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Carbon monoxide production and emission by some Scottish soils

By J. M. MOXLEY[1] and K. A. SMITH[2]†, [1] *Soils Dept, SAC* and* [2] *Institute of Ecology and Resource Management, University of Edinburgh, School of Agriculture Building, West Mains Rd, Edinburgh EH9 3JG, Scotland, UK*

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ABSTRACT

When mineral soils from woodland, grassland and arable environments in Central Scotland were air-dried, they became net sources of CO; production rates were greatly increased by oven-drying at 104°C. The soils also produced CO after sterilisation by autoclaving and gamma irradiation. It was concluded that the CO production process involved non-biological decomposition of humic materials; addition of such materials to soils enhanced production. When moist, the soils were normally net sinks for CO, but in the presence of 1000 ppmv of acetylene (an inhibitor of microbial oxidation of CO), they became net sources. Net CO emission was observed in a peatland, in the field, during the wetter months of the year. Here, the CO production was apparently due to a different process from that responsible for production in the dried soils, probably involving anaerobic microbial activity. A possible upper limit of 0.2 Tg y^{-1}, for emissions of CO from northern hemisphere wetlands, was calculated on the basis of this part of the study.

1. Introduction

Carbon monoxide, CO, is an important trace gas as it is the main atmospheric sink for the hydroxyl radical, $OH^{\cdot}$, which oxidises many other trace gases, including radiatively active ones such as methane. In the troposphere it is also involved in the production of ozone in the presence of sufficient NO_x, but where the latter is very low CO acts as a sink for ozone (Wayne, 1991).

The sources and sinks of CO are finely balanced, and to predict changes in CO mixing ratio, it is important to have better estimates of the size of all significant sources and sinks. Soils are generally thought to be a net sink for CO, which is oxidised to CO_2 by microorganisms. Measurements have been made mainly in temperate regions, with moist, aerobic soils; there are few data for waterlogged or arid soils in the tropics or high latitudes, but those field measurements that have been made in arid regions, and laboratory work, suggest that soils may be net sources of CO when dry, and that production rates are enhanced when the soil is rewetted (Smith et al., 1973; Conrad and Seiler, 1982, 1985a). CO production is increased in autoclaved soils, suggesting that it is a non-biological process (Smith et al., 1973). In the field, emission occurs in the dark as well as in the light, which suggests that the CO production process is not photochemical (Conrad and Seiler, 1985a). In the tropics, soils were found to be net sinks for CO at night, and net sources in the daytime, attributed to the strong temperature dependence of the non-biological production of CO (Scharffe et al., 1990; Sanhueza et al., 1994). This production is thought to be due to the oxidation of

† Corresponding author.
e-mail: k.a.smith@ed.ac.uk
* Current address: 17 Woolfords Cottages, by West Calder, Lanarkshire, Scotland EH55 8LH, UK.

humic acids and other phenolic substances in the soil under aerobic conditions (Conrad and Seiler, 1985b). In field experiments, CO production was shown to depend on the total organic carbon (TOC) content of the soil (Conrad and Seiler 1985a). At the outset of this investigation it was not known whether CO production by aerobic soils is mainly restricted to soils from tropical and arid regions, or whether soils from cool temperate regions which normally act as a sink for CO become sources under some conditions.

Net CO production (37 μg CO m^{-2} h^{-1}) has also been reported from cores of water-logged tundra soils incubated in the laboratory, and attributed to a biogenic process, possibly linked to methane production (Funk et al., 1994). However, to date, the only direct field measurements of CO production by waterlogged soils have been in rice paddies, where fluxes in the range of 12–110 μg CO m^{-2} h^{-1} have been recorded (Conrad et al., 1988, Khalil et al., 1990). There is also evidence from airborne measurements that there are sources of CO close to the ground in the Amazon basin (Harriss et al., 1990; Kirchoff and Marinho, 1990) and the North American tundra (Gosink and Kelly, 1979; Ritter et al., 1992, 1994). However, it is not clear whether the CO is emitted from the soil, or directly from the vegetation. The North American tundra source had a strength of up to 2.4 mg CO m^{-2} h^{-1} (Ritter et al., 1994). Modelling work by Potter et al. (1996) suggested that CO emissions due to the oxidation of soil organic carbon, mainly in the tropics, may offset a significant portion of the global CO sink in soils.

To allow better estimates to be made of CO fluxes to and from different soil types, it is important to know more about the processes leading to CO production. This investigation used laboratory incubations to explore factors affecting CO production by aerobic soils, and field measurements over a one year period to investigate CO fluxes from a peatland site, which was waterlogged during the winter, but drier in summer.

2. Material and methods

2.1. Gas analysis

Carbon monoxide mixing ratios were measured using an RGA3 Reduction Gas Analyser (Trace Analytical, Menlo Park, California, USA) — a dedicated gas chromatograph with a mercury vapour detector (Seiler et al., 1980). Purified compressed air (zero grade, BOC Speciality Gases, Guildford, UK) at a flow rate of 20 ml min^{-1} was used as the carrier gas. The instrument was fitted with a 1 ml sample loop which was filled by flushing with a 5-ml sample from a syringe. A 1000 ppbv CO in air standard (prepared gravimetrically by BOC Speciality Gases, Guildford, UK) was used for calibration. This standard had not been cross-calibrated against international reference standards, but the supplier claimed an accuracy of better than $\pm 1\%$ of the nominal mixing ratio.

2.2. Laboratory studies

Details of the soils studied are given in Table 1. Except where otherwise stated, the soil samples used were from 0–10 cm depth. The soils were passed though a 2 mm mesh sieve to remove roots and stones, and stored in a refrigerator at 4°C for up to 2 weeks prior to use. Drying, when required, was carried out at either room temperature or 104°C, to constant weight. Soil sterilisation was done either by autoclaving for 30 min or gamma irradiation with a dose of >25 kGy in a cobalt 60 unit.

Measurements of CO production rates were made in triplicate. For each soil, 20 g was placed in a 1.5 l air-tight glass preserving jar sealed with a rubber gasket. The atmosphere in the jar at the start of each experiment was normal ambient air, with an initial CO mixing ratio of about 150 ppbv. With no soil in the jar, there was a very low rate of change of CO mixing ratio ($\leqslant 0.06$ ppbv h^{-1}), possibly due to the rubber gasket. Each jar had 3 holes drilled in the lid to accommodate inlet and outlet tubes and a septum to allow samples to be taken using a gas-tight glass syringe, with a PTFE plunger that did not need to be greased. The jars were incubated at room temperature (ca. 25°C). 5-ml gas samples were taken from each jar for gas analysis at 30 min intervals for 6 h. CO mixing ratios generally increased linearly over this period, and fluxes were calculated from the regressions through all 12 points (equilibrum mixing ratios were not reached for several days).

During some incubations, carried out with field-moist soils, 1000 ppmv acetylene (an inhibitor of microbial oxidation of CO; Bédard and Knowles, 1989) was added to the headspace in the jar. In

Table 1. *Details of Scottish soils sampled for laboratory studies of CO production*

Origin	Land use	pH[a)]	Organic C ($g\,kg^{-1}$)	Texture
Cowpark field, Glencorse Mains, Midlothian	grassland (cut for silage)	6.7	33	sandy clay loam
	mixed woodland	6.7	60	sandy clay loam
Bush Estate, Midlothian	arable	6.5	17	sandy loam
	coniferous woodland	4.0	76	sandy loam
	deciduous woodland (wet area)	4.0	73	sandy loam
	(dry area)	4.3	20	sandy loam
Gullane, E. Lothian	arable	8.7	11	loamy sand
	mixed woodland	8.3	31	loamy sand

[a)] In H_2O.

others, a solution of the nitrification inhibitor dicyandiamide (DCD) was used, to give a concentration of 100 mg kg^{-1} fresh soil; an equal volume of water was added to other replicates to provide a control. To investigate the effect of light on CO production by dried soils, samples of all the soils from Bush (Table 1) were air dried at room temperature, and the CO production rate measured in the light and in the dark. To see whether there was an optimum water content for CO production, soils from Bush and Gullane were dried to constant weight at room temperature rewetted with deionised water to give a range of water contents for each soil, and then incubated as described above.

To investigate further the effects of sterilisation, drying and wetting of soils, and the interactions between them, and to try to determine which components of soil organic matter were responsible for the production, a series of 2^4 factorial experiments were carried out. The experiments were repeated for each of 4 soils (woodland and arable soils from Gullane, dry deciduous woodland and arable soils from Bush), and with 6 different organic materials. The materials used, chosen to represent different classes of soil compounds, were cellulose, glucose, humic acid, sodium acetate, starch, and sucrose (Fluka Chemie AG, Buchs, Switzerland). In this experiment, drying was carried out at room temperature to constant weight; sterilisation was by gamma irradiation; organic material additions were of 0.025 g organic material g^{-1} soil, and wetting was with 0.25 ml deionised water g^{-1} soil. Treatments were carried out in the order drying, sterilisation, addition of organic material, wetting. The experiment was repeated using each of the six organic materials with each of 4 different soils (arable soil and soil from the dry area of deciduous woodland at Bush, and arable and woodland soil from Gullane).

2.3. *Field measurements*

Measurements of CO fluxes were made approximately once a fortnight at Springfield Farm, Leadburn, Midlothian, Scotland, UK (55°47′N, 3°14′W, Ordnance Survey grid reference NT 221562) from 23 February to 19 December 1995. The mean annual temperature for this site was 7.5°C, and the rainfall 803 mm (C Flechard, pers. comm.). Flux chambers made of PVC, 38.5 cm i.d., 20 cm high (Smith et al., 1995) were used, inserted 6 cm into the ground. The 14 cm high head space was closed with a removable aluminium lid, fitted with a rubber gasket to make a gas-tight seal while fluxes were being measured. A sampling port with a tap was installed in the lid. Measurements made in the absence of soil, with the chambers standing in water to make a seal, showed that they produced some CO, 2.5 μg m^{-2} h^{-1} at 25°C in the light, which was very much smaller than the rates of CO production from the soil.

The peat layer at the site was 30 cm deep, and had a pH of 3.2. The vegetation consisted mainly of mosses such as *Sphagnum* and *Polytrichum*, and sedges (*Carex ovalis* and *C. nigra*) in the wetter areas, while the drier areas were dominated by grasses, especially *Deschampsia flexuosa*, *Molinia*

caerulea, *Eriophorum vaginatum*, *E. angustifolium*, *Festuca ovina* and *F. rubra*. There were also scattered patches of heathers (*Erica tetralix*, and *Calluna vulgaris*) and bilberry (*Vaccinium myrtillus*). Three chambers were used, one enclosing mainly *Sphagnum*, on an area of wetter ground, with the others, on an intermediate and a dry area, respectively, enclosing a mixture of species, with some dead or dying material present.

During sampling periods, the lids were placed on the chambers, and 5 ml samples withdrawn every 5 min for 20 min, using gas-tight syringes which could be closed with 3-way taps while they were transported by car back to the laboratory for analysis. This procedure only allowed the determination of net CO fluxes, and did not allow separate measurements of CO production and CO oxidation to be made directly.

Experiments with a 1000 ppbv standard showed that the CO mixing ratio in the syringes could change by up to 0.5% (5 ppbv) h^{-1}. These changes were thought to be due to leaks. Samples were normally analysed within 3 h of collection, so the maximum change in CO mixing ratio to be expected was $\leqslant 1.5\%$ of the initial value. As the syringes were known to leak at temperatures below 10°C, in winter they were kept in a polystyrene box containing a hot-water bottle. On each occasion that gas samples were taken, soil samples were collected from within 1 m of each chamber for analysis. Soil samples were normally taken from 3 different locations per chamber, and bulked together prior to analysis. From June 1995 to February 1996, samples of the soil atmosphere were taken from 30 cm long brass tubes, 0.4 cm in diameter, capped by rubber septa. Triplicate sets of tubes were inserted to 3, 6, 9, 12, 15, 18, 21, 24, and 27 cm depths close to the wettest and driest chambers, to determine CO mixing ratio profiles. The water table depth was also recorded, by making dip-stick measurements in a 2 cm diameter well, lined with plastic pipe, The water content of duplicate samples of soil was determined gravimetrically. On each sampling occasion, the soil temperature at 10 cm was measured, using an electronic temperature probe placed outside the chamber within 5 cm of the chamber wall.

3. Results

3.1. Laboratory incubations

All the soils, which other measurements (Moxley and Smith, 1997) had demonstrated to be normally sinks for CO, were converted into sources by drying. CO mixing ratios generally showed linear increases over 6 h. Table 2 and Fig. 1 show the rates of CO production from soils which had been dried at either room temperature or 104°C, and which had then either been left dry or re-wetted to maximum water holding capacity. ANOVA showed that both increasing the drying temperature and rewetting the soil significantly increased the rate of CO production ($p < 0.05$ for both factors; $n = 3$). Rewetting after drying at the higher temperature had a dramatic effect on CO production, compared with the effect at 25°C. The average increase in production when dry soil was

Table 2. *CO production rates from dried soils*

Soil	Total organic carbon (%)	CO production rate (mg CO kg^{-1} dry soil h^{-1})			
		dried at 25°C		dried at 104°C	
		dry	rewetted	dry	rewetted
Cowpark, grassland	3.3	4.2	4.2	6.5	74.8
Cowpark, woodland	6.0	6.6	14.0	11.9	151.0
Gullane, arable	1.1	1.8	2.8	2.7	17.8
Gullane, woodland	3.1	2.4	5.0	3.9	63.3

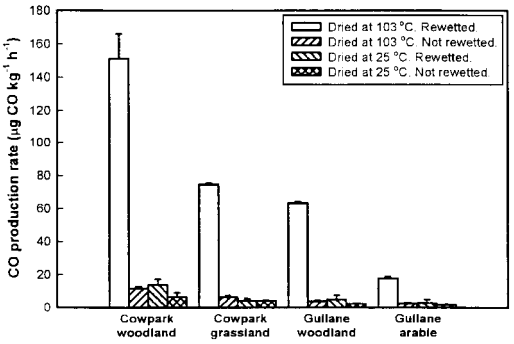

Fig. 1. Effect of drying and rewetting on soils from 4 sites. Error bars show 1 standard error; $n=3$.

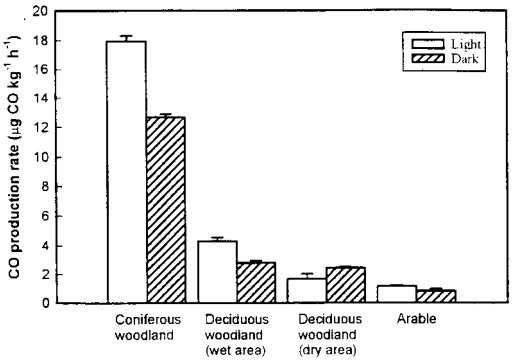

Fig. 3. Effect of light on CO production by dry soils from Bush. Error bars show 1 standard error; $n=3$.

rewetted was twelve-fold after drying at 104°C, but was only up to two-fold after drying at 25°C.

Fig. 2 shows that there was a highly significant relationship between TOC content and CO production rate ($r^2=0.72$, $p<0.01$, $n=7$).

The rate of CO production by the coniferous woodland soil was significantly faster ($p<0.05$) in the light than in the dark (Fig. 3). For the soil from the wet area of deciduous woodland the faster rate in the light was not quite significant ($0.05<p<0.10$; $n=3$), and there was no difference between light and dark for the other two soils.

Sterilisation by both autoclaving and by gamma irradiation enhanced CO production in fresh, air dried and rewetted soils (Fig. 4), showing that CO production could not be a biological process. In many cases, sterilisation by either method noticeably changed the smell of the soil to a more "vinegary" one, typical of organic acids, presumably due to organic matter decomposition.

Net CO production also occurred when microbial CO oxidation was inhibited by acetylene (Fig. 5a). When DCD solution was added, no CO production was observed except in the arable soil from Bush which had the lowest CO oxidation rate of the soils examined (Fig. 5b). In the other soils tested there was still net CO oxidation, but at a reduced rate, in the presence of DCD, com-

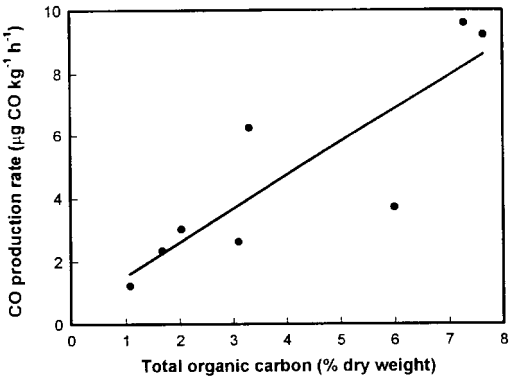

Fig. 2. Relationship between TOC content and rate of CO production by soils air dried at room temperature and not rewetted.

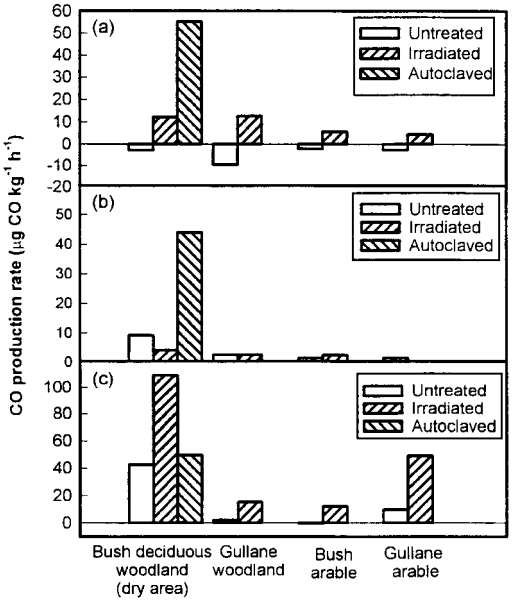

Fig. 4. Effect of sterilising soils on CO production: (a) fresh soil; (b) soil air dried at ~25°C; (c) as (b), but rewetted with 0.25 ml H_2O g^{-1} soil.

pared with the control. No CO production was observed when jars containing 1 ml l^{-1} acetylene or 1 ml DCD solution, but no soil, were incubated.

The experiments on the effects of different water contents gave contrasting results between different soils. There were optimum water contents for CO production, varying from about 20% for the Bush deciduous woodland soils to about 25% for the coniferous woodland soil (Fig. 6a). For the Gullane soils (Fig. 6b) and for the arable soil from Bush (Fig. 6a), net CO production was much lower or even negative, with some indication of minima at 15–20% water content.

Rates of CO production when soils were incubated in the jars did not change significantly as a result of prior storage in the dry state for periods of up to 6 months, but during incubation the CO mixing ratios reached plateaux at 2000–4000 ppbv after about a week (Fig. 7). Rewetted soils regained their ability to oxidise CO, so that after 20–30 h the oxidation rate began to exceed the production, and mixing ratios fell towards zero (Fig. 8). This recovery was faster for unsterilised soils than for sterilised soils (data not shown).

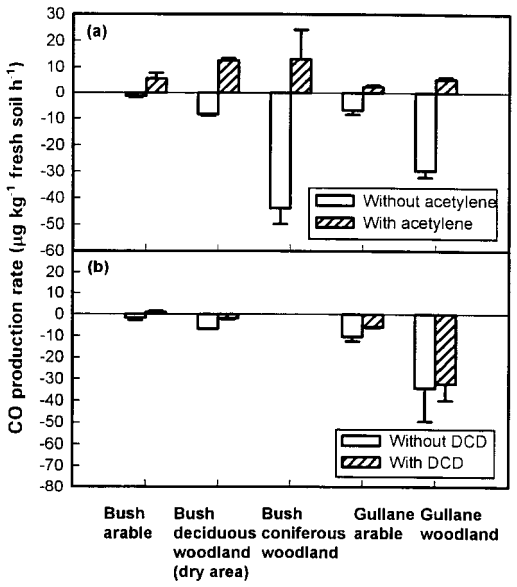

Fig. 5. (a) The effect of acetylene on CO fluxes. Error bars show 1 standard error. $n = 3$; (b) the effect of dicyandiamide (DCD) on CO fluxes. Error bars show 1 standard error; $n = 3$ for soil from Gullane and 2 for soils from Bush. Negative rates (oxidation) are normalised to a mixing ratio of 100 ppbv.

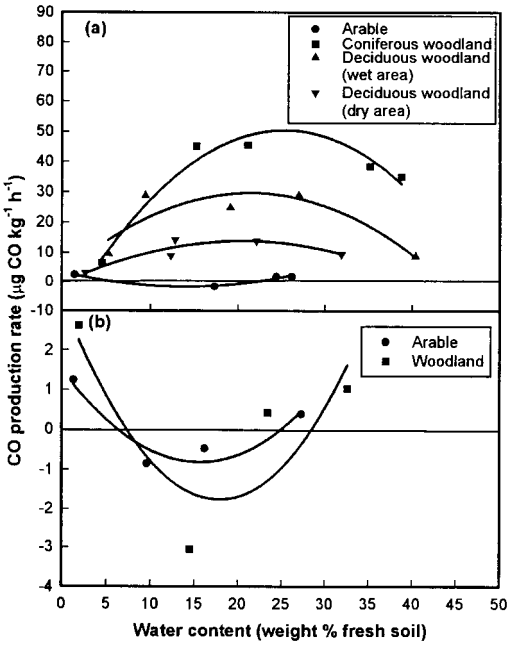

Fig. 6. Relationship between water content and CO production rate for soils air dried at ~25°C and rewetted. (a) Bush; (b) Gullane.

It was only possible to complete the factorial experiments for some of the organic additives (humic acid, glucose and sodium acetate) with the soil from the dry deciduous woodland at Bush because with some of the other additives a peak appeared during the gas chromatographic analysis between the H_2 and CO peaks, preventing a quantitative measurement of CO. Experiments showed that the peak was not due to CH_4, C_2H_2 or HCOOH. Other gaseous hydrocarbons were not investigated; nor was HCN, for safety reasons. The manufacturers of the analyser were unable to suggest a cause.

The results of the factorial experiments are summarised in Table 3. In all cases but two, sterilisation of the soil significantly increased CO production. For all soils, except the one from the dry deciduous woodland area at Bush, this treatment had the most significant effect. Drying and wetting of soils also had a significant effect in most cases, as did their interaction. The only organic substrate which consistently increased CO production was humic acid, although glucose, sodium acetate and sucrose also increased CO

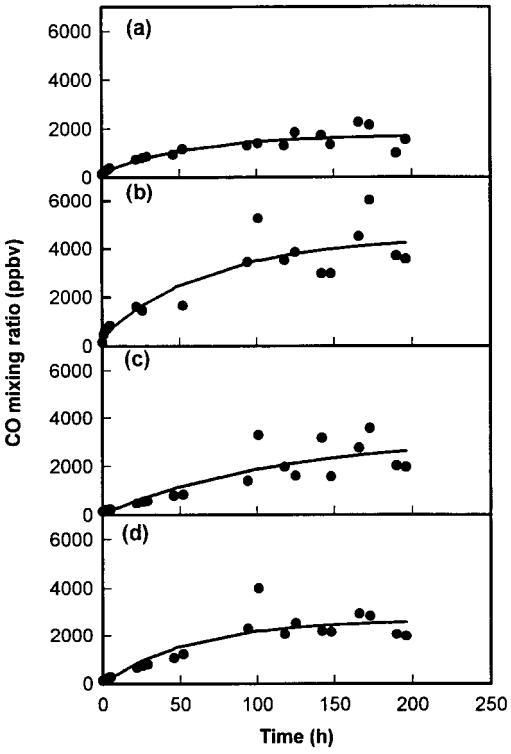

Fig. 7. Changes in CO mixing ratio over air dried soils without rewetting: (a) Cowpark grassland; (b) Cowpark woodland; (c) Gullane arable; (d) Gullane woodland.

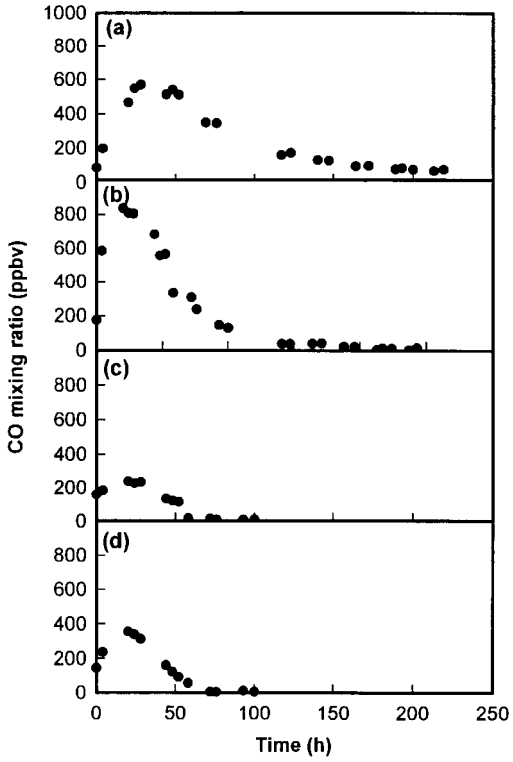

Fig. 8. Changes in CO mixing ratio over air dried soils after rewetting: (a) Cowpark grassland; (b) Cowpark woodland; (c) Gullane arable; (d) Gullane woodland.

production from the Bush arable soil, but their effects were much smaller than that of humic acid. Sodium acetate significantly increased CO production by soil from the deciduous woodland area at Bush. The interaction between drying, sterilisation and wetting was significant for all additives with most soils, except for the Gullane arable one, where it was only significant when humic acid was added. To see whether any of the organic additives produced or removed CO in the dry or wet states, 5-g samples of each material were incubated in the 1.5 l jars when dry, and also when wetted with 0.25 ml deionised water g^{-1}. None of the dry organic materials produced changes in CO mixing ratio of more than 30 ppbv over a six hour period, equivalent to a maximum of 1.8 µg CO kg^{-1} additive h^{-1}: far lower than rates of CO production for dried soils. When wetted, all the organic materials produced CO. In most cases the rate was <10 mg CO kg^{-1} h^{-1}, but for humic acid it was 165 mg CO kg^{-1} h^{-1}. When the organic materials were oven-dried at 104°C prior to incubation, the humic acid produced CO at a rate of 13 mg CO kg^{-1} h^{-1}. Rewetting the oven-dried materials resulted in rates of 173, 40 and 12 mg CO kg^{-1} h^{-1} for humic acid, starch and cellulose, respectively. The other materials produced <10 mg CO kg^{-1} h^{-1}.

To see whether the rate of CO production by humic acid varied with pH, as suggested by Conrad and Seiler (1985b), 5 g samples of were rewetted with 0.25 ml g^{-1} of deionised water (pH 7), 0.25 N NaOH and KOH (pH >13) and 0.25N HCl and H_2SO_4 (pH <1). There were no significant differences ($p>0.05$) in CO production rate.

3.2. *Field measurements*

Equilibrium CO mixing ratios were not reached during the 20 min chamber closure periods. At the

Table 3. *Effect of treatments and additives on CO production by dry soils*

Soil	Drying A	Sterilisation B	Organic material C	Wetting D	Interaction AD	Other interactions
Gullane arable	none	all except sodium acetate and glucose	humic acid only	humic acid only	humic acid only	ABD: humic acid only
Gullane woodland	✓	✓	humic acid only	✓	✓	BD: all except glucose and starch ABD: all
Bush arable	✓	✓	glucose humic acid sodium acetate sucrose	✓	✓	AB: glucose and starch BD: all except cellulose and humic acid ABD: all ABCD: sodium acetate
Bush deciduous woodland (dry area)[a)]	✓	✓	humic acid and sodium acetate	✓	✓	AB: humic acid BD: all ABD: all

A ✓ shows that the variable or interaction had a significant positive effect with all additives. Capitals show variables, and groups of capitals show interactions, e.g., ABD is the interaction between variables A, B and D, i.e., between drying, sterilising and wetting.

[a)] Results for trials with glucose, humic acid and sodium acetate only.

driest location, CO was oxidised most of the time, while at the wettest location it was produced most of the time. At the chamber where the soil water status was intermediate, there was a mixture of oxidation and production. Oxidation of CO occurred in all chambers during a period of warm, dry weather in the summer, and CO production tended to occur during cooler, wetter weather in the winter (Fig. 9). Over the whole period, the wettest chamber position was a net source of CO, with a mean production rate of 7.6 mg CO m^{-2} h^{-1}, while the soils in the other two chambers were net sinks. In addition to these discernible general trends, strong inverse correlations were also observed between the initial ambient CO mixing ratio at the time of chamber closure (which varied widely between 137 and 882 ppbv) and net CO production. This is illustrated for one of the chambers in Fig. 10. There was a significant correlation ($p<0.05$) between CO production rate and soil water content for the driest chamber only, and no correlation with temperature for any chamber.

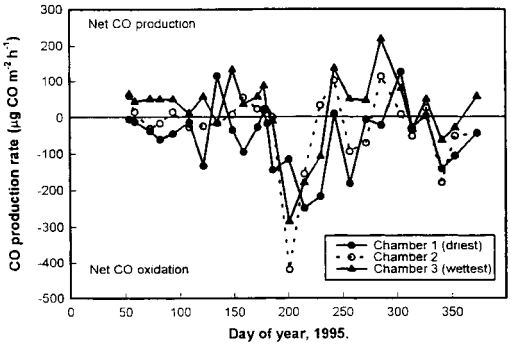

Fig. 9. Seasonal variation in CO production rate on peat land at Springfield Farm, Leadburn, Midlothian, Scotland.

CO mixing ratios generally increased sharply with increasing depth below the surface (Fig. 11). There were significant correlations ($p<0.05$)

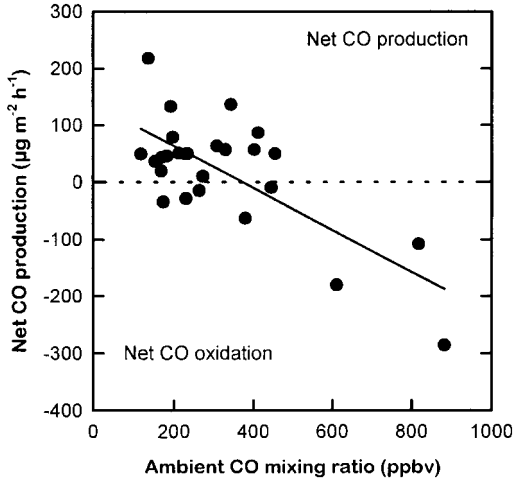

Fig. 10. Relationship between net CO production and ambient CO mixing ratio at beginning of chamber enclosure period, chamber 3 (wettest location), Leadburn.

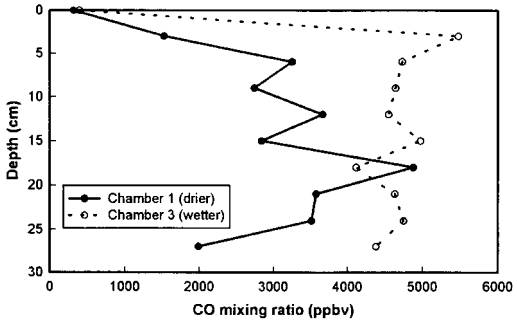

Fig. 11. Change in CO mixing ratio with depth at Leadburn, 13/10/95. Water table depth at chamber 1 = 3 cm, at chamber 3 = 8 cm. Chamber 1 oxidised 22.1 µg CO m^{-2} h^{-1}; chamber 3 produced 218 µg CO m^{-2} h^{-1}.

between the depth at which the increase in mixing ratio occurred and the water table depth ($r^2 = 0.38$ for the driest chamber and 0.27 for the wettest, $p < 0.05$ for both chambers; $n = 13$). There were also significant correlations between net CO production rates and the position of the water table ($r^2 = 0.47$ for the driest chamber, $p < 0.01$; $r^2 = 0.27$ for the wettest, $p < 0.05$; $n = 13$).

4. Discussion

It is clear from the laboratory incubation experiments that CO can be produced by soils formed in a cool temperate environment such as that of southeast Scotland, when they are in an air-dry state, and particularly when they have been rewetted. In other work during this project, the arable soil at the Bush site (Table 1) was found to be a net source of CO in the field on one occasion in dry summer conditions, when the temperature was 22°C (Moxley and Smith, 1997). Earlier, in work by Conrad and Seiler (1980) near Mainz, Germany, small production rates were detected on occasions throughout the year, but only when the chamber over the soil surface was flushed with virtually CO-free air ($\leqslant 20$ ppbv, below the compensation point). It appears that production in the field is much greater in hotter climates, where soils are subjected to much higher daytime temperatures (up to >40°C), as shown both by Conrad and Seiler (1985a) in two arid locations in South Africa and one in Andalusia, Spain, and by Sanhueza et al. (1994), for a tropical savannah soil in Venezuela.

The temperature at which our incubations were carried out (ca. 25°C) was close to the maximum normally found in the uppermost few mm of the soil profile, in our conditions. This is likely to have resulted in higher values for fluxes than would have been observed if the incubations had been made at, say, annual mean soil temperatures (ca. 10°C for Bush and Gullane), but the trends between soils and treatments are unlikely to have been greatly affected.

It is clear that CO production in the dry Scottish soils cannot have been caused by biological activity, as it was generally enhanced by sterilisation (as previously reported for soils from other regions: Smith et al., 1973; Conrad and Seiler, 1980) and by inhibitors of microbial activity (Conrad and Seiler, 1980). This may be because the conditions required to kill microorganisms also break down soil organic matter, or because CO is generally formed in soils but production is usually masked by a higher rate of microbial oxidation. This latter explanation certainly appears to fit Conrad and Seiler's (1980) study using atmospheres with CO above and below the compensation point, and our experimental results with acetylene, a known inhibitor of microbial oxidation of CO.

DCD, which inhibits nitrifiers (one of the groups capable of oxidising CO: Jones and Morita, 1983) did not have as large an effect as acetylene, suggesting that these organisms were only responsible for part of the CO oxidation. However, it is

also possible that DCD in solution was not distributed as evenly through the soil as the gaseous acetylene.

In our work, the dried soils, whether sterilised or not, retained their ability to produce CO for considerable periods of time, but once rewetted gradually regained their capacity to oxidise it, as active microbial populations became reestablished, and sterilised soils were recolonised. It is possible that drying of soils, especially at higher temperatures, breaks down some components of the soil organic matter, which are partially oxidised to CO. In unsterilised soils with high organic matter contents, which had high CO production rates when dried, the rates increased when water was added up to a maximum, and then decreased. The increase may have been caused by increasing dissolution of organic matter, while the decrease beyond the maximum may have been caused by hindered gaseous diffusion as the soil pores became water-filled. In unsterilised soils with lower organic matter contents, CO production decreased to a minimum as water content increased, then increased again. It is likely that, in these soils, increases in the biological oxidation of CO with water content outweigh any increases in CO production, leading to a net decrease in production with water content. However, once the soil becomes waterlogged, and gaseous diffusion is reduced, the CO oxidation rate decreases, and the balance tilts in favour of production.

The data in Fig. 6 and Table 1 suggest that low pH/high OM soils have a greater tendency than high pH/low OM ones to emit CO. However, as the soils were rewetted immediately prior to the measurement of CO production, it is possible that the active CO-oxidising microbial population had not returned to the normal level in moist soil; earlier work has shown that net oxidation increases with soil OM content (Moxley and Smith, 1997).

The linear relationship we found between TOC content and the rate of CO production by dry soils (Fig. 3) is in agreement with Conrad and Seiler's (1985a) findings for arid subtropical soils, suggesting that the relationship may well be globally applicable.

The factorial experiments showed that sterilisation was the factor that caused the most significant increase in CO oxidation. The effects of drying the soil and wetting it, as well as the interaction between these two factors, were also significant. The significance of the interaction suggests that CO production is caused by a breakdown of soil organic matter into smaller molecules which oxidise to CO. The oxidation is increased if water is present. This agrees with the finding in the experiments with unamended soil that the interactions between sterilisation (which also breaks down soil organic matter), and wetting the soil, and between sterilisation, drying and wetting were significant. Humic acid was the only organic material which significantly enhanced CO production in most cases. Sugars, polysaccharides and acetate had no significant effect. These observations agree with the results of Conrad and Seiler (1985b). Humic acid itself was not a source of CO when dry if stored at room temperature, but became one after storage at 104°C, and when wetted. The conditions which induced CO production from humic acid were similar to those which induced it in soils (i.e. drying at high temperatures and rewetting). Exposure to high temperatures, followed by rewetting, also induced CO production by starch and cellulose, but to a lesser extent than humic acid.

In contrast to Conrad and Seiler's results we found that the pH did not affect the rate of CO production from moist humic acid. A possible reason for the difference is that they mixed their humic acid with sand and so increased the surface area. However, both their work and ours shows that humic acid can produce CO, and suggests that the breakdown of it and other phenolic compounds may be responsible for CO production in soils.

The results from the field experiments clearly show that waterlogged peat can produce CO in a temperature regime ranging from 3 to 18°C. The temperature was measured routinely at 10 cm depth. There was little variation with depth (data not shown) and production occurred well below the surface, unlike that from dried aerobic soils; therefore the measured temperatures are regarded as reasonably representative of production conditions. It is improbable that this production at depth would have been much affected by the disturbance caused to the surface by chamber installation, in contrast with, for example, the known effects on CO_2 and N_2O production processes driven by root exudates and mineralisation in surface layers (Matson et al., 1990).

The production of CO in the peat is most unlikely to have been brought about by the same

process as that operating in dry soils. It is far more likely to have been due to anaerobic microbial activity (Zavarzin and Nozhevnikova, 1977; Conrad and Thauer, 1983; Funk et al., 1994). Conrad and Seiler (1980) cited older work in which CO mixing ratios were found to increase with depth in anaerobic soils, and this was also observed in this study (Fig. 11). It is likely that the CO is produced in anaerobic zones at or just above the water table, and that some or all of it is oxidised in aerobic zones above the water table before reaching the atmosphere.

The large effect of variations in ambient CO mixing ratio on net CO production (Fig. 10) is attributable to the effect on CO oxidation, which is a first-order reaction and thus increases with [CO]. This could explain why CO production displayed no clear temperature dependence. The cause of the variations in ambient CO is unknown.

The pattern of CO mixing ratios in sampling tubes below the water table was very variable, but this may be a reflection of the difficulty in obtaining a large enough gas sample (at least 2 ml from a tube with a volume of 3.8 ml). Further investigation of CO production under controlled anaerobic conditions is needed.

There was considerable variability in the size of the CO fluxes at the different chamber locations on the peat site, which makes scaling up difficult. However, it is useful to establish the likely order of magnitude of wetland emissions. On the basis of the mean flux at the chamber in the wettest location, and taking the area of northern hemisphere wetlands to be $2.9 \times 10^{12}\,m^2$ (Matthews and Fung, 1987: total for forested and nonforested bog), these wetlands could only emit of the order of $0.2\,Tg\,y^{-1}$ CO. This agrees well with other published estimates. Although they are probably not globally important sources of CO, northern wetlands could be locally important in regions where there are few anthropogenic sources of CO. More field data on CO fluxes from wetlands, both in the mid to high northern latitudes and elsewhere, is required, to provide a more reliable assessment of the overall wetland source strength.

5. Conclusions

CO production is a process which normally occurs in soils from cool temperate environments as well as from warmer ones, but is often masked by oxidation. An excess of production over oxidation generally occurs after drying at ambient and higher temperatures, and when CO oxidation is halted by the addition of acetylene or by sterilisation. CO production in aerobic soils appears to be caused by a chemical rather than a biological process that is enhanced by autoclaving and the addition of water after drying. It increases with the amount of soil organic matter, and is probably caused by the breakdown of organic materials, in particular humic acid. The mechanism for this is not clear.

In wet peatland, CO production occurs in anaerobic regions at or just above the water table. Some of the CO produced may be oxidised as it passes through aerobic regions prior to escaping to the atmosphere. This CO production is probably a biological process, but further laboratory work is needed in anaerobic conditions to confirm this. Although not important on a global scale, emissions of CO from wetlands could be regionally significant sources.

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