FACTORS CONTROLLING N_2O EMISSIONS FROM SOILS: A STUDY USING A NOVEL SOIL MONOLITH/FLUX CHAMBER SYSTEM

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DECLARATION

I, Petra Elisabeth Thomson, declare that this thesis was composed by myself, and the work carried out by myself, except for the instances detailed in the text and acknowledgement.

Petra Thomson

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ABSTRACT

Soils are the most important source of N_2O emissions to the atmosphere, with denitrification and nitrification being the major processes responsible for production of the gas. Although much is known about factors controlling these processes and N_2O fluxes from them, it is still difficult to obtain accurate N_2O emission estimates due to the highly heterogeneous nature of soils. Better estimates can only be achieved by a combination of direct measurements in key ecosystems and by quantifying the relationships between fluxes and the controlling parameters, as an aid to modelling and upscaling.

The aim of this project was to quantify the effects of various soil and environmental parameters on N_2O emissions to the atmosphere, making measurements in a semi-controlled environment, where it was more possible to control these parameters than in the field. The system consisted of 12 soil monoliths (1 m diameter and ca. 60 cm deep) from three contrasting soils (a sandy loam, a clay loam and a peaty gley). The headspaces of the monolith casings were converted to flux chambers by fitting them with aluminium lids and each chamber was connected to an ECD gas chromatograph. Gas sampling and analysis, and recording of information from temperature probes and transducer tensiometers, were completely automated.

Soil water content, temperature (including diurnal temperature variation), organic matter input and respiration all had major effects on N_2O emissions. Using boundary line analysis (summarising data from several experiments), quadratic relationships between water-filled pore space (WFPS) and log-transformed N_2O fluxes from the sandy loam and clay loam soils were established; the optima for emissions were 90 and 92% WFPS, respectively. The relationships between temperature and log-transformed N_2O data were linear, and Q_{10}-values up to 7.5 for the sandy loam soil and 9.4 for the clay loam soil were observed. The high optimum WFPS for emissions and the high Q_{10}-values indicate that denitrification was the major process involved. Diurnal maxima in N_2O flux were observed, which sometimes coincided with the

temperature maxima in the uppermost 5 cm, but on other occasions the flux maxima were delayed by several hours; this was attributed to N_2O production taking place at greater depths. Significant relationships were observed between N_2O emissions, and CO_2 emissions from respiration, following incorporation of a grass-clover mixture into the sandy loam and clay loam soils. The overall effect of respiration on log-transformed N_2O emissions from the sandy loam and clay loam soils could be described with a rectangular hyperbola, where the rate of the N_2O emission increase at first rose steeply with the respiration rate, but then slowed down drastically when the respiration rate was greater than 20 mg CO_2-C m^{-2} h^{-1}. No boundary line could be defined for water-filled pore space, temperature and respiration from the peaty gley soil. However, when data from single experiments were analysed, relationships could be established. Strong interactions between all the factors controlling N_2O emissions were observed.

CONTENTS

1. INTRODUCTION

1.1. Nitrous Oxide in the Atmosphere

Nitrous oxide (N_2O) in the atmosphere is of major environmental concern:

a) it is a greenhouse gas, and

b) it is involved in the destruction of the ozone layer.

The anthropogenic greenhouse effect

Solar short-wave radiation is the ultimate energy source for the earth's climate (Houghton *et al.*, 1995; Whyte, 1995). Most of it is absorbed by land, ocean and ice surfaces. The incoming radiation is balanced by outgoing radiation from the long wave infra-red spectrum. Some of this is absorbed by radiatively active gases (greenhouse gases) in the atmosphere, of which the most important ones are water vapour (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and ozone (O_3) (Houghton *et al.*, 1995). This keeps the earth's surface and the troposphere about 33°C warmer than it would be otherwise, and is called the natural greenhouse effect (MacDonald, 1989; Houghton *et al.*, 1995; Whyte, 1995). A simple diagram of the greenhouse effect is shown in Fig. 1.1. The enhanced or anthropogenic greenhouse effect is caused by an increase of the concentration of the greenhouse gases (exclusive of water vapour) in the atmosphere and by adding new ones, like chlorofluorocarbons (CFCs), due to human activities since the industrial revolution (MacDonald, 1989; Houghton *et al.*, 1995).

Trends in the atmospheric N_2O concentration were summarised by Prather *et al.* (1995). In pre-industrial times the N_2O concentration was about 275 ppbv, with a range of 260 to 285 ppbv. Since then N_2O concentrations have risen by about 15% and reached 311 ppbv in 1992. During the 1980s the increase was about 0.25% per year, with a strong year-to-year variation. N_2O has an atmospheric lifetime (defined as the ratio of the atmospheric concentration to the total rate of removal) of 120 ±30 years and has, therefore, a long-term effect on the earth's climate.

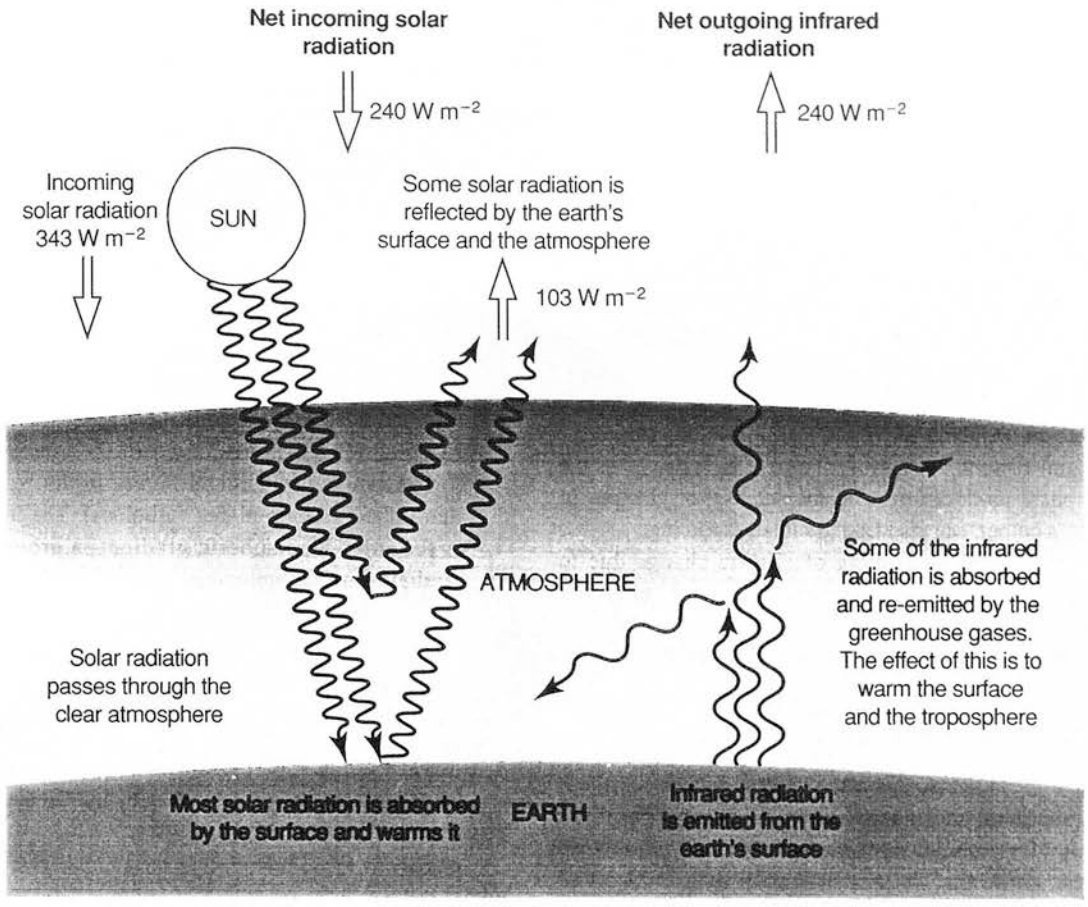


Fig. 1.1. A simplified diagram illustrating the global long-term radiative balance of the atmosphere. Net input of solar radiation (240 Wm^{-2}) must be balanced by net output of infrared radiation. About a third (103 Wm^{-2}) of incoming solar radiation is reflected and the remainder is mostly absorbed by the surface. Outgoing infrared radiation is absorbed by greenhouse gases and by clouds keeping the surface about 33°C warmer than it would otherwise be (Houghton *et al.*, 1995).

N_2O is a much stronger greenhouse gas than CO_2; molecule for molecule the radiative forcing due to N_2O (defined as the net radiative imbalance (in W m^{-2}) at the tropopause, after allowing for stratospheric temperatures to re-adjust to radiative equilibrium, but with surface and tropospheric temperature held fixed at their unperturbed values), is 206 times that of CO_2 (Shine *et al.*, 1995). The total radiative forcing of the main greenhouse gases (excluding O_3) is currently 2.45 W m^{-2}, to which N_2O contributes about 5 to 6%, or 0.14 W m^{-2} (Shine *et al.*, 1995). The contribution of the other greenhouse gases is shown in Fig. 1.2.

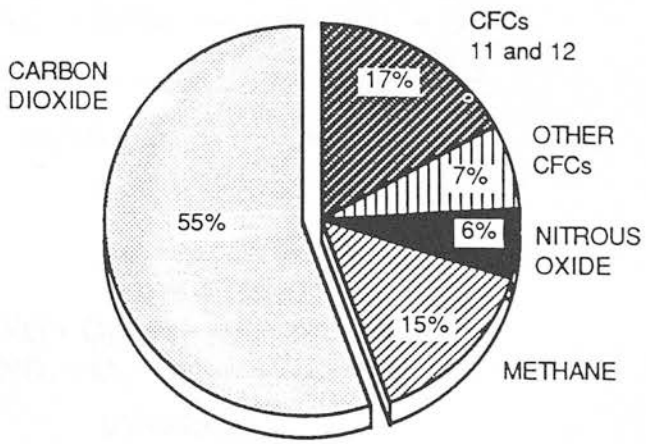


Fig. 1.2. The contribution from each of the human-made greenhouse gases (excluding ozone) to the change in radiative forcing from 1980 to 1990 (Houghton *et al.*, 1990).

Destruction of stratospheric ozone

N_2O is inert in the troposphere; however, in the stratosphere it is destroyed mostly by photodissociation by sunlight and through reaction with excited oxygen atoms, $O(^1D)$ (McElroy and McConnell, 1971; Crutzen and Ehhalt, 1977):

$$N_2O \xrightarrow{\text{UV radiation (< 337 nm)}} N_2 + O(^1D)$$

$$N_2O \xrightarrow{\text{UV radiation (< 250 nm)}} NO + N$$

$$O(^1D) + N_2O \longrightarrow 2NO$$

$$O(^1D) + N_2O \longrightarrow N_2 + O_2$$

Transformation of N_2O is the major process producing nitric oxide (NO) in the stratosphere, which is involved in the destruction of the ozone layer by the following catalytic reactions (Crutzen and Ehhalt, 1977; Crutzen, 1979):

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O(^1D) \longrightarrow NO + O_2$$

net: $O(^1D) + O_3 \longrightarrow 2O_2$

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
$$NO_3 \xrightarrow{\text{UV radiation}} NO + O_2$$

net: $2O_3 \longrightarrow 3O_2$

For a doubling of the N_2O concentration in the atmosphere, these reactions would lead to a reduction of 3 to 5% of the stratospheric O_3, assuming otherwise constant atmospheric conditions (Bolle *et al.*, 1986).

Badr and Probert (1993) suggested that the oxidation of N_2O in the stratosphere can also contribute to the acid rain problem, due to the subsequent formation of nitric acid (HNO_3) in the lower stratosphere. N_2O leads also to an increase of tropospheric O_3 (Wang and Sze, 1980).

1.2. Sources and Sinks

Table 1.1 shows the sources and sinks of atmospheric N_2O. Of the 14.7 Tg N yr^{-1} emitted to the atmosphere about 65% is derived from soils, making them the largest

single source. It is estimated that around 37% of the soil contribution originates from cultivated soils. However, this is likely to be an underestimate, since no attempt has been made so far to divide tropical soils into natural and cultivated ones (Prather *et al.*, 1995). Industrial sources account for approximately 1.3 Tg N yr^{-1}, and comprise several small sources like adipic acid production (Thiemans and Trogler, 1991), nitric acid production (Watson *et al.*, 1992), motor vehicles, particularly when fitted with catalytic converters (Dasch, 1992; Khalil and Rasmussen, 1992), and fossil fuel combustion (Watson *et al.*, 1992). Because all of these sources only emit small amounts of N_2O, their actual strength is very difficult to estimate (Khalil and Rasmussen , 1992; Prather *et al.*, 1995).

The main sink for N_2O is the destruction in the stratosphere, as outlined in Section 1.1., which accounts for 12.3 Tg N yr^{-1}. It has also been suggested that soils can act as a sink for N_2O, as well as being a source (Blackmer and Bremner, 1976; Donoso *et al.*, 1993); however, no estimate of the sink strength is available to date.

Taking the atmospheric increase into account the total annual N_2O emissions should be 1.5 Tg N yr^{-1} higher than estimated from the known sources (see Table 1.1). This can be attributed to the large uncertainty range for some sources, rather than to the likelihood of major unidentified sources (Prather *et al.*, 1995). If the current emission rate remains unaltered the atmospheric N_2O concentration will reach about 400 ppbv over the next two centuries, corresponding to an additional radiative forcing of 0.3 W m^{-2} (Schimel *et al.*, 1996). A reduction of more than 50% in emissions would be needed to hold atmospheric concentrations at the present level (Houghton *et al.*, 1995).

Table 1.1. Estimated sources and sinks of N_2O typical of the last decade (Tg N yr^{-1}) (Prather *et al.*, 1995).

	Range	Likely
Atmospheric increase	3.1 - 4.7	3.9†
Sinks		
stratosphere	9 - 16	12.3
soils	?	
Total Sinks	9 - 16	12.3
Implied total sources (atmospheric increase + total sinks)	13 - 20	16.2

Identified sources	**Range**	**Likely**
Natural		
oceans	1 - 5	3
tropical soils		
wet forests	2.2 - 3.7	3
dry savannas	0.5 - 2.0	1
temperate soils		
forests	0.1 - 2.0	1
grasslands	0.5 - 2.0	1
Total identified natural sources	6 - 12	9
Anthropogenic		
cultivated soils	1.8 - 5.3	3.5
biomass burning	0.2 - 1.0	0.5
industrial sources	0.7 - 1.8	1.3
cattle and feed lots	0.2 - 0.5	0.4
Total identified anthropogenic	3.7 - 7.7	5.7
TOTAL IDENTIFIED SOURCES	**10 - 17**	**14.7**

† The observed atmospheric increase implies that sources exceed sinks by 3.9 Tg(N)/yr.

1.3. N_2O Production and Emissions from Soils

The most important processes responsible for N_2O production in soils are biological denitrification and nitrification. Both these processes are dominant driving forces in the biological nitrogen cycle (Robertson and Kuenen, 1991), shown in Fig. 1.3. During chemo-denitrification N_2O is also produced, and may lead to significant N_2O losses at times in neutral to alkaline soils (Mosier *et al.*, 1983). Other processes during which N_2O is released from soils are dissimilatory and assimilatory NO_3^--reduction to NH_4^+ by bacteria (Smith and Zimmerman, 1981; Bleakley and Tiedje, 1982; Mosier *et al.*, 1983). The latter process can also be carried out by fungi and yeasts (Bollag and Tung, 1972; Bleakley and Tiedje, 1982; Umarov, 1990). These two processes can contribute substantially to N_2O emissions from soils. For example, Robertson and Tiedje (1987) found that 77 - 100% of N_2O produced in two soils came from sources other than denitrification or nitrification. However, at present, very little is known about the mechanism of N_2O evolution from these processes (Mosier *et al.*, 1983; Umarov, 1990). Because of this, only biological denitrification and nitrification will be considered in this work.

1.3.1. Biological denitrification

Biological denitrification is defined as anaerobic bacterial respiration, during which nitrate (NO_3^-) and nitrite (NO_2^-) are reduced sequentially through NO and N_2O to N_2 (Aulakh *et al.*, 1992). The commonly accepted pathway (Knowles, 1981; Payne, 1981) is:

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

Denitrification species are largely limited to the genera *Pseudomonas*, *Bacillus* and *Paracoccus*, but the reduction is catalysed by *Thiobacillus denitrificans* and also by *Chromobacterium*, *Corynebacterium*, *Hyphomicrobium* and *Serratia* (Alexander, 1977). Denitrifying bacteria are aerobic, but use NO_3^- and NO_2^- as electron acceptors

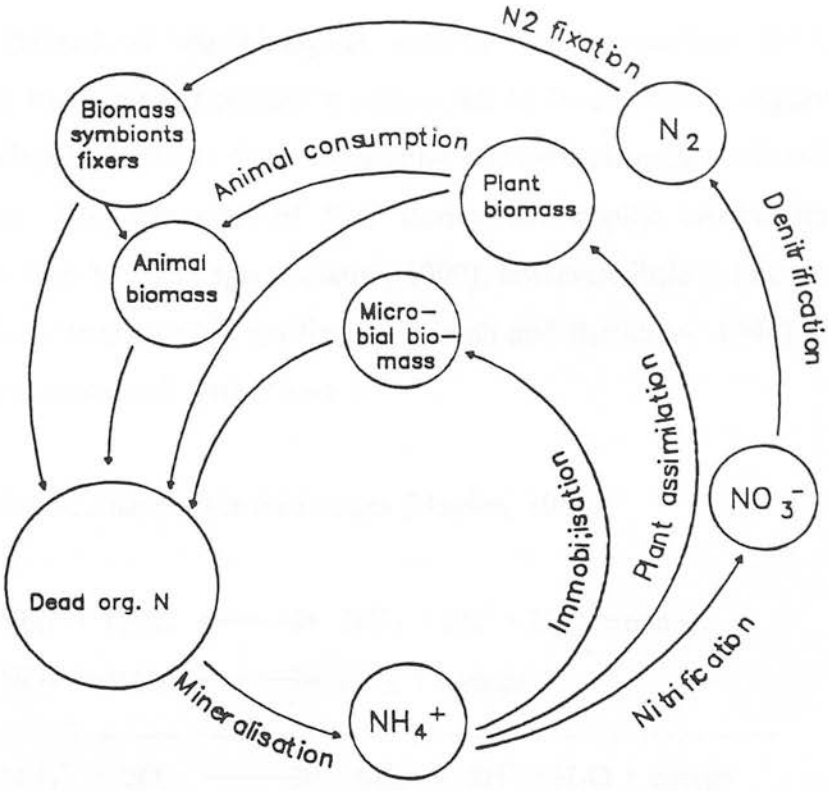


Fig. 1.3. The nitrogen cycle (adapted from Jansson and Persson, 1982).

for growth in the absence of O_2 (Alexander 1977; Knowles, 1981), thus denitrification is usually associated with anaerobic soils. However, denitrification can also occur in anaerobic microsites in otherwise aerobic soils (Parkin, 1987). These microsites form when the oxygen consumption exceeds the oxygen supply (Tiedje *et al.*, 1984), usually around particulate organic matter, like pieces of decaying plant material, earth worm casts or dead cells (Svensson *et al.*, 1986; Parkin, 1987; Christensen *et al.*, 1990). They can also form when a diffusion barrier of mainly water-filled pores limits the oxygen diffusion into soil aggregates (Smith, 1990). Not all denitrifiers can carry out the complete reduction from NO_3^- to N_2 (Ingraham, 1981; Knowles, 1982; Robertson and Kuenen 1991).

1.3.2. Nitrification

Nitrification is defined as the biological oxidation of ammonium (NH_4^+) by chemoautotrophic bacteria or of organic N compounds by heterotrophic organisms to NO_2^- and NO_3^- (Groffman, 1991). Both autotrophic and heterotrophic nitrification are aerobic processes. The formation of N_2O during autotrophic nitrification was established more than 50 years ago (Umarov, 1990); however, little is known about N_2O evolution from heterotrophic nitrification (Granli and Bøckman, 1994) and this process will not be considered further here.

Autotrophic nitrification happens in two stages (Haynes, 1986):

$$\text{I. } NH_4^+ + 1\tfrac{1}{2}O_2 \longrightarrow NO_2^- + 2H^+ + H_2O + \text{energy}$$

$$\text{II. } NO_2^- + \tfrac{1}{2}O_2 \longrightarrow NO_3^- + \text{energy}$$

$$\text{Overall: } NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O + \text{energy}$$

The first stage is carried out by bacteria from the genera *Nitrosomonas*, *Nitrosococcus*, *Nitrospira* and *Nitrosolobus* (these are also called ammonium oxidizers); the second stage by *Nitrobacter* (also called nitrite oxidizers). Of these five, only *Nitrosomonas* and *Nitrobacter* are encountered frequently (Alexander, 1977). These chemoautotrophic bacteria use CO_2, carbonates or bicarbonate as carbon source and obtain their energy by oxidising NH_4^+ or NO_2^- (Alexander, 1977).

It is thought that at least two mechanisms are responsible for N_2O evolution during autotrophic nitrification (Groffman, 1991):

a) Ammonium oxidizers can use NO_2^- when O_2 is limiting and produce N_2O. This process is called nitrifier denitrification (Poth and Focht, 1985).

b) Intermediates between and NH_4^+ and NO_2^-, or NO_2^- itself, can chemically decompose to N_2O (a type of chemodenitrification), especially under acidic conditions (Ritchie and Nicholas, 1972; Minami and Fukushi, 1986).

1.3.3. Factors controlling N_2O emissions from soils

Factors affecting the N_2O production from denitrification and nitrification, and N_2O emissions from soils, have been reviewed by Sahrawat and Keeney (1986), Bouwman (1990) and Granli and Bøckman (1994). The main controlling factors are soil aeration and water status, NO_3^- and NH_4^+ concentrations, organic matter supply, soil temperature and soil pH. Both denitrification and nitrification can occur simultaneously in the soil, and the controlling factors affect the two processes in different ways. They also affect how much of the produced N_2O is further reduced to N_2 and how much can escape from the soil. To show the complexity of this, Firestone and Davidson (1989) developed the "hole-in-the-pipe" model, which was expanded by Davidson (1991). The model shows that N_2O fluxes are regulated on three levels (Fig. 1.4):

I. Factors affecting the denitrification and nitrification rates (the amount of N flowing through the pipe).
II. Factors affecting the relative proportion of the end products produced (size of hole in the pipe).
III. Factors that affect gaseous diffusion through the soil into the atmosphere.

In the following section the effect of each main controlling factor on each of the three levels will be discussed.

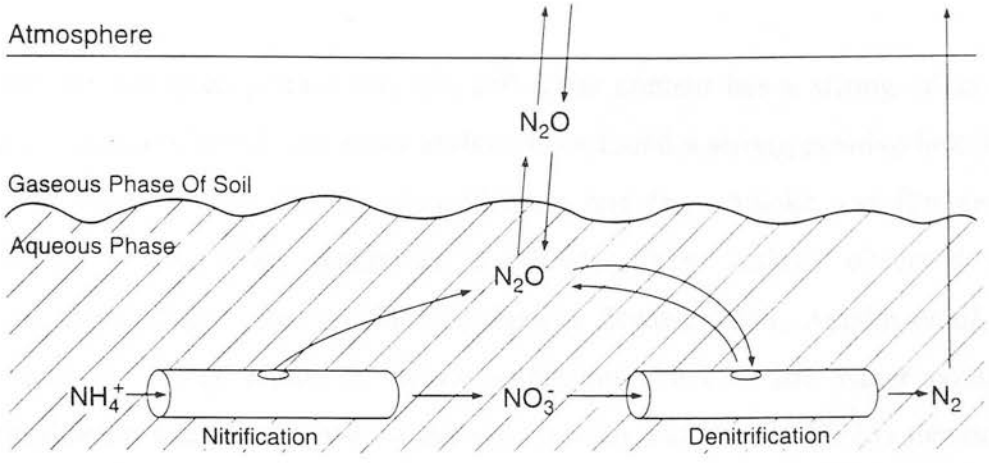


Fig. 1.4. Three levels of regulation of N_2O flux: (I) the rates of nitrification and denitrification (amount of N flowing through the pipes); (II) the ratios of end products (the size of the holes of the pipes); and (III) diffusion and consumption of N_2O prior to escape from the soil to the atmosphere (Granli and Bøckman, 1994; redrawn from Davidson, 1991).

1.3.3.1. Soil aeration and water status

Soil aeration and water status are discussed together, since they are closely related:

a) water replaces air in the soil and

b) water affects O_2 diffusion into the soil.

Thus the water content can be used as an indicator to describe soil aeration. The aeration is also affected by the O_2 consumption by soil microorganisms (the activity of which is affected by the soil water content) and plant roots.

Denitrification is an anaerobic process, which is inhibited by the presence of O_2 (Parkin and Tiedje, 1984; Burton and Beauchamp, 1985; Arah *et al.*, 1991). In general, denitrification rates are low at O_2 concentrations of more than 3% and increase drastically when O_2 falls below 2% (Parkin and Tiedje, 1984; Tiedje *et al.*, 1984). The O_2 concentration also affects the N_2O/N_2 ratio from denitrification. O_2

reduces the activity and delays the synthesis of N_2O reductase relative to the NO_3^- and NO_2^- reductase, thus leading to an increase of the N_2O/N_2 ratio as the O_2 concentration increases (Focht, 1994; Fillery, 1983; Tiedje, 1988; Masscheleyne, *et al.* 1993).

As has already been pointed out, the soil water content has a strong effect on the aeration status of a soil, and many authors have found a strong positive link between the soil water content and the denitrification rate (e.g. Aulakh and Rennie, 1985; Benckiser *et al.*, 1986; Koops *et al.*, 1996). Other authors observed marked denitrification peaks after rainfall or irrigation (Ryden, 1983; Aulakh *et al.*, 1983; Jarvis *et al.* 1991). However, below a threshold limit in soil water content, no denitrification activity is usually observed. Aulakh and Rennie (1985) demonstrated that denitrification was often negligible below a volumetric water content of 40 to 50% and de Klein and van Logtestijn (1996) observed threshold levels ranging from 71 to 83% water-filled pore space (WFPS), depending on soil type, which were equivalent to field capacity.

The soil water content has also a strong effect on the N_2O/N_2 ratio, which decreases with increasing water contents (Rolston *et al.*, 1982; Weier *et al.*, 1993).

In contrast to denitrification, nitrification is an aerobic process, and therefore requires oxygen. Keeney *et al.* (1985) showed that the nitrification rate was inversely related to the CO_2 concentration in the soil. When O_2 becomes limited, the nitrification rate slows down, but the overall N_2O production increases (Goreau *et al.*, 1980).

Like all microbiological processes, nitrification requires water, and the rate will increase with increasing water contents (Goodroad and Keeney, 1984; Tietema *et al.*, 1992). However, the rate will only increase up to the point where O_2 becomes limited, and the optimum water content for nitrification is around 50 to 60% WFPS (Linn and Doran, 1984; Skopp *et al.*, 1990).

N_2O emissions by denitrification and nitrification from soils tend to be highest at water contents of 45 to 75% WFPS, which are usually equivalent to values around field capacity (Fig. 1.5) (Davidson, 1991). Under these conditions both nitrification and denitrification can occur simultaneously in the soil, and either process can be the main contributor to the N_2O production (Klemedtsson *et al.*, 1988; Parton *et al.*, 1988; Davidson, 1992). When the soil water content falls below field capacity denitrification rates will be low, and the N_2O/NO_3^- ratio from nitrification will decrease with decreasing water contents. Above field capacity nitrification is limited, but denitrification rates increase substantially. However, if the soil water content is high enough to restrict gas diffusion, N_2O will be trapped in the soil and will be further reduced to N_2. Thus flooded soils usually only emit very small quantities of N_2O (Denmead *et al.*, 1979a, Terry *et al.*, 1981). However, Minami (1987) measured relatively large fluxes from a flooded rice field.

Many authors find a positive correlation between soil water content and N_2O emissions (Foluronso and Rolston, 1985; Klemedtsson *et al.*, 1988; Skiba *et al.*, 1992; Rodriguez and Giambiagi, 1995), and marked N_2O emissions are often observed after rainfall or irrigation (Freney *et al.*, 1985; Mosier *et al.*, 1991; Corre *et al.*, 1995). Soils that undergo drying and wetting cycles emit more N_2O than those that are wet for prolonged periods of time (Letey *et al.*, 1981; Smith and Patrick, 1983).

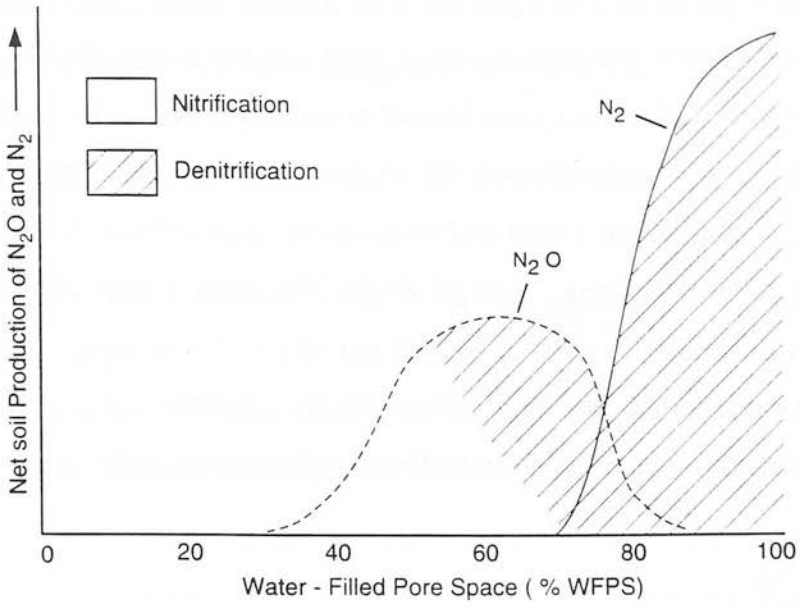


Fig. 1.5. Model of the relationship between WFPS of the soil and the relative fluxes of N_2O and N_2. The emitted N_2O derives both from nitrification and denitrification (Granli and Bøckman, 1994, after Davidson, 1991).

1.3.3.2. Mineral N availability

Sufficient soil mineral N concentrations are one prerequisite for denitrification and nitrification, and thus N_2O production, to occur. The dependence of denitrification and nitrification on mineral N (NO_3^- for denitrification and NH_4^+ for nitrification) has been shown to follow Michaelis-Menten kinetics (Klemedtsson *et al.*, 1977; Focht and Verstraete, 1977):

$$R = \frac{M \times N}{K_m + N}$$

where: R = Denitrification or nitrification rate
M = Maximum denitrification or nitrification rate
N = NO_3^- or NH_4^+ concentration
K_m = NO_3^- or NH_4^+ concentration that gives a denitrification or nitrification rate of 50% of the maximal value.

For nitrification K_m values seem to be in the range of 1 to 10 mg N kg soil^{-1} or mg N litre culture^{-1} (Hofman and Lees, 1953; Lees and Simpson, 1957; Mosier *et al.*, 1983), and very high NH_4^+ concentrations in the soil can be toxic for nitrifiers (McIntosh and Frederick, 1958). Reported K_m values for denitrification vary a lot. For example, Yoshinari *et al.*, (1977) reported values of less than 2 mg N kg soil^{-1}, Klemedtsson *et al.* (1977) observed a value of 4 mg N kg soil^{-1}, and Malhi *et al.* (1990) obtained values in the range of 117 to 138 mg N kg soil^{-1}. The difference can be explained by other soil variables affecting denitrification (e.g. soil water content or organic C concentration), which can override the effect of NO_3^- on denitrification (Aulakh *et al.*, 1992).

High NO_3^- concentrations inhibit the reduction of N_2O to N_2, and the N_2O/N_2 ratio increases with increasing NO_3^- concentrations (Blackmer and Bremner, 1978; Terry and Tate, 1980; Vinther, 1984). Yoshida and Alexander (1970) showed in a study using liquid cultures that the N_2O/NO_3^- ratio increases with increasing NH_4^+ concentrations, and Blackmer *et al.* (1980) came to the some conclusion from an experiment using soils.

In natural soils the microbes would have to compete with plants for mineral N, and thus both denitrification and nitrification can be limited by mineral N. It is thus not surprising that fertiliser additions to soils simulate the denitrification (e.g. Egginton and Smith, 1986a) and nitrification rates (e.g. Hutchinson and Brams, 1992), and often N_2O emission peaks are observed after fertiliser applications (Breitenbeck *et al.*, 1980; Duxbury *et al.*, 1982, Conrad *et al.*, 1983; Clayton *et al.*, 1997). Apart from the amount of fertiliser added, the form in which it is added also seems to have an effect on the extent of N_2O-N losses from agricultural land. In a recent review Bouwman (1994) showed that N_2O-N losses from different fertilisers were in the order of organic/organic-mineral mixtures ≅ anhydrous ammonia > ammonium-nitrate ≅ NO_3^--based > urea ≅ NH_4^+-based from a range of sites. Eichner (1990) in another review came to a similar conclusion for grassland: ammonium-nitrate > anhydrous ammonia > NO_3^--based > urea.

1.3.3.3. Available carbon

One of the most important prerequisites for denitrification is the presence of available C:

a) it is the reducing agent (electron donor) for denitrification (Beauchamp *et al.*, 1989), and

b) the respiration of available C may under certain circumstances create anaerobic conditions in the soil (Parkin, 1987; Christensen *et al.*, 1990).

Available C sources for denitrification include soluble carbohydrate, organic acids, amino acids, glycerol, fatty acids and phenolic acids (Beauchamp *et al.*, 1989). Some of these are the breakdown products of more complex C forms like proteins, lipids and lignin, and all are provided by soil organic matter, root exudates, plant residues and manures.

The close relationship between C and denitrification has often been demonstrated in laboratory and field studies (Paul and Beauchamp, 1989; Drury *et al.*, 1991; Iqbal, 1992; Bergstrom and Beauchamp, 1993), and marked denitrification peaks are often observed after organic matter applications (e.g. plant residues) to a soil (Aulakh *et al.*, 1991a; Dorland and Beauchamp, 1991). Burford and Bremner (1975) found that the water-soluble or readily decomposable C content is better correlated to the denitrification rate than the total organic C content of a soil. Similar results were obtained by Schipper *et al.* (1994); in their study they showed that denitrification was not dependent on the total C content of the soil, but on the labile C content after anaerobic decomposition.

The organic C content of a soil also affects the N_2O/N_2 ratio, and low ratios are observed at high available C contents (Elliot *et al.*, 1990; Vinther, 1984; Weier *et al.*, 1993).

In contrast to denitrification, autotrophic nitrification is only indirectly affected by the organic C content of a soil. During the mineralisation of organic matter, NH_4^+ is

released and made available for nitrification (Hayes, 1986). However, this strongly depends on the C/N ratio of the of the organic material, and adding material with a high C/N ratio (e.g. straw) will immobilise NH_4^+ (Powlson, 1993). The organic C content may also affect the N_2O/NO_3^- ratio; if, for example, organic material is added to a soil, the subsequent increase in respiration rate can lead to O_2 limitation, and the N_2O/NO_3^- ratio will increase (Granli and Bøckman, 1994).

Taking into account the effect of organic C on denitrification and nitrification, it is not surprising that N_2O emissions are also closely linked to the soil organic C (Bremner and Blackmer, 1981; Robertson and Tiedje, 1984; Iqbal, 1992). Adding organic material to the soil often enhances N_2O emissions (Paul *et al.*, 1993; Flessa *et al.*, 1995), and organic fertilisers often lead to higher N_2O-N losses from a soil than when fertilised with mineral fertilisers with a similar N content (Christensen, 1983a; Benckiser *et al.*, 1987). However, this may only be the case if organic C is limiting denitrification, and other studies have shown higher N_2O emissions from soils fertilised with NO_3^- than from those fertilised with slurry (Egginton and Smith, 1986b; Hansen *et al.*, 1993). Often there is a time lag observed between the organic C application and the N_2O emission peak, which is attributed to the time it takes for organic N to mineralise and nitrify to NO_3^- (Flessa *et al.*, 1995; Lovell and Jarvis, 1996). Similar observations have been made by Bergstrom *et al.* (1994); they observed that N_2O production in a soil was highest when the soil was amended with NH_4^+ and glucose, rather than with just either NH_4^+ or glucose. They concluded that the NH_4^+ increased the NO_3^- concentration in the soil via nitrification, which then stimulated denitrification in the presence of the glucose.

1.3.3.4. Soil temperature

Like all microbiological processes, denitrification and nitrification rates increase with increasing temperatures up to an optimum, above which they decline again. The optimum temperature for denitrification is between 60 and 70°C (Nommik, 1956; Bremner and Shaw, 1958), and for nitrification between 25 and 35°C (Bock *et al.*, 1986; Haynes, 1986). However, it has been suggested that the reported optimum

temperature for denitrification might be too high for true biological denitrification, and that at high temperatures chemodenitrification may be dominant (Keeney *et al.*, 1979). Malhi *et al.* (1990) reported a much lower optimum temperature for denitrification of around 40°C.

Apart from the overall reaction rate the N_2O/N_2 and N_2O/NO_3^- ratios are also affected by temperature. The N_2O/N_2 ratio decreases with increasing temperatures (Nommik, 1956; Keeney *et al.*, 1979; Vinther, 1990), whereas the N_2O/NO_3^- ratio increases with increasing temperatures (Bremner and Blackmer, 1981; Goodroad and Keeney, 1984; Yoshida and Alexander, 1970). The decreasing N_2O/N_2 ratio observed from denitrification does not necessarily mean that N_2O emissions from denitrification decline with increasing temperatures, since the overall increase of reaction rate may override the effect of the decreasing ratio (Smith, 1997).

Taking all the above facts into account it becomes apparent that N_2O emissions generally increase with increasing temperatures, and many authors find a strong correlation between the two variables (Freney *et al.*, 1979; McKenney *et al.*, 1980; Brumme, 1995; Smith *et al.*, 1995; Maag and Vinther, 1996). The rate of increase can be described as a Q_{10} value, which is the relative increase in reaction rate over 10°C, and for biological reactions is usually around 2. However, often very high Q_{10} values are observed for N_2O production and emissions (Nommik, 1956; Christensen, 1983a; Brumme, 1995), and these indicate that other factors also affect the reaction rate. Smith (1997) suggests that high Q_{10}s are the result of an increase in anaerobic volume in the soil caused by increasing temperatures, and this process is further discussed in Chapter 4 (Section 4.2.3).

The effect of temperature on N_2O fluxes leads to a strong diurnal variation in emissions (Denmead *et al.*, 1979b; Conrad *et al.*, 1983; Yamulki *et al.*, 1995), and part of the often observed seasonal variation can also be explained by temperature (Bremner *et al.*, 1980; Armstrong, 1983).

1.3.3.5. Soil pH

Denitrification increases with increasing soil pH values up to about 7.0 to 8.0 (Bremner and Shaw, 1958; Focht, 1974; Bryan, 1981); below a pH value of about 6.0 the N_2O/N_2 ratio will increase with decreasing pH values (Koskinen and Keeney, 1982; Weier and Gilliam, 1986; Eaton and Patriquin, 1989).

Nitrification, too, increases with increasing soil pH values, and has an optimum at about 7.0 to 8.0 (Focht and Verstraete, 1977; Bock *et al.*, 1986). In acid soils autotrophic nitrification tends to be slow, and generally ceases at pH values below 4.5 (Sahrawat, 1982; Duggin, 1991). At low pH values, like those observed in acid forest soils, heterotrophic nitrification may be the dominant process (Kuenen and Robertson, 1988; Killham, 1986). Above pH values of 7.5 the activity of NO_2^- oxidizers is restricted due to NH_3 toxicity (Morrill and Dawson, 1967). Goodroad and Keeney (1984) found that the N_2O/NO_3^- ratio increases with increasing pH, but no other study is known to confirm this.

The effect on soil pH on N_2O emissions is not clear, and different studies come to different conclusions. For example, Weier and Gilliam (1986) found that liming a soil increased the soil pH from about 4.2-5.0 to 6.6-7.6, which resulted in a large increase in N_2O emissions. Similarly, Bremner and Blackmer (1978) found higher N_2O emission rates from a soil with a pH of 7.8 compared to soil with lower pH values. In contrast, Brumme and Beese (1992) observed that N_2O fluxes decreased after liming an acid forest soil, and N_2O emissions measured by Nägele and Conrad (1990) also decreased when the pH was raised (from 4.0 to 7.0). One reason for these differing results could be that in different studies either nitrification or denitrification was the dominant process. For example when nitrification is the dominant process N_2O emissions should increase with an increasing soil pH. In contrast, due to the decreasing N_2O/N_2 ratio from denitrification observed at higher pH levels, it could be that a decrease in N_2O emissions may occur when the pH values increase, depending on the overall increase of the denitrification rate.

1.4. Measurement of N_2O Fluxes

Different methods of measuring N_2O fluxes from soils have been reviewed by Mosier (1990). Two basic methods can be distinguished:

a) chamber methods, and

b) micrometeorological methods.

1.4.1. Chamber methods

There are two types of chamber methods, open and closed ones.

Closed chambers

For this method a box which is open at the bottom is inserted into the soil, thus enclosing a small area of surface, and then gas samples are withdrawn periodically from inside the chamber. Alternatively, a cylinder or a frame (a box without top or bottom) can be inserted into the soil, which is then fitted with a lid for measurements. Fluxes can be calculated from the gas concentration change over time. For designs of different chambers see IAEA (1992); an example is shown in Fig. 1.6. The advantages of this method are that it is simple, relatively cheap, sensitive and no electrical supply is needed. The disadvantages are that the build-up of N_2O in the chamber can restrict normal gas diffusion, and that normal atmospheric pressure fluctuations are eliminated. The first problem can be overcome by short sampling periods (Jury *et al.*, 1982), and the second by inserting a small vent into the chamber (Hutchinson and Mosier, 1981).

Open chambers

The basic design is the same as for closed chambers, except that air from outside the chamber is continuously drawn through it and forced to flow over the enclosed soil surface. The gas flux can be calculated from the concentration difference between the inflowing and outflowing air, the flow rate and the enclosed area. For examples of open chambers see Denmead (1979), and Sebacher and Harriss (1982). The main advantage of this method is that they maintain environmental conditions more closely to the outside of the chamber than closed chambers do. The main disadvantage is that

the method is sensitive to pressure deficits inside the chamber, which can lead to an overestimation of the gas flux. This problem can be overcome by ensuring that the air inlet is larger than the air outlet (Denmead, 1979).

The drawback of both chamber types is that solar radiation can alter the soil temperature inside the chamber. Furthermore, the large spatial variability observed in N_2O fluxes from soils (Folorunso and Rolston, 1984; Ambus and Christensen, 1995) make it necessary to use relatively large numbers of replicate chambers to obtain a reliable flux estimate, and this makes the use of chamber methods labour-intensive.

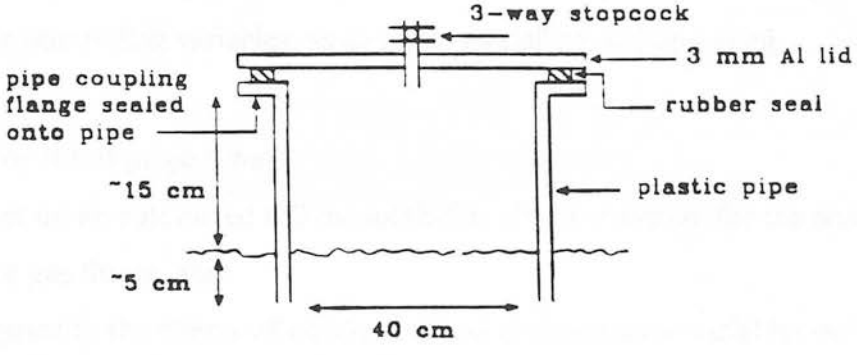


Fig. 1.6. An example of a cylindrical chamber (Smith *et al.*, 1995).

1.4.2. Micrometeorological Methods

The basic concept of micrometeorological methods is that gas transport is accomplished by the motion of the atmosphere which displaces parcels of air (eddies) from one level to another (Denmead, 1983). The three main approaches are eddy correlation, flux gradient and mass balance calculations, and they are described by Thom (1975), Denmead (1983) and Fowler and Duyzer (1989). The main advantage of micrometeorological methods is that they integrate the fluxes over a large area, and thus overcome the problem of spatial variability. However, the methods require large uniform areas with a minimum of air turbulence, and constant atmospheric conditions during the measuring period (Mosier, 1990). Thus the methods are not suitable for all

field situations. Further disadvantages are that micrometeorological methods are not as sensitive as chamber methods and cannot measure very small fluxes. They are also expensive methods, requiring complex equipment.

1.5. Aims of this Project

From Table 1.1 it can be seen that the estimated source strength for soils shows a very wide range, which clearly shows a need to improve N_2O flux estimates. However, due to the highly heterogeneous nature of soils it is difficult to obtain accurate emission estimates. Better estimates can only be achieved by a combination of direct measurements in key ecosystems and by quantifying the relationships between fluxes and the controlling variables, as an aid to modelling and upscaling.

The aim of this project was

a) to set up an automated soil monolith-flux chamber system for the study of trace gas fluxes, and

b) to quantify the effects of various soil and environmental variables on N_2O emissions to the atmosphere, by making measurements with the system in a semi-controlled environment, where it was more possible to control these variables than in the field.

It was hypothesised that a significant proportion of the overall N_2O emissions from soils occur as intense but short-lived flushes after perturbations of the soil (e.g. after rainfall, mineral N and organic matter applications, etc.). However, little is known about the intensity and duration of such flushes. It was further hypothesised that the soil water content would have a strong influence on the occurrence of these N_2O flushes, in particular that major emission increases would take place when critical threshold values of the soil water content were exceeded, causing the onset of anaerobiosis. Another variable leading to short-lived emission peaks was expected to be the diurnal cycling of the soil temperature. The time of the occurrence of the daily flux peak would be expected to depend on the progress of the diurnal "heating wave"

down the soil profile and the depths at which the N_2O production occurred. Available carbon strongly affects the soil respiration rate, and thus the aeration status of the soil. Therefore, the application of organic matter to the soil, like the addition of water, could be expected to lead to the development of anaerobic zones, resulting in N_2O emission peaks. Further, it was considered likely that the three above-mentioned variables (soil water content, temperature and respiration rate) have a strong interacting effect on N_2O emissions, whereas one variable on its own might have little effect on the fluxes. From this, a further possibility to be tested was whether there might be a "dominant" variable that has a stronger and more important effect on N_2O fluxes from soils than the other variables.

It was also the intention to study the effect of mineral N on N_2O fluxes, and different amounts and types of fertilisers were applied to the soil monoliths on several occasions. However, in practice none of these applications caused any significant flux changes, and the results are not discussed in this thesis.

2. MATERIALS AND METHODS

2.1. Soil Monolith-Flux Chamber System

Gas flux measurements to establish relationships between soil and environmental variables and N_2O fluxes were made using a large soil monolith-flux chamber system, set up in a semi-controlled environment. Such a system has a number of advantages over field studies, and laboratory studies using sieved soil or small soil cores. In the field it is often impracticable to obtain information to establish relationships between soil variables and N_2O fluxes because of the vagaries of the weather. For example, the desired range of soil water contents may be unattainable in the time available. Furthermore, prolonged time series of measurements at the desired sampling frequency may be logistically impracticable. Laboratory studies overcome these problems, but because sieved soil or small soil cores are usually used, the information obtained may not be representative for soils in the field. By using large soil monoliths, and disturbing the soil as little as possible during the collection and the subsequent studies, an attempt was made to maintain as much as possible of the physical integrity of the soil structure, to minimise the introduction of artefacts such as changes in the aeration regime.

Such monoliths, cropped with grass, were earlier used by Webster and Dowdell (1982) to study N_2O emissions after fertiliser addition, by a manual chamber method. They have also proved suitable for studies of pesticide dynamics (Leake, 1991; Yon, 1992), N leaching (Webster *et al.*, 1992), and soil aeration and crop growth (Cannell *et al.*, 1984, 1985).

2.1.1. Collection and installation of soil monoliths

The method adopted for collecting the monoliths was that described by Belford (1979). The only modification made for this study was to change the dimensions of the casings, to an outer diameter of 1 m, with a length of 0.75 m and a wall thickness

of 7 mm. They were made of glass fibre-reinforced polyester with an inert epoxy resin coating on the inner side.

To obtain a soil monolith the casing was pushed vertically a few cm into the soil with a hand-operated hydraulic ram or by the tines of a fork-lift on a tractor, and the soil around it was excavated by hand (see Appendix I, Plate A1.1). This process was repeated until the casing was at a depth of approximately 60 cm, when a large pit was dug around it and a steel cutting plate was forced underneath, again using a hydraulic ram, to separate the monolith from the soil below (see Appendix I, Plate A1.2). After temporarily packing the headspace with large chipboard discs, a square cover plate was placed on the top of the casing and joined to the cutting plate by long threaded rods, thus firmly securing the monolith between the two plates. The monolith was then lifted out of the pit by the fork lift (see Appendix I, Plate A1.3), and inverted, and about 5 cm of soil was removed from the bottom and replaced with gravel. Notches were cut into the bottom edge of the casing to allow exit of drainage water, and finally a mild steel base plate 1.05 m in diameter, with a 10 cm high rim (into which a drainage pipe was fitted) was attached. After that the monolith was re-inverted and the cover plate and packing were removed. The monolith was then transported to the laboratory, where the annular space between the base plate and the monolith casing was filled with gravel, and sealed with Araldite 2001 epoxy resin. In due course the monoliths were installed on supporting brick walls in a greenhouse (Fig. 2.1; see also Appendix I, Plate A1.4).

The monolith side walls were insulated with glass fibre mats, coated with reflecting aluminium foil on one side to minimise lateral heat flow. The bases were insulated with rock wool (see Appendix I, Plate A1.4).

2.1.2. Soils

Four replicate monoliths were obtained as described above, from each of three soils with different drainage characteristics:

a) a sandy loam alluvium (no Series name) that had been in arable cultivation,

b) a clay loam glacial till of the Winton Series (Ragg and Futty, 1967) under ryegrass (both from the Bush Estate about 10 km south of Edinburgh), and

c) a peaty gley of the Carter Series (Muir, 1956) from an upland forest near the Scotland-England border.

(Note: Eight of these soil monoliths had been collected and were partly installed before I started this project).

Details of the soils are shown in Table 2.1. The grass crop on the Winton soil was incorporated by removing the turf to a depth of ca. 5 cm, then removing a further 5 cm of the topsoil, after which the turf was put back in small pieces upside down and covered with the removed topsoil. This procedure was carried out to simulate the rotational ploughing of grass leys on this soil, and to permit simultaneous experiments under fallow conditions on both mineral soils.

During the collection of the peaty gley monoliths gaps up to a few millimetres wide had developed between the soil and the glass fibre casings, attributed to rocking of the casings through using the tines of a fork-lift rather than a hydraulic ram to push the casings into the soil. To ensure that water applied to the top of these monoliths would not pass down the sides inside the casings, and also to ensure that gas exchange occurred through the surface, the gaps between the soil and the casing were sealed with paraffin wax.

2.1.3. Monoliths as flux chambers

The head spaces of the monoliths were converted into closed gas flux chambers (Mosier 1989) approximately 15 cm high by fitting them with lids (104.5 × 108 cm) made from 3 mm aluminium sheets. Each lid was stiffened by a steel frame, which in turn was attached by hinges to a vertical free-standing steel frame (Fig. 2.1). These lids were driven by battery (12 V)-powered actuators (LINAK UK Ltd, Smethwick). On the upper rim of the monolith case natural rubber tubing (12.5 mm i.d., 17 mm o.d.) was fastened with "Unibond General Purpose Sealant" to make a tight gas seal when the lids were pressed down into place (Fig. 2.1). After the lids had been in

Table 2.1. Sites from which monoliths were collected, and soil types and soil characteristics.

	Site A	Site B	Site C
Date collected	spring 1991	spring 1991	summer 1992
Location	Bush (Crofts), Lothian	Bush (Cowpark), Lothian	Kielder Forest, Northumberland
Grid Reference	NT 245 653	NT 238 627	NY 654 923
Elevation	190 m	180 m	295 m
Soil Series / Major soil sub-group	unclassified alluvium	Winton / Brown forest soil with gleying	Carter / Poorly drained peaty gley
Texture (%)	Sandy loam †	Clay loam†	Fine loamy sand (overlaying clay loam / clay)‡
Drainage	well drained	restricted	waterlogged below ca. 50 cm depth
pH	5.7	5.5	3.7§
Organic Carbon (%)	2.7	3.2	52§
Total org. Nitrogen (%)	0.14	0.18	1.8§
Vegetation	Wheat	Ryegrass	Sitka spruce

† Topsoil
‡ beneath organic layer (32 - 48 cm depth)
§ Peat layer

Acknowledgement: I would like to thank M. Pore from MLURI for providing the soil details for the peaty gley soil, L. Swan for supplying the total organic nitrogen data for the mineral soils, and Dr. I.P. McTaggart for providing the remaining soil characteristic data for the minerals soils.

operation for some time they tended to move slightly out of position, making the gas seal unreliable. This problem was overcome by fitting each lid with a gasket of flexible rubber draught excluder, so that following closure the two rubber surfaces made adequate contact all round the circumference. This was verified by placing a high-powered electric torch in each flux chamber after dark, closing the chamber, and examining the junction between the rubber seals for any light emission.

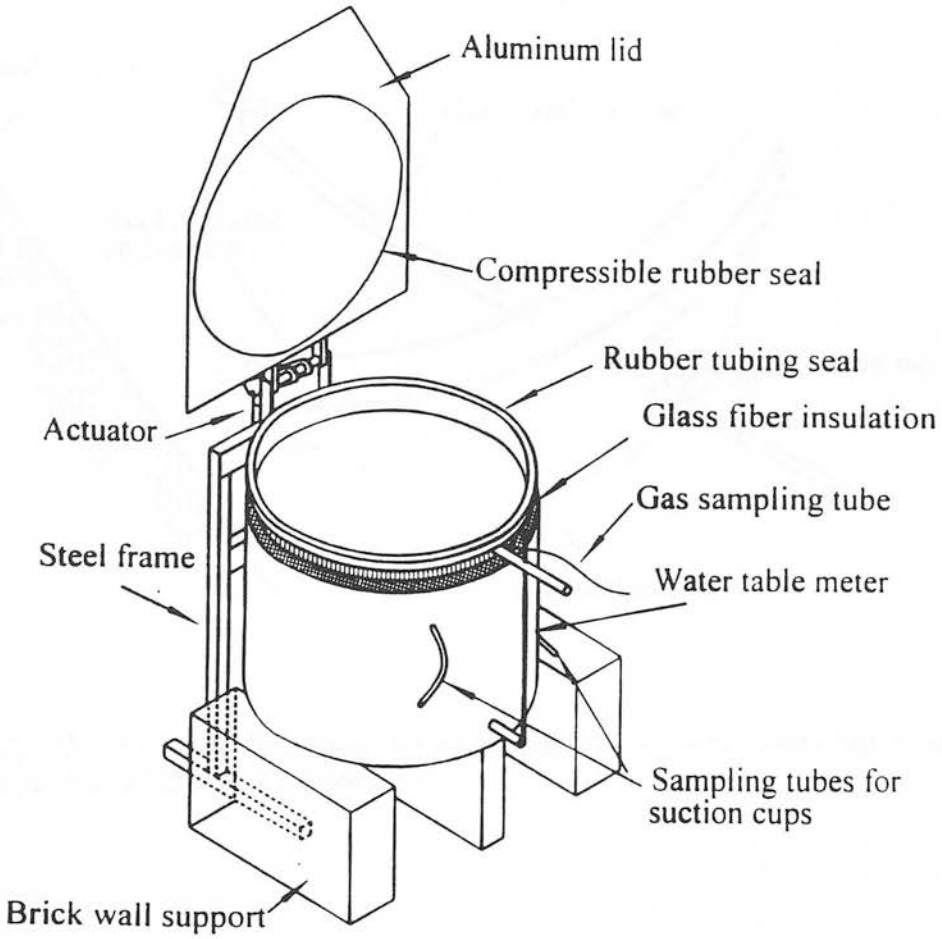


Fig. 2.1. Soil monolith as flux chamber, showing aluminium lid supported by steel frame actuator, gas seals and sampling tubes.

A gas sampling port, consisting of a three way stopcock, held in place by a short piece of thick-walled neoprene rubber (9 mm o.d., 3 mm i.d.), was inserted through each monolith casing approximately 5 cm above the soil surface. A piece of Teflon tubing (5 mm o.d., 2 mm i.d.) ca. 50 cm long, leading to the centre of the flux chamber, was attached to the inner end of the gas sampling port (Fig. 2.2).

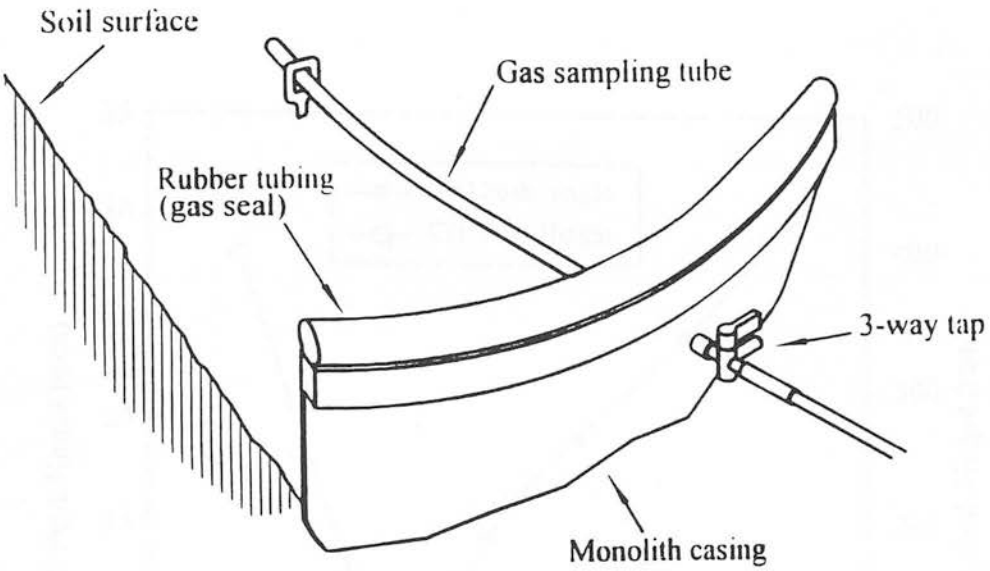


Fig. 2.2. Detail of monolith casing above soil surface, showing 3-way tap used as gas sampling port and Teflon gas sampling tube.

2.1.4. Gas analysis system

Gas samples were analysed with a Philips PU 4500 gas chromatograph (Pye Unicam Ltd., Cambridge) equipped with an electron capture detector, a 1.5 m long, 4 mm i.d, stainless steel column packed with Porapak Q (50 - 80 mesh size), and a 15 cm long brass pre-column (4 mm i.d.) with the same filling, for back-flushing. Dinitrogen was

used as carrier gas. A short analysis time (3 min) was achieved by using a relatively high column oven temperature (55°C) and a carrier gas flow rate of 50 ml min^{-1}.

At elevated temperatures, ECD response to an increase in temperature is positive for N_2O but negative for CO_2 (Christensen, 1983b). Thus an optimum temperature can be selected for the determination of both gases. Tests carried out showed that, for the system used in this study, a detector temperature of 270°C gave adequate sensitivity for both N_2O and CO_2 (Fig. 2.3).

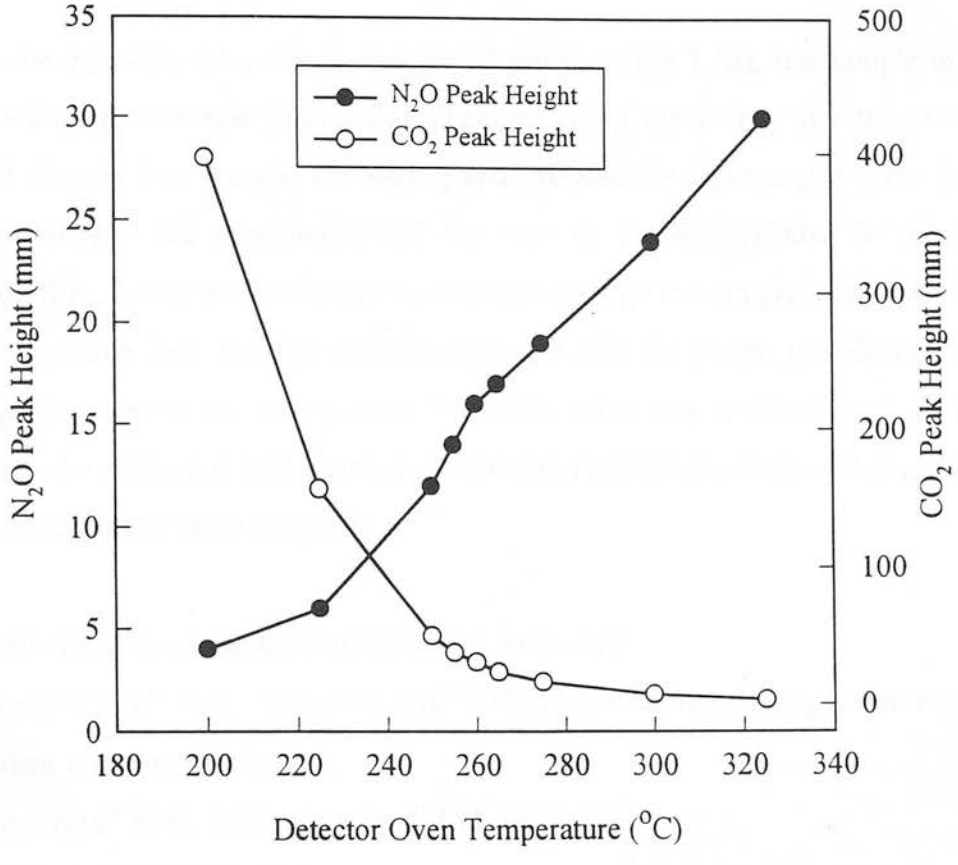


Fig. 2.3. Sensitivity of GC detector to ambient N_2O and CO_2 concentrations at different detector temperatures. Peak heights were recorded with a Philips chart recorder (attenuation: 4, range: 10 mV).

The gas chromatograph was also equipped with an auto-injector (designed by Dr. J.R.M. Arah), consisting of a 16-port multiposition valve (Valco Europe, Schenkon, Switzerland) and a 10-port 2-position injection valve (also Valco). Both valves were electrically operated (240 VAC). Electrical interference from other equipment in the greenhouse with the injection valve, causing it to malfunction, was overcome with a mains filter.

Each flux chamber was connected to the 16-port valve by Teflon tubing (3 mm o.d., 1.5 mm i.d.) ca. 9 m long. The common outlet port of this valve was connected to the 10-port valve, which was fitted with a 1 ml sample loop and had a small diaphragm pump (50 Hz, 240 V, flowrate: 120 ml min^{-1}) attached to one port (Fig. 2.4).

When the injection valve was in the "load" position (Fig 2.4a), the sample loop was filled with a gas sample from a flux chamber, using the pump, and the carrier gas flowed directly into the gas chromatograph. Meanwhile a purge gas (also pure N_2) flowed through the pre-column and the vent to the atmosphere. In the "inject" position (Fig. 2.4b), the carrier gas flowed first through the sample loop, then through the pre-column into the gas chromatograph, while the purge gas flowed directly through the vent to the atmosphere. When the valve was switched back to its load position, the purge gas back-flushed all unwanted substances in the sample still in the pre-column out to the atmosphere.

For calibration three standard gas mixtures were used:

- 0.31 µlitre $litre^{-1}$ N_2O, 350 µlitre $litre^{-1}$ CO_2 (air containing these gases at normal ambient concentrations);
- 1 µlitre $litre^{-1}$ N_2O, 3000 µlitre $litre^{-1}$ CO_2 (in N_2);
- 10 µlitre $litre^{-1}$ N_2O (in N_2).

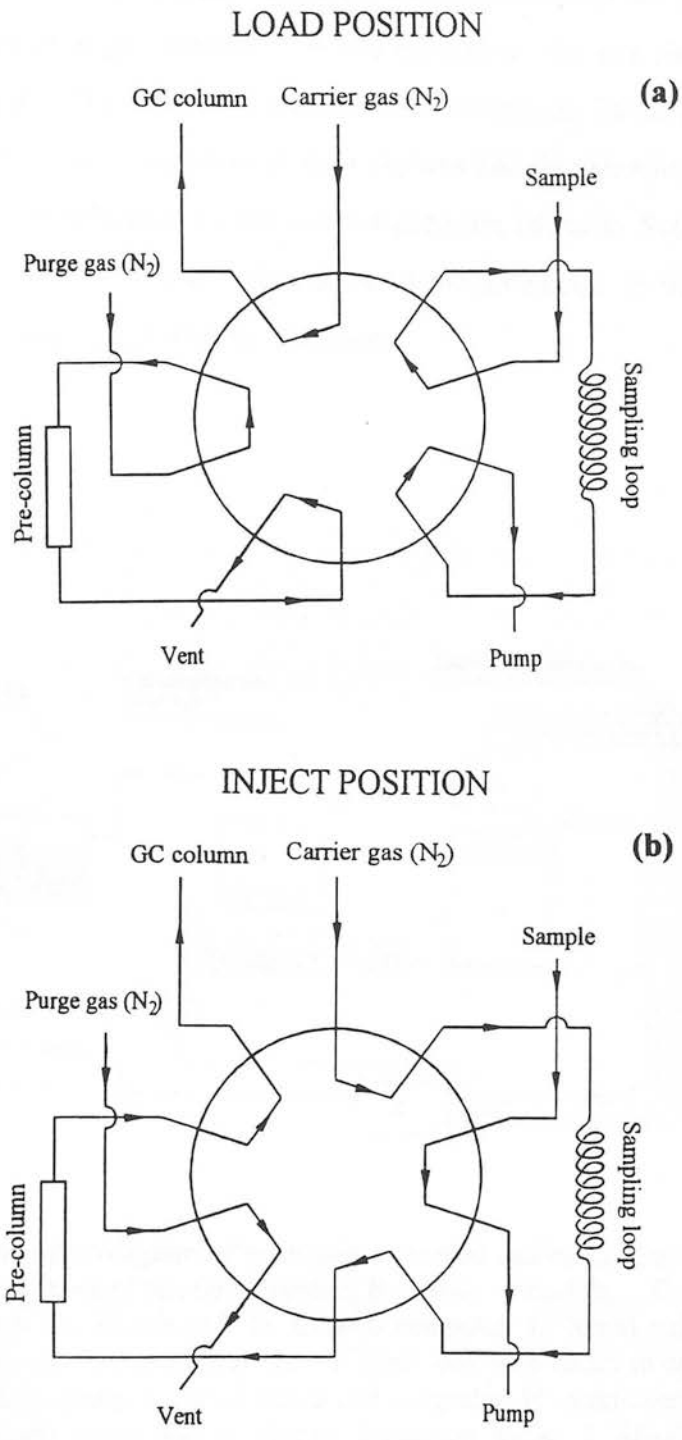


Fig. 2.4. Flow diagram of the Valco 10-port 2-position valve of the auto-injector.
a) Load position. The pump fills the sampling loop with gas from the flux chamber; unwanted substances from the previous gas sample still in the pre-column are back-flushed out of the system via the vent.
b) Inject position. The gas sample in the sampling loop is injected into the GC via the pre-column.

Each standard cylinder was connected to a separate port of the 16-port valve with stainless steel tubing (1.5 mm o.d., 0.8 mm i.d.), via one-way solenoid valves (Fig. 2.5). Samples from the standard cylinders were injected into the gas chromatograph in the same manner as gas samples from the monoliths. The gas chromatograph outputs were recorded with a Hewlett Packard A9600 integrator. Initially, a manual reset was necessary after each 5-h period of data capture and downloading. This problem was overcome by modification of the control program (done in September 1994 by Dr. J.R.M. Arah), and the system then allowed measurements to be made for up to 99 flux measurement cycles without attention.

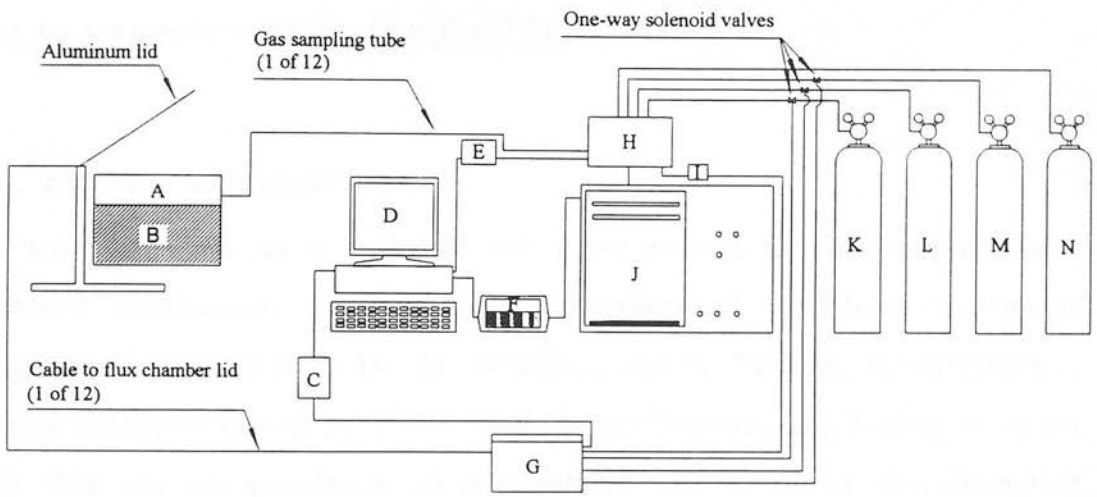


Fig. 2.5. Schematic diagram of computer-controlled automated gas sampling and analysis system: A: Headspace of gas flux chamber; B: Soil monolith; C: Relay multiplexer daughter boards for PC-labcard; D: Control computer; E: Serial valve interface for auto-injector; F: Hewlett Packard integrator; G: Metal box with relays to operate actuators of gas flux chamber lids, pump, solenoid valves and integrator; H: Auto-injector consisting of a 16-port multiposition valve and a 10-port 2-position valve; I: Diaphragm pump; J: Gas chromatograph; K, L, M: Standard gas mixtures for calibration; N: Carrier and purge gas (N_2).

2.1.5. Computer control

The monolith chamber lids, the pump, the auto-injector, solenoid valves and data capture were all controlled by the same PC computer program (written in Power-Basic by Dr. J.R.M. Arah). For this automation it was necessary to fit the computer with a PC-labcard (PCL-711S, Integrated Measurement System Ltd., Southampton, UK) and two corresponding relay multiplexer daughter boards (PCLD-788). These were linked with a series of normally open relays, arranged in a metal box (Fig. 2.5) together with a 12 V lead-acid battery (to provide power for the relays and the actuators of the flux chamber lids) and a trickle battery charger.

Each flux chamber lid required two relays, one for closing and one for opening. To switch the pump on and off, another two relays were needed. Three more relays opened the solenoid valves linked with the standard gas cylinders and a further relay switched the integrator on and off. The two Valco valves were controlled by the computer via a serial valve interface (Fig. 2.5).

2.1.6. Monolith instrumentation

Soil water potential, as an index of soil water content, in each monolith was monitored continuously with a laboratory-constructed recording tensiometer (designed and assembled by Dr. M. O'Sullivan and R. Mackie), incorporating a pressure transducer (model no. PT2P15G1C, Sensor Technics UK, Rugby), at 20 cm depth. The soil and greenhouse air temperatures were measured with thermistor temperature probes (model no. CS-U-V10-2V, Grant Instruments Ltd., Barrington, UK). To obtain a mean temperature gradient for each soil type, each of the four replicate monoliths from one soil type contained a single probe (inserted horizontally through the monolith casing) at a different depth (5, 10, 20 and 30 cm). The temperature probes were attached to metal rods (40 cm long), so that the tip of the probe could reach the centre of the monolith. No temperature probes were installed at a depth greater than 30 cm because preliminary recordings showed that there was no significant temperature difference between 30 and 50 cm depth. Both the tensiometers and temperature probes were connected to Grant SQ1202 data loggers.

The drainage pipe at the bottom of each monolith casing could be fitted with a "water table meter" consisting of a neoprene rubber bung with a hole in the middle to which a 77.5 cm long transparent piece of plastic tubing (6 mm i.d.) was attached in a vertical position (Fig. 2.1).

After the monoliths were in use for approximately 2 years (November 1994) they were also equipped with soil solution samplers (3 in each monolith at 12.5 cm depth). Each sampler consisted of a round-bottom tapered-neck ceramic cup (2.2 cm o.d., 2.3 mm wall thickness and 7 cm long), fastened to a 20 cm long piece of ABS tubing (14 mm i.d., 21 mm o.d.) (Fig. 2.6). To sample the soil solution the sampler was connected to a brown Winchester bottle (2.5 l), to which a vacuum of approximately -67 kPa was applied. The solution was then collected for approximately 24 h.

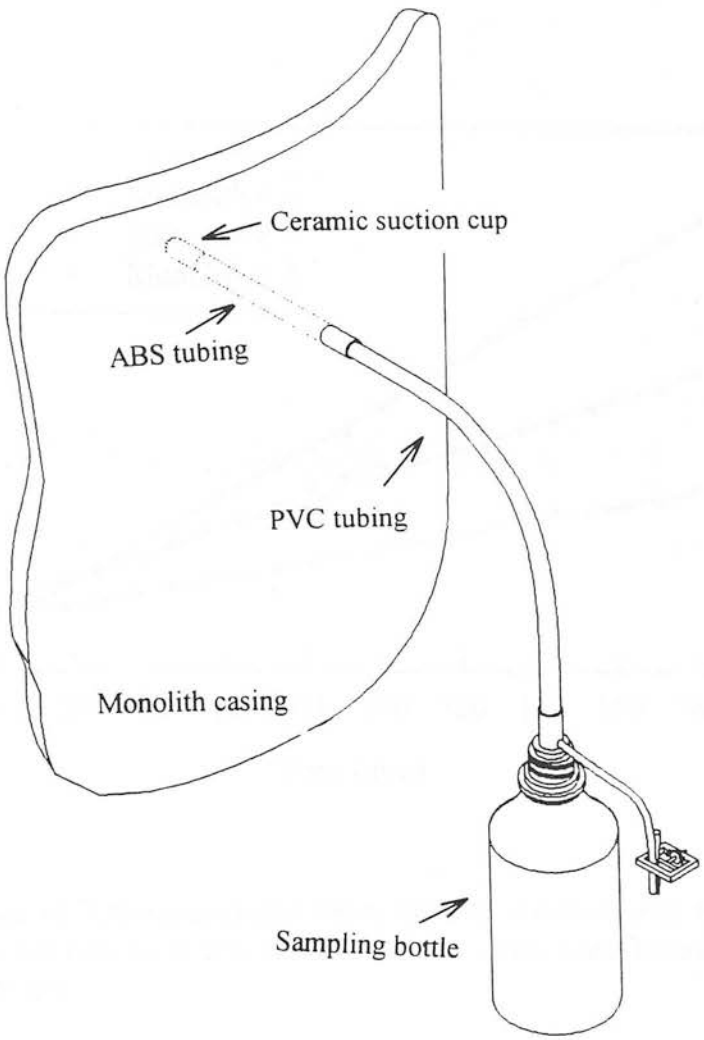


Fig. 2.6. Soil solution sampler, showing ceramic suction cup inserted into the soil and connected to the sampling bottle.

2.1.7. Gas flux measurement

Measurements of N_2O and CO_2 fluxes were normally made at 4-hourly intervals throughout the period of each experiment. The closure period of the gas flux chambers was usually 1 hour and a gas sample from each chamber was taken immediately after the lids closed and just before they opened again. Tests have demonstrated that the increase of the N_2O concentration in the headspace of the flux chambers was linear for time periods longer than 1 hour (see Fig. 2.7 as an example).

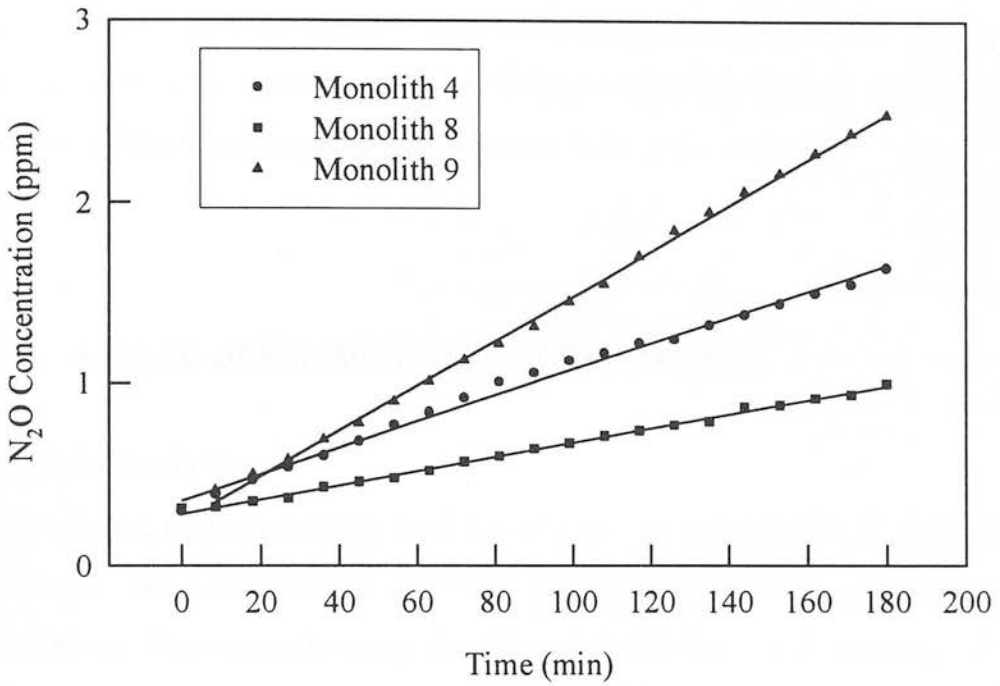


Fig. 2.7. Increase of N_2O concentration inside the flux chambers over time (showing one monolith of each soil type as an example: monolith 4 - sandy loam, monolith 8 - clay loam, monolith 9 - peaty gley.

Initially, the diaphragm pump attached to the injector valve pumped air from each flux chamber for 1 min, to ensure that the connecting tubing and the sampling loop of the auto-injector were adequately flushed, and filled with air from the headspace of the flux chamber. However, it was found that high N_2O emissions could produce memory effects due to adsorption of N_2O by the Teflon tubing. This problem was overcome by flushing the tubing with ambient air for 5 min between flux measurement cycles.

During each flux measurement cycle a reading from the pressure transducer tensiometers and the temperature probes was also recorded.

2.1.8. Pre-treatment of mineral soil monoliths

Soil samples taken at the beginning of this project (see Section 2.2.2) revealed that NO_3^- had accumulated in the mineral soil monoliths to very high concentrations (706 ±522 and 263 ±143 mg N kg^{-1} in the sandy loam and clay loam, respectively). This was presumably due to high mineralisation and nitrification rates during the long time period these monoliths had been kept for in the greenhouse prior to experimentation. It was decided to remove the NO_3^- by leaching and denitrification, and to achieve this the monoliths were periodically flooded and drained for 5 months.

2.2. Analysis of Soil Solutions and Soil Samples

2.2.1. Soil solution

Soil solution from the ceramic suction cup samplers was sampled approximately every fortnight, and was analysed for NO_3^- and NH_4^+. Both ions were determined by continuous flow analysis using the methods of Crooke and Simpson (1971) and Selmer-Olsen *et al.* (1981), except that the NO_3^--N procedure used copper and hydrazine in place of cadmium as a reducing agent.

2.2.2. Soil analysis

Prior to any experiments 4 small soil cores (18 mm i.d.) were taken at 0-5, 5-10 and 10-20 cm depth from each monolith. The 4 replicates from each depth were bulked and then analysed for NO_3^- and NH_4^+. For this, 20 g of fresh soil were weighed into a 350 ml plastic beaker and shaken with 100 ml of 1M KCl extracting solution for one hour. The extracts were then analysed using the same method as for the soil solutions (see Section 2.2.1).

2.2.3. Conversion of soil water potential to water-filled pore space

In order to establish general relationships between the soil water content and N_2O fluxes, the soil water potentials were converted into water-filled pore space (WFPS) values. WFPS was preferred to soil water potentials in order to make it easier to compare the data from this project with published data from other studies, since WFPS is more commonly measured than soil water potential. For this conversion it was necessary to know the relationship between the volumetric water content and soil water potential (water release characteristics of the soils), and the total pore space of the soils.

To obtain the water release curves, one soil core (73 mm i.d., 50 mm high) from each monolith was taken (done by J.P. Parker) at 10 and 30 cm depth (middle point of the soil cores), and the volumetric water content at saturation, -1, -2, -5, -10 and -20 kPa was determined with suction tables using the method of Ball and Hunter (1988) (done by E. Robertson). After this the mean volumetric water contents for each pair of cores at each water potential value were used to draw the water release curves (see Appendix II). The mean values were taken to represent the average water release characteristics for the whole topsoil. The relationship between volumetric water content and soil water potential was logarithmic for the mineral soils and linear for the peaty gley soil, and can be described by the following equation:

$$y = a + (b \times x)$$

where: $y = \log(|kPa|)$ for the mineral soils or kPa for the peaty gley soil
x = volumetric water content
a = intercept (value of y when x is zero)
b = slope (increase of y per unit of x)

To convert soil water potential into volumetric water content the above equation is solved for x:

$$x = (y - a) / b$$

To obtain values for the parameters a and b linear regression was used (see Appendix II for the values for individual monoliths). Because the relationship between volumetric water content and soil water potential for the mineral soils was logarithmic the water content value at saturation (zero potential) had to be omitted.

To determine the total pore space of the soils a further set of soil cores similar to those the one sampled for the water release curve analysis was taken from each soil monolith, and the bulk density measured using the method described by Ball and Hunter (1988) (done by J.P. Parker and E. Robertson). From this the total pore space could be calculated with the following equation:

$$\varepsilon_{tot} = 100(1 - (\rho_b / \rho_p))$$

where: ε_{tot} = total pore space (percent of total volume)
ρ_b = bulk density
ρ_p = particle density

For the mineral soils a particle density of 2.65 Mg m^{-3} (g cm^{-3}) was assumed. However, the peaty gley soil had a very high organic material content (which has a particle density of approximately 1.4) and the particle density for this soil was calculated as follows:

$$\rho_p = ((m / 100) \times 2.65) + ((n / 100) \times 1.40)$$

where: ρ_p = particle density
m = percentage of mineral soil
n = percentage of organic material

The percentage of the organic material of the soil was determined as loss on ignition (Allen, 1989) (done by L. Swan).

The WFPS values were then obtained with the following equation:

$$WFPS = 100(\phi / \varepsilon_{tot})$$

where: ϕ = volumetric water content (percent)
ε_{tot} = total pore space

2.3. Statistical Analysis

To establish relationships between soil variables and N_2O fluxes regression analysis and correlations were used. To perform these tests SigmaStat (Jandel Scientific, 1994a) was used. As is shown in Chapters 3, 4 and 5, regression analysis was not a suitable tool for describing general relationships between soil variables and N_2O fluxes over longer time periods, and boundary line analysis was used as an alternative. The concept and use of this method is described in Chapter 6, Section 6.2.

2.3.1. Regression analysis

There are three types of regressions: linear, nonlinear, and multiple linear regressions (Mead and Curnow, 1983). Linear and nonlinear regressions describe the response of a dependent variable to an independent one, for example, the response of crop growth to different amounts of fertiliser added to the soil. The simplest relationship is when the response follows a straight line (Mead and Curnow, 1983; Watt, 1993), which is expressed as:

$$y = a + bx$$

where: y = dependent variable
a = intercept
b = slope
x = independent variable.

The intercept describes the value of y when x is zero (e.g. crop growth without fertiliser additions), and the slope is the rate of increase of y per unit x (e.g. increase in crop growth per kg fertiliser added).

Not all relationships are linear, and in this case the data can either be transformed (e.g. log-transformed) to make the response linear, or nonlinear regression analysis can be used (Mead and Curnow, 1983).

Multiple linear regression describes the response of a dependent variable to two or more independent variables (Mead and Curnow, 1983), which is expressed in the following equation:

$$y = a + b_1x_1 + b_2x_2 + ... + b_nx_n$$

where: y = dependent variable
a = intercept (value y when all independent variables are zero)
$b_1, .., b_n$ = slope (rate of increase for each independent variable)
$x_1, .., x_n$ = independent variable.

The strength of the dependence of one variable to one or more others is expressed as an r^2 value (regression coefficient or coefficient of determination), which varies from 0 to 1. It is the proportion of the variation in y accounted for by x (Watt, 1993). If r^2 equals 0 no relationship exists between the variables, and if r^2 equals 1 the model describes all of the variation observed in the dependent variable.

Regression analysis is a parametric test for which certain assumptions have to be met to make it valid (Watt, 1993). These are:

a) normal distribution of the residuals (difference between predicted and observed value),

b) homogeneity of variance of residuals (they should show no tendency to increase or decrease as x increases), and

c) independence between the y variables.

Small violations of these assumptions are usually accepted, e.g. if the residuals are almost but not quite normally distributed; however, if larger ones occur, the regression should be dismissed.

2.3.2. Correlation

Correlations describe the degree of the linear association between two variables (Mead and Curnow, 1983). The strength of the association is described by the r value

(correlation coefficient), which has a range from -1 to 1. An r value of 0 indicates that no correlation exists between two variables, an r value near 1 indicates a strong positive linear correlation (both variables increase together), and an r value near -1 shows a strong negative linear correlation (one variable decreases as the other one increases). Correlation does not mean causation; it could be that the two examined variables respond independently to a third one (Watt, 1993).

There are two types of correlations: Pearson product-moment correlation and Spearman rank correlation. The Pearson product-moment correlation is a parametric test, which means that the data of both variables should be normally distributed and have a similar variability, whereas the Spearman rank correlation is a non-parametric or distribution-free test (Watt, 1993).

In this study the assumptions for regression analysis to be valid were often not met, and the Spearman rank correlation was chosen to demonstrate an association between two variables. Spearman rank correlation has also the advantage that it is less sensitive to outliers and slight nonlinearity of the data than Pearson product-moment correlation.

3. EFFECTS OF SOIL WATER CONTENT ON N_2O FLUXES

3.1. Mineral Soils - Fallow

3.1.1. Methods

Two wetting experiments were carried out to study the effect of soil water content on N_2O fluxes from the fallow mineral soils. These investigations were made in connection with two fertiliser experiments:

- **1st wetting experiment:** On 25th October 1993, at the beginning of the experiment, 5 g N m^{-2} as $Ca(NO_3)_2$ (equivalent to 50 kg N ha^{-1}) was added to two replicate monoliths of each soil type (monoliths 2, 3, 5 and 8). The remaining two replicates were used as unfertilised controls.

- **2nd wetting experiment:** At the beginning of this study, on 24th March 1994, two replicate monoliths of each soil type (monoliths 1, 3, 5 and 7) received 10 g N m^{-2} as $Ca(NO_3)_2$ (equivalent to 100 kg N ha^{-1}), the other two (monoliths 2, 4, 6 and 8) 10 g N m^{-2} as $(NH_4)_2SO_4$.

(Note: As mentioned in Chapter 1 (Section 1.5), fertiliser additions had no effect on N_2O emissions from fallow soil monoliths and the results are not discussed here.)

Before the fertiliser was applied the monoliths were allowed to dry out for a period of time (27 days before the 1st wetting experiment and 20 days before the 2nd wetting experiment). A few days after the fertiliser applications the drainage pipes of the monolith casings were blocked with the "water table meters", and the soils were repeatedly irrigated over 3.5 months (1st experiment) and 4 months (2nd experiment) until the soils were eventually saturated. All applications were made with a sprayer, with a flow rate of 2 l min^{-1}. Initially 5 mm of tap water were added to each monolith on each irrigation date. Rainfall data from a field site at the Bush estate near Edinburgh collected for nearly 2 years (supplied by Dr. I.P. McTaggart) revealed that this is a typical daily rainfall value in the south-east of Scotland; on 158 days out of 249 rainy days rainfall of up to 5 mm was measured, whereas rainfall over 15 mm was only observed on 14 days. However, with this amount of water the water tables rose

too slowly for the experiments to be completed, and subsequently larger water amounts were added (Tables 3.1, 3.2). On some occasions the amount of water added to each soil monolith varied in order to achieve similar soil water potentials and water table heights in each replicate monolith. The time intervals between irrigation events also varied because it took different lengths of time for the N_2O emissions to reach their maxima after the water addition (Tables 3.1, 3.2).

Gas flux and soil water potential measurements were made as described in Chapter 2 (Sections 2.1.4 and 2.1.6, respectively).

Table 3.1. Dates and amount of water added to fallow soil monoliths during first wetting experiment.

	Amount of water added (mm)							
	Sandy loam				Clay loam			
	Monolith No.							
Date	1	2	3	4	5	6	7	8
1-Nov-9	5	5	5	5	5	5	5	5
4-Nov-9	5	5	5	5	5	5	5	5
8-Nov-9	5	5	5	5	5	5	5	5
12-Nov-9	5	5	5	5	5	5	5	5
15-Nov-9	5	5	5	5	5	5	5	5
22-Nov-9	5	5	5	5	5	5	5	5
6-Dec-9	10	none	none	none	none	10	10	10
14-Dec-9	10	5	5	5	5	5	5	10
12-Jan-9	10	10	10	10	10	10	10	10
24-Jan-9	20	10	10	10	10	10	15	20
14-Feb-9	20	20	15	15	10	10	15	20

Table 3.2. Dates and amount of water added to fallow soil monoliths during second wetting experiment.

	Amount of water added (mm)							
	Sandy loam				Clay loam			
	Monolith No.							
Date	1	2	3	4	5	6	7	8
20-Apr-94	10	10	10	10	10	10	10	10
29-Apr-94	10	10	10	10	10	10	10	10
6-May-94	10	10	10	10	10	10	10	10
12-May-94	10	10	10	10	10	10	10	10
18-May-94	10	10	10	10	10	10	10	10
24-May-94	15	15	15	15	10	10	10	10
31-May-94	20	20	20	20	10	10	10	10
7-Jun-94	10	10	10	10	10	10	10	10
14-Jun-94	15	15	15	15	15	15	15	15
24-Jun-94	20	20	20	20	15	15	15	15
5-Jul-94	25	20	20	20	20	20	20	20
29-Jul-94	20	20	20	20	20	20	20	20
17-Aug-94	20	20	20	20	20	20	20	20

3.1.2. Results

3.1.2.1. 1st wetting experiment

The effects of water additions to the fallow sandy loam and clay loam soils on N_2O fluxes and soil water potentials during the 1st wetting experiment are shown in Figures 3.1 and 3.2. The daily mean soil water potentials before the first water application ranged from -7.4 to -9.6 kPa in the sandy loam soil and from -7.8 to -8.4 kPa in the clay loam soil, and the daily mean N_2O emissions from 19.2 to 30.0 μg N_2O-N m^{-2} h^{-1} and 11.9 to 26.4 μg N_2O-N m^{-2} h^{-1} in the sandy loam and clay loam soil, respectively. The first water application had no effect on N_2O fluxes, despite increasing the daily mean soil water potentials in the sandy loam soil to -4.1 to -8.5 kPa and in the clay loam soil to -3.7 to - 4.9 kPa. In fact, the first drastic flux change from most soil monoliths was only observed after the 5th irrigation, when the N_2O emissions increased 2.5 and 3.4 times on average from the sandy loam and clay loam soils, respectively (Table 3.3). In some monoliths, however, smaller flux increases

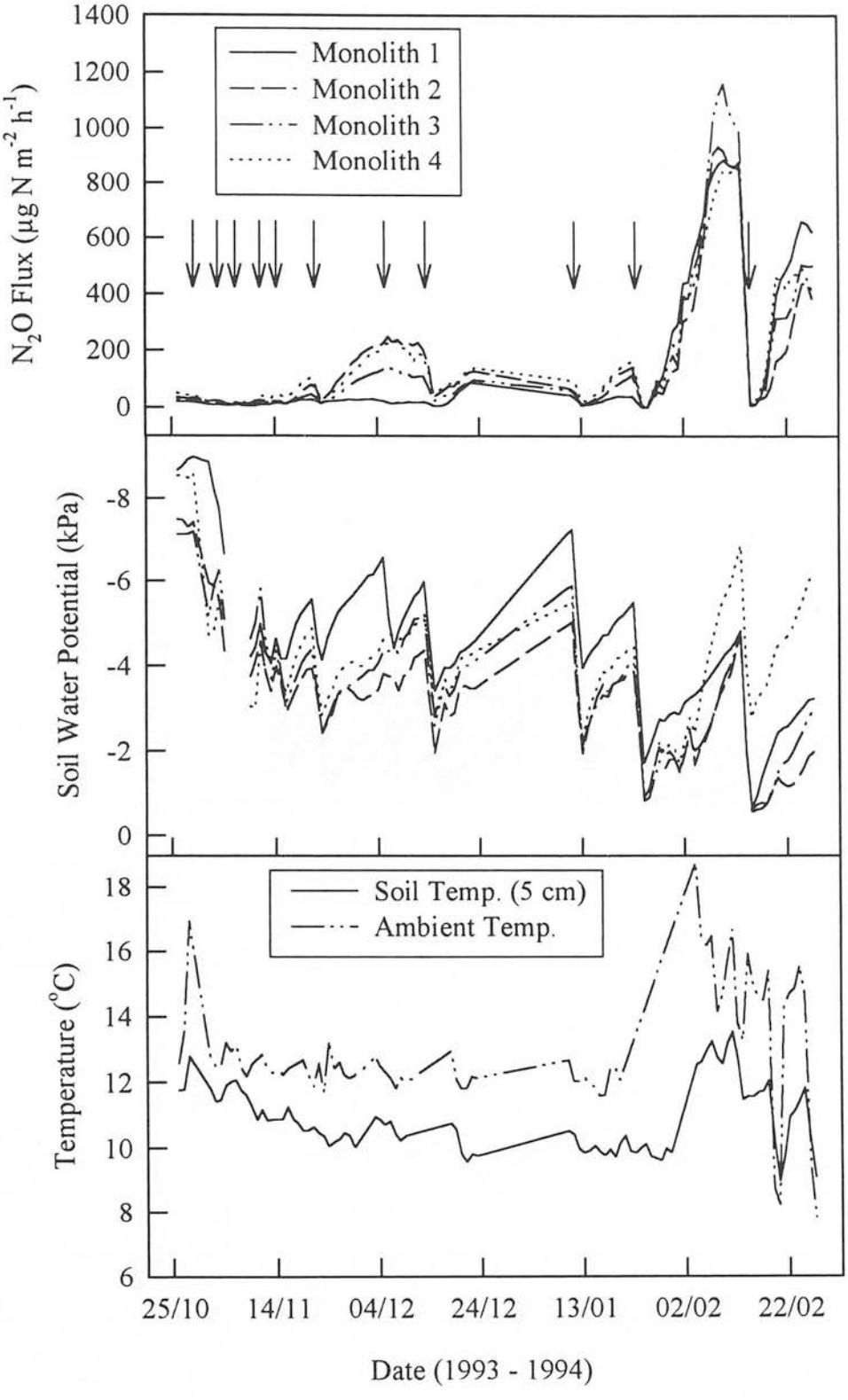


Fig. 3.1. N_2O fluxes, soil water potentials and soil temperatures, fallow sandy loam soil, 1st wetting experiment. Arrows indicate wetting events.

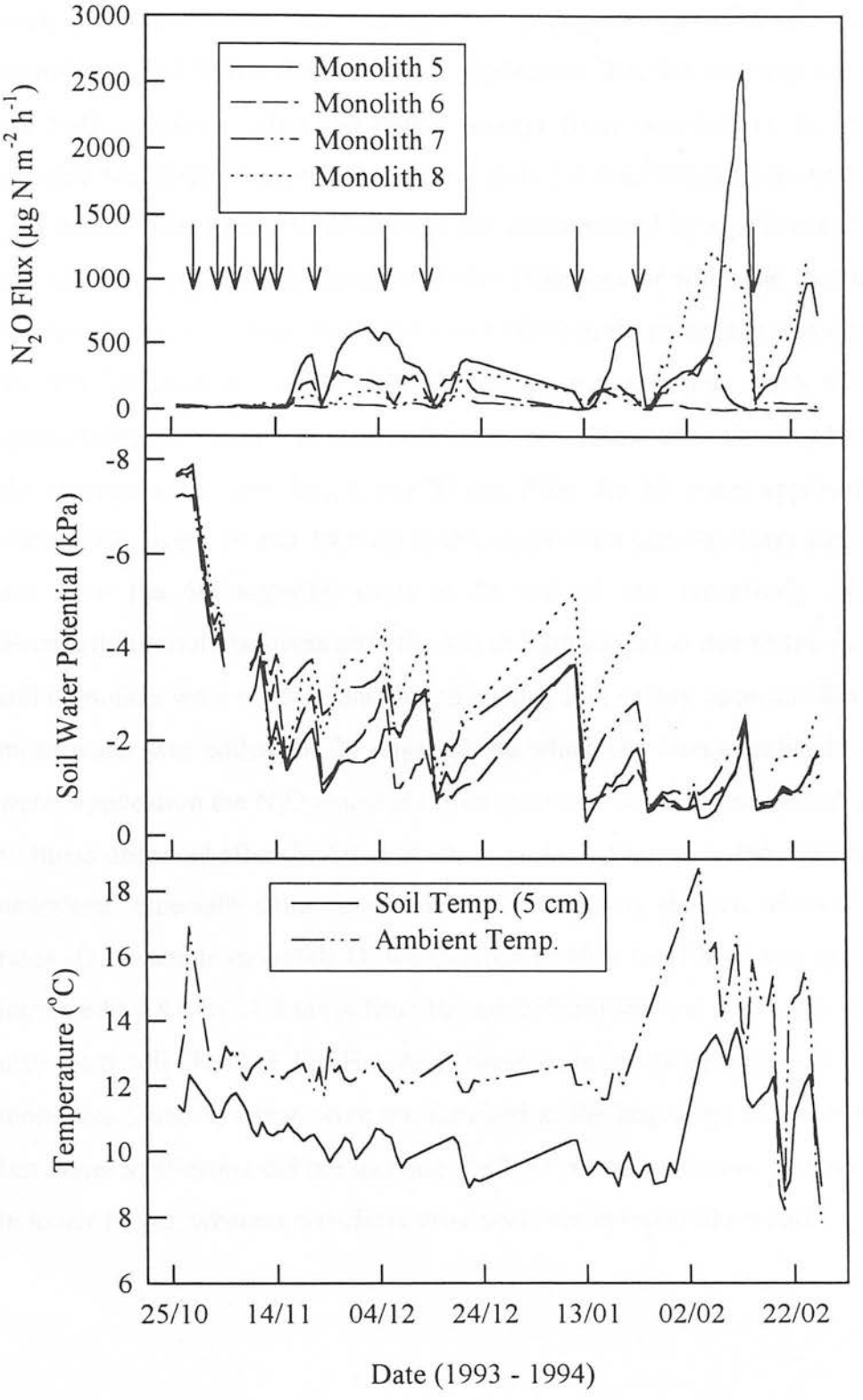


Fig. 3.2. N_2O fluxes, soil water potentials and soil temperatures, fallow clay loam soil, 1st wetting experiment. Arrows indicate wetting events.

were observed earlier; for example the emissions approximately doubled from monolith 4 and 8 after the third water application. The 6th watering event resulted in the N_2O emissions rising still higher (except from monolith 1), but this time the increase was larger from the sandy loam soil (2.4 times) than from the clay loam soil (1.4 times). These flux increases were not accompanied by significant changes in the soil water potentials immediately after the irrigations or when the flux maxima were reached; however, a large rise in the water tables in the monoliths was observed. After the 4th irrigation no water tables (measured approximately 24 h after the water application) were visible in the sandy loam monoliths, but in the clay loam monoliths the average water table height was 50 cm. After the 5th water application the mean water tables were 36 and 19.5 cm in the sandy loam and clay loam soil, respectively, and after the 6th watering event at 28 and 14 cm, repectively. No conclusive observations could be made after the 7th and 8th irrigation due to the fact that not all soil monoliths were watered and due to missing flux values. After the 8th irrigation no more water was added for 29 days, during which the fluxes declined. After the 9th water application the N_2O emissions from most monoliths again reached similar values to those observed after the 5th and 6th irrigations. Extremely large increases in N_2O emissions, especially from monoliths which previously showed relative low emission rates (for example monolith 1), were observed after the 10th water application; they increased by 8.0 to 21.4 times from the sandy loam soil and 4.1 to 9.6 times from the clay loam soil (Table 3.3). However, these large increases were not observed from monoliths 6 and 7, which were not fertilised at the beginning of the experiment. The last water application did not increase the N_2O emissions further, but actually resulted in lower fluxes, whereas no effects were observed in monoliths 6 and 7.

Table 3.3. Maximum N_2O fluxes between watering events during first wetting experiment, and associated soil water potentials.

		Daily mean N_2O Flux ($\mu g\ N\ m^{-2}\ h^{-1}$)								Daily mean soil water potential (kPa)							
		Sandy Loam Soil				Clay Loam Soil				Sandy Loam Soil				Clay Loam Soil			
Watering		Monolith No.								Monolith No.							
Event	Date	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
1	01-Nov-93	12.78	26.86	17.90	26.15	11.23	19.96	17.45	13.83	-7.65	-5.47	-6.41	-5.66	-4.32	-4.91	-4.64	-4.95
2	04-Nov-93	11.34	21.84	17.34	24.21	23.55	13.80	32.07	28.67	*	*	*	*	*	*	*	*
3	08-Nov-93	13.07	29.39	24.74	50.92	27.92	18.07	28.69	61.27	-5.01	-4.78	-5.84	-4.88	-3.80	-4.41	-4.18	-4.52
4	12-Nov-93	19.16	26.30	24.04	61.22	52.56	17.61	24.77	57.32	-4.93	-4.41	-4.89	-4.89	-2.76	-3.58	-4.14	-2.56
5	15-Nov-93	36.00	99.06	58.17	112.97	429.83	227.25	28.70	111.99	-5.68	-4.13	-4.50	-5.03	-2.42	-3.14	-3.80	-3.67
6	22-Nov-93	29.62	248.75	148.76	235.40	627.22	289.81	46.42	140.65	-6.18	-3.77	-4.36	-4.63	-1.63	-0.93	-2.05	-1.05
7	06-Dec-93	20.90	-	-	-	-	257.21	50.35	90.59	-5.40	-	-	-	-	-1.50	-2.80	-3.89
8	14-Dec-93	*	*	*	*	387.67	286.57	115.65	*	*	*	*	*	-1.66	-0.95	-2.31	*
9	12-Jan-94	41.52	116.9	143.44	165.3	634.90	207.88	149.41	128.47	-5.50	-4.07	-4.10	-4.69	-1.76	-1.03	-2.16	-4.02
10	24-Jan-94	887.76	936.51	1161.51	853.11	2594.86	44.04	407.42	1231.59	-4.30	-3.35	-3.79	-5.68	-2.35	-0.65	-1.06	*
11	14-Feb-94	660.74	443.20	508.33	498.34	990.26	9.10	66.68	*	-3.04	-1.89	-2.50	-5.57	-1.65	-1.61	-0.73	*

Note: On 6th December 1993 only monoliths 1, 6, 7 and 8 were watered to achieve similar soil water potentials in all four replicates of each soil type.

* Missing values

For the whole experiment no simple relationship between water content and N_2O fluxes could be established; but, between consecutive watering events a strong dependence was observed. Adding water to the soils usually resulted first in a decline in the N_2O emissions, and then, as the water front moved down the soil profile, in a rise. The time elapsed before the flux maxima were reached varied between 2 and 20 days, and depended on the water status of the soil. Wet soils with a high water table usually needed longer before the maxima occurred, which tended to be slightly earlier in the clay loam soil than in the sandy loam soil. After some irrigation events, however, fluxes increased immediately after the water application, but the emission peak lasted only for approximately 4 h before the usual flux decrease occurred. On most occasions the soil monoliths were watered again when the flux maxima were reached. When the soils were left unwatered for longer the fluxes started to decrease slowly, while the soil water potentials increased.

Fig. 3.3 shows as an example the relationship between N_2O flux and soil water potential for all data points over the 13-d period between 2 watering events in January 1994 for the sandy loam. All monoliths followed the same regression line ($r^2 = 0.82$, $p < 0.01$), except monolith 1 ($r^2 = 0.70$, $p < 0.01$). The most likely reason for this difference is that drier conditions were observed in monolith 1, which resulted in a slower flux increase after the water application.

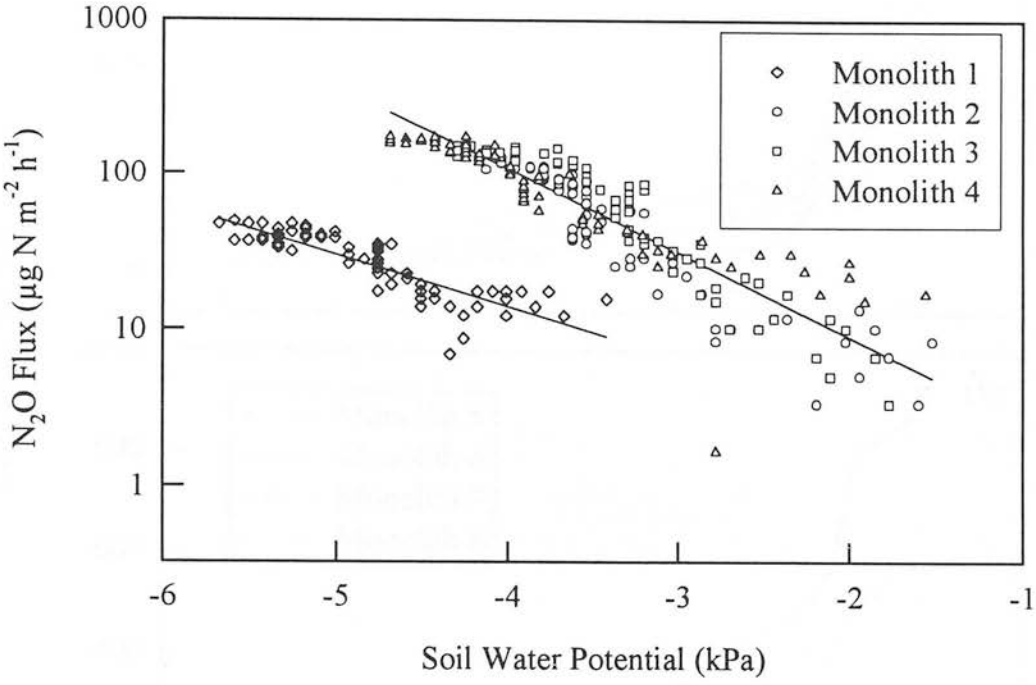


Fig. 3.3. Relationship between soil water potential and N_2O fluxes between two watering events (12th to 24th January 1994). Monolith 1: $r^2 = 0.7$, $p < 0.01$; Monoliths 2 - 4: $r^2 = 0.82$, $p < 0.01$.

Throughout the whole experimental period the clay loam soil monoliths were generally wetter than the sandy loam soil monoliths, and the mean N_2O fluxes from the clay loam soil were higher than from the sandy loam soil (Figs. 3.1, 3.2), though the differences were not significant. The total cumulative N-loss ranged from 179 to 963 mg N m^{-2} and 408 to 457 mg N m^{-2} from the clay loam soil and the sandy loam soil, respectively (Fig. 3.4). When monoliths 6 and 7, which had low N-losses towards the end of the experiment due to suspected nitrate depletion, were excluded the mean N-loss from the clay loam soil (838 ±125 mg N m^{-2}) was about twice as high as from the sandy loam soil.

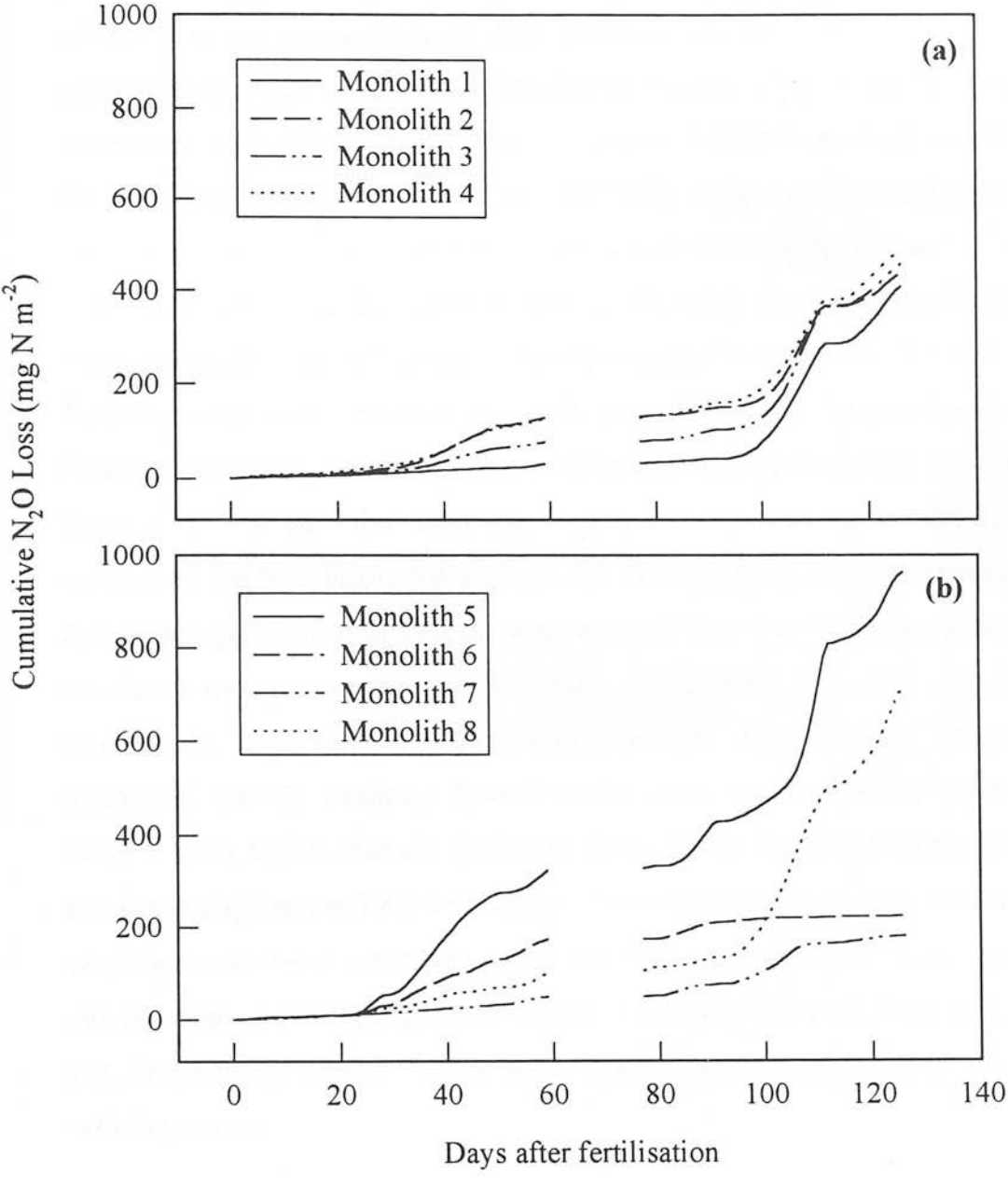


Fig. 3.4. Cumulative N_2O loss from (a) sandy loam soil, (b) clay loam soil, 1st wetting experiment.

3.1.2.2. 2nd wetting experiment

The results from this experiment, shown in Figs. 3.5 and 3.6, were very similar to that of the first wetting experiment (see previous section). Before the first water application the soils were much drier than at the beginning of the first wetting up experiment, with daily mean soil water potentials ranging from -10.8 to -20.5 kPa in the sandy loam soil and from -16.1 to - 30.0 kPa in the clay loam soil, and the daily mean N_2O emissions were slightly lower (3.4 to 13.1 μg N_2O-N m^{-2} h^{-1} from the sandy loam soil, 6.1 to 20.7 μg N_2O-N m^{-2} h^{-1} from the clay loam soil). After the first water application the daily mean soil water potential increased to -7.5 and -5.4 kPa from the sandy loam and clay loam soil, respectively, and, in contrast to the first fertiliser experiment, the N_2O emissions from most monoliths started to increase (see Table 3.4). The next five irrigations caused the soil water potentials to increase further and the N_2O fluxes continued to rise slowly after each water application. The first drastic N_2O emission increase was observed after the 7th watering event, when the fluxes increased by 4.7 and 2.7 times in the sandy loam and clay loam soil, respectively. Extremely large N_2O fluxes occured after the 9th, 10th and 11th irrigations, with the maximum fluxes from the sandy loam soil during this experiment being 5 times higher than the maximum fluxes during the first fertiliser experiment, and in the clay loam soil 2.5 times higher. These high emissions were accompanied by very high soil water potentials during the first 24 h after the water applications, ranging from -1.2 to -2.1 kPa and -0.9 to -1.3 kPa in the sandy loam and clay loam soil, respectively. Lower N_2O emissions were observed again after the last two watering events.

In contrast to the first wetting up experiment during this investigation no trend in N_2O flux difference between the sandy loam and clay loam soil could be seen, and the mean cumulative N-loss from the sandy loam soil was 2370 ±172 mg N m^{-2} and from the clay loam soil 2570 ±256 mg N m^{-2} (Fig. 3.7).

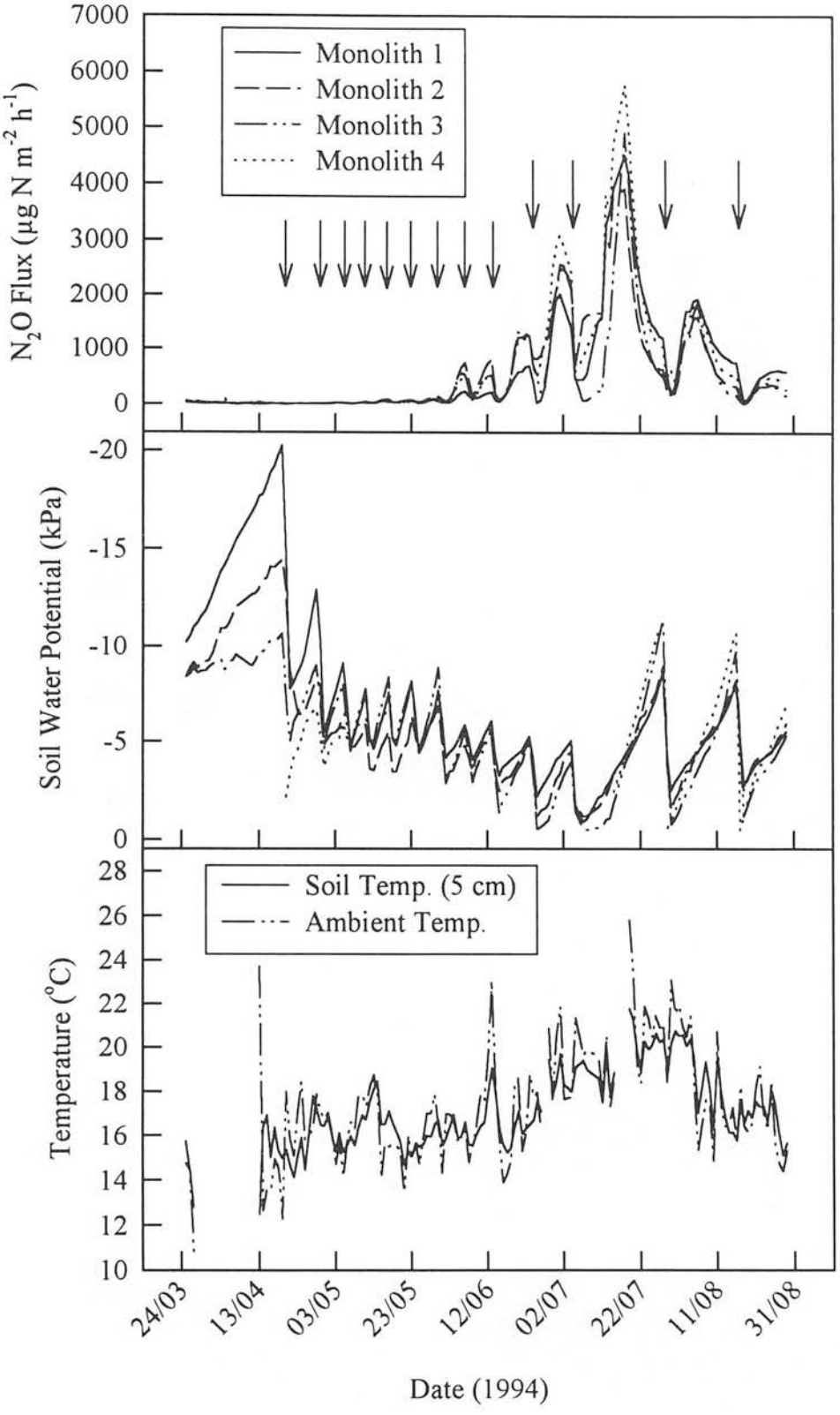


Fig. 3.5. N_2O fluxes, soil water potentials and soil temperatures, fallow sandy loam soil, 2nd wetting experiment. Arrows indicate wetting events.

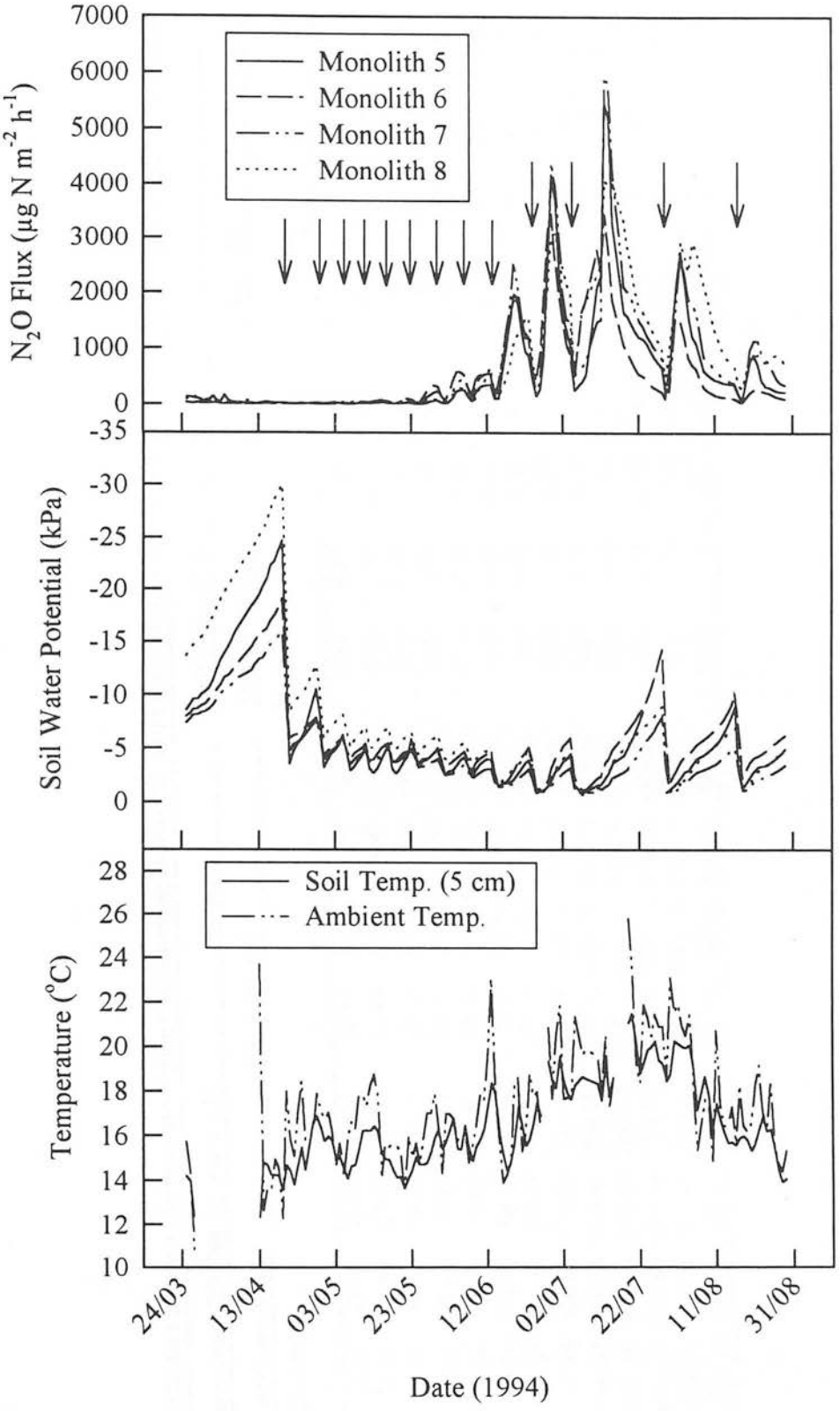


Fig. 3.6. N_2O fluxes, soil water potentials and soil temperatures, fallow clay loam soil, 2nd wetting experiment. Arrows indicate wetting events.

Table 3.4. Maximum N_2O fluxes between watering events during second wetting experiment, and associated soil water potentials.

		Daily mean N2O Flux (µg N m-2 h-1)								Daily mean soil water potential (kPa)							
		Sandy Loam Soil				Clay Loam Soil				Sandy Loam Soil				Clay Loam Soil			
Watering		Monolith No.								Monolith No.							
Event	Date	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
1	20-Apr-94	12.30	17.78	11.84	16.28	28.16	11.25	16.74	23.92	-12.03	-8.21	-7.25	-5.12	-11.82	-6.53	-7.68	-12.10
2	29-Apr-94	30.45	31.89	27.07	24.97	25.18	14.51	38.47	21.59	-8.30	-5.70	-6.93	-5.19	-4.90	-5.15	-5.06	-7.11
3	06-May-94	44.50	44.01	31.30	30.31	25.12	16.29	51.64	19.60	-7.64	-5.91	-7.07	-6.82	-5.16	-5.45	-4.93	-7.03
4	12-May-94	96.61	81.82	57.80	61.17	38.10	55.96	77.17	57.80	-6.72	-5.11	-6.80	-6.83	-3.88	-5.00	-4.40	-6.27
5	18-May-94	75.88	72.23	44.83	53.87	24.30	107.18	53.63	39.53	-8.18	-5.00	-6.80	*	-4.29	-4.77	-3.94	-5.93
6	24-May-94	102.75	142.49	80.92	117.57	70.40	342.86	244.00	93.00	-7.67	-6.86	-6.79	*	-4.63	-4.66	-4.05	-5.98
7	31-May-94	231.27	742.36	574.07	478.68	269.18	576.76	465.88	298.28	-5.89	-4.80	-4.90	*	-3.93	-4.14	-4.09	-5.33
8	07-Jun-94	238.88	814.64	530.20	570.71	354.48	550.35	764.36	501.03	-4.43	-5.22	-5.67	*	-5.81	-4.59	-5.45	-4.95
9	14-Jun-94	696.62	1266.66	1302.66	1221.23	1972.52	1883.06	2519.48	1551.70	-5.29	-4.75	-4.54	*	-2.13	-2.93	-1.79	-4.88
10	24-Jun-94	2027.51	2577.99	2509.69	3092.52	4170.11	3461.55	4408.94	3102.71	-4.26	-3.37	-3.29	*	-2.11	-3.20	-1.59	-3.13
11	05-Jul-94	4515.07	3926.97	4916.38	5778.44	5464.70	3457.01	5949.72	4084.87	-4.30	-4.34	-3.92	-4.31	-2.22	-3.58	-1.46	-2.16
12	29-Jul-94	1940.06	1610.62	1871.49	1897.23	2730.38	1480.46	2747.35	2930.16	-4.47	-4.76	-3.58	-4.40	-2.35	-3.84	-1.75	-1.64
13	17-Aug-94	636.74	369.79	426.21	517.75	896.16	287.64	1149.24	895.07	-5.00	-4.45	-3.27	-4.82	-2.90	-4.34	-1.84	-2.86

* Missing values

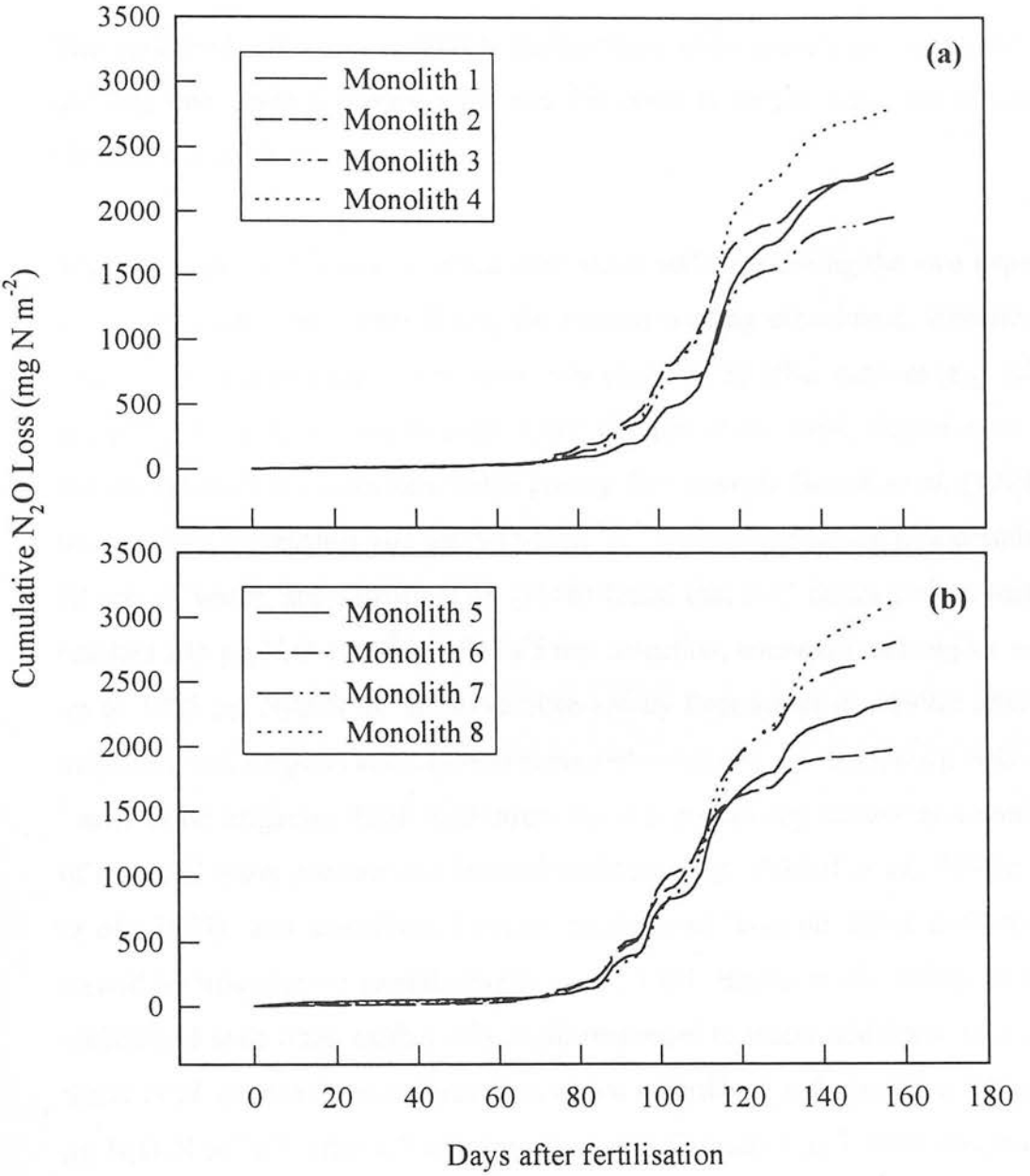


Fig. 3.7. Cumulative N_2O loss from (a) sandy loam soil, (b) clay loam soil, 2nd wetting experiment.

3.1.3. Discussion

The measured soil water potentials during these two experiments, especially during the first one, seem relatively high, and this point is further discussed in Chapter 6 (Section 6.2.3.1.).

The maximum N_2O fluxes observed after water additions during the two experiments were very high, particularly during the second wetting experiment. Emission peaks after rainfall and irrigation were commonly observed by other authors (e.g. Mosier *et al.*, 1981, 1991; Cates and Keeney, 1987; Clayton *et al.*, 1994; Coyne *et al.*, 1994), but the extent of the emissions varied greatly. For example Guenzi *et al.* (1994) found that N_2O fluxes reached 108 μg N_2O-N m^{-2} h^{-1} after irrigating soil in a cornfield with 32 mm of water, and Mosier *et al.* (1986) found that N_2O fluxes from a barley field reached 245 μg N_2O-N m^{-2} h^{-1} after a 5 mm irrigation; whereas much higher emissions up to 1025 μg N_2O-N m^{-2} h^{-1} were observed by Bronson *et al.* (1992) after furrow irrigation, and Delgado *et al.* (1996) measured emissions up to 8330 μg N_2O-N m^{-2} h^{-1} after flood irrigation. High N_2O fluxes like this are usually caused by a combination of high soil water content and fertiliser additions (e.g. Velthof *et al.*, 1996a; Clayton *et al.*, 1997), and sometimes fertiliser applications have no effect until the soil is wetted by irrigation or rainfall (Slemr *et al.*, 1984; Brams *et al.*, 1990). In contrast, unfertilised soils often exhibit only small responses to water additions. In a study by Slemr *et al.* (1984) the emissions from a bare unfertilised soil rose from 20 to only 35 μg N_2O-N m^{-2} h^{-1} after a 7 mm irrigation, and Conrad *et al.* (1983) observed a flux increase of only 15 μg N_2O-N m^{-2} h^{-1} (from 5 μg N_2O-N m^{-2} h^{-1}) after heavy rain showers, again from an uncultivated soil, presumably because of substrate limitation.

Most long term studies show that high fertiliser-induced N_2O emissions only last for a relatively short period of time, after which low or no fluxes are measured regardless of the soil water content (Ryden and Lund, 1980; Mosier and Hutchinson, 1981; Slemr and Seiler, 1984). In this investigation, however, high fluxes persisted over the whole study period from all monoliths, except from monoliths 6 and 7 after the

second last irrigation during the first fertiliser experiment. This, together with the fact that fertiliser additions had no effect on N_2O fluxes, is a strong indication that nitrogen from mineralisation during these two experiments was available in ample amounts and was not limiting microbiological activities. Subsequent N measurements from the soil solution collected, at 10 to 15 cm depths with ceramic cup suction samplers (data not shown), always showed very high NO_3^- concentrations, with values never being below 25 mg l^{-1} in the mineral fallow soils. The only evidence for N restriction was observed during the first wetting experiment from monoliths 6 and 7, after the last two irrigations. The fluxes from these two monoliths were very low compared to the other two replicates from the clay loam soil, and did not respond at all to the last water application. Monoliths 6 and 7 were not fertilised at the beginning of this experiment, and it is possible that the soils at the end of the experimental period were depleted in mineral N.

During the time periods immediately following irrigation and until the maximum emissions were reached, the soils were very wet and the soil water potentials did not fall below field capacity (-5 kPa), which is a strong sign that most of the N_2O emitted during these two experiments was derived from denitrification (see also Chapter 1, Section 1.3.3.1). Evidence for this was shown by Skiba *et al.* (1993), where N_2O emissions from a sandy loam soil derived mainly from denitrification when the soil was wet, but from nitrification during drier conditions, and Parton *et al.* (1988) suggested that denitrification is only a significant source of N_2O when soils become very wet.

The immediate reduction of N_2O fluxes and the delayed flux maxima after water additions observed in this study was also noticed by other workers. Shepherd *et al.* (1991) found that N_2O fluxes were reduced by 20% after irrigation, but increased again as the soil dried out (a very similar result to that shown in Fig. 3.3). Mulvaney and Kurtz (1984) showed that fluxes from soil cores virtually ceased when the soil was saturated by water applications, and then increased as the soil dried out, with maximum emissions occurring 2 to 9 days after the watering, and Byrnes *et al.* (1993) observed emission peaks in fallow rice soils 5 days after simulated rainfall events. The

reduction in the N_2O emissions was due either to a creation of a diffusion barrier of water-filled pores between the zone of production and the surface (Benckiser, 1994; Guenzi *et al.*, 1994), or to the N_2O being reduced to N_2 before it could escape from the soil. The former explanation seems more likely; the fact that immense N_2O emissions occurred relative shortly after the water additions, whereas the soil water potentials often stayed above field capacity, suggests that some redistribution of water occurred, causing enough pores to unblock to allow emission to resume. The time lag observed before maximum fluxes are reached can be explained by (a) the time it takes for anaerobic zones, where denitrification can take place, to form in the soil, and to reactivate the synthesis of the denitrifying enzymes after the water application (Smith and Tiedje, 1979a; Sexstone *et al.*, 1985a), and (b) the time it takes for any N_2O formed to diffuse out of the soil (Jury *et al.*, 1982; Leffelaar, 1986). The fact that the time lag between watering and the occurrence of the flux maxima tended to be slightly shorter in the clay loam soil than in the sandy loam soil can be explained by the water status of the soils. The clay loam soil monoliths were usually wetter and had higher water tables than the sandy loam soil monoliths. Therefore, more anaerobic zones would be expected to form faster in the clay loam soil than in the sandy loam soil, and due to the higher water tables these microsites would be closer to the soil surface, thus reducing the time of diffusion to the soil surface. In contrast to this the occasional short-lived emission peaks immediately after watering were most likely caused by a nonbiological process (suggested by the brevity of the peak), possibly a displacement of N_2O-enriched air by water.

Repeatedly watering the soil monoliths resulted in increasing N_2O emissions with each irrigation, except after the last water addition during the first wetting experiment, and the last two additions in the second wetting experiment, respectively (Figs. 3.1, 3.2, 3.5, 3.6). This can partly be explained by the soil water content, and the relationships between the maximum daily mean fluxes in-between watering events, and their associated soil water potentials, which are shown in Fig. 3.8 (note: It has to be pointed out that the soil water potential was only measured at one depth, and the relationship might look slightly different if the water potential had been measured at a different depth. The implications of measuring water potential at only one depth are

further discussed in Chapter 6, Section 6.2.3.1). The figure indicates that N_2O emissions tend to increase exponentially. A Spearman rank correlation analysis showed a significant correlation between soil water potential and fluxes, with correlation coefficients ranging from 0.76 to 0.93 ($p < 0.01$). However, it is also clear from Fig. 3.8 that soil water potentials alone can not explain the increase in N_2O emissions with each successive irrigation. For example in Fig. 3.8b it can be seen that at a soil water potential of around -2.4 kPa two very different N_2O emissions were measured. Similarly Fig 3.8c shows three very different flux values at around -4.5 kPa. These differences are far too large to be just sampling variation (e.g. slight measuring errors), and strongly point to the fact that other parameters were also responsible for increasing the N_2O emissions. It seems likely that a combination of three other factors was responsible:

(a) Temperature From Figs. 3.1, 3.2, 3.5 and 3.6 it can be seen that very high N_2O emission rates were accompanied with an increase in soil temperature (measured at 5 cm depth). Smith *et al.* (1995) and Brumme (1995) found large increases of N_2O emissions even with small temperature changes, and the mechanism responsible for this phenomenon is discussed in detail in the next Chapter.

(b) Height of water table As pointed out in Section 3.1.2.1. some watering events did not result in a significant change in soil water potentials, but in a rise in the water table approximately 24 h after the irrigation. This is a little surprising since the water table height should be reflected in the soil water potential; however, it could have been caused by small measuring errors from the transducer tensiometers. Higher N_2O evolution in soils with high water tables than from soils with lower water tables were also observed by Kliewer and Gilliam (1995) and Velthof *et al.* (1996a). High water tables 24 h after irrigating indicate that the water front was moving down the soil profile slowly, thus allowing more time for anaerobic microsites to build up, which was followed by higher denitrification rates. Also, in soils with high water tables the denitrification would occur closer to the soil surface, resulting in higher N_2O concentrations close to the soil surface, which then could escape more easily from the soil before reduction to N_2. Similar results were obtained by Gilliam *et al.* (1978), who found high N_2O concentrations in the soil profile when the denitrification occurred in the topsoil, but no N_2O when it took place in the subsoil. The

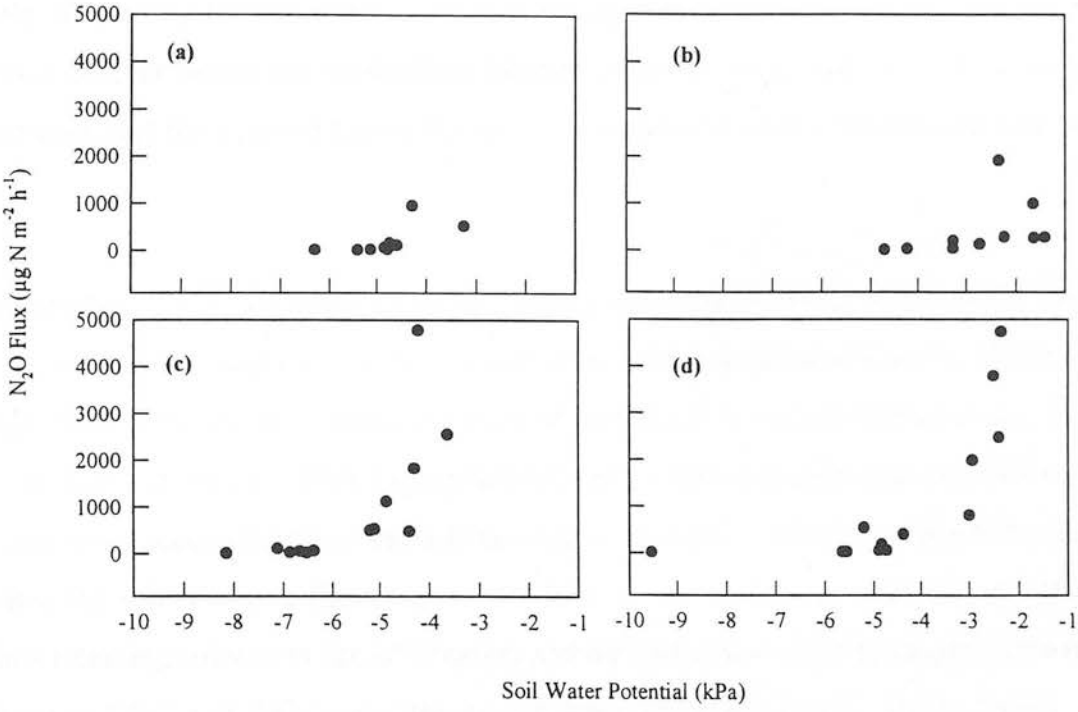


Fig. 3.8. Relationship between maximum N_2O fluxes from fallow soil monoliths between watering events and their associated soil water potentials. (a) Sandy loam, first wetting experiment; (b) clay loam, first wetting experiment; (c) sandy loam, second wetting experiment; (d) clay loam, second wetting experiment.

denitrification rate closer to the soil surface would also be likely to be higher than further down the soil profile due to higher concentrations of available nitrate and carbon.

(c) Accumulation of denitrification enzymes During both experiments the soils rarely dried out below -10 kPa. Thus the conditions were favourable for denitrification to proceed unhindered for prolonged periods of time (it was assumed that no other factors were limiting the process), leading to more and more denitrification enzymes being synthesized. This is in agreement with Dendooven *et al.* (1996), who showed that denitrifiers that experience long periods of wetness were better adapted to anaerobic conditions and produced more enzymes than those which encountered shorter ones. Likewise, Højberg *et al.* (1996) found that denitrification enzymes only

increased after long rainy periods rather than short ones. It is also interesting that Clayton *et al.* (1997) found that N_2O emissions after fertiliser applictions were not only affected by the soil water content at the time of the application, but also by the water content before the application. Higher emissions were observed when the soil had been wet for a period before the fertiliser application than when the soil had been dry.

Higher N_2O fluxes are often observed when soils undergo drying and wetting cycles than when a soil is constantly wet (Letey *et al.*, 1981; Smith and Patrick, 1983), and high denitrification rates can be observed when dry soil is wetted (Patten *et al.*, 1980; Groffman and Tiedje, 1988). Drying soil kills part of the soil microbial population and leads to an accumulation of degradable organic material, which is rapidly mineralised when the soil is wetted (Sorensen, 1974; Kieft *et al.*, 1987; van Gestel *et al.*, 1993), thus releasing substrates for nitrification and denitrification. During longer periods of dryness NO_3^- and NO_2^- can also accumulate (Davidson *et al.*, 1993; Granli and Bøckman, 1995). Letey *et al.* (1981) postulated that high N_2O fluxes during drying and wetting cycles are caused by the fact that the N_2O reduction after wetting a soil is slower than the nitrate reduction leading to an initial accumulation of N_2O. If the soil dries out within 1 to 3 days, insufficient time will have elapsed for the N_2O reduction, and N_2O can escape from the soil. In the current study, however, it is believed that neither of the processes outlined in this section were responsible for the high N_2O emissions observed, or for the N_2O emission increase after each successive water application. One reason is that the soils between the watering events did not dry out sufficiently to kill off the microbial population and lead to an increase of labile organic matter. If this had happened flushes of CO_2 emissions would have occurred after the water applications, which was not observed (Figs. 3.9, 3.10). The process suggested by Letey *et al.* (1981) might have occurred to a certain extent, but again the soils did not dry out enough to completely stop the N_2O reduction.

The fact that during the first wetting experiment no significant increases in N_2O emissions were observed after the first 4 irrigations can be explained by the short time

intervals between the watering events. Due to inexperience not enough time was allowed to pass for the fluxes to reach their maxima before more water was applied.

Higher maximum N_2O fluxes between watering events occurred during the second wetting up experiment than during the first one. This can be explained by the soil temperature. The first wetting experiment was carried out over the autumn and winter months, during which time the temperature in the greenhouse was kept between 12 and 15°C, and the daily mean soil temperatures at 5 cm depth varied from about 9 to 12°C. Only during the last month of the experiment was the greenhouse temperature increased, and the soil temperatures rose to about 13 to 14°C. The second wetting up experiment was done during the spring and summer months, during which much higher daily mean soil temperatures (up to about 22°C) were observed, for prolonged periods of time, than during the first wetting experiment. This led to generally higher respiration rates during the second wetting up experiment, and particularly in July the maximum respiration rates were 2.5 to 3 times higher than the maximum rates during the first wetting experiment (Figs. 3.9, 3.10). This would have led to higher denitrification rates during the second wetting experiment; the exact mechanism is discussed in the next chapter.

During the first wetting experiment, higher N_2O-N losses occurred from the clay loam soil than from the sandy loam. This can be explained by the water status of the soil. Generally the clay loam was wetter and had higher water tables than the sandy loam throughout the whole experimental period, and these wetter conditions would favour higher denitrification rates. It could be argued that due to the high water content in the clay loam the diffusion of the N_2O out of the soil would be restricted, thus leading to lower N_2O emissions due to further reduction to N_2. However, the water tables in the monoliths were relatively high and the N_2O had only a short distance to pass through to the soil surface. It is also possible that the clay loam soil had a higher content of organic matter than the sandy loam. The former monoliths came from a field under grass, whereas the sandy loam soil monoliths were collected from arable land, though it is questionable whether differences were still significant after both soil types had remained fallow for an extended period. Higher N_2O fluxes from fine

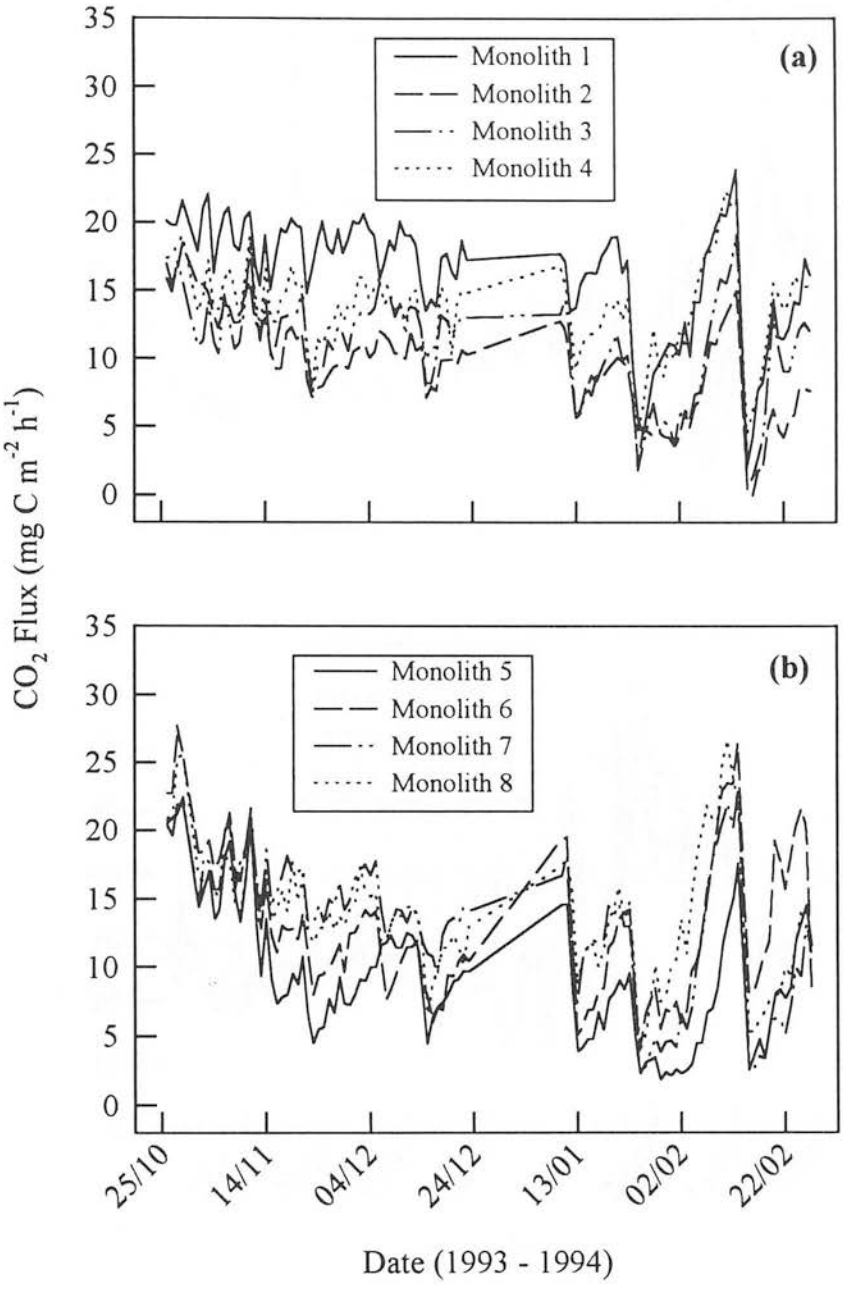


Fig. 3.9. CO_2 flux during 1st wetting experiment. (a) sandy loam, (b) clay loam.

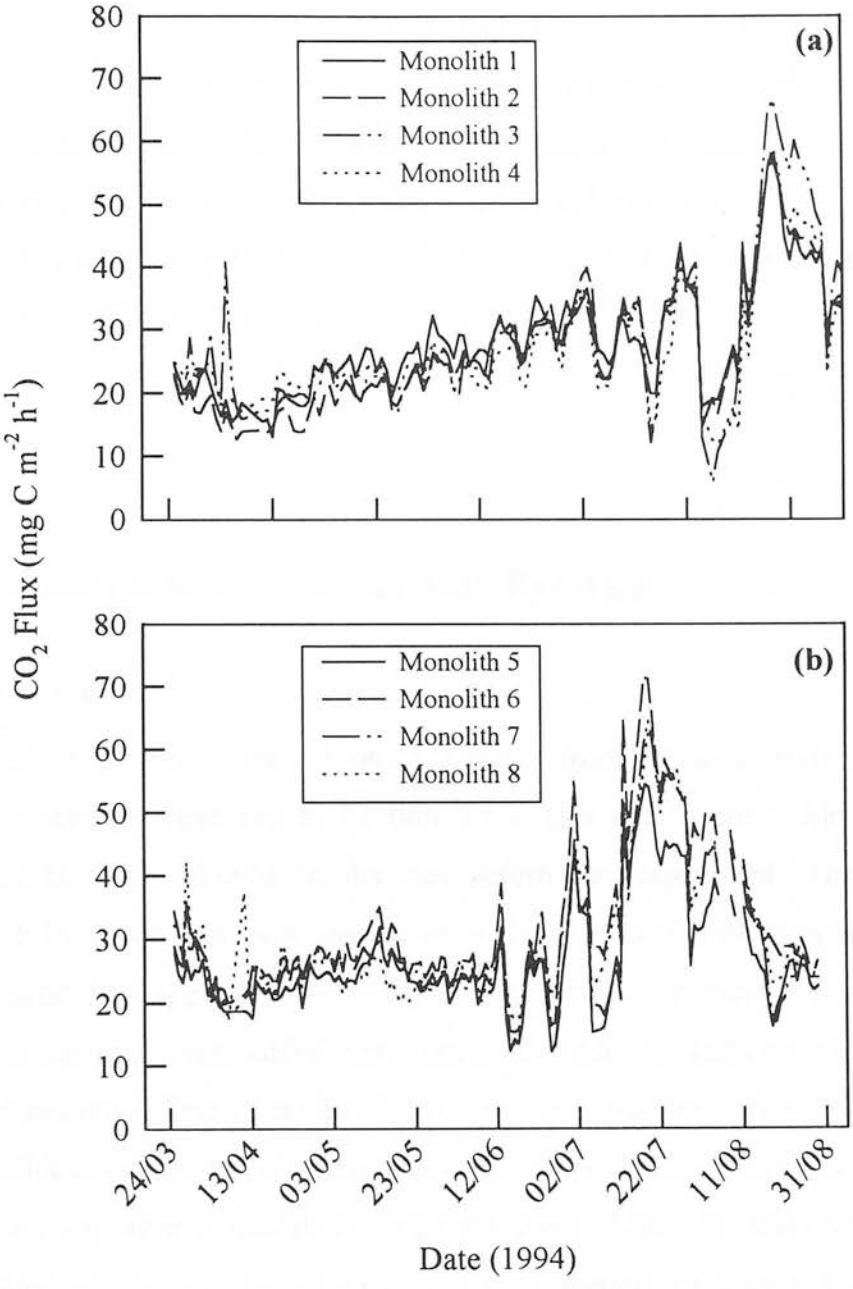


Fig. 3.10. CO_2 flux during 2nd wetting experiment. (a) sandy loam, (b) clay loam.

textured soils than coarse texured soils are commonly observed, and the findings from this study are in good agreement with the results from other work (e.g. Matson *et al.*, 1990; Skiba *et al.*, 1992; Velthof and Oenema, 1995). However, other factors can often override the effect of texture (Granli and Bøckman, 1994), and during the second wetting experiment no differences in N_2O emissions could be detected between the clay loam soil and the sandy loam soil.

3.2. Mineral Soils - Cropped with Ryegrass

3.2.1. Methods

The effect of water content on N_2O fluxes from grassland soils was studied in a similar way as described in Section 3.1.1. (for details see Table 3.5). Again the monoliths were allowed to dry out before the experiment. Then two replicate monoliths of each soil type were sown with ryegrass (*Lolium perenne* L.; amount of seed used: 25.4 g per monolith - equivalent to the recommended 1 oz./sq. yd.), and 5 mm of tap water were added immediately after that. No fertiliser was applied prior to this experiment. During the first 5 months of this experiment the drainage pipes of the monolith casings were left open to simulate more natural conditions, where the water drains away after a rainfall or irrigation event. Then the water table meters were attached again in order to keep the soils wetter, to create a more favourable environment for N_2O production. During the last month of this experiment the soils were fertilised. On 27th October 1995 one replicate of each soil type received 10 g N m^{-2} as $Ca(NO_3)_2$, the other replicate was used as a control. Throughout this experiment the grass was either cut short or just trimmed along the monolith casings in order to prevent it from hanging over the edges of the cases, and thus obstructing the gas seal of the flux chamber.

Gas flux and soil water potential measurements were made as described in Chapter 2 (Sections 2.1.4 and 2.1.6, respectively).

Table 3.5. Dates and amount of water added to mineral soil monoliths cropped with ryegrass.

	Amount of water added (mm)			
	Sandy loam		Clay loam	
	Monolith No.			
Date	2	3	5	7
07-Apr-95	5.0	5.0	5.0	5.0
10-Apr-95	2.7	2.7	2.7	2.7
12-Apr-95	2.7	2.7	2.7	2.7
13-Apr-95	2.7	2.7	2.7	2.7
18-Apr-95	2.7	2.7	2.7	2.7
22-Apr-95	2.7	2.7	2.7	2.7
24-Apr-95	2.7	2.7	2.7	2.7
26-Apr-95	2.7	2.7	2.7	2.7
27-Apr-95	2.7	2.7	2.7	2.7
29-Apr-95	2.7	2.7	2.7	2.7
02-May-95	2.7	2.7	2.7	2.7
05-May-95	2.7	2.7	2.7	2.7
09-May-95	2.7	2.7	2.7	2.7
11-May-95	5.4	5.4	5.4	5.4
15-May-95	5.0	5.0	5.0	5.0
18-May-95	2.7	2.7	2.7	2.7
23-May-95	10.0	10.0	10.0	10.0
26-May-95	10.0	10.0	10.0	10.0
02-Jun-95	10.0	10.0	10.0	10.0
09-Jun-95	10.0	10.0	5.0	5.0
16-Jun-95	10.0	10.0	10.0	5.0
19-Jun-95	5.0	5.0	10.0	10.0
26-Jun-95	35.0	35.0	20.0	20.0
05-Jul-95	25.0	45.0	15.0	10.0
14-Jul-95	15.0	15.0	10.0	10.0
27-Jul-95	15.0	15.0	10.0	10.0
04-Aug-95	15.0	15.0	10.0	10.0
15-Aug-95	25.0	25.0	25.0	20.0
25-Aug-95	25.0	25.0	20.0	15.0
15-Sep-95	25.0	25.0	20.0	20.0
19-Sep-95	15.0	15.0	10.0	15.0
03-Oct-95	15.0	20.0	20.0	10.0
23-Oct-95	20.0	20.0	20.0	10.0
27-Oct-95	2.0	2.0	2.0	2.0
06-Nov-95	10.0	10.0	10.0	10.0

3.2.2. Results

The results of this experiment are shown in Figs. 3.11 and 3.12. During the first 6 weeks small amounts of water (2.7 mm) were applied to the monoliths at short time intervals (approximately every second day) to help the seeds to germinate and to establish the grass ley. Emission peaks were observed after some of these watering events, however no statement can be made of the extent of the peaks, since there was not enough time between irrigation events for the N_2O fluxes to re-adjust to changing water contents.

As the grass grew, the soil water potentials in both soil types decreased slowly from about -6 kPa in the sandy loam soil and about -5.5 kPa in the clay loam soil at the beginning of the experiment to a range of -13 to -17 kPa and -20 to -24 kPa over the first 7 weeks in the sandy loam soil and clay loam soil, respectively. During this period of time the N_2O emissions gradually declined. At the start of this investigation the maximum fluxes from the sandy loam soil ranged from 31 to 129 μg N_2O-N m^{-2} h^{-1} and in the clay loam soil from 53 to 101 μg N_2O-N m^{-2} h^{-1}. These emissions then decreased to very low rates, and the minimum mean values were 12.5 and 6.7 μg N_2O-N m^{-2} h^{-1} from the sandy loam soil and clay loam soil, respectively.

In contrast to the fallow mineral soils, the soil water potentials between irrigation events reached relatively low values (down to -35 and - 48 kPa in the sandy loam soil and clay loam soil, respectively), and the soils dried out faster after the water applications. Applying water to the soils usually had no effect on N_2O fluxes from the clay loam soil monoliths, and only on two occasions was a small short-lived emission peak from the sandy loam soil monoliths observed. One of these peaks occurred soon after the grass ley was established (26 May 95) and the other one after a very large amount of water was applied (26 June 95). Compared to emission peaks from the fallow mineral soil (see Section 3.1.) these peaks were very small, and the general trend over the summer months was a decline of N_2O fluxes until very low emissions and even negative fluxes were observed.

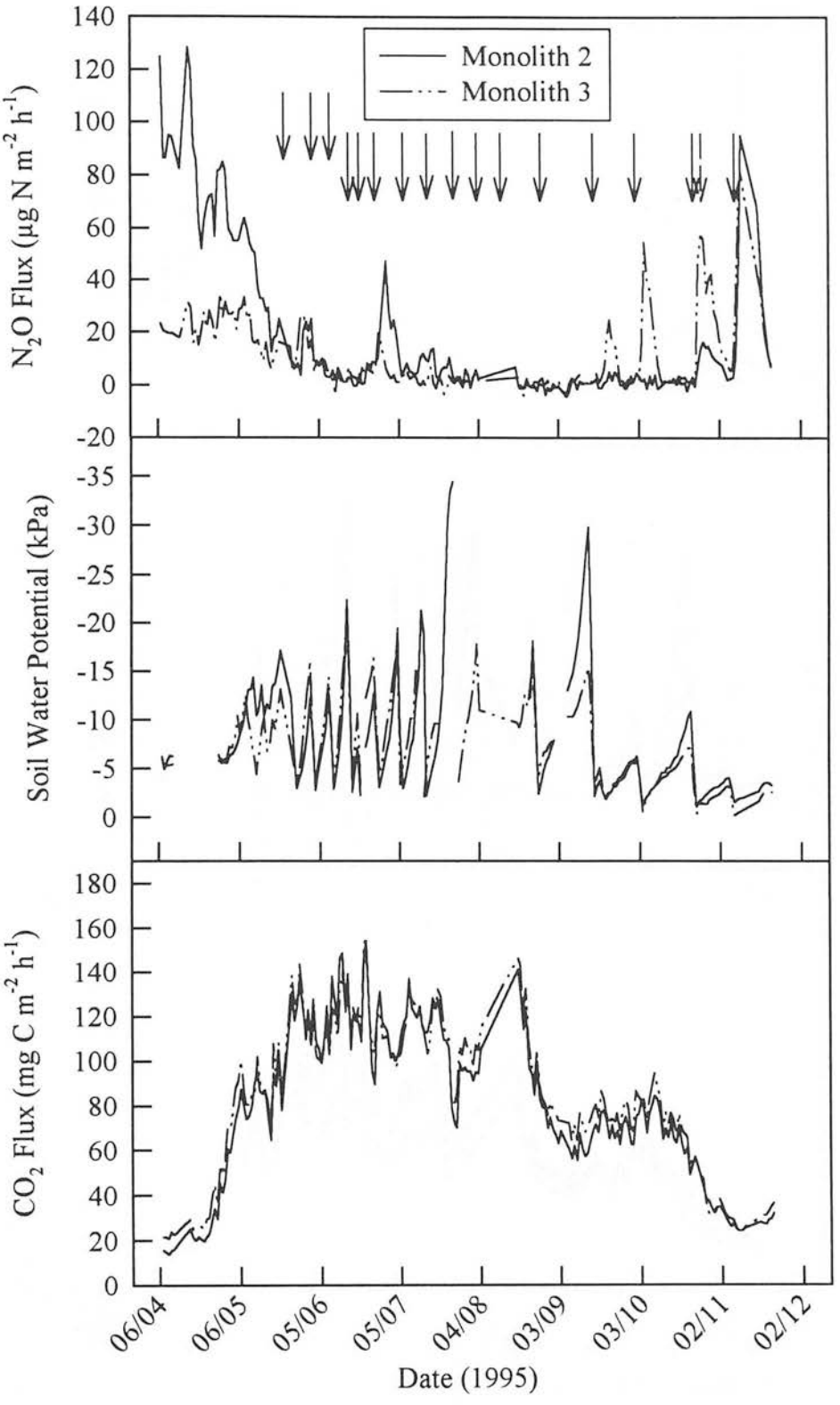


Fig. 3.11. N_2O fluxes, soil water potentials and CO_2 fluxes, sandy loam soil sown with ryegrass. Solid arrows indicate later wetting events (details of all wetting events are given in Table 3.5). Broken arrow indicates date of fertiliser application.

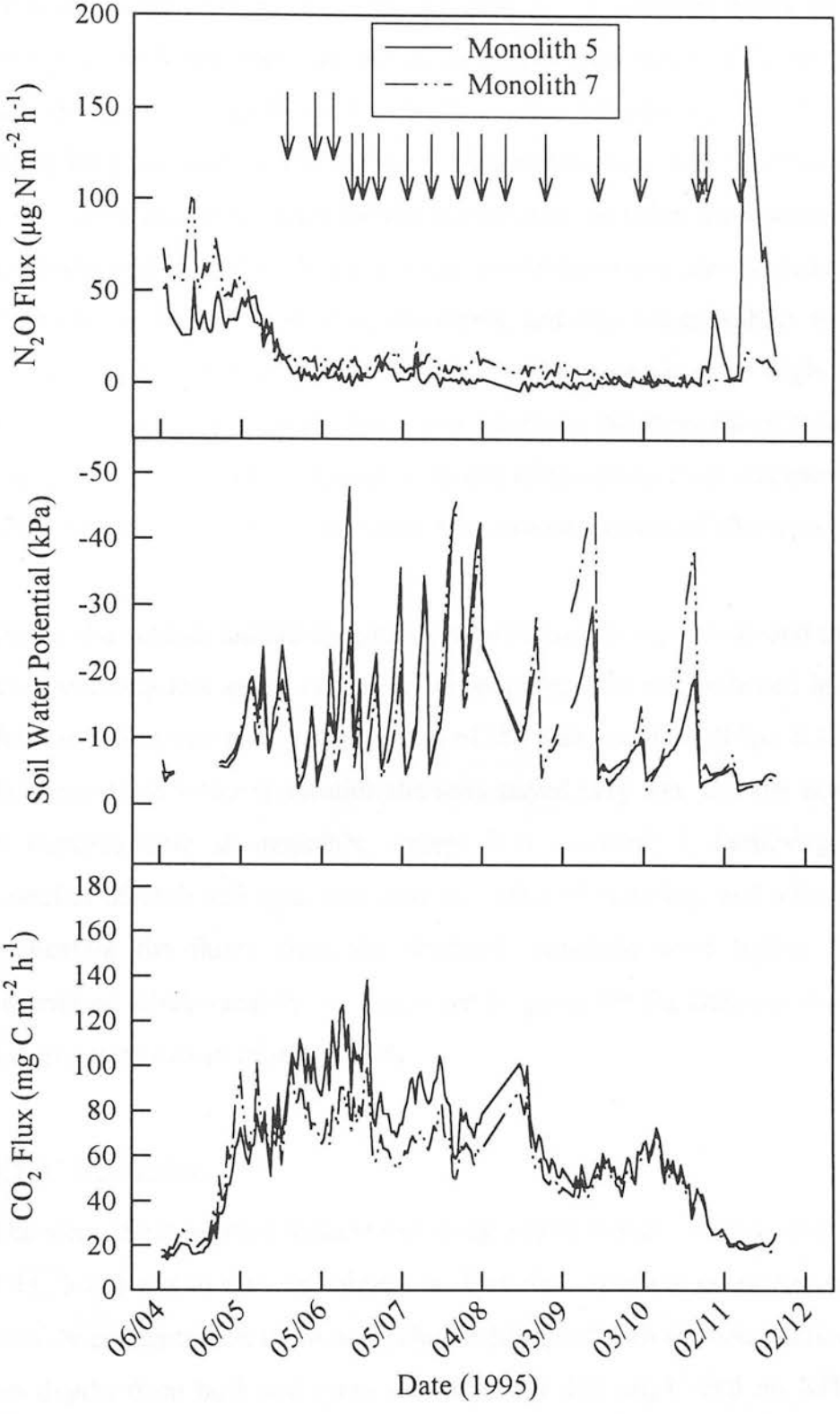


Fig. 3.12. N_2O fluxes, soil water potentials and CO_2 fluxes, clay loam soil sown with ryegrass. Solid arrows indicate later wetting events (details of all wetting events are given in Table 3.5). Broken arrow indicates date of fertiliser application.

After the water table meters were attached to the drainage holes of the monolith casings a rise in the water tables was measured after watering the soils, but usually they declined very quickly and were always low before irrigating. A similar pattern would have occurred before the water table meters were attached (but obviously this could not be detected). After the water applications a water front would exist high up in the soil profile, and while some water would then move slowly down the profile, a proportion would be taken up by the plants, and thus not contribute to the raising of the water tables, which during this experiment were never as high as during the wetting experiments with the fallow soil monoliths. No response of N_2O flux to water applications was observed, except from one of the sandy loam soil monoliths (no. 3), where small emission peaks occurred, with maxima measured after two to three days.

During the autumn months the grass was growing less vigorously and the growth rate was extremely low at the end of the experiment. This was reflected in a decrease of the respiration rate and in a reduction of the water up-take (Figs. 3.11, 3.12). After the second last water application the soils stayed very wet, and the emissions started to increase from all monoliths, except from monolith 7. Fertilising one replicate monolith of each soil type enhanced the effect of watering, and after the last water application the fluxes from the fertilised monoliths were higher than from the unfertilised. Unfortunately, no figure can be given for the emission maxima after the last irrigation due to missing values.

3.2.3. Discussion

The main effect of plant roots in this study was to reduce the soil water content (Figs. 3.11, 3.12) and to take up mineral N. Five days after the grass was sown the mean NO_3^--N concentration in the soil solution (sampled with ceramic suction cups at 12.5 cm depth) from both soil types was just over 100 mg l^{-1} and no NH_4^+-N could be detected. By the 5th October, before the fertiliser application, the mean NO_3^--N concentration had declined to 0.9 mg l^{-1} in the sandy loam soil, and during the whole experimental period, the NH_4^+-N concentrations were very low (the highest value that

was measured was 0.05 mg l^{-1}). Unfortunately, no values can be given for the clay loam soil because the soil was too dry to obtain any soil solution.

The N_2O emissions decreased from around 125 and 25 μg N_2O-N m^{-2} h^{-1} from the sandy loam monoliths, and from around 53 and 73 μg N_2O-N m^{-2} h^{-1} from the clay loam monoliths to values generally below 10 μg N_2O-N m^{-2} h^{-1} from both soil types as the grass became established, and this also coincided with the decrease in NO_3^- in the soil solution. The grass evidently provided a significant sink for the available N in the soil, and the growth both diminished the available substrate for N_2O *and* dried out the soil by transpiration. The likely early effect of this would have been to dry the soil below the threshold for denitrification (Davidson, 1991). Later on during the summer months very low soil water potentials of down to about -50 kPa were observed between watering events. These conditions were not so dry that mineralisation and nitrification would have been inhibited, but the active grass sink would have prevented any accumulation of the mineral N to provide a source of N_2O. This has also been observed in field experiments (Clayton, 1997)

Similar results were obtained by Clayton *et al.* (1997). N_2O fluxes from unfertilised grassland measured for 2 years were consistently low, and fluxes from fertilised plots only increased when the soil was wet at the time of fertilisation or shortly afterwards. Any fertiliser applied was taken up relatively quickly by the plants. However, data from the literature show conflicting results for the effect of plants on N_2O emissions; e.g. Cribbs and Mills (1979) measured higher N_2O fluxes from soils planted with tomato plants than from unplanted soil, whereas Aulakh *et al.* (1982) and Duxbury *et al.* (1982) reported higher emissions from fallow soils than from planted soils.

Changes in N_2O emissions due to plants are generally associated with denitrification, and plants can affect the denitrification rate in several ways. Several studies have shown that denitrification is stimulated by the presence of plant roots, and this can be attributed to an increase of soil organic matter due to root exudates (e.g. sugars and amino acids) and dead root material (e.g. sloughed off root cells and root hairs), as

well as decreasing oxygen concentrations in the soil due to root respiration (Stefanson, 1972; Rolston *et al.*, 1979; Klemedtsson *et al.* , 1987). Root exudation seems particularly high when plants are damaged, e.g. due to cutting grass (Scaglia *et al.*, 1985; Beck and Christensen, 1987). However, Guenzi *et al.* (1978), Smith and Tiedje (1979b) and Heinemeyer *et al.* (1988) pointed out that denitrification rates only increase when sufficient NO_3^- is present, and growing plants compete with micro-organisms for mineral N. In contrast to this, Haider *et al.* (1987) found that the denitrification rate was not stimulated by growing plants, even when the NO_3^- concentration and the water content of the soil were favourable for the process. In a previous study (Haider *et al.*, 1985) they pointed out that even though plants do increase the soil organic matter content, it is not in an easily available form for the microorganisms; and Bakken (1988) concluded that the stimulating effect of plants on denitrification due to root respiration may be more important than root exudation. It also has to be pointed out that even if plants do increase the denitrification rate, this may not necessarily lead to an increase of N_2O fluxes due to a change in the N_2O/N_2 ratio, which tends to decrease in the presence of plants (Vinther, 1984; Klemedtsson *et al.*, 1987).

The observation of increasing N_2O fluxes towards the end of the experiment can be explained by the rate of plant growth. As pointed out in the previous section the growth rate was strongly reduced in the autumn months, leading to a reduced water uptake by the plants. Similarly the uptake of mineral N would also be diminished. Thus, conditions became more favourable for N_2O emissions to occur. The fact that the N_2O fluxes started to increase immediately after the second last irrigation, 4 days before the fertiliser application, suggests that mineral N from mineralisation had accumulated again and was available in large enough quantities for nitrification and denitrification to occur, and that the microbes did not have to compete with the plants. The observed soil water potentials were above field capacity at the time when maximum fluxes occurred, indicating that denitrification was the major process responsible for the emissions.

It seems that monolith 3 had a particularly high mineralisation rate, since emission peaks were observed approximately 5 weeks earlier than from the other monoliths. The occurrence of N_2O flux peaks was also favoured by a relative high water content in the sandy loam soil monoliths compared to the clay loam soil monoliths (Figs. 3.11, 3.12).

From this data, and other work, it can be concluded that in general soils with plants emit less N_2O during the growing season than fallow soils, due to the uptake of mineral N and drier conditions, unless fertiliser is applied during wet conditions. Rainfall and irrigation usually has no effect because of the lack of mineral N and the rapid uptake of the water by the plants, re-creating well aerated conditions before any anaerobic zones can form.

3.3. Organic soil

3.3.1. Methods

The effect of soil water content on the peaty gley soil was examined in the same way as on the fallow mineral soils, except that the soils were not fertilised prior to the experiments (see Section 3.1.1.). This experiment was carried out twice (for details see Tables 3.6 and 3.7).

Gas flux and soil water potential measurements were made as described in Chapter 2 (Sections 2.1.4 and 2.1.6, respectively)

Table 3.6. Dates and amount of water added to peaty gley soil monoliths during the first wetting experiment .

Amount of water added (mm)

Date	Monolith No. 9	10	11	12
25-Aug-93	5	5	5	5
30-Aug-93	5	5	5	5
06-Sep-93	5	5	5	5
27-Sep-93	5	5	5	5
04-Oct-93	5	5	5	5
11-Oct-93	5	5	5	5
18-Oct-93	5	5	5	5
25-Oct-93	5	5	5	5

Table 3.7. Dates and amount of water added to peaty gley soil monoliths during the second wetting experiment .

Amount of water added (mm)

Date	Monolith No. 9	10	11	12
14-Feb-94	10	10	10	10
01-Mar-94	10	10	10	10
17-Mar-94	10	10	10	10
30-Mar-94	10	10	10	10
20-Apr-94	10	10	10	10
29-Apr-94	10	10	10	10
06-May-94	10	10	10	10
15-May-94	10	10	10	10
18-May-94	10	10	10	10
25-May-94	10	10	10	10

3.3.2. Results

Figs. 3.13 and 3.14 show the results from these experiments; compared to the fallow mineral soils, the N_2O emissions observed were relatively low. The maximum emissions did not exceed 550 μg N_2O-N m^{-2} h^{-1}, whereas fluxes up to about 6000 μg N_2O-N m^{-2} h^{-1} were measured from the mineral soils.

The effect of water additions on N_2O fluxes from the peaty gley soil was very different from the fallow effect on the mineral soils. The usual pattern of rapidly instantly decreasing N_2O emissions after irrigating, followed by a gradual flux increase as the water front moved down the profile, which was observed in the mineral soils, was not observed frequently in the peaty gley soil. Adding water to the latter either increased or decreased the N_2O fluxes, depending on the soil water status of the monoliths. At the beginning of the experiments, after the first two irrigations the emisions tended to increase, whereas subsequent watering events led to a decrease in fluxes. It has to be pointed out though that this is a broad generalisation and that this pattern was not always observed from all monoliths, e.g. the N_2O fluxes from monolith 12 during the second wetting up experiment decreased during the whole experiment (Fig. 3.14).

In contrast to the mineral soils, good relationships between the soil water potentials and the N_2O fluxes were observed from some peat gley monoliths over the whole time period for each experiment, and two examples are given in Figs. 3.15a and 3.15b. The first one shows the relationship in monolith 9 during the first wetting up experiment. The N_2O emissions increased until the soil water potential reached field capacity, and then as the soil got wetter they decreased again and reached very low values (< 5 μg N_2O-N m^{-2} h^{-1}) at a soil water potential of just above -3 kPa. Increasing the soil water potential further had no effect on N_2O fluxes. Between -2.5 and -6.5 kPa the relationship can be described with a quadratic equation, with a regresion coefficient of $r^2 = 0.80$ ($p < 0.0001$). The second example (from monolith 11 during the second wetting up experiment) shows a very simliar result. Again a quadratic relationship was observed ($r^2 = 0.83$, $p < 0.0001$), with a flux optimum at about field capacity. However, in contrast to example 1, the N_2O emissions were decreasing until a soil

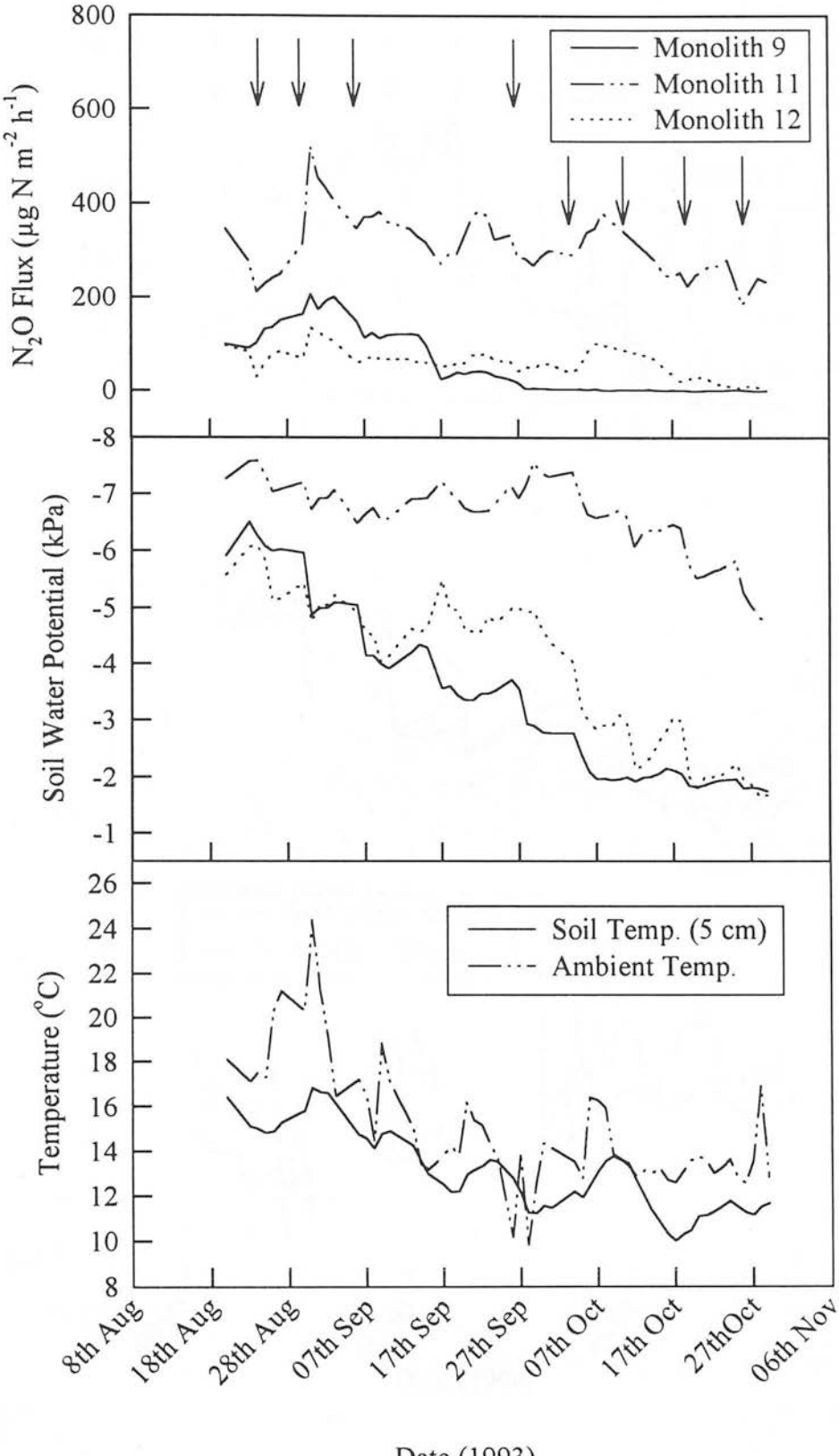


Fig. 3.13. N_2O fluxes, soil water potentials and soil temperatures, peaty gley soil, 1st wetting experiment. Arrows indicate wetting events.

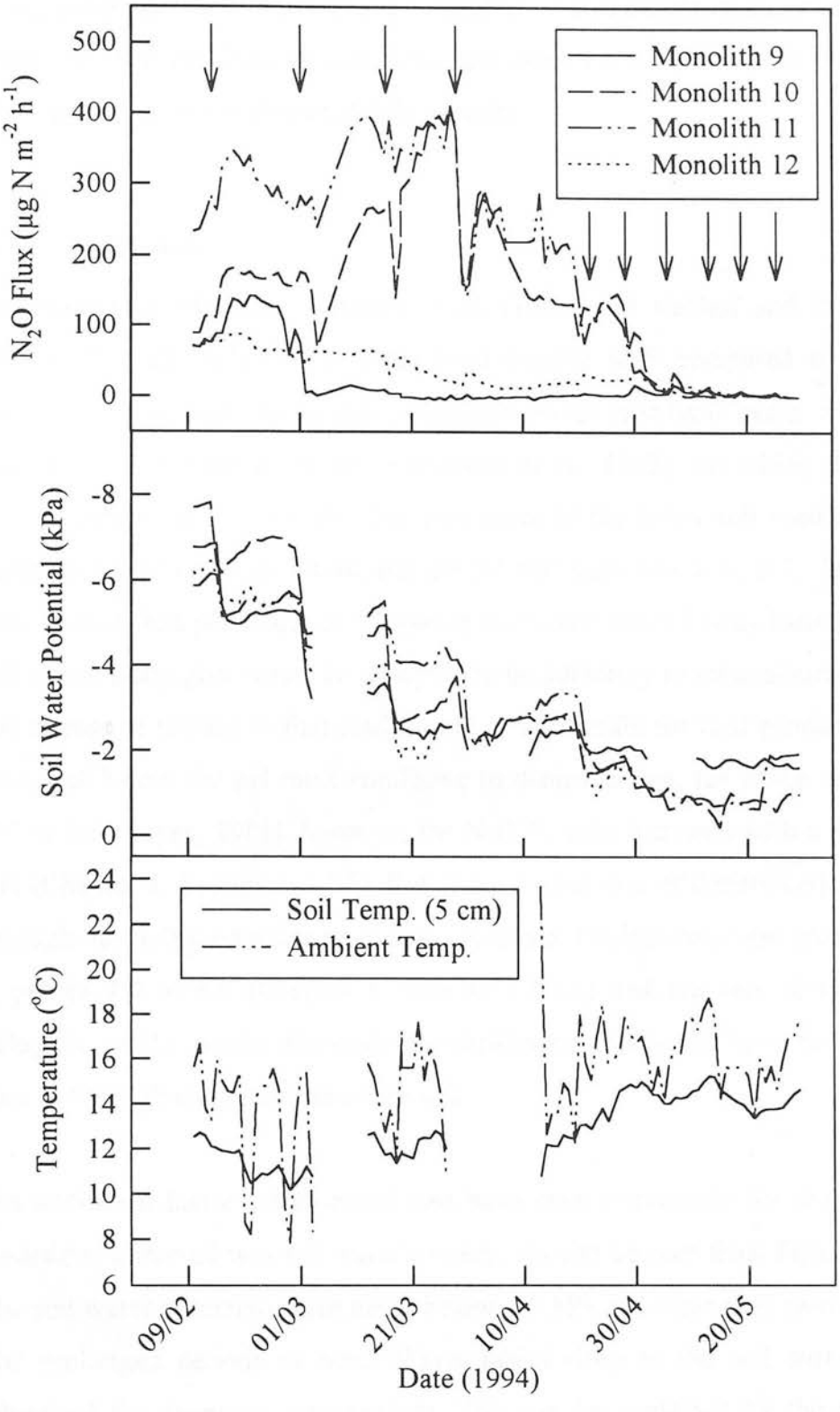


Fig. 3.14. N_2O fluxes, soil water potentials and soil temperatures, peaty gley soil, 2nd wetting experiment. Arrows indicate wetting events.

water potential of around -1 kPa was reached. Unfortunately, such good relationships were not observed from all monoliths, and even if a trend could be established, the flux optimum was not always at field capacity.

3.3.3. Discussion

In contrast to this study Duxbury *et al.* (1982) and Velthof and Oenema (1995) measured much higher N_2O fluxes from organic soils compared to mineral soil. However, these experiments were conducted on fen type basin peats, which generally have a low C/N ratio of 15 to 35 (Naucke *et al.*, 1993), but which also commonly have a neutral or alkaline pH. The peat layer of the forest soil used in the present study had a C/N ratio of 24-40, but the pH was extremely low: 3.7. In contrast, the mineral soils had pH values of 5.7 (sandy loam soil) and 5.5 (clay loam soil). The low pH of the peaty gley would be expected to be inhibitory to mineralisation and thus to the release of mineral N that could serve as a substrate for N_2O production, and was also well below the pH most conducive to denitrification, for which the optimum is 7.0 to 8.0 (Bryan, 1981), however, the N_2O/N_2 ratio increases with a decreasing soil pH (Chapter 1, Section 1.3.3.5). But if the overall rate of denitrification is restricted enough the N_2O production would also decrease. Nitrification rates are also highest at a pH of 7.0 to 8.0 (Chapter 1, Section 1.3.3.5) and are very slow in acid soils (Duggin, 1991). But in this study the nitrification rate would have been low anyway due to the high water content of the soil.

An additional factor which could also have been responsible for the relatively low emissions observed was soil water content. As can be seen from Figs. 3.13 and 3.14 the soil water potentials were never below -10 kPa and often they were above -5 kPa for prolonged periods of time. Water tables close to the soil surface were also observed for extensive time periods. This can be explained by the texture of the subsoil, which below approximately 50 cm was a clay. This strongly restricted the drainage of the monoliths, and the soil never dried out as much as the mineral soils in-between irrigation events. Conditions like this inhibit nitrification, and although they promote denitrification, the end product is usually N_2 (Chapter 1, Section 1.3.3.1).

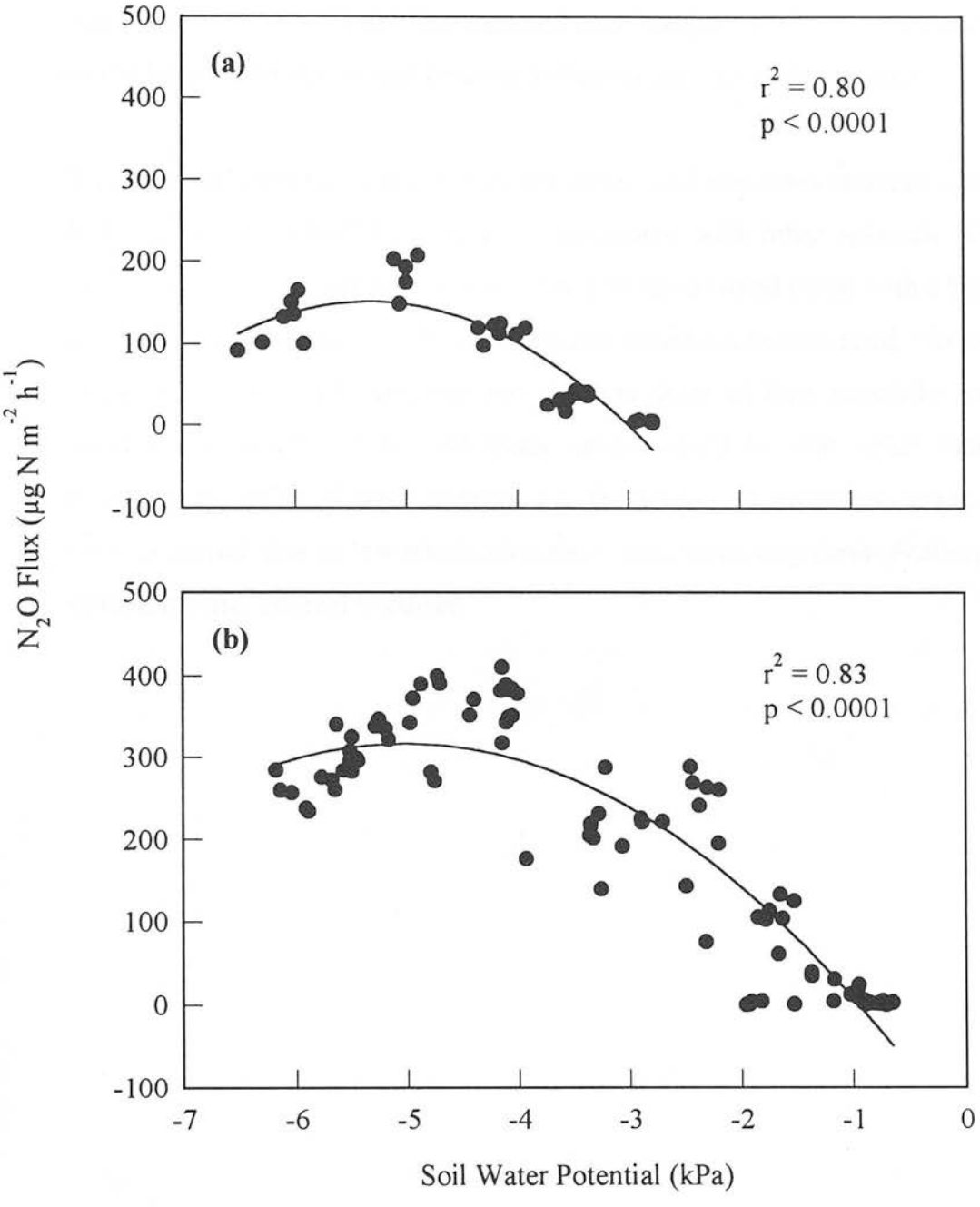


Fig. 3.15. Relationships between N_2O flux and soil water potential. (a) Monolith 9 during 1st wetting experiment. (b) Monolith 11 during 2nd wetting experiment.

Peat is a very porous material, and the total porosity of the topsoil was 91%. This can explain why the flux decrease immediately after water additions observed from the mineral soils, was not commonly detected from the peaty gley soil. After adding water to the latter, there still would be some soil pores open to let N_2O escape.

The observed optimum soil water potential for N_2O emissions at about field capacity from some soil monoliths is in good agreement with other research (Chapter 1, Section 1.3.3.1). At this water content denitrification would occur with a high N_2O/N_2 ratio, and the diffusion of N_2O out of the soil would not be restricted. No explanation can be given as to why this was not observed from all four monoliths during both wetting experiments. The most likely cause would be that other factors were obscuring the effect of water content, e.g. the nitrate concentrations in the soil could have decreased due to low nitrification rates, thus restricting denitrification when the optimum water content occurred.

4. EFFECTS OF TEMPERATURE ON N_2O FLUXES

Three aspects of the effect of temperature on N_2O fluxes were examined:

(a) the effect of diurnal temperature cycles,

(b) general relationships between temperature and N_2O fluxes over longer time periods, and

(c) combined effects of temperature and soil water content.

4.1. Diurnal Flux Cycles

4.1.1. Methods

The effect of diurnal temperature cycles on N_2O emissions was studied in connection with the wetting experiments during the summer months of 1994 and in June 1995 (using all 12 monoliths), when large diurnal temperature variations were observed in the greenhouse. As usual, six flux and temperature measurements were taken per 24-h period. For details on the measurement of the soil and greenhouse temperature see Chapter 2, Section 2.1.6. Gas flux measurements were made as described in Chapter 2, Section 2.1.7.

4.1.2. Results

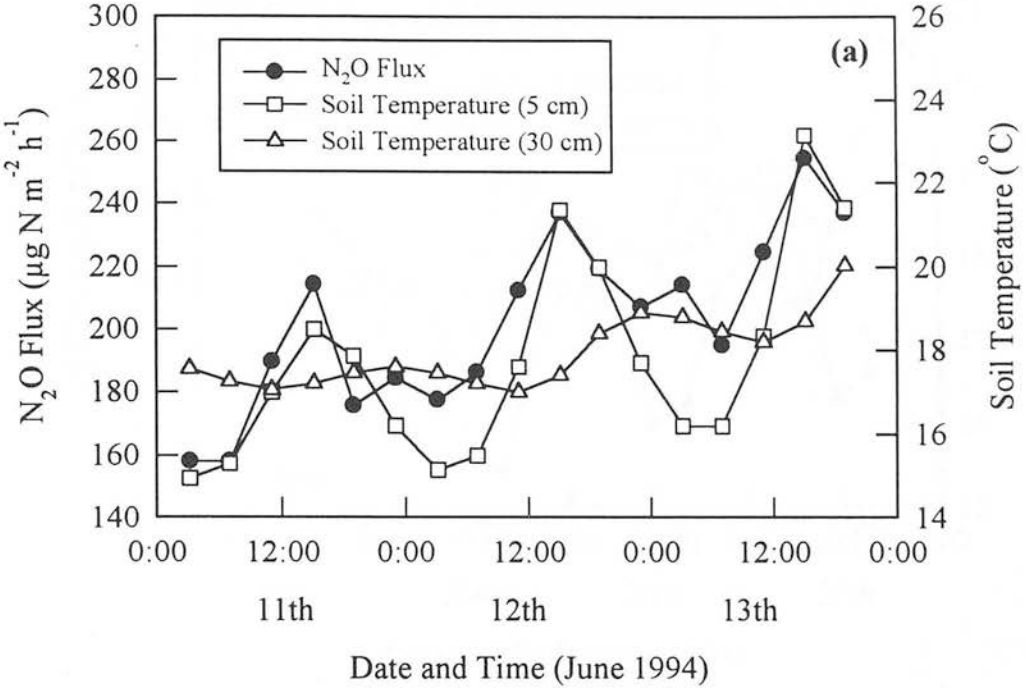
From spring to early autumn, diurnal temperature cycles were detectable in the soil monoliths. The highest soil temperature during each cycle, and the largest amplitude in the cycles, were measured at the shallowest depths where temperature probes were placed (5 and 10 cm). In the mineral soils the temperature maxima occurred at around 1500 h and the minima around 0700 h (Fig. 4.1a). The highest temperatures measured at 5 cm depth were around 25°C, and amplitudes as high as 9°C were observed. At 20 and 30 cm the maxima and minima showed a time lag of approximately 4 to 8 h, and had a lower amplitude (usually 1 to 2°C). The peaty gley soil exhibited the same

variation in the uppermost 5 cm as the mineral soils, but at 10 cm depth the maxima were observed at around 2300 h and the minima at 1100 h (Fig. 4.2a), while cycling at 20 and 30 cm depth was negligible. However, the measured maximum temperatures (up to 21°C) were lower than those observed from the mineral soils, and the temperature cycling was far less pronounced, with amplitudes around 2 to 3°C. From October to the end of March the heating in the greenhouse was switched on, and the ambient temperature was kept at around 15°C at day and night. No diurnal cycling of the soil temperature was observed during these months

Diurnal N_2O flux cycles were observed when diurnal temperature cycling was prominent and when other soil variables (e.g. WFPS) were not completely overriding the temperature effect. However, the relationship between flux and temperature was not constant. Flux maxima occurred at different times of the day and correlated with soil temperatures at different depths. Fig. 4.1a shows diurnal N_2O cycling in one of the sandy loam soil monoliths as an example. Emissions followed closely the soil temperature pattern at 5 and 10 cm depths, but a small emission peak was also observed late at night or in the early morning, coinciding approximately with the temperature maximum at 20 cm depth.

An example with a different diurnal N_2O flux pattern from a peaty gley soil monolith is shown in Fig. 4.2a. Here the emissions followed the soil temperature at 10 cm with a time lag of about 4 h, and had a daily maximum at around 0300 h and a daily minimum in the late morning or early afternoon.

In both examples, on average the daily maximum fluxes were approximately 55 μg N_2O-N m^{-2} h^{-1} higher than the daily minimum fluxes (equivalent to increases of 30% in the sandy loam and 40% in the peaty gley), and a good relationship between the N_2O emissions and the soil temperature was observed. In the sandy loam the r^2-value was 0.77 ($p < 0.0001$) (Fig. 4.1b; soil temperature at 5 cm depth taken for the regression analysis) and in the peaty gley $r^2 = 0.51$ ($p = 0.0006$) (Fig. 4.2b; with the soil temperature at 10 cm depth and time lag taken into account). Assuming that the



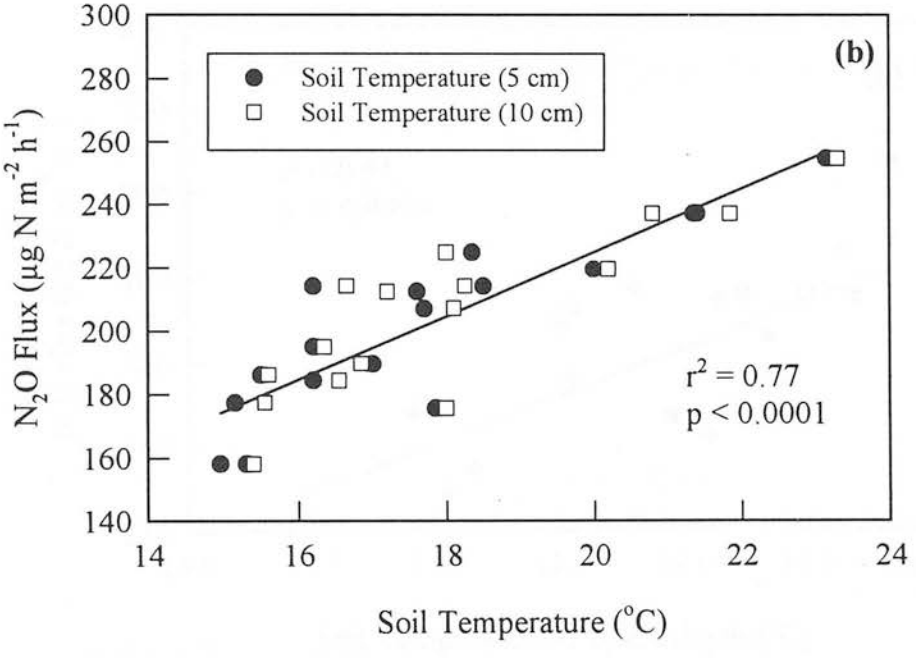
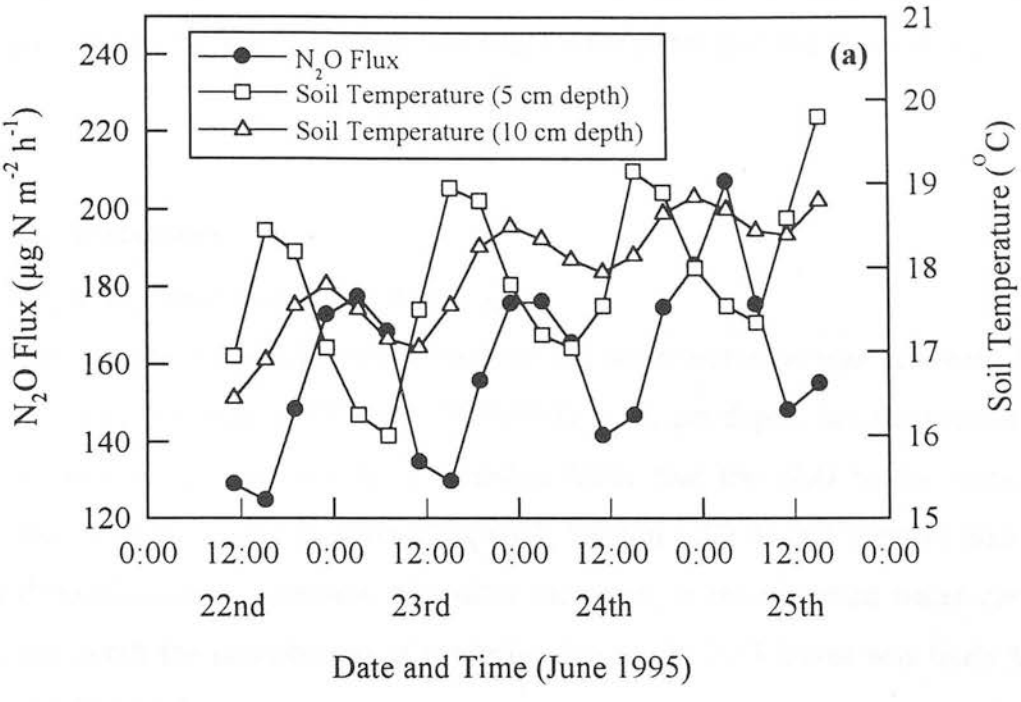


Fig. 4.1. (a) Diurnal temperature and flux cycles in a sandy loam soil monolith. (b) Relationship between soil temperatures and N_2O fluxes (regression line is through the data points relating to temperature at 5 cm depth).



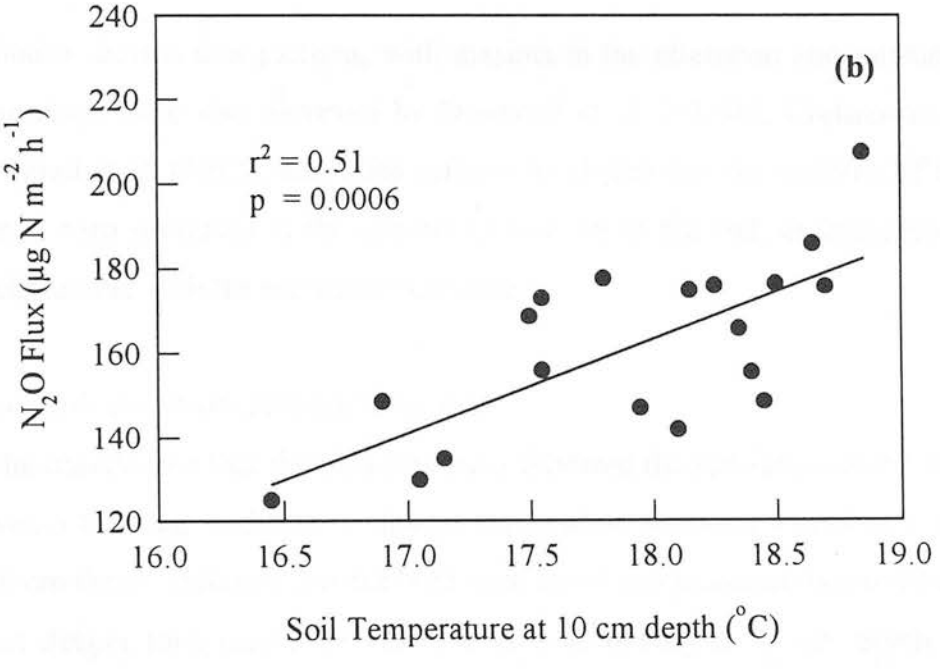


Fig. 4.2. (a) Diurnal temperature and flux cycles in a peaty gley soil monolith. (b) Relationship between soil temperatures and N_2O fluxes (time lag taken into account).

majority of the N_2O from the sandy loam was formed in the topsoil (see discussion), a Q_{10} value of 1.6 was calculated, whereas for the peaty gley the Q_{10} was 4.1.

4.1.3. Discussion

Example 1 - Sandy Loam Soil (Fig. 4.1)

During the three days of measurement the soil water potential was between -5.1 and -6.2 kPa (equivalent to 85 and 84% WFPS) at 20 cm depth, but the topsoil would have been drier than that. It is therefore likely that the N_2O in the topsoil was produced mainly by nitrification (Chapter 1, Section 1.3.3.4), but possibly also in part by denitrification in anaerobic microsites. However, at the observed water content at 20 cm depth the contribution of denitrification to the N_2O fluxes was likely to have been substantial.

Similar diurnal flux patterns, with maxima in the afternoon and minima in the early morning, were also observed by Denmead et al. (1979b), Christensen (1983a) and Conrad et al. (1983), and these authors concluded that the majority of the N_2O must have been produced in the uppermost few cm of the soil, as indicated by the close relationship with the topsoil temperature.

Example 2 - Peaty gley soil (Fig. 4.2)

The observation that the N_2O emissions followed the soil temperature at 10 cm depth with a time lag, and that no diurnal temperature variation was observed at or below 20 cm depth, indicates that the N_2O must have been produced below 10 cm depth, but not deeper than maybe 18 cm. The lack of cycling at 20 cm depth, and the low observed temperature amplitudes at 5 cm depth, were probably caused by the insulating effect of the litter and peat layer. Subsequent N_2O concentration profile measurements (taken at 5, 10, 20 and 30 cm depth) always showed the highest concentration at 10 cm depth (data not shown). The relatively high Q_{10} value (4.1) suggests that most of the N_2O must have been produced by denitrification (see Section 4.2.3).

Blackmer *et al.* (1982) and Yamulki *et al.* (1995) measured similar N_2O flux patterns, and came to the same conclusion that the N_2O was produced at a greater depth than the top few cm.

Our data, and the results from other researchers, strongly indicate that, in order to obtain good flux estimates, several measurements per day have to be taken, and, as Blackmer *et al.* (1982) concluded, due to the fact that the times when flux maxima and minima occur alter, no ideal time of the day exists when reliable daily mean fluxes can be measured.

4.2. General Relationships between Temperature and N_2O Fluxes

4.2.1. Methods

To obtain a more general relationship between temperature and N_2O fluxes, the daily mean temperature and flux values were recorded from 20 October 1993 to 5 April 1995 (the time period from the beginning of the first wetting experiment done with the fallow mineral soils to the beginning of the wetting experiment done with the mineral soil monoliths planted with ryegrass). No data from the monoliths planted with ryegrass were taken because the effects of the plants on N_2O fluxes were strongly overriding the effects of other variables, and created relatively dry conditions, through transpiration, that were unfavourable for emissions to occur (Chapter 3, Section 3.2.3).

In addition, to "purify" the relationship and to eliminate the overlapping effect of the soil water content, the data set was reduced to the flux values at their optimum water content for N_2O emissions to occur, and the associated temperature values. For the optimum soil water content values for the mineral soils see Chapter 6. No general optimum water content value could be established for the peaty gley soil monoliths, but because on some occasions the highest N_2O emissions were observed at field capacity (Chapter 3, Section 3.3.2) this value was chosen.

To examine the data, the N_2O fluxes were first log-transformed, and then Spearman rank correlation and regression analyses were carried out. For this the soil temperature at 5 cm depth was chosen; although the N_2O would not always be produced at 5 cm depth, the temperature at that depth would drive the soil temperature at greater depths, and likewise would be affected by the soil temperature above the 5 cm depth.

Both the whole and the reduced data sets were analysed for each monolith separately and for the mean values of each soil type.

For details of the measurement of the soil and greenhouse temperature see Chapter 2, Section 2.1.6. Gas flux measurements were made as described in Chapter 2, Section 2.1.7.

4.2.2. Results

Mineral soils

Fig. 4.3 shows the effect of soil temperature on N_2O fluxes from the sandy loam and clay loam soils, based on the mean values for all the 4 replicates. Both soil types showed a very similar pattern, which was also observed from all single monoliths (data not shown). The Spearman rank correlation showed that temperature and N_2O fluxes were positively correlated (Table 4.1), but the correlation coefficients were relatively low (< 0.3), with the exception of monolith 7 ($r = 0.41$). The low r values reflect the high variability of the data, and no further analysis was carried out with the whole data set, since due to the low association observed between the two variables, regression analysis would only account for an insignificant percentage of the variability.

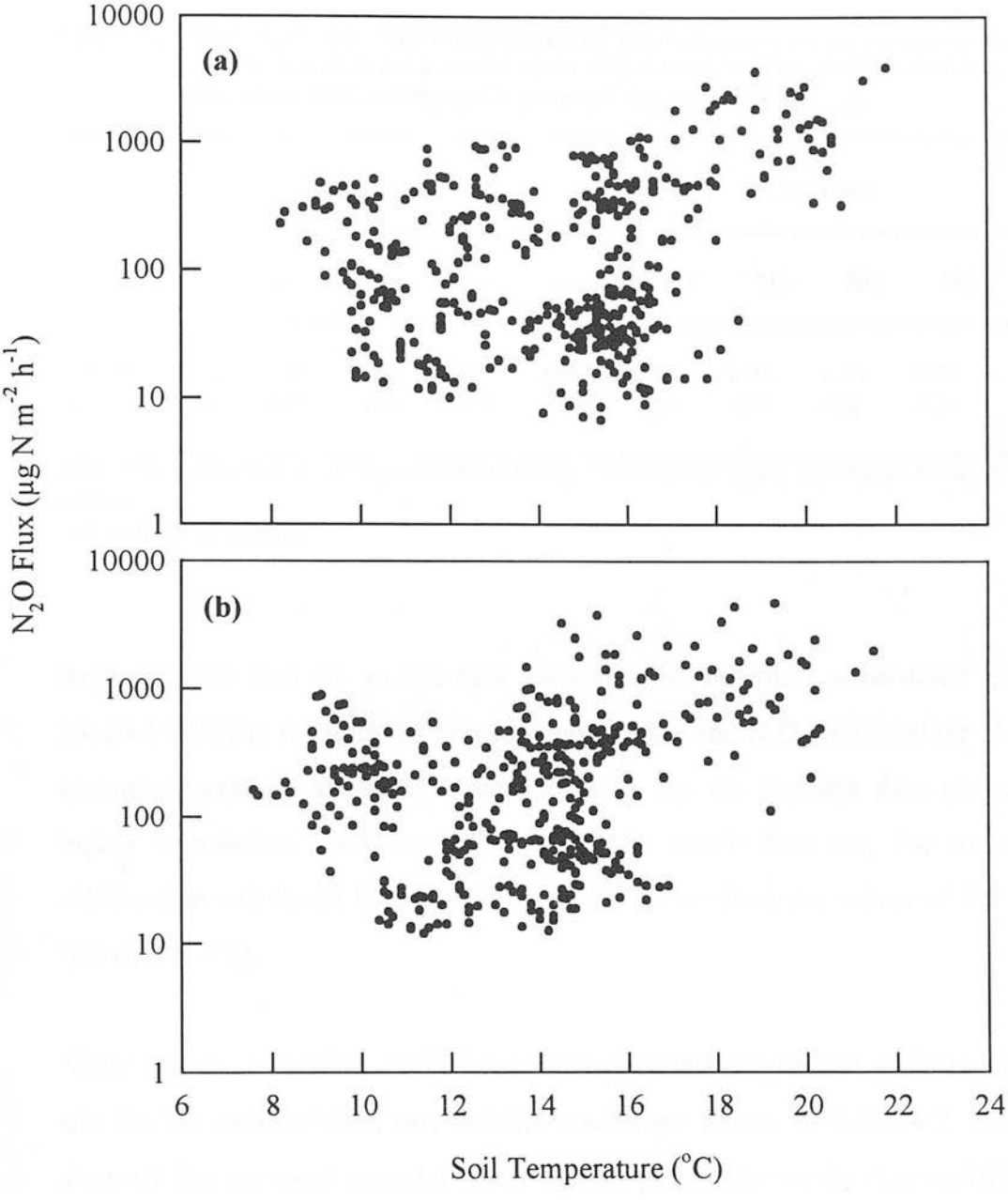


Fig. 4.3. Relationship between soil temperature at 5 cm depth and N_2O fluxes (full data set); (a) sandy loam, (b) clay loam.

Table 4.1. Spearman rank correlation coefficients (r) between soil temperature at 5 cm depth and N_2O fluxes from sandy loam soil monoliths (M1 to M4) and clay loam soil monoliths (M5 to M8), and from mean values of each soil type.

	Sandy loam					Clay loam				
	M1	M2	M3	M4	mean	M5	M6	M7	M8	mean
r value	0.24	0.20	0.22	0.19	0.22	0.08	0.28	0.41	0.24	0.23
N	428	427	428	428	428	426	428	428	426	428

Note: The correlation is not significant for M5 ($p = 0.097$), but highly significant for all others ($p < 0.001$).
N = number of samples

Reducing the data set to the flux values at the optimum water-filled pore space showed a clearer relationship between temperature and N_2O emissions (see Fig. 4.4 as example), and the Spearman rank correlation for the reduced data set resulted in higher correlation coefficients than from the whole data set, but no significant relationship was found for monoliths 4 and 5, or for the mean values of the clay loam soil (Table 4.2).

Since higher correlation coefficients were observed, regression analysis was carried out for the reduced data set, and the results are shown in Table 4.3. The analysis showed that for most monoliths only a small percentage of the flux variability could be accounted for. Furthermore, not all regressions were significant, and for most one or two of the assumptions necessary for the regression to be valid (see Chapter 2, Section 2.3.1) were not met. Exceptions were observed from monoliths 3, 7 and 8, and from the mean values of the sandy loam soil, with r^2 values of 0.418, 0.720, 0.491 and 0.361, respectively, and Q_{10} values of 16.2, 69.2, 28.8 and 15.1, respectively.

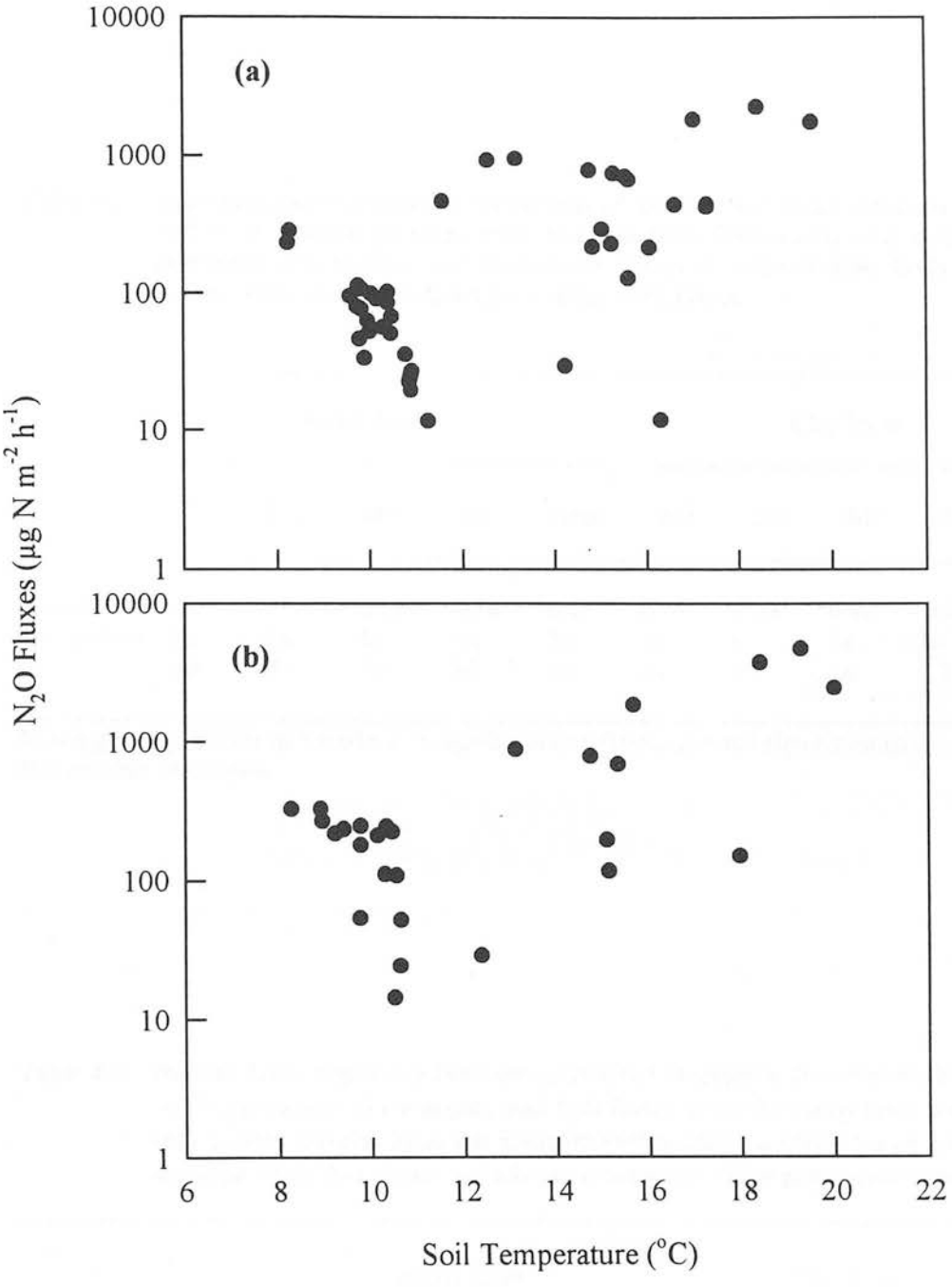


Fig. 4.4. Relationship between soil temperature at 5 cm depth and N_2O fluxes (reduced data set); (a) sandy loam, (b) clay loam.

Table 4.2. Spearman rank correlation coefficients (r) between soil temperature at 5 cm depth and N_2O fluxes from sandy loam soil monoliths (M1 to M4) and clay loam soil monoliths (M5 to M8), and from mean values of each soil type. Only flux values at their optimum water-filled pore space were taken.

	Sandy loam					Clay loam				
	M1	M2	M3	M4	mean	M5	M6	M7	M8	mean
r value	0.50	0.43	0.62	0.18	0.47	0.35	0.38	0.81	0.66	0.26
Significance	hs	hs	hs	ns	hs	ns	s	hs	hs	ns
N	69	57	30	63	44	24	55	18	22	27

hs = highly significant ($p < 0.01$), s = significant ($p < 0.05$), ns = not significant ($p \geq 0.05$)
N = number of samples

Table 4.3. Results from regression analyses carried out to explain the relationship between soil temperature (5 cm depth) and N_2O fluxes from the sandy loam soil monoliths (M1 to M4) and clay loam soil monolith (M5 to M8), and from mean values of each soil type. Only flux values at their optimum water-filled pore space were taken.

	Sandy loam					Clay loam				
	M1	M2	M3	M4	mean	M5	M6	M7	M8	mean
r^2 value	0.272	0.163	0.418	0.038	0.361	0.117	0.125	0.720	0.491	0.372
Significance	hs	s	hs	ns	hs	ns	s	hs	hs	s
N	70	57	30	63	44	24	55	18	22	27
Normality Test	f	f	p	p	p	f	p	p	p	f
Homogeneity Test	p	p	p	f	p	p	f	p	p	p

N = number of samples
hs = highly significant ($p < 0.01$), s = significant ($p < 0.05$), ns = not significant ($p \geq 0.05$)
f = failed, p = passed

The results from the Spearman rank correlation analysis showed that for both the whole and the reduced data sets soil temperature and N_2O fluxes were associated, but not for all monoliths, and for the whole data set the link was weak. Regression analysis carried out with the reduced data set showed some significant relationships with high r^2 values, but for most monoliths and the mean from the clay loam the regression was not valid, because some of the necessary assumptions were not met. However, even without statistical backing a clear trend of increasing N_2O emissions with increasing soil temperatures was observed (Figs. 4.3, 4.4)

Peaty Gley Soil

The data from the peaty gley soil monoliths and their mean values showed a very clustered pattern (see Fig. 4.5 as an example), and no statistical analysis could be carried out. Reducing the data set to flux values at their optimum WFPS improved the situation very slightly, but only for monoliths 11 and 12 (Fig. 4.6). The emission values from these monoliths first increased with increasing temperatures, then they levelled off, and from monolith 11 they declined again at the highest temperatures. A Spearman rank correlation analysis, which could be carried out for monolith 12, showed a highly significant relationship between the soil temperature at 5 cm depth and N_2O fluxes (untransformed and log-transformed data), with a correlation coefficient of 0.74 ($p < 0.001$).

The data from these two individual monoliths, and also from the whole data set, seem to indicate an optimum temperature for N_2O emissions from the peaty gley soil at about 12 to 15°C, above which the N_2O is further reduced to N_2. However, this could be an artefact due to the clustering of the data.

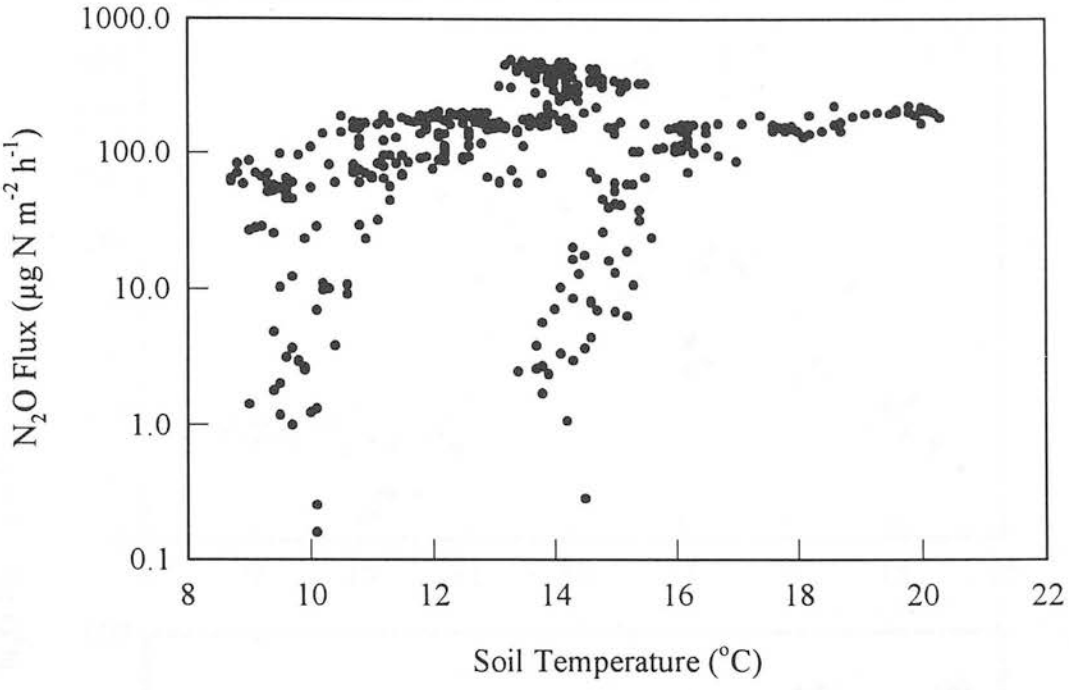


Fig. 4.5. Relationship between soil temperature at 5 cm depth and N_2O fluxes from peaty gley (full data set).

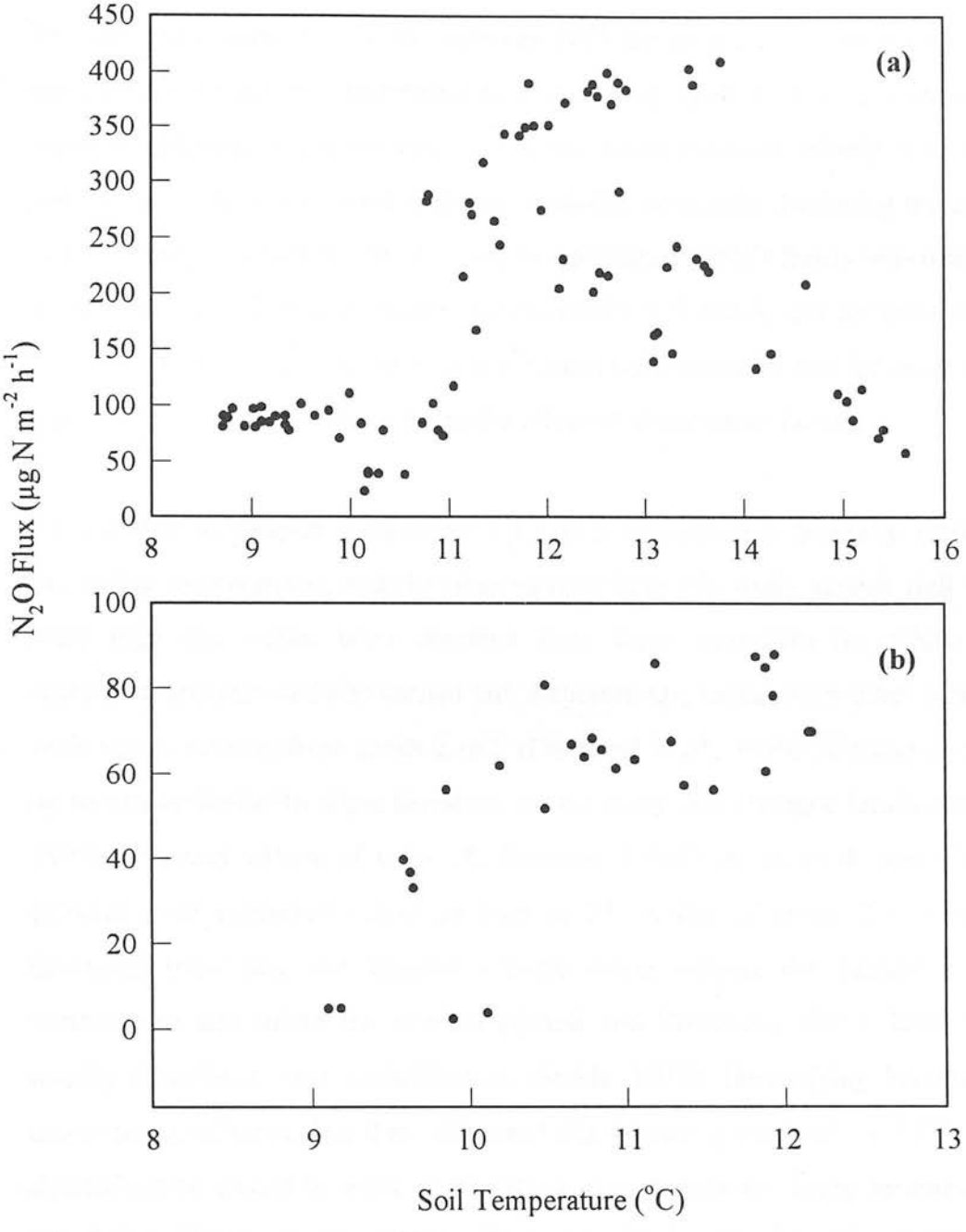


Fig. 4.6. Relationship between soil temperature at 5 cm depth and N_2O fluxes from peaty gley (reduced data set); (a) Monolith 11, (b) Monolith 12. Note the different scales on the x-axes and y-axes.

4.2.3. Discussion

Mineral Soils

The low correlation coefficients between N_2O fluxes and soil temperature obtained from the Spearman rank correlation analysis for the whole data set are not surprising, when considering that many more variables, which fluctuate widely over long time periods, also affect N_2O production and emission from soils. Reducing the data set to those points for which the WFPS was an optimum for N_2O fluxes improved matters slightly, and significant regressions for monoliths 3, 7 and 8, and for the mean values from the sandy loam, with reasonable r^2 values were obtained, but for most monoliths this still could not take into account the effect of all the other factors.

As outlined in Chapter 1 (Section 1.3.3.4) N_2O emissions generally increase with increasing temperatures, and the observations from this study agreed well with this. Very high Q_{10} values were obtained from those monoliths for which a linear regression analysis could be carried out. Reported Q_{10} values from other work show a wide range, varying from about 2 to 3 (Denmead *et al.*, 1979b; Conrad *et al.*, 1983) up to values similar to those measured in this study. For example Smith *et al.* (1995, 1997) observed values of 6 to 15, Brumme (1995) up to 14.4, and Christensen (1983a) even measured values as high as 23. A Q_{10} of about 2 is common for biological processes, and significant larger values indicate that factors others than temperature also affect the process (Granli and Bøckman, 1994). High Q_{10}'s are usually associated with denitrification (Smith, 1997). Denitrifying bacteria require anaerobic conditions, but they also need the aerobic generation of NO_3^-, and thus denitrification should be more significant wherever there are many aerobic-anaerobic interfaces (Tiedje *et al.*, 1984). These interfaces exist in soil aggregates with anaerobic centres, which form or expand whenever the oxygen consumption exceeds the supply rate. This can either happen when a high water content restricts the oxygen diffusion into the centre of a soil aggregate or when the respiration rate is high (e.g. near decaying organic matter like a piece of leaf) (Smith, 1990). Sexstone *et al.* (1985b) and Højberg *et al.* (1994) showed experimentally that denitrification occurs in such anaerobic centres, particularly when C and N are not limiting the process.

Moreover, Parkin and Tiedje (1984) showed that there is a strong relationship between the denitrification rate and the anaerobic volume fraction of the soil. Temperature has a strong positive effect on the respiration rate of soils, and can thus lead to the creation and expansion of anaerobic sites (Renault and Sierra, 1994). This increase in anaerobic volume, combined with the usual Q_{10} of 2 per unit volume of anaerobic soil, can lead to very high "apparent" Q_{10} values for denitrification and thus N_2O production and emissions (Renault and Sierra, 1994; Smith, 1997). However, the extremely large Q_{10} value observed from monolith 7 (reduced data set) seems unrealistically high, and is most likely an artefact caused by other interfering factors.

Peaty Gley Soil

Unfortunately, the strong clustering of the data from the peaty gley soil made the interpretation extremely difficult, and the observed temperature optimum for N_2O emissions was most likely an artefact (each cluster seemed to respond differently to temperature). Unfortunately, no explanation for the clustering could be found. Reducing the data to the values at the optimum WFPS appeared to give a clearer picture for two monoliths, but this too could be an artefact, because field capacity might not be the true optimum water content for emissions (Section 4.3.1).

Furthermore, there is no indication in the literature of an optimum temperature for N_2O emissions under natural conditions. As pointed out in Chapter 1 (Section 1.3.3.4) both nitrification and denitrification have temperature optima, but they are much higher than the apparent optimum observed for N_2O emissions from the peaty gley soil. Increasing the soil temperature leads to a decrease in the N_2O/N_2 ratio from denitrification (Chapter 1, Section 1.3.3.4), and this, in theory, could lead to an optimum temperature for N_2O production. However, the overall increase of the denitrification rate with increasing temperature usually outweighs the effect of the decreasing N_2O/N_2 ratio, and no references reporting decreasing N_2O fluxes with increasing temperature could be found.

In conclusion, the observation from this study has to be treated with extreme care and not be taken as a final result without further experimentation.

4.3. Combined Effects of Temperature and Soil Water Content

4.3.1. Methods

Combined effects of temperature and soil water content were examined for short time periods when diurnal flux cycles were observed, and for the whole data set used to establish a general relationship. To analyse short time periods multiple linear regression was used, but this seemed inappropriate for the whole data set. Some authors (Shepherd *et al.*, 1991; Clayton *et al.*, 1997) have tried to use multiple linear regression to explain N_2O emissions measured in the field, and could only account for a very low percentage of the variation. This can be explained by the fact that several prerequisites have to be met simultaneously for N_2O emissions to occur (e.g. a reasonable soil water content with an adequate N supply), and this makes the use of a multiplicative model more suitable (Elliot and de Jong, 1993). However, developing such a model is much more complex than multiple linear regression analysis, and could not be carried out in the framework of this study. Instead the combined relationship was visualised using the 3-D mesh plot function from SigmaPlot (Jandel Scientific, 1994b).

4.3.2. Results

Fig. 4.7 shows an example of the combined effect of temperature and soil water content on N_2O emissions from a clay loam soil monolith over 3 days between two watering events. During this time period the soil dried out slowly, with the water potential changing from -4.8 to -6.5 kPa, and the daily mean N_2O fluxes increased from 22 to 52 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$. This flux increase was attributed to a downward moving water front after irrigating the soil (for a detailed analysis of the processes involved, see Chapter 3). However, superimposed on the increasing trend were

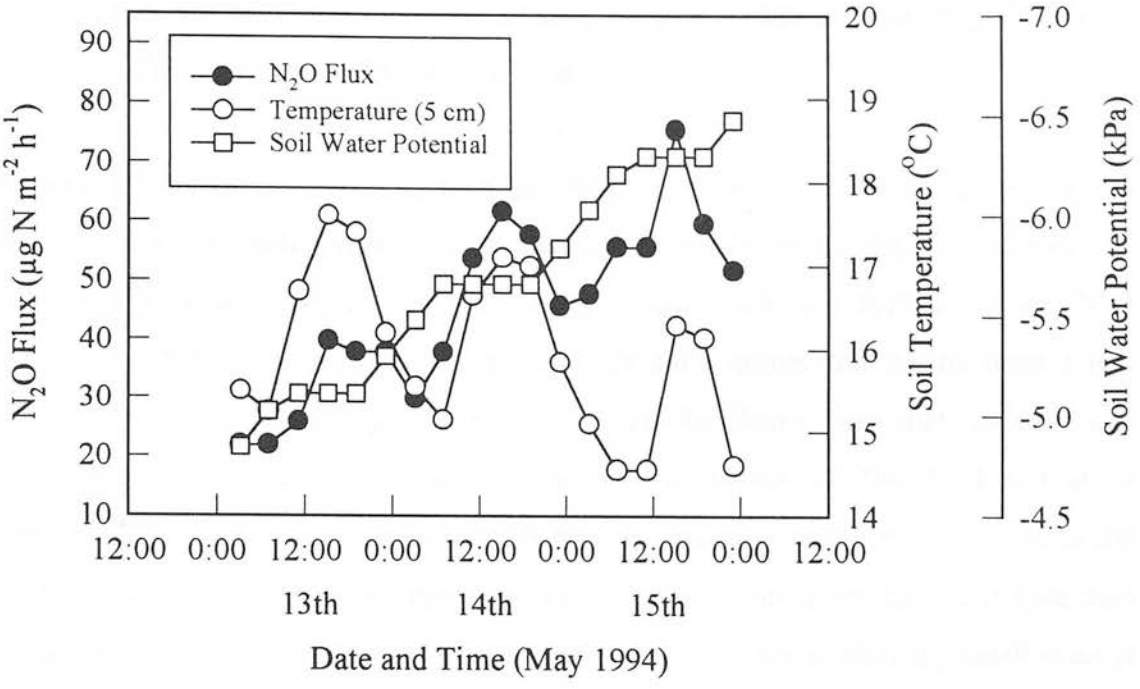


Fig. 4.7. N_2O fluxes, soil temperatures at 5 cm depth and soil water potentials in a clay loam soil monolith.

diurnal flux cycles caused by diurnal temperature variation. Both the temperature maxima at 5 cm depth and the flux maxima occurred at 1500 h, the temperature minima at 0700 h, and the flux minima either at 2300 h or 0300 h. A multiple linear regression analysis showed that both soil temperature and soil water potential were highly significant in explaining the flux variation ($r^2 = 0.88$, $p < 0.0001$). When a regression analysis was carried out using only the soil water potential, only 64% of the flux variation was accounted for. No significant relationship could be detected between soil temperature and emissions, and this can be explained by the fact that the daily temperature and flux minima were out of phase, and because the daily mean temperature was decreasing over the measuring period while the daily mean N_2O emissions were increasing. Similar combined relationships were observed many times, but sometimes the diurnal N_2O emission cycles were superimposed on a decreasing

flux trend as the soil dried out, or on an emission peak, when after an irrigation event the fluxes first increased and then decreased.

Generally N_2O fluxes increased with increasing temperatures, but the extent of the increase was strongly influenced by the soil water content. Fig. 4.8 shows the relationship between the soil temperature at 5 cm depth, the WFPS and the N_2O fluxes for all three soil types (values are both daily means and means from the 4 replicates of each soil type), and from this it can be clearly seen that both the soil temperature and the WFPS strongly affect the extent of the N_2O emissions simultaneously. The strongest increase in fluxes caused by temperature was when the soil water content was at its optimum value for N_2O emissions to occur (see also Chapter 6). Likewise, at low temperatures the emissions were relatively small even at the optimum water content. The extreme "spikiness" observed from the peaty gley soil can be explained by the trend of the data to form clusters (Section 4.2.2).

4.3.3. Discussion

Clayton *et al.* (1997) carried out the same analysis as shown in Fig. 4.8 with field data from a clay loam soil, and the results from their study and the present one are remarkably similar. They too demonstrated that the highest N_2O emissions occur at an optimum WFPS for N_2O and high temperatures, and that high values from both variables have to coincide. It is also worth mentioning that the optimum WFPS in both studies was above field capacity (which is usually thought to give maximum emissions) (Chapter 1, Section 1.3.3.1). This strongly points to the fact that most of the N_2O was produced by denitrification, and this aspect is further discussed in Chapter 6 (Section 6.2.3.1).

As has already been pointed out, the largest emission increase with increasing temperature occurred when the water content was at its optimum value for N_2O to occur. At lower water contents nitrification would become more and more significant, and the N_2O flux increases would be low compared to increases associated with denitrification. As denitrification becomes more important the flux increases are

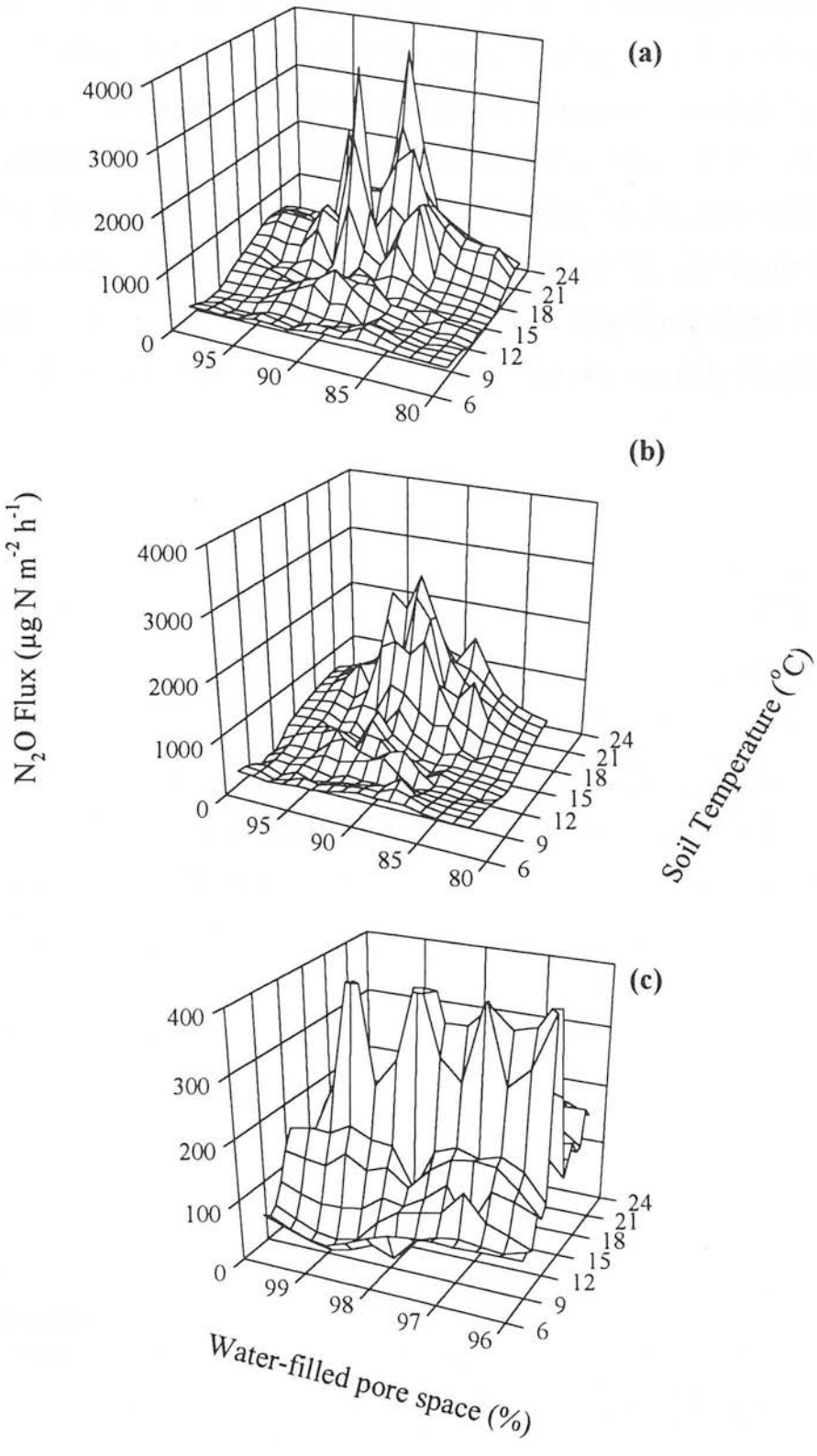


Fig. 4.8. 3-D mesh plots of relationships between N_2O fluxes, water-filled pore space and soil temperature. (a) sandy loam, (b) clay loam, (c) peaty gley. Note the differences in scales for N_2O flux and WFPS in (c).

strongly driven by the formation of anaerobic zones, leading to large apparent Q_{10} values (Section 4.2.3). The highest Q_{10} values resulting from denitrification are likely to be observed at relatively low water contents, when only a small fraction of the total soil volume is initially anaerobic (Renault & Sierra, 1994, Smith, 1997). Thus the *relative* flux changes caused by temperature is likely to decrease with an increasing water content. This was also observed by Craswell (1978), who found that at a water content of 0.7 kg kg^{-1} the denitrification rate was eight times higher at 30°C than at 20°C, whereas at a water content of 0.8 kg kg^{-1} the rate was only four times higher.

5. EFFECTS OF SOIL RESPIRATION ON N_2O FLUXES

In this Chapter short-term changes in N_2O emissions after the stimulation of respiration by the incorporation of plant residues into the mineral soils, as well as general relationships between soil respiration and N_2O fluxes and interactions with the soil water content, are described.

5.1. Effect of Crop Residues

5.1.1. Methods

An experiment to examine the effect of incorporating crop residues was carried out on the mineral soils in December 1994. A grass-clover mixture (875 g fresh weight, 39 g N kg^{-1} DW, 423 g C kg^{-1} DW), harvested from a field site, was applied to each of two replicate monoliths of the sandy loam and clay loam soils and incorporated into the soil to about 10 to 15 cm depth. This amount of grass-clover mixture was equivalent to that grown on an area 5 times larger than the surface area of one monolith, because at the time of the collection the plants were very short (approximately 1 to 2 cm), and also because no root biomass was sampled. The topsoil of the monoliths which did not receive any plant material was also mixed.

Ten days before the grass-clover mixture was applied, all replicates of both soil types had been fertilised with 10 g N m^{-2} as NH_4NO_3 to make sure that the soils were not deficient in mineral N, and 6 days before the grass-clover application 5 mm of water were added to all monoliths. The greenhouse temperature was kept at about 15°C during this experiment.

Gas flux measurements were made as described in Chapter 2, Section 2.1.7.

5.1.2. Results

Before the start of the experiment, the CO_2 emissions from all monoliths of the mineral soils were very similar, with mean fluxes (taken over 2.5 days) of 20.5 ±2.6 and 20.4 ±0.8 mg CO_2-C m^{-2} h^{-1} from the sandy loam and clay loam, respectively. Adding the grass-clover mixture resulted in rapid increases in the soil respiration rate, which reached maxima within 6 h. Similar CO_2 emissions were observed from both soil types (143 ±2 and 153 ±6 mg CO_2-C m^{-2} h^{-1} from the sandy loam and clay loam, respectively), and these fluxes declined very quickly and levelled off to about 53 ±1.7 mg CO_2-C m^{-2} h^{-1} from the sandy loam and 64 ±0.2 from the clay loam after about 2 days (Fig. 5.1). During a period of about 3 days after the organic matter application 5450 ±112 and 6260 ±101 mg CO_2-C m^{-2} h^{-1} was lost from the sandy loam and clay loam, respectively.

Three days after the experiment began the soil monoliths were irrigated with 10 mm of water, and this resulted in a second smaller CO_2 emission peak from both soil types, within 3 h of the water application. Again, the observed maxima were very similar from the two soils: 99 ±9 mg CO_2-C m^{-2} h^{-1} from the clay loam, 112 ±5 from the sandy loam. Subsequent water additions caused further emission peaks from some but not all four monoliths, and the maxima of these were only about a third of the first flux peak. At the end of January 1995 no differences in CO_2 emissions from monoliths that had received organic matter and those that had not could be detected (Fig. 5.2).

During the whole time period (12 December 1994 to 31 January 1995) the CO_2 emissions from the untreated monoliths stayed fairly constant (around 18.2 ±0.2 and 17.8 ±0.6 mg CO_2-C m^{-2} h^{-1} from the sandy loam and clay loam, respectively), and did not respond to any water additions.

The N_2O emissions before the grass-clover application (means over a 2.5 day period) were 9 ±3.6 and 29 ±3.7 µg N_2O-N m^{-2} h^{-1} from the two sandy loam soil monoliths and 63 ±6.5 and 31 ±3.2 µg N_2O-N m^{-2} h^{-1} from those clay loam monoliths that were

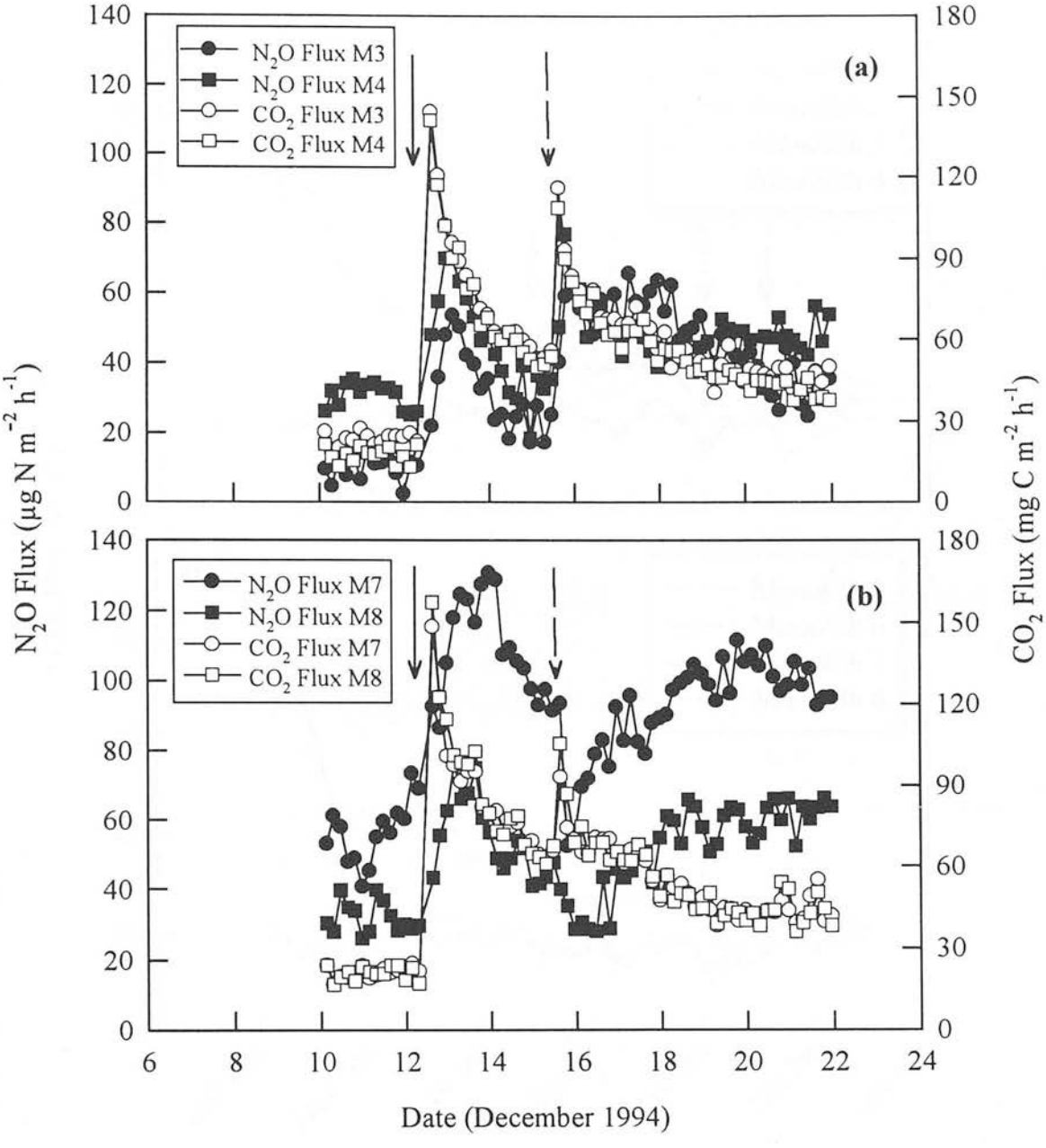


Fig. 5.1. CO_2 and N_2O fluxes from two replicate monoliths of each of (a) the sandy loam and (b) the clay loam. Six measurements per 2-h period were taken. Solid arrow indicates application of grass-clover mixture, broken arrow indicates water application.

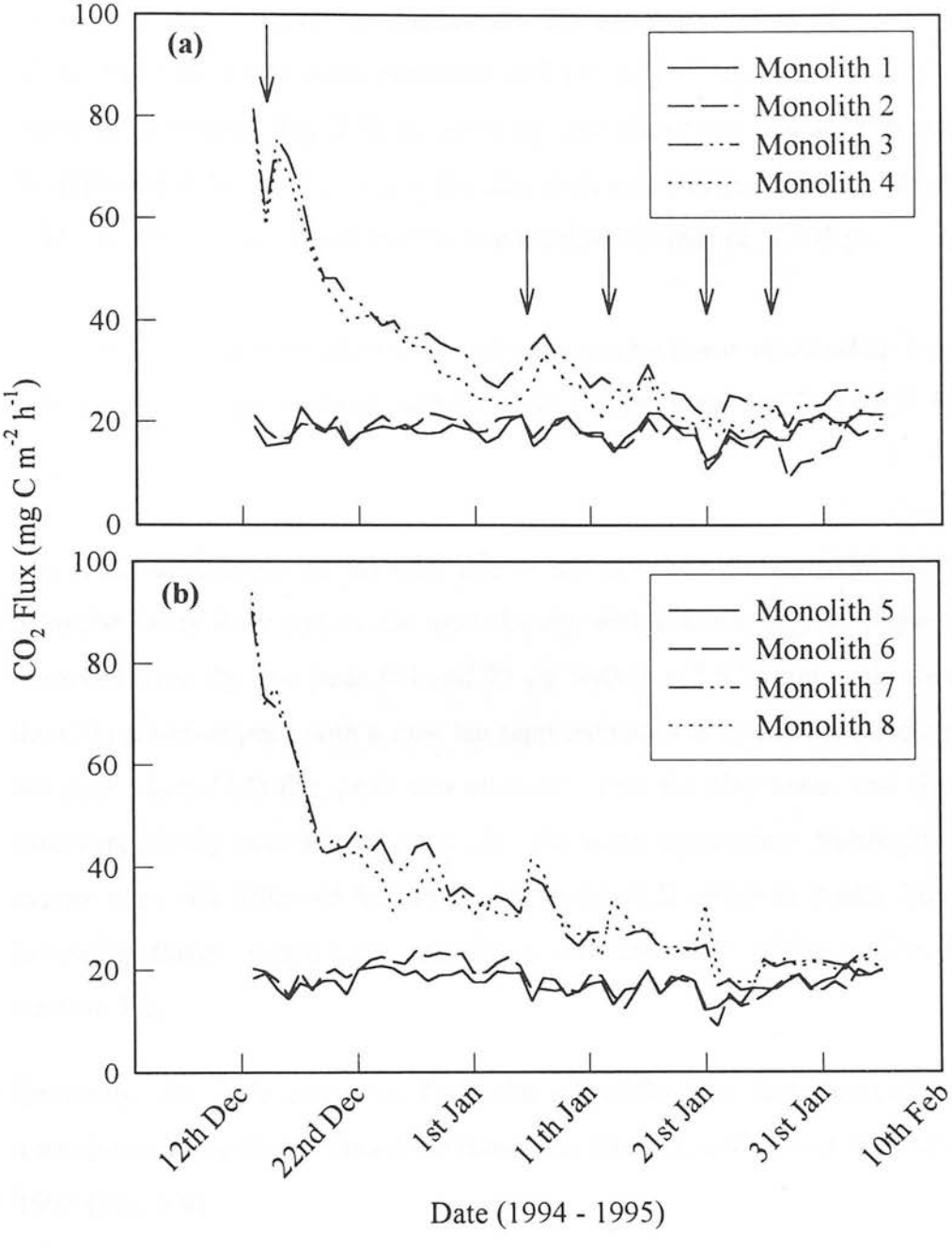


Fig. 5.2. CO_2 fluxes from (a) the sandy loam and (b) the clay loam. Monoliths 2, 3, 7 and 8 received a grass-clover mixture on 12 December 1994; remaining monoliths were left untreated. Arrows indicate water application.

to receive the grass-clover mixture. Large emission peaks, that followed the CO_2 flux peaks with a time lag of about 10 h from the sandy loam and about 14 h from the clay loam, were observed after the application. The maxima reached 54 and 70 μg N_2O-N m^{-2} h^{-1} from the sandy loam monoliths and 125 and 77 μg N_2O-N m^{-2} h^{-1} from the clay loam monoliths (Fig. 5.1). In the sandy loam these high emission rates lasted only for approximately 4 h, whereas in the clay loam soil they persisted for about 12 to 16 h. The fluxes then decreased quickly and levelled off after ca. 1.5 days.

When the time lag was taken into account a strong linear relationship between CO_2 and N_2O fluxes was observed, with r^2 values ranging from 0.487 to 0.851 ($p < 0.001$) (Fig. 5.3).

The water application on the third day of the experiment resulted in the N_2O fluxes from the sandy loam soil to rise immediately, with maxima slightly higher than were observed from the first peak (63 and 77 μg N_2O-N m^{-2} h^{-1}), and again they followed the CO_2 emission peak with a time lag (approximately 6 h) and then declined quickly. No such sharp N_2O flux peak was observed from the clay loam, and the emissions rose very slowly over several days after the water application. Subsequent watering events were not followed by rapidly occurring N_2O emission peaks, but by slowly increasing fluxes, which were associated with the water additions (see Chapter 3, Section 3.1).

Generally, the N_2O emissions from the monoliths that had received the organic amendment were higher than from those that had not, until about the end of January 1995 (Fig. 5.4)

5.1.3. Discussion

The incorporation of shoot material only, rather than a mixture of shoot and root material probably resulted in a more dramatic increase in respiration than would have resulted from, say, experiments where a grass ley is ploughed into the soil. Roots have

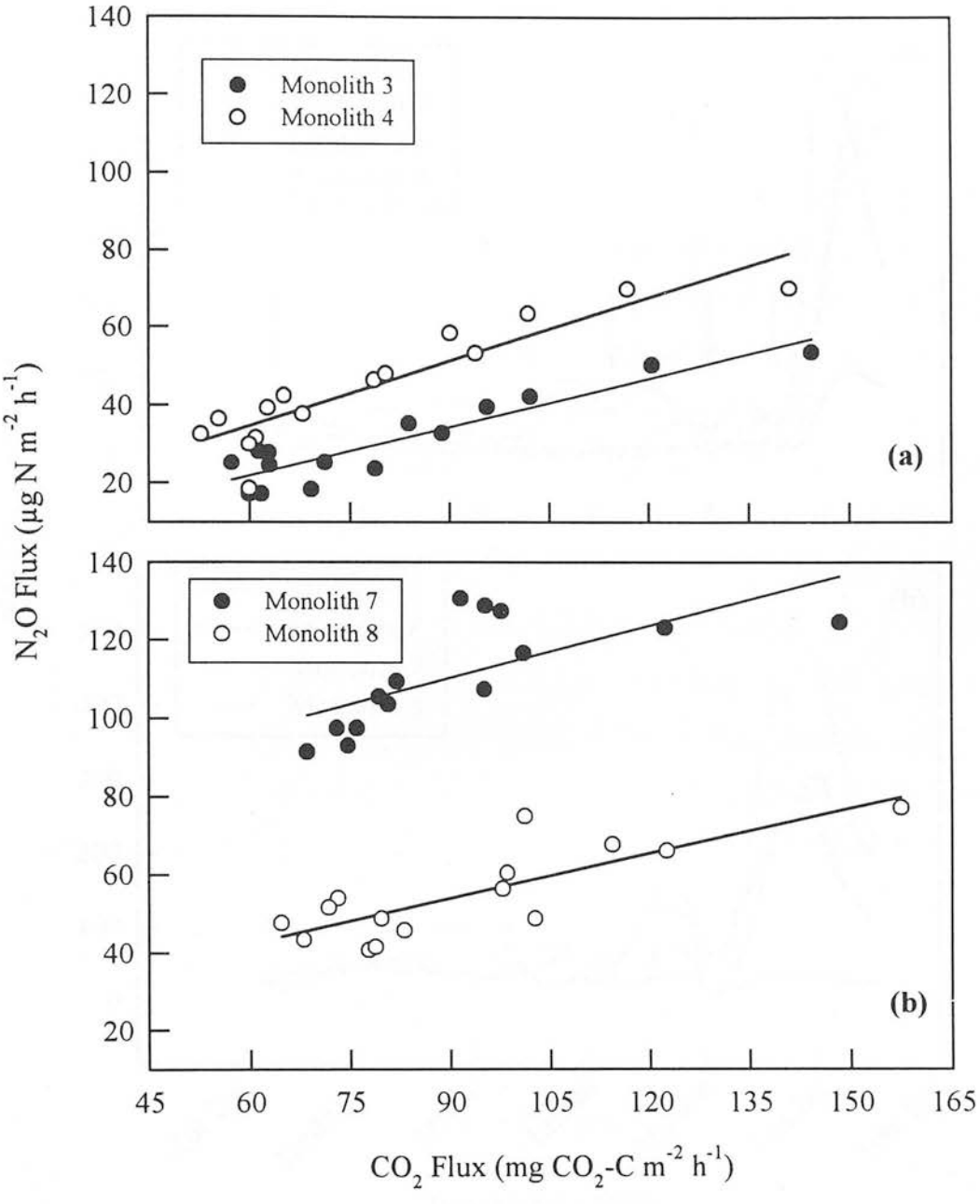


Fig. 5.3. Relationship between CO_2 and N_2O emissions from (a) the sandy loam and (b) the clay loam. Time lag between CO_2 and N_2O fluxes taken into account. Monolith 3: $r^2 = 0.851$, $p < 0.001$; Monolith 4: $r^2 = 0.828$, $p < 0.001$; Monolith 7: $r^2 = 0.487$, $p < 0.01$; Monolith 8: $r^2 = 0.659$, $p < 0.001$.

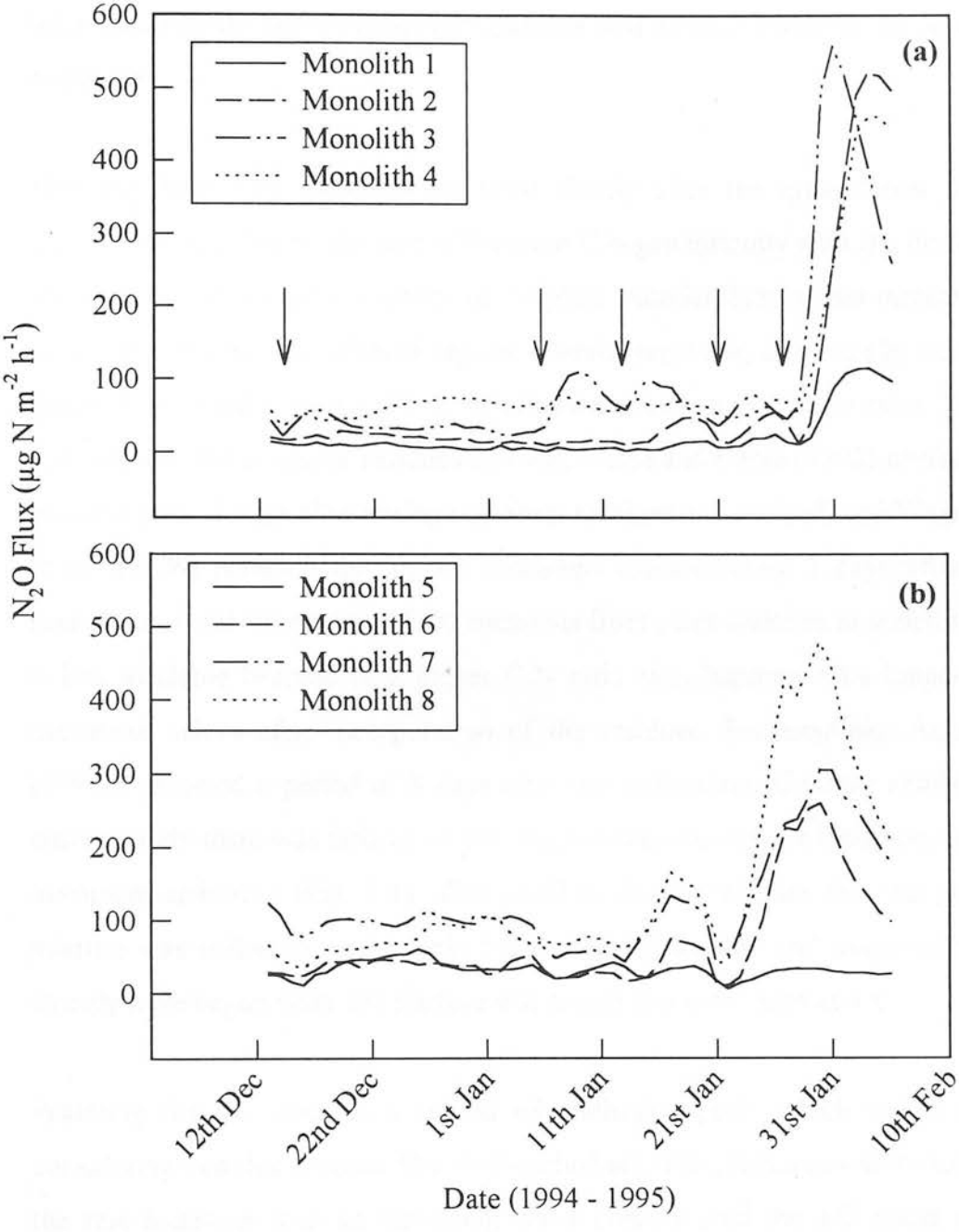


Fig. 5.4. N_2O fluxes from (a) the sandy loam and (b) the clay loam. Monoliths 2, 3, 7 and 8 received a grass-clover mixture on 12 December 1994, remaining monoliths were left untreated. Arrows indicate water application.

a larger C/N ratio than shoots, and therefore decay more slowly and may even immobilise N. Nevertheless, the effect of the incorporation provided useful information on the speed of the N_2O response, and its relationship to the actual rate of respiration.

The very high CO_2 emissions observed shortly after the grass-clover application indicate that rapid mineralisation of the plant C began instantly after the incorporation, which reflects the high availability of the plant material. Similar fast increases in CO_2 fluxes after the incorporation of organic material were also observed by several other researchers. Aulakh *et al.* (1991a, b) observed maximum emission rates 2 to 3 days after incorporating legume residues into soil, Flessa and Beese (1995) measured a first emission peak 3 days after mixing sugarbeet residues into the soil, and Wagner-Riddle *et al.* (1996) detected the highest emissions approximately 2 days after applying sucrose to a soil. In contrast, CO_2 emissions from plant residues in which the carbon is less available because of a higher C:N ratio than legumes take longer to reach maximum values after incorporation of the residues. For example, Aulakh *et al.* (1991b) reported a period of 8 days after the application of wheat residues. In the current study there was little or no time lag between the residue incorporation and the maximum emissions (Fig. 5.1). This could be due to the fact that the grass-clover mixture was collected several days before the application, and mineralisation could already have begun while the mixture was stored in a cold room at 4°C.

Watering the soil initiated a second mineralisation peak, which is not surprising, considering that this process, like all microbial activities, requires water, and generally the rate increases with an increasing water content until the soil starts to become anaerobic (Linn and Doran, 1984; Quemada and Cabrera, 1997).

The observed N_2O emissions after the plant residue application were most likely caused by denitrification. At the time of the organic matter incorporation the soils were neither restricted in NH_4^+ nor NO_3^- due to the previous fertiliser application. Adding fertiliser did not increase the N_2O fluxes, despite the fact that the soil water potentials (-9.5 ±1.7 and -7.0 ±0.6 kPa in the sandy loam and clay loam, respectively)

were at a level expected to favour N_2O emissions from both nitrification and denitrification, thus indicating that even before the fertiliser was applied ample mineral N was present in the soil. It is therefore unlikely that any NH_4^+ resulting from mineralisation would have caused any flux increases via nitrification, and likewise, any NO_3^- formed by nitrification after the mineralisation would not have resulted in higher denitrification rates. The only possible factor that could have caused the flux increase was therefore the increase in available C. Autotrophic nitrification would not be influenced by the amount of available C, but denitrification is a heterotrophic process, which is strongly affected by available carbon (see also Chapter 1, Section 1.3.3.3). However, it cannot be excluded that heterotrophic nitrification also contributed to the N_2O emissions.

At the time of the incorporation of the organic material the soil water potentials were -13.0 ±4.9 and -7.5 ±1.4 kPa (equivalent to 85 and 87% WFPS) in the sandy loam and clay loam, respectively, and the observed time lag between the CO_2 and N_2O fluxes was most probably caused by the time it took for anaerobic zones to form after the increased demand for oxygen due to high mineralisation rates (Parkin, 1987; Leffelaar, 1986; Smith, 1990). Evidence for this was given by Christensen *et al.* (1990), who measured a time lag of 5 days before the denitrification rate increased after the addition of dead *E. coli* cells to soils with a water content of 180 g kg^{-1} dry matter, whereas when the cells were added to an anaerobic soil slurry the denitrification was stimulated within 2 h.

Similar relatively fast responses of N_2O emissions to those observed in this study were also observed by Wagner-Riddle *et al.* (1996) after the application of sucrose and by Loro *et al.* (1997) when liquid cattle manure was applied to soil. However, other studies show a longer time lag between the application of organic matter and maximum denitrification rate and N_2O emissions (Aulakh *et al.*, 1991b; Paul *et al.* 1993; Lovell and Jarvis, 1996), and this can be possibly explained by a slower mineralisation rate restricting the formation of available C, and/or mineral N if this was limiting nitrification and denitrification before the application. Flessa and Beese (1995) and Lovell and Jarvis (1996) attributed N_2O emission peaks observed after

relatively long time periods (17 and 13 days, respectively) following organic matter applications to increasing NO_3^- concentrations in the soil following nitrification. Comfort *et al.* (1990) observed two N_2O emission peaks after injecting liquid dairy manure into the soil, and again the second peak (occurring after 16 days) was explained by increasing NO_3^- concentrations.

Strong relationships between CO_2 and N_2O emissions, like those observed in this study, were also detected by Wagner-Riddle *et al.* (1996), who found a linear relationship between hourly CO_2 and N_2O emissions for 3 days following a sucrose addition, with an r^2 value (0.87) similar to those observed in this work. Other researchers have found a strong association between the respiration and denitrification rates. For example, Breland (1994) observed a positive correlation ($r = 0.68$) between the two from soils kept in a controlled unaltered environment for 132 days, and Aulakh *et al.* (1991a) found that the respiration and denitrification rates followed the same time pattern.

The N_2O emission peak, that followed the initial respiration peak, lasted longer in the clay loam soil than in the sandy loam soil (Fig. 5.1), and this can probably be explained by a slower diffusion rate of oxygen back into the soil aggregates after the respiration rate decreased.

No explanation can be given as to why the water addition after three days following the grass-clover application did not result in N_2O emission peaks from the clay loam similar to those from the sandy loam. It could have been that the soil water content acted as a strong diffusion barrier, but this is unlikely. After approximately 12 to 16 h after watering (the time lag by which the N_2O peak was expected to occur) the water potentials at 20 cm depths were -3.6 and -3.7 kPa in monoliths 7 and 8, respectively, but the potentials at the depths where the organic amendment was located would have been lower. Enough soil pores would therefore have been air-filled to allow fast gas diffusion. Furthermore, a similar water potential was also observed in monolith 3 (-3.7 kPa) at the time of the peak maxima, though monolith 4 was drier (-7.8 kPa). The slow N_2O flux increase after watering observed from the clay loam was most likely

caused by the watering event itself, and not linked to the organic matter application (see also Chapter 3, Section 3.1).

For about 6 to 7 weeks N_2O emissions were higher from monoliths that had received the organic amendment than from those that had not, but because of the inter-monolith variability before and during the experiment it cannot be concluded that the enhancement was caused by the grass-clover application for the whole of this period.

5.2. General Relationships between Respiration and N_2O Fluxes

5.2.1. Methods

For this examination the same data set used for analysing general relationships between soil temperature and N_2O fluxes (see Chapter 4, Section 4.2.1) was taken. Again, analysis was first carried out with the whole data set, and then with a data set containing only flux values at the optimum water content for N_2O emissions to occur. This was done using Spearman rank correlation and linear regression analysis. Some data sets showed a more nonlinear relationship (the N_2O flux increase at higher respiration rates was slower than at lower rates), and for these nonlinear regression analysis, fitting a quadratic line to the data sets, was carried out. Both the whole and the reduced data sets were analysed for each monolith separately and for the mean values of each soil type.

5.2.2. Results

Mineral soils

Fig. 5.5 shows the effect of soil respiration on N_2O fluxes from the sandy loam and clay loam soils (based on the mean values for all 4 replicates). A very similar pattern was observed from both soil types, which was also detected from all single monoliths (data not shown). The data showed very high variability, but a general trend could be

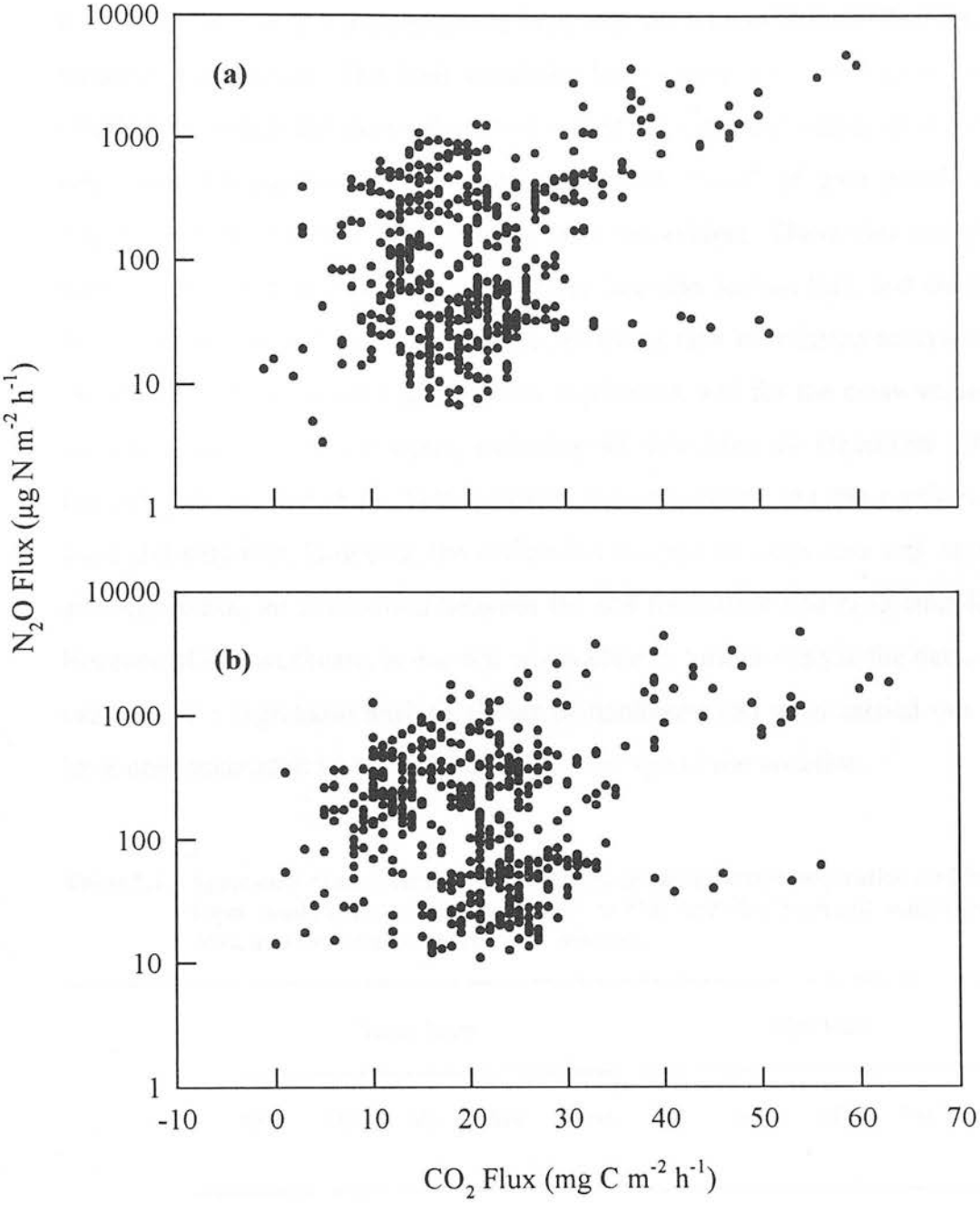


Fig. 5.5. Relationship between soil respiration rates and N_2O fluxes (full data set); (a) sandy loam, (b) clay loam.

detected; fluxes first increased as the soil respiration rate increased, and then levelled off. It has to be pointed out that the levelling off effect was caused by the fact that the N_2O flux data were log-transformed, and that the untransformed data showed the tendency to increase. The high variability led to very low correlation coefficients (Table 5.1), which for monoliths 5 and 6, and for the mean values of the clay loam soil, were not significant. In Fig. 5.5 (a and b), "lines" of data points with high respiration rates but low N_2O emission rates are evident. These data are the results from the grass-clover application experiment (see also Section 5.1), and clearly do not fit in with the other data. Therefore the Spearman rank correlation analysis for those monoliths which received a grass-clover application, and for the mean values of each soil type, was carried out again, excluding all data from 12 December 1994 to 31 January 1995 (Table. 5.2). This improved the correlation, but the r values obtained were still very low. However, the correlation analysis for both data sets showed that, although weak, an association between the soil respiration and N_2O emission exists. Because of this weakness, is was not worthwhile to further analyse the data, since, for example, if a regression analysis (linear or nonlinear) had been carried out, it would have only accounted for an insignificant percentage of the variation.

Table 5.1. Spearman rank correlation coefficients (r) between soil respiration and N_2O fluxes from sandy loam soil monoliths (M1 to M4) and clay loam soil monoliths (M5 to M8), and for mean values of each soil type.

	Sandy loam					Clay loam				
	M1	M2	M3	M4	mean	M5	M6	M7	M8	mean
r value	0.35	0.26	0.23	0.18	0.23	0.08	0.08	0.13	0.14	0.04
significance	hs	hs	hs	hs	hs	ns	ns	s	s	ns
N	479	478	479	479	479	477	479	479	477	479

hs = highly significant ($p < 0.01$), s = significant ($p < 0.05$), ns = not significant ($p \geq 0.05$)
N = number of samples

Table 5.2. Spearman rank correlation coefficients (r) between soil respiration and N_2O fluxes from two sandy loam soil monoliths (M3 and M4) and two clay loam soil monoliths (M7 and M8), and for mean values of each soil type from all 4 replicates. Data from grass-clover application experiment excluded.

	Sandy loam			Clay loam		
	M3	M4	mean of all 4 replicates	M7	M8	mean of all 4 replicates
r value	0.28	0.29	0.33	0.16	0.24	0.13
significance	hs	hs	hs	hs	hs	s
N	428	428	428	428	426	428

hs = highly significant ($p < 0.01$), s = significant ($p < 0.05$), ns = not significant ($p \geq 0.05$)
N = number of samples

Reducing the data set to the flux values at their optimum water-filled pore spaces produced a more obvious trend (Fig. 5.6) and improved the correlation coefficients, which for some monoliths (e.g. monoliths 3 and 7) were relatively high (Table 5.3). The association between soil respiration and N_2O fluxes was now significant for all monoliths and for the mean values of each soil type, and regression analysis was carried out. Both linear and nonlinear (quadratic) regression was used, but only for the mean values of each soil type were significant higher r^2 values obtained from the nonlinear regression. The results are summarised in Table 5.4, and show that for most monoliths less than 50% percent of the variation could be accounted for. Furthermore, over half of the regression analyses were not valid, because they either failed the normality or the homogeneity test, or both.

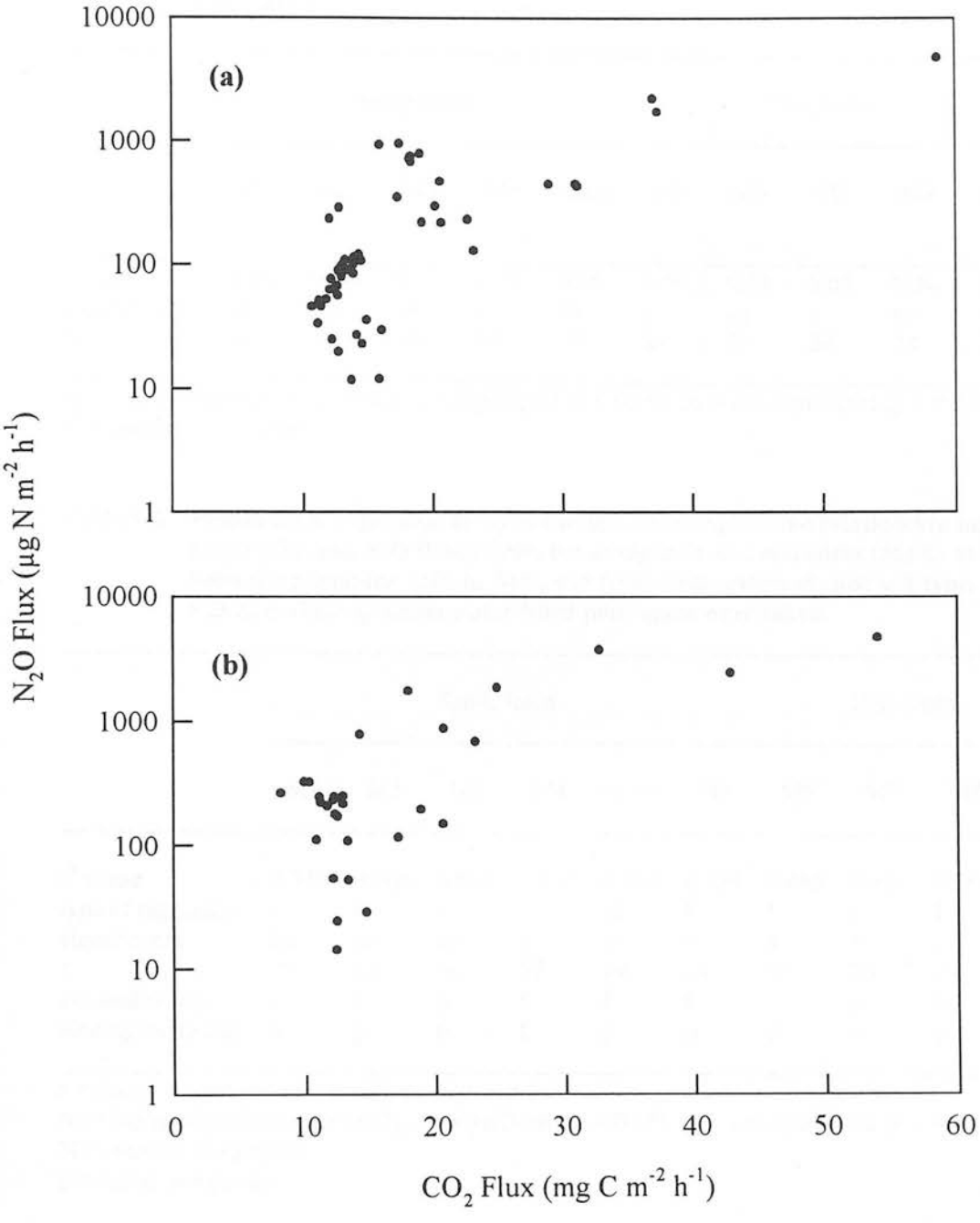


Fig. 5.6. Relationship between soil respiration rate and N_2O fluxes (reduced data set); (a) sandy loam, (b) clay loam.

Table 5.3. Spearman rank correlation coefficients (r) between soil respiration and N_2O fluxes from sandy loam soil monoliths (M1 to M4) and clay loam soil monoliths (M5 to M8), and for mean values of each soil type. Only flux values at their optimum water-filled pore space were taken.

	Sandy loam					Clay loam				
	M1	M2	M3	M4	mean	M5	M6	M7	M8	mean
r value	0.55	0.56	0.73	0.32	0.69	0.56	0.12	0.65	0.36	0.34
significance	hs	hs	hs	s	hs	s	ns	s	ns	ns
N	71	63	36	67	49	24	55	20	24	31

hs = highly significant ($p < 0.01$), s = significant ($p < 0.05$), ns = not significant ($p \geq 0.05$)
N = number of samples

Table 5.4. Results from regression analysis carried out to explain the relationship between soil respiration and N_2O fluxes from the sandy loam soil monoliths (M1 to M4) and clay loam soil monoliths (M5 to M8), and from mean values of each soil type. Only flux values at their optimum water-filled pore space were taken.

	Sandy loam					Clay loam				
	M1	M2	M3	M4	mean	M5	M6	M7	M8	mean
r^2 value	0.312	0.268	0.531	0.151	0.545	0.333	0.085	0.411	0.366	0.479
type of regression	l	l	l	l	nl	l	l	l	l	nl
significance	hs	hs	hs	s	hs	s	s	s	s	hs
N	71	63	36	67	49	24	55	20	24	31
Normality test	f	f	p	f	f	f	f	p	p	p
Homogeneity test	p	p	p	f	p	p	p	p	p	p

l = linear regression, nl = nonlinear regression
hs = highly significant ($p < 0.01$), s = significant ($p < 0.05$), ns = not significant ($p \geq 0.05$)
N = number of samples
f = failed, p = passed

As for the results obtained when examining the relationships between soil temperature and N_2O fluxes (Chapter 4, Section 4.2), these data show that although Spearman rank correlation provided evidence for an association between soil respiration and N_2O fluxes and showed that a general trend of the relationship between the two

variables is identifiable, regression analysis, in this case, is not a good tool to describe the relationship.

Peaty Gley Soil

The data from the peaty gley soil monoliths and their mean values again showed a clustered pattern (Fig. 5.7), though not as strong as that observed from the relationship between soil temperature and N_2O fluxes (see Chapter 4, Section 4.2.2). Due to the clustering, no statistical analysis could be carried out. No reason for the clustering can be given.. However, there seemed to be a similar trend to that observed for the mineral soils; the log-transformed N_2O fluxes appeared to level off at high respiration rates (Fig. 5.7a), but the plot of the untransformed data (Fig. 5.7b), in which the higher flux values were not "compressed", showed that there was an optimum at a respiration rate of around 30 mg C m^{-2} h^{-1}.

The partial data set containing only the flux values at the optimum WFPS for emission showed a clearer relationship between the respiration rate and N_2O fluxes from monolith 12 (Fig. 5.8), but not for the other three or the mean values. A Spearman rank correlation analysis showed that log-transformed N_2O data and CO_2 emissions from monolith 12 were positively correlated ($r = 0.92$; $p < 0.01$).

5.2.3. Discussion

Mineral and peaty gley soils

The results described in this Chapter, like those from the analysis of the relationship between temperature and N_2O fluxes (Chapter 4, Section 4.2), are not surprising, considering that N_2O fluxes from soils are affected by an interaction of many variables, which fluctuate over time. Reducing the data set to those points for which the WFPS was at an optimum for N_2O fluxes took account of the effect of soil water content, and a more clearer relationship between soil respiration and N_2O fluxes was observed. However, the effect of other variables was still noticeable. Despite this some general conclusions can be drawn.

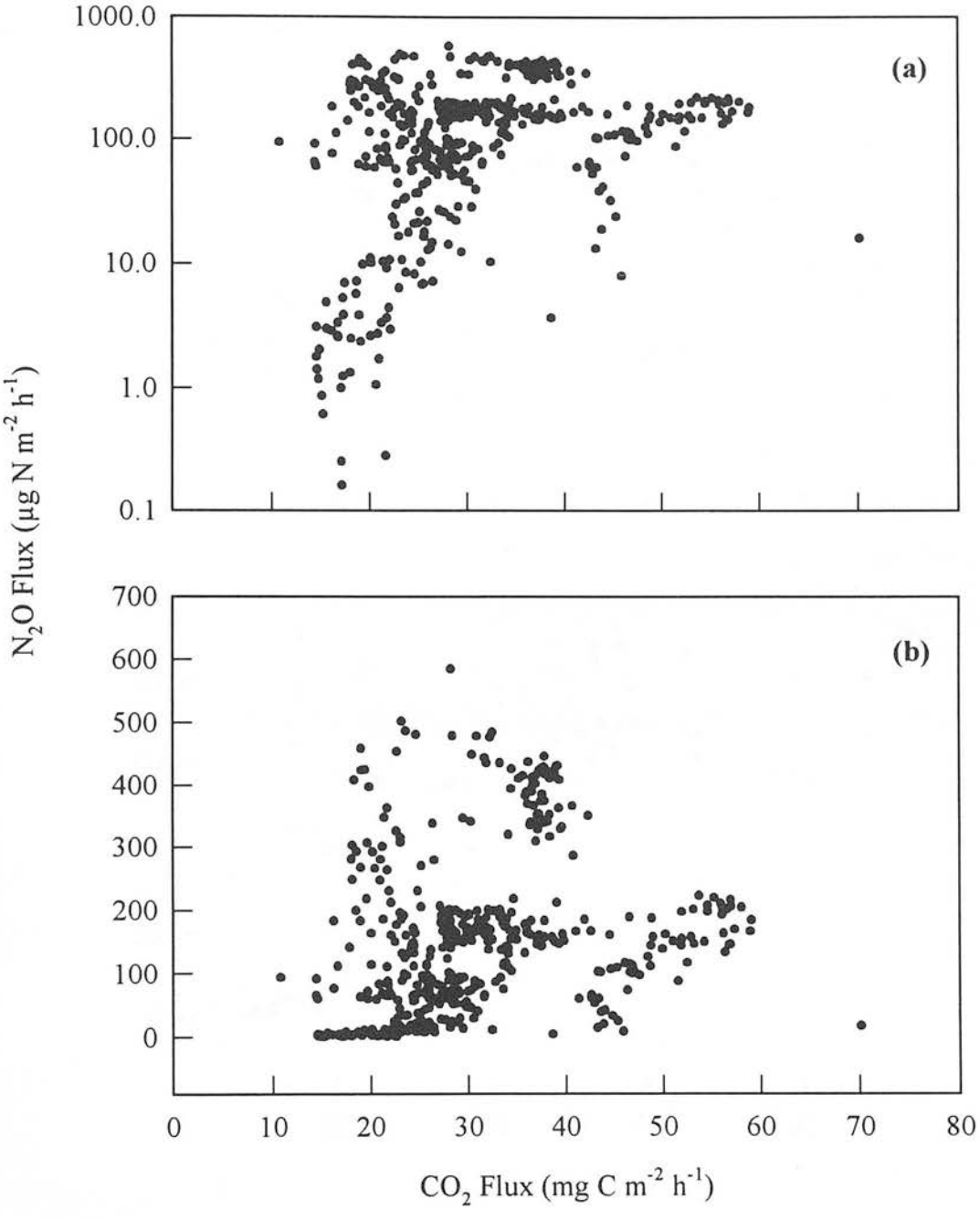


Fig. 5.7. Relationship between soil respiration rate and N_2O fluxes from the peaty gley (full data set). Note the different scales of the y-axis: (a) log-transformed data, (b) untransformed data.

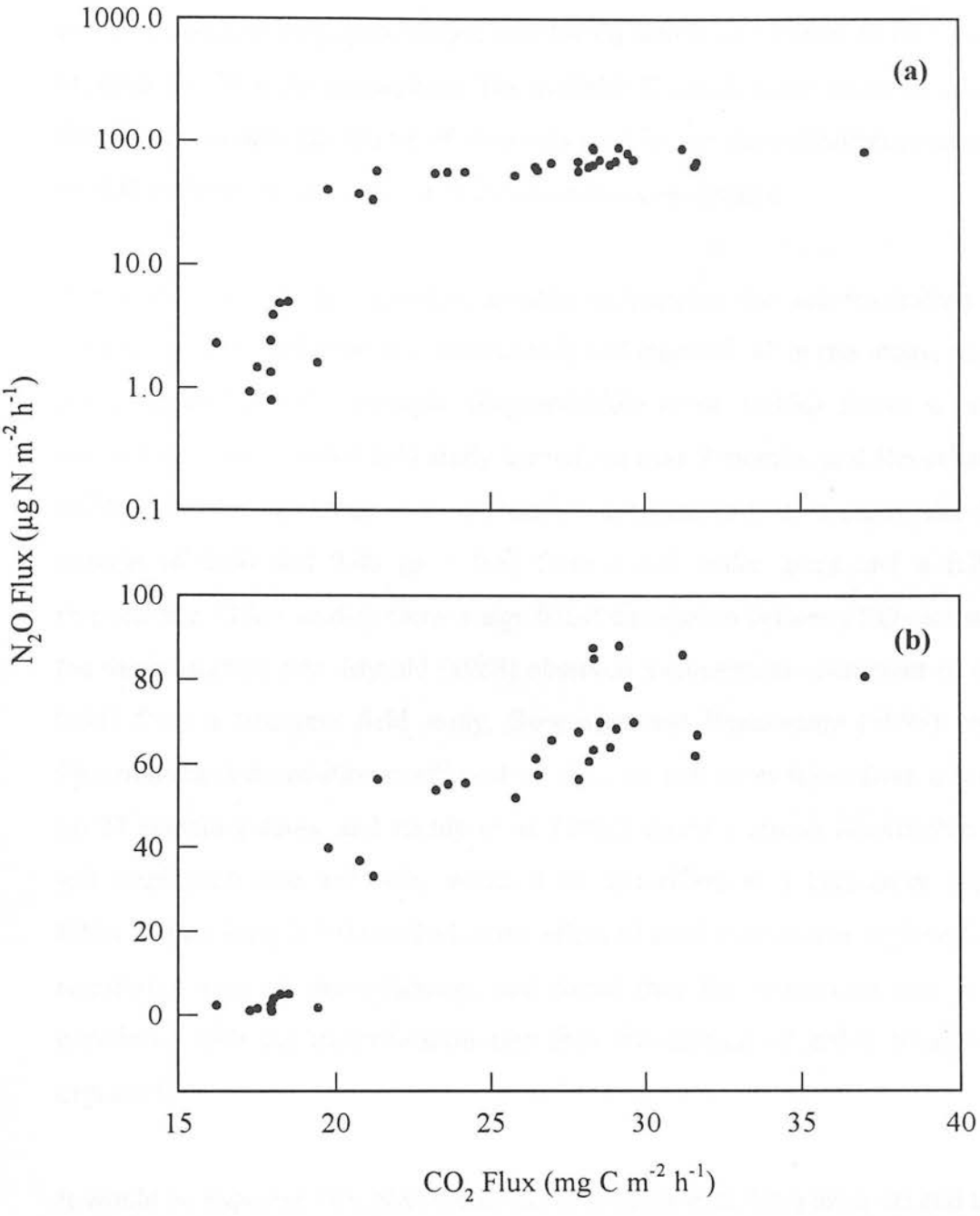


Fig. 5.8. Relationship between soil respiration rate and N_2O fluxes from Monolith 12 (peaty gley) (full data set). Note the different scales of the y-axis: (a) log-transformed data, (b) untransformed data.

Soil aerobic respiration is an important factor influencing N_2O fluxes from soils. It is responsible for the creation or enlargement of anaerobic zones in which denitrification can take place, through providing a sink for O_2 which is too great to be overcome by O_2 diffusion from the atmosphere. The available C which is the essential substrate for this process is also the source of electrons used in the denitrification process leading to N_2O emission which goes on in the anaerobic sites created.

This is reflected in the significant association between the soil respiration rate and N_2O fluxes observed from the mineral soils and monolith 12 in this study, and also by other researchers. For example Wagner-Riddle *et al.* (1996) found a correlation coefficient of 0.49 from a field study carried out over 7 months, and Beauchamp *et al.* (1996) reported Spearman rank correlation coefficients from a study also lasting 7 months of 0.60 and 0.40 ($p < 0.5$) from a soil under grass and a fallow soil, respectively. Other studies show a significant correlation between CO_2 emissions and the denitrification rate. Myrold (1988) observed a correlation coefficient of 0.36 ($p < 0.01$) from a two-year field study, Bergstrom and Beauchamp (1993) reported a Spearman rank correlation coefficient of 0.42 for soil cores taken from a barley field on 27 sampling dates, and Reddy *et al.* (1982) found a strong relationship between soil respiration rate and NO_3^- removal by denitrifiers in a laboratory experiment. Elliot and de Jong (1993) looked at the effect of total and soluble organic C, and the respiration rate on denitrification, and found that the respiration rate was better correlated with the denitrification rate than the amount of either total or soluble organic C.

It would be expected that N_2O emissions (untransformed data) level off and ultimately decrease, with increasing respiration rates, because:

a) The denitrifier population cannot grow indefinitely, and once a "saturation concentration" of available C is reached, any further increases will have no effect on the denitrification rate. Furthermore, as more C becomes available in a soil the N_2O/N_2 ratio is shifted towards N_2 (see Chapter 1, Section 1.3.3.3), and this could lead to an absolute decrease in N_2O emissions, even if total denitrification increases.

b) Anaerobic zones can also not expand indefinitely, and generally the largest relative increase will be observed at low respiration rates, when only a small fraction of the soil is initially anaerobic. At higher respiration rates a higher fraction of the soil will be anaerobic and the relative increase will be smaller (Smith, 1997), thus leading to a reduction in the denitrification rate increase as the soil respiration increases. Also, at very low oxygen concentrations lower N_2O/N_2 ratios are observed than at higher concentrations (see Chapter 1, Section 1.3.3.1), and again this could lead to decreasing N_2O fluxes.

The reason why the data for the mineral soils of this study did not tend to level off was most likely caused by the range of respiration rates measured, which were probably never high enough to bring into effect the mechanisms discussed in the previous paragraph. In contrast, the peaty gley soil showed an optimum respiration rate for N_2O flux, but this may have been an artefact caused by the clustering of the data, and no firm conclusion can be drawn.

5.3. Combined Effects of Respiration and Soil Water Content

5.3.1. Methods

To study the combined effects of soil water content and respiration on N_2O fluxes the whole data set was used, and the effects were visualised using the 3-D mesh plot function from SigmaPlot (Jandel Scientific, 1994b) (see also Chapter 4, Section 4.3.1).

When two (or more) variables are used to predict another variable the driving variables should ideally be independent from each other. The respiration rate of a soil depends on the soil water content (Linn and Doran, 1984, Quemada and Cabrera, 1997), and it could be argued that at high water contents the respiration rate would be high, and, due to multicolinearity, this would inevitably lead to high N_2O emissions. However, the soil respiration rate depends also on other factors (e.g. temperature), and no simple relationship between soil water content and respiration would exist for

a data set obtained over longer time periods, thus diminishing the effect on multicolinearity.

5.3.2. Results

Fig. 5.7 shows the combined effects of soil water content and respiration rate on N_2O fluxes from all three soil types (values are both daily means and means from the 4 replicates of each soil type). The mineral soils exhibited a very similar pattern, and the results are very like those observed from the combined effects of soil water content and soil temperature on N_2O fluxes (see Chapter 4, Section 4.3). It can be clearly seen that both the soil water content and the respiration rate affect the N_2O fluxes strongly, and that they also interact. The highest N_2O emissions were observed when the soil water content was around the optimum value for N_2O emissions to occur and when high respiration rates were measured. Respiration had the strongest effect at the optimum water-filled pores space for N_2O emissions to occur, and, likewise, at high respiration rate the soil water content had the strongest effect.

No clear trends could be detected from the peaty gley soil, and again this was caused by the clustering of the data.

5.3.3. Discussion

The strong interacting effect of both soil water content and respiration rate is not surprising, considering that both the soil water content and the respiration rate have a strong influence on the soil aeration. The occurrence of large anaerobic zones in a soil would be expected at high respiration rates and high water contents, because (a) the soil respiration would consume a lot of O_2, and (b) the high water content would restrict the diffusion of atmospheric O_2 back into the soil. However, the combination of the two factors will only enhance N_2O emissions up to a certain soil water content; above that the diffusion of N_2O out of the soil will be hindered, and further reduction to N_2 will take place (see Chapter 1, Section 1.3.3.1).

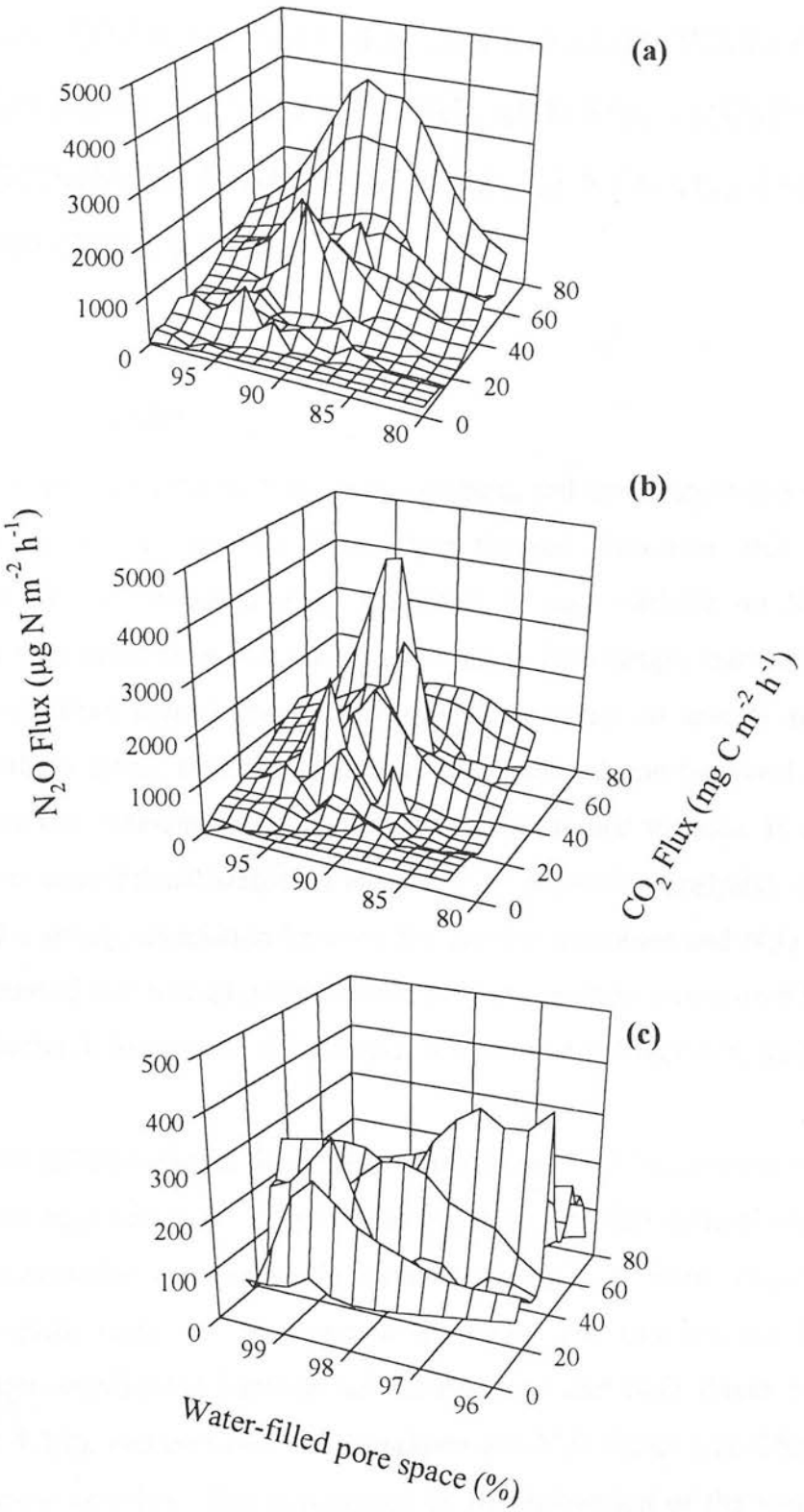


Fig. 5.9. 3-D mesh plots of relationships between N_2O fluxes, water-filled pore space and soil respiration rate. (a) sandy loam, (b) clay loam, (c) peaty gley. Note the differences in scales for N_2O flux and WFPS in (c).

6. RESPONSE OF N_2O FLUXES TO SOIL WATER CONTENT, TEMPERATURE AND SOIL RESPIRATION: BOUNDARY LINE ANALYSIS, GENERAL DISCUSSION AND CONCLUSIONS

6.1. Introduction

All three variables examined, soil water content, soil temperature and respiration, had very strong effects on N_2O fluxes from the soil. However, this could only be satisfactorily demonstrated when the effect of each variable on N_2O fluxes was studied over short time periods of a few days, for example between two watering events or when diurnal temperature cycling occurred on several successive days. During these times, variables other than the examined one remained fairly constant, and were not "contaminating" the effects of the studied variable. It was possible to carry out conventional statistical analysis (e.g. regression analysis), and this always showed a strong association between the variable examined and N_2O emissions, and demonstrated that a large proportion of the flux variation was caused by this variable (see Chapter 3, Section 3.1.2.1; Chapter 4, Section 4.1; Chapter 5, Section 5.1).

When the effects between the driving variables and N_2O fluxes were examined over a period of approximately 1.5 years, in order to establish general relationships, the strong association between single variables on N_2O emissions, observed over short time periods, could not be detected any more. For example the Spearman rank correlation coefficients between soil temperature and N_2O fluxes (see Chapter 4, Section 4.2.2), and between soil respiration and N_2O fluxes (see Chapter 5, Section 5.2.2) were very low. This was caused by the interaction of the variables and their high temporal fluctuation. An attempt was made to take account of some of the interactions by reducing the data set to N_2O flux values at the optimum water-filled pore space for emission, and by using the 3-D mesh plot function of Sigma Plot. The reduced data sets usually showed improved Spearman rank correlation coefficients,

but when regression analyses were carried out these were often invalid, due to the violation of the necessary assumptions (see Chapter 2, Section 2.3.1). The 3-D mesh plots are a useful tool, but they can only show trends. Furthermore, the strong clustering observed in the data from the peaty gley soil made it impossible to use any statistic for the whole data sets, or for most of the reduced sets.

From all this it became apparent that in this study conventional statistical analysis could not be used to establish general relationships between driving variables and N_2O fluxes from soils, and that alternative methods had to be applied. One such method is "boundary line analysis" and this, as is discussed below, has been found to be a very useful tool.

6.2. Boundary Line Analysis

6.2.1. The concept of boundary line analysis

The concept of boundary line analysis was developed by Webb (1971, 1972). It makes use of the fact that biological material has an upper limit of development or response. For example an apple can only grow to a certain size, and a microbial population cannot grow indefinitely. Therefore in any cause-and-effect relationship between two variables there is a maximum response for any level of the causal factor in a given situation. If enough data can be obtained, for which other interacting variables are not limiting the response of the dependent variable, an edge may appear on an array of data. The data points that make up this edge can be used for regression analysis to obtain a line of best performance, called the boundary line. Deviations from this line only occur due to measurement errors and to variability of the biological material. The remaining data all lie underneath the boundary line, and represent situations for which other factors limit the response of the examined variable. The boundary line will only

be visible if the limits of response in a given situation are reached, and will not appear at all if there is no cause-and-effect relationship between the associated variables.

For modelling purposes this concept can be used to obtain equations for the maximum response of each variable, which will be incorporated in the model. For example, Livingston and Black (1987) used boundary line analysis for modelling stomatal conductance, and Elliot and de Jong (1993) and Bergstrom and Beauchamp (1993) used the concept to model denitrification. All these authors found that their models worked reasonably well. A very similar approach was used by Parton *et al.* (1996) to model N_2 and N_2O production from nitrification and denitrification. To obtain the functions for the response of denitrification to NO_3^- concentration and soil respiration, they only used the maximum denitrification rates for a given NO_3^- level and soil respiration rate.

Defining the boundary line

The selection of data points used to obtain the equation of the boundary line may seem somewhat arbitrary. However, Webb (1972) suggested a method of selecting the best points from the mass of data, which can then be used for regression analysis, and this method is demonstrated in this Section with the soil temperature data from the sandy loam soil as an example.

First, all the log-transformed N_2O data from the whole data set (20 October 1993 - 5 April 1995) were sorted by the soil temperature at 5 cm depth and then put into classes of 1°C. For example, all data from 8.50°C to 9.49°C were put into one class, and the class was named the 9°C class. For each class the logarithm of the maximum N_2O emission rate was taken and put into a table (Table 6.1). From the table it is apparent that the log values for the N_2O emissions increased fairly steadily with increasing soil temperatures, up to 19°C. However, it is also evident that some data pairs (indicated by *) do not fit into this trend. For instance the value at 11°C is lower than at 10°C, whereas in fact it should be higher. It was assumed that the possible maximum response was not reached due to the limitation of other factors, and the data pair was rejected. The highest flux was observed at 22°C, but the emission

increase from 19 to 22°C was negligible. There were too few data points above 19°C to show adequately whether the boundary line had a genuine point of inflexion, so in this analysis the last 3 data pairs were rejected. All the remaining pairs were then used for regression analysis. Although it was not necessary in this example, any obvious outliers should also be rejected when carrying out this procedure.

Table 6.1. Maximum log-transformed N_2O fluxes from the sandy loam soil (mean of all 4 replicates) observed in each temperature class (soil temperature at 5 cm depth). Data taken for regression analysis to define boundary line.

Temperature	log(N_2O)
8	2.45
9	2.68
10	2.71
11	2.61*
12	2.95
13	2.98
14	2.96*
15	2.90*
16	3.05
17	3.26
18	3.45
19	3.57
20	3.45*
21	3.50*
22	3.60*

* rejected data pairs

The data were analysed in this way for each single monolith and for mean values of each soil type.

6.2.2. Results

6.2.2.1 Mineral soils

Effect of water-filled pore space on N_2O fluxes

The effect of water-filled pore space (WFPS) on the mean log-transformed N_2O fluxes from the mineral soils is shown in Fig. 6.1. The relationship was described by a quadratic equation, and the data clearly showed that there was an optimum WFPS for maximum N_2O emissions to occur. This optimum was around 90% (equivalent to a soil water potential of -4.2 kPa) for the sandy loam and around 92% (equivalent to -2.5 kPa) for the clay loam. When the data from each monolith were analysed separately the range for the sandy loam was 86 to 96%, and for the clay loam 88 to 96%. A t-test showed no significant difference between the two means. The r^2 values from the regression analysis carried out to obtain the boundary line for the mean values from the sandy loam and clay loam were 0.96 and 0.99 ($p < 0.0001$), respectively.

Effect of soil temperature on N_2O fluxes

The log-transformed N_2O flux data showed a linear response to the soil temperature at 5 cm depth (see Fig. 6.2 as an example), and the measured Q_{10} values for the mean values of the sandy loam and clay loam were 7.5 and 9.4, respectively. The Q_{10}'s from the single monoliths were 5.2, 7.3, 4.5 and 3.7 from the sandy loam and 5.9, 6.3, 7.5 and 6.4 from the clay loam. It is obvious that when these values are averaged for each soil type, the mean value obtained differs from the one obtained by the boundary line analysis carried out for the mean values of the 4 replicates from each soil type. This can be explained by the fact that, for each replicate, different data pairs were taken or rejected to define the boundary line, and that the highest flux observed in each temperature class might not be the one that made up the mean value for that class. Therefore, no statistical test was carried out to compare the means from the two soil types. Again, high r^2 values (0.95 and 0.96 ($p < 0.0001$) for the means of the sandy loam and clay loam, respectively) from the regression analysis were observed.

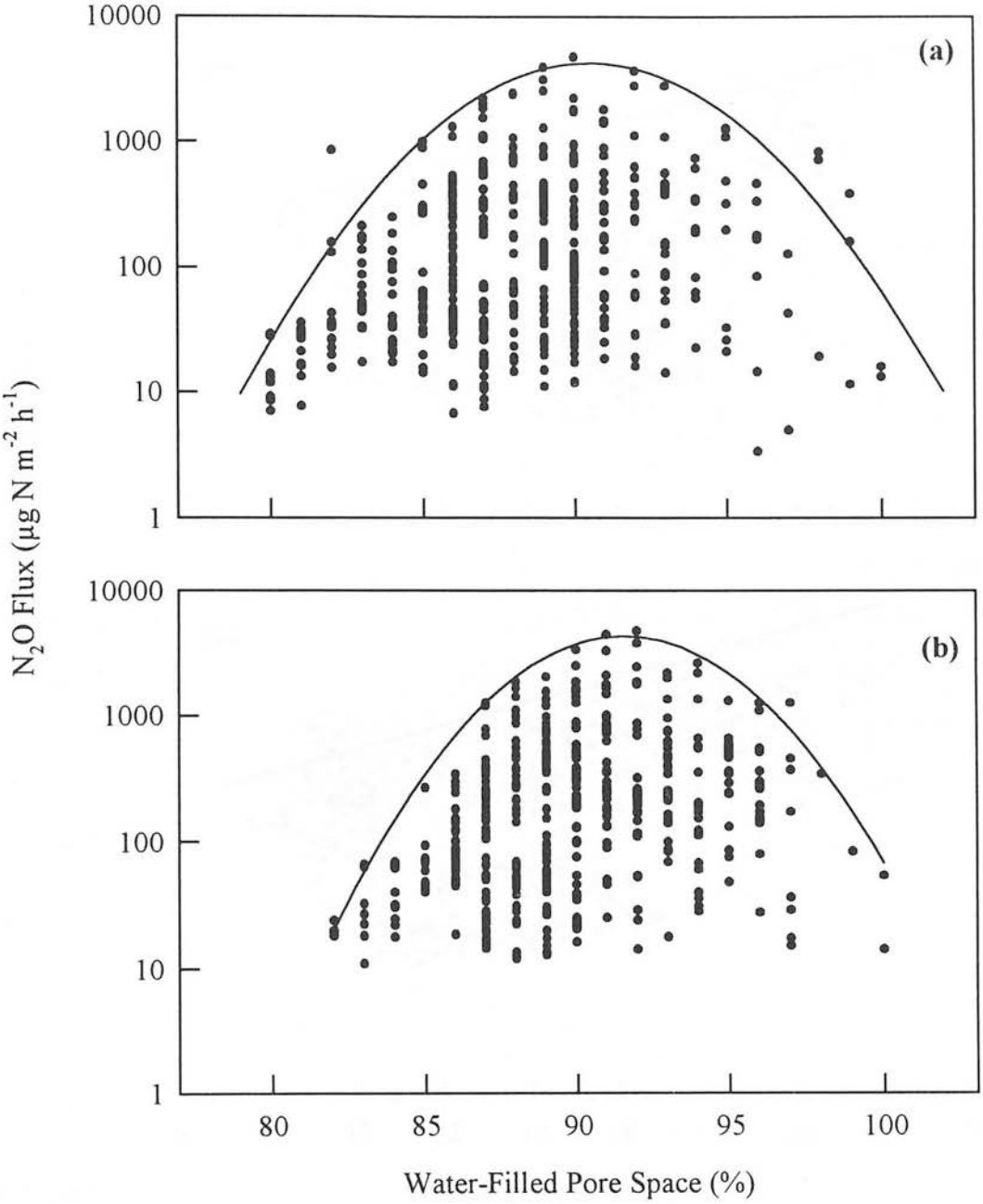


Fig. 6.1. Scattergram and boundary line for N_2O fluxes plotted versus water-filled pore space for (a) sandy loam and (b) clay loam.

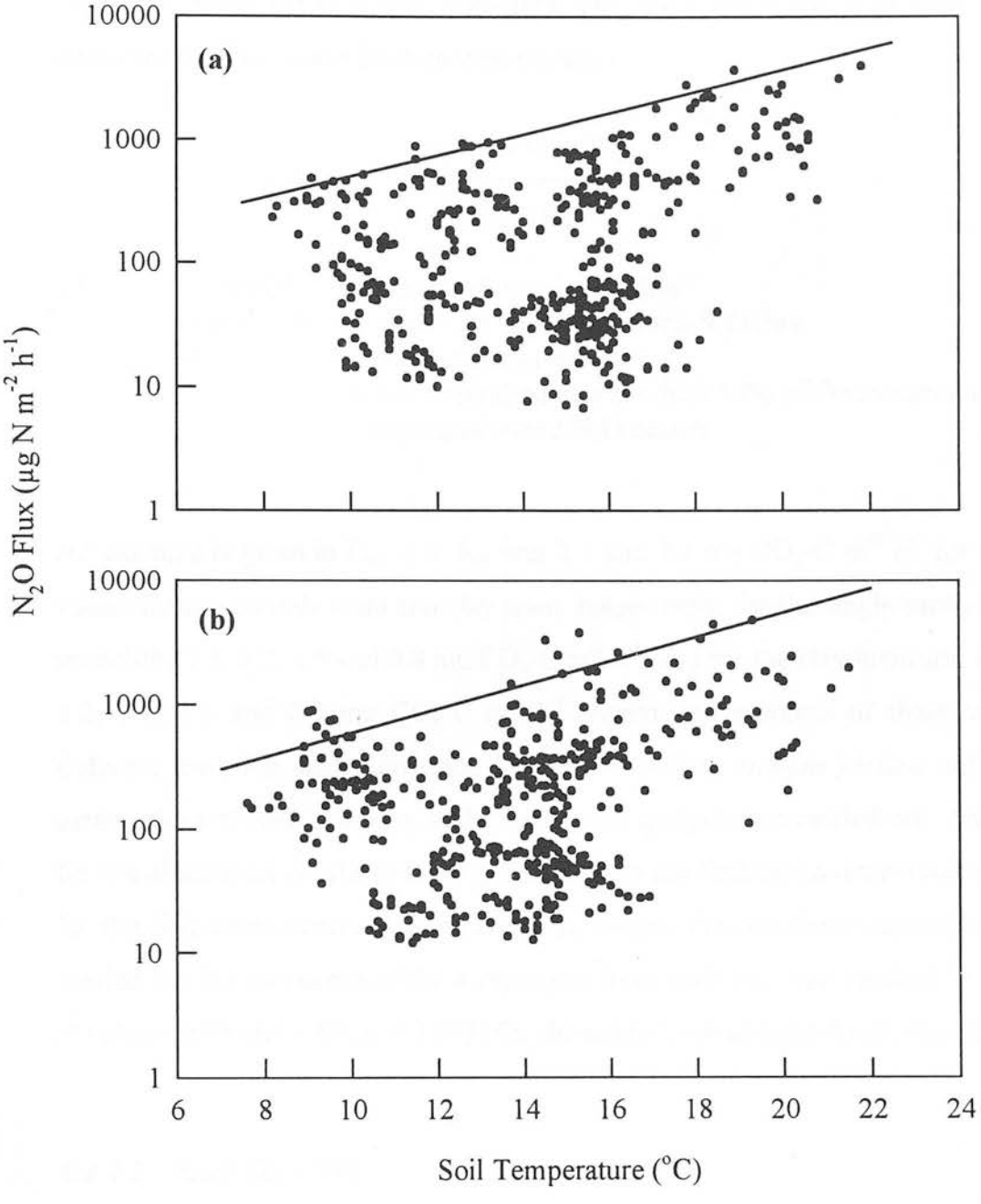


Fig. 6.2. Scattergram and boundary line for N_2O fluxes plotted versus soil temperature at 5 cm depth for (a) sandy loam and (b) clay loam.

Effect of soil respiration on N_2O fluxes

The relationship between soil respiration and log-transformed N_2O data was best described by a Michaelis-Menten type equation:

$$\log(N_2O) = \frac{Max(N_2O) \times R_s}{K_m + R_s}$$

where: $\log(N_2O)$ = log-transformed N_2O flux
$Max(N_2O)$ = maximum log-transformed N_2O flux
R_s = soil respiration rate
K_m = soil respiration rate at which 50% of the maximum log-transformed N_2O occurs.

An example is given in Fig. 6.3. K_m was 2.1 and 3.1 mg CO_2-C m^{-2} h^{-1} for the mean values from the sandy loam and clay loam, respectively, for the single sandy loam soil monoliths 1.5, 0.7, 1.9 and 0.8 mg CO_2-C m^{-2} h^{-1}, and for the clay loam soil monoliths 1.2, 3.6, 1.6 and 0.9 mg CO_2-C m^{-2} h^{-1}. Again, the averages of these values are different from the values obtained from the boundary analysis carried out with the mean values of each soil type, and no statistical analysis was carried out. The reasons for the differences are the same as given above in the Section on temperature response for the differences observed in the mean Q_{10} values. The non-linear regression analysis carried out for the means of the 4 replicates from each soil type resulted in very high r^2 values (0.95 and 0.89 ($p < 0.001$) for the sandy loam and clay loam, respectively).

6.2.2.2. Peaty Gley Soil

No boundary lines could be defined for the relationships between the three examined variables, WFPS, soil temperature and respiration, and N_2O fluxes (untransformed and log-transformed values) from the peaty gley soil. For example, Fig. 6.4 shows the scattergram of the WFPS plotted against log-transformed N_2O fluxes and untransformed fluxes. If a boundary line was to be defined for the log-transformed data it would be more or less just a horizontal line; for the untransformed data a

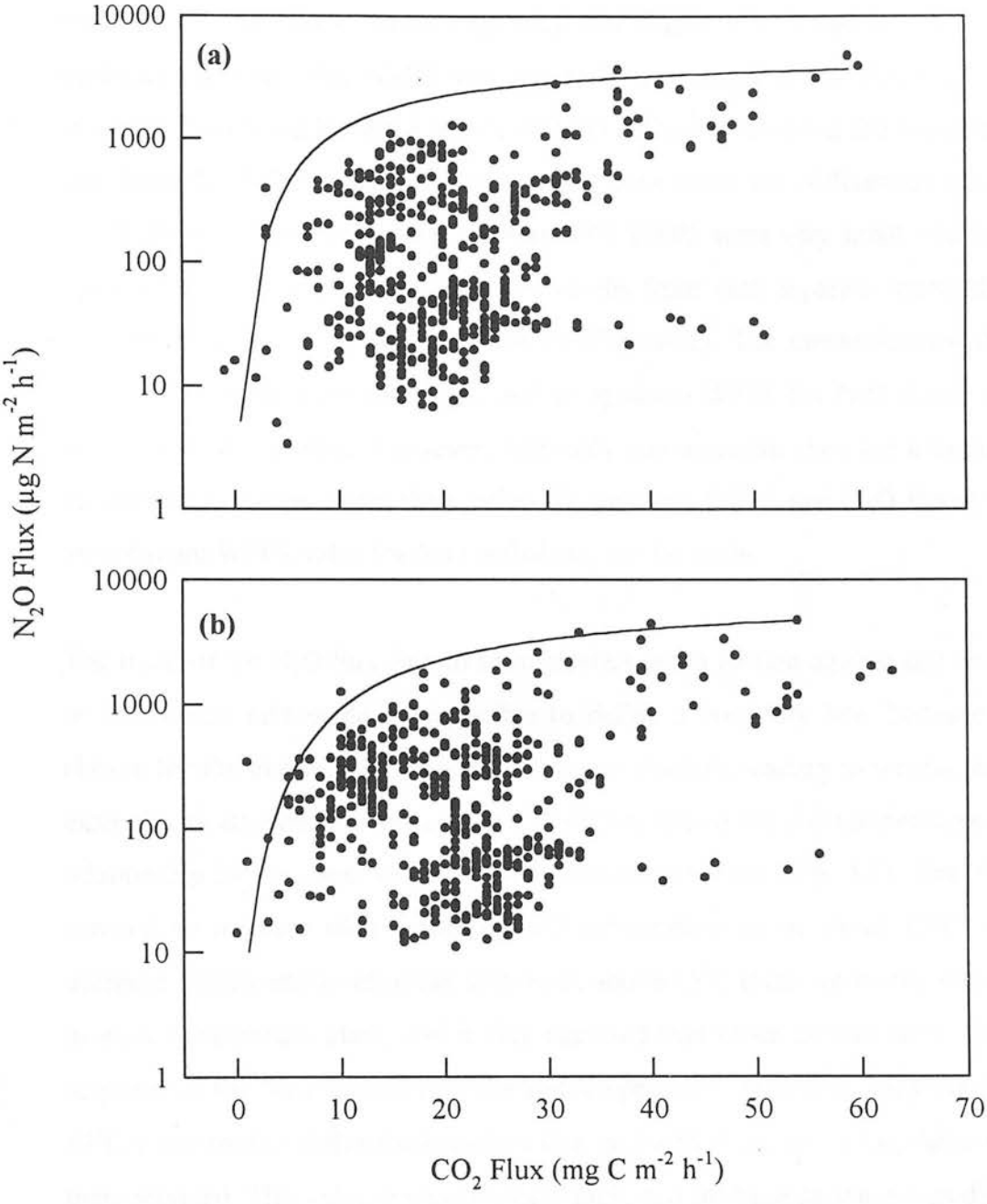


Fig. 6.3. Scattergram and boundary line for N_2O fluxes plotted versus soil respiration rate for (a) sandy loam and (b) clay loam.

sharp increase of N_2O emissions from 95 to 96% WFPS was observed. Between 96 and 99% WFPS the fluxes still increased, and there seemed to be an optimum value at 99% WFPS. At 100% WFPS only very low fluxes were observed. The apparent optimum value of 99% WFPS was caused by one single point; this was an outlier resulting from a sudden large release of N_2O caused by draining the monolith after it had been flooded for 3 days. Without this data point the differences between the maximum emissions in the range of 96 to 99% WFPS were very small, and no distinct optimum value could be identified. The results from each separate monolith showed very similar patterns, except monolith 10 (Fig. 6.4c). The untransformed data from monolith 10 show a boundary line, and an optimum WFPS for N_2O fluxes at around 98% could be identified. However, with only one monolith showing a boundary line no general statement about the relationship between WFPS and N_2O fluxes, or about an optimum WFPS value for N_2O emissions, can be made.

The trend of the N_2O flux data to form clusters when plotted against soil temperature or respiration rate made it impossible to define a boundary line, because the data chosen for the line would come from different clusters, leading to wrong results. For example, an attempt was made to fit a boundary line to the soil temperature-N_2O flux relationship for the mean values of all 4 monoliths (see also Fig. 4.5). The N_2O fluxes showed an increase with increasing soil temperature up to about 13°C, then they declined slightly and levelled off. However, above 15°C there were only very few data in each temperature class, and it was assumed that other factors were limiting the response of the N_2O emissions to the soil temperature. Therefore, only the data up to 13°C were used to define the boundary line, and with these data a Q_{10} value of 49 was then obtained. This value is unrealistically high, and the boundary line was dismissed.

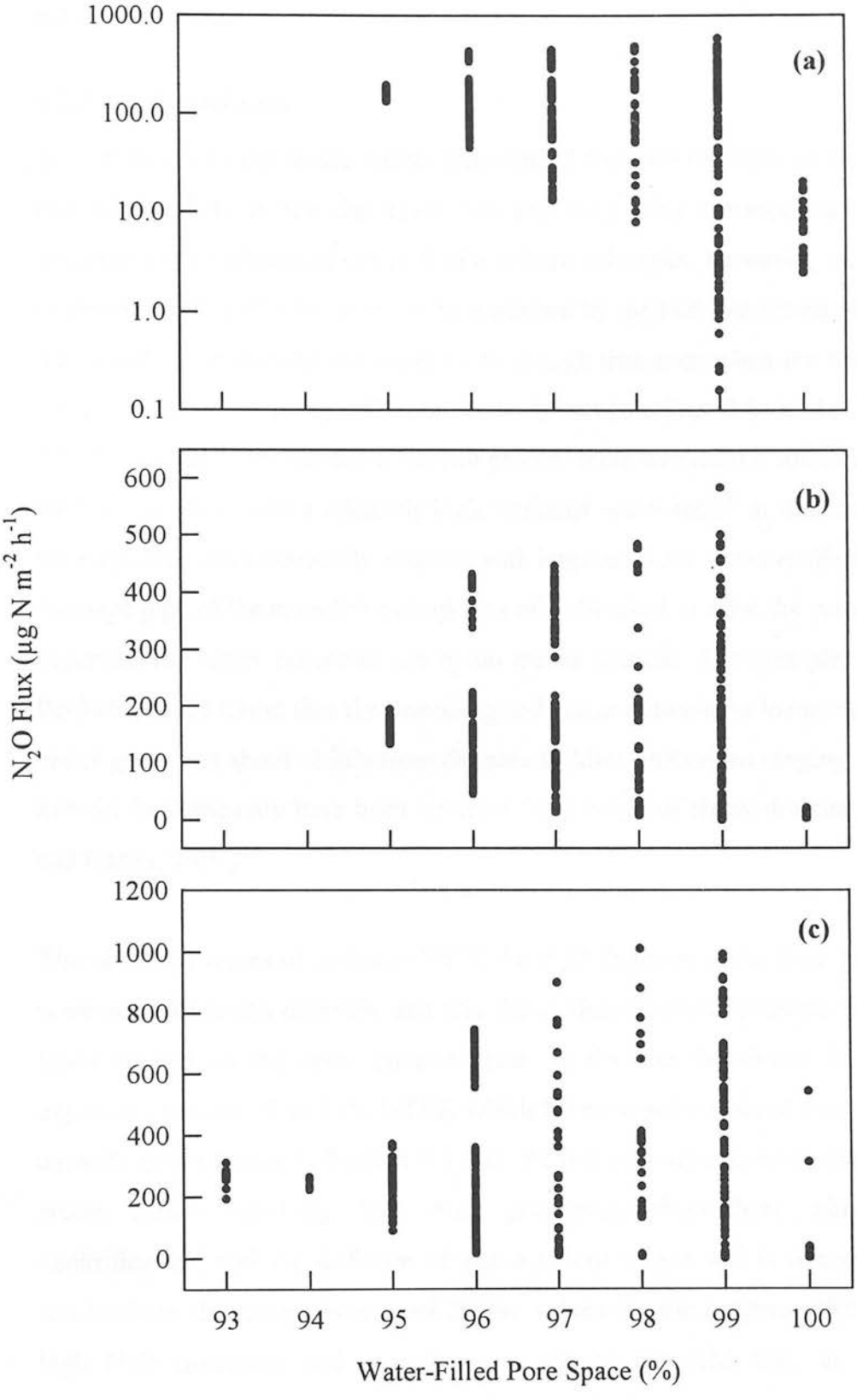


Fig. 6.4. Scattergram and boundary line for N_2O fluxes plotted versus water-filled pore space for the peaty gley soil; (a) mean values - log-transformed, (b) mean values - untransformed, (c) Monolith 10 (note the differences in scales for N_2O flux in all three graphs).

6.2.3. Discussion

6.2.3.1. Mineral soils

The of WFPS values in the fallow soils ranged from 80 to 100% in the sandy loam and 82 to 100% in the clay loam (see Fig. 6.1). This corresponds to soil water potential values of around -24 to 0 kPa in both soil types. However, most values fell in the range -10 to 0 kPa. This can be explained by the fact that (a) no plants grew on the monoliths to take up the water (note though that even when the monoliths were planted with reygrass they still remained fairly wet (see Figs. 3.11 and 3.12 in Section 3.2.2)), (b) due to the depths of the soil profiles there was no soil suction below about 60 cm (thus there was a relatively high "artificial water table" at that depth), and (c) the monoliths were frequently irrigated with large amounts of water. Furthermore, the drainage pipe of the monolith casings was often blocked to raise the water tables. The observed soil water potentials are by no means unusual. For example, Webster and Beckett (1972) found that the prevailing soil water potential in loams and clay loams under grass was about -2 kPa from October to May, and values ranging from -3 to -8 kPa for field capacity have been reported for a range of freely draining soils (Reeve and Carter, 1991).

The observed values of optimum WFPS for N_2O fluxes to occur from both soil types were not statistically different, and this shows that the N_2O emissions from both soil types depend on the same aeration status of the soil. Maximum N_2O fluxes are expected at about 45 to 75% WFPS, which for most soils is about equivalent to field capacity (see Chapter 1, Section 1.3.3.1). At this soil water content the soil aeration status allows relatively high N_2O production from both nitrification and denitrification, and the diffusion of the N_2O out of the soil is not restricted. The results from this study show much higher values for the optimum WFPS favouring high N_2O emissions, and normally it would be expected that, at these values, nitrification would be severely restricted and denitrification would have a low N_2O/N_2 ratio, thus small N_2O fluxes would occur (see Chapter 1, Section 1.3.3.1). However, for the soils used in this study field capacity (-5 kPa) corresponds to around 86 and 88% WFPS for the sandy loam and clay loam, respectively. Thus, the high WFPS

values are not as high as they seem, as they are only marginally above field capacity for both soil types. It has to be pointed out though that the soil water content was only determined at one depth, 20 cm (to install more than one tensiometer per monolith would have disturbed the soil profile too much, due to their size), and that no information can be given about the soil water content at other depths. If the soil water content had been measured at a different depth, other values for optimum WFPS's might have been obtained. It also has to be stressed that the obtained optimum WFPS's relate to N_2O fluxes and not to N_2O production (which may have occurred at a different depth from that at which the soil water content was measured). However, the highest N_2O emissions in this study were detected when the soils were very wet and high water tables were observed (see Chapter 3, Section 3.1.2). In this situation it seems reasonable to assume that the soil water content was high enough to restrict the aeration of the soil, thus limiting nitrification, and that denitrification took place close to the soil surface (which means that it may well have occurred at the same depth at which the soil water content was measured). Hence it seems likely that the high emission rates observed in this study derived predominantly from denitrification.

Further evidence for this is given by the high Q_{10} values observed, which are usually associated with denitrification (see Chapter 4, Section 4.2.3). The clay loam soil showed higher Q_{10} values than the sandy loam soil, both for the mean values of the 4 replicate monoliths, and generally also from the separate monoliths. Although it cannot be proven statistically whether the difference is significant, the results still show a trend which can be explained by the texture of the soils. The finer texture of the clay loam restricts diffusion of gases more than the coarser texture of the sandy loam; thus, if the soil respiration rate increases with increasing temperature (see Chapter 4, Section 4.2.3), the clay loam is more susceptible to the creation and enlargement of anaerobic zones.

To describe the relationship between soil respiration rate and log-transformed N_2O fluxes different equations were tested (e.g. exponentials), but the relationship was fitted best by a Michaelis-Menten equation. However, it has to be stressed that, due to

the log-transformation of the N_2O data, this is not the true mechanism which describes the association between soil respiration and N_2O fluxes in this study. Therefore, the observed K_m values have no direct biological meaning.

Very high r^2 values were observed for all boundary lines describing the relationships between the three examined variables and N_2O. This is not surprising, taking into account that the boundary line describes the dependence of one variable on another, without the interference of other ones. It is therefore questionable, whether, unlike the situation for ordinary regression analysis, r^2 values have a meaningful use in boundary line analysis.

6.2.3.2. Peaty gley soil

As already mentioned in Section 6.2.2.2 no boundary line could be defined for the relationships between soil temperature and respiration, and N_2O fluxes, due to the clustering of the data. However, no clustering was observed for the association between WFPS and N_2O emission, but despite this, no boundary line could be identified. This could partly be due to the narrow range of measured WFPS's, ranging for the mean values of all 4 replicates from 95 to 100%. Thus the optimum value could lie outside this range. However, this is unlikely since lower fluxes were observed at 95% WFPS for the mean values, and at lower WFPS values for monolith 10, than at higher values, except at 100% WFPS (Fig. 6.4). It could be that a wider range of WFPS's provide optimum conditions for large N_2O emissions, rather than a narrow range. For monolith 10, for example, the optimum WFPS for high N_2O emissions was around 98 - 99%. But since a boundary line was only visible in this monolith no conclusions can be drawn.

6.3. General Discussion and Conclusions

6.3.1. Performance of the sampling system

The fully automated gas sampling system came into operation in September 1993 and the automatic conversion of measured N_2O concentrations into gas fluxes was integrated into the system in June 1994. The system remained in almost continuous use and had worked without any major breakdown, until the completion of experimental measurements in November 1995. It could be left unattended for up to 99 flux measurement cycles.

The N_2O concentration in ambient air measured with the system typically showed a fluctuation of $\pm$ 0.009 µlitre litre^{-1}. For the flux chamber size, with a 60 min closure period, this corresponds to an error of $\pm$1.4 µg N_2O-N m^{-2} h^{-1}, which is insignificant compared with the range of emission rates observed during this project. It should be noted that this precision for N_2O was achieved at a suboptimal temperature, with a much reduced response, in order to measure CO_2 simultaneously (Fig. 2.3). The purpose of the system was to measure these two gases and other variables simultaneously, in a generally high-flux environment, and the operational parameters chosen were a necessary, and generally satisfactory, compromise in this regard.

When all 12 monoliths were in operation it was possible to take gas flux measurements at minimum intervals of 3 h. More frequent measurements could be taken if fewer monoliths were being used. The system was thus a very useful tool for studying problems of temporal variations in N_2O fluxes.

Coefficients of variation between all four replicates of each soil type were calculated for each N_2O flux measurement for approximately two months at the start of the experimental period in 1993, when the soil water potentials were around field capacity. The average value for the sandy loam was 48% ($\pm$15.5), for the clay loam soil 71% ($\pm$30) and the peaty gley 85% ($\pm$21). These values were generally lower than those reported from other studies where smaller gas flux chambers were used

(Folorunso and Rolston, 1984; Christensen et al., 1990; Ambus and Christensen, 1995). Ambus et al. (1993) observed that the coefficient of variation decreases with increasing size of gas flux chambers. However, Ambus and Christensen (1994) observed CV's from small chambers similar to the CV's measured in this study. The relatively low CV's for the large monolith flux chambers suggests that this benefit of increasing size has not been negated by variability induced by disturbance due to collection and transport of the monoliths.

In conclusion, the automated gas sampling and analysis system had a high potential for producing detailed data on the fluxes of N_2O and CO_2, and their relationship with fluctuating soil and environmental variables. Because of their size and relative lack of disturbance, the soil monoliths were fairly representative of soil structures in the field, but by establishing them in a semi-controlled environment it was possible to manipulate single controlling factors and their interactions in a way that cannot be done in the field. The response of N_2O fluxes to changes of soil and environmental variables can be very diverse, depending on the previous state of the soil; the frequency and continuity of measurements of gas fluxes, water potentials, and temperatures made possible by the automation helped the interpretation of the processes governing the emissions.

6.3.2. Controls of N_2O gas fluxes

As has been shown in Chapters 3, 4, 5 and this Chapter (Section 6.2), all three examined soil variables had a very strong effect on N_2O emissions. Water applications were usually followed by increasing N_2O emissions after one to two days, which peaked after several days. However, substantial emissions, which lasted only for a few hours, were sometimes measured shortly after a water application (Chapter 3, Section 3.1.2). Changes in the soil temperature, particularly diurnal temperature cycling, also led to short-lived emission peaks (Chapter 4, Section 4.1.2). In addition, large short-lived emission peaks also resulted from the addition of organic matter to the soils (Chapter 5, Section 5.1.2). All this strongly points to the fact that a large proportion of the overall emissions from soils can occur as intense but short-lived flushes after

perturbation of the soil, as hypothesised in Chapter 1 (Section 1.5). In many studies attempting to estimate N_2O emissions, flux measurements were made relatively infrequently due to the difficulties (cost and labour) involved with intense sampling. With such a sampling regime it is easy to miss flux peaks (e.g. if no measurements are taken for a few days after rainfall) and to incur significant errors in the estimates of the N_2O emissions. For example, if the diurnal flux cycling from Monolith 9 shown in Fig. 4.2 had been ignored and the fluxes had been measured only daily at 1100 h, the cumulative N_2O-N loss over the three days would have been underestimated by 15%. If the amplitude of the flux cycling had been bigger and/or more emission peaks had been missed, the error would have been even larger. This highlights the need for long sampling periods with frequent measurements if accurate meaningful N_2O flux estimates are to be obtained. An automated sampling system, like the one used in this study, is an ideal tool for this since, although initially expensive, it does not require much labour, once it has been set up.

The extent and duration of the observed N_2O emission peaks were determined by the soil variables examined, and could be related to individual variables, providing that the other ones remained fairly constant. For example, the N_2O fluxes between two watering events usually correlated very well with the soil water potentials. However, between each pair of irrigation events the relationship was slightly different. For example, the time when emissions started to increase and the speed of the actual increase varied greatly. Similarly, over short time periods diurnal flux cycles could be observed when other variables were not overriding the effect of the soil temperature. But again no common relationship could be established, since N_2O fluxes correlated with soil temperatures at different depths at different times. When the whole data set was used to establish relationships no significant associations could be found.

As in this work, various studies have tried to explain the relationships between soil variables and N_2O fluxes using conventional statistics, and while some authors found good correlations and regressions between N_2O fluxes and the variables examined in their studies (e.g. Mosier *et al.*, 1983; Velthof *et al.*, 1996b), most workers, particularly in long-term experiments, were unable to show relationships (e.g.

Shepherd *et al.*, 1991; Flessa *et al.*, 1995; Clayton *et al.*, 1997). The main reason for this failure to establish relationships is the fact that the controlling variables interact and one or more prerequisites have to be met before emissions can take place (e.g. water content will only have an effect on fluxes if there is enough mineral N in the soil). The interpretation of relationships between N_2O fluxes and driving variables can be made easier if the data are put into classes (e.g. temperature classes or ranges of WFPS) (e.g. Brumme, 1995; Smith *et al.*, 1998). Another, more effective approach, is the application of boundary line analysis used in this study. With this it is possible to examine the effect of one controlling variable on N_2O emissions, while eliminating the effects of other variables (see this chapter, Section 6.2.1). Therefore it is possible to gain a very clear insight into the relationship between two variables. The only disadvantage of boundary line analysis is that it requires relatively large data sets. In this study boundary line analysis worked very well for the fallow mineral soils, but unfortunately not for the peaty gley soil (no satisfactory reason can be given why it did not work). Despite the advantages of boundary analysis over conventional statistical analysis, to my knowledge no study to date exists where boundary line analysis has been used explicitly to examine the relationships between N_2O fluxes and controlling variables, although Parton *et al.* (1996) used a rather similar approach to derive functions for N_2O modelling (see this chapter, Section 6.2.1).

Of the three variables examined in this study (soil water content, soil temperature, and respiration rate), the first of these had the strongest effect on N_2O fluxes from the fallow soil monoliths, since mineral N was not limiting the N_2O production (see Chapter 3, Section 3.1.3), and substantial emissions were observed even at low soil temperatures and respiration rates (see Figs. 6.2, 6.3). When the soils were too dry or too wet no N_2O emissions were observed, regardless of whether the temperature was at a value which generally favoured N_2O fluxes. It has also been shown in this study that the three variables examined strongly interacted with each other (e.g. soil water content had the strongest effect on N_2O fluxes at high temperatures) (see Chapter 4, Section 4.3.2 and Chapter 5, Section 5.3.2).

It was hypothesised in Chapter 1 (Section 1.5) that major N_2O emission increases would occur when the soil water content exceeded certain threshold values. In the event, the largest relative flux increases were usually observed when the soil water content changed from that which was equivalent to field capacity to wetter conditions for a few days (see also Fig. 3.8). When the soils dried rapidly to values below field capacity no major changes in emissions were observed. However, large emission peaks could also occur when the soils were drier than field capacity, and as was discussed in Chapter 3 (Section 3.1.3) the largest N_2O emissions were observed when other soil variables were interacting with the soil water content. Due to this interacting effect of soil variables it is difficult to give a precise threshold value.

Soil water content has a very strong effect on soil aeration (Chapter 1, Section 1.3.3.1), and in Chapters 4 (Section 4.2.3) and 5 (Section 5.2.3) it has been discussed how the soil temperature and the respiration rate of a soil may affect the N_2O fluxes indirectly by having a strong effect on the soil aeration. Few studies to date have made this connection, and it is concluded that soil aeration is the main controlling variable for N_2O fluxes, provided that mineral N and organic C are not limiting.

For the soil monoliths cropped with ryegrass, the presence of the plants was overriding all other controlling variables. The plants provided a strong sink for mineral N, and due to transpiration the soils always dried out very quickly after irrigation events (see Chapter 3, Section 3.2.3). Thus in a situation like this, apart from the soil aeration, the mineral N content is also a major controlling factor, and both variables need to be at sufficient values simultaneously for N_2O emissions to occur.

In a normal field situation soils are usually only left fallow from the end of one growing season to the beginning of the next one. During this period the mineral N content in the soil is generally relatively low since the crop would have taken up most of it, and mineralisation would be low due to low temperatures, and winter leaching of nitrate commonly occurs. Consequently N_2O emissions would be low during this period. Furthermore during the winter months temperatures might also fall to levels

low enough to severely restrain nitrification and denitrification. During the growing season N_2O emissions would normally be low due to the presence of plants.

In conclusion, in a normal field situation N_2O emissions are predominantly controlled by mineral N and soil water content. N_2O emissions from field soils are usually relatively low, except after fertiliser applications in wet enough conditions for nitrification and denitrification to occur (Slemr *et al.*, 1984; Brams *et al.*, 1992; Clayton *et al.*, 1997).

The high N_2O emissions observed in this study were caused mainly by denitrification rather than nitrification (see Section 6.2.3). This does not mean that nitrification has not contributed to N_2O emissions, but unlike denitrification nitrification seems not to have resulted in very large fluxes during this study. It appears that nitrification might have been responsible for relatively low "background" emissions (e.g. Chapter 4, Section 4.1), but that large flux peaks, for example caused by irrigation (Chapter 3, Section 3.1) or plant residue applications (Chapter 5, Section 5.1), occurred more sporadically and were predominantly caused by denitrification. This seems also to be the case in typical field situations in Scotland. For example, Clayton *et al.* (1997) measured large flux peaks only at WFPS values in the range from around 80 to 90%, indicating that denitrification was responsible for these emissions.

In summary, the most significant findings of this work were as follows:

- Accurate N_2O flux estimates need frequent measurements throughout the period of interest.

- Boundary line analysis provided an excellent tool for examining the association between N_2O emissions and controlling variables in the fallow mineral soils, and significant relationships could be established.

- All three controlling variables that were investigated strongly interacted with each other.

- All three of these variables affect soil aeration, which is the main controlling variable for N_2O fluxes provided that mineral N and organic C supplies are not limiting nitrification and denitrification.

- Denitrification was the main soil process responsible for the large emission peaks observed in this study.

6.4. Future Work

Although this work contributed to an improvement in our understanding of N_2O fluxes from soils and their controlling variables, there are still a lot of questions to be answered, and here are some suggestions for future work:

- The boundary line analysis carried out in this study should be used for modelling the data from this study.

- Boundary line analysis should also be used to examine the relationships between N_2O fluxes and controlling factors other than the ones used in this study, and then a predictive model should be developed employing all the variables (preferably with field data).

- The automated soil monolith-flux chamber system could be used to study the N_2O fluxes from soil types other than those used in this work, or to study other greenhouse gases. It could also be modified for use in the field.

- As no clear estimates can be given of the actual contribution from nitrification or denitrification to the measured N_2O emissions, further experiments to distinguish between the two processes would be useful (this would probably be a laboratory experiment).

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Appendix I

Plate A1.1. Collection of large soil monolith. Picture shows the monolith casing with cutting ring at the bottom, and a jack being inserted below an anchored steel frame.

Plate A1.2. Under-cutting the monolith. A steel plate is forced with a jack horizontally under the monolith.

Plate A1.3. Removing the monolith from the pit. The monolith with steel under-cutting frame attached is hoisted out of the pit by a front-loader.

Plate A1.4. Complete monolith-flux chamber system assembled in the greenhouse. Picture shows monoliths with some lids closed, and control computer and gas chromatograph in the background.

Appendix II

Water Release Curves

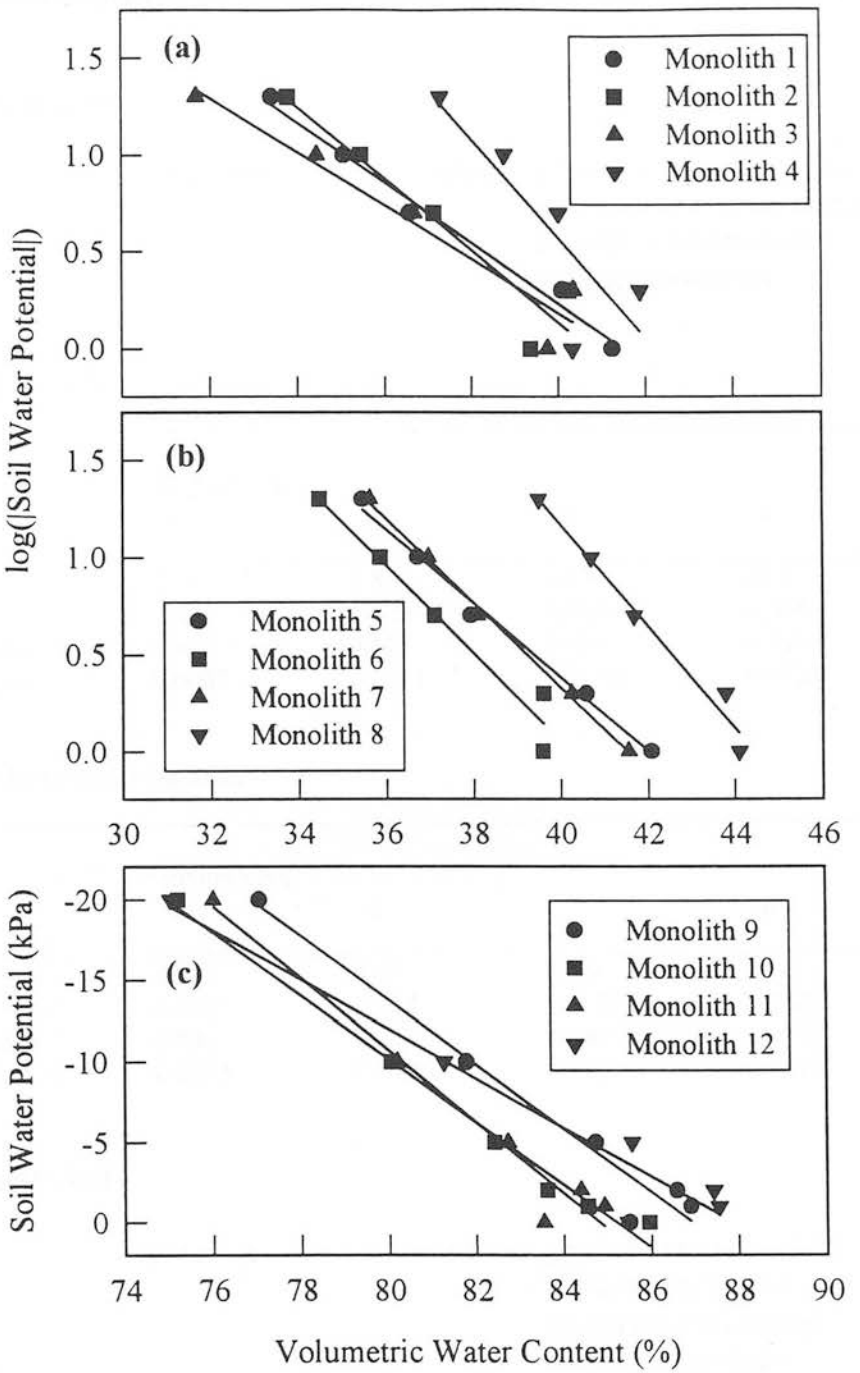

Fig. AII.1. Moisture release curves for (a) the sandy loam, (b) the clay loam and (c) the peaty gley soil monoliths. (a) and (b) Soil water potential values changed to positive sign before log transformation. Note the differences in scales for the soil water potential and the volumetric water content in (c). For the regression parameters see next page.

Regression analysis for moisture release curves (see Fig. AII.1 on previous page):

Mineral Soils

$y = a + bx$ where: y = log(|soil water potential|)
x = volumetric water content
a = regression intercept
b = regression slope

Sandy Loam Soil Monoliths:

	Monolith No. 1	2	3	4
a	6.51	7.56	5.73	10.8
b	-0.157	-0.185	-0.139	-0.256
r2 value	0.987	0.899	0.926	0.712
p value	0.0007	0.0141	0.0088	0.0723

Clay Loam Soil Monoliths:

	Monolith No. 5	6	7	8
a	8.00	9.06	9.00	11.6
b	-0.190	-0.225	-0.2.17	-0.262
r2 value	0.991	0.957	0.997	0.977
p value	0.0004	0.0039	< 0.0001	0.0015

Organic Soil

$y = a + bx$ where: y = soil water potential
x = volumetric water content
a = regression intercept
b = regression slope

Peaty Gley Soil Monoliths:

	Monolith No. 9	10	11	12
a	-172.4	-166.4	-188.4	-134.1
b	1.98	1.95	2.22	1.53
r2 value	0.961	0.987	0.962	0.938
p value	0.0006	< 0.0001	0.0006	0.0015

Appendix III

Publications arising from this study

Refereed Papers

SMITH, K.A.; CLAYTON, H.; McTAGGART, I.P.; THOMSON, P.E; ARAH, J.R.M and SCOTT, A. (1995). *The measurement of nitrous oxide emissions from soil by using chambers*. Philosophical Transactions of the Royal Society London A **351**, 372 - 338.

SMITH, K.A.; THOMSON, P.E.; CLAYTON, H.; McTAGGART, I.P. and CONEN, F. (1998). *Effects of temperature, water content and mineral nitrogen on emissions of nitrous oxide by soils*. Atmospheric Environment, in press.

THOMSON, P.E.; PARKER, J.P.; ARAH, J.R.M; CLAYTON, H. and SMITH, K.A. (1997). *Automated soil-monolith chamber system for the study of trace gas fluxes*. Soil Science Society of America Journal **61**, 1323 - 1330.

Published Abstracts

Smith, K.A.; Ball, B.C.; Dobbie, K.E.; McTaggart, I.P. and Thomson, P.E. (1995). *Nitrous oxide emission and methane uptake by soils: Relationships with soil nitrogen dynamics, physical factors and land use, and estimates of regional fluxes*. Annales Geophysicae **13**. Supplement II, C400.

Thomson, P.E.; Parker, J.; Smith, K.A.; Clayton, H. and Arah, J.R.M. (1994). *An automated monolith lysimeter system for study of factors affecting N_2O emissions from soils*. Annales Geophysicae **12**. Supplement II, C392.

Poster Papers

Smith, K.A.; Ball, B.C.; Dobbie, K.E.; McTaggart, I.P. and Thomson, P.E. (1995). *Nitrous oxide emission and methane uptake by soils: Relationships with soil nitrogen dynamics, physical factors and land use, and estimates of regional fluxes*. EGS XX General Assembly in Hamburg (3rd - 7th April 1995).

Smith, K.A.; Thomson, P.E.; McTaggart, I.P. and Parker, J.P. (1996). *Investigation of soil and environmental processes responsible for the production of nitrous oxide in soils, and development of a predictive model of net fluxes*. TIGER II Review Meeting in Grange-over-Sands (29th January - 2nd February 1996).

Smith, K.A.; Thomson, P.E.; McTaggart, I.P.; Parker, J.P.; Clayton, H. and Crichton, I.C. (1997). *Investigation of soil and environmental processes responsible for the production of nitrous oxide in soil*. Final TIGER II Review Meeting in Manchester (7th - 9th January 1997).

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