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UV-induced carbon monoxide emission from living vegetation

D. Bruhn1,2, K. R. Albert1, T. N. Mikkelsen1, and P. Ambus1

1Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), 2800 Kgs. Lyngby, Denmark
2Centre for Earth, Planetary, Space and Astronomical Research, The Open University, Walton Hall, Milton Keynes MK76AA, UK

Correspondence to: D. Bruhn (dan.bruhn@open.ac.uk)

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Abstract. The global burden of carbon monoxide (CO) is rather uncertain. In this paper we address the potential for UV-induced CO emission by living terrestrial vegetation surfaces. Real-time measurements of CO concentrations were made with a cavity-enhanced laser spectrometer connected in closed loop to either a chamber on a field of grass or a plant-leaf scale chamber. Leaves of all plant species that were examined exhibited emission of CO in response to artificial UV radiation as well as the UV component of natural solar radiation. The UV-induced rate of CO emission exhibited a low dependence on temperature, indicating an abiotic process. The emission of CO in response to the UV component of natural solar radiation was also evident at the natural grassland scale.

1 Introduction

Carbon monoxide (CO) is a reactive gas which, in part, controls the oxidizing capacity of the atmosphere (IPCC, 2001). Carbon monoxide can lead to the formation of ozone (O3), and since CO is a main reactant of hydroxyl (OH) radicals, which are the principal sink for atmospheric methane (CH4), CO also indirectly affects the atmospheric CH4 levels (IPCC, 2001). Carbon monoxide is therefore an important trace gas in the atmosphere (IPCC, 2001). Estimated total global source strengths and estimated total sink strengths are very similar (IPCC, 2001), but large uncertainties remain about the strength of the individual natural terrestrial direct sources (Potter et al., 1996; Guenther, 2002), which adds a great uncertainty to estimates of the net CO burden (360 Tg CO yr−1, IPCC, 2001).

All natural terrestrial direct CO emissions, in the range of 50–200 Tg CO yr−1, have hitherto been ascribed by the IPCC (1995, 2001) to photo-induced CO emission by living plants (cf. Tarr et al., 1995). However, in the studies underlying the photo-induced CO emission by living plants, which were incorporated into previous global CO budgets (IPCC 1995, 2001), the UV component of (sun)light was not considered (Seiler and Giehl 1977; Seiler et al., 1978). In studies of photochemically induced release of CO by dead plant material, it was demonstrated that the more energy-rich UV light had a very significant impact on the total CO emission (Tarr et al., 1995; Schade et al., 1999a; Derendorp et al., 2011). The aim of this study was thus to examine the potential of UV-induced CO emission from living plants in relation to plant species and environmental conditions. Experiments were carried out under controlled laboratory conditions and under in situ field conditions.

2 Materials and methods

2.1 Plant material

Leaves were freshly excised from well-watered plants grown in pots in the greenhouse (Brassica oleracea capitata f. alba, Ficus elastica, Zea mays), and from trees (Acer platanoides, Corylus avellana) and grasses growing in the vicinity of the laboratory (dominated by Deschampsia flexuosa and with minor occurrences of Achilla millefolium and Plantago lanceolata). Ecosystem analysis was focused on the grass vegetation that occurred on a sandy loam soil and received no fertilizer or other chemical treatment.
2.2 Measurement system

Real-time measurements of [CO], corrected for H₂O interference, were conducted by off-axis enhanced cavity spectroscopy (Los Gatos N₂O/CO analyzer, LGR Inc, Mountain View, CA, USA) connected to either an ecosystem Plexiglas chamber or a leaf scale Walz chamber (3010-GWK1, Heinz Walz GmbH, Effeltrich, Germany). We used the LGR in the low-flow configuration with a flow of 3.3 L per minute, 55 cc per sec. The LGR internal volume was 411 cc. The Synflex tubing connecting the LGR to the chamber (Waltz or Plexiglas) was 6 mm outer diameter, 3 mm inner diameter, and the length was 3.20 m (inlet line plus outlet line total 6.20 m).

2.2.1 Natural grassland–atmosphere CO exchange

Natural grassland–atmosphere CO exchange measurements were conducted under in situ conditions on natural vegetation and under ambient conditions, in September and October 2011 at DTU Risø campus (55°41′N, 12°05′E) between 09:00 and 17:45. A UV-transparent Plexiglas chamber (45 × 45 × 25 cm³; PAR transmission 83 %; UV-B transmission 91 % incl. water condensation on inside of chamber walls) was placed on a stainless steel collar pushed into the ground. A water-filled groove on top of the collar ensured a gas-tight seal between collar and chamber. The chamber was equipped with an internal fan to ensure mixing and thermocouples measuring air temperature. To exclude solar UV radiation in some experiments, a larger UV-opaque chamber (60 × 60 × 85 cm³, transmitting only 32 % UV-B, but 96 % PAR) was placed around the grassland chamber. For measurements in the dark, the chamber was covered by light-excluding metal foil. Photosynthetic active radiation (PAR; 400–700 nm) and UV-B (280–315 nm) were measured next to the chamber and adjusted as mentioned transmittance. This transmittance was verified according to the above-mentioned transmittance. This transmittance was verified after each measurement of gas exchange. The average temperature increase in the chamber was 2.98 °C, with a standard error of 1.29 °C during measurements. Blank chamber emissions of CO were examined by placing the chamber over an inert surface (PTFE foil) under different light regimes. The analysis revealed no detectable CO emissions from the chamber itself.

2.2.2 Exchange of CO by leaves

A temperature-controlled and well-mixed Walz leaf chamber with a UV-transparent quartz glass lid was used for leaf measurements. For light- and UV-exposure experiments, the lid was fitted with varying sizes of apertures to ensure that only the sample of interest inside the chamber received light. For sun exposure, the chamber was placed on a table outside the lab. For artificial UV exposure, lamps were positioned at varying distances from the lid of the chamber in the lab (see Bruhn et al., 2009). For dark measurements the entire lid was covered with layers of black cloth. A UV-opaque filter (transmitting only 17 % of UV-B, but 91 % of PAR) was used to examine the UV effect. Both PAR and UV-B (280–315 nm) were measured next to the chamber and adjusted as described in Sect. 2.2.1. The Walz chamber release of CO was characterized in the laboratory in relation to chamber temperature (T) as 0.15 × 10⁻⁶ × e⁰.⁰⁵T nmol CO m⁻² h⁻¹, and this value was subtracted from all calculations of CO emission rates. Exposed leaf areas were ca. 100 to 225 cm².

2.2.3 Calculation of exchange rates

The exchange of CO between the surface and atmosphere was calculated based on the changes in chamber CO concentration over time. A steady CO concentration change was commonly observed (R² > 0.95) within time windows lasting a minimum of 5–15 min, and rates were derived from linear regressions. Thus, the rate is derived from the observed slope and the treatment effects derived from the change in slopes. For the grass field: the full sun gross rate was calculated by subtracting the rate measured in full sun from the rate measured dark, and the UV-induced gross rate was calculated by subtracting the rate measured in full sun from the measured rate when UV-B was excluded.

3 Results and discussion

3.1 Natural grass field–atmosphere CO exchange

3.1.1 Darkness

Under dark conditions, the natural grass field was a significant sink for atmospheric CO (−2819 ± 210 nmol CO m⁻² h⁻¹, mean ± SE, n = 24, Fig. 1a). The measured uptake rate of CO in the dark can be approximated as the product of the CO diffusion coefficient of the topsoil and the CO concentration profile in the topsoil profile (Potter et al., 1996) according to Fick’s first law. Therefore, CO uptake in the grass field is in agreement with the expectation of an active microbial community in the grass field oxidizing the CO (Potter et al., 1996; King and Weber, 2007).

3.1.2 Natural sunlight

In response to natural sunlight, the grassland exhibited a net CO release of 1281 ± 334 nmol CO m⁻² h⁻¹ (Fig. 1b). The photo-induced gross release rate of CO, 4099 ± 334 nmol CO m⁻² h⁻¹ for the grassland (Fig. 1b), was calculated as the difference between the rates measured in natural sunlight and the rate in darkness.

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This photo-induced release of CO from the grassland very likely has its origin in the living vegetation. Firstly, the ground was fully covered with green leaves of grassland species, and the soil was not exposed to light. Secondly, the estimated release of CO from the natural grass field is similar to that of excised grass leaves from the grass field (Fig. 1c, Sect. 3.2). To date no other study has explicitly examined the potential of CO emission from living vegetation in response to the full natural spectrum of sunlight. However, a recent study by Galbally et al. (2010) of soil–atmosphere CO exchange in a semiarid Eucalyptus sp. ecosystem was conducted with chambers exposed to natural sunlight, although neither the transparent chamber area nor potential discrimination of certain wavelengths was clearly specified. In that study Galbally et al. reported CO release (net) rates of ca. 3000 nmol CO m$^{-2}$ h$^{-1}$ in the Eucalyptus sp. ecosystem, in the same range as the gross rate estimated for the grassland studied here. Even though the authors ascribe the CO release to have predominantly originated in the organic soil and plant litter (Eucalyptus sp.), it is noteworthy that the Eucalyptus sp. ecosystem had a 50 % leaf cover, and furthermore the ground was covered with lichens and mosses. Thus, it may be speculated that a substantial part of the measured CO emission in the Eucalyptus sp. ecosystem in response to natural sunlight may have originated from living vegetation rather than plant litter.

3.1.3 Effects of UV

The effects of natural UV irradiance on gross CO emission rates were tested under field conditions by shielding the measurement chamber with an almost completely UV-opaque chamber with little effect on total PAR transmission (Fig. 1a). In response to this, the gross CO emission rates were approximately halved for the natural grass field to 2466 ± 273 nmol CO m$^{-2}$ h$^{-1}$ (Fig. 1b).

As the UV-opaque field chamber transmitted 32 % UV-B, the CO emission from the natural grass field in response to natural solar PAR only was estimated by calculating the value at 0 % UV from a linear extrapolation of the relationship between the data points (100 % PAR and 32 % UV, 2466 ± 273 nmol CO m$^{-2}$ h$^{-1}$, and 100 % PAR and 100 % UV, 4099 ± 334 nmol CO m$^{-2}$ h$^{-1}$). This resulted in a value of 1697 nmol CO m$^{-2}$ h$^{-1}$. Interestingly, this value is very similar to the value of 1467 nmol CO m$^{-2}$ h$^{-1}$ measured in Brassica oleracea capitata f. alba leaves in response to 789 nmol photons m$^{-2}$ s$^{-1}$ artificial PAR in the laboratory (data not shown; 789 nmol photons m$^{-2}$ s$^{-1}$; PAR was the mean level during field measurements).

The actual value of CO emission from the natural grass field in response to natural solar UV radiation can thus be calculated as 4099 nmol CO m$^{-2}$ h$^{-1}$ minus 1697 nmol CO m$^{-2}$ h$^{-1}$, resulting in 2402 nmol CO m$^{-2}$ h$^{-1}$.

Fig. 1. (a) Measured natural grass field net CO emission rates in dark, sunlight and UV-excluded sunlight. Measurements were conducted with a Plexiglas chamber at ambient temperature (grass field [$T = 21.38 \, ^\circ\text{C}; \, n = 22$]). Values shown are means ± S.E. The order of treatments (dark, full sunlight and sun screened for UV) was alternated between replicates. For the Plexiglas grass field chamber measurements the mean (± S.E.) level of UV-B (280–315 nm) was 0.50 ± 0.01 Wm$^{-2}$ and the mean (± S.E.) PAR was 711 ± s.e. 16 µmol photons m$^{-2}$ s$^{-1}$. (b) Calculated ecosystem gross rates of CO emission. (c) CO emission rates (mean ± S.E., n = 4) of leaves cut from the natural grass field. Measurements were conducted with a temperature-controlled chamber at 25 °C. The order of treatments (full sun and sun screened for UV) was alternated between replicates. For the temperature-controlled chamber measurements the mean (± S.E.) level of UV-B (280–315 nm) was 0.51 ± 0.03 Wm$^{-2}$ and the mean (± S.E.) PAR was 789 ± S.E. 47 µmol photons m$^{-2}$ s$^{-1}$.
Figure 2. The effect of solar radiation on the CO emission rates (ER) by leaves (mean ± S.E. of ERlight – ERdark). Measurements were conducted with a temperature-controlled chamber at 25 °C. The order of treatments (full sun and dark) was alternated between replicates. For the temperature-controlled chamber measurements the mean (± S.E.) level of UV-B (280–315 nm) was 0.51 ± 0.03 Wm$^{-2}$ and the mean (± s.e.) PAR was 789 ± E.E. 47 µmol photons m$^{-2}$ s$^{-1}$.

A study by Tarr et al. (1995) on the effect of artificial light on CO production by leaf litter indicated that UV-irradiation was a stronger catalyst than visible light. A similar response has been reported for photo-induced carbon dioxide production in terrestrial plant litter (Brandt et al., 2009).

3.2 Leaf–atmosphere CO exchange

3.2.1 Natural sunlight

Freshly excised green leaves of six different plant species exhibited rates of net (i.e. after subtracting rates from dark measurements) CO release ranging from 965 to 2396 nmol CO m$^{-2}$ h$^{-1}$ (mean 1740 nmol CO m$^{-2}$ h$^{-1}$) when exposed to natural sunlight (Fig. 2). These rates are of the same magnitude as the gross rates (i.e. incl. dark rates) reported by Tarr et al. (1995) by green leaves, 1800 nmol CO m$^{-2}$ h$^{-1}$ in response to simulated sunlight (650 Wm$^{-2}$ UV-B + UV-A + PAR), and those by Yonemura et al. (1999) by green leaves, 1300 to 1550 nmol CO m$^{-2}$ h$^{-1}$ in response to 490 Wm$^{-2}$ PAR (without UV). In comparison, Seiler et al. (1978) reported a mean photo-induced CO production by living plants of 386 nmol m$^{-2}$ h$^{-1}$ in response to 50 Wm$^{-2}$ PAR (without UV).

Photo-induced CO emissions from leaf litter are typically 5 to 10 times higher than from living plants (Tarr et al., 1995; Schade et al., 1999a; Yonemura et al., 1999).

3.2.2 Effects of UV

Rates of CO emission by green leaves increased near-linearly with increasing intensity of UV-B and UV-A (Fig. 3). Such linear irradiance responses have been previously reported for Vicia faba and Platanus acerfolia (Seiler and Giehl, 1977), Oryza sativa (Yonemura et al., 1999), and Sequoiadendron gigantum (Derendorp et al., 2011).

The CO emission at specific irradiance intensities increased with decreasing wavelength of the radiation, as illustrated by the greater response in CO emissions under UV-B compared to UV-A (compare slopes in Fig. 3). Similar results have been found for leaf litter (Tarr et al., 1995; Schade et al., 1999a).

Schade et al. (1999b) suggested cellulose to be the main precursor for UV radiance-induced CO emission from dried leaf matter. Cellulose was recently also found to emit CH$_4$ in response to UV radiance; however, only at much lower rates compared to that of other structural components (Vigano et al., 2008). The exact nature of the origin of the produced CO in fresh leaves remains unclear, but it may be cellulose. UV-induced emission rates of CO from dead plant material have been observed to be oxygen dependent in several studies (Tarr et al., 1995; Yonemura et al., 1999; Derendorp et al., 2011). In studies on green lima bean leaves, Tarr et al. (1995)
indicated that the photo-production of CO occurred inside the leaves. However, this could not be confirmed by Yonemura et al. (1999).

We suggest that the process per se may be photolysis, and therefore the extrapolation of UV effects would only be compromised by a change in the source. This has important implications for future up-scaling.

We did not test the effects of a directly measured water status. However, we did measure the CO emission of dried material (litter), and found, as others (Tarr et al., 1995; Yonemura et al., 1999; Derendorp et al., 2011), that the CO emission is about one order of magnitude larger in dried leaves compared to that of fresh leaves. Hence, more knowledge is also needed in order to evaluate how a higher degree of leaf desiccation may increase rates of CO emission. Schade et al. (1999b) speculated that during senescence and leaf death, the colouring changes to darker leaf colours cause a greater degree of light absorption, which may explain higher rates of UV radiance-induced CO emission from dried leaf matter.

### 3.2.3 Effects of temperature

The effect of temperature \( T \) on the CO emission rate, \( ER \), can be described by the exponential function \( ER(T) = \alpha e^{\beta T} \) (Fig. 4). Under UV-B, \( F.\ elastica \) exhibited a temperature response of the UV-induced (\( ER_{UV} \) minus \( ER_{dark} \)) CO emission with \( \alpha = 6861 \text{ nmol CO m}^{-2} \text{ h}^{-1} \) and a temperature sensitivity \( \beta = 0.029 \). In contrast, \( B.\ oleracea \) exhibited a temperature response of the UV-induced (\( ER_{UV} \) minus \( ER_{dark} \)) CO emission with \( \alpha = 12 087 \text{ nmol CO m}^{-2} \text{ h}^{-1} \) and a temperature sensitivity \( \beta = 0.008 \). In darkness, the mean temperature response of the emission of the two plant species resulted in \( \alpha = 11 \text{ nmol CO m}^{-2} \text{ h}^{-1} \) and a temperature sensitivity \( \beta = 0.104 \). Thus, the mean temperature sensitivity under UV-B is so low that it indicates an abiotic process (Derendorp et al., 2011). In darkness, however, the temperature sensitivity for the green leaves resembled the activation energy associated with biological processes.

### 3.3 Relevance of measured rates

The global net burden of CO is 360 Tg CO yr\(^{-1} \) (IPCC 2001). Photo-induced CO emission from living plants has long been recognized and has been estimated to contribute globally with 50–200 Tg CO yr\(^{-1} \) (cf. Tarr et al., 1995). Importantly, though, this global estimate is not taken into account by the IPCC (IPCC, 2001). Further, this estimate is based solely on studies regarding the visible part (400–700 nm) of the solar spectrum, as the potential effects of light with shorter wavelengths were not examined in the underlying experimental studies (Seiler and Giehl, 1977; Seiler et al., 1978). Therefore, we still await a proper global estimate of UV radiance-induced CO emission by living vegetation. Our study provides the first in situ measurements at ambient conditions of ecosystem CO emission by living plants in response to natural solar UV irradiation. Importantly, we found that in the studied natural grass field the photo-induced CO emission due to natural solar UV radiation is more than half of the value of that due to the total solar spectrum at the Earth’s surface. This may imply that the previous global estimate of photo-induced CO emission from living plants of 50–200 Tg CO yr\(^{-1} \) (cf. Tarr et al., 1995) should perhaps be doubled. Thus, future global budgets need to include CO emission caused by natural UV irradiance.

We do propose that future global estimates may be possible based on the results presented in the current paper. The number of plant species tested was limited, but we do not consider this a major concern, given the relatively low variation between species in CO emission rates under UV (Fig. 2). A more variable selection of test species with an even greater variability in leaf surface characteristics may be needed to confirm this. This would also allow for further testing of our finding that the CO emissions from excised leaves are similar to those from attached leaves. In this context it is noteworthy that the current global scale numbers for CO adopted by the IPCC are derived from fewer plant species (Seiler et al., 1978). Therefore, we still await a proper global estimate of UV radiance-induced CO emission by living vegetation. Our study provides the first in situ measurements at ambient conditions of ecosystem CO emission by living plants in response to natural solar UV irradiation. Importantly, we found that in the studied natural grass field the photo-induced CO emission due to natural solar UV radiation is more than half of the value of that due to the total solar spectrum at the Earth’s surface. This may imply that the previous global estimate of photo-induced CO emission from living plants of 50–200 Tg CO yr\(^{-1} \) (cf. Tarr et al., 1995) should perhaps be doubled. Thus, future global budgets need to include CO emission caused by natural UV irradiance.

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It is possible that the otherwise natural breakdown of trace gasses by UV radiation in the presence of OH radicals is partially or completely unnoticed in a laboratory scale setup as used in the current study. The lifetime of OH radicals in the atmosphere is less than one second (Isaksen and Dalsøren,
2011), whereas potential formation rates under the current experimental conditions are unknown. Importantly, though, CO depletion by radicals is already a known sink and thus already accounted for (IPCC, 2001).

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