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UV-induced carbon monoxide emission from living vegetation

D. Bruhn[1,2], **K. R. Albert**[1], **T. N. Mikkelsen**[1], **and P. Ambus**[1]

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

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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 an ecosystem chamber or a plant-leaf scale chamber. Leaves of all examined plant species 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 rather 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 ecosystem scale.

1 Introduction

Carbon monoxide (CO) is a reactive gas and the oxidizing capacity of the atmosphere is controlled in large part by levels of CO (Potter et al., 1996). Carbon monoxide can lead to the formation of O_3, and since CO is a main reactant of hydroxyl (OH) radicals, the principal sink for atmospheric methane (CH_4), CO also indirectly affects the atmospheric CH_4 levels (IPCC, 2001). Carbon monoxide is therefore an important trace gas in the atmosphere (Schade et al., 1999b). 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 on the net CO burden.

All natural terrestrial direct CO emissions, in the range of 50–200 Tg CO yr^{-1}, have hitherto been ascribed by 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 in previous global CO budgets (IPCC, 1995, 2001), the UV-component of (sun)-light was not considered (Seiler and

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Giehl, 1977; Seiler et al., 1978). In studies of photo-chemically induced release of CO by dead plant material, it was demonstrated that the more energy-rich UV light had a very important 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*), from trees (*Acer platanoides*, *Corylus avellana*) and grasses growing in the near vicinity of the laboratory (dominated by *Deschampsia flexuosa* and with minor occurrence of *Achilla millefolium* and *Plantago lanceolata*). Ecosystem analysis was deployed to 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 H_2O interference, were conducted by off-axis enhanced cavity spectroscopy (Los Gatos N_2O/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).

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2.2.1 Ecosystem-atmosphere CO exchange

Ecosystem-atmosphere CO exchange measurements were conducted under in-situ conditions on natural vegetation and under ambient UV-B conditions, in September and October 2011 at DTU Risø campus (55°41′ N, 12°05′ E). A UV-transparent Plexiglas chamber (45 × 45 × 25 cm^3; 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 cm^3, transmitting only 32 % UV-B, but 96 % PAR) was placed around the ecosystem 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) was measured next to the chamber with a LiCor LI-250A Light Meter and Gigahertz–Optik UV-1102 detector, respectively. 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 light- and UV-exposure experiments, the lid was fitted with varying size of apertures to ensure that only the sample of interest inside the chamber received light. For sun exposure, the chamber was placed outside the lab. For artificial UV exposure, lamps were positioned at varying distances to 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. The Walz chamber release of CO was characterized in the laboratory in relation to chamber temperature (T) as 0.15 × 10

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$^{-6} \times e^{0.05T}$ 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 cm^2.

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. A steady CO concentration change was commonly observed ($R^2 > 0.95$) within time-windows lasting a minimum of 10 min, and rates were derived from linear extrapolations.

3 Results and discussion

3.1 Ecosystem-atmosphere CO exchange

3.1.1 Darkness

Under dark conditions, the grassland ecosystem was a significant sink for atmospheric CO (Fig. 1). The measured uptake rate of CO in the dark can be approximated as the product of the CO diffusion coefficient of the top soil and the CO concentration profile in the top soil profile (Potter et al., 1996) according to Fick's first law. Therefore, CO uptake in the grassland is in agreement with the expectation of an active microbial community in the grassland oxidizing the CO (Potter et al., 1996; King and Weber, 2007).

3.1.2 Natural sunlight

In response to natural sun-light the grassland exhibited a net CO release of 1628 ± 309 (mean $\pm$ SE, $n = 27$, measurements in four plots) nmol CO m^{-2} h^{-1} (Fig. 1). The photo-induced gross release rate of CO can be calculated as the difference between the rates measured in natural sun-light and the rate in darkness, equal to 4437 ± 464 nmol CO m^{-2} h^{-1} for the grassland.

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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 grassland is similar to that of excised grass leaves (Fig. 1, Sect. 3.2). 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} (Tarr et al., 1995). Importantly, though, this global 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). 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 were 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 is 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 effect 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. 1). In response to this, the gross CO emission rates were approximately halved for the grassland. A study

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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).

Thus, in addition to the global estimates of photo-induced CO emission by living vegetation in response to incident visible light (Seiler and Giehl, 1977; Seiler et al., 1978) amounting to 50–200 Tg CO yr^{-1} (Tarr et al., 1995) future global budgets need to include CO emission caused by natural UV irradiance. For future chamber measurements addressing CO exchange it is thus important to use UV-transparent materials when constructing chambers.

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 W m^{-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 W m^{-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 W m^{-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).

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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. 4). 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 proven in leaf litter (Tarr et al., 1995; Schade et al., 1999a).

The exact nature of the origin of the produced CO remains unclear, but UV-induced emission rates of CO from dead plant material are in several studies observed to be oxygen dependent (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 photoproduction of CO occurred inside the leaves. This could however 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.

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, the mean temperature re-

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sponse of the UV-induced (ER_{UV} subtracted ER_{dark}) CO emission of the two plant species resulted in $\alpha = 9410\,\mathrm{nmol\,CO\,m^{-2}\,h^{-1}}$ and a temperature sensitivity, $\beta = 0.017$. In darkness, the mean temperature response of the emission of the two plant species resulted in $\alpha = 11\,\mathrm{nmol\,CO\,m^{-2}\,h^{-1}}$ 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 for the global scale

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). However, 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 a further testing our finding that the CO emissions from excised leaves is similar to that from attached leaves. In this context it is noteworthy that the current global scale numbers for CO adopted by IPCC are derived from fewer plant species (Seiler et al., 1978, see Tarr et al., 1995 for discussion) than used in current study.

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, in particular when the rate of carrier gas is fast enough. 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 "simply" an important CO-sink. This sink is, however, already a known sink and thus already accounted for (IPCC, 2001). If such mechanism is in operation, which cannot be concluded from the current study, the observed CO release rates should be considered net rates. Nevertheless, the measured UV-induced rate of CO emission is still very relevant and important to extrapolate. This is because net CO release is a combination of

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CO release and CO uptake. Indeed, all gross rates of CO uptake and CO release are necessary to extrapolate in order to fully close the global CO budget.

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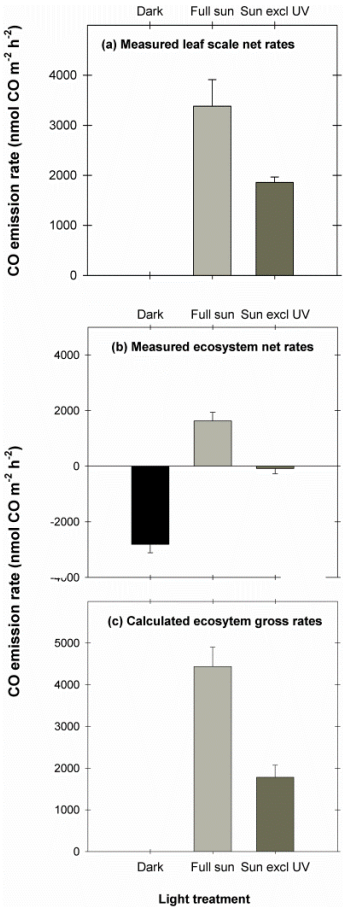

Fig. 1. Caption on next page.

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Fig. 1. (a) Leaf CO emission rates (mean ± s.e.). Measurements were conducted with a temperature controlled chamber at 25 °C (cut vegetation [$n = 4$] from the grassland ecosystem. Values shown are means ± s.e. 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 $0.51 \pm 0.03\,W\,m^{-2}$ and the mean (± s.e.) PAR was 789 ± s.e. 47 µmol photons $m^{-2}\,s^{-1}$. **(b)** Measured ecosystem net CO emission rates in dark, sunlight and UV-excluded sunlight. Measurements were conducted with a Plexiglas chamber at ambient temperature (grass ecosystem [$T = 21.38$ °C; $n = 22$]; sand [$T = 13.03$ °C; $n = 7$]).Values shown are means ± s.e. The order of treatments (dark. full sun. and sun screened for UV) was alternated between replicates. For the Plexiglas ecosystem and sand measurements the mean (± s.e.) level of UV-B (280–315 nm) was $0.50 \pm 0.01\,W\,m^{-2}$ and the mean (± s.e.) PAR was 711 ± s.e. 16 µmol photons $m^{-2}\,s^{-1}$. **(c)** Calculated ecosystem gross rates of CO emission.

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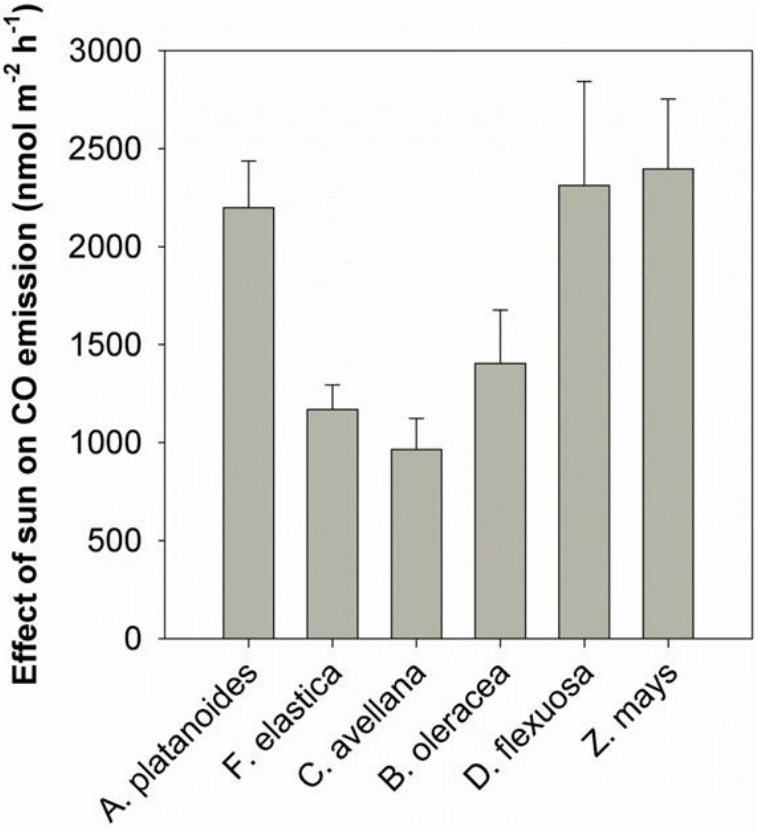

Fig. 2. The effect of solar radiation on the CO emission rates (ER) by leaves (mean ± s.e. of $ER_{light} - ER_{dark}$). Measurements were conducted with a temperature controlled chamber at 25 °C The order of treatments (full sun and dark) was alternated between replicates. For the temperature controlled chamber measurements the mean (± s.e.) level of UV-B (280–315 nm) was 0.51 ± 0.03 W m^{-2} and the mean (± s.e.) PAR was 789± s.e. 47 µmol photons m^{-2} s^{-1}.

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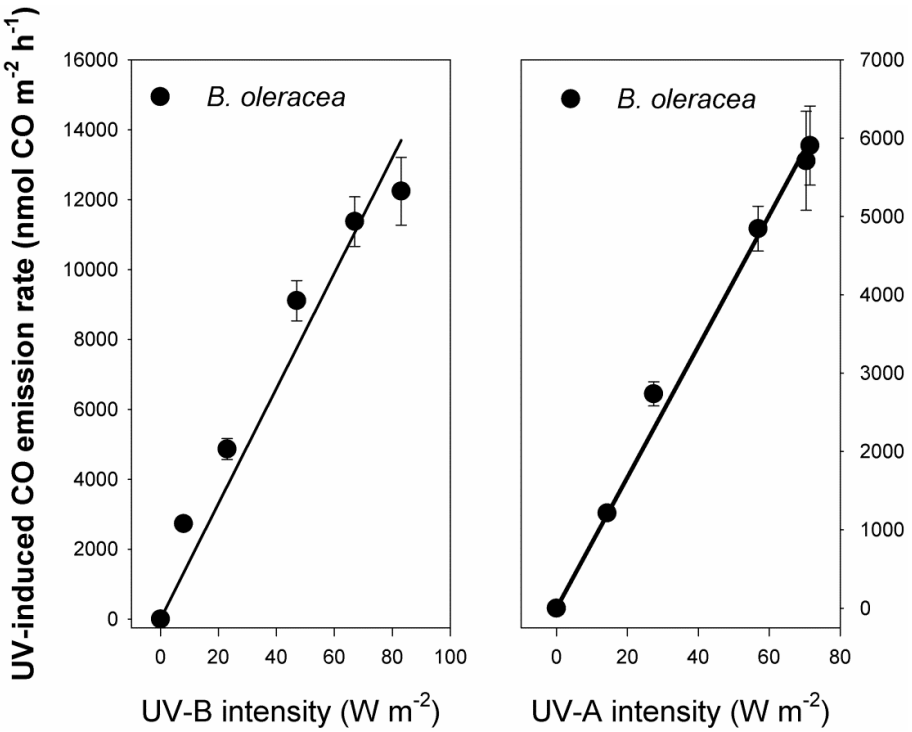

Fig. 3. The UV-irradiance response of CO emissions by leaf (mean ± s.e. of $ER_{light} - ER_{dark}$) at 25°C. The lines indicate the position of the linear regressions lines intercepting at (0, 0) and slopes of 160 and 89 for *B. oleracea* (UV-B) and *B. oleracea* (UV-A), respectively. The regression coefficients (R^2) are 0.96 and 0.98, respectively.

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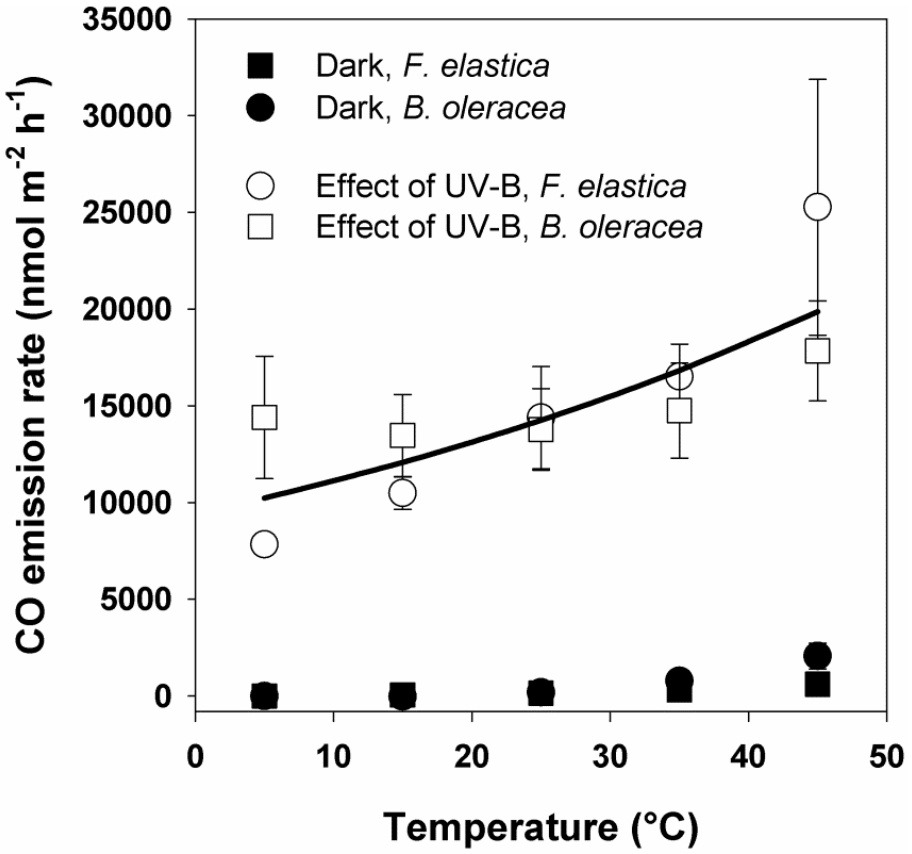

Fig. 4. Temperature dependence of UV-induced CO emission rate (ER) by leaf ($ER_{light} - ER_{dark}$) and dark CO emission rate (mean ± s.e.). The full line represents an exponential regression to data for leaves. See Sect. 3.2.3 for equation coefficients.

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