# Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes

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## Summary

This review examines the interactions between soil physical factors and the biological processes responsible for the production and consumption in soils of greenhouse gases. The release of $CO_2$ by aerobic respiration is a non-linear function of temperature over a wide range of soil water contents, but becomes a function of water content as a soil dries out. Some of the reported variation in the temperature response may be attributable simply to measurement procedures. Lowering the water table in organic soils by drainage increases the release of soil carbon as $CO_2$ in some but not all environments, and reduces the quantity of $CH_4$ emitted to the atmosphere. Ebullition and diffusion through the aerenchyma of rice and plants in natural wetlands both contribute substantially to the emission of $CH_4$; the proportion of the emissions taking place by each pathway varies seasonally. Aerated soils are a sink for atmospheric $CH_4$, through microbial oxidation. The main control on oxidation rate is gas diffusivity, and the temperature response is small. Nitrous oxide is the third greenhouse gas produced in soils, together with NO, a precursor of tropospheric ozone (a short-lived greenhouse gas). Emission of $N_2O$ increases markedly with increasing temperature, and this is attributed to increases in the anaerobic volume fraction, brought about by an increased respiratory sink for $O_2$. Increases in water-filled pore space also result in increased anaerobic volume; again, the outcome is an exponential increase in $N_2O$ emission. The review draws substantially on sources from beyond the normal range of soil science literature, and is intended to promote integration of ideas, not only between soil biology and soil physics, but also over a wider range of interacting disciplines.

## Introduction

Soil and its use contribute substantially to the 'greenhouse effect', i.e. the enhanced warming of the earth's surface and lower atmosphere as a result of increased emissions of carbon dioxide and trace gases into the atmosphere by human activity, over and above any warming due to natural processes. The most important individual greenhouse gas is carbon dioxide, $CO_2$, but substantial contributions to global warming are also made by methane, $CH_4$, and nitrous oxide, $N_2O$. Although the absolute quantities of these gases being emitted is small compared with that of $CO_2$, they are far more effective in absorbing infrared radiation and thus contributing to global warming: 1 kg of $CH_4$ has a warming potential 23 times greater than 1 kg of $CO_2$, over a 100-year period, while the warming potential of 1 kg of $N_2O$ is nearly 300 times greater (Ramaswamy *et al.*, 2001). Roughly a third of $CH_4$ emissions and two-thirds of

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$N_2O$ emissions to the atmosphere come from soils (Prather *et al.*, 1995).

A further contribution to global warming comes indirectly from tropospheric ozone, which is produced by light-catalysed reactions involving nitric oxide, NO, and organic compounds (e.g. isoprene, monoterpenes) emitted by vegetation. Nitric oxide is a natural product emitted from soil as well as from combustion. Soil, particularly in its undisturbed natural state, also acts as a sink for methane already in the atmosphere.

These gases are all produced (or consumed) as a result of microbial processes in the soil, but the size of the fluxes between the soil and the atmosphere depends heavily on soil physical factors. Soil temperature and water content directly affect production and consumption of greenhouse gases, through their effects on microorganism and root activity. Gas diffusivity, which depends on the air-filled porosity (and thus varies inversely with water content), controls the movement of the gases to and from the atmosphere; it also affects soil aeration, and thus indirectly controls the capacity of the

soil to produce or consume $CO_2$, $N_2O$ and $CH_4$. This review examines the interactions between the controlling physical factors and the biological processes responsible for trace gas production and consumption in soils.

## Physical controls on $CO_2$ emission from soil

### Temperature

Carbon dioxide ($CO_2$) emissions resulting from respiration in soil and vegetation are the principal sources from which this gas enters the atmosphere, being 10–15 times greater than emissions of $CO_2$ from fossil fuels (Raich & Schlesinger, 1992). Field data indicate that most temperate and boreal forests are significant sinks for $CO_2$ (Goulden *et al.*, 1996), with soil respiration being the main determinant of carbon balance in European forests (Valentini *et al.*, 2000). Global circulation models (GCMs) have shown that there is a potential for significant acceleration of global warming due to feedbacks in the carbon cycle. According to Cox *et al.* (2000), forest ecosystems that are now net sinks for $CO_2$ might become net sources after about 2050, if projected temperature rises become a reality. However, another recent study has suggested that the temperature sensitivity of soil respiration may be independent of the mean annual temperature of the soil across a wide variety of ecosystems and average temperatures (Giardina & Ryan, 2000). In view of these uncertainties, characterizing the temperature response for forest soils is particularly important, because these soils contain more than 70% of the world's pool of C in the soil (Post *et al.*, 1982; Xu & Qi, 2001a).

The release of $CO_2$ from soil organic matter by heterotrophic respiration, and (where roots are present) the release by autotrophic root respiration, generally increase exponentially with temperature. The temperature response is usually expressed as a $Q_{10}$ value,

$$Q_{10} = \text{Respiration rate at } (T + 10)/\text{respiration rate at } T, \quad (1)$$

where $T$ is the temperature in K.

Figure 1 shows the wide scatter of $Q_{10}$ values for the temperature response found in 16 studies reviewed by Raich & Schlesinger (1992). Many of the discrepancies may stem from simple differences in experimental procedure, e.g. making temperature measurements at different depths without taking account of the damping of the diurnal temperature cycle with depth (Figure 2). For example, Goulden *et al.* (1996), Moore *et al.* (1996) and Davidson *et al.* (1998) measured soil temperatures at 2, 5 and 10 cm depth, respectively, and found corresponding diurnal $Q_{10}$s for $CO_2$ flux of 2.2, 2.7 and 4.2. Davidson *et al.* (1998) argued that the substantial differences between their own observed $Q_{10}$ and those published in the other projects might be at least partly explained by the decrease in diurnal variation in temperature with depth. They commented that 'ideally, temperature dependence of $CO_2$ production would be
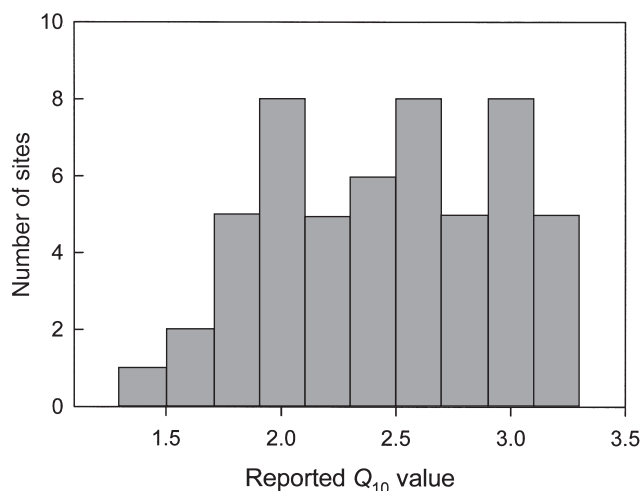


**Figure 1** Distribution of reported $Q_{10}$ values for soil respiration. (Drawn from data contained in Raich & Schlesinger, 1992).
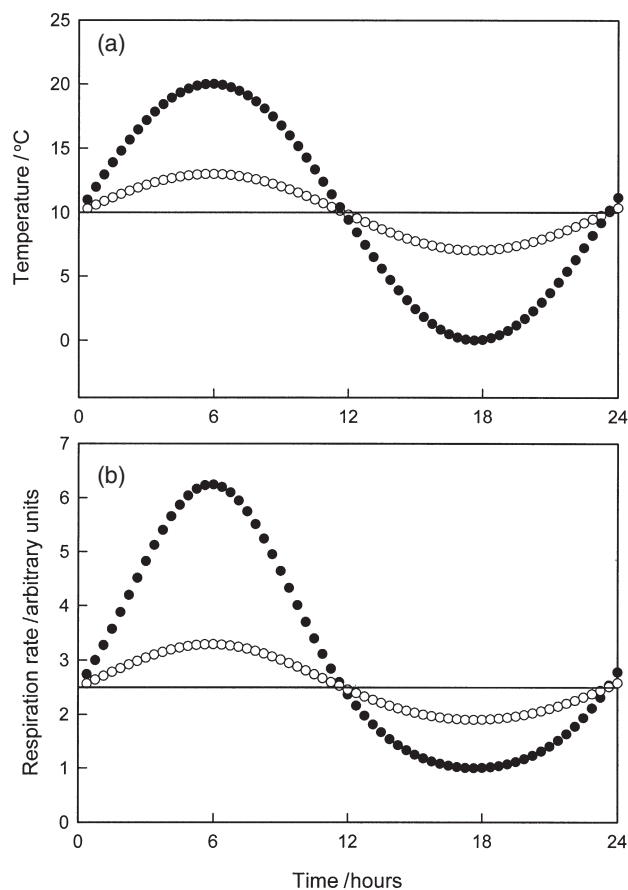


**Figure 2** (a) Idealized diurnal temperature wave at surface (solid circles) and 10 cm depth (open circles). (b) Corresponding diurnal fluctuation in respiration rate at surface (solid circles) and 10 cm depth (open circles). For convenience of illustration, the time when the diurnal mean temperature is reached for each depth is adjusted to time = 0, so that the maxima and minima coincide, whereas in reality these points are progressively delayed (offset to the right) with increasing depth.

determined, both in field measurements and in models, for each soil horizon, rather than relating total soil $CO_2$ efflux to the temperature of some arbitrarily chosen depth'. Xu & Qi (2001a) have related $Q_{10}$ measurements to temperature readings at various depths, in a pine plantation in the Sierra Nevada of California, and found an increase in $Q_{10}$ with increasing depth in the soil.

Although Davidson *et al.* (1998) and Xu & Qi (2001a) recognized the potential impact of greater or lesser diurnal variations in temperature in producing different $Q_{10}$ values for soil respiration, there is another related factor that may well contribute to observed differences in temperature response between different studies. This factor, which has not (as far as we can ascertain) been previously considered by workers in this field, is the increased average rate of microbial activity to be expected over the temperature cycle in the uppermost layers of the soil compared with that at greater depths. This difference depends simply on the combination of a physical variable, the diurnal 'wave' of temperature variation in the soil and its changing amplitude with depth (Figure 2a; see also, for example, Parton, 1984), and the non-linearity of the temperature response of soil respiration. As can be seen in Figure 2, the symmetry of the waves at different depths above and below the mean temperatures (Figure 2a) is accompanied by an asymmetry in the respiration rate curves (Figure 2b). The total respiration in the surface layer over the 24-hour cycle will thus be greater than that at 10 cm depth, even though the mean temperatures are the same, provided no other factor becomes limiting. In the illustration in Figure 2(b), based on a $Q_{10}$ value of 2.5, the total respiration at the surface is 19.6% greater than at 10 cm depth.

In general, the greater the diurnal swing in temperature, the greater will be the mean respiration rate, even though the mean temperature is the same, and this will apply to differences of location as well as to differences in depth at the same point in the landscape. Thus the prediction is that an exposed soil in a sunny climate, but with the same mean diurnal temperature as a shaded forest soil, will respire more on average in the surface layers in conditions where moisture content is not limiting. In practice, however, the unshaded environment is more likely to create suboptimal conditions for respiration. These interactions need to be investigated experimentally, so that future modelling of the effects on soil carbon stocks of, say, a 2–3° increase in mean temperature as a result of global warming can take better account of differences in environmental conditions.

Organic soils, on which a large proportion of boreal forests are located, have thermal conductivities and thermal diffusivities one quarter to one eighth of those of mineral soils (Figure 3). They therefore damp the diurnal temperature wave more than mineral soils do. The impact of this effect on differences in respiration rate between organic and mineral soils also needs to be investigated before any satisfactory upscaling of respiration measurements at particular study sites to a regional or national basis can be achieved.

## Soil water content and aeration

Soil water content (in particular water-filled pore space, WFPS) is another variable that affects the rate of respiration (e.g. Xu & Qi, 2001b). There is a wide range of water contents within which there is little change in the rate, but as the soil dries there comes a point at which microbial activity is inhibited, and respiration decreases. Rey *et al.* (2002) investigated the relation between soil respiration, volumetric water content, $\theta$, and the temperature of the soil, for a Mediterranean site. Whereas during the winter and part of spring and autumn
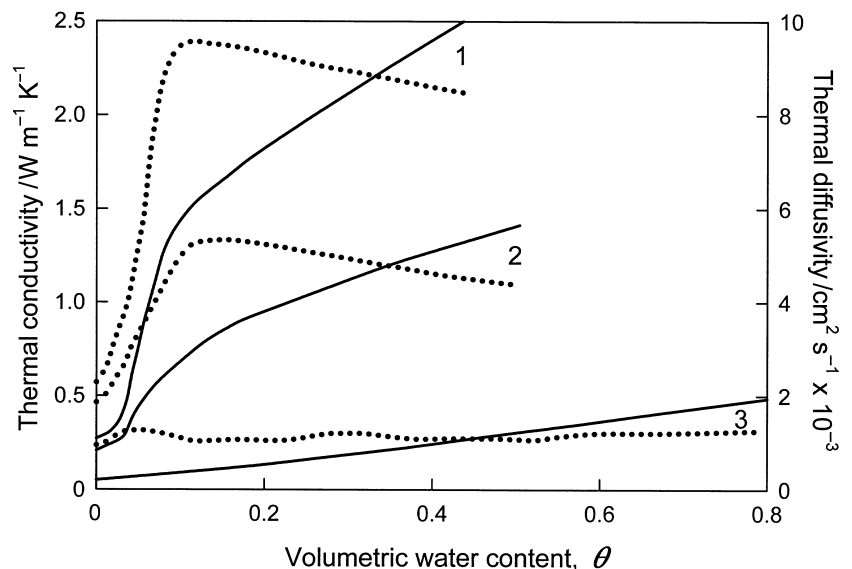


**Figure 3** Variation of soil thermal conductivity (solid curves) and diffusivity (broken curves) with volumetric water content for (1) quartz sand, (2) loam, and (3) peat. (Drawn from data contained in de Vries, 1975).

(whenever $\theta$ was $> 20\%$) soil respiration was controlled by temperature, during the dry summer respiration was limited by the lack of water (Figure 4a). Rey *et al.* developed a simple empirical model that simulated very closely the observed annual variation in soil respiration (Figure 4b). Earlier, a regression model linking the same variables, by Hanson *et al.* (1993), explained between 50 and 74% of the variability in $CO_2$ flux, and performed similarly for data from several topographical locations. Kicklighter *et al.* (1994) established that there was an exponential relationship between monthly mean $CO_2$ emissions from temperate forest soils and monthly mean air temperatures:

$$M = 27.5 \exp(0.068T), \tag{2}$$



where $M$ is the monthly evolution of $CO_2$ from the soil, in g C $m^{-2} month^{-1}$, and $T$ is the mean monthly air temperature in °C.

A more detailed, process-based, model has been described by Fang & Moncrieff (1999). This takes into account the production of $CO_2$ by the respiration of plant roots and microorganisms, and the transport of gases in the soil: $CO_2$ from soil to atmosphere and $O_2$ in the opposite direction.

In very wet soils, aeration is restricted because a large proportion of the pores are filled with water. Respiration is also restricted, and $CO_2$ flux decreases, but not as much as when lack of water is the limiting factor.

The depth to the water table has an important effect on soil respiration. Moore & Dalva (1993), Oechel *et al.* (1998) and Davidson *et al.* (1998) have shown that water tables, because of their effect on $O_2$ supply to the decomposer microflora, are the major control on $CO_2$ emission in high latitudes in soils with thick organic layers. This has become a topical issue, following the Kyoto Protocol, because of the potential role of afforestation in offsetting fossil fuel emissions of greenhouse gases. The greater proportion to date of forests in the UK have been planted on peat and peaty gley upland soils. These forests are accumulating carbon in the tree biomass, but one major effect of the trees on the soil environment is to lower the water table, well below the depth prevailing under the previous herbaceous vegetation (Figure 5). The likely consequence of this is an enhanced rate of oxidation (Silvola, 1986; Trettin *et al.*, 1996), thus counteracting, to some extent, the photosynthetic uptake by the forest. Reported rates of loss of C from drained afforested peats range from 1.2–3.7 t C ha$^{-1}$ year$^{-1}$ in Norway (Braekke, 1987) to 6–9 t C ha$^{-1}$ year$^{-1}$ in Scotland (Harrison *et al.*, 1995). However, Minkkinen *et al.* (2002) have concluded that peat drainage for forestry in Finland (usually with a water drawdown of $< 40$ cm) has increased C sequestration in the peat as well as in the tree stands. Thus there is still much work to be done to quantify the net effects on the C balance over whole forest rotations, in various environments. There are also implications for the balance of the non-$CO_2$ greenhouse gases $CH_4$ and $N_2O$ (see below).

## Physical controls on $CH_4$ emission and soil oxidation

### $CH_4$ emission: diffusion and ebullition processes

The concentration of methane in the atmosphere has more than doubled since the preindustrial era, from about $0.7 \times 10^{-6}$ mol mol$^{-1}$ to more than $1.7 \times 10^{-6}$ mol mol$^{-1}$ today. The lifetime of $CH_4$ in the atmosphere is quite short, $c.10$ years. Most atmospheric methane ($\geq 90\%$) is destroyed by oxidation by UV-created hydroxyl radicals (OH), while 5–10% is removed from the atmosphere by diffusion into aerobic topsoils, where it is oxidized by soil microorganisms (Prather *et al.*, 1995). No single source is responsible for the atmospheric increase, but soils contribute about 40% of total emissions (Prather *et al.*, 1995).
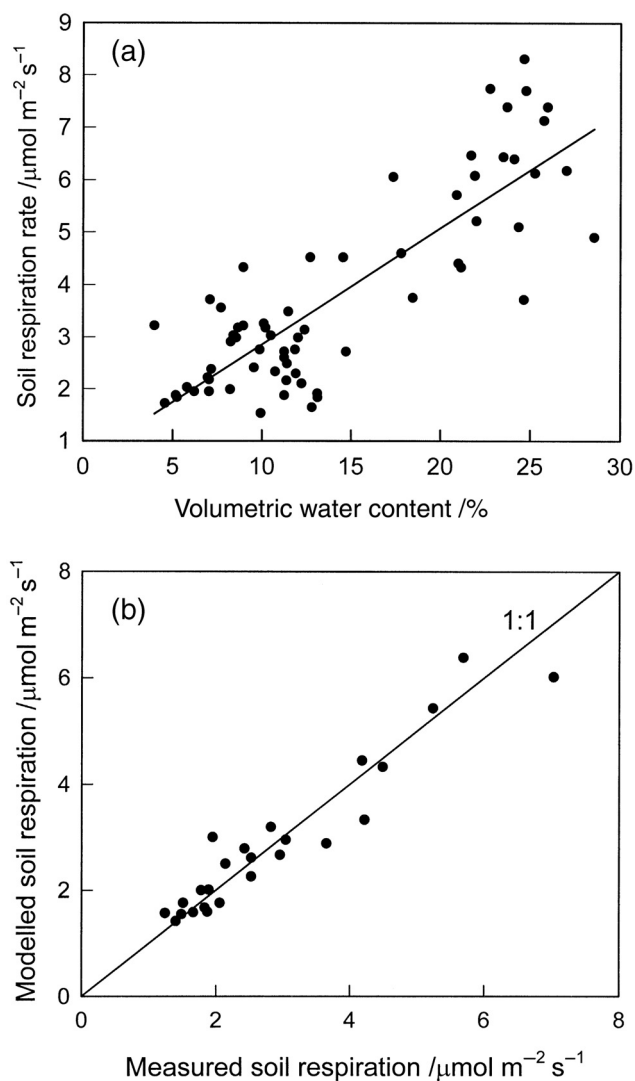
Figure 4 (a) Change in respiration rate in a Mediterranean soil with changing water content. The solid line is the regression line; $r = 0.83$, $P = 0.01$. (b) Modelled against measured respiration rate in the same soil. (Drawn from data contained in Rey *et al.*, 2002).
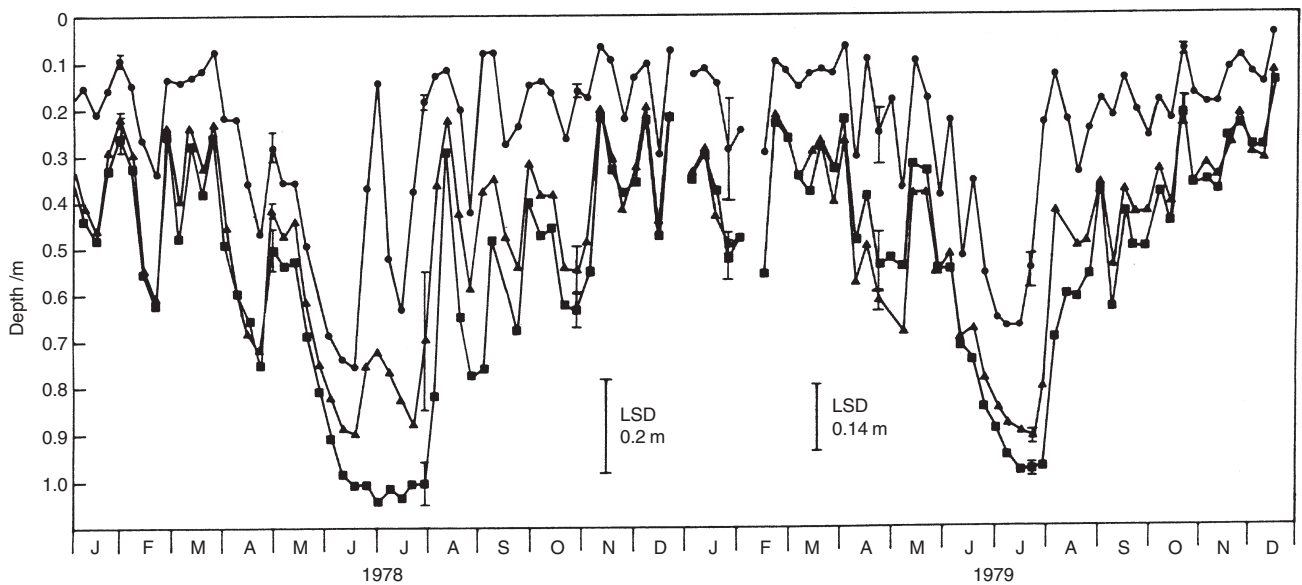
**Figure 5** Mean depth to water table under *Molinia caerulea* grassland (circles), Sitka spruce (*Picea sitchensis*, triangles) and lodgepole pine (*Pinus contorta*, squares). LSD, least significant difference. (From King *et al.*, 1986).

Methane is formed in soils by the microbial breakdown of organic compounds in strictly anaerobic conditions, at a very low redox potential. Production of $CH_4$ does not begin until reduction of molecular oxygen, nitrate, iron(III), manganese(IV) and sulphate (all of which maintain a higher potential) is complete (Ponnamperuma, 1972). Such low redox conditions usually require prolonged waterlogging, as is common in natural wetlands and flooded rice fields, as well as in lake sediments.

The $CH_4$ formed in flooded soils and sediments can migrate to the surface and be emitted into the atmosphere by one of three different pathways. First, diffusion can take place in solution towards the surface, in the course of which a substantial proportion of the $CH_4$ (10–40% in rice paddies, for example: Krüger *et al.*, 2002) is oxidized. Second, sufficient gas may be produced for bubbles to form in the water layer, and force their way to the surface – the process of ebullition. The speed of this process prevents any significant oxidation (Conrad, 1989). The third route is via the continuous air spaces – aerenchyma – of vascular plants which are adapted to life in flooded environments (e.g. Thomas *et al.*, 1996; Lloyd *et al.*, 1998; see Figure 6). These structures have evolved to transport oxygen needed for root respiration and cell division, but serve equally well as channels for the transport of methane from the root environment to the atmosphere.

In natural northern wetlands, methane emissions have been found to vary considerably with the type of vegetation present, but the greatest differences in flux appear to be brought about by the depth to the water table. Figure 7 shows the logarithmic increase in methane emissions from peat monoliths taken from a blanket bog as the measured depth to the water table diminishes from 40 cm or so to zero (MacDonald *et al.*, 1998). A very similar trend has been found by Liblik *et al.* (1997), for the combined results of six studies in boreal America.

Liblik *et al.* (1997) also reported $CH_4$ concentrations in the water in saturated peat 6000 times atmospheric concentration, and similar concentrations have been reported elsewhere. The concentration of $CH_4$ in gas bubbles reaching the surface of a bog or a paddy field is another indicator of how large concentrations in the root zone can be. Bubble concentrations in a rice paddy in Vercelli, northern Italy were 0.025–0.15 mol $CH_4$ $mol^{-1}$ (2.5–15% $CH_4$), and showed a clear increase as the season progressed (Conen, 2000; Marik *et al.*, 2002; Table 1). Those measured by Krüger *et al.* (2002) at the same site followed a similar trend, and these workers also found 1–4% $CH_4$ in the plant stems, i.e. concentrations which, though large, were substantially less than in the bubbles. Thus there is a concentration gradient between the root zone and the plant stems, and between the stems and the air outside, which promotes emission of $CH_4$ via diffusion through the plants; this applies to both rice plants and species growing in natural wetlands.

Arah & Stephen (1998) and Walter & Heimann (2000) have published process-based models of methane emission from wetlands. The models are essentially one-dimensional, treating the surface as if it were flat rather than the irregular mixture of hummocks and hollows that actually exists. In the model of Walter & Heimann, diffusion, plant-mediated transport, and ebullition – the three different transport mechanisms by which methane can move from the zone of formation to the atmosphere – are modelled explicitly.
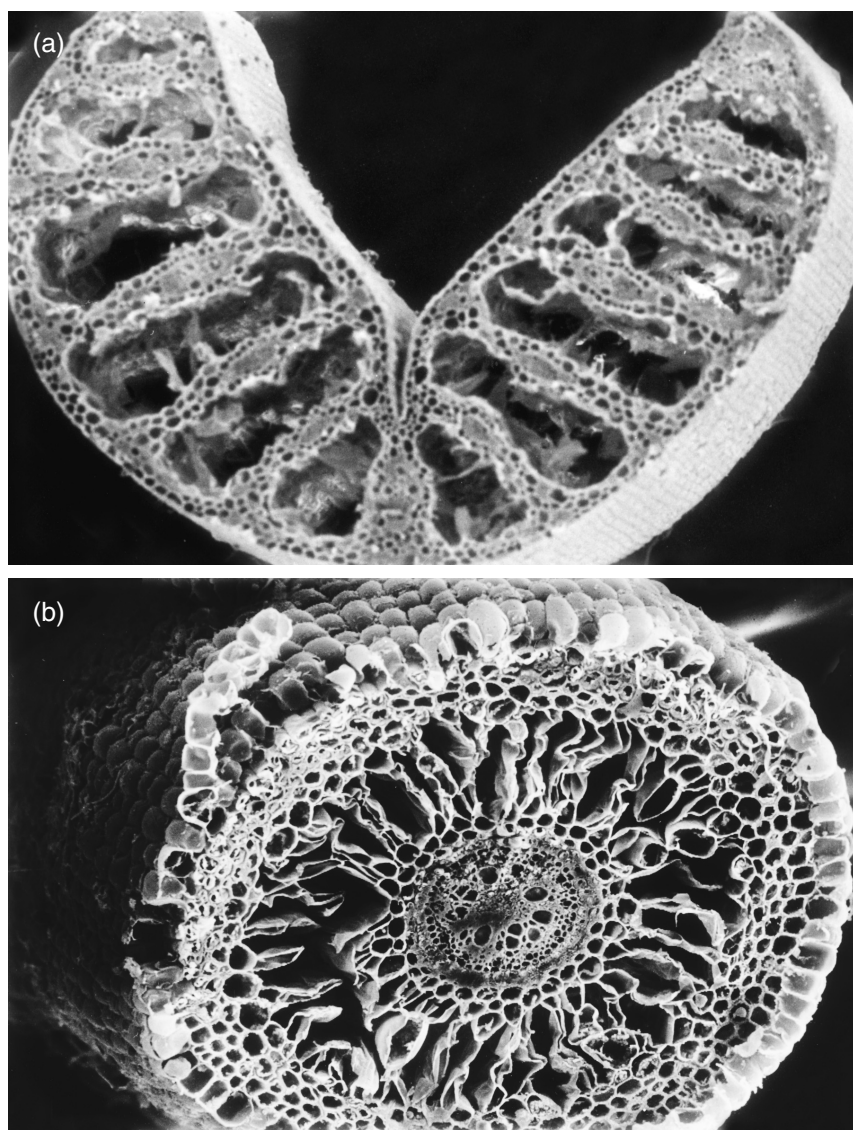
**Figure 6** Electron micrographs showing aerenchyma in (a) leaf of *Eriophorum angustifolium* and (b) root of *Molinia caerulea* at *c.*150 mm depth. (Reprinted from Thomas *et al.* (1996) with permission from Elsevier).

*CH$_4$ oxidation: effects of controls on diffusion and temperature*

About 30 Tg of atmospheric CH$_4$ per year (Prather *et al.*, 1995) is oxidized to CO$_2$ by aerobic soil bacteria which are adapted to living on this very small concentration of substrate. Oxidation is most rapid in coarse-textured forest soils with well-developed soil structure and a surface organic layer through which gases can readily diffuse (Smith *et al.*, 2000). However, Brumme & Borken (1999) have shown that the inhibition of litter decomposition in acid conditions in some forest soils can reduce substantially the entry of atmospheric CH$_4$ into the soil. The resulting accumulation of multiple layers of leaves from deciduous trees acts in wet conditions as an effective barrier against gas exchange by diffusion, and retards CH$_4$ oxidation considerably. This effect has been neatly demonstrated by an experiment in which litter from
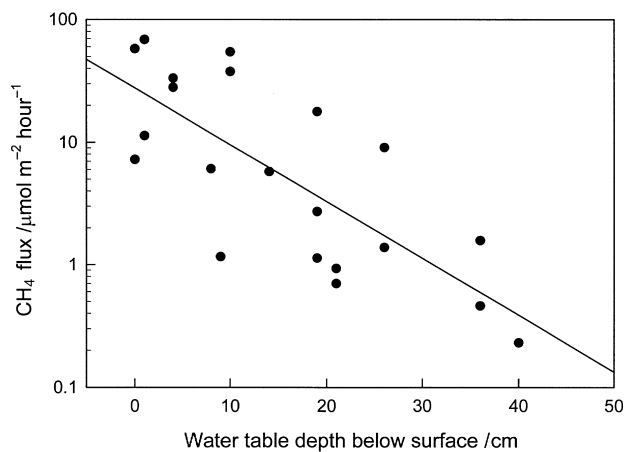


**Figure 7** Relation between depth to water table and CH$_4$ flux in monoliths from a Scottish wetland. The solid line is the regression line; $r = 0.79$, $P < 0.01$. (Drawn from data contained in MacDonald *et al.*, 1998).

**Table 1** Methane concentration in gas bubbles reaching the water surface of a rice paddy, Vercelli, Italy (Conen, 2000; Marik *et al.*, 2002)

| | CH$_4$ in bubbles /% | |
|---|---|---|
| Growth stage | 1998 | 1999 |
| Tillering | 11.0 | 2.5 |
| Flowering | 15.0 | 6.9 |
| Significance of increase from tillering to flowering | $P < 0.01$ | $P < 0.001$ |

spruce and beech stands in a German forest was exchanged. Replacement of spruce needles by beech leaves retarded the oxidation, whereas the reverse process had the opposite effect (Figure 8).
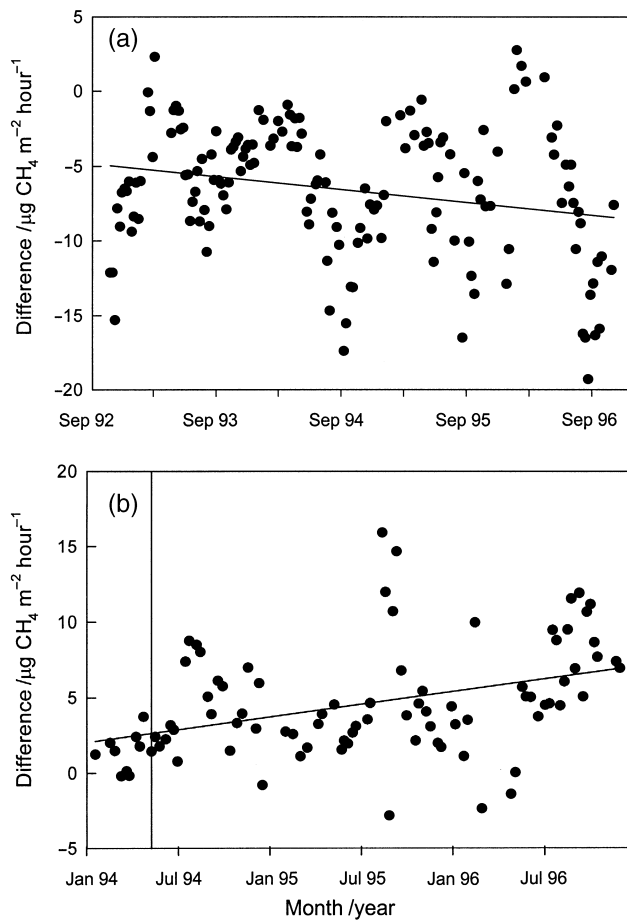


**Figure 8** Effect of exchanging spruce and beech litter between sites on CH$_4$ oxidation in soil. (a) Difference between chambers receiving beech litter and control chambers in a spruce stand. (b) Difference between chambers receiving spruce litter and control chambers in a beech stand; vertical line indicates date when litter first exchanged. In both experiments, the differences are highly significant ($P < 0.01$); they show maxima in late summer and minima in winter, but also gradually increase with time, as shown by the regression lines. (Drawn from data contained in Brumme & Borken, 1999).

The effect of soil temperature on oxidation is small, with reported $Q_{10}$ values of the order of 1.4 (e.g. Born *et al.*, 1990; Crill, 1991). Increases in oxidation rates in summer are due mainly to drier soil, and only secondarily to increases in temperature (Brumme & Borken, 1999). The small temperature response is attributed to limitations imposed by the supply of available methane substrate, due to the combined effects of diffusion resistance and small atmospheric concentration. Data compiled by Smith *et al.* (2000) show steady decreases in oxidation rate with increasing dry bulk density of the soil and with increasing proportion of water-filled pore space: both factors reduce gas diffusivity. Ball *et al.* (1997) showed the link between oxidation rate and measured gas diffusivity (Figure 9). Earlier, Keller & Reiners (1994) found a linear relationship between CH$_4$ oxidation rate and diffusivity values calculated from WFPS measurements on the soil.

Several models of methane oxidation, of varying complexity, have been published. That of Dörr *et al.* (1993) simulates methane oxidation gradients in the soil. Ridgwell *et al.* (1999) developed a process-based model in which methane oxidation is controlled by gas diffusivity when microbial activity is great and by microbial activity at large diffusivities. The model of Potter *et al.* (1996) is simpler; it assumes that gas diffusivity is
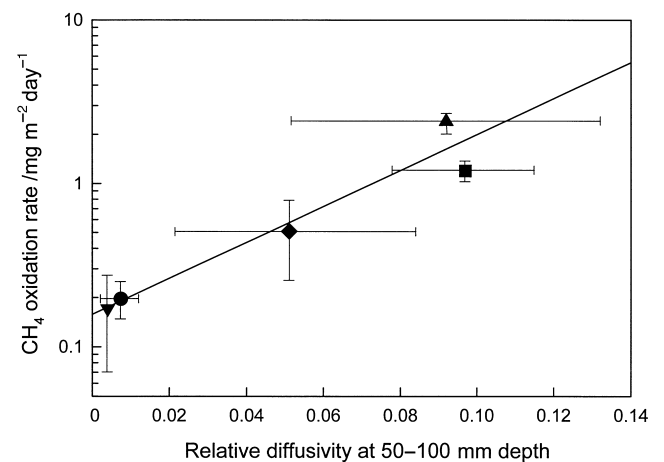


**Figure 9** Relation between rate of CH$_4$ oxidation and relative gas diffusivity in some northern European soils. The solid line is the regression line ($r = 0.96$, $P < 0.01$); the error bars indicate $\pm$ 1 standard deviation for each data point. (Drawn from data contained in Ball *et al.*, 1997).

the major control, and thus it predicts maximum methane oxidation rates in dry soil. This is an oversimplification, because oxidation decreases as soils become very dry and microbial activity is inhibited (e.g. Dobbie & Smith, 1996). Del Grosso *et al.* (2000a) have developed the model of Potter *et al.* to take account of this limitation.

## Physical controls on $N_2O$ and NO emissions

### Diffusion of $O_2$ and $N_2O$

Nitrous oxide, $N_2O$, and nitric oxide, NO, are produced in soil mainly in the course of two contrasting microbial processes: nitrification of ammonium, $NH_4^+$, to nitrite, $NO_2^-$ and thence to nitrate, $NO_3^-$, and denitrification of nitrate to $N_2O$ and ultimately to molecular nitrogen, $N_2$.

Nitrification is an aerobic process, but when the supply of $O_2$ is limited by diffusional constraints the nitrifying bacteria can use nitrite as an electron acceptor and reduce it to NO and $N_2O$ (Poth & Focht, 1985; Bollmann & Conrad, 1998). The process may be simply represented as follows:

$$NO, N_2O \text{ (emission)}$$
$$\uparrow$$
$$NH_4^+ \Longrightarrow NO \Longrightarrow NO_2^- \Longrightarrow NO_3^-.$$
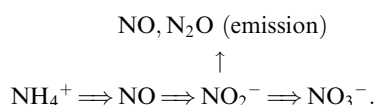
Thus the rate of nitrification, the rate of $N_2O$ production, and the ratio of $N_2O$ to nitrate produced during nitrification all increase as the soil WFPS increases (Table 2). Production of NO by nitrification is generally much faster than the corresponding production of $N_2O$, and this is reflected in the ratios in which the two gases are emitted from aerated soils. Data
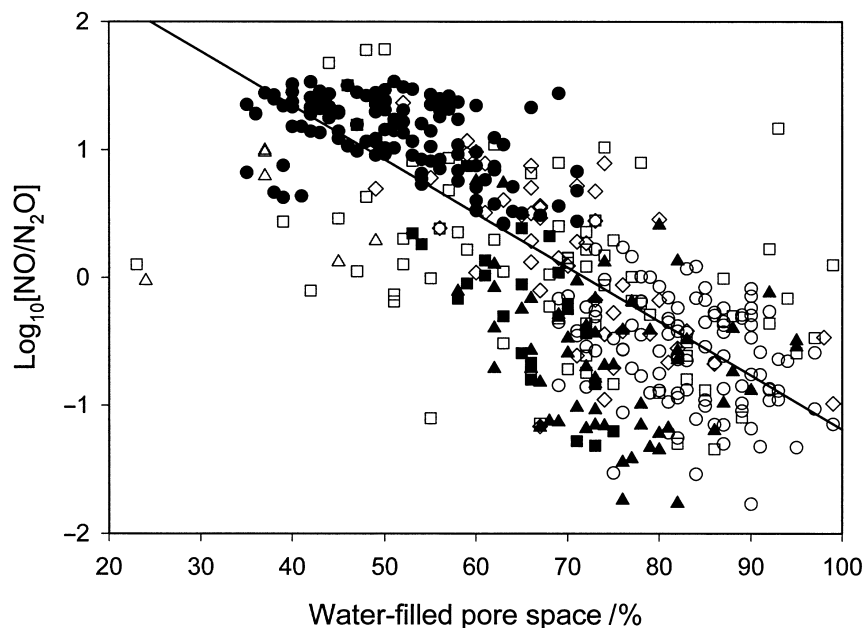
**Table 2** Effect of soil water-filled pore space (WFPS) on rate of nitrification, rate of $N_2O$ production, and ratio of $N_2O$ to nitrate produced (Goodroad & Keeney, 1984)

| | Soil WFPS /% | | |
| --- | --- | --- | --- |
| | 18 | 36 | 54 |
| Rate of nitrification[a] | 1.0 | 1.5 | 1.7 |
| Rate of $N_2O$ production[a] | 1.0 | 1.6 | 7.4 |
| Ratio ($N_2O$-N/$NO_3^-$-N)$\times 10^3$ | 1 | 1 | 5 |

[a]Rate at 18% WFPS normalized to 1.0.

from seven studies compiled by Davidson & Verchot (2000) show mean ratios of NO-N/$N_2O$-N well in excess of 10 at 40% WFPS or drier (Figure 10).

The other microbial process that is a major source of $N_2O$ is anaerobic denitrification, involving the reduction of nitrate via nitrite and NO, to $N_2O$ and $N_2$:

$$N_2O \text{ (emission)}$$
$$\uparrow$$
$$NO_3^- \Longrightarrow NO_2^- \Longrightarrow NO \Longrightarrow N_2O \Longrightarrow N_2.$$

The necessary conditions for the process occur when respiratory consumption of $O_2$ in the soil by plant roots and soil microorganisms exceeds the rate of replenishment by diffusion from the atmosphere, and anaerobic microsites within the soil profile are created. Nitrate is the chemical species that most readily acts as an electron acceptor, once $O_2$ has been exhausted, and so the onset of denitrification, unlike methane production, can be rapid.



**Figure 10** Relation between water-filled pore space in the soil and the ratio of NO emissions to $N_2O$ emissions, for measured fluxes $>1 \text{ g N ha}^{-1} \text{day}^{-1}$ in the TRAGNET database (http://www.nrel.colostate.edu/projects/tragnet/). The solid line is the regression ($r = 0.75$, $P < 0.001$). The different symbols represent different sites and land uses in Costa Rica (■, ▲, ○, ◊), Germany (●), Mexico (□) and USA (△). (Drawn from data contained in Davidson & Verchot, 2000).
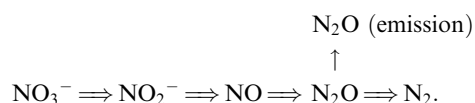
**Table 3** Emissions of gases from drained and undrained organic soils, converted to $CO_2$ equivalents in terms of global warming potential (from Kasimir-Klemedtsson *et al.*, 1997)

| Soil and crop | $CO_2$ /kg ha$^{-1}$ year$^{-1}$ | $N_2O$ /kg ha$^{-1}$ year$^{-1}$ | | $CH_4$ /kg ha$^{-1}$ year$^{-1}$ | | Total /kg $CO_2$ equivalent |
|---|---|---|---|---|---|---|
| | | Actual | $CO_2$ equivalent | Actual | $CO_2$ equivalent | |
| Undrained peat, fen | −600 | 0 | 0 | 200 | 4900 | 4300 |
| Undrained peat, bog | −900 | 0 | 0 | 100 | 2500 | 1600 |
| Drained, grass | 11 000 | 9 | 2880 | < 0.1 | 2 | 13 900 |
| Drained, cereals | 20 000 | 15 | 4800 | 1.1 | 27 | 24 800 |
| Drained, row crop | 70 000 | ND | ND | ND | ND | > 70 000 |

ND, not determined.

The fraction of the total gaseous products of anaerobic denitrification that is actually emitted to the atmosphere as $N_2O$ depends heavily on the structure and wetness of the soil. If an $N_2O$ molecule can readily diffuse from the site of production into an oxygenated pore it has a good chance of being emitted to the atmosphere rather than being reduced to $N_2$. On the other hand, $N_2O$ produced well below the surface of a saturated soil clod is much more likely to be reduced to $N_2$ than to escape. The distribution of source regions in a soil producing substantial fluxes of $N_2O$ is inherently more complex than the corresponding distribution in a wetland soil emitting methane; the former is essentially a three-dimensional mosaic of anaerobic microsites producing $N_2O$ within an otherwise aerobic matrix, whereas the latter is usually a one-dimensional system of oxygenated layers above a highly reduced anaerobic layer in which $CH_4$ forms.

The denitrification pathway to $N_2O$ has been established as having to go via NO, yet NO is virtually absent from gaseous emissions in wet soils where anaerobic conditions occur. As can be seen in Figure 10, the mean NO-N/$N_2O$-N ratio diminishes rapidly with increasing WFPS, to about 3–5 in the 50–60% WFPS range, and to much less than 1 at or in excess of 80% WFPS. This is attributed to a greater tendency for NO than $N_2O$ to be consumed by the denitrifying organisms (Firestone & Davidson, 1989). Thus NO emission from denitrifying soils is usually detected only in highly artificial experimental conditions, for example when the NO is swept out of a column of soil by a stream of $O_2$-free gas (Johansson & Galbally, 1984).

### Changes in depth to water table

As mentioned in the section above dealing with $CO_2$ emissions, lowering of the water table in organic soils can have significant effects on trace gas emissions. Table 3, taken from Kasimir-Klemedtsson *et al.* (1997), shows the emissions of $N_2O$ (and of $CH_4$ and $CO_2$) from undrained wetlands and drained organic soils converted to agricultural use in Scandinavia. The $N_2O$ emissions following draining had a global warming potential of about 25% of those of $CO_2$, whereas in flooded conditions

$N_2O$ was not detectable, presumably because any $N_2O$ produced during denitrification was completely reduced to $N_2$. Similar results are being obtained by our group in a plantation forest in northern England (Smith *et al.*, 2003). Yet another environment where flooding prevents $N_2O$ emission and draining promotes it is the rice paddy. However, the use of one or more brief drainage episodes during the rice growing season (e.g. Neue, 1997), or delaying flooding after sowing, produces a beneficial 'trade-off' with reduced $CH_4$ emission that considerably reduces the overall contribution to global warming (Leip *et al.*, 2002).

### Temperature

Many research studies have reported non-linear (exponential) increases in $N_2O$ emission rate with increasing temperature. The temperature dependence is commonly and conveniently expressed in terms of the $Q_{10}$ value, Equation (1) above, as for $CO_2$, but observed values for the $Q_{10}$ for $N_2O$ emission range up to 10 or more, compared with the general range of 2–3 for most biochemical processes. For example, Brumme (1995) observed a $Q_{10}$ of 14.4 for a forest soil in Germany. An explanation for this marked response is provided by the theory of anaerobic zone development in soils (e.g. Leffelaar, 1979, 1986; Smith, 1980, 1997; Li *et al.*, 2000). An increase in temperature leads to an increase in the size of the zones, because of increased respiration causing larger gradients in $[O_2]$ and thus rendering more of the soil volume devoid of oxygen (Figure 11).
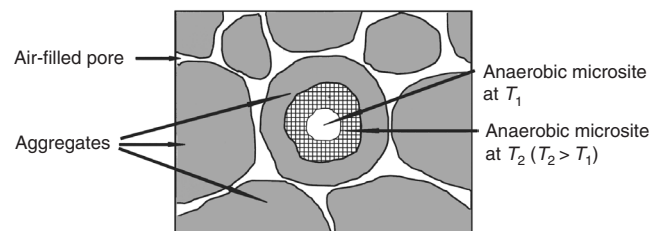


**Figure 11** Conceptual relation between the size of an anaerobic microsite and the soil temperature.
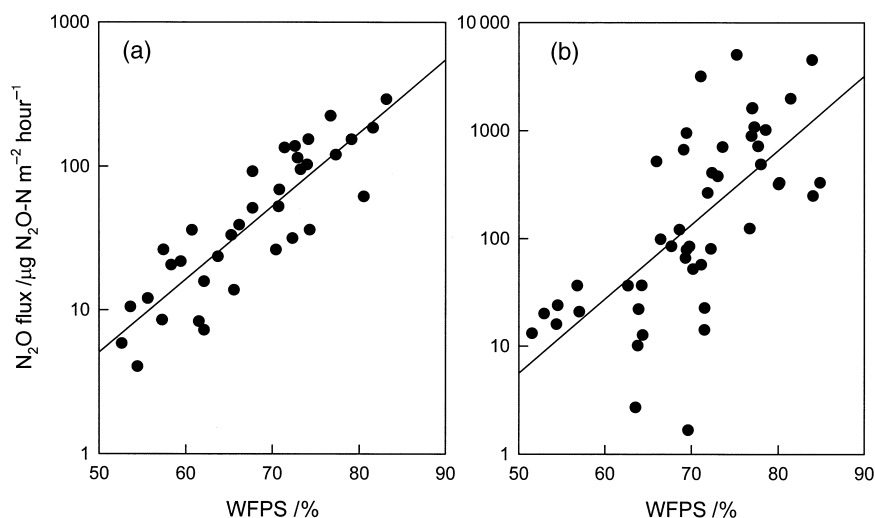
**Figure 12** Similar relations between soil water-filled pore space (WFPS) and $N_2O$ flux in widely contrasting environments. (a) Old-growth tropical forest in Costa Rica (drawn from data contained in Keller & Reiners, 1994). (b) N-fertilized grassland on glacial till soil in southeast Scotland (drawn from data contained in Smith & Dobbie, 2002).

It also leads to an increase in the rate of denitrification per unit anaerobic volume (with a $Q_{10}$ of 2 or so). The overall change in the rate of $N_2O$ production in a soil mass (as is observed by a chamber measurement) is then the product of these two factors (Smith, 1997). An increase in soil WFPS, and the consequent decrease in $O_2$ diffusion rate within the soil, has a similar effect on the system to that induced by a rise in temperature, and thus $N_2O$ production and emission increase exponentially with WFPS (Keller & Reiners, 1994; Dobbie & Smith, 2001; Smith & Dobbie, 2002; Figure 12).

Several models of $N_2O$ emissions, embracing emissions both from agricultural soils and from natural ecosystems, have been published. The most complex, diffusion-based, models calculate the soil anaerobic fraction in which denitrification can occur (e.g. Arah & Smith, 1989; Renault & Stengel, 1994). These models are likely to require too many parameters to be applicable over sufficiently large areas to be useful for predicting fluxes, but they do provide a better understanding of the processes responsible for emissions, and the sensitivity of the fluxes to changes in particular variables. Qualitatively, the trends predicted by these models are borne out by observation, in particular the very large $Q_{10}$ values for $N_2O$ emission that are sometimes observed (Brumme, 1995; Smith, 1997). There are also several 'process-oriented' simulation models of intermediate complexity (e.g. Li *et al.*, 1992a,b, 2000; Engel & Priesack, 1993; Parton *et al.*, 1996; Del Grosso *et al.*, 2000b) and empirical models such as that relating flux to WFPS, temperature and soil mineral N content (Conen *et al.*, 2000).

## Concluding remarks

We hope that this paper, in an issue of the Journal devoted to soil biology, will introduce many more soil scientists to the effect of biogeochemical cycling within soils on the composition of the atmosphere and on global warming. Our review has had to be illustrative rather than fully comprehensive, but it should provide insight into the subject for those not previously familiar with it. We further hope that it provides a bridge between soil physics and soil biology, by demonstrating the key roles played by soil physical factors in controlling the biological processes responsible for the exchange of greenhouse gases between soil and atmosphere. It should also provide a bridge to the wider scientific literature. As readers will observe from the bibliography, this is a subject that transcends traditional subject boundaries, and one in which relevant material is as likely to turn up in a meteorological journal as in one devoted to soil science. The choice of journal is often more to do with the publishing tradition of the research group concerned than to a strict classification of the material presented. One often hears complaints about the 'compartmentalization' of science; we hope that this paper will help readers to cross some of those compartment boundaries and lead towards greater integration of our science.

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