad (3)$$

Broader in scale, an atmospheric relative uptake (ARU; estimated to be ~6; ref. 4) at the local to continental scales can be used to examine the influence of vegetative uptake (and other processes) on the amplitude of the seasonal variations of atmospheric COS and CO_2 (or on vertical gradients observed over terrestrial ecosystems[3,4]):

$$ARU = \frac{([COS]_{spring\_max} - [COS]_{fall\_min})}{([CO2]_{spring\_mas} - [CO2]_{fall\_min})} \times \frac{[CO2]_{annual\_mean}}{[COS]_{annual\_mean}} \quad (4)$$

It is generally recognized that the amplitudes of seasonal CO_2 mixing ratio variations throughout the Northern Hemisphere are determined largely by seasonal changes in terrestrial NEE (ref. 15) and inserting equation (2) into equations (3) and (4) provides a potential window to assess GPP/NEE at scales that are not possible at present by other means.

Here we directly explore the links between COS and ecosystem GPP by attempting the first ecosystem-scale eddy covariance flux measurements of COS (F_{cos}), and compare them to estimates based on simultaneous measurements of net CO_2 flux (NEE). We carried out five field campaigns in three pine forests along a steep precipitation gradient (280–710 mm annual precipitation), and in summer and winter crop fields (cotton and wheat, respectively).

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We used a specially designed mobile laboratory that included an eddy covariance system centred on a fast (20 Hz) CO_2/H_2O infrared gas analyser (IRGA) and a three-dimensional sonic anemometer mounted on a pneumatic mast (4–28 m). The system was complemented by a quantum cascade laser (QCL) system capable of measuring COS and CO_2 at 1 Hz (ref. 10) housed in the temperature-controlled mobile laboratory with air sampling from an intake adjacent to the anemometer.

Background mixing ratios (±s.d.) of CO_2 and COS were on average 391 ± 1.5 μmol mol^{-1} and 500 ± 11 pmol mol^{-1} respectively, with little diurnal variations during the campaigns (Fig. 1 for a typical day). These levels are consistent with the background records for this latitude (ref. 4, see also http://www.esrl.noaa.gov/gmd/), and the local station in the global observation records (http://www.weizmann.ac.il/GGI/). The small diurnal variations presumably indicated that rigorous atmospheric mixing overwhelmed the influence of any local vegetation or other processes on mixing ratios.

Canopy eddy covariance flux measurements showed that all sites were sinks for both CO_2 and COS with typical daily cycles peaking around midday (Fig. 1). As indicated above, NEE measurements were based simultaneously on the two analysers, and the comparison between them (Fig. 1) indicated <10% loss of flux in the slow rate measurements. This provided confidence in the COS flux measurements that were obtainable only with the 1 Hz QCL measurements. We also note that although each campaign lasted over a week, the challenges associated with setting up the new and demanding COS measurements at each site reduced the number of successful campaign days.

Midday NEE ranged between −3.9 and −20.4 μmol m^{-2} s^{-1} and peak F_{COS} ranged between −50 and −90 pmol m^{-1} s^{-1}, in the dry forest and the cotton field (during the leaf expansion stage). Within this range, the daily sum and daily mean values were obtained and reported in Table 1. As expected, night-time NEE showed small positive fluxes reflecting ecosystem respiration (2.6 ± 1.4 μmol m^{-2} s^{-1}, on average across sites). The night-time F_{COS} signal was characterized by a relatively low signal/noise ratio, averaging (±s.d.) across sites at $+3.9 \pm 8.6$ pmol m^{-2} s^{-1}, emission rates that corresponded to ~6% of the mean midday uptake rates (see example in Fig. 1). To further constrain the soil contribution to F_{COS}, several soil cores (~15 cm deep) were collected near the medium-precipitation forest site and on

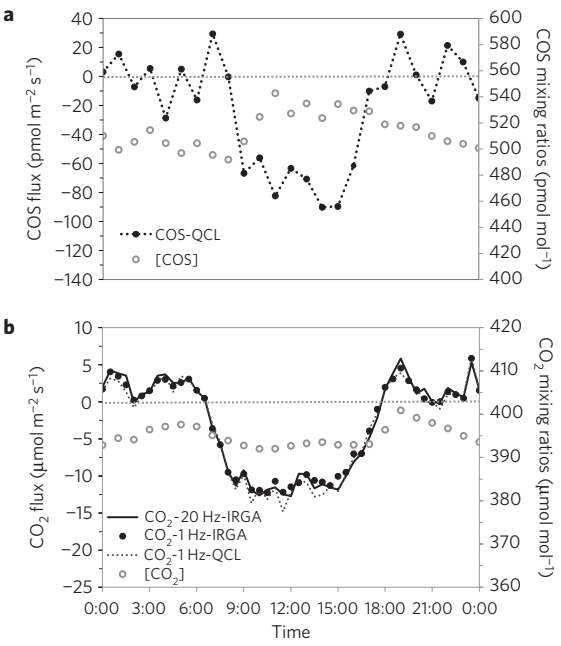

Figure 1 | Daily changes in mixing ratios and fluxes of CO_2 and COS. **a**,**b**, Typical diurnal cycles in the atmosphere–vegetation COS flux (F_{COS}) above a cotton field, and in the atmospheric COS mixing ratios (pmol mol^{-1}) ~3 m above the vegetation canopy (**a**), and in the atmospheric CO_2 mixing ratios (μmol mol^{-1}) and net ecosystem CO_2 exchange (NEE; μmol m^{-2} s^{-1}) measured both with the 20 Hz IRGA and the 1 Hz QCL, with the latter used also for F_{COS} (**b**). Flux loss due to the slow measurements was <10% and often near zero.

Table 1 | Exchange fluxes of CO_2 and COS in five field campaigns.

	NEE	F_{COS}	ERU	GPP	
	(mmol m^{-2} d^{-1})	(μmol m^{-2} d^{-1})	Daytime	GPP_{COS}	GPP_{Re}
			Daytime sum		
	(mmol m^{-2} d^{-1})	(μmol m^{-2} d^{-1})		(mmol m^{-2} d^{-1})	(mmol m^{-2} d^{-1})
Cotton	−538±29	−1,764±65	2.5	1,024±51	889±46
Wheat	−678±89	−1,098±100	1.3	636±26	680±27
Pine-280	−74±30	−573±239	6.0	329±19	126±6
Pine-520	−424±28	−1,161±142	2.4	458±23	479±20
Pine-710	−414±21.5	−1,060±150	2.0	618±22	503±17
Average	−425±223	−1,131±423	2.8±1.8	612±261	535±281
			Daytime mean		
	(μmol m^{-2} s^{-1})	(pmol m^{-2} s^{-1})		(μmol m^{-2} s^{-1})	(μmol m^{-2} s^{-1})
Cotton	−13.7±7.6	−43.2±25.5	2.4±0.3	20.6±12.4	17.1±11.8
Wheat	−18.5±13.3	−31.0±22.5	1.3±0.8	16.1±7.5	17.2±7.2
Pine-280	−2.9±1.4	−22.9±23.5	6.1±2.3	8.3±5.2	3.2±1.4
Pine-520	−10.5±6.7	−33.8±33.1	2.5±0.7	10.6±6.3	11.9±5.5
Pine-710	−10.2±4.8	−27.8±38.6	2.1±0.9	15.3±13.9	13.3±5.8
Average	−11.2±5.7	−31.8±7.6	2.9±1.8	14.1±4.8	12.5±5.7

Fluxes were measured by the eddy covariance technique in winter (wheat) and summer (cotton) crops and three pine forests along a precipitation gradient (mean annual precipitation indicated). Net ecosystem exchange of CO_2 (NEE) and COS (F_{COS}) are reported as average daytime sum, and mean values for 9:00–17:00. Number of days averaged for each site varied ($n = 2$–6; see Supplementary Information). Ecosystem relative uptake is the ratio of F_{COS}/NEE normalized by the respective ambient mixing ratios (~390 μmol mol^{-1} for CO_2 and 500 pmol mol^{-1} for COS). GPP_{COS} was obtained from F_{COS} and the ambient mixing ratios using equation (2). GPP_{Re} was obtained using night-time NEE (ref. 19). Daytime sum values represent means for the successful campaign days with s.d. values indicated.

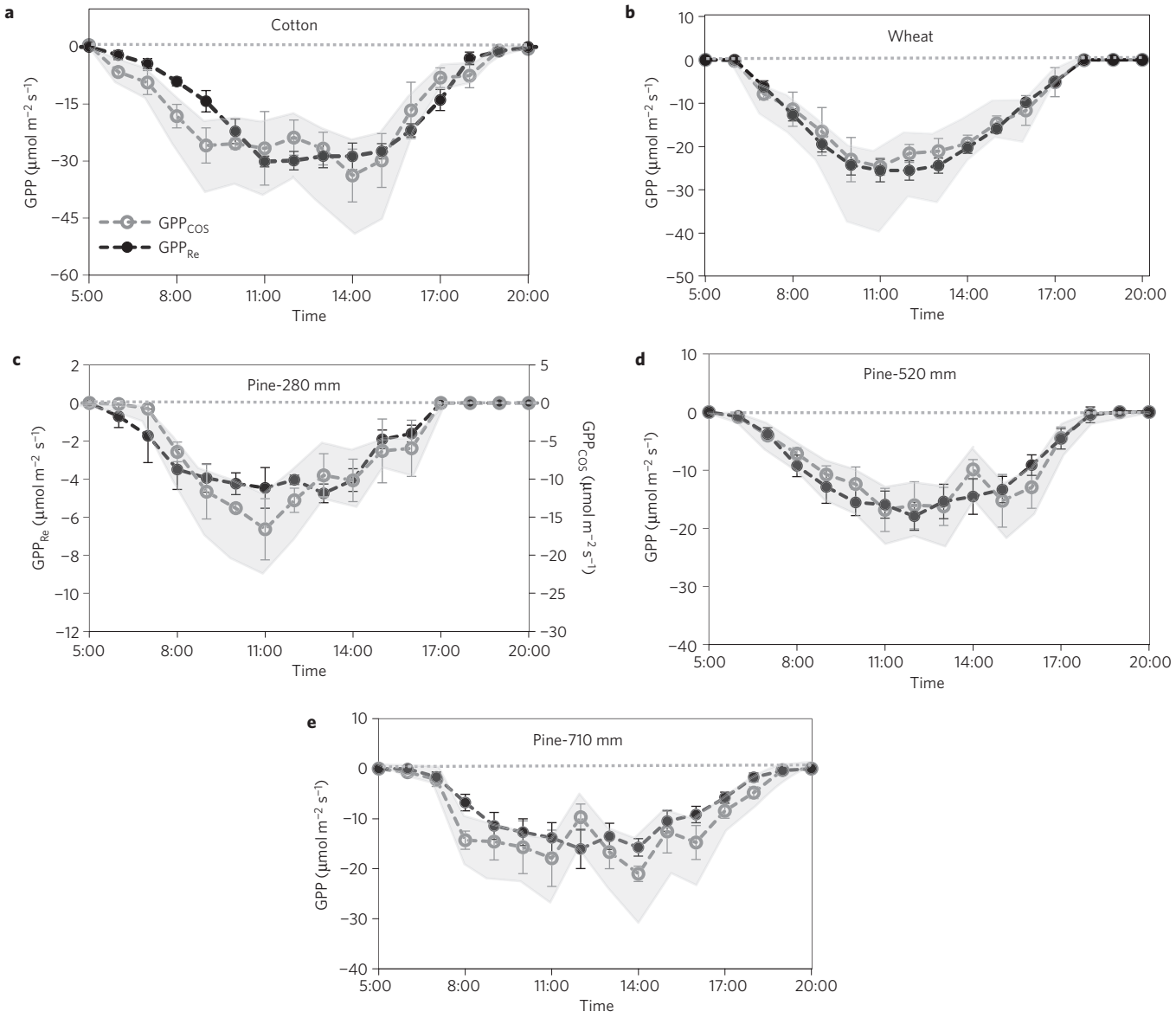

Figure 2 | Diurnal cycles in photosynthetic GPP. a–e, Average diurnal cycles in GPP in summer cotton and winter wheat fields (**a**,**b**), and in three pine forests along a precipitation gradient (**c**–**e**; mean annual precipitation is indicated). GPP was estimated directly from eddy covariance measurements of F_{COS} (GPP_{COS}, grey circles), or indirectly on the basis of night-time NEE measurements extrapolated to daytime to account for ecosystem respiration (GPP_{Re}, black circles). Shading indicates uncertainty in the GPP estimate associated with variations in LRU between 1 and 2. The number of measurement days represented by each data point varied (see Supplementary Information).

the Weizmann campus, and sealed in specially constructed gas exchange chambers for gas exchange measurements. The results indicated a mean uptake rate across cores and measurement conditions of $-6.6\,pmol\,COS\,m^{-2}\,s^{-1}$, which is within the range of -0.2 to $-13.3\,pmol\,m^{-2}\,s^{-1}$ previously reported[16–19]. The combined records of soil cores and field data (mean values of -6.6 and $+3.9\,pmol\,COS\,m^{-2}\,s^{-1}$) indicate soil fluxes much smaller than daytime uptake, and possibly near zero. A possible explanation is competitive inhibition of the COS uptake by the relevant enzymes due to high soil CO_2, and the slow rate of non-enzymatic COS hydration[20]. Further work with increased precision is clearly required to more accurately quantify the soil component.

Using equation (2) and the proposed mean LRU of 1.6 (ref. 6; $LRU^* \sim 1.5$), we estimated GPP (GPP_{COS}) on an hourly basis at all sites (Fig. 2; night-time GPP = 0 by definition not shown) and report them as daytime mean values, and daily sums (Table 1). The results were compared with GPP_{Re} estimated by a widely used indirect approach based on night-time NEE representing ecosystem respiration (Re), which is, in turn, extrapolated to daytime values by applying temperature corrections. GPP_{Re} is then obtained from daytime NEE and estimated Re as GPP = NEE + Re (ref. 21). Both approaches have limitations at present, and neither one can serve as an accurate reference[5]. However, GPP_{COS} measurements offer an independent, direct approach, not based on an extrapolated estimate for daytime respiration. Nevertheless, we estimate magnitudes for GPP on the basis of COS fluxes (GPP_{COS}) at all sites and along the climate gradient, which are comparable to those from the more traditional methodology (GPP_{Re}). In all cases GPP estimates from both methods show similar daily cycles and climatic effects (Fig. 2), and values that agree to within ±15% on average (better than ±10% excluding the dry pine forest). Note that the GPP_{COS} values were not adjusted for possible soil contributions. Although this is not necessarily universally applicable, we justify this here given the near-zero night-time fluxes and our soil chamber measurements

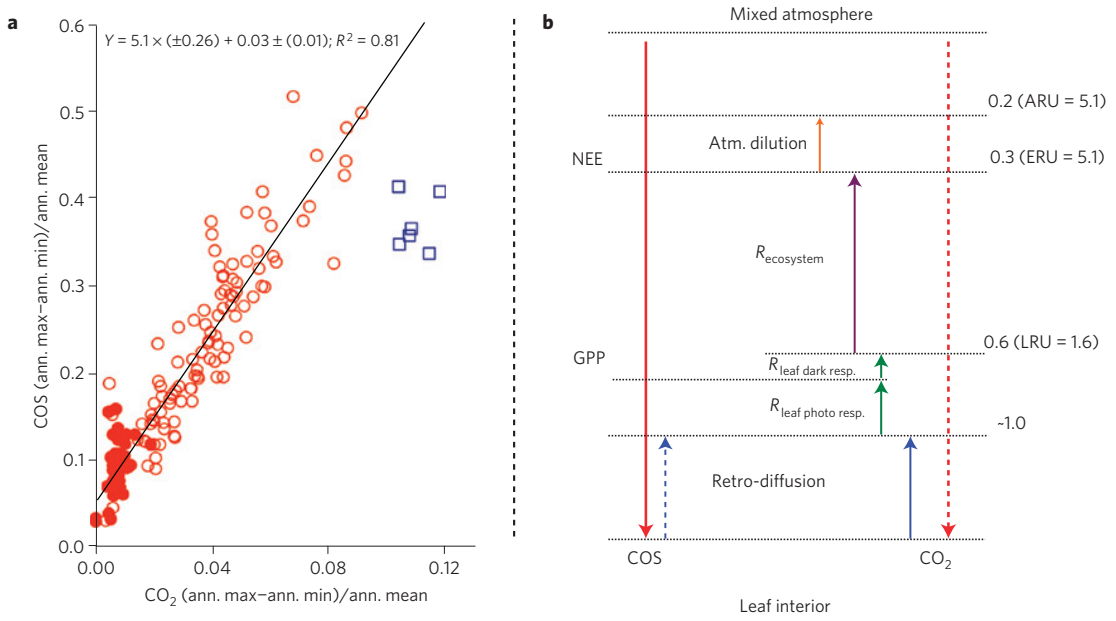

Figure 3 | Relative uptake of COS versus CO_2. a, ARU (equation (4)) is the slope (model II linear regression) of seasonal peak-to-peak drawdown of COS versus CO_2 across 15 global sampling stations with up to 12 years of data. Each point represents one year and station; $n = 147$. Stations in the Northern and Southern hemispheres are indicated by empty and filled circles, respectively. Distinct data from Wisconsin USA (squares) and three outliers (outside scale) were excluded from the regression. **b**, The increasing COS/CO_2 flux ratio as respiratory processes diminish net CO_2, but not COS, fluxes with increasing scale (see Supplementary Information for theory), which shows the evolution of the observed ARU slope of 5.1 in **a**.

noted above. We realize that on average, GPP_{COS} values were slightly higher than GPP_{Re} (by ~6% without considering the unusual dry forest site; Table 1), which may result from some soil COS uptake.

An uncertainty in the application of the COS/CO_2 approach presented here is introduced by the use of a constant LRU value[6–9,22,23]. LRU is related to leaf Ci/Ca (ratio of leaf internal to ambient CO_2 concentrations; see the discussion in the Supplementary Information), which is a relatively conservative parameter in non-stressed plants. It is, however, significantly different in C3 and C4 plants with, consequently C4 LRU of about 1 (ref. 7). Within the same vegetation type, a potential contributor to variations in LRU is variations in the leaf internal conductance (g_m) to COS and CO_2 (refs 9,22). It is generally assumed that stomatal conductance (g_s) dominates the diffusion of both COS and CO_2 into leaves, with g_s/g_m of ~0.2 (refs 6,22). However, for example, under environmental stress, internal conductance, g_m, may decrease, and more so for CO_2 with its longer path to the site of carboxylation in the chloroplast, compared with COS hydrolysed closer to the gas/air interface. In this case, higher g_s/g_m and consequently higher LRU values may be expected. This perspective is important because it indicates that LRU may vary mostly upwards compared with the mean value reported[7,9,22,23]. The sensitivity of inferred GPP_{COS} to the value taken for LRU exhibits a power-law type behaviour (Supplementary Fig. S3), indicating that GPP_{COS} has a low sensitivity to variations in LRU values above the observed mean value of 1.6. In addition, the robustness of the estimated LRU = 1.6 across a wide range of plant species and functional groups[7], and the good agreement of GPP_{COS} versus GPP_{Re} reported here, based on it, may indicate that in reality, the uncertainty around LRU may have a relatively small influence on estimates of GPP in non stressed plants.

Although ERU is not necessary for estimating GPP, it is an important link of ecosystem- and atmospheric-scale measurements, and allows comparison to reported ARU (equation (4)) values (for example, ref. 4). Estimated ERU based either on the daily sums of F_{COS} and NEE or the daytime mean values (about 9:00–17:00) for each site indicated a mean ERU of about 2.9 ± 1.7 for both cases (Table 1). This value is consistent with the expected values reported on the basis of less direct approaches of 2.8–4.3 (refs 3,5,9). A higher ERU value of ~6 was observed in our dry forest site. This site, however, is characterized by a relatively extensive biological soil crust[24], which could enhance the soil uptake of COS and consequently ERU (consistent with $GPP_{COS} \gg GPP_{Re}$ at this site). This suggests the need for a more detailed examination of biological soil crust effects (see ref. 25). Combining equations (2) and (3) yields ERU/LRU = GPP/NEE, and using the mean daytime ERU value of 2.9 and LRU* of 1.5 suggests a mean daytime GPP/NEE of ~2. Including night-time NEE in calculating ERU increases the mean, diurnally based ERU to 4.1 and implies a mean GPP/NEE value for our sites of ~2.7, consistent with accepted values[26]. Note, however, that although these comparisons provide confidence in the new approach, we do expect ERU to vary, and F_{COS}/F_{CO2} measurements such as proposed here could provide a major tool to identify and quantify this dynamics over space and time.

Finally, as noted above, high-precision measurements of atmospheric COS are performed routinely at now 15 sampling sites around the world, with measurement records being as long as 12 years at some sites (a continuation of work in ref. 4). Combining this record with the CO_2 measurements (http://www.esrl.noaa.gov/gmd/) at these same sites, we obtained a robust estimate of ARU (equation (4) and Fig. 3a) of 5.1 ± 0.2, which is lower than the first estimate made with fewer data[4] but consistent with the ecosystem values, of 4.1, observed in this study (and with vertical gradients above ecosystems[3,4]). This atmospheric perspective seems to demonstrate the dominant influence of the land biosphere on the seasonal COS/CO_2 relationships, with LRU of 1.6 increasing to ERU of 4.1, levelling off with ARU of 5.1 (see Fig. 3b for a schematic of this evolution). This may be further supported by ARU values excluded from the global regression line (indicated in Fig. 3a) from Wisconsin that probably reflect the influence of intensive agricultural activities, and the large contribution of C4 vegetation, as data from this site exhibit an ARU of 3.5 ± 0.2, approximating ecosystem-scale ERU values (Table 1). Considered together, the concentration and flux measurements of COS presented here show that the evolution of the COS/CO_2 relative uptake can be accurately

traced from the leaf, through the ecosystem to the continental scale (Fig. 3b). This is significant because the GPP_{Re} approach can be applied only at the ecosystem scale; at the global atmospheric scale, COS could provide the only means to assess net photosynthesis or GPP in the land biosphere.

Methods

Five field campaigns of 7–14 days each were carried out during 2011–2012 (one during summer 2011, the rest during the winter/spring local active period). Three of the campaigns were carried out in pine forests (predominantly *Pinus halepensis*) along the precipitation gradient in Israel (see Supplementary Information for conditions during the campaigns): dry site (31° 20′ 49.2″ N 35° 03′ 07.2″ E; precipitation 280 mm), which is a permanent flux site[27] and allowed an inter-comparison of flux measurements between the permanent and mobile flux systems; intermediate site (31° 47′ 34.5″ N 35° 00′ 11.5″ E; precipitation 520 mm); wet site in northern Israel (33° 00′ 00.5″ N 35° 30′ 40.5″ E; precipitation 710 mm). Two campaigns in crop fields: Cotton field during summer and peak leaf expansion (31° 50′ 51.5″ N 34° 46′ 34.2″ E; irrigation 550 mm); wheat field during winter (31° 53′ 07.1″ N 34° 53′ 09.2″ E; irrigation 540 mm). A newly designed mobile flux measurement system was used in all campaigns, based on the 30 m pneumatic mast of a 12-ton 4 × 4 truck and a complete eddy flux system. The laboratory provided an air-conditioned instrument facility (cellular communication, 18 KVA generator, 4200 W UPS). Flux, meteorological and radiation measurements rely on an eddy-covariance system that provides CO_2, sensible and latent heat fluxes using a three-dimensional sonic anemometer (R3, Gill Instruments) and closed-path CO_2/H_2O IRGA (Li-Cor 7200) using CarboEuroflux methodology, and EddyPro Software (www.licor.com/). Air temperature and relative humidity (HMP45C probes, Campbell Scientific) and air pressure (Campbell Scientific sensors) were measured ∼3 m above the canopy. Energy fluxes rely on radiation sensors including solar radiation (0.29–4.0 μm; CMP21, Kipp and Zonen), long-wave radiation (4.0–100 μm; CRG4, Kipp and Zonen) and photosynthetic radiation (PAR, 0.4–0.7 μm; PAR-LITE2) sensors. All sensors are installed in pairs facing up and down, and they are connected using differential mode through a multiplexer to a data logger (Campbell Scientific). A mid-infrared dual-QCL spectrometer (Aerodyne Research) was used to measure COS and CO_2 concentrations at a frequency of 2,056 cm^{-1} with a thermoelectrically cooled detector as described previously[10], at a rate of 1 Hz. The inlet tube of the measurements was installed next to a sonic anemometer. A calibration gas mixture for COS was obtained from the National Oceanic and Atmospheric Administration Global Monitoring Division[4] (NOAA-GMD); CO_2 was calibrated against laboratory tanks that undergo periodic inter-comparison with the NOAA-GMD laboratory. We computed 30-min and 60-min mean fluxes using Eddy-pro 3.0 software. The ratio of the 20 Hz fluxes of CO_2 from the Li-Cor to the 1 Hz measurements of the Li-Cor and the QCL for each 30-min interval provided an estimate of flux loss by instrumental smoothing of high-frequency fluctuations[28] (Fig. 1). GPP for each site was estimated using equation (2), and using the conventional approach of estimating ecosystem Re. The latter was carried out using a regression of NEE on turbulent nights against temperature, followed by extrapolating the derived night-time Re–temperature relationship to daytime periods and the relationship: GPP = NEE + Re (ref. 21). Atmospheric mixing ratios for both COS and CO_2 were obtained by the NOAA-GMD global observations network (www.esrl.noaa.gov/gmd) as described in detail in ref. 4.

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Author contributions

D.Y. conceived the study. D.A. performed all COS measurements. D.A., E.R., U.D. and F.T. carried out all of the field measurements and data analysis. S.A.M. provided the atmospheric data. D.Y. and D.A. wrote the paper with discussions and contributions to interpretations of the results from all co-authors.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to D.Y.

Competing financial interests

The authors declare no competing financial interests.