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Photodegradation leads to increased carbon dioxide losses from terrestrial organic matter

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Abstract

CO_2 production in terrestrial ecosystems is generally assumed to be solely biologically driven while the role of abiotic processes has been largely overlooked. In addition to microbial decomposition, photodegradation – the direct breakdown of organic matter (OM) by solar irradiance – has been found to contribute to litter mass loss in dry ecosystems. Previous small-scale studies have shown that litter degradation by irradiance is accompanied by emissions of CO_2. However, the contribution of photodegradation to total CO_2 losses at ecosystems scales is unknown. This study determined the proportion of the total CO_2 losses caused by photodegradation in two ecosystems: a bare peatland in New Zealand and a seasonally dry grassland in California. The direct effect of solar irradiance on CO_2 production was examined by comparing daytime CO_2 fluxes measured using eddy covariance (EC) systems with simultaneous measurements made using an opaque chamber and the soil CO_2 gradient technique, and with night-time EC measurements under the same soil temperature and moisture conditions. In addition, a transparent chamber was used to directly measure CO_2 fluxes from OM caused by solar irradiance. Photodegradation contributed 19% of the annual CO_2 flux from the peatland and almost 60% of the dry season CO_2 flux from the grassland, and up to 62% and 92% of the summer mid-day CO_2 fluxes, respectively. Our results suggest that photodegradation may be important in a wide range of ecosystems with exposed OM. Furthermore, the practice of partitioning daytime ecosystem CO_2 exchange into its gross components by assuming that total daytime CO_2 losses can be approximated using estimates of biological respiration alone may be in error. To obtain robust estimates of global ecosystem–atmosphere carbon transfers, the contribution of photodegradation to OM decomposition must be quantified for other ecosystems and the results incorporated into coupled carbon–climate models.

Keywords: abiotic decomposition, carbon cycle, carbon dioxide (CO_2) emission, eddy correlation, grassland, peatland, photodegradation, rain pulse, respiration, solar radiation

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Introduction

Microbial decomposition of organic matter (OM) is regarded as one of the dominant processes resulting in CO_2 production in terrestrial ecosystems (Grace & Rayment, 2000; Janzen, 2004). Temperature, moisture and substrate quality are generally considered the main factors controlling decomposition because of their strong influence on decomposer activity (Luo & Zhou, 2006). However, abiotic processes like physical fragmentation by wind and water, leaching, and photodegradation (Vanderbilt *et al.*, 2008) can also contribute to decomposition of litter and soil organic matter (SOM). Of these, photodegradation is well known to be important in cycling of aquatic OM (Zepp, 2003), but the relevance of photodegradation in OM cycling in terrestrial ecosystems is poorly understood (Brandt *et al.*, 2009; Smith *et al.*, 2010; Throop & Archer, 2009).

Photodegradation is the process by which solar irradiance directly breaks down the compounds of OM, increasing CO_2 fluxes through either photochemical mineralization or microbial facilitation. Photochemical mineralization is the direct breakdown of OM to CO_2 and has been demonstrated in the absence of microbial activity (Anesio *et al.*, 1999; Brandt *et al.*, 2009). Microbial facilitation is the breakdown by solar irradiance of large organic compounds into smaller molecules that can subsequently be degraded by microbes (Gallo *et al.*, 2006, 2009; Day *et al.*, 2007; Henry *et al.*, 2008).

Photodegradation can contribute to mass loss of litter in sparsely vegetated arid and semi-arid environments (see review Throop & Archer, 2009). Litter mass loss has been found to be greater under ambient solar irradiance than reduced irradiance using a range of filters blocking different wavelength bands (Austin & Vivanco, 2006;

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Brandt *et al*., 2007; Day *et al*., 2007; Gallo *et al*., 2009). Supplemental UV-B irradiance may also increase mass loss (Rozema *et al*., 1997; Smith *et al*., 2010), although not always (Gehrke *et al*., 1995; Newsham *et al*., 1997; Verhoef *et al*., 2000; Moody *et al*., 2001).

Photodegradation is likely most important in arid and semi-arid regions with open canopies, large amounts of standing dead material, and high radiative loads (Austin & Vivanco, 2006; Throop & Archer, 2009) and where microbial activity is inhibited by water limitation and possibly by exposure to high UV irradiance (Gehrke *et al*., 1995; Pancotto *et al*., 2003; Austin & Vivanco, 2006; Brandt *et al*., 2009; Smith *et al*., 2010). Although previously UV-B irradiance was considered to be responsible for the vast majority of photodegradation, irradiance in other parts of the solar spectrum (i.e. UV-A and visible) can also contribute to OM decomposition and gaseous carbon losses (Anesio *et al*., 1999; Austin & Vivanco, 2006; Brandt *et al*., 2009).

Field studies of photodegradation have focussed on mass loss of litter (Austin & Vivanco, 2006; Brandt *et al*., 2007; Day *et al*., 2007; Henry *et al*., 2008) but have not determined the contribution of photodegradation to ecosystem scale CO_2 losses. Our objective was to determine the extent to which photodegradation contributed to CO_2 losses from two contrasting ecosystems: an exposed de-vegetated peatland in New Zealand and an annual (seasonally dry) grassland in California. These ecosystems were selected because they had significant surface OM exposed to high ambient levels of solar irradiance when microbial activity was low due to water limitation. CO_2 fluxes were measured using a combination of eddy covariance (EC), chamber and soil CO_2 gradient measurements that allowed us to determine the potential influence of solar irradiance on the CO_2 flux. These field studies were complemented with a controlled experiment where instantaneous CO_2 fluxes were measured from peat that was alternately exposed to and shaded from natural solar irradiance in a small transparent container.

Site descriptions and methods

Peatland study site

The peatland study site was an exposed, de-vegetated peat bog at Torehape, in the Hauraki Plains of the North Island of New Zealand (37°19′S, 175°27′E, 3 m elevation). The vegetation and the top 1 m of peat had been removed as part of a peat mining operation. Measurements started directly after mining had finished. A further 8 m of peat remained and the site remained un-vegetated throughout the study. The site was drained to make mining activities possible with drains approximately 40 m apart. Lanes of bare peat between drains were 900 m long. Dominant vegetation before mining at Torehape was *Sporadanthus ferrugineus* over a lower storey of *Empodisma minus* and *Sphagnum cristatum* (Schipper *et al*., 2002). Dry bulk density of the peat (depth 0–150 mm) was 0.135 g cm^{-3}, and OM content was 92%, measured by loss on ignition. Mean annual air temperature at a nearby climate station was 15.2 °C and average rainfall 1150 mm yr^{-1} (1970–2000). During the experiment water table depth varied from 0.45 m during summer to 0.05 m during winter. Volumetric moisture content (VMC) measured at 50 mm depth varied from 0.49 m^3 m^{-3} during summer to 0.68 m^3 m^{-3} during winter. In summer, the surface peat got very dry and formed a dry crust over the surface, leading to much drier surface conditions than the VMC at 50 mm implied.

Grassland study site

EC measurements of CO_2 flux were made at an annual grassland site (Vaira Ranch, part of the AmeriFlux network) located in the lower foothills of the Sierra Nevada, near Ione, CA (38.4133°N; 120.9508°W, 129 m elevation). The soil is an Exchequer very rocky silt loam (Lithic xerorthents). Soil bulk density at the surface (0–300 mm) was 1.43 ± 0.10 g cm^{-3}. The site was relatively flat and upwind fetch exceeded 200 m. Species composition included *Brachypodium distachyon*, *Hypochaeris glabra*, *Trifolium dubium*, *Trifolium hirtum*, *Dichelostemma volubile* and *Erodium botrys* (Xu & Baldocchi, 2004). The measurements of soil CO_2 flux using a belowground CO_2 flux gradient system were collected at a companion site (Tonzi Ranch) located 2 km from the grassland site (38.4311°N, 120.966°W, 177 m elevation). This site is composed of oak/grass savanna. The soil is an Auburn very rocky silt loam (Lithic haploxerepts) with a soil bulk density at the surface (0–30 cm) of 1.64 ± 0.11 g cm^{-3} (Baldocchi *et al*., 2004). Species of annual herbs and exotic grasses in the understory included *Brachypodium distachyon*, *Hypochaeris glabra*, *Bromus madritensis* and *Cynosurus echinatus* (Baldocchi *et al*., 2006). The climate of the region can be described as Mediterranean, with hot and dry summers and cool and wet winters. Mean annual air temperature at a nearby climate station was 16.3 °C and average rainfall 559 mm yr^{-1} (1959–1977) (Baldocchi *et al*., 2004). The general absence of precipitation during summer (May–November) causes the grass to die (Xu *et al*., 2004) and limits soil respiration (Tang & Baldocchi, 2005).

Instrumentation EC and flux processing

CO_2 fluxes were measured using the EC technique (Baldocchi, 2003). At the peatland, EC measurements were made over a period of 2 years (Jun 2005–May 2007). Instruments were mounted at 1.5 m above the peat surface until March 2007 and thereafter at 2.5 m. The system consisted of a sonic anemometer (CSAT-3, Campbell Scientific Inc. (CSI), Logan, UT, USA) and an open-path infrared H_2O/CO_2 gas analyser (LI-7500, LI-COR Inc., Lincoln, NE, USA). A CR23x datalogger (CSI) sampled signals of the CSAT-3 and the LI-7500 and calculated raw fluxes. At the grassland the EC system was mounted at 2.0 m above the ground. It consisted of a sonic anemometer (Model 1352, Gill Instruments Ltd, Lymington, UK) and a LI-7500 gas analyser. Raw data were recorded on a laptop computer. At both sites the sampling rate was 10 Hz. To compute half-hourly CO_2 fluxes from the raw data at the peatland we applied coordinate rotation (McMillen, 1986), corrected for sonic temperature (Schotanus *et al.*, 1983) and high-frequency loss (Moore, 1986) and added the density correction term (Webb *et al.*, 1980). We refer to Xu & Baldocchi (2004) and Baldocchi *et al.* (2004) for detailed information on computational procedures applied to the grassland data.

EC data filtering

For the peatland, EC data were only used when footprint analyses (Schuepp *et al.*, 1990) showed that 80% or more of the flux originated from the bare peat. Further data were discarded when wind direction was from behind the tower to avoid possible flow distortion. Data were discarded also when rainfall or dew caused unreliable readings from the LI-7500 or when friction velocity was $<0.2\,\mathrm{m\,s^{-1}}$. The friction velocity threshold was chosen conservatively to ensure only the very best data were used for analysis. Because of these strict criteria we discarded 89% of the data points, leaving ∼4000 half-hourly averages of CO_2 flux for analysis.

For the grassland, data were only used for the period in 2007 when vegetation had senesced. Data were selected for periods when the soil VMC at 50 mm was $<0.038\,\mathrm{m^3\,m^{-3}}$ to ensure that photosynthesis was zero. Data were discarded when collected during rainfall, and 7 days thereafter. No gap-filling of missing data was applied for either site.

Additional field measurements

At the peatland, repeated chamber measurements were made using a LI-8100 automated soil CO_2 flux system (LI-COR Inc.). We used a long-term chamber (LI-8100-101, soil collar 200 mm in diameter) to measure the temporal variation of the CO_2 fluxes from one collar installed 10 m from the EC system. Measurements were made every 15 min. A SP Lite pyranometer (Kipp & Zonen, Delft, the Netherlands) mounted at 2.4 m was used to measure incident solar irradiance ($K\downarrow$, wavelengths between 400 and 1100 nm). Soil temperature at 5 mm was measured using an averaging thermocouple (four prongs) buried close to the EC tower and long-term chamber. VMC was measured at 50 mm depth using a CS615 water content reflectometer (CSI) calibrated in the lab for peat.

At the grassland, measurements of soil respiration were collected using a belowground CO_2 flux gradient system (Tang *et al.*, 2003). Soil CO_2 concentrations were measured using probes at depths of 0.02, 0.08, 0.16 and 0.24 m. The profile was measured approximately 20 m away from trees, and tree roots had negligible influence on the measurements, based on transect measurements of soil respiration using a manual chamber system (Tang & Baldocchi, 2005). CO_2 concentrations in the soil air were measured by solid-state infrared gas analyzer probes (GMT 222 and GMT 221, Vaisala, Helsinki, Finland). Soil CO_2 efflux rates were computed using flux–gradient theory. Refer to Tang *et al.* (2003) and Baldocchi *et al.* (2006) for detailed descriptions of the measurements and flux calculations. We used a four-component net radiometer (CNR1, Kipp & Zonen) mounted at 2.5 m to measure incident solar irradiance ($K\downarrow$, wavelengths between 310 and 2800 nm) and upward longwave radiation. The latter was used to calculate the surface temperature. Soil VMC was measured with frequency-domain reflectometer probes (ML2x, Delta-T Devices, Burwell, Cambridge, UK) at a depth of 50 mm.

Container experiment

To confirm the direct control of solar irradiance on CO_2 effluxes an additional small-scale chamber experiment was conducted, whereby CO_2 fluxes from air-dried peat were measured in a small closed chamber (volume 270 mL). To make the distinction between the chamber used in the field (see previous section) and this small home-made closed chamber, we will refer to the latter as the 'container.' We replaced the top of the polystyrene container with a quartz plate 3.175 mm thick (GM Associates Inc., Oakland, CA, USA) to increase transmittance to 0.91, 0.93 and 0.93 for visible (400–700 nm), UV-A (320–400 nm) and UV-B (280–320 nm) irradiance, respectively, as measured by a Cary 100 UV-Vis spectrophotometer (Varian Inc., Palo Alto, CA, USA). A thin layer of peat in the container (approximately 4 g, just sufficient to cover the bottom of the container) was alternately shaded from and exposed to sunlight. CO_2 concentration was measured every second using a LI-8100 infrared gas analyser (LI-COR Inc.) in runs of 140 or 200 s. The container was flushed with ambient air after every 10 runs. Because of the fast response of the CO_2 flux to changes in temperature and irradiance conditions, fluxes were calculated from the change in CO_2 concentration over 1 min, beginning 6 s after the run started (i.e. 7–66 s). The first 6 s of each run were discarded to allow for travel time of air from the container to the infra-red gas analyser. The shorter run length ensured temperatures between sun and shade runs overlapped, thus allowing direct comparison between sun and shade runs of equal mean temperature. Test runs ($n = 14$), where the empty container was exposed to sunlight, confirmed that uptake or release of CO_2 by the container materials in response to exposure to irradiance was negligible (0.0159 and $0.0055\,\mu\mathrm{mol\,CO_2\,m^{-2}\,s^{-1}}$ for sun and shade runs, respectively) and not significantly different from zero.

Peat temperature was measured with four thermocouples of which the average was used. Average peat temperatures ranged from 35 to 65 °C and were representative of surface temperatures occurring in the field: surface temperatures of up to 60 °C were observed during summer at the peatland. The experiment ran over 3 days (February 3–5, 2009) during 5 h centered on midday. On each day, a new peat sample was used. The total number of runs used in the analyses was 114 (57 with the container shaded, 57 with the container exposed).

Estimation of cumulative CO_2 losses

To calculate yearly CO_2 losses from the peatland, a model was constructed using lookup tables of EC fluxes defined by bins of VMC at 50 mm depth (three bins with equal number of data points: VMC $< 0.50\,m^3\,m^{-3}$, $0.50\,m^3\,m^{-3} <$ VMC $< 0.56\,m^3\,m^{-3}$ and VMC $> 0.56\,m^3\,m^{-3}$), incident solar irradiance (bins of $100\,W\,m^{-2}$) and soil temperature at 5 mm depth (bins of 2 °C). Each bin required a minimum of five data points to make an average. To estimate the irradiance-induced part of the flux for each time step, we took the difference between the CO_2 flux from the lookup table, and the estimated dark (night-time) CO_2 flux at the same temperature and in the same moisture bin. Night-time CO_2 fluxes were estimated using two different regression equations of CO_2 flux as a function of soil temperature for each soil moisture class. As a conservative estimate of the night-time flux, we used a linear regression between soil temperature and measured flux ($R^2 = 0.64$, 0.45, 0.24 for dry, medium and wet soil moisture classes, respectively). As a second estimate of night-time flux, we fitted the Lloyd and Taylor equation (Lloyd & Taylor, 1994; $R^2 = 0.76$, 0.71, 0.02 for dry, medium and wet soil moisture classes, respectively). By combining the daytime value for the CO_2 flux from the lookup table with the two estimates for night-time flux and summing the values over the year, two estimates were calculated for annual contribution of photodegradation to the total CO_2 flux.

For the grassland site, a very similar but slightly simpler method was used to estimate the cumulative contribution of irradiance-induced CO_2 flux to the total CO_2 flux during the dry season. A lookup table of EC fluxes, defined by bins of incident solar irradiance (bins of $100\,W\,m^{-2}$) and surface temperature (bins of 2 °C), was made using the data from the dry season. Soil moisture was not used for the lookup table because the values of soil VMC were very low with a very narrow range during the senescent period ($0.03\,m^3\,m^{-3} <$ VMC $< 0.038\,m^3\,m^{-3}$); therefore no effect of moisture was expected. Night-time CO_2 fluxes were estimated using the median value of all night-time EC measurements during the dry period, because night-time EC flux showed no clear trend with surface temperature (data not shown). An estimate for the cumulative contribution of photodegradation to the total CO_2 flux during the dry season was calculated by subtracting the estimated night-time flux from the daytime value for the CO_2 flux from the lookup table and summing all half-hourly values for the dry season.

Statistics

We tested whether solar irradiance explained a statistically significant proportion of variation in abiotic flux (here defined as 'the CO_2 flux measured using EC minus CO_2 flux measured using chamber or soil probes') in addition to the variation explained by temperature and soil moisture. The multiple regression analysis was carried out using the RAR1 procedure in GENSTAT (Version 11.1.0.1535). Fitted terms were: a constant, temperature, soil moisture content and solar irradiance. The analysis used residual maximum likelihood to model correlated regression errors for contiguous blocks of observations (i.e. within observation days).

To test whether the differences between CO_2 fluxes measured by EC and those measured by chamber or soil probes were significantly different from zero at different levels of solar irradiance a one-sample *t*-test was used (95% significance level, MATLAB, Version 7.3.0.267, R2006b). Before testing, flux differences were binned by incoming solar irradiance (bin width $150\,W\,m^{-2}$) and averaged daily by bin to avoid issues with correlated data within observation days.

Results

Effect of solar irradiance on CO_2 fluxes – field experiments

To examine the effect of incident solar irradiance ($K\downarrow$) on the CO_2 fluxes measured by EC fluxes, we first compared them with fluxes measured by chamber (chamber fluxes) and soil probes (probe fluxes) for different levels of solar irradiance. At night ($K\downarrow = 0\,W\,m^{-2}$), EC fluxes agreed well with chamber and probe fluxes (Fig. 1).

However, during the day ($K\downarrow > 0\,W\,m^{-2}$) there was a large discrepancy between EC fluxes and fluxes measured by chamber and soil probes. This discrepancy increased with increasing incident solar irradiance (Fig. 1b and d). At the peatland, the average difference between EC and chamber fluxes at high irradiances ($K\downarrow$ around $1000\,W\,m^{-2}$) was almost $2\,\mu mol\,m^{-2}\,s^{-1}$ (Fig. 1b). The EC flux was approximately 2.5 times larger than the chamber flux in those instances. At the grassland, the average difference between EC and probe fluxes at high irradiances was $1.1\,\mu mol\,m^{-2}\,s^{-1}$ (Fig. 1d). The EC flux was 12 times larger than the probe flux in those instances.

Multiple regression analyses confirmed that for both sites the effect of solar irradiance explained a significant proportion of variation in the discrepancy between the EC CO_2 fluxes and chamber or soil CO_2 fluxes in addition to the variation explained by soil temperature and soil moisture ($P < 0.001$, Table 1).

To visually separate the controls of temperature and solar irradiance on CO_2 fluxes, we compared day- and night-time measurements made using EC in the same temperature ranges (Fig. 2). This comparison showed that solar irradiance had a direct effect on CO_2 fluxes measured by EC. At both sites, CO_2 fluxes were much greater during the day than at night when comparing fluxes measured at equal temperatures (Fig. 2), further suggesting that photodegradation was an important process explaining the difference between day- and night-time EC fluxes. At the peatland, the effect of irradiance on the CO_2 flux was most pronounced when the surface peat was dry, but could also be observed when the peat was moist (Fig. 3).

Effect of solar irradiance on CO_2 fluxes – container experiment

Exposing peat to sunlight in the transparent container markedly increased CO_2 flux (Fig. 4). CO_2 fluxes in the

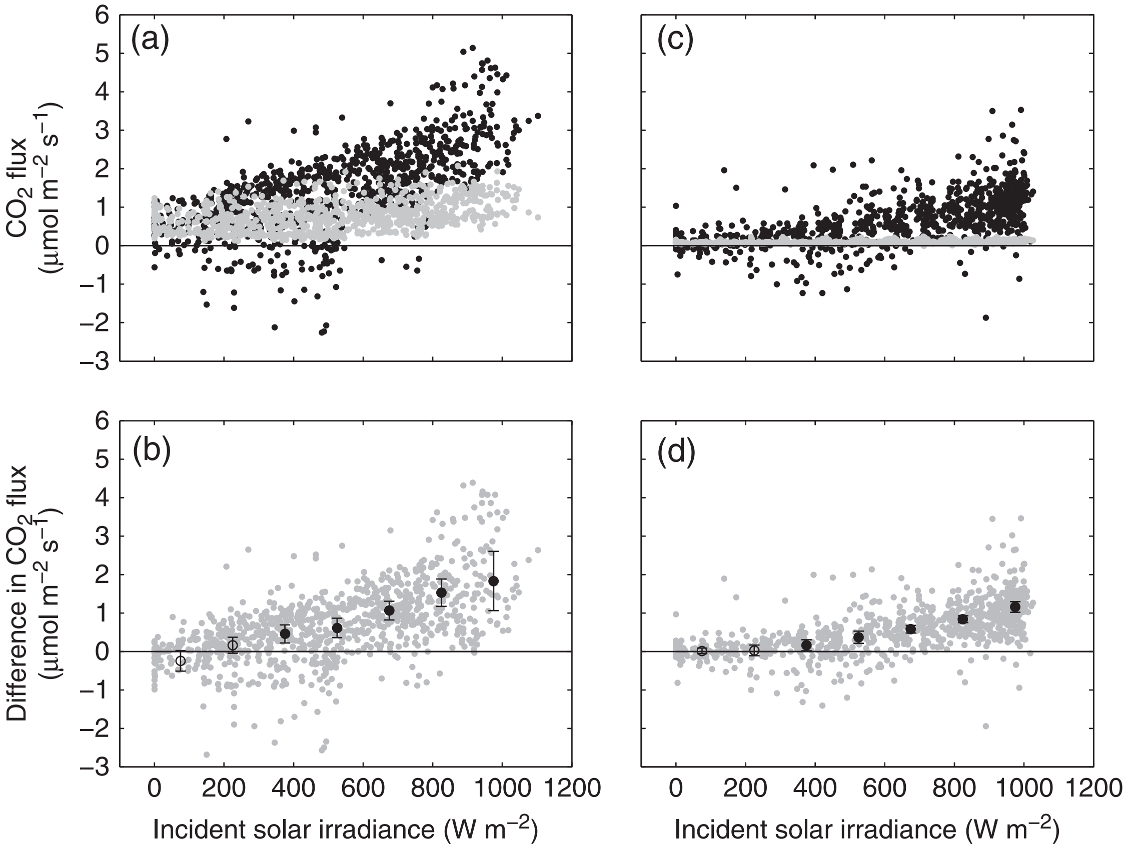

Fig. 1 Illustration of the effect of irradiance on CO_2 fluxes measured at the peatland (a and b) and the grassland (c and d). Fluxes were measured by eddy covariance (black points, a and c), opaque chamber (for peatland, gray points in a) and soil CO_2 probes (for grassland, gray points in c). Gray points in (b and d) are the difference in flux between total CO_2 flux (from EC) and biological CO_2 flux (from chamber or probes). Positive values depict instances where the EC system measured larger CO_2 fluxes than the chamber or probes. Black circles in (b and d) are daily averaged bin averages with error bars showing 95% confidence intervals. For the open circles, the difference between the total and biological CO_2 flux were not statistically different from zero (one sample *t*-test at a 95% significance level). For the filled symbols, the difference was statistically different from zero.

Table 1 Estimates of parameters of multiple regression analyses on peatland and grassland data

Parameter	Estimate coefficient	Standard error	*t*-statistic	*P* value
Peatland (n = 908)				
Constant	−1.2	1.43	−0.82	0.415
Soil temperature	0.042	0.013	3.3	0.001
Soil moisture content	−0.20	2.5	−0.08	0.937
Solar irradiance	0.0019	0.00020	9.2	<0.001
Grassland (n = 885)				
Constant	−0.48	0.64	−0.76	0.448
Surface temperature	0.025	0.00603	4.2	<0.001
Soil moisture content	−7.1	20	−0.35	0.728
Solar irradiance	0.00065	0.00015	4.3	<0.001

Multiple regression equation with abiotic flux (here defined as 'the CO_2 flux measured using eddy covariance minus the CO_2 flux measured using chamber or soil probes') as dependent variable and temperature, soil moisture content and solar irradiance as independent variables. The percentage of the variance that was explained by the total regression was 27.0% and 24.7% for the peatland and grassland regressions, respectively. The number of observations is represented by *n*.

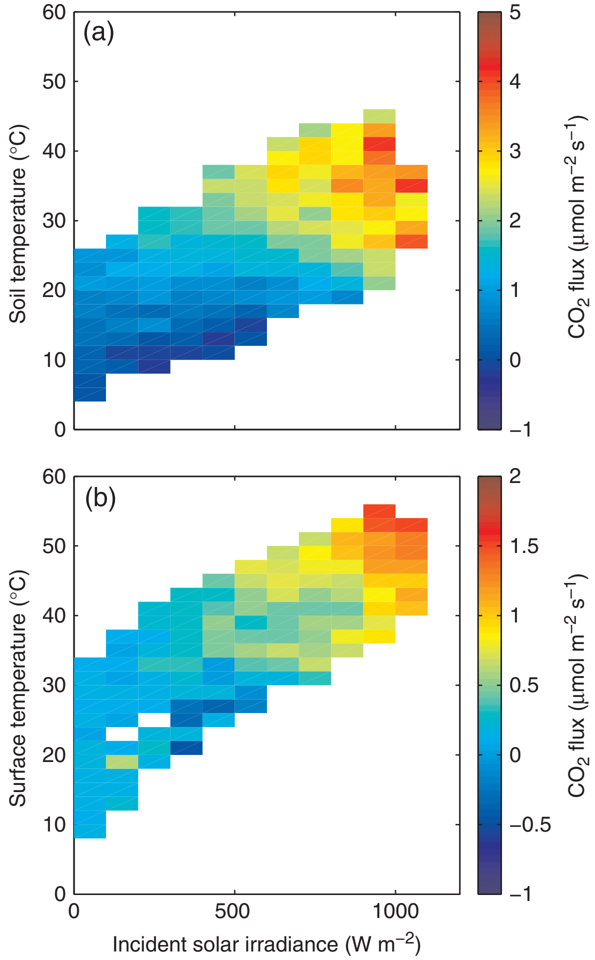

Fig. 2 Effect of solar irradiance and temperature on CO$_2$ fluxes measured by eddy covariance above (a) the bare peatland and (b) the annual grassland. CO$_2$ fluxes were averaged across intervals defined by incident solar irradiance (bin width 100 W m^{-2}) and temperature (bin width 2 °C). Note that the scales on the color axes are different between panels. For the peatland, similar graphs with data split into three groups based on volumetric moisture content of the peat are shown in Fig. 3.

dark (irradiance = 0 W m^{-2}) were around zero because low moisture availability constrained microbial decomposition. Even at high temperatures (>60 °C) CO$_2$ fluxes in the dark remained around zero while fluxes from peat exposed to sunlight were over 0.5 µmol m^{-2} s^{-1} at the same temperature (Fig. 4). The increase in CO$_2$ concentration on exposure to solar irradiance was nearly instantaneous (Fig. 5), and the immediate effect on the rate of increase in CO$_2$ concentration caused by passing clouds can clearly be seen (Fig. 5g and h). We observed small negative fluxes in the dark (Fig. 4) that were likely due to adsorption of CO$_2$ to the plastic or desiccant in the tubing at higher temperatures, even though we confirmed that the container materials did not emit or take up CO$_2$ by exposing the empty container to solar irradiance. However, the temperature in the container was generally higher when peat was present compared with the empty container because the peat was still warm after absorbing solar irradiance in the sun run preceding the shade run. We suspect that this absorption is affected by temperature only (Fig. 4) which means that shaded and exposed measurements made at the same temperature are still comparable.

Estimates of the contribution of irradiation-induced CO$_2$ fluxes

For the peatland, the total CO$_2$ losses for June 2005–May 2007 averaged 269 g C m^{-2} yr^{-1}. The estimate of the annual contribution of photodegradation to the total flux depended on the equation used to model the biological fluxes in the dark and ranged from 34 (using the Lloyd and Taylor equation) to 66 g C m^{-2} yr^{-1} (using a linear equation), representing 13% and 25% of total CO$_2$ flux, respectively.

For the grassland, the contribution of photodegradation could only be estimated for the dry season when no uptake of CO$_2$ by photosynthesis was taking place. During the entire 2007 dry season, the CO$_2$ loss from the grassland was estimated to be 27 g C m^{-2} (or 0.314 g C m^{-2} day^{-1}), of which approximately 16 g C m^{-2} (or 0.186 g C m^{-2} day^{-1}) was irradiation induced, equalling almost 60% of the total dry season CO$_2$ flux.

Discussion

Size of the irradiance-induced flux

During midday on sunny days in summer, when incoming solar irradiance and temperature were highest, the CO$_2$ efflux due to photodegradation contributed as much as 62% and 92% of the total half-hourly CO$_2$ flux from the peatland and grassland, respectively. The magnitude of the annual carbon loss via photodegradation at the peatland (34–66 g C m^{-2} yr^{-1}) was substantial compared with net ecosystem production (NEP) documented for other ecosystems [e.g. average NEP across a range of ecosystems was 181 g C m^{-2} yr^{-1} (Baldocchi, 2008)].

Our estimates of photodegradation at the peatland (34–66 g C m^{-2} yr^{-1}) and the grassland (16 g C m^{-2} for the dry season) were much greater than the estimate made by Brandt *et al.* (2009), who extrapolated measurements made from sterile litter in microcosms to field conditions. They estimated irradiance-induced CO$_2$ loss of 4 g C m^{-2} yr^{-1} from litter in a desert grassland in New Mexico assuming that 100% of the surface area

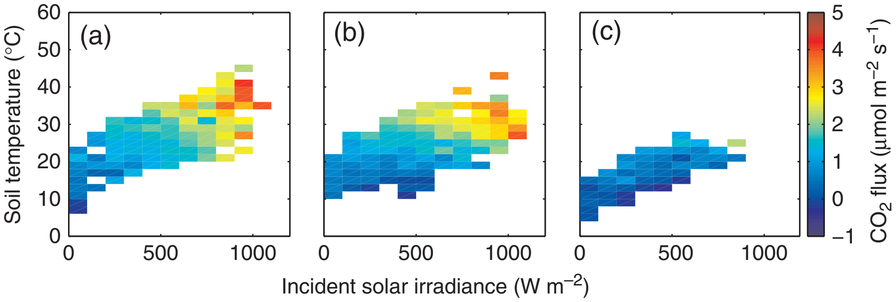

Fig. 3 Effect of solar irradiance and soil temperature on CO_2 fluxes measured by eddy covariance at the peatland for different soil moisture contents. CO_2 fluxes were averaged by intervals defined by incident solar irradiance (bins width 100 W m^{-2}) and soil temperature at 5 mm depth (bin width 2 °C) under (a) dry (volumetric moisture content of peat at 50 mm depth VMC <0.5 m^3 m^{-3}, (b) moist (0.5 m^3 m^{-3}$<$VMC$<$0.56 m^3 m^{-3}) and (c) wet (VMC >0.56 m^3 m^{-3}) conditions.

was covered with litter. The causes of the difference between our measurements and their estimate are likely due to differences in substrate species/quality and experimental conditions (e.g. sterile conditions in the microcosms vs. nonsterile conditions in the field and partial blocking of irradiance by the sides of the microcosm).

For the grassland, the irradiance-induced CO_2 losses formed almost 60% of the total CO_2 flux during the dry season. This is at the upper end of the range of estimates (32–60%) of the contribution of photodegradation to mass loss in dry ecosystems given by Austin & Vivanco (2006) and Gallo *et al*. (2009). Even though the percentage contribution of photodegradation to the total CO_2 flux at the grassland site was high, the absolute CO_2 fluxes during dry seasons are generally much lower than during wet seasons when microbes are not limited by moisture (e.g. Xu & Baldocchi, 2004; Xu *et al*., 2004). For example, annual average ecosystem respiration at the grassland site from 2000 to 2006 was estimated to be >900 g C m^{-2} yr^{-1} (Ma *et al*., 2007). However, compared with the average net ecosystem exchange (NEE) for the same years (38 g C m^{-2} yr^{-1}; Ma *et al*., 2007) the dry season irradiance-induced flux of 16 g C m^{-2} yr^{-1} was substantial.

Potential pathways of irradiance-induced CO_2 production

There are two possible pathways for irradiance-induced CO_2 production from OM: the direct abiotic process of photochemical mineralization and the indirect process of microbial facilitation, whereby partial breakdown of OM by irradiance enhances subsequent microbial activity. In the container experiment, photochemical mineralization was the sole pathway leading to CO_2 loss because the dry peat samples did not support biological activity. At the grassland, low microbial respiration rates measured under dry conditions also strongly suggested photochemical mineralization as the main pathway for CO_2 loss. While we deliberately excluded data from wetter periods when microbial facilitation may have been important, there is evidence that this process may also contribute to CO_2 losses during the dry season. Previous studies observed large pulses of CO_2 resulting from rapid microbial respiration following small, infrequent rain events (Xu & Baldocchi, 2004; Xu *et al*., 2004). Such pulses are common during dry seasons in a wide range of semi-arid ecosystems (Fierer & Schimel, 2003; Huxman *et al*., 2004; Jarvis *et al*., 2007) but uncertainty still exists about the origin of the labile carbon that is mineralized after these wetting events (Jarvis *et al*., 2007). At the grassland, cumulative carbon losses via the pulses were found to be larger at exposed sites than at shaded sites (Xu *et al*., 2004). We suggest that this difference between shaded and unshaded sites might partly be attributed to partial breakdown of the OM by solar irradiance before rain, making substrates more available to microbes at the unshaded sites. This hypothesis for asynchronous microbial facilitation also fits very well with the observation that the size of the CO_2 pulses tends to be proportional to the length of time since the last rainfall event (Jarvis *et al*., 2007; Sponseller, 2007).

Potentially affected ecosystems

Photodegradation may be an important contributor to CO_2 loss in a wide range of ecosystems where SOM, litter and/or standing dead material are exposed to solar irradiance (Throop & Archer, 2009). Those affected might include arid and semi-arid ecosystems, barren peat areas in tundra, bare burnt areas, ecosystems that are sparsely vegetated like shrublands, savannas and other grasslands, agricultural sites after cultivation or harvest (especially when crop residues are left on the surface), deciduous forests after leaf fall, ecosystems during prolonged drought or ecosystems with a naturally large amount of exposed standing dead material like peat bogs. The magnitude of photodegradation in these ecosystems is likely to be <34–$66\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$ that we found at our peatland because the conditions will be less favorable for photodegradation. Most ecosystems have smaller amounts of accumulated exposed OM (especially arid and semi-arid ecosystems) or dead OM is only exposed to solar irradiance during part of the year (e.g. harvested cropland or ecosystems during seasonal drought like the Californian grassland). In some ecosystems, OM will be exposed to levels of incoming solar irradiance that are lower than in our study (e.g. exposed peat in tundra in boreal regions or deciduous forests where litter will only be exposed in winter).

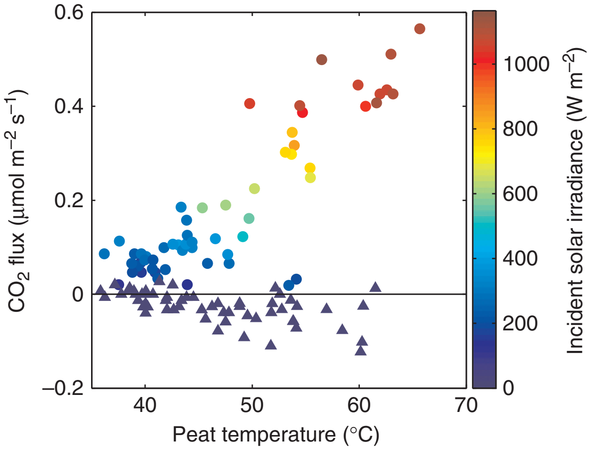

Fig. 4 CO_2 flux from air-dried peat measured in a container transparent to visible and UV light alternately exposed to solar irradiance (colored circles) and shaded (triangles).

Implications for measurements and modelling

There are several important implications of photodegradation for the current approaches to measurement and interpretation of CO_2 fluxes. Opaque chambers and soil CO_2 profiles are commonly used to measure CO_2 efflux. However, they may significantly underestimate actual CO_2 losses because they do not measure the irradiance-induced portion of the CO_2 flux. For example, at our sites, chamber and soil probe measurements underestimated the total CO_2 efflux by as much as 62% and 92% for the peatland and grassland, respectively, when the contribution of photodegradation to the total CO_2 flux was at its maximum. Also, for studies which aim to measure net ecosystem exchange of CO_2 of vegetated ecosystems using transparent chambers placed over plants, it is important that the chambers are transparent not only to photosynthetically active radiation, but also to radiation in the UV wavelengths. Otherwise, the photodegradation component of the CO_2 efflux might be underestimated, leading to overestimates of net CO_2 sequestration.

Additionally, in many ecosystem studies of CO_2 exchange using EC, models based on night-time measurements are used to estimate daytime respiration rates to enable partitioning of daytime NEE into photosynthesis and respiration (Falge *et al.*, 2002; Reichstein *et al.*, 2005). However, this approach does not take into account

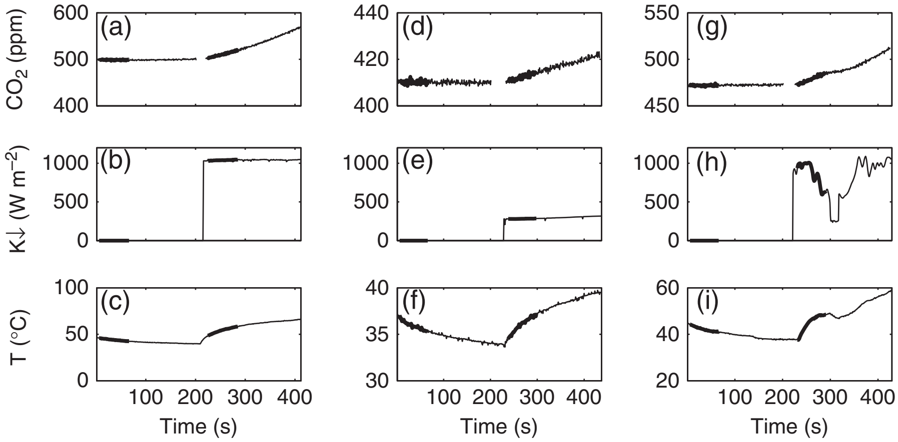

Fig. 5 Example data of the small scale container experiment. CO_2 molar fraction (a, d and g), incident solar irradiance (b, e and h) and peat temperature (c, f and i) during three sets of two consecutive runs: runs 8 and 9 (a, b and c), with CO_2 fluxes of −0.01 and 0.39 µmol m^{-2} s^{-1}, respectively; runs 80 and 81 (d, e and f) with CO_2 fluxes of 0.01 and 0.09 µmol m^{-2} s^{-1} respectively; runs 86 and 87 (g, h and i) with CO_2 fluxes 0 and 0.29 µmol m^{-2} s^{-1}, respectively. Individual runs were 200 s long. Bold lines indicate the CO_2 concentration data that were used for flux calculation (60 s) and the matching irradiance and temperature data. The container was shaded from the sun when irradiance (K↓) was 0 W m^{-2}. Please note that scales on *y*-axes differ between graphs of CO_2 concentration (top panels) and graphs of temperature (bottom panels).

photodegradation (a daytime-specific pathway of CO_2 loss) and consequently might underestimate both daytime total CO_2 losses and CO_2 uptake by photosynthesis.

Conclusions

We have demonstrated that solar irradiance contributes directly to ecosystem CO_2 losses through photodegradation of OM. Previously solar irradiance has been assumed to contribute to CO_2 losses only indirectly by regulating temperature, which in turn controls microbial respiration.

The grassland data showed that photodegradation can be responsible for a substantial portion of CO_2 losses in a natural ecosystem during the dry season. Because the ecosystems potentially affected by photodegradation comprise very large areas on a global scale [e.g. arid and semi-arid ecosystems cover $\sim$30% of the Earth's land surface (Lal, 2004)], even small contributions from photodegradation to CO_2 fluxes could represent large fluxes of carbon when summed globally. These losses are currently unaccounted for by carbon cycling models.

Small-scale laboratory studies have started to elucidate how wavelength, litter species, litter density, irradiance intensity and moisture affect OM decomposition and CO_2 loss through photodegradation (e.g. Brandt *et al*., 2009; Smith *et al*., 2010), but it is essential to extend this work to natural field conditions and appropriate scales. Quantifying the role of irradiance-induced CO_2 losses in the field will be challenging; particularly problematic is separating CO_2 fluxes into photodegradation, biologically driven decomposition and photosynthesis in systems where water does not limit biological activity. Despite these challenges, it is crucial that we conduct further studies in a wide variety of ecosystems to increase our understanding of the importance and drivers of photodegradation. This knowledge is needed for gaining insight into the response of carbon cycling in terrestrial ecosystems to climate change (Austin & Vivanco, 2006) and for continued development of coupled carbon-climate models.

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