

CO emissions from degrading plant matter

(I). Measurements

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ABSTRACT

CO emissions from degrading deciduous leaf and grass matter have been investigated in laboratory and field measurements. CO emissions are induced both photochemically and thermally. Photochemical CO production can be described by a 2nd-order polynomial in light intensity and exhibits a hysteresis effect, not previously reported. Humid material showed higher CO emissions than dry material. A preliminary, relative action spectrum for the photochemically induced CO emissions is presented. Although UV irradiation caused most of the CO production, visible light also caused up to 40% of the emissions. We propose a cleavage of the cellulose chain as the important step prior to CO production. Thermal CO emissions from degrading plant material obey an Arrhenius type equation (presented for several species in this paper), but emissions are lower than those induced photochemically. During our field measurements on dry grasses in a South African savanna we found a strong influence of incident radiation intensity and temperature on measured CO fluxes. Solely photochemical CO production from the grasses is calculated by subtraction of soil fluxes and thermally induced grass CO emissions from the total CO emissions. CO emissions and hysteresis differ between the grasses investigated and may be interpreted by the grass' colour and their architecture. Deposition of CO on the soils was much lower than CO emission from the dry grasses during daytime. Nighttime data show that possible thermal CO production from the grasses may partially compensate for CO deposition on the soils for several hours after sunset depending on temperature.

1. Introduction

Carbon monoxide (CO) is an important atmospheric trace gas in the atmosphere. In the background atmosphere CO is the main reactant of the OH radical, thereby strongly influencing its concentrations in the atmosphere. In addition, CO oxidation can lead to either production or consumption of tropospheric ozone depending on NO_x mixing ratios (Crutzen, 1994). However, the global CO budget, as recently reevaluated by the IPCC (1994), includes major uncertainties, such

as the amount of CO deposited on soils, or the amount of CO that is photochemically produced in plants.

Currently, natural sources of CO in the atmosphere are believed to constitute approximately 50% of its global source strength (Khalil and Rasmussen, 1990). However, especially in remote, unpolluted regions, natural CO emissions may account for a much larger fraction of total emissions, because efficient CO production from the oxidation of natural non-methane hydrocarbons (NMHCs) may be more restricted to NO_x-rich areas (Harris et al., 1990; Hatakeyama et al., 1991; Miyoshi et al., 1994). Previously investigated direct CO emissions include those from green plants (Wilks, 1959; Troxler and Dokos, 1973;

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Fischer and Lüttge, 1978; Bauer et al., 1979; Fischer and Lüttge, 1979; Lüttge and Fischer, 1980; Seiler and Conrad, 1987), and from soils (Conrad and Seiler, 1982; Conrad and Seiler, 1985a, 1985b; Scharffe et al., 1990; Zepp et al., 1997). Recently, Sanhueza et al. (1994a) and Zepp et al. (1996) found that dead savanna grasses emit CO in the dark thereby affecting the total CO flux between the soil and the atmosphere, and Zepp et al. (1997) showed that soil-atmosphere CO fluxes can be influenced by CO photoproduction in the soil surface layer of recently burned plots. Further, Tarr et al. (1995) showed that senescent leaves and dead brown leaves as well as a dead grass material emit CO when irradiated with simulated sunlight, therefore, plant litter should be included in the list of potential CO sources.

Until now, very little data on CO emissions from dead plant matter in the dark have been presented. Zepp et al. (1996) gave activation energies for a savanna soil, grass, and a "litter composite", while other data on organic material are restricted to soil organic matter and phenolic model compounds (Conrad and Seiler, 1985b, 1985c). Conrad and Seiler (1985c) inferred phenolic structures in soil organic matter to be the primary source of the CO production.

The amount of CO emitted from green leaves upon solar irradiation was measured by Seiler and Giehl (1977), Seiler et al. (1978), and Bauer et al. (1979). Besides their measurements of CO emissions from green leaves, Bauer et al. (1979) mentioned that senescent leaves also produced CO under the influence of light. They concluded that the production was of abiological, photochemical origin, whereas Fischer and Lüttge (1978, 1979) and Lüttge and Fischer (1980) believed it to be a by-product of photorespiration. Bauer et al. (1979) estimated a global CO source from photochemical CO production in green plants of 70 Tg CO yr^{-1} , a value similar as that by Seiler and Conrad (1987) who estimated an amount of $75 \pm 25 \text{ Tg yr}^{-1}$ globally, including year-round emissions from tropical ecosystems, assuming similar CO emissions during the dry season, when dead plant matter prevails. However, Tarr et al. (1995) measured a much higher CO emission per irradiated leaf area for senescent and dead leaves than for green leaves in the laboratory. They also found that CO emissions were reduced in a nitrogen atmosphere and that variation of carbon dioxide concentrations did

not influence the CO photoproduction. Tarr et al. (1995) concluded from their mechanistic studies, that the CO production is a photooxidation process in or on the leaves. Though they did not present CO emissions as a function of irradiation intensity, they presumed emissions to be linear with light intensity and calculated the possible CO source in tropical savannas to be 30 to 60 Tg yr^{-1} on the basis of an average daily solar irradiation and a five month duration of the dry season. On a global basis they estimated a source value of 60 to 90 Tg CO yr^{-1} .

Here, we show results of a detailed study on CO emissions from degrading plant matter. Field measurements on CO emissions from different grasses in an African savanna are presented, soil fluxes as well as ambient CO mixing ratios are discussed, and grass CO emission dependencies on incident solar irradiation are determined. Our laboratory measurements show that CO emissions grow quadratically with light intensity, and this work was extended to give a preliminary action spectrum of the CO emission for a savanna grass and European beech (*Fagus sylvatica*) leaves. We also present results from the evaluated dependence of photochemically-induced CO emissions on leaf moisture. Possible mechanisms for CO production are discussed in Section 6.

2. Experimental

2.1. Field site description

The field measurements were carried out in the Nylsvely Nature Reserve in South Africa, 24.65°S , 28.7°E , approximately 200 km north of Johannesburg. The nature reserve has been a study site for numerous scientific campaigns and was described comprehensively by Scholes and Walker (1993). We report results from a site at the edge of the floodplain, where the sandstone derived sandy soil has a pale reddish alluvial horizon that is poor in nutrients. Its pH (1:2.5 in 0.01 M CaCl_2) was 3.9 and the TOC was 0.3% in the top 5 cm.

Nearly all grasses grew in tufts, occupying more than half the soil surface area, the remainder mostly being bare ground. Grass heights were between 1 and 1.5 m depending on species. Measurements were conducted in late July and early August 1996 during a period of clear skies

and intense solar radiation. The aboveground parts of all grasses were dead and dry. Little biomass was found on the soil as litter; almost all biomass was standing dead matter.

2.2. Field measurement setup

Prior to a measurement cycle, a grass tuft was chosen based on its representative appearance. A steel cylinder, 32 cm ID, 30 cm deep, was then hammered into the soil around the tuft so that it topped the soil surface by approximately one centimeter. Care was taken not to disturb the aboveground parts of the plant. Two 3 cm OD steel bars, 70 cm high, were fixed outside the steel cylinder. They were topped by additional bars in order to reach the same height as the standing dead plant matter. In addition, another steel cylinder of the same diameter but 12 cm high and coated inside with teflon was hammered into the soil directly beside the grass tuft on bare ground down to approximately half its depth. On the

following day, a teflon 0.05 mm FEP film (DuPont, 1985) chamber was built around the grass, and measurements were started on the next day. A schematic representation of the field setup is given in Fig. 1.

The soil in the "soil-chamber" was cleared from litter, and the air was blown inside the chamber at an angle to create turbulence. The chamber was closed on top with teflon-film, which had several 2 mm holes through which excess air escaped from the chamber.

The "grass-chamber" consisted of a 1.2 m high teflon-film sack around the grass tuft. At the top it was tightened around a plexiglass-ring (Fig. 1) which could be varied in height along the outside steel bars. At the bottom we tightened the teflon-film sack around the soil steel cylinder with a strong o-ring. In the middle it was held in position via four teflon ventilators. These were fixed to the outside steel bars by strong magnets which could also be varied in height. Each ventilator produced an air-flow of approximately 700 l min^{-1} , so that

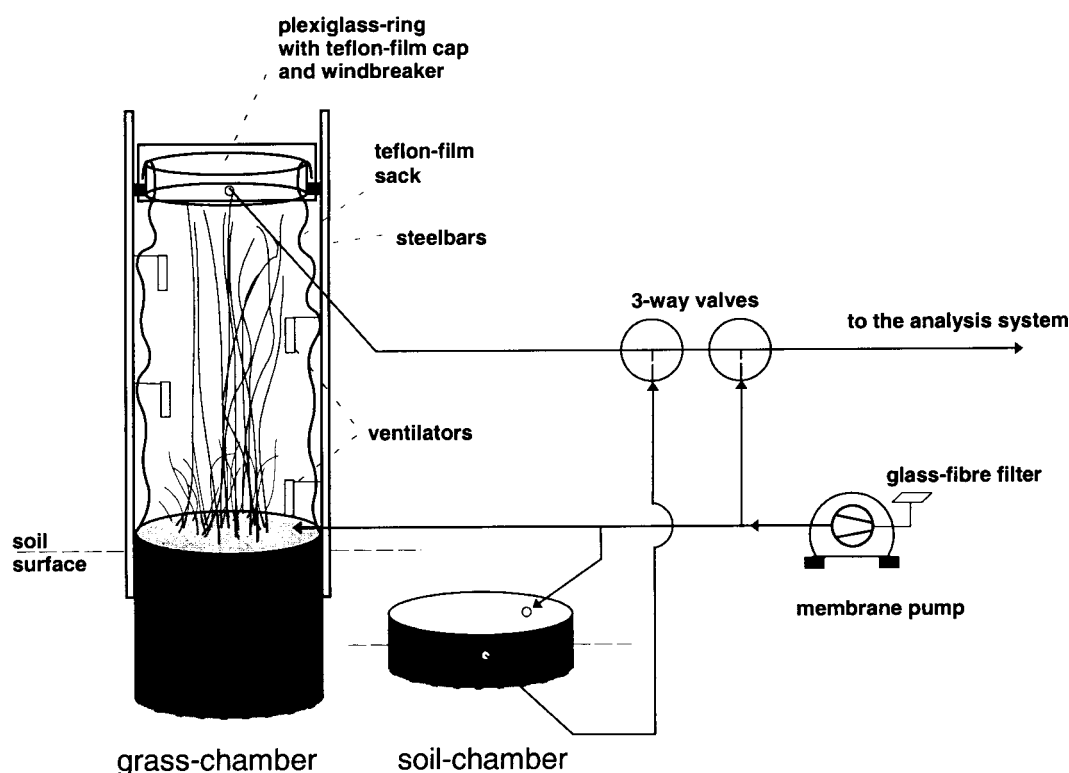


Fig. 1. Schematic presentation of the field measurement setup.

the air inside the grass-chamber was sufficiently mixed. As for the soil-chamber, air exited the chamber via a number of holes in a teflon-film cap on top of the chamber. In addition, a wind-breaker was built to keep ambient air from mixing with chamber air when strong wind produced turbulence outside the chamber. The chamber could be protected from sunlight by wrapping it in plastic bags, in order to distinguish between photochemical or thermal CO production.

All analytical instrumentation was placed a few meters away from the chambers, and was protected from direct sunlight and wind-blown dust by a shelter. Power was provided by a generator placed approximately 150 m downwind of the measurement site. Ambient air was pulled in through a glass-fibre filter to remove dust, and was pumped into the flux chambers near the ground. A 3/8" OD teflon-tube provided a flux of 31 to 34 l min⁻¹ to the grass-chamber, whereas only 5 to 8 l min⁻¹ flowed through a 1/4" thick-wall teflon-tube to the soil-chamber.

2.3. Laboratory setup

Measurements were conducted with a specially designed analysis system comprised of a solar simulation device, and a pyrex glass chamber for leaf exposures, described here briefly. The solar radiation simulator was an Osram HMI 1200W lamp in a commercial housing, which allowed the movement of a reflector focusing the lamp's radiance cone. To change the light intensity in an experiment, the reflector was moved to a previously evaluated position where the lamp's irradiation intensity in the chamber was known. Changes in light intensity on the chamber, either random or due to non-homogeneity of the irradiance cone, were found to be less than 10%.

To examine the relation of different wavelengths on CO emissions several filters were used: A 4 mm Makrolon[®] disc (polycarbonate, cutoff: 405 nm; Cadillac Plastic, Mainz-Kastel, Germany) was used to block all UV radiation, a 4 mm soda-lime glass (cutoff: 335 nm) was used to filter UV-B but retain most of the UV-A radiation, and several pyrex-glass discs were used to filter shortwave UV-B radiation (cutoff: 300 nm for 2 mm pyrex, 315 nm for 6 mm pyrex). Total irradiation was also measured under the different filters and the

light intensity was re-adjusted to the desired value by focusing the lamps radiance cone.

For the evaluation of the relative action spectrum of CO emissions in the visible part of the spectrum the Makrolon[®] disc was used together with commercially available thin polymer film color filters (Lee Filters, Andover, Hampshire, UK, which either acted as a bandpass filter ($\lambda_{\text{max}} = 420 \text{ nm}$, 460 nm, 505 nm, and 525 nm, blue to green colours) or as a cutoff filter (cutoff at 500 nm, 565 nm, and 615 nm, yellow to red colours). We measured light intensity with a PAR (Photosynthetic Active Radiation; photon flux density) sensor (Skey, Campbell Sci., UK) and re-adjusted light intensity via focusing. All values of CO emissions were normalized to a photon flux of 400 $\mu\text{mol m}^{-2} \text{s}^{-1}$ PAR.

In the UV part of the spectrum, leaves were exposed to an array of Philips TL/05 UV-A, or TL/12 UV-B lamps. The first had a radiance maximum at 365 nm with a band width at half intensity of approximately 65 nm, the latter had a radiance maximum at 306 nm and a band width at half intensity of approximately 50 nm. The UV intensity was measured with UV-A and B sensors (Cole-Parmer, USA), and CO emissions were extrapolated to a photon flux of 400 $\mu\text{mol m}^{-2} \text{s}^{-1}$.

The exposure chamber was a pyrex glass tube with an ID of 24 cm and a height of 15 cm. Air could be admitted through an inlet tube at half height and extracted through an outlet tube at 2/3 height. The chamber had an additional connection to introduce a temperature probe via a septum. Bottom and top of the chamber were closed with highly light transparent teflon FEP foil (DuPont, 1985) tightened around the glass with strong o-rings. The top foil had several little holes through which air could leave the inner volume, producing a constant upflow of air inside the chamber. Air was blowing inside the chamber at a slant to produce turbulence, thereby mixing the chamber air. The outlet tube was positioned higher and away from the inlet tube in order to extract air which had equilibrated inside the chamber.

The bottom 3–5 cm of the chamber were placed in a water bath, used for cooling or heating during experimental evaluations of photochemical or thermal CO production. A known weight of leaves chosen at random was placed at the bottom of the chamber to give an optically thick layer, and

so every result represented an average of emissions from a number of leaves which were different in shape, colour and chemical composition. The leaf temperature was measured with two probes inside and on top of the leaf layers. The maximum temperature difference between these positions was 5°C, and an average was used for evaluations of thermally induced emissions and for temperature corrections.

The chamber was used only in the dynamic mode, and air was mixed from synthetic air (Messer Griesheim, Germany), compressed air, CO₂ and CO standard mixtures in air. Fluxes were adjusted with flow controllers to provide a total flux of either 3 or 4 l min⁻¹. The mixture was passed through a water bottle kept at 0°C to provide a constant humidity, then flushed into the chamber. The extracted air was split: 200 ml min⁻¹ was introduced into the sample loop of the CO analyzer, while the rest passed through a CO₂ and a H₂O infrared analyzer. Thick wall teflon tubing (1/4" OD PFA) and valves were used for gas transport to the chamber as well as to the analysis instruments.

2.4. Analytical instruments

CO₂ and H₂O were measured with commercial infrared analyzers (Heraeus/Rosemount, Hanau, Germany). Differences in measured CO₂ mixing ratios of 6 µmol mol⁻¹ were considered significant at the 95% confidence level. H₂O differences in measured mixing ratios of 0.1% were considered significant at the 95% confidence level.

CO was measured with an RGA3 instrument (Trace Analytical, Menlo Park, CA), based on gas chromatographic CO separation and a HgO detector (Seiler et al., 1980). The instrument has been extensively described by Novelli et al. (1991) and is commonly used for CO measurements in the low nmol mol⁻¹ range (Scharffe et al., 1991; Novelli et al., 1994; Sanhueza et al., 1994a, 1994b; Zepp et al., 1996). We used synthetic air as the carrier gas (40 ml min⁻¹) and kept the separation columns at 130°C. The backflush timing of column one (Unibeads® 1S) was 24 s, and was controlled by the data logger. We calibrated the CO analyzer with a 14.5 µmol mol⁻¹ CO standard (Deuste Steinger, Muehlhausen, Germany). The standard was diluted with CO-free air and we generated a calibration line for the instrument from

120 nmol mol⁻¹ to 500 nmol mol⁻¹ once each month. Secondary calibration gases, high purity air in steel cylinders, were calibrated to the primary standard, and were on the NOAA scale (Novelli et al., 1991, 1994) within the measurement error. The instrument response was linear above 100 nmol mol⁻¹ CO, and the reproducibility was better than 1% at the 99% confidence level. The standard error for mixing ratios higher than 150 nmol mol⁻¹ was approximately 2% and a difference between mixing ratios of 4 or 8 nmol mol⁻¹ CO was considered to be significant at the 95% confidence level during the laboratory or field measurements, respectively. The CO analyzer was calibrated in Germany before and after the expedition. The calibration lines were identical (t-test at the 95%-level). In the field, the instrument stability during the day was checked by a secondary calibration gas of 78 ± 3 nmol mol⁻¹ introduced three times consecutively every two hours. Corrections had to be made for only two days, when the otherwise stable instrument response differed by more than 10% during the course of that day.

2.5. Trace gas flux measurements

In the field air from inside the chambers was extracted by a small membrane pump at a flow between 0.5 and 1.0 l min⁻¹. The first 3-way valve (Fig. 1) controlled whether chamber or ambient air (behind the big membrane pump) was measured. The second 3-way valve controlled which chamber was measured. The system was controlled by a data logger (21X, Campbell Sci. Inc., UK) which collected data every 5 seconds, and stored them as 30 second averages. A complete measurement cycle of 6 min included 2 min of ambient air, 2 min of soil-chamber air, and 2 min of grass-chamber air measurements. This order was chosen in accordance to the throughflux times of the chambers. Gas fluxes to the chambers were checked several times during each daytime measurement series by a portable gas meter. Sample tests in the field showed that there was no contamination from either the membrane pump (on ambient air mixing ratios) or from the grass-chamber (on chamber air mixing ratios). However, the soil-chamber showed some CO production when irradiated by direct sunlight. During our flux measurements, we blocked direct sunlight to the soil

chamber with a plastic bag to create an environment similar to the soil conditions underneath the tufted grass.

The laboratory measurements were also controlled by the data logger. Samples were introduced onto the GC column of the CO analyzer every 2 minutes (when a high flux through the chamber (4 l min^{-1}) had been chosen) or every 3 min (when a low flux (3 l min^{-1}) had been chosen). In the first case, every 7th measurement a 3-way valve was switched and the controlled air mixture entering the chamber was analyzed as a reference. In the latter case, the reference measurement was carried out every 6th measurement. Each hour a secondary calibration gas was processed to check instrument stability. Therefore, a complete cycle of one hour included 30 (or 20) chromatograms of which 4 (or 3) were reference CO mixing ratios and one was an instrument calibration.

The trace gas flux, Q , emitted from the dead plant matter was calculated from the measured mixing ratios as, for example in the case of CO,

$$Q_{\text{CO}} = ([\text{CO}]_{\text{chamber}} - [\text{CO}]_{\text{ambient}}) \times F \quad (\text{molec. s}^{-1}), \quad (1)$$

where $[\text{CO}]$ denotes the mixing ratios, and F is the gas flux through the respective chamber.

Under field conditions the total maximum uncertainty of the calculated flux rates was estimated to be 1.5×10^{14} molec. CO s^{-1} . In the laboratory, the relative maximum error of calculated fluxes was always smaller than 5%.

2.6. Reference data

During the field measurements meteorological data (including air T, P, rH, incident radiation, and soil-T) were collected from a location approximately 50 m upwind of the chambers, in the direction of the floodplain. Furthermore, we collected radiation data from a platform located at the grass top height, i.e. total solar irradiation with a Pyranometer, as well as PAR, UV-A and UV-B flux. Temperature data were taken from the soil (3–5 cm depth) between the chambers, from the top soil in the soil chamber (surface), and from the base of the grass tuft inside the grass-chamber. After completion of the measurement series all the grass which had been inside the chamber was cut just above the surface, combined with the addi-

tional litter from inside the chamber, weighed, and dried overnight at 100°C . All grass material was later taken to Germany, where its thermal CO production was assessed.

For the field and laboratory measurements, the measured dry weight, referred to as gdw, serves as the reference quantity of thermal CO production from the dead plant material. In addition, a part of the dry sample was ground and analyzed for its total organic carbon and nitrogen contents as well as its pH (0.1 g in 2 ml 0.01 M CaCl_2). Fluxes determined from laboratory irradiations refer to the surface area of the glass chamber covered with the substrate as the reference quantity of emissions, and were corrected for temperature. The different leaf materials used in our laboratory studies are described in Subsection 6.1.

3. Results and discussion

3.1. Ambient CO mixing ratios in the southern hemisphere and at the Nylsvey Nature Reserve

CO mixing ratios at southern hemisphere remote coastal stations such as Cape Grim, Tasmania (Fraser et al., 1986), and Cape Point, South Africa (Brunke et al., 1990), are substantially lower than over the continents where sources such as non-methane hydrocarbon (NMHC) oxidation (Zimmerman et al., 1988), and especially biomass burning (Crutzen et al., 1985; Kirchhoff and Marinho, 1989) add to the natural background. Additionally, CO emissions from plants, primarily in the tropics (Seiler and Giehl, 1977; Fischer and Lüttge, 1978; Lüttge and Fischer, 1980; Jacob and Wofsy, 1990; Harriss et al., 1990), and from soils (Conrad and Seiler, 1980, 1982; 1985a; Scharffe et al., 1990; Sanhueza et al., 1994a, 1994b; Zepp et al., 1996), can be direct natural, ground-based CO sources. Tropospheric CO mixing ratios in the southern hemisphere, as in the northern hemisphere, show a distinct seasonal behaviour with maximum values during winter and minimum values during summer (Seiler et al., 1984; Brunke et al., 1990; Fraser et al., 1986; Brenninkmeijer et al., 1992). A comparison with model data on methane oxidation indicated that the CO sources are mainly active during the SH winter months (Seiler et al., 1984).

As yet, relatively few CO measurements in remote, continental areas of the southern

hemisphere exist. Seiler and Junge (1970) reported on CO mixing ratios between 100 and 140 nmol mol⁻¹ in “unpolluted air” at a remote site near Pretoria, South Africa, not far from our measurement site. Kirchhoff and Marinho (1990) found CO mixing ratios between 70 and 140 nmol mol⁻¹ in samples from several locations in South America, with most samples around 100 nmol mol⁻¹. Approximately the same mixing ratios were found by Conrad and Seiler (1982) for the Karoo semidesert and the Namib desert in southern Africa. In another publication, Kirchhoff and Marinho (1989) reported some very high CO concentrations (250 nmol mol⁻¹) at a remote site in the “Pantanal” in the southwest of Brazil, a feature readdressed in a recent publication by Novelli et al. (1998).

CO ambient mixing ratios at the Nylsvey remote site were measured between 16 July and 3 August, and were very variable on a day to day basis. The lowest measured mixing ratios near 80 nmol mol⁻¹ occurred on 24 July, the highest near 200 nmol mol⁻¹ on 16 July and on 2 August. The high values at the beginning of August were most probably due to nearby biomass burning which could be seen from the measurement site during the late evening of 31 July.

In addition to day to day variability, CO mixing ratios were generally low during morning hours, increased during the day and reached maximum values in the afternoon. This feature might either be explained by a daytime rise of the boundary layer height along with vertical down mixing of polluted air masses at higher altitudes, or by advection of polluted air masses from anthropogenic sources in the north. The site is approximately 10 km SE of the highway N1, and approximately 50 km and 100 km S to SSW of urban centers with populations of more than 10 000, so that the Nature Reserve was not protected from anthropogenic sources during our measurement campaign. We note that residential/domestic stationary burning and road traffic are thought to constitute approximately half of the South African total CO emissions (Scholes and van der Merwe, 1996).

Meteorological conditions at the measurement site were characterized by stable wind directions from NE, and a distinct wind speed pattern, shown in Figs. 2a, b. During the night, wind speeds steadily decreased, and the direction shifted to the

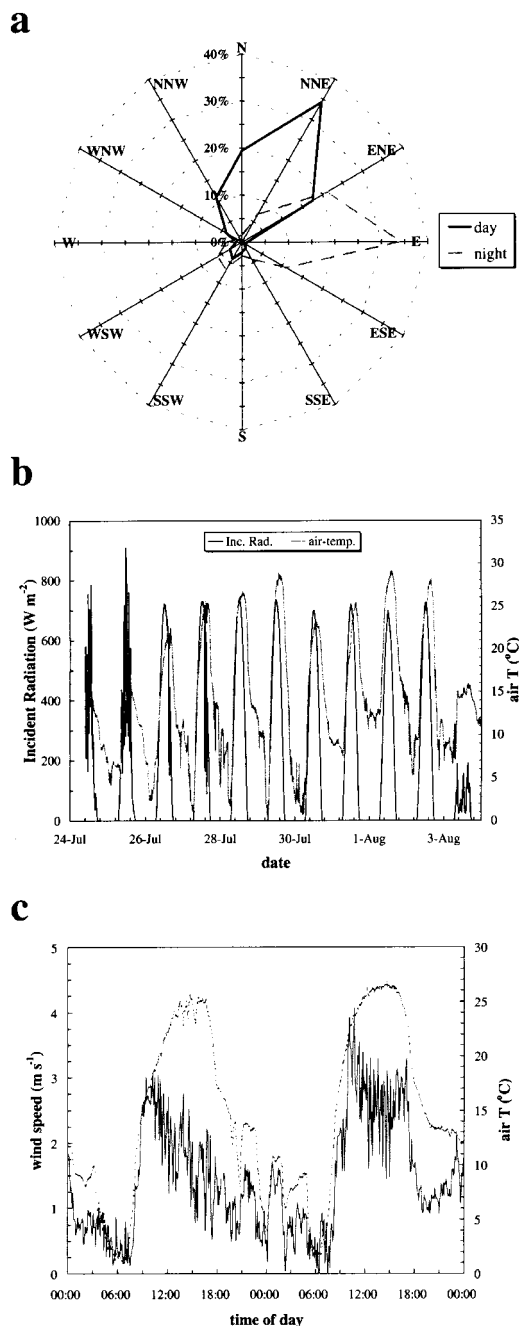


Fig. 2. (a) Wind directions at the field site. “Day” values represent hours between 9 am and 5 pm, whereas “night” values represent hours between 8 pm and 4 am. (b) Variation of incident radiation and air temperature during the field measurements. (c) Wind speed and air temperature during two days in July 1996.

east, possibly due to the topography, which forced minor air movements along the E–W direction of the floodplain. As can be seen from Fig. 2c, the measurement period at the end of July exhibited a series of cloudless days, resulting in high incident solar irradiation with warm temperatures during the day and strong cooling, almost to the frost-point, at night. Nighttime temperatures are positively correlated with wind speeds (Fig. 2b) and infer the formation of strong nighttime inversions.

Increases of the CO mixing ratios of 30 nmol mol^{-1} within six hours (Fig. 3) can only partly be explained by reactive hydrocarbon oxidation ($\leq 3 \text{ nmol mol}^{-1}$ in the dry season; L. Otter, University of the Witwatersrand, pers. comm.), or the direct photochemical CO production from dead plant matter at the surface, as we have measured it. For example, the latter can account for an 8 nmol mol^{-1} increase at most if an average CO emission from the dead grasses of $1 \times 10^{12} \text{ molec. CO cm}^{-2} \text{ s}^{-1}$ (ground area) is assumed. During 29 July, wind speeds showed the same pattern as during the days before (Fig. 2b), and suggest that the planetary boundary layer rose quickly after sunrise, which could have lead to a vertical down mixing of polluted air from higher altitudes. Therefore, we assume that most of the observed variability was due to polluted air masses transported to our measurement site.

3.2. Soil trace gas emissions

Soil respiration emissions averaged between $40 \times 10^{12} \text{ molec. CO}_2 \text{ cm}^{-2} \text{ s}^{-1}$ ($\approx 0.7 \text{ g C}$

$\text{m}^{-2} \text{ d}^{-1}$) and $100 \times 10^{12} \text{ molec. CO}_2 \text{ cm}^{-2} \text{ s}^{-1}$ (soil humidity $\approx 1\% \text{ w/w}$), which is in accordance with previous data for the dry season given by Scholes and Walker (1993) and Zepp et al. (1996). CO₂ emissions were well correlated with top soil temperature and often reached two maxima: one in the morning, probably due to increased moisture availability in the form of dew, and one during the temperature maximum in the afternoon.

As soil CO fluxes were only measured in connection to total CO fluxes between the grass-soil system and the atmosphere, they are discussed here only briefly: Soil CO exchange showed the behaviour previously described by Conrad and Seiler (1985a). A daytime variation of the CO fluxes between the soil and the atmosphere during 28 July is shown in Fig. 4, together with measured soil temperatures. The soil typically acted as a net sink for CO. Only during the hottest part of the day, when topsoil temperatures exceeded 25°C , did the soil act as a net CO source. This compensation point temperature characteristic agrees with investigations by Conrad and Seiler (1985a). Average CO net deposition velocities at three different plots at the measurement site ranged from 0.7 to $1.9 \times 10^{-2} \text{ cm s}^{-1}$ for topsoil temperatures between 11°C and 18°C , decreasing with prolonged dryness. At another site a CO net deposition velocity of $(4.8 \pm 0.6) \times 10^{-2} \text{ cm s}^{-1}$ at a topsoil temperature of $4 \pm 1^\circ\text{C}$ was observed during the night. The latter plot was characterized by a dark reddish sandy soil with a higher pH and organic carbon content. In addition, soil

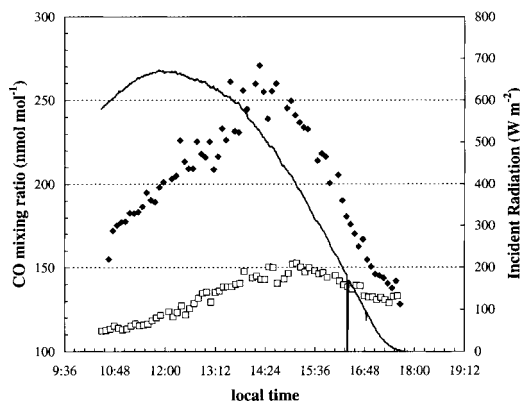


Fig. 3. Variation of solar irradiance (solid line), ambient (open squares) and grass chamber (solid diamonds) CO mixing ratios during 29 July 1996. Local time is local mean solar time plus 10 min.

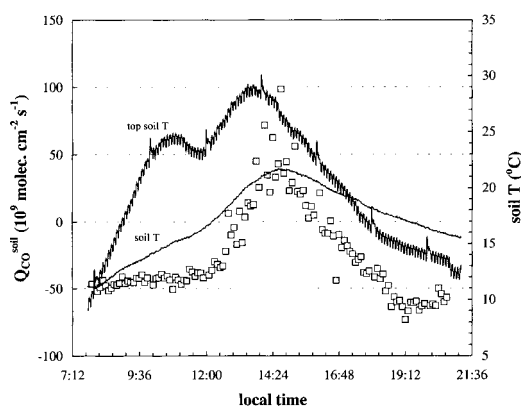


Fig. 4. Development of soil CO fluxes (open squares) and soil temperature during 28 July in the soil-chamber.

moisture was higher at that site due to 8 mm of rain two days before, and we expect that soil moisture is responsible for most of the observed variability. Our values are in favourable agreement with the results of Conrad and Seiler (1985a) for comparable soils in Andalusia, Spain, and the Transvaal, South Africa.

3.3. Dark CO emissions

Approaching sunset, CO mixing ratios in the grass chamber rapidly dropped and reached near ambient mixing ratios after sunset (data not shown). In the field experiments, CO deposition on the soil in the grass chamber was not determined directly. However, mixing ratios in the grass chamber were not significantly different from ambient, and the CO production in the grass chamber after sunset was confirmed by switching off the circulating pump: 2 to 3 measurement cycles (~ 15 min) revealed an increase in CO mixing ratio in the grass chamber and a decrease in the soil chamber, both significantly different from ambient. As the soil chamber data always exhibited a CO deposition shortly before and after sunset, we imply a non-photochemical CO source in the grass chamber, most probably thermal CO production from the dead dry grass matter.

We have measured several dry biomasses, deciduous leaves and grasses in the laboratory for their thermal CO production in the dark, and found that CO emissions rise exponentially with leaf temperatures. They can generally be described by an Arrhenius type equation, of which an example is shown in Fig. 5. The Arrhenius parameters evaluated for several dry grasses and other leaf material were calculated from linear regressions, and are summarized in Table 1 in Subsection 6.1. Q_{CO}^T denotes the thermal CO emission flux, E_a is the activation energy and A is the pre-exponential factor. An additional database for deciduous leaves and several model compounds for leaf chemical composition has been given by Schade (1997). Thermal CO production was not connected with CO₂ emissions, dropping at temperatures higher than 35°C. This points to a physical rather than a microbial CO source mechanism. Furthermore, it was found that most of the biomasses and other materials tested for CO emission had similar activation energies, implying a

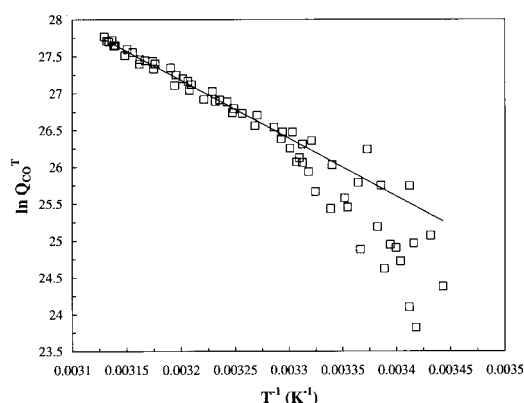


Fig. 5. An Arrhenius-plot for the grass *Trachypogon* sp., including the linear regression for temperatures between 30°C and 50°C. The calculated activation energy was $66 \pm 3 \text{ kJ mol}^{-1}$ and the A -factor was $6.0 \times 10^{22} \text{ molec. CO gdw}^{-1} \text{ s}^{-1}$.

similar chemical precursor group for CO production.

A nighttime measurement between 31 July and 1 August exhibited nearly stable ambient CO mixing ratios, even though a constant CO deposition on the soil of approximately $40 \times 10^9 \text{ molec. CO cm}^{-2} \text{ s}^{-1}$ was found. The constant $[\text{CO}]$ implies the presence of a nighttime source of CO, probably from the grass, approximately equal to the measured sink. A similar result was presented by Scharffe et al. (1990) for a Venezuelan savanna during the later part of the rainy season. They assumed the source to have come partly from termites and partly from local forest vegetation. Here, we propose another explanation, involving thermal CO production from standing dead plant matter and litter: At the end of the rainy season, a substantial amount of standing dead grass material has accumulated. Assuming an activation energy of 65 kJ mol^{-1} and an A -factor of $10^{23} \text{ molec. CO gdw}^{-1} \text{ s}^{-1}$ (Schade, 1997) for thermal CO production and a total amount of approximately 500 gdw m^{-2} of dead plant material, a CO emission of $14 \times 10^9 \text{ molec. cm}^{-2} \text{ s}^{-1}$ at a temperature of 20°C is calculated. Thus, a significant portion of the inferred CO source could have derived from dead grass matter. This conjecture is further supported by the results of the nighttime measurements shown in Fig. 6. Although the fluxes are within the total estimated measurement error, a clear trend of decreasing CO flux from the

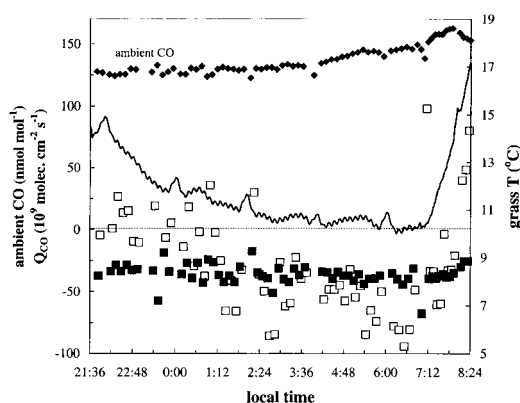


Fig. 6. Nighttime variation of CO fluxes in the soil chamber (solid squares) and in the grass chamber (open squares) (based on ground area), and development of ambient CO mixing ratios (solid diamonds) from 31 July to 1 August 1996. The solid line shows the grass temperature decrease during the night and its immediate increase after sunrise.

grass-chamber can be seen which parallels the grass temperature decrease. Ambient CO mixing ratios during this time remained almost constant until the early morning, when the wind transported contaminated air from biomass burning to the site (Fig. 6).

3.4. Photochemically induced CO emissions

3.4.1. Laboratory results. All biomass samples tested showed steadily increasing CO emissions with increasing irradiation intensity. Emissions could be up to ten times higher than those induced thermally in the dead organic matter and in almost all cases the increase was non-linear with light intensity, even after correction for simultaneously occurring thermal CO emissions via calculated Arrhenius parameters. This is demonstrated in Fig. 7, which depicts the functional dependence of photochemical CO emissions from a savanna grass (*Trachypogon sp.*) on incident irradiation from the solar simulator. As in this example, the dependence could generally be described by the second order polynomial

$$Q_{\text{CO}}^{\text{hv}} = a \times J_e + b \times J_e^2, \quad (2)$$

where $Q_{\text{CO}}^{\text{hv}}$ is the specific CO flux in $\text{molec. cm}^{-2} \text{s}^{-1}$ (irradiated leaf area), J_e is incident irradiation intensity in W m^{-2} , and a and b are constants which were calculated by a multili-

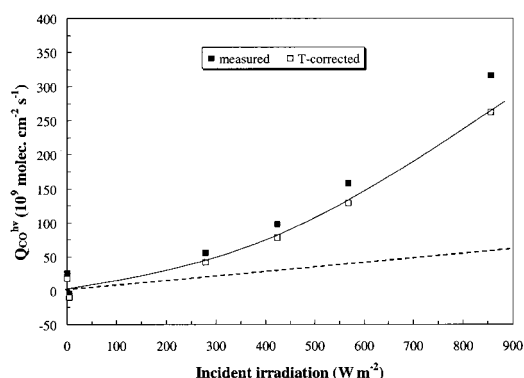


Fig. 7. Variation of photochemically induced CO emissions with incident radiation intensity J_e for the dry savanna grass *Trachypogon sp.* After temperature correction (open squares) of the measured values (solid squares) the functional dependence on light intensity is still non-linear. It obeys the second order polynomial given in eq. (2) (black regression line), the dashed line showing the linear term.

near regression. The parameter a varied only slightly within the different biomass groups with an average for all brown deciduous leaves of $(3.7 \pm 1.2) \times 10^{12} \text{ molec. J}^{-1}$ (1 sd), and $(5.8 \pm 2.1) \times 10^{11} \text{ molec. J}^{-1}$ (1 sd) for grasses. Deciduous leaves showed approximately a factor of two higher emissions than grasses. In addition to the observed quadratic increase with irradiation intensity, the CO emissions at a lower irradiation intensity often showed hysteresis effects, depending on the (higher) irradiation intensity of the previous measurement, as will be discussed with the field results.

Photochemically induced CO emissions were also dependent on irradiation wavelength (Tarr et al., 1995) as well as on leaf moisture. When deciduous leaves were irradiated under different UV filters, the CO emissions decreased notably, as can be seen from the example of relative CO emissions from beech leaves (*Fagus sylvatica*) shown in Fig. 8a. The most prominent decrease occurred after we had covered the chamber with the Makrolon[®] disc, so we conclude that the UV-A part (330–400 nm) of the simulated sunlight was most effective in CO photoproduction. We evaluated this aspect in more detail with the colour filters and UV-lamps, and calculated the relative action spectra of dry, dark brown beech leaves (*Fagus sylvatica*), and of a South American dry,

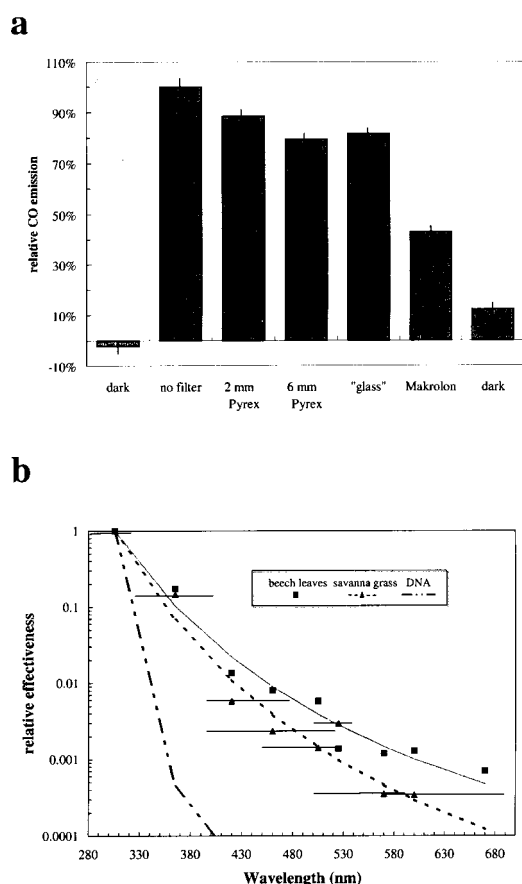


Fig. 8. (a) CO emissions from brown beech leaves (*Fagus sylvatica*) for a fixed irradiation intensity under different cut-off filters, relative to emissions without a filter (second bar). "Glass" depicts a commercial soda-lime glass (window-glass). Error bars represent 95% confidence intervals. The dark measurements were done before the irradiations, and thereafter. b) Calculated action spectra for the investigated dry biomass species *Fagus sylvatica* (squares) and *Trachypogon sp.* (triangles), compared to the relative DNA action spectrum (intercepted line). The gray, solid line and the dotted line are exponential fits to the data points for the equation $y = a \times \exp(-b/x)$. The horizontal bars represent the width at half height of the respective bandpass colour filter, with the exception of the last two points where they refer to the range from zero transmission to maximum transmission for the respective cut-off filter. Essentially no CO was emitted from *Trachypogon* under red light.

reddish brown savanna grass (*Trachypogon sp.*), shown in Fig. 8b. CO emissions were normalized to the emission at 306 nm, the maximum radiation wavelength of the UV-B lamps. Relative CO emissions from both beech leaves and the savanna grass decreased exponentially with increasing wavelength, but were still induced by visible light. Both action spectra were very similar, except that the relative effectiveness of emissions from the savanna grass under green light irradiation was higher than under blue and yellow light. We note that an analogous variation has been observed by Valentine and Zepp (1993) for CO emissions from fresh waters. For comparison, Fig. 8b includes the relative action spectrum of DNA damage, which is much steeper in the UV part of the spectrum.

Evaluation of the influence of leaf moisture (expressed as percent weight per fresh weight) was carried out only with deciduous leaf biomasses, and an example is shown in Fig. 9. CO emissions were always found to decrease as the material dried out. The decrease was linear but its slope was different for different leaf species, and could be as high as $-5.0 \pm 2.6\% \%^{-1}$ (relative emissions change per absolute moisture change) in ash leaves (*Fraxinus pennsylvanica*) (Schade, 1997). A corresponding decrease by $1\% \%^{-1}$ in a range from 50% to 20% moisture content has been previously reported by Hon (1975a) for the production of radicals in irradiated cellulose. The results suggest that water may take part in the CO emitting mechanism in which case we can assume that a hydrolysis plays an important role.

Part of these results have previously been

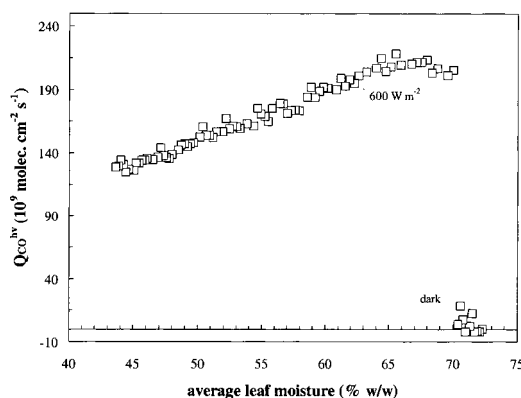


Fig. 9. Variation of CO emissions from moist oak leaves (*Quercus robur*) at a fixed light intensity.

described by Tarr et al. (1995), however, these authors could not observe the non-linear dependence on incident irradiation because they measured only at one light intensity. Additionally, they did not report on CO emissions caused by irradiation at wavelengths in the visible, which can cause approximately 40% of the total emissions, as shown in Fig. 8a. Furthermore, the dependence on leaf moisture has not been previously evaluated. As wetting can induce drastically higher CO emissions for certain leaf species, extrapolations from data retrieved from dry leaves can lead to underestimates.

3.4.2. Field results. The photochemically induced CO emission fluxes ($Q_{\text{CO}}^{\text{hv}}$) are derived by subtracting thermally induced CO fluxes (Q_{CO}^{T}) and soil CO fluxes ($Q_{\text{CO}}^{\text{soil}}$) from the total CO fluxes ($Q_{\text{CO}}^{\text{tot}}$):

$$Q_{\text{CO}}^{\text{hv}} = Q_{\text{CO}}^{\text{tot}} - Q_{\text{CO}}^{\text{soil}} - Q_{\text{CO}}^{\text{T}}. \quad (3)$$

This calculation presumes that the soil CO fluxes in the grass chamber are comparable to the soil CO fluxes in the soil chamber. Since CO deposition on the soil increases with increasing CO concentrations (Conrad and Seiler, 1985a), and CO concentrations were always higher inside the grass chamber, $Q_{\text{CO}}^{\text{soil}}$ values may have been underestimated at least during daylight hours. Q_{CO}^{T} was calculated using Arrhenius parameters of thermal CO production from the respective grass and the measured dry weight, as evaluated under controlled conditions in the laboratory (Subsection 3.3).

The CO fluxes from two grasses, *Tristachya rehmannii* and *Schizachyrium sanguineum*, were followed for several days. We had chosen these grasses based on their appearance in terms of colour and architecture: *Tristachya* was light yellow with only some parts showing darker colours, e.g. the remainders of spikelets. The grass was dense at its base with several shoots up to 120 cm. The majority of dead savanna grasses have a similar appearance. In contrast, *Schizachyrium* appears dark reddish brown in colour. It was less dense at its base but had much more shoots, which gave it a more uniform structure. Together, these two grass species may represent the range of different colours and architectures exhibited by dead dry grasses.

The fluxes determined based on eq. (3) are

shown in Fig. 10a, b (fluxes are given as chamber CO fluxes, because areal references of CO fluxes are different: ground area for $Q_{\text{CO}}^{\text{soil}}$, and irradiated grass surface area for $Q_{\text{CO}}^{\text{hv}}$). The dark reddish brown grass emits approximately twice as much CO as the light yellow grass. Both grasses show a hysteresis effect, i.e., a significantly higher CO emission for a given light intensity in the afternoon than in the morning. The hysteresis effect is much stronger for the dark grass than for the light grass. Furthermore, Fig. 10b shows a strong rise of CO emissions for *Schizachyrium* during midday hours, what are probably a result of the higher ratio of UV radiation to total radiation found with lower solar zenith angles. At midday, the UV-A to total incident solar radiation ratio at our site was 5% to 10% higher than 2 h before or after noon.

We note that a similar result was presented by Zepp et al. (1997, Fig. 5) for soil CO emissions as influenced by sunlight on a previously burned plot in Canada. However, the authors did not address the observed non-linear increase of emissions with light intensity.

Around noon of 30 July, we totally wrapped the outside of the grass chamber with black plastic bags for a period of 30 minutes to further evaluate the contribution of photochemical and thermal CO production on total CO emissions. A dramatic and continuous decrease of CO emissions down to approximately one third of initial CO emissions in the light occurred, whereas grass chamber temperatures during the dark period dropped only slightly. Fig. 11 shows the development of CO emissions from *Tristachya rehmannii* with incident irradiation during that day, as calculated from equation 3. Interestingly, $Q_{\text{CO}}^{\text{hv}}$ did not drop to zero as might be expected. That phenomenon can neither be explained by temperature gradients in the chamber nor by the soil CO fluxes because these were much lower than the grass CO fluxes. Furthermore, after removal of the black cover (arrow in Fig. 11), CO emissions did not recover immediately to pre-darkening values but increased slowly to overtake morning values about 1 h later.

A similar feature occurs in the evening, and is shown in Fig. 10b: For *Schizachyrium sanguineum* on 28 July the temperature corrected CO emission values, while steadily decreasing, persisted for three hours after sunset, as illustrated by the inset graph. We explain this behaviour to be a result of

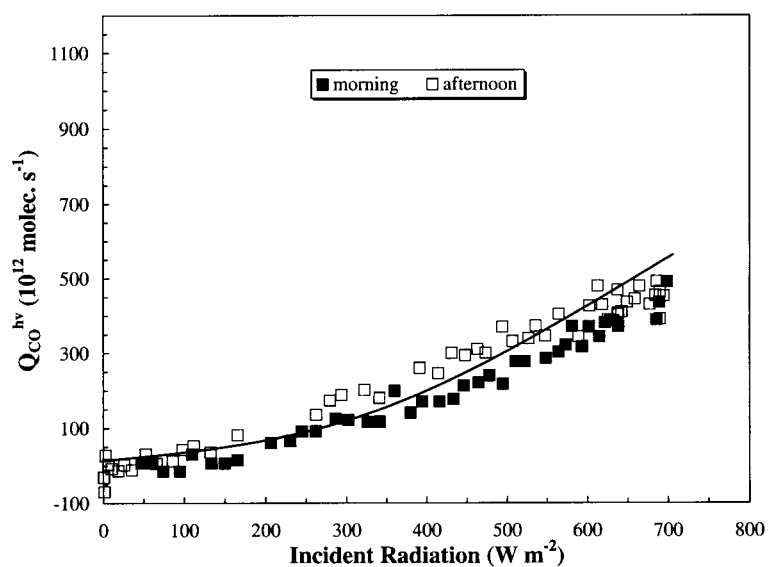
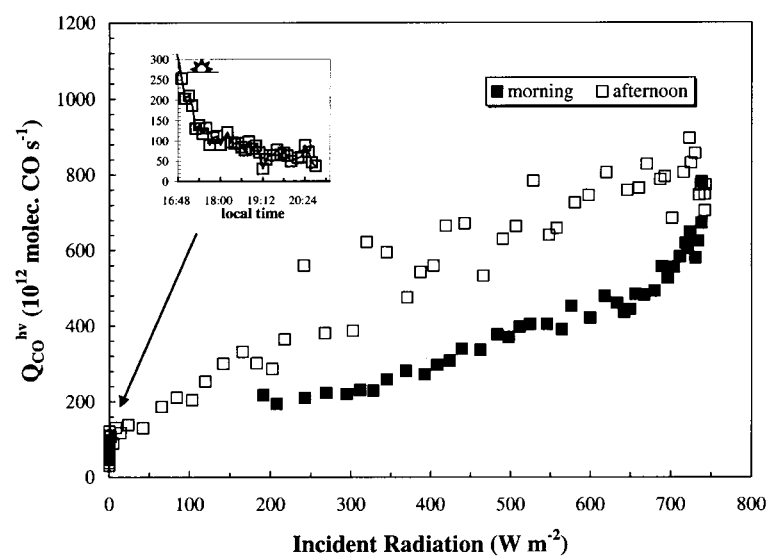
a**b**

Fig. 10. (a) Calculated, solely photochemical CO emissions from *Tristachya rehmannii* versus incident irradiation intensity. A non-linear increase and the hysteresis effect can be noticed (morning values smaller than afternoon values). Flux is given as chamber flux. (b) Same as (a), but for *Schizachyrium sanguineum*. The inset graph shows the time development of Q_{CO}^{hv} after sunset which occurred around 17:30 local time.

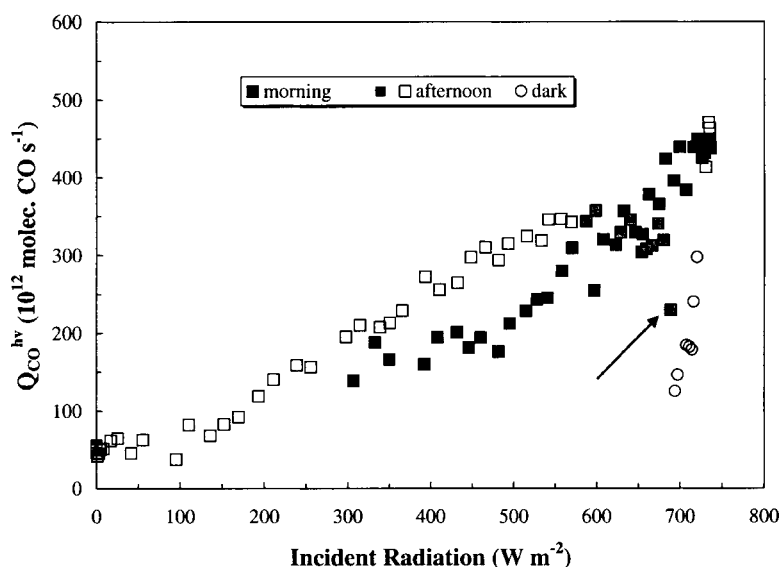


Fig. 11. Same as Fig. 10 for *Tristachya rehmannii* on 30 July. The values during the darkening experiment are shown as open circles, and are left at the position of actual incident radiation to demonstrate how litter emissions behave before, during, and after the darkening (see text). The latter ones are depicted in gray for identification, an arrow pointing to the first value after removing the black cover.

the two-step photochemical CO production mechanism, which is outlined in detail in Section 6.

4. Conclusions

We have presented CO emissions from various kinds of degrading plant matter in the laboratory and under field conditions. The results show that CO is produced thermally as well as photochemically from the plant matter, the latter being the dominant source during the day in the field, and more important on a diurnal basis. The dependence on incident irradiation exhibits a linear plus quadratic increase with light intensity and a hysteresis effect, which seems to be dependent on the grass' appearance in terms of colour and architecture. Investigation of the effects of different wavelengths of irradiation shows that the UV-A part of the solar spectrum will be most efficient in CO production from degrading leaf and grass matter. However, CO production from visible radiation can contribute up to 40% of the total emissions. Due to the hysteresis effect, which we presume to be due to an accumulation of a CO precursor in the dead plant material, probably carbonyl groups,

and the influence of moisture, actual CO emission in the field will depend on present and past weather conditions: Wet leaf litter emits more CO than dry leaf litter, and clear skies produce more CO than partly cloudy skies, because intermittent radiation mostly decreases CO precursor accumulation.

Bare soil CO fluxes showed the expected diurnal variation described previously. However, our nighttime data suggest that thermal CO production from the dead savanna grasses could partially compensate for simultaneous soil CO deposition. Thermal CO production from the grasses follows the Arrhenius equation, so that a possible compensation of soil CO deposition strongly depends upon temperature. We measured Arrhenius parameters for several kinds of decaying biomasses. We also found that moisture enhances thermal CO production (see, e.g., Table. 1). Therefore, we expect moist and fresh litter layers like they occur in the tropical rain forest to be potential sources of CO.

The data on photochemical and thermal CO production in degrading plant matter presented in this study are used in the accompanying paper to estimate a global gross source of CO production

in standing dead plant material and litter (Schade and Crutzen, this issue).

5. Acknowledgements

We are indebted to Luanne Otter for her help and company during the field measurements as well as for sampling fallen leaves from deciduous trees in the Nylsvley Nature Reserve. Thanks to Bob and Mary Scholes for useful comments on how to handle the field measurement data, and three anonymous reviewers for their valuable comments. We also like to thank Orlando Vargas, Joel Alvarado and Tania Brenes from the La Selva Biological Station in Costa Rica for sampling a litter composite from the tropical rain forest, and Jesine Quesada for organization.

6. Appendix

6.1. Plant material

In this study, we examined CO emissions from deciduous leaves and grasses. Deciduous leaves were chosen because they constitute the biggest portion of plant litter on a dry matter basis while grasses were chosen because they are the dominant species in "open" ecosystems where light reaches the ground unintercepted.

Deciduous leaves were sampled at different times after leaf fall. Leaves were collected from the university campus and its botanical garden in Mainz, Germany, except for leaves from *Fagus sylvatica* (European beech, the dominant tree in central Europe), which were sampled throughout the year at a beech forest site approximately 50 km north-west of Mainz. Species studied included beech (*Fagus sylvatica*, *Fagus orientalis*), birch (*Betula* sp.), oak (*Quercus robur*, *Quercus* sp.), maple (*Acer platanoides*, *Acer sacharinum*), ash (*Fraxinus pennsylvanica*, *Fraxinus augustifolia*), elm (*Ulmus laevis*, *Ulmus pumila*), poplar (*Populus canadensis*, *Populus nigra* var. *italica*), and chestnut (*Aesculus hippocastanum*). Savanna grasses, sampled previously in Africa and stored in the institute in the dark for 2 months to 5 years, included *Hyparrhenia cymbia*, *Capillipendulum parviflorum*, *Schizachyrium sanguineum*, *Tristachya rehmannii*, and *Eragrostis pallens*. Additionally, a typical grass from South American savannas, *Trachypogon* sp.,

which had also been stored for several years in the institute, and an annual grass from the university campus, *Bromus hordeaceus*, collected in the summer of 1995, were analyzed for their CO emissions in the laboratory.

The deciduous leaves were kept in polyethylene bags in a refrigerator at 5°C for at least two days prior to a measurement to allow for moisture equilibration. Leaf samples of 10 to 40 g fresh weight were then taken out of the bag for CO emission measurements without further treatment, the dry weight of a sample was measured after emission measurements and drying of the material at 100°C overnight. The handling was similar for the grasses except that they had been stored at room temperature prior to analysis.

Thermal CO production from the various litters was measured from air-dry material and followed an Arrhenius type equation. The Arrhenius parameters calculated for several selected grass and leaf biomasses are given in Table 1. They served as the basis for the estimate on global thermally induced CO emissions from litter pool values (Schade and Crutzen, this issue).

6.2. Origin of CO production from degrading plant matter

Due to our laboratory results (data not shown), the dominating chemical source of CO is most probably plant cellulose (Schade, 1997), which can either be photolyzed to give CO directly (Hon, 1979, and references therein), or accumulates carbonyl groups from the photochemical oxidation of the OH groups in the cellulose. Minor sources include plant lignin and polyphenols, chemical constituents which are also thought to be the major precursors of thermal CO production in soils (Conrad and Seiler, 1985b) and litter (Zepp et al., 1996; Schade, 1997).

An explanation for the observed dependencies on solar irradiation intensity, and the hysteresis effect, is a two-step photochemical mechanism of CO production, which we have outlined in detail below. The quadratic rise of CO emissions with irradiation intensity is obtained when two photons are absorbed to produce one CO molecule, that is, in the second step an intermediate product produced by absorption of the first photon is photolyzed to give CO. That intermediate accumulates at high irradiation intensities and consti-

Table 1. Evaluated Arrhenius parameters and measured thermal CO emissions at 25°C of some degrading grasses (upper panel), as well as temperate (middle panel) and tropical (lower panel) deciduous leaf matter

Biomass (latin name)	$E_a \pm 2 \text{ sd}$ (kJ mol ⁻¹)	A-factor (molec. gdw ⁻¹ CO s ⁻¹)	Q_{CO}^1 (25°C) (molec. gdw ⁻¹ CO s ⁻¹)	T (range)	Approximate age (leaves), or origin
<i>Trachypogon</i> sp.	66 ± 3	6.0 × 10 ²²	1.3 × 10 ¹¹	30–50°C	South America
<i>Capillipendulum parvif.</i>	81 ± 3	2.4 × 10 ²⁵	1.1 × 10 ¹¹	30–50°C	West Africa
<i>Hyparrhenia cymbia</i>	67 ± 6	5.6 × 10 ²²	< 1 × 10 ¹¹	30–50°C	West Africa
<i>Tristachya rehmannii</i>	65 ± 6	2.5 × 10 ²²	≈ 1 × 10 ¹¹	30–60°C	Nylsvley
<i>Schizachyrium sanguineum</i>	77 ± 7	2.9 × 10 ²⁴	≈ 1 × 10 ¹¹	40–60°C	Nylsvley
<i>Eragrostis pallens</i>	39 ± 2	2.6 × 10 ¹⁸	3.5 × 10 ¹¹	20–65°C	Nylsvley
<i>Bromus hordeaceus</i> l.	66 ± 5	8.3 × 10 ²²	2.5 × 10 ¹¹	20–60°C	Mainz, campus
European beech (<i>Fagus sylvatica</i>)	84 ± 4	9.6 × 10 ²⁶	2 × 10 ¹²	20–60°C	2 months
	87 ± 12	6.3 × 10 ²⁶	4 × 10 ¹¹	20–40°C	7 months
	90 ± 4	2.2 × 10 ²⁸	3 × 10 ¹²	4–27°C	4–5 months (wet)
	90 ± 8	1.2 × 10 ²⁸	2 × 10 ¹²	5–25°C	4–5 months (wet)
	54 ± 3	5.7 × 10 ²¹	7 × 10 ¹²	10–70°C	freshly fallen (dry)
	84 ± 8	4.2 × 10 ²⁵	0.6 × 10 ¹²	30–80°C	more than 1 year
oak (<i>Quercus robur</i>)	69 ± 4	6.7 × 10 ²³	0.9 × 10 ¹²	30–65°C	about 1 year
maple (<i>Acer saccharinum</i>)	84 ± 40	9.3 × 10 ²⁴	≤ 0.1 × 10 ¹²	35–65°C	about 1 year
ash (<i>Fraxinus pennsylv.</i>)	85 ± 6	3.4 × 10 ²⁷	1 × 10 ¹²	15–50°C	1 month
Poplar (<i>Populus nigra</i>)	89 ± 3	3.8 × 10 ²⁷	1.2 × 10 ¹²	25–55°C	1 month
<i>Terminalia sericea</i>	119 ± 3	3.1 × 10 ³²	5.0 × 10 ¹¹	15–65°C	Nylsvley
<i>Burkea africana</i>	88 ± 1	5.4 × 10 ²⁶	2.5 × 10 ¹¹	15–65°C	Nylsvley
<i>Combretum zeyheri</i>	89 ± 2	2.2 × 10 ²⁷	8.0 × 10 ¹¹	20–70°C	Nylsvley
Rain forest mixture ^a	75 ± 3	5.0 × 10 ²⁴	3.5 × 10 ¹¹	15–65°C	Costa Rica, dry
Rain forest mixture ^a	74 ± 2	1.0 × 10 ²⁵	1.2 × 10 ¹²	15–75°C	Costa Rica, wet

^aMixture of species sampled in a rain forest area in Costa Rica.

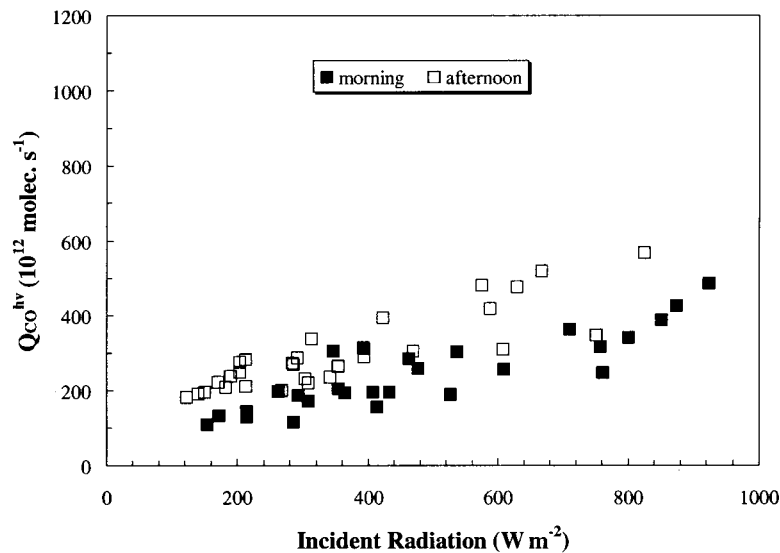


Fig. 12. Same as Figs. 10, 11 but for *Schizachyrium sanguineum* during a partly cloudy day.

tutes the source for the hysteresis effect. When that accumulation is hindered, as, e.g., due to clouds, the CO production is dominated by another, direct CO emitting mechanism (Schade, 1997). Furthermore, the results infer that a possible intermediate is also a CO source in the dark, so it will not be accumulated from day to day.

The CO emissions shown in Figs. 10, 11 were all measured during cloudless days prevailing during the measurement period (Fig. 2). Results from *Schizachyrium sanguineum*, obtained on a partly cloudy day (25 July) are shown in Fig. 12. Despite higher solar irradiation intensities were encountered due to additional reflection when a cloud passed by, CO emissions during these episodes were lower, and the dependence of CO emission on incident radiation seemed to be linear. Daily integrated CO emissions weighed by the available light were 40% lower than during cloudless days. Nevertheless, the hysteresis effect could still be discerned.

A photochemical mechanism to explain this behaviour of CO emissions can be hypothesized, based on the various results shown here for beech leaf litter under different environmental conditions, and several chemical model compounds investigated in the laboratory (Schade, 1997). Here, we address only the major features: CO emissions probably take place via two different reaction pathways: One emission pathway is proportional to incident radiation intensity, J_e , and one is proportional to its square, J_e^2 . Within the chemical model compounds irradiated only recycled paper, α -cellulose and methylcellulose emitted CO in approximately equal amounts to the degrading plant material, thus, we believe that the cellulose chain is the dominating photochemical source of CO. After direct photochemical or photosensitized cleavage of the α -glycosidical carbon bond in the cellulose chain, several different radicals can be formed (Hon, 1976a, 1976b, 1979, and references therein), a few of which are depicted in Fig. 13. The important radicals to be produced are the ones which carry the radical function at C-atom 1 (approximately in the middle), and possibly also the oxy-radical down the left chain of the mechanism. CO via this mechanism would be emitted "promptly". Hence, this mechanism is proportional to J_e . It is supported by the linear effect of water on CO emissions (Fig. 9), because the hydrolysis seen in the

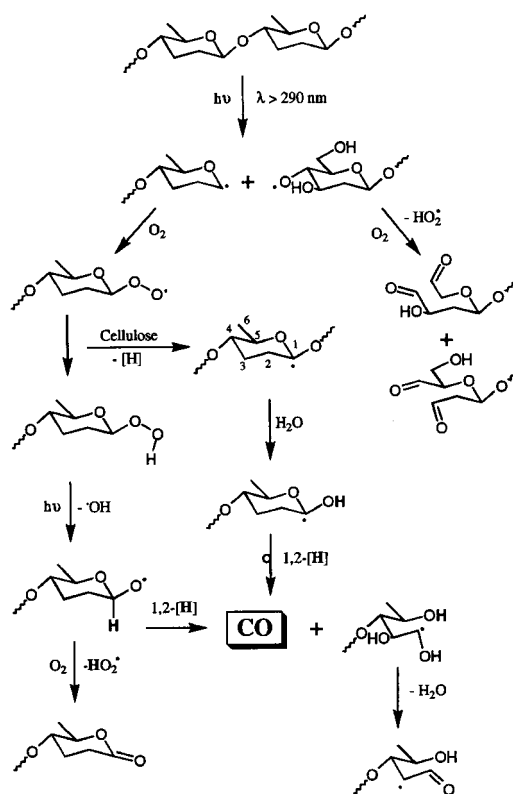


Fig. 13. Presumed chemical mechanism for a CO production proportional to incident irradiation intensity. The first step is a cleavage of the α -glycosidical bond in the cellulose chain. Only one photon is absorbed to produce one molecule of CO emitted.

middle of Fig. 13 has an order of reaction of one. It is further supported by the result that irradiation under a nitrogen atmosphere still produces substantial amounts of CO (30% to 40%; Schade, 1997), because the radical in question to produce CO can be generated simply by H-atom abstraction from C-atom 1. This can be achieved by a photosensitizer such as Fe^{3+} , humic acid or quinones (Wells, 1961a, 1961b; Hon, 1975b; Atherton et al., 1993; Hendry et al., 1994; Pillinger et al., 1996).

As can also be seen from Fig. 13, during these and similar photochemical transformations carbonyl-groups are produced in the material which are additional photochemical precursors of CO via the Norrish Type I cleavage. This explains the observed quadratic dependence of CO emissions on irradiation intensity, and the hysteresis effect,

seen in Figs. 10, 11. The latter is due to the accumulation of these groups in the material (Hon, 1979; Tolvaj and Faix, 1995). More carbonyl groups are formed in the presence of high irradiation intensities than in the presence of low irradiation intensities. As the decay of carbonyl groups is a slow reaction compared to their production from alcohol groups, increasing radiation intensities during the day result in the buildup of a reservoir of carbonyl groups. This may reach a maximum at noon and represents an additional precursor pool from which there is delayed CO emission. The greater the portion of CO emitted from such a pool, the greater is the hysteresis effect. The difference in the observed hysteresis between the two grasses, as well as the difference in total CO emissions at a certain light intensity, could be a result of their different appearance. Leaf colour during senescence and death is influenced by condensation reactions of polyphenols, which can act as photosensitizers. The delayed CO production mechanism predicts that CO emissions are proportional to the photosensitizer concentration, hence, the darker grass, which has a

stronger light absorption, is expected to show higher CO production.

Our results indicate that carbonyl groups are also degraded in the dark. Photochemically produced radicals in the plant material do not disappear instantaneously after removal of radiation, and thus could still attack carbonyls, possibly resulting in the observed dark source of CO (Fig. 10b). Hence, the slow decline after darkening or after sunset may reflect radical decay in the dead plant material. Additionally, the difference in CO emissions for the same grass at similar light levels could be explained by a missing accumulation of carbonyls during prior light levels under cloudy conditions. The linear dependence on incident radiation during 25 July (Fig. 12) may therefore reflect the dominance of promptly emitted CO over delayed CO emission. Direct irradiation of the dead plant matter was probably not long enough to accumulate a significant amount of carbonyls as during cloudless days. Therefore, we presume that photochemically induced CO emissions are generally the highest during cloudless days because of a significant accumulation and photolysis of carbonyls in the dead plant matter.

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