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Soil Microbial Processes and the Cycling of Atmospheric Trace Gases [and Discussion]

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Soil microbial processes and the cycling of atmospheric trace gases

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Soil microbial processes involved in the flux between soil and atmosphere of the atmospheric trace gases methane (CH_4), hydrogen (H_2), carbon monoxide (CO), carbonyl sulphide (OCS), nitrous oxide (N_2O), and nitric oxide (NO) are reviewed. The flux of a trace gas between soil and atmosphere is usually the result of simultaneous production and consumption reactions, so that a compensation concentration exists, at which the net flux is zero. With some of the trace gases, different suites of processes operate at different gas concentrations, so that the processes that consume a trace gas that is produced within the soil are often different from those that consume the trace gas entering the soil from the atmosphere. Certain groups of soil microorganisms can metabolize more than one of these trace gases. The processes involved in the cycling of a trace gas in anoxic wetland soils are often different from those operating in upland soils.

1. Introduction

Junge (1972) pointed out that virtually all the atmospheric gases undergo cycles which are more or less dominated by the biosphere. Only a few species (e.g. O_3, Rn) exhibit cycles which are purely governed by physical-chemical reactions. The main sources and sinks for atmospheric trace gases in the biosphere are the ocean, soils, vegetation, and animals: for detailed reviews see Buat-Menard (1986), Bouwman (1990), Sharkey *et al.* (1991), and Khalil (1993).

The sources and sinks in soils include (1) abiotic chemical reactions (e.g. the production of CO from soil organic carbon (Conrad & Seiler 1985*a*)), (2) 'fortuitous' biochemical reactions that do not support microbial growth (e.g. hydrolysis of OCS (Kesselmeier 1992)), (3) biochemical reactions by the extracellular enzymes present in soil (e.g. oxidation of H_2 (Conrad *et al.* 1983*a*)), and (4) metabolic reactions that support the growth of microorganisms (e.g. oxidation of CH_4 (King 1992)).

In most of these processes microorganisms are either directly or indirectly involved. Soils probably show the highest abundance and diversity of microorganisms in nature, and thus it is no wonder that soils are involved in and can even dominate the cycling of many atmospheric trace gases. Table 1 lists a selection of atmospheric trace gases for which soils are important sources and/or sinks, and which are all (with the possible exception of H_2) of importance in atmospheric chemistry and thus of considerable concern with respect to climate and to global change. To understand and predict changes in the source and sink strengths of

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Table 1. *Contribution of the soil to the cycling of atmospheric trace gases*

trace gas	lifetime (days)	mixing ratio (ppbv)	total budget ($\mathrm{Tg\ a^{-1}}$)	annual increase (%)	contribution (%) of soils to total budgets as		impact	ref.
					source	sink		
N_2O	60 000	310	15	0.2–0.3	70	?	stratospheric chemistry; greenhouse effect	1–4
CH_4	4000	1700	540	< 0.8	60	5	greenhouse effect; tropospheric & stratospheric chemistry	4–7
H_2	1000	550	90	0.6	5	95	insignificant	8,9
OCS	> 350	0.5	1.2	?	25	?	aerosol formation	10–12
CO	100	100	2600	1.0[a]	1	15	tropospheric chemistry	8,13
NO	1	< 0.1	60	?	20	?	tropospheric chemistry	3,14

(1) Khalil & Rasmussen 1992; (2) Bouwman 1990; (3) Davidson 1991; (4) Prinn 1994; (5) Cicerone & Oremland 1988; (6) Khalil & Rasmussen 1990*a*; (7) Steele *et al.* 1992; (8) Conrad 1988; (9) Khalil & Rasmussen 1990*b*; (10) Andreae & Jaeschke 1992; (11) Chin & Davis 1993; (12) Möller 1984; (13) Khalil & Rasmussen 1990*c*; (14) Conrad 1990.

[a] The long-term trend has recently reversed; CO is now decreasing by about 6% per year (Novelli *et al.* 1994).

these trace gases, it is necessary to know the processes involved in generating the net flux at the soil–atmosphere interface.

2. Diffusion of trace gases

The net flux of a trace gas is usually the result of production, consumption, and transport within the soil column. Whether produced or consumed, the diffusional flux of a trace gas is basically controlled by Fick's law and thus is proportional to the actual diffusion coefficient in soil and to the concentration gradient of the trace gas. The actual diffusion coefficient is difficult to determine, being affected by the temperature and air-filled porosity of the soil. In particular, the distribution of water has drastic effects on diffusion. In well-aerated soils ('upland soils'), the diffusional flux is dominated by diffusion in the air-filled soil pores, since the molecular diffusion coefficient in water is about four orders of magnitude lower than in air. In addition, many of the trace gases (in table 1 all except N_2O) are not very soluble in water. However, in watersaturated flooded soils ('wetland soils'), diffusion is entirely within the water phase until the trace gas reaches the water–atmosphere interface or a plant root, from where it may be transported to the atmosphere by gas mass flow or by diffusion through the plant's gas vascular system (Armstrong 1979; Schütz *et al.* 1991). Some of the differences between upland and wetland soils are depicted in figure 1.

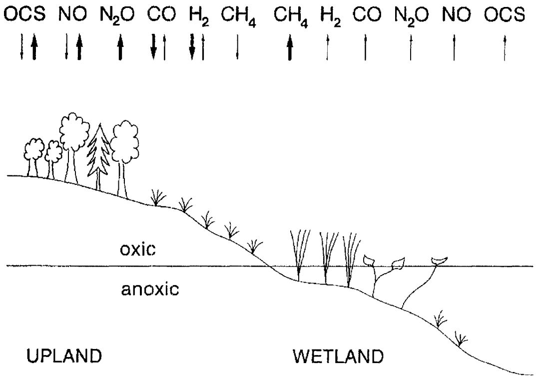

Figure 1. Flux of trace gases between upland and wetland soils and the atmosphere. Thick arrows represent major fluxes, thin arrows minor fluxes.

3. Simultaneous production and consumption of trace gases in soil

Two different situations exist. The first is where production and consumption processes are more or less homogeneously distributed within the soil, a situation typical of upland soils, but also of anaerobic processes occurring within the anoxic zones of wetland soils. The second is where production and consumption processes are spatially separated, as is usual in wetland soils, where the deeper anoxic soil layers (sites of production) are covered at the surface with a shallow oxic layer (site of consumption). The roots of aquatic macrophytes that penetrate the anoxic zones of wetland soils are often surrounded by a thin oxic layer, which also provides a site for aerobic consumption processes (Conrad 1989; Schütz *et al.* 1991).

In upland soils, the existence of both production and consumption reactions can be infered if it can be shown that there is a compensation concentration at which the two processes are in equilibrium and at which no net flux is observed. In oxic upland soils this is almost always true, with compensation concentrations established for H_2 (Seiler 1978; Conrad & Seiler 1980*a*), CO (Seiler 1978; Conrad & Seiler 1985*b*), OCS, N_2O (Seiler & Conrad 1981) and NO (Johansson & Galbally 1984; Remde *et al.* 1989). The compensation concentrations for N_2O are usually so high that upland soils are almost always a source of atmospheric N_2O. This may also turn out to be the case for OCS. By contrast, the compensation concentrations for H_2 are usually so low (except at sites with biological N_2 fixation (Conrad & Seiler 1980*a*)), that upland soils almost always act as a sink for atmospheric H_2 (Seiler 1978; Conrad 1988). On the other hand, the compensation concentrations for CO (Conrad & Seiler 1980*b*, 1985*b*; Scharffe *et al.* 1990) and NO (Slemr & Seiler 1984, 1991) vary with changing soil conditions and are in a range such that soil may dynamically change from acting as a source to acting as a sink. An example is shown in figure 2, where the CO compensation concentration changes during the day. During the hot hours of the day it is higher than the atmospheric CO concentration, so that there is a net flux of CO from the soil into the atmosphere. If the CO concentration is increased experimentally, CO is taken up by the soil until the compensation concentration is once again reached.

There is, as yet, no firm evidence for a CH_4 compensation concentration. However, a compensation concentration may exist, since tropical upland soils are

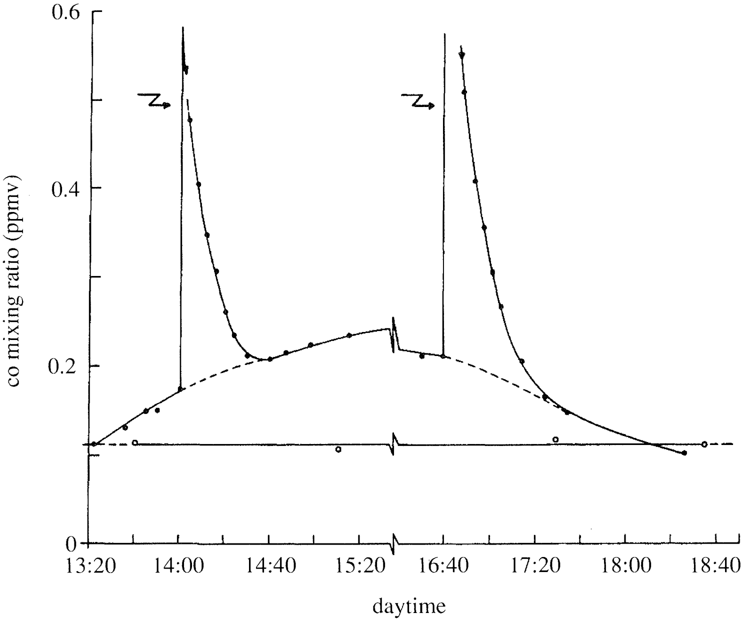

Figure 2. Diurnal change of the CO concentration outside (○) and inside (●) a chamber covering the surface of a savanna soil in the Transvaal (South Africa). The CO concentrations inside the chamber represent CO compensation concentrations between release and uptake by the soil. The arrows indicate injection of CO into the chamber. Adapted from Conrad and Seiler (1985*c*).

sometimes sources of atmospheric CH_4, especially during the rainy season (Keller *et al.* 1986, 1993). However, in most upland soils CH_4 production seems to be marginal, probably because CH_4-producing bacteria require strictly anoxic and reduced conditions and thus are inactive in well-aerated upland soils (Cicerone & Oremland 1988; Conrad 1989; Reeburgh *et al.* 1993). Methane uptake by upland soils seems to be limited by diffusion from the atmosphere into the soil (Dörr *et al.* 1993) and from the air-filled pore space into the soil aggregates (Koschorreck & Conrad 1993). It is also limited by the activity of methanotrophic bacteria, which typically occur in subsurface soil layers and on the larger soil grains (Bender & Conrad 1994), and by the threshold and affinity for CH_4 of the methanotrophic population (see below; Bender & Conrad 1992, 1993).

In wetland soils, oxidation of CH_4 in the overlying oxic soil layer diminishes the flux of CH_4 to the atmosphere from the deeper water-saturated, anoxic soil (Reeburgh *et al.* 1993). It is also possible that CH_4 is oxidized during its passage through the oxic layers surrounding the roots of these plants that penetrate the anoxic layers. The role of transport and oxidation in the cycling of CH_4 in paddy fields has recently been reviewed by Conrad (1993).

4. Gas concentration and microbial activity

Microorganisms metabolizing trace gases at atmospheric concentrations must be able to deal with gas concentrations that are typically in the picomolar to nanomolar range. These low concentrations are unfavourable for synthesis of cellular biomass (Conrad 1984). Interestingly, many of the processes involved in the consumption of trace gases at atmospheric concentrations are fortuitous reac-

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Table 2. *Microorganisms and reactions important in production or consumption of trace gases in soil*

gas	trace production	consumption at elevated concentrations	consumption at atmospheric concentrations
CH_4	methanogens	common methanotrophs; nitrifiers	unknown methanotrophs; nitrifiers
H_2	fermenting bacteria; N_2-fixing bacteria	Knallgas bacteria; anaerobic chemolithotrophs[a]	abiotic soil hydrogenases
CO	chemical conversion of soil organic carbon; anaerobic chemolithotrophs	carboxydotrophs; anaerobic chemolithotrophs	nitrifiers; oligotrophic bacteria
OCS	thiocyanate hydrolase	carbonic anhydrase	carbonic anhydrase
N_2O	denitrifiers; DNRA[b];	denitrifiers	denitrifiers
NO	denitrifiers; DNRA; nitrifiers; chemical decomposition of NO_2^-	denitrifiers; methanotrophs; heterotrophic bacteria	denitrifiers; methanotrophs; heterotrophic bacteria

[a] Anaerobic chemolithotrophs are methanogens, homoacetogens, sulphate reducers, etc.
[b] DNRA is dissimulatory reduction of nitrate to ammonium.

tions that do not serve microorganisms for growth (table 2). This is the case with the oxidation of CO by ammonium-oxidizing nitrifiers (Jones & Morita 1983*a*; Jones *et al.* 1984), of H_2 by soil hydrogenases (Conrad & Seiler 1981; Conrad *et al.* 1983*a*; Schuler & Conrad 1990), of OCS by the carbonic anhydrase present in various CO_2-fixing bacteria (Protoschill-Krebs & Kesselmeier 1992), and of NO by heterotrophic bacteria (Baumgärtner *et al.* 1995, unpublished work). In all these cases, the trace gases are oxidized rather than reduced and the enzymes involved have the high affinity and the low threshold required for reaction with a trace gas at atmospheric concentrations. This is also true for atmospheric CH_4 which, however, is probably not fortuitously but 'usefully' oxidized by an unknown methanotrophic population (Bender & Conrad 1992). Similarly, atmospheric CO seems to be oxidized to some extent by unknown oligotrophic microorganisms (Conrad & Seiler 1982).

Only N_2O and (to some extent) NO seem to be consumed by reduction processes in aerated upland soils. Such soils normally contain anoxic microsites (Sexstone *et al.* 1985; Zausig *et al.* 1993) which are presumably where the reduction occurs. Reduction of NO and N_2O mainly involves the well-known denitrifiers that catalyse the sequential reduction of nitrate → nitrite → NO → N_2O → N_2 (Knowles 1982; Tiedje 1988; Zafiriou *et al.* 1989; Remde & Conrad 1991). However, consumption of atmospheric NO in upland soils seems to involve two additional reactions, (i) fortuitous oxidation by heterotrophic bacteria (see above) and (ii) consumption by methanotrophic bacteria (Krämer *et al.* 1990).

Frequently, however, the microorganisms involved in the consumption of trace gases at atmospheric concentrations are not those which have been isolated on the basis of their ability to use one of the trace gases for growth at high gas concentrations (percent level). This is obviously true for the commonly known methanotrophs (CH_4) (Conrad 1984; Bender & Conrad 1992; King 1993), the Knallgas bacteria (H_2) (Conrad 1988), and the carboxydotrophic bacteria (CO)

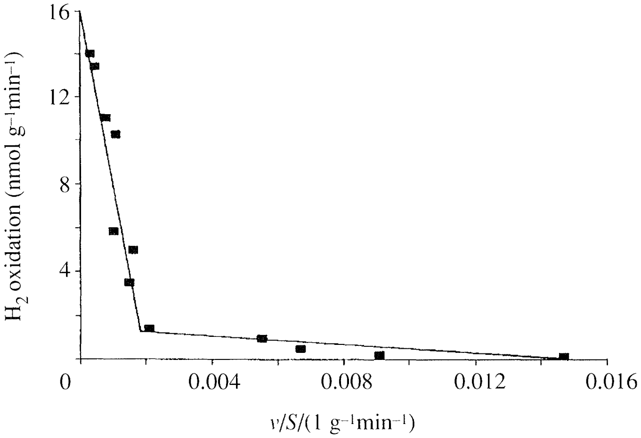

Figure 3. Eadie–Hofstee plot of the kinetics of H_2 oxidation in a meadow soil, revealing two activities with K_m values of 19 and 1450 ppmv H_2, respectively. Adapted from Häring & Conrad (1994).

(Conrad 1988). All these bacteria can only use trace gases at elevated concentrations (table 2). For this reason they are probably only active adjacent to special spots (e.g. anoxic microsites, root nodules; see below) in the soil where the trace gases are produced at such high rates that elevated concentrations are generated. Thus, Knallgas bacteria contribute to the oxidation of the relatively high H_2 concentrations found in the vicinity of H_2-producing root nodules of legumes (LaFavre & Focht 1983; Popelier *et al.* 1985; Cunningham *et al.* 1986; Schuler & Conrad 1991). Kinetic experiments demonstrate the existence in soil of both Knallgas bacteria, with low affinity for H_2 and soil hydrogenases, with high affinity for H_2 (figure 3; Schuler & Conrad 1990; Häring & Conrad 1994). Schuler & Conrad (1991) showed that the H_2 compensation concentration was relatively large when nodulated legumes grown on sterile soil were inoculated with Knallgas bacteria. The Knallgas bacteria could only consume the H_2 produced by the legumes down to concentrations of about 13 ppmv H_2. The consumption of H_2 to still lower concentrations was only possible if the soil hydrogenases were also active, i.e. in non-sterile soil. However, it is likely that the soil hydrogenases operate in tandem with the H_2-oxidizing bacteria, since the soil hydrogenases are reversibly inhibited by exposure to high H_2 concentrations (Conrad & Seiler 1981). Knallgas bacteria presumably first reduce the H_2 concentration to a level that allows the soil hydrogenases to operate.

The importance of these microorganisms for reducing the flux of trace gases into the atmosphere is most evident in wetland soils (e.g. rice fields), where the metabolites CH_4, H_2, N_2O and NO are produced at potentially high rates but released into the atmosphere at drastically reduced rates. Consumption of H_2 is achieved by various anaerobic chemolithotrophic bacteria (methanogens, homoacetogens, sulphate reducers, etc.) within the anoxic environment (Conrad 1989) and, in addition, by the aerobic Knallgas bacteria at the anoxic–oxic interface (Schütz *et al.* 1988). Consumption of CH_4 is achieved by the common methanotrophic bacteria at the anoxic-oxic interface (King 1990; Conrad & Rothfuss 1991; Bosse *et al.* 1993; Bender & Conrad 1994). Nitrous oxide and NO are effectively consumed within the anoxic environment by sequential reductive denitrification to N_2, thus reducing the flux into the atmosphere to very low rates (Freney & Denmead 1992; Galbally *et al.* 1987), but in this case by the same denitrifying bacteria which act on NO and N_2O at atmospheric concentrations.

5. Microorganisms producing or consuming more than one trace gas

Certain species of microorganism are capable of metabolizing more than one trace gas; see table 2. Autotrophic nitrifiers are involved in the oxidation of CO (Jones & Morita 1983*a*; Jones *et al.* 1984) and probably also of CH_4 (Hyman & Wood 1983; Jones & Morita 1983*b*; Castro *et al.* 1994). Methanotrophs can also be involved in heterotrophic nitrification and thus in the cycling of NO and N_2O (Yoshinari 1985; Knowles & Topp 1988; Krämer *et al.* 1990). The significance of the bioversatility of these organisms for the turnover of trace gases in soil deserves further investigation. Several types of anaerobic H_2-consuming chemolithotrophic bacteria (methanogens, homoacetogens, sulphate reducers, etc.), which play an important role in the control of CH_4 production in anoxic wetland soils (Conrad 1989), also have the potential to produce and consume CO (Diekert & Wohlfarth 1994). However, the significance of this potential for the turnover of CO in wetland soils is largely unexplored (Conrad *et al.* 1983*b*, 1988).

6. Cycling of trace gases in wetland and upland soils

Whereas wetland soils are always sources, upland soils can act both as sources or sinks of atmospheric trace gases (figure 1). For the most part, we do not know whether the microorganisms living in anoxic microsites within upland soils are the same as those living in anoxic wetland soils. Interestingly, strictly anoxic methanogenic bacteria that typically occur in anoxic wetland soils also occur in low numbers in upland soils which have never been flooded (Mayer & Conrad 1990); they are even found in desert soils (Peters & Conrad 1995). As a first approach, we may therefore assume that although the species might be different, the reactions that they catalyse are the same in both environments.

However, anaerobic microorganisms are both more abundant and more active in wetland than in upland soils. This is obvious for production processes such as CH_4 production (Conrad 1989). In principle, it is also true for H_2 which is produced in large amounts by fermenting bacteria in wetland soils, but converted to CH_4 (among other products) so that only small amounts of H_2 escape into the atmosphere (Schütz *et al.* 1988). In upland soils, on the other hand, H_2 production by fermentation is negligible (Conrad 1988). Instead, it is produced by biological N_2 fixation in legumes (Conrad & Seiler 1980*a*), whose root nodules provide a highly specialized low-O_2 environment, allowing the O_2-sensitive nitrogenase to be active within oxic soils.

Very little is known about how the production of CO and OCS differ in upland and wetland soils. In oxic upland soils, CO is mainly produced during the chemical oxidation of soil organic matter (Conrad & Seiler 1985*a*, *b*). In anoxic wetland soils, CO can also be produced by anaerobic chemolithotrophs during metabolism (Diekert & Wohlfarth 1994). The production processes of OCS are mostly unknown, except for one reaction, the hydrolysis of thiocyanate ($SCN^- + H_3O^+ \rightarrow OCS + NH_3$) by microorganisms containing the enzyme thiocyanate hydrolase (Kelly *et al.* 1993; Katayama *et al.* 1992). This enzyme may be active in both wetland and upland soils (Minami & Fukushi 1981).

The difference between upland and wetland soils is also seen in consumption processes, for example H_2 consumption. In contrast to upland soils, where soil hydrogenases and, to some extent, also Knallgas bacteria collaborate (Conrad 1988), consumption of H_2 in wetland soils is achieved by anaerobic chemolithotrophs (Conrad 1989, 1995). A similar difference exists for CO consumption. Ammonium-oxidizing nitrifiers, oligotrophic bacteria, and (to some extent) carboxydotrophic bacteria all contribute to CO consumption in upland soils (Conrad 1988; Mörsdorf *et al.* 1992), whereas it is likely that anaerobic chemolithotrophs dominate CO turnover in wetland soils. The methanotrophs active in wetland soils differ in their kinetics from those in upland soils, since the former are exposed to elevated CH_4 concentrations, whereas the latter are exposed to atmospheric concentrations of CH_4 (see above; Bender & Conrad 1992, 1994). Anaerobic CH_4-oxidizing microorganisms seem to play an important role in marine sediments (Alperin & Reeburgh 1984; Iversen & Joergensen 1985), but have not yet been isolated.

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Discussion

K. A. Smith (*SAC, Edinburgh, U.K.*). In the course of work done in the U.S.A. over 20 years ago (Smith *et al.* 1973), which was primarily intended to study soil *uptake* of CO, I found that sterilized soils released CO, so presumably this was by a non-biological process. Does Dr Conrad believe that his observations of CO emission from soils in hot, dry conditions were due to non-biological production?

R. Conrad. Yes, I can confirm that Dr Smith's observation that CO production in soil is largely due to non-biological processes that are also active in sterilized soil. CO is probably produced by thermal decomposition of humic material (Conrad & Seiler 1985*a*).

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