MEASUREMENT AND MODELLING OF N_2O AND CH_4 EMISSIONS FROM SOILS

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Declaration

I, Franz Conen. hereby declare that this thesis was composed by myself, and that the work described was carried out by myself. except where stated otherwise in the text. The work presented has not been submitted in any previous application for a degree.

Franz Conen

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General introduction

The composition of the atmosphere has been subject to alterations since very early times and has so far mainly been influenced by the development of plant life. Before the occurrence of oxygenic photosynthesis about 2.7 billion years ago, O_2 was absent from the atmosphere and CO_2 concentrations were 100-1000 times higher than at present. By their photosynthetic activity, plants absorbed CO_2 and released O_2, a process that led to today's values of 21% O_2 and 0.035% of CO_2 (Rozema *et al.*, 1997). The increase in O_2 has also led to the gradual development of a stratospheric ozone layer that absorbs most of the damaging part of solar UV radiation. This development has allowed for the evolution of plants above protective water surfaces (Caldwell, 1979) and other forms of terrestrial life. The carbon removed from the early atmosphere is now mainly stored in the form of fossil fuels, as soil organic matter or in forests.

Apart from such fundamental changes that took place over millions of years, recent history has seen relatively small but fast alterations of the atmospheric composition, mainly related to human activity. These changes mainly consist of increases in the trace gases present in the atmosphere. Despite their small concentrations, these gases are of particular significance, because they absorb infrared radiation emitted from the earth's surface and reemit it. Thus they play an important role in the energy balance of the earth. Increasing trace gas concentrations lead to increasing global temperatures. The effects of this so-called "greenhouse effect" are expected to be detrimental to the global population. Apart from rising sea levels, the effect is expected to lead to a more vigorous hydrological cycle, with longer and more severe droughts in some parts of the world, and more severe flooding in other parts. Also, a shift in the competitive balance between species may occur and result in a die-back of forests (IPCC, 1997). This would aggravate an already highly undesirable trend.

Today, there are three trace gases which are of major concern. These are carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Also chlorofluorocarbons

(CFCs) contribute to the greenhouse effect. However, their production has been banned by the 'Montreal-Protocol' because of their destructive influence on the stratospheric ozone layer. CFCs are purely man-made gases that did not exist in the atmosphere before the industrial revolution, whereas CO_2, CH_4, and N_2O are partly of biogenic origin and were already present in the atmosphere. Since about 1750, these latter gases have undergone a marked increase. By 1990, CO_2 had increased by about 30 %, CH_4 by 145 %, and N_2O by 15 % (IPCC, 1994). The increase in CO_2 is related to the burning of fossil fuels, deforestation, and the opening up of virgin lands whereby soil organic matter has been oxidised. The additional CH_4 originates from fossil sources, e.g. leaking gas wells and vented coal mines (pit-gas). Also, biogenic sources have increased as a result of the growing human population. Rice paddies have been expanded and herds of ruminants increased. In both, CH_4 is produced by incomplete fermentation of organic material. N_2O is mainly of biogenic origin, being produced in soils and animal manure either by nitrification of ammonium, or by denitrification of nitrate. Natural soils tend to have very low levels of ammonium and nitrate and thus tend to produce only very small amounts of N_2O. However, this has changed dramatically since mineral nitrogen fertilisers were introduced and are being used in increasing quantities. This trend is expected to continue, to meet the food demands of a growing global population. Growing atmospheric concentrations of N_2O are also undesirable because of their destructive effect on the stratospheric ozone layer (Crutzen, 1974). This was the initial reason why interest in the measurement of N_2O from soils evolved.

Since political agreements have been signed relating to the reduction of net greenhouse gas emissions by many countries (Rio de Janeiro, 1992; Kyoto, 1998), it has become increasingly important to improve methods for the measurement and estimation of trace gas emissions. While this might be relatively easy for industrial emissions, where controlled processes and point sources are involved, it is much more difficult for emissions from biogenic sources on large land surfaces. For example, it is easy to quantify CO_2 emissions from fossil fuel burning. Statistics on fuel consumption are available from the institutions where fuel tax is levied. Knowing the amount of

CO_2 that is produced by burning a certain amount of fuel, it is possible to calculate the total amount of CO_2 from this source. To estimate the amount of N_2O and CH_4 emitted from agricultural soils is by far more complicated and leads to less well defined estimates. Even if it were possible to reliably model the processes involved, there would still be the problem of obtaining the input data needed to run the resulting model. Direct measurement requires high inputs of labour and materials and is therefore limited to small areas. Thus it is hard to provide reliable national or global estimates. This is reflected in the larger uncertainties in emission estimates for these gases. For example for N_2O from agricultural soils, global estimates range from 0.6 to 14.8 Tg N y^{-1} (IPCC, 1997). In agriculture, N_2O and CH_4 are the most important trace gases; CO_2 is only of minor significance, except where organic soils are utilised (Kasimir-Klemendtsson *et al.*, 1997).

While a lot of work has been done on the methodologies of measuring and estimating terrestrial trace gas emissions, there are still some open fundamental questions. This thesis explores some of these questions. Its scope is necessarily limited to the techniques that have been applied within the course of this work. The studies involving N_2O were supported in part by a MAFF (Ministry of Agriculture, Fisheries and Food) funded project on quantifying emissions from fertilised agricultural soils (Grant No. CC0214). All studies involving CH_4 and rice plants were part of the EC funded RICEOTOPES project (Grant No. CT97-0408), looking into fluxes and isotopic signatures of CH_4 from rice paddies.

After the literature review (Chapter I), issues related to the so-called closed chamber technique are investigated in Chapters II and III. This is a method, which involves the covering of a small area (usually < 1 m^2) with some type of inverted container and the monitoring of the changing gas concentrations within the headspace so created. While N_2O was used as a target gas in the work described in these chapters, the results are also applicable to other gases. Chapter IV explores the possibility of predicting N_2O emissions through related soil parameters. A simple model has been developed on the basis of closed chamber measurements and the simultaneous measurement of related soil water and mineral N contents, and temperature. This was then verified against data sets obtained by the same methods. Chapter V describes an automated system of closed chambers for the measurement of CH_4 from rice paddies and results obtained with this system over two growing seasons. It includes some technical aspects and an illustration of seasonal variability and variations in the pathways of CH_4 emission. Chapters VI and VII investigate two possibilities of measuring CH_4 from rice on a larger scale than it is possible with closed chambers.

In a general discussion, the different approaches to estimating trace gas emissions from land surfaces previously discussed are compared and an outlook on possible future developments is given.

CHAPTER I

Literature review

This literature review is intended to provide a baseline on which this thesis has been built, rather than as a comprehensive review of the literature relevant to the topics covered by the individual Chapters in the thesis, three of which have been published or accepted for publication. The review in this Chapter is therefore complementary to the coverage of the literature in each of the ensuing Chapters (II-VII).

There is an abundance of literature on measurements and modelling of N_2O and CH_4 emissions from soils. While most of the literature on N_2O emissions is concerned with agricultural soils (e.g. Ryden and Lund 1980; Bronson *et al.*, 1997; Tsuruta *et al.*, 1997; Dobbie *et al.*, 1999), literature on CH_4 emissions is often dealing with natural wetlands (e.g. Fan *et al.*, 1992, Gallagher *et al.*, 1994; Kuhlmann *et al.*, 1998), but also with rice paddies (e.g. Holzapfel-Pschorrn and Seiler, 1986; Yagi *et al.*, 1996; Bronson *et al.*, 1997; Khalil *et al.*, 1998a).

The technical issue of the measurement of N_2O seems to have attracted attention mostly at an early stage, in the late 1970s and early 1980s. It was the possible systematic errors involved in the closed chamber technique that were discussed. Analytical limitations at that time did not allow for the application of micrometeorological techniques. One of the first to look into errors involving the chamber technique was Denmead (1979). He identified the feed-back effect of the chamber on soil gas concentrations and also found that depressurisation causes over-estimation of flux. This was later confirmed by Christensen (1983), who observed increased N_2O emissions after reducing the inlet of a chamber from which air was continuously withdrawn. At about the same time, Matthias *et al.* (1980) proposed a simple chamber technique for measuring N_2O emissions from soils. Probably the paper in this field most often referred to is by Hutchinson and Mosier (1981). They proposed an improved chamber design that was intended to overcome the suppression of turbulence-induced pressure fluctuations by closed chambers. The same paper also proposed a model and a procedure for correcting for changes in the gas concentration gradient between the soil and the chamber atmosphere. This was an improvement of an earlier model by Matthias *et al.* (1978). Later models describing gas flux from the soil covered by a closed chamber are essentially refinements of these earlier works, building on the same assumptions (Healy *et al.*, 1996, Gao & Yates, 1998).

One outcome of the modelling was the recommendation to keep the chamber closure as short as possible and the chamber height as large as possible (Healy *et al.*, 1996). This is to avoid accumulation of large headspace concentrations and their feedback effect on gas flux from the soil. Another important issue of the closed chamber technique, the spatial variability of N_2O flux, has received surprisingly little attention so far. The largest fluxes measured with individual chambers can be several orders of magnitude larger than the mean of a larger chamber population (Ball *et al.*, 1997). On grazed grassland, Clayton *et al.* (1994) found coefficients of variation between 59 and 183 % for a total of 16 chambers (0.4 m diameter). Dobbie *et al.* (1999) reported from coefficients of variation between 68 and 83% for a set of 6 chambers (0.4 m diameter) on a ungrazed grassland site. The problem of spatial variability might be reduced by increasing the number of replicate chambers, or by integrating flux over larger areas. Chambers of very large surface areas (tens of square metres) were used in some studies (Galle *et al.*, 1994; Smith *et al.*, 1994). The possibility of applying the dynamic wind gradient method in connection with GC/ECD analysis to measuring N_2O emissions from soil has been explored by Arah *et al.* (1994). The sensitivity of the analysis system limited the application to fluxes > 100 g N_2O-N ha^{-1} d^{-1}. Using tuneable diode laser trace gas analysers (TDLTGA), Wagner-Riddle and Thurtell (1998) were able to monitor N_2O fluxes well below 20 g N_2O-N ha^{-1} d^{-1} by the gradient method over several years. The eddy covariance technique has been applied on a campaign basis (Hargreaves *et al.*, 1994; Wienhold *et al.*, 1995; Laville *et al.*, 1999). However, apart from the study by Wagner-Riddle and Thurtell (1998), it is only the closed chamber technique that has so far been applied in long-term measurements of N_2O from soils. It is also the preferable technique in process studies as it can be applied in experiments with small field plots undergoing different treatments (i.e. Clayton *et al.*, 1997; Velthof *et al.*, 1997; Dobbie *et al.*, 1999).

The closed chamber technique is also the preferred measurement technique for determining CH_4 emissions. In rice paddies, the most used design involves relatively large, transparent boxes ranging from 0.055m^2 (Khalil *et al.*, 1998a) to 1.44 m^2 (Yagi *et al.*, 1996). Some are fitted with a lid that is closed for about one hour for measurement and otherwise stays open (i.e. Schütz *et al.*, 1989; Butterbach-Bahl *et al.*, 1997). Others are placed into position over the plants only during the measurement period, and rest on permanently inserted foundations (Khalil *et al.*, 1998). Yet another chamber type was used by Yagi *et al.* (1996). This involves a box with three square flanges (0.2 x 0.2 m) fitted with shutters. When a measurement is to be made, the shutters are closed, at other times the chamber is vented by a fan drawing air through one of the open shutters.

Possible effects of closed chambers on rice plants and CH_4 flux from paddy fields have been studied in detail by Butterbach-Bahl (1993). The main concern raised is a temperature increase within the chamber and a resulting increase in CH_4 flux. Werle (1999) suspected that the fan mixing the air within the closed chamber creates turbulence above the natural level, accelerating gas exchange and leading to an over-estimation of the flux. Micrometeorological techniques have been applied to measuring CH_4 from wetlands on a campaign basis (e.g. Fan *et al.*, 1992; Gallagher *et al.*, 1994). Over several years, CH_4 mixing ratios and observations of stable isotope ratios and ^{222}Rn activity were used to generate flux estimates from a wetland region in the Hudson Bay Lowland (Worthy *et al.*, 1998; Kuhlmann *et al.*, 1998). Simpson *et al.* (1995) used micrometeorological methods to measure CH_4 flux from rice. Their results were about twice as high as parallel chamber measurements. However, conditions were not ideal for a direct comparison in this case. In an experiment undertaken specifically for inter-comparison of methods, Werle (1999) measured only about half of the flux determined by parallel chamber measurements. The chamber measurements in this intercomparison were carried out as part of this thesis (Chapter V).

Emissions and processes involved in the emission of N_2O and CH_4 have been modelled at different levels. Models can be useful in understanding processes involved in production and emission of trace gases. For example, the interference of a closed chamber in the emission process can be modelled as discussed earlier. Models can also be used to predict emissions, or interpret observed changes in atmospheric trace gas concentrations. Smith (1980) presented a process model describing the development of anaerobic zones in soil aggregates of otherwise aerated soil. Anaerobic conditions are a pre-requisite for denitrification and thus, N_2O formation by this route. A similar model has been produced and experimentally verified by Sierra *et al.* (1995). Such a model can be used as a submodel in a more complex process model. An example of a process model describing N_2O formation driven by rainfall and resulting decomposition and denitrification has been proposed by Li *et al.* (1992). Another example of a relatively complex N_2O model has been given by Parton *et al.* (1996). A comparison of the performance of these two models, and two others, can be found in Frolking *et al.* (1998). A process model for predicting CH_4 emissions from rice paddies has been developed by Cao *et al.* (1995). CH_4 emissions from wetlands have been described in a process model by Walter *et al.* (1996). Process models usually suffer from the problem of requiring input data that is only rarely available. Therefore, more empirical models have been brought forward. Probably the most relevant one so far is by Bouwman (1996). The current IPCC "Phase II methodology" for producing national inventories of N_2O from agricultural land is based on it, assuming a default emission factor of 1.25% of all the nitrogen added to the soil plus a background emission of 1 kg N_2O-N $ha^{-1}y^{-1}$ (IPCC 1997). This procedure does not account for climate, management practice, irrigation, soils, crop types and other variables, and thus efforts are currently underway to develop improved methodologies for estimating N_2O emissions from agricultural soils, taking account of regional and seasonal variations (Smith *et al.* 1999). An empirical model specifically for grassland on peat soil has been developed by Velthof *et al.* (1996). Huang *et al.* (1998) developed a semi-empirical model for CH_4 emissions from rice paddies that is based on relatively easily obtainable parameters. An example of inverse modelling is given by Kroetze *et al.* (1999), undertaking to close the global N_2O budget retrospectively for the period from 1500 to 1994.

CHAPTER II

A re-examination of closed flux chamber methods for the measurement of trace gas emissions from soils to the atmosphere

(A version of this Chapter has been published in the *European Journal of Soil Science*, December 1998, **49**, 701-707.)

1 Introduction

Static flux chambers are widely used for measuring trace gas emissions from soil. They are cheap, straightforward to use and can be applied under a wide range of conditions (Smith *et al.*, 1995). Commonly, static chambers seal a certain volume of atmosphere above the soil surface for 20-60 minutes to allow trace gas fluxes to accumulate to a concentration that can be determined by gas chromatographic (or infra-red) analysis. The surface areas covered vary considerably from 0.008 m^2 (Ambus and Christensen, 1994) to 0.49 m^2 (Clayton *et al.*, 1994). Potential sources of systematic errors in the use of static chambers have been discussed by a number of authors and have been summarized by Mosier (1990).

In this chapter, one potential error involved in using sealed static chambers is examined, namely the exclusion of ambient pressure fluctuations. Hutchinson and Mosier (1981) proposed that under undisturbed conditions pressure fluctuations caused by wind turbulence promote the mixing of soil air with the atmosphere. This effect could enhance the transfer of trace gases such as N_2O, whereas otherwise the transfer is driven by diffusion only (Kimball and Lemon, 1971). To enable ambient pressure fluctuations to occur also inside a static chamber, Hutchinson and Mosier (1981) proposed an improved chamber design including a vent tube for pressure equilibration. They considered losses due to diffusion along the vent tube negligible. In contrast to dynamic chambers with forced air flow, such a vented chamber is still a static chamber for accumulation of trace gases, but is responsive to atmospheric pressure fluctuations. Since that publication appeared, Hutchinson & Mosier's design has been used by several groups of scientists (e.g. Flessa *et al.*, 1995; Velthof & Oenema, 1995), while others, (e.g. Ambus & Christensen, 1994) and our own group (Clayton *et al.*, 1994), have used a sealed (unvented) design.

Whereas a sealed chamber might suppress pressure fluctuations caused by wind turbulence and therefore lead to smaller fluxes than those measured with a vented chamber, which allows pressure equilibration, there is also the possibility that depressurization due to the Venturi effect can lead to a flow of air enriched in trace gas from the soil into the chamber, as indicated by the arrows in Figure 1, and thus to an over-estimation of fluxes. This hypothesis was investigated in the experiments below.

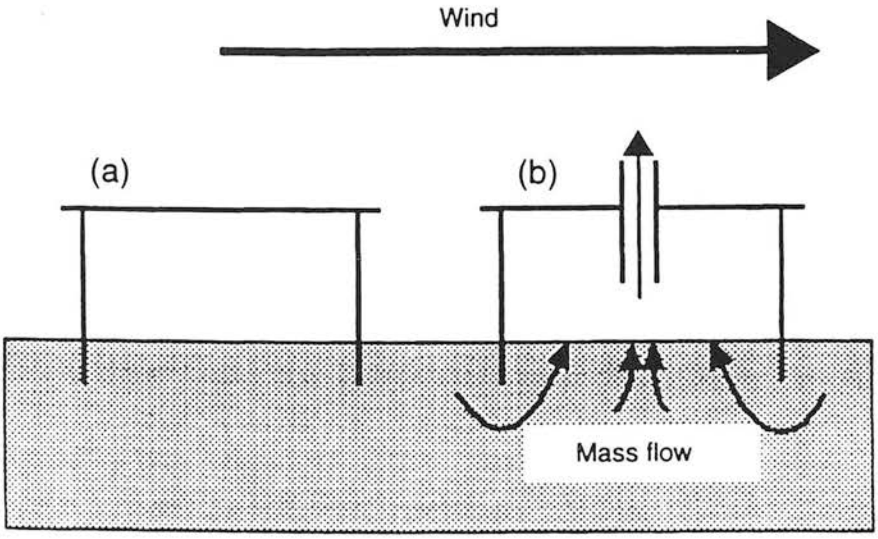


Figure 1: *Cross section through (a) sealed (b) vented chambers.*

2 Materials and methods

2.1 *Field experiment*

Field experiments with vented and sealed chambers took place between 7 March and 16 May 1997 at Langhill Farm and Glencorse Mains, both ca 10 km south of Edinburgh. The soil at Langhill is a sandy clay loam (65% sand, 14% silt, 21% clay) with 12.1% organic matter in the upper 10 cm, pH 5.5 (in water), a bulk density of 1.18 g cm^{-3} in the top 5 cm and is used as pasture for cattle. The soil at Glencorse Mains is a clay loam (36% sand, 40% silt, 24% clay) with 5.5% organic matter, pH 5.5 (in water), bulk density 1.20 g cm^{-3} in the top 5 cm. The field sampled is managed as grassland cut for silage. On ten days measurements were made on the sandy clay loam at Langhill, covering different environmental conditions such as water-filled pore space (WFPS), windspeed and NH_4^+ and NO_3^- concentrations in the soil (Table 1). On five days measurements were made on the clay loam at Glencorse Mains, covering the environmental conditions given in Table 1. Each day when measurements were made, eight replications of both vented and sealed chambers were sampled. The chambers consisted of plastic rings, 40 cm in diameter and 20 cm high (Clayton *et al.*, 1994; Smith *et al.*, 1995), which were inserted 7 cm deep into the soil more than 4 weeks before the first measurement and left in place throughout.

To overcome the problem of spatial variation adding to the variation due to venting or non-venting, the same rings, or chamber bases, were tested as vented and sealed chambers by covering them either with a closed 5 mm thick aluminium lid for the sealed treatment or with a similar lid containing a vent tube (16 cm long, 1 cm inner diameter) for the vented treatment. Measurements were taken between 10:00 and 12:00 hours, with half of the chamber bases first being covered with sealed and half with vented lids for 45 minutes. Gas samples were taken with evacuated 20-ml aluminium flasks through three-way stopcocks in the lids. After the first 45 minute sampling, the lids were removed from the bases of the chambers for 15-20 minutes. During a second 45-minute closure and sampling period, previously sealed chambers were covered with vented lids and previously vented chambers were covered with sealed lids. All gas samples were analysed using the automated gas chromatographic analysis system described by Arah *et al.* (1994).

Table 1: *Environmental conditions at field sites at the time of measurement*

Site	Date	Soil temp. at 5 cm (°C)	WFPS top 10 cm (%)	Wind speed at 2m height ($m\ s^{-1}$)	NO_3^--N top 10 cm ($mg\ kg^{-1}$)	NH_4^+-N top 10 cm ($mg\ kg^{-1}$)	Air permeability top 10 cm ($10^{-8}\ cm^2$)
Langhill Farm	07-Mar-97	6.9	40.2	2.5	7.2	6.47	2300
	13-Mar-97	7.6	44.0	3.0	4.4	11.04	1200
	17-Mar-97	9.0	55.0	1.0	56.4	64.10	170
	18-Mar-97	8.8	45.6	4.0	51.3	33.28	890
	19-Mar-97	9.3	49.8	1.3	32.0	9.04	420
	21-Mar-97	6.6	58.8	0.8	38.6	55.87	86
	24-Mar-97	7.3	42.6	1.3	40.6	18.14	1500
	26-Mar-97	9.1	43.2	6.0	30.8	13.18	1400
	04-Apr-97	6.4	46.4	1.0	28.9	11.79	770
	08-Apr-97	9.8	47.9	2.0	53.4	13.53	590
Glencorse Mains	17-Apr-97	9.9	59.4	0.5	17.9	46.50	132
	22-Apr-97	8.4	62.3	1.5	21.1	32.20	96
	01-May-97	11.9	61.7	6.0	10.7	22.70	103
	09-May-97	9.8	83.4	1.8	1.8	20.00	10
	16-May-97	11.7	74.2	4.5	1.2	12.60	27

Wind speed was measured at the beginning and end of each measurement at 2 m height. Total soil porosity was calculated from measurements of dry bulk density, assuming a particle density of 2.6 g cm^{-3} . Water content was measured gravimetrically, converted to a volumetric basis and then divided by total porosity and multiplied by 100 to give % water-filled pore space (WFPS). NO_3^- and NH_4^+ were determined by KCl extraction and automated continuous-flow analysis. Air permeability was determined on intact soil cores with different WFPS taken from the upper most 10 cm at the end of the experiment according to the method developed by Ball *et al.* (1981). Functions for the correlations between WFPS and soil air permeability for both sites were determined and used to calculate the air permeability for the specific days when gas samples were taken (Table 1).

Since the same locations and chamber bases were used for sealed and vented chambers, spatial variation played no role in the comparison (Hogg & Ledolter, 1992), and this made the comparison more sensitive than it might otherwise have been. Statistical differences between the two methods were assessed by means of the paired-sample *t*-test.

2.2 *Laboratory experiment*

For the laboratory experiment, a smaller version of a vented chamber (10 cm diameter, 13 cm height) was built from Perspex, with a vent tube of 4 mm i.d., 4.9 cm long. The chamber was pushed 3 cm deep into a 5-litre bucket, filled with air-dry sand (10% coarse sand, 84% medium sand, 6% fine sand and silt). A micromanometer (model MP30mbDμ, Air Instrument Resources Ltd., Chalgrove, Oxford, England) was used to measure pressure differences between the inside and the outside atmosphere of the chamber at different wind speeds, created by an electric fan placed at various distances from the chamber and measured with an airflow meter (model TA400, Airflow Developments Ltd., High Wycombe, England). The probe of the airflow meter was installed for this purpose at the same height above the chamber as the top of the vent tube (2 cm), and aligned to the air flow direction.

In an experiment to determine the relation between wind speed and flow rate out of the chamber, the vent tube was transformed into a simple flow meter by fitting it with a float consisting of a spherical piece of duck's down. A short piece of thin wire in the upper and lower part of the vent tube prevented the down from escaping. Calibration with a bubble flow meter indicated that the down began to float at a flow rate of 1.3

ml s^{-1} (replicate measurements: 5; standard error: 0.18). An electric fan was again used to generate wind over the vent tube at various velocities, depending on its distance from the chamber.

3 Results and discussion

3.1 *Field measurements*

On the sandy clay loam at Langhill Farm, faster average N_2O emission occurred on all sampling dates with vented chambers than with sealed chambers. Fluxes from sealed chambers ranged from 9 g to 243 g N_2O-N ha^{-1} day^{-1}, and for the vented treatment from 14 to 450 g N_2O-N ha^{-1} day^{-1}. On six out of ten days, the observed differences were significant (paired *t*-test for means, $p<0.05$) (Figure 2a). The difference was greatest at the highest wind speed (6 m s^{-1}) on 26 March 1997, when the vented chambers gave 5 times larger values than did the sealed chambers. Calculating average daily emissions between individual measurements by linear interpolation (as is commonly done in emission studies), the total emission determined with vented chambers was 233% of what was measured with sealed chambers during the same period.

No correlation could be identified between the relative difference in measured flux rates and WFPS or NO_3^- or NH_4^+ concentrations in soil. A weak correlation ($r=0.75$; $p<0.1$) was found for the percentage increase in flux due to venting, and average wind speed.

In contrast, on the wetter and less permeable clay loam at Glencorse Mains (Figure 2b), vented chambers indicated lower emissions than sealed chambers. However, the differences were much smaller. Where fluxes were within the range of 0 - 3 g N_2O-N ha^{-1} day^{-1}, only one significantly smaller average ($p= 0.01$) was measured with vented chambers. On two occasions with larger fluxes sealed chambers recorded emissions of 193 g and 73 g N_2O-N ha^{-1} day^{-1} , whereas vented chambers yielded only 90% and

80% of those values. However, these differences were not significant (Figure 2b). Total N_2O emissions measured with vented chambers over the observation period were 88% of the emissions measured with sealed chambers.

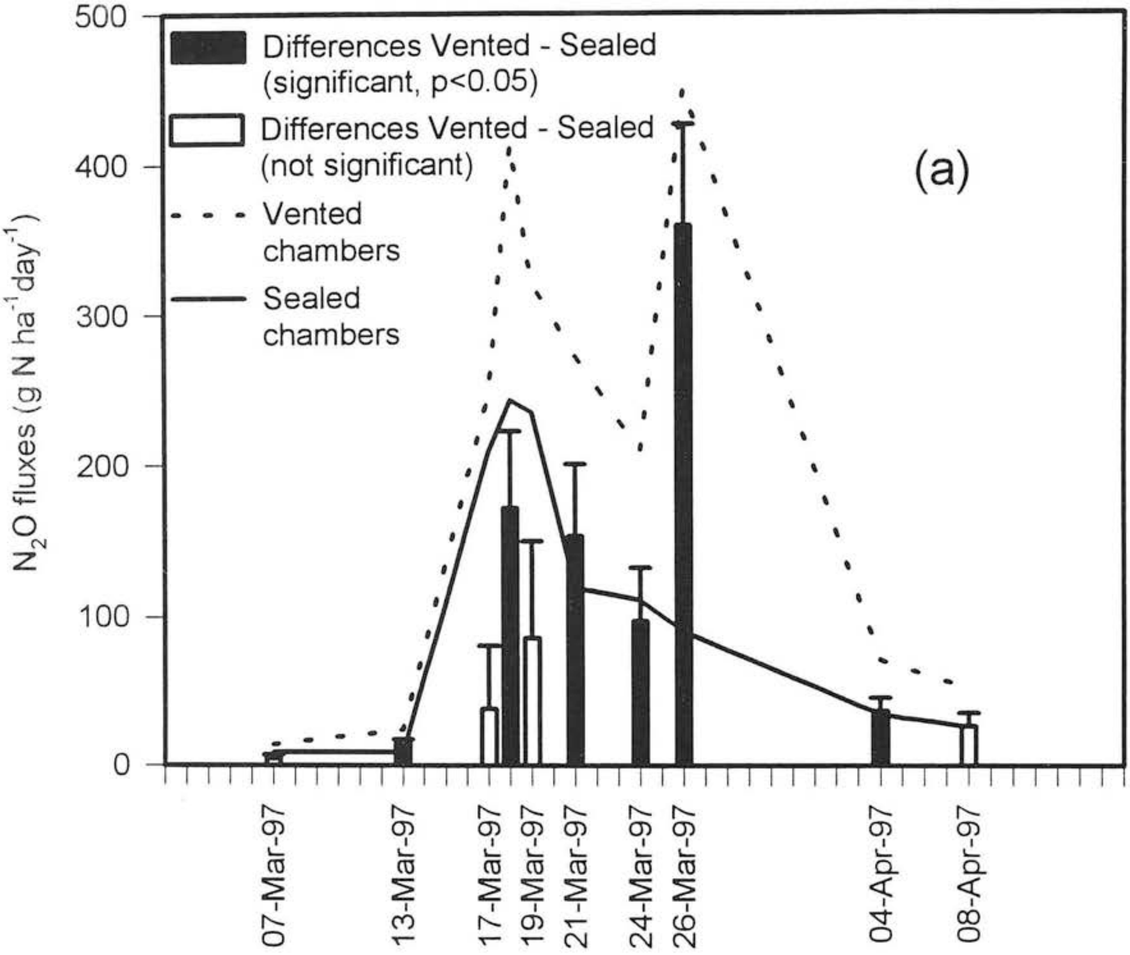


Figure 2a: *N_2O fluxes measured with vented and sealed chambers at a site with a fairly large air permeability, Langhill Farm. The differences between the two chamber designs have been determined on eight chamber bases, each covered consecutively with a vented and a sealed lid. This gave eight distinct values for flux differences due to venting on each day, measurements were made. The means of these differences, ±1 standard error, are shown.*

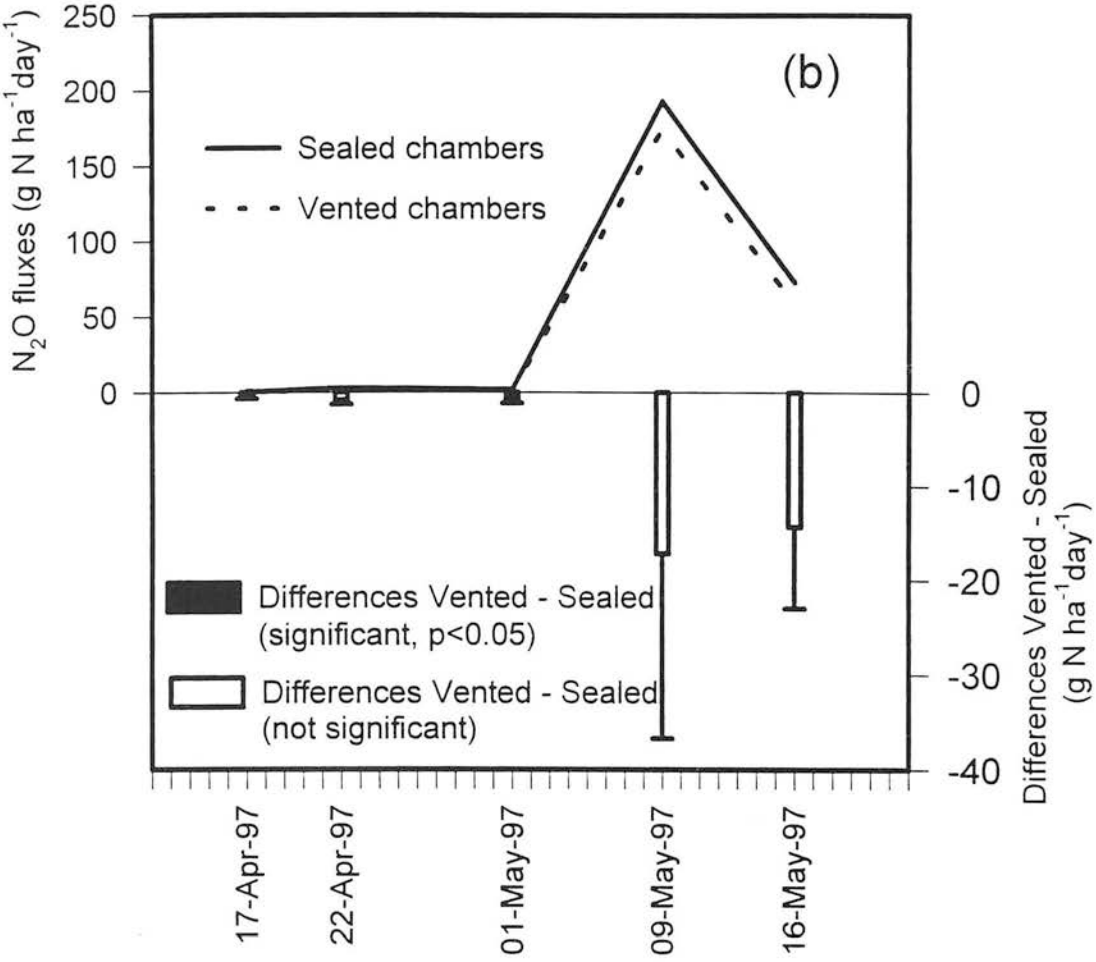


Figure 2b: *N_2O fluxes measured with vented and sealed chambers at a site with smaller air permeability, Glencorse Mains.*

On the lighter, drier and more permeable soil, the scale of observed differences between vented and sealed chambers was much larger than expected for turbulent mixing effects. Results of an earlier study (Kimball & Lemon, 1971) indicated little influence of natural air turbulences upon gas exchange through media of small particle size. Therefore, another effect must have contributed to the observed increase in fluxes under vented conditions. As it is very unlikely that the processes of N_2O formation are affected by venting, the most likely cause of increased N_2O concentrations is the mass flow of air with larger concentrations of N_2O from the soil atmosphere to the interior of the vented chamber, induced by a pressure deficit within the chamber over extended periods.

3.2 Factors affecting soil gas flow

The principles of gas stream flow from soil into large enclosed spaces have been studied in detail in a different context, namely the entry of ^{222}Rn into buildings (Mowris and Fisk, 1988; Nazaroff, 1992; Riley *et al.*, 1996). Stating that a small depressurization is sufficient to drive soil gas through cracks in the floor, Nazaroff (1992) concluded that advective entry of radon-bearing soil gas is the dominant source of indoor radon in most homes in which the concentrations are large. For the same reason, Mowris and Fisk (1988) concluded that exhaust ventilation is ineffective for houses on more permeable soils, unless other measures are taken. When the drop in pressure inside a house below outside atmospheric pressure increased from 4 Pa to 10.9 Pa, the rate at which ^{222}Rn entered almost tripled (Mowris and Fisk, 1988).

Denmead (1979) found that on the much smaller scale of chambers used for measuring trace gases, a pressure deficit of 100 Pa causes a 10-fold increase in measured N_2O emissions. Christensen (1983) observed increased N_2O emissions after reducing the inlet of a chamber from which air was continuously withdrawn and attributed the effect to a depressurization of the chamber, resulting in air being drawn out of the soil. To reduce significant over- or under-estimations in CO_2 emissions with flow-through chambers, Fang & Moncrieff (1996) developed a chamber operating at less than 0.1 Pa pressure difference.

To return to the chambers used in this study, small depressurizations are likely to have been caused by wind blowing over the open end of the vent pipe (Venturi effect). In the context of wetland aeration, this effect has already been found to drive the convective flow of air through hollow, dried and broken stems of *Phragmites australis* (Armstrong *et al.*, 1991).

The pressure of a flowing fluid, a, is related to the density, ρ, and velocity, V, by

$$a = 0.5\rho V^2 . \tag{1}$$

If this equation is applied to the vented chambers, where the velocity of air at the upper end of the vent tube is the wind speed, V_1, and the velocity at the end of the tube inside the chamber is V_2, which is also that at the ground surface outside the chamber and equals zero, then the pressure difference (Δp) between ambient and chamber atmosphere is given by

$$\begin{aligned}\Delta p &= a_2 - a_1 \\ &= 0.5\rho V_2^2 - 0.5\rho V_1^2 \\ &= 0.5\rho\,(V_2^2 - V_1^2).\end{aligned} \tag{2}$$

For $V_2 = 0$ and $\rho = 1.2$ kg m^{-3}, and with V_1 in m s^{-1}, then

$$\Delta \mathrm{p} = 0.6V_1^2 \tag{3}$$

in Pa.

For a steady wind of 2 m s^{-1}, this gives a pressure deficit inside the chamber of 2.4 Pa; for a wind speed of 4 m s^{-1} the deficit is already 9.6 Pa and so on. Because of this sensitivity to wind speed, and the dependence of wind speed on the height above the surface, the height of the vent tube is important. The wind speed given in Table 1 for a height of 2 m has to be divided by 2 to get the approximate wind speed at the height of the vent tube (25 cm) (Vitkevich, 1960).

The order of magnitude of the quantity of soil gas which is moved due to pressure differences is described by Darcy's equation (Kirkham, 1946):

$$q_v = (K\,\eta^{-1})\,(\Delta p\,\Delta L^{-1}), \quad (4)$$

where q_v is the volumetric flow rate per unit cross section, K is the air permeability, η is the viscosity of air, Δp is the pressure difference and ΔL is the path length.

3.3 *Laboratory experiments*

To test the assumptions made above about depressurization and resultant mass flow, the small chamber in the laboratory was first used with the micromanometer. Good agreement was obtained between predicted and measured pressure differences between the inside and outside of the chamber over a range of wind velocities from 0.8 to 2.0 m s^{-1} (Figure 3).

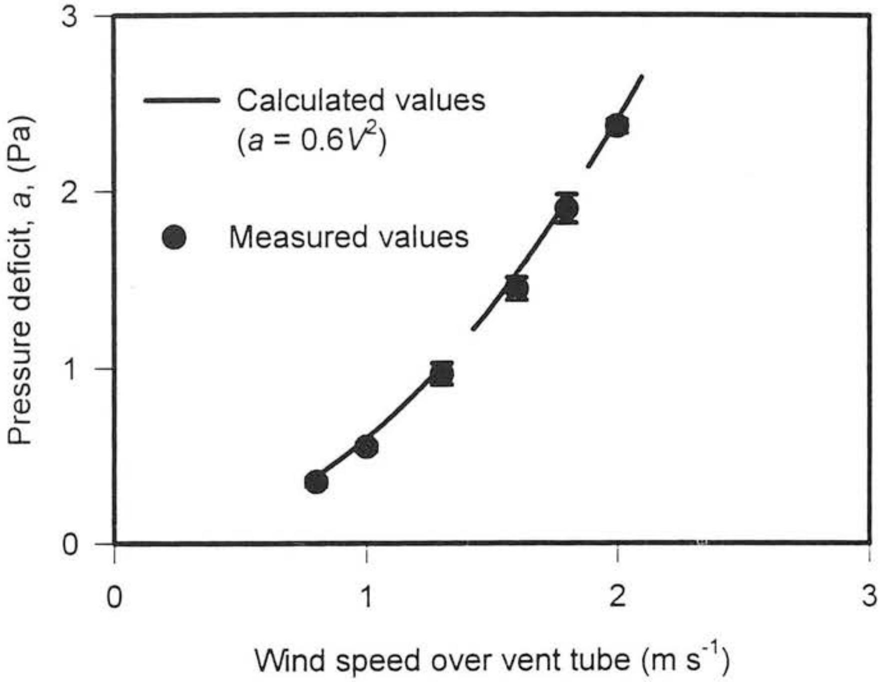


Figure 3: *Comparison of predicted and measured pressure deficits inside a small vented chamber at different wind speeds above the vent tube (measured values are the mean of 6 replications; error bars indicate ±1 standard error).*

These are not short-lived pressure deficits resulting from pressure waves caused by wind, as mentioned by Kimball and Lemon (1971), but continuous pressure differences which can be maintained only by a steady removal of air from the chamber, caused by the Venturi effect (Sabersky *et al.*, 1999). Following this, the chamber with the vent tube transformed into a flow meter was used to determine the flow rate of air out of the chamber. The electric fan was moved towards the chamber until the indicator in the vent was in a floating position (i.e. 1.3 ml s^{-1} flow rate). The wind speed measured above the tube was 3 m s^{-1} under these conditions. To verify the equations given above for this system, the average path length of soil air was assumed to be the length of a half-circle with a radius half the radius of the chamber (i.e. 7.8 cm). For air permeability, values of 10^{-6} cm^2 and 10^{-7} cm^2 were used. The first is for uniform, medium sand, the second for clean, well-graded sand and gravel (Nazaroff, 1992). The permeability of the sand used (a mixture of 10% coarse sand, 84% medium sand, 6% fine sand and silt) was probably between those two values. The calculated flow rates according to above equations (3, 4) were 0.32 ml s^{-1} and 3.2 ml s^{-1} for air permeability values of 10^{-6} cm^2 and 10^{-7} cm^2 respectively. The observed flow rate of 1.3 ml s^{-1} was thus well within the range of the theoretical prediction.

3.4 Calculated effect of wind in the field

For the chambers used in the field experiments, the effect of wind speed at vent height and air permeability on the flow rate of air from the soil into the chamber is shown in Figure 4. The isarithms of flow rate have been calculated for a chamber volume of 16.3 litres and an area of 0.126 m^{-2} with equations 3 and 4, assuming the average path length of air through the soil to be 30 cm. For better visualization, the flow rate is given in chamber volumes (16.3 litres) per 45 min (observation period). The open and closed circles in Figure 4 indicate the wind speed at vent height and the air permeability of the soil on the days measurements were made in the field at the two sites. This shows that on the more permeable soil at Langhill Farm the influx of soil air into the chamber ranged from less than 0.1 to more than 10 chamber volumes during the time of the measurement (45 min). On six out of ten days the inflow of soil air was more than one chamber volume. On the less permeable soil at Glencorse Mains, the inflow of soil air tended to be less and only on one out of five days was more than one chamber volume. This could explain why, on the latter site, vented chambers did not show increased fluxes as a result of venting. The tendency to smaller fluxes with vented chambers, and in one case a significantly smaller average, leads to the conclusion that losses by diffusion through the vent tube had a larger effect than the increase in concentration caused by inflowing soil gas.

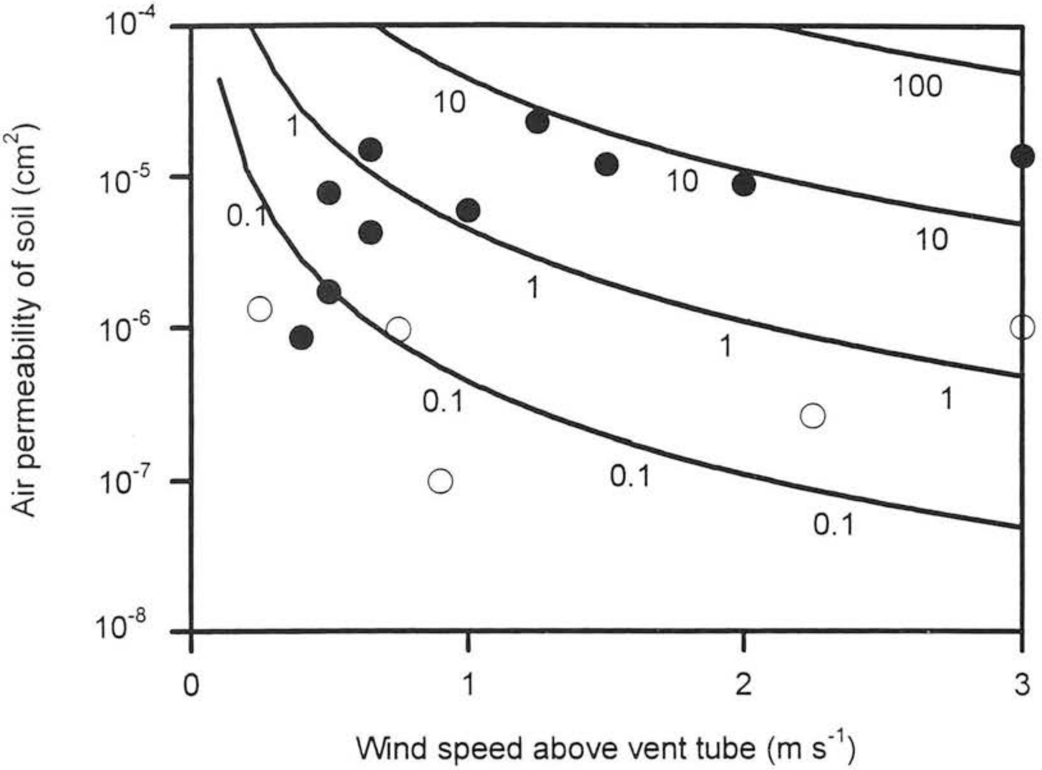


Figure 4: *Calculated effect of wind speed above the vent tube and air permeability of the soil on mass flow of air from the soil into a vented chamber. The isarithms of flow rate are given in chamber volumes per 45 min period for a chamber with an area of 0.126 m^2 and a volume of 16.3 litres. The conditions of wind speed above the vent tube and air permeability at the field sites are indicated for the days on which flux measurements were made (● Langhill, ○ Glencorse Mains).*

The difference in air permeability probably explains most of the observed differences in response to venting on the two sites. There might also have been a contribution from another effect. The soil at Glencorse Mains gave significant N_2O fluxes only at WFPS exceeding 60%, whereas, at Langhill, large fluxes were observed even at WFPS values less than 45%. This seems to suggest that, at Glencorse Mains, N_2O was produced predominantly when aeration was restricted and NO_3^- denitrified. This is likely to happen in the centres of larger soil aggregates (Sierra *et al.*, 1995; Smith, 1980). By definition, these locations are also the most likely to be by-passed by soil air flow, which tends to occur predominantly through the larger pores because of exponentially decreasing resistance to flow with increasing pore diameter. On the soil at Langhill Farm, which contains more organic matter, N_2O production is likely to be less concentrated in poorly aerated aggregate centres but rather where available carbon is concentrated and where there is much biological activity and therefore demand for oxygen. It is also possible that a larger part of the emissions came from nitrification, which happens where the soil is well aerated. Thus, apart from being more permeable and more susceptible to gas movements in bulk, than the soil at Glencoarse Mains, this soil may in addition be more likely to produce N_2O in the aerated parts of its structure.

4 Conclusions

The error caused by isolating sealed static chambers from ambient pressure fluctuations is considered to be fairly small under conditions found in most agricultural soils. By adding a vent tube to the chamber, as commonly practised, this error might be reduced, but new and more important sources of error are likely to be introduced. One such source is the depressurization of the chamber by the Venturi effect and subsequent flushing of soil air into the atmosphere in the chamber. On light and permeable soils this effect can lead to significant overestimation of fluxes. A second, smaller, source of error is diffusion losses through the vent tube. This can induce an underestimation of fluxes where soils have low air permeability and slow inflow of soil air with large concentrations of N_2O into the chamber. The results of this study therefore lead to the conclusion that the potentially beneficial effect of venting static chambers is outweighed by the disadvantages. Sealed static chambers should be preferred in trace gas measurements.

Note added after this chapter had been published. Studying dynamic chambers, Lund *et al.* (1999) found that over-pressurising the inside of a chamber by 0.5 Pa, as compared to the outside atmosphere, could lead to a reduction in measured CO_2 flux of up to 70%. This was related to a downward flow of air through the soil air-filled pore space.

CHAPTER III

An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere

(A version of this Chapter will be published in the *European Journal of Soil Science*, March 2000, **50**)

1 Introduction

In the previous chapter (II) it was concluded that sealed chambers were preferable to vented ones because they are not subject to the potentially serious artefacts caused by depressurisation. This means, the possible minor artefact of suppressing ambient pressure fluctuations probably has to be accepted when using chambers for the measurement of trace gas exchange between soil and the atmosphere. Another artefact that needs to be considered in closed chambers is their effect on the concentration gradient between the soil gas phase and the atmosphere. This issue has been approached theoretically in a number of published models that predict the accumulation of trace gases in closed chambers. These models include the assumption that there is a constant concentration of the target gas either at the interface between the soil and the atmosphere (Gao and Yates, 1998), or at a plane within the soil profile (Hutchinson and Mosier, 1981; Healy *et al.*, 1996) during the chamber closure period. However, Denmead (1979) had referred earlier to a 'readjustment of the N_2O concentration in the soil air whenever the N_2O concentration in the chamber air changes from ambient'. These models conclude that the increase in concentration in the chamber leads to a decrease in the relative difference in concentration between the soil air near the surface and the atmosphere in the chamber, and therefore a decrease in the flux intensity with time should be observed. The corollary of this is that the graph of chamber concentration against time will be non-linear, and thus samples need to be taken at several time intervals during closure to calculate the flux.

In contrast, there is considerable direct experimental evidence from studies on a range of arable, grassland and forest soils of linear increases in gas concentration with time, after chamber closure. Matthias *et al.* (1980) found that this was the typical pattern observed for N_2O in arable soil in Iowa. Yamulki and Jarvis (1999) report linear increases in a study on grassland. The same was observed by Thomson (1998) in studies using monoliths of arable, grassland and forest soil. For radon (^{222}Rn), accumulations in a chamber were found to be linear over 6 hours (Dörr and Münnich, 1990).

The assumption in current models that the concentration of the target gas in the soil gas phase is constant at a certain depth for the limited time of chamber deployment has apparently never been tested in an experiment with natural soil. Nay *et al.* (1994) tested closed chambers with a model system consisting of a chemical source supplying CO_2 into a footspace covered by polyurethane foam to simulate a porous soil layer. The CO_2 diffused through the foam into different types of chambers placed on the top surface. However, the authors regulated the CO_2 concentration in the footspace to keep it constant; thus the experiment could not show what happens when constant gas production occurs *in situ*.

In this chapter, a different approach to the problem is proposed, which is based only on the assumption of a constant production rate of the target gas within the soil profile. This assumption is present also in previous models. However, it may not have been always built into the model simulations. The main conclusion from the modelling presented here has been compared with measurements made in a simple laboratory experiment, using a system comprising a soil monolith and flux chamber similar to that described by Thomson. *et al.* (1997), but on a smaller scale.

2 Materials and methods

2.1 Model

The model developed here is based on the main assumption of a constant production of the target gas at a certain depth within the soil profile. Further assumptions are made, which are unlikely to affect the model in principle, but which are a simplification of the complex spatial inhomogeneity of natural soils. Thus, production and consumption are considered to occur in the same location and to be independent of the surrounding target gas concentration. This allows net production to be related to a certain depth only. Also, the model soil is assumed to have a homogeneously distributed air-filled porosity (and thus the same diffusivity) at all depths, which is also constant throughout the period of interest. It is also assumed that the gas emitted from the soil surface mixes readily in the atmosphere, or in the headspace of the chamber. N_2O is used as an example of a target gas, which has a diffusivity in air of 1.43×10^{-5} m^2 s^{-1} (Pritchard and Currie, 1982). Diffusivity is calculated in the soil in a way similar to that of Healy *et al.* (1996) as $D_{air} \times \theta \times \theta^{1/3}$, where θ is the air-filled porosity of the soil. The model treats the different soil depth as cells of 1 cm height. The lowest cell, at 30 cm depth, is assumed to be sealed at the bottom by an impermeable layer. The uppermost cell represents the atmosphere. This cell has an indefinite height when no chamber is in place, but it has the same height as the chamber when a situation with the closed chamber in place is simulated. Gas exchange occurs between the cells according to Fick's law of diffusion:

$$J = -D\frac{c_b - c_a}{d}, \qquad (1)$$

where J is the flux, D is the diffusion coefficient, c_b is the gas concentration in cell b, c_a is the gas concentration in cell a, and d is the vertical distance between the bottom of cell a and the bottom of cell b.

The gas concentration within a cell was calculated in 6-second time steps as follows:

$$c_i = c_{i-1} + \frac{J_{i-1}A}{V} + c_\mathrm{p}, \tag{2}$$

where c_i is the concentration at time step i, $c_{i\text{-}1}$ is the concentration at the previous time step, c_p is the concentration increase due to gas production within the cell during one time step, J_{i-1} is the net flux resulting from gas diffusion into and out of the cell during the previous time step, A is the area of the horizontal cross-section of the cell, and V is the air volume of the cell.

V can be defined as

$$V = \theta\, hA\ , \tag{3}$$

where θ is the air-filled porosity, and h is the cell height.

Combining Equations (1) to (3), one gets:

$$c_i = c_{i-1} + \frac{-D\dfrac{c_{i-1} - c_{(a)i-1}}{d}A \ + \ D\dfrac{c_{i-1} - c_{(c)i-1}}{d}A}{\theta\ hA} + c_\mathrm{p}, \tag{4}$$

where $c_{(a)\,i\text{-}1}$ is the concentration in neighbouring cell a at time step i-1, and $c_{(c)\,i\text{-}1}$ is the concentration in neighbouring cell c at time step i-1.

In this equation A cancels out, leaving the following equation:

$$c_i = c_{i-1} + \frac{-D\dfrac{c_{i-1} - c_{(a)i-1}}{d} \ + \ D\dfrac{c_{i-1} - c_{(c)i-1}}{d}}{\theta\ h} + c_\mathrm{p}. \tag{5}$$

To test this one-dimensional model first situations were simulated without a chamber and compared them prior to, and at, the steady state indicated by the general form of Equation (1). Then concentration changes with closed chambers of different heights were simulated. Simulations were also made with different values for soil porosity and diffusivity. Initial concentrations were assigned to each cell as expected under steady-state conditions for the particular values of *D*, *J* and source depth, and the changes over a 30-minute interval were simulated. A linear regression was fitted to the chamber concentration over time and the flux into the chamber was calculated as the slope of this regression multiplied by the chamber height. This value was then compared with the total source strength, i.e. the flux under undisturbed conditions.

2.2 *Experiment*

A soil core (24 cm diameter, 13 cm height) with associated plants, encased in a PVC cylinder, was taken from a grassland site at Glencorse Mains, 10 km south of Edinburgh and brought to the laboratory on 16 February 1999. The soil had a clay loam texture (36% sand, 40% silt and 24% clay), an organic matter content of 5.5% and a bulk density of 1.05 g cm^{-3}. It was fertilized the following day with ammonium nitrate at a rate equivalent to 100 kg N ha^{-1} and subjected to three series of measurements on 25 February, 3 March and 8 March 1999. No water lost by evapotranspiration was added during this period, so as to get results for different soil moisture contents. The first series of measurement was made near field capacity.

The plastic cylinder enclosing the core was closed at the base with a cap of the same material, which had been fitted with a soil air sampler consisting of a perforated plastic tube (5 mm internal diameter, 0.45 m length), laid out in a circle and embedded in a 1-cm high layer of medium sand. The sides of the core were sealed to the cylinder with wax to prevent gas movement. The 7 cm of the plastic cylinder protruding above the top of the core acted as a flux chamber that could be closed with a gas-tight plastic lid.

Gas samples from the space below the core, and from the space above the core, were taken at 20-minute intervals and analysed on-line through 0.6 m long, 4 mm diameter Teflon® tubes connected to the automated gas chromatographic analysis system described by Arah et al. (1994). Ambient temperature during the measurements was constant at 20 °C.

3 Results

3.1 Model

The model was capable of reproducing the accumulation of a soil concentration profile when no chamber was in place. The initial concentration in the soil profile was set equal to atmospheric concentration (0.31×10^{-6} m^3 m^{-3}). Soil porosity was set at 20% and D at 1.673×10^{-6} m^2 s^{-1}. Concentrations increased quickly at the beginning and the rate of increase declined as steady state conditions were approached. This general pattern was independent of source strength. However, graphical illustration was clearer when weak sources were used in the simulation; the example shown in Figure 1 is for a constant source of 12 μg N_2O-N m^{-2} h^{-1}, equally distributed between 8 and 13 cm depth.

Examples of simulations of concentration profiles under a closed chamber are shown in Figure 2. Soil conditions were the same as in the previous simulation. This time, however, the atmosphere above the soil was an enclosed headspace with a height of 10 cm (Figure 2a). Concentrations started to increase within the soil profile as soon as the chamber was closed. This increase began with the first 6-second time step and included the layer where the source was located. However, changes below the source became smaller with increasing depth. The increase in chamber concentration was almost linear ($r^2 = 0.9994$). Nevertheless, the flux calculated from the concentration increase within the chamber was only 84% of the source strength. Under certain circumstances, chamber concentrations were found to increase above concentrations in the soil below the source. Such behaviour was found when the source was close to the surface, the soil was highly porous, and the chamber was shallow (5 cm). An example is shown in Figure 2b. Many simulations were run, and it was found that the proportion of the total flux that was measured was independent of the strength and depth of the source. It was also independent of whether the source was concentrated in a shallow layer, or whether it was evenly distributed within a layer several centimetres thick. However, the proportion depended on the air-filled porosity and associated diffusivity, as well as on the height of the chamber.

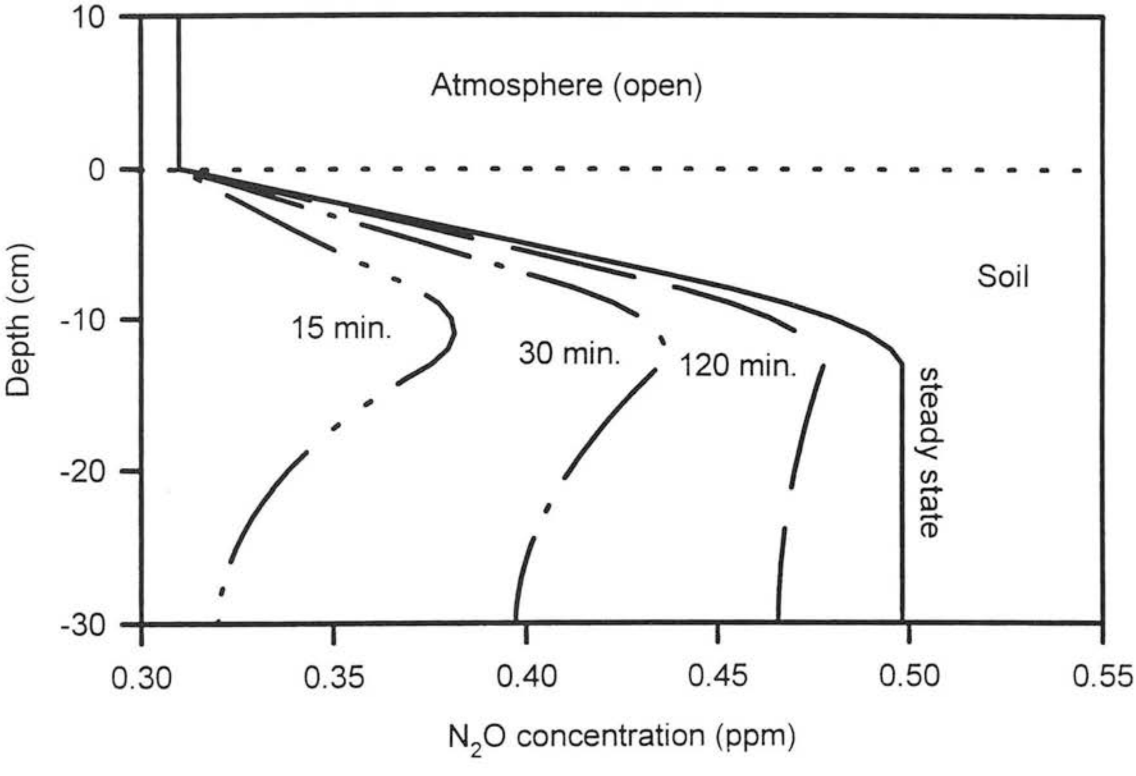


Figure 1: *Development of an N_2O concentration profile within a soil of 20% air porosity, diffusivity of 1.673×10^{-6} m^2 s^{-1}, and no initially enhanced N_2O concentrations. The soil surface is open to the atmosphere. The N_2O source forming this profile starts producing at a constant rate at time 0 and is of a total strength of 12 μg N_2O-N m^{-2} h^{-1}. The theoretical steady state concentrations (——) are approached with declining speed. Profiles are shown for 15 min. (— • • — • •), 30 min. (— • — •), and 120 min. (— — —).*

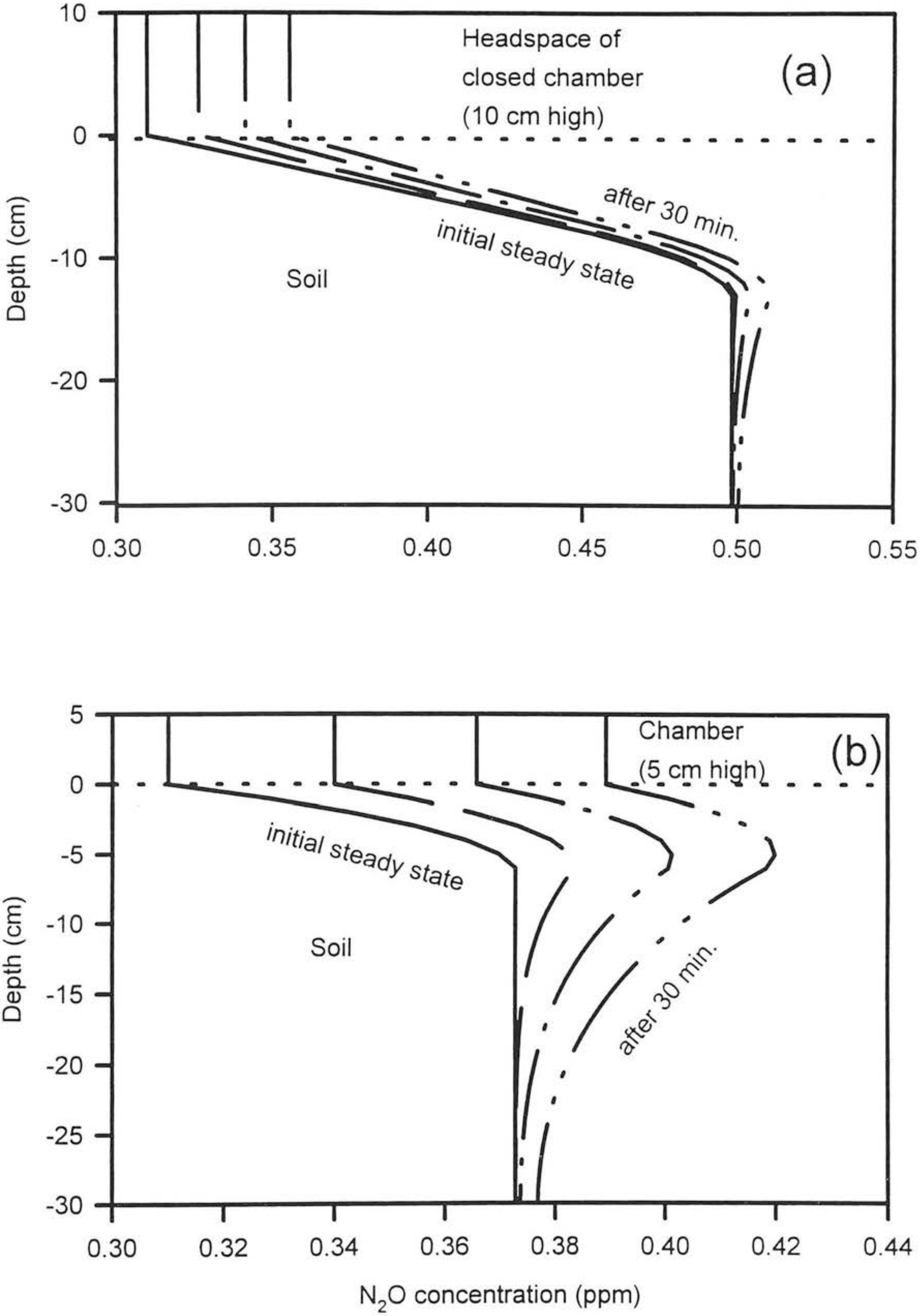


Figure 2: (legend on next page)

Figure 2: *Development of a N_2O concentration profiles in a soil with 20% air porosity, diffusivity of 1.673×10^{-6} m^2 s^{-1}, and initially steady state concentrations at time 0 (——). (a) The N_2O source (12 μg N_2O-N m^{-2} h^{-1}) is evenly distributed between 8 and 13 cm depth and the soil is covered with a 10-cm-high chamber. (b) The N_2O source (12 μg N_2O-N m^{-2} h^{-1}) is evenly distributed between 0 and 5 cm depth and the soil is covered with a 5-cm-high chamber. As concentrations increase within the headspace of the chamber, they also increase within the entire soil profile. Profiles are shown for 10 min. (— — —), 20 min.* (— • — •), *and 30 min.* (— • • — • •) *after chamber closure.*

For gas concentrations, the unit [ppm] (parts per million) is used in this thesis as short-hand for the SI-unit [m^3 m^{-3} x 10^{-6}].

Table 1 shows some results of the simulations. The proportion of the total production rate (J_m) that was represented by the flux into the chamber was found to be between 72% for a 5-cm high chamber on soil with an air-filled porosity of 20%, and 99% for a 30-cm high chamber on a soil with an air-filled porosity of 5%. The concentration increase with time was always close to linear ($r^2 > 0.99$) and became more and more so with increasing height of the chamber and decreasing soil porosity.

Table 1: *Linearity and proportion of total net N_2O production (J_m) measured with chambers of different height and on soils with different air porosity and a total depth of 30 cm.*

θ (%)	D ($m^2 s^{-1} \times 10^{-6}$)	Chamber height (cm)	r^2 (*)	J_m (%)
20	1.673	5	0.9978	72
20	1.673	10	0.9994	84
20	1.673	20	0.9998	92
20	1.673	30	0.9999	94
10	0.664	5	0.9995	86
10	0.664	10	0.9999	93
10	0.664	20	1	96
10	0.664	30	1	97
5	0.264	5	0.9999	93
5	0.264	10	1	97
5	0.264	20	1	98
5	0.264	30	1	99

(*) of linear regression; concentration over time

3.2 Experiment

Emissions were largest, at 388 μg N_2O-N m^{-2} h^{-1}, during the first series of measurements. The concentration in the chamber exceeded 20×10^{-6} m^3 m^{-3} at the end of the closure period (Figure 3a). Successive measurements as the soil dried out gave decreasing values of 67 and 29 μg N_2O-N m^{-2} h^{-1} respectively (Figure 3b, c). The concentration increase in the headspace was found, on all three occasions, to be virtually linear ($r^2 > 0.9983$) over the entire period of closure, which ranged between 200 and 280 minutes. Also, increases in N_2O concentrations were observed below the source of N_2O production in the sand at the bottom of the core. These were less in amplitude and were delayed relative to the changes in the headspace concentration (Figure 3a, b, c). When the soil was relatively dry, the concentrations in the chamber increased until they exceeded concentrations in the soil at the bottom of the core (Figure 3c).

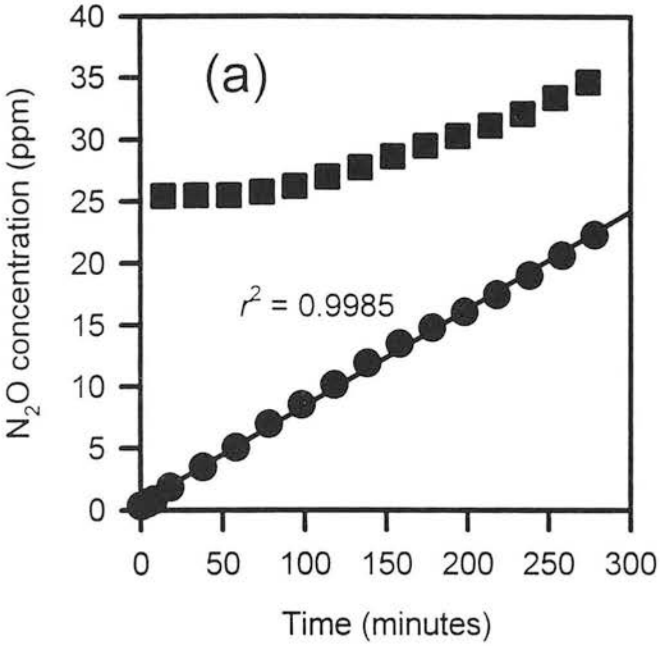
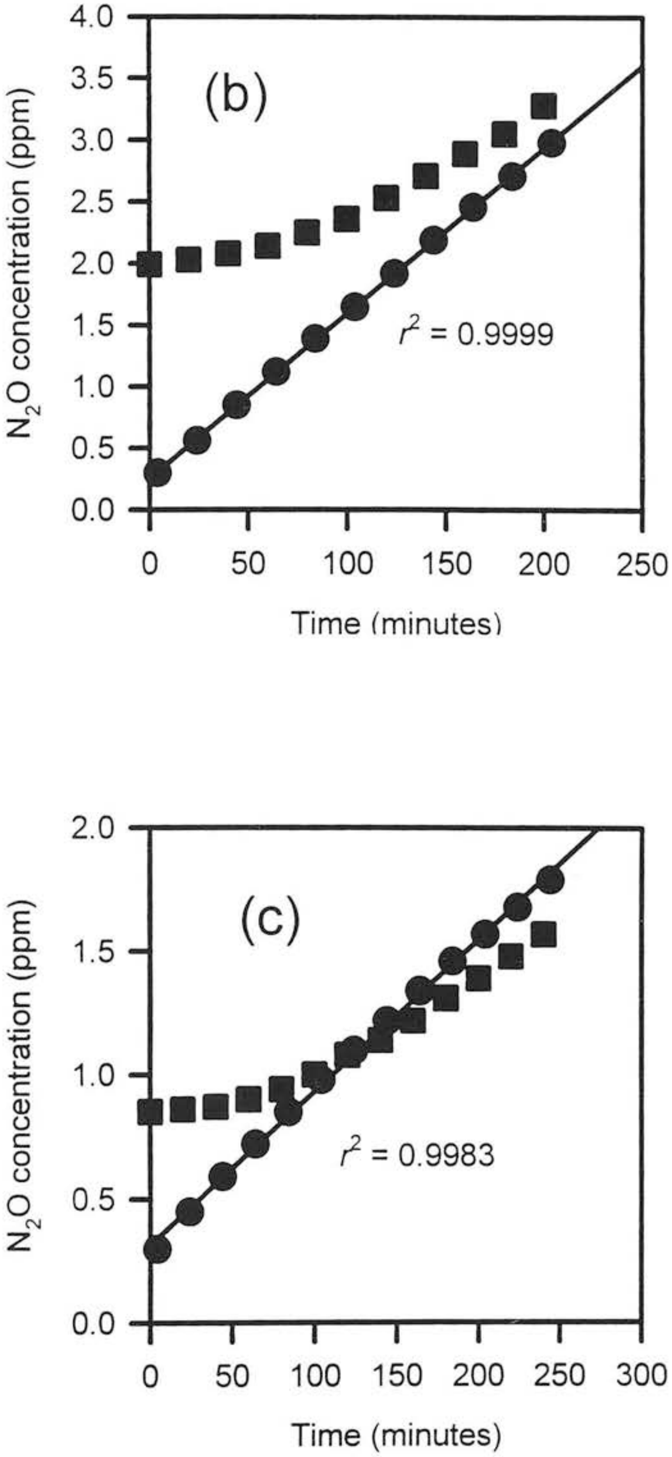


Figure 3a: *Measured changes in N_2O concentrations below the source of N_2O production (–) and in the headspace (●) of soil core for a wet core with low air-filled porosity. A linear regression (continuous line) has been fitted to the headspace concentration over time.*



Figures 3b, c: *Measured changes in N_2O concentrations below the source of N_2O production (□) and in the headspace (●) of soil core (b) core at intermediate air-filled porosity; (c) relatively dry soil core. A linear regression (continuous line) has been fitted to the headspace concentration over time.*

4 Discussion

In this modelling approach it was found that soil gas concentrations increased throughout the soil profile as soon as gas exchange between soil and atmosphere was intercepted by a closed chamber. The increases were detectable even after the first time step of the simulation, 6 seconds after closure. The other main outcome of the model simulations was the increase in soil concentrations of the target gas at a depth greater than the source. This was supported by the experimental measurements. These results indicate that the presented approach offers advantages over the concept of a constant concentration, or a plane of constant concentration, of a target gas in the soil profile as assumed in previous models (Gao and Yates, 1998; Hutchinson and Mosier, 1981; Healy *et al.*, 1996).

It was found that the concentration increases in the chamber headspace were either linear or very nearly so. Even the largest departure from linearity ($r^2 = 0.9978$) found for the shallow chamber (5 cm) on the soil with 20% air-filled porosity was so small that it would be difficult to detect under field conditions by repeated sampling during the closure. Nevertheless, fluxes calculated from the increase in chamber concentrations were always less than the fluxes we expected under undisturbed conditions. This was because a proportion of the gas produced was stored within the soil profile rather than being emitted at the surface, as would be expected under undisturbed equilibrium conditions between gas production and gas emission. The proportion of flux missed is directly related ($r^2 = 0.99$) to the ratio of the total air volume within the soil profile underneath the chamber to the chamber's volume (Figure 4). This suggests that corrections could be made to measured fluxes, if the total soil air volume is known. The under-estimation of the flux can be calculated approximately from the regression in Figure 4 as

$$J_{\mathrm{e}} = 0.24 \frac{V_s}{V_c} \tag{6}$$

where J_e is the proportion of the flux that is missed, V_s is the total soil air volume underneath the chamber, and V_c is the chamber's volume.

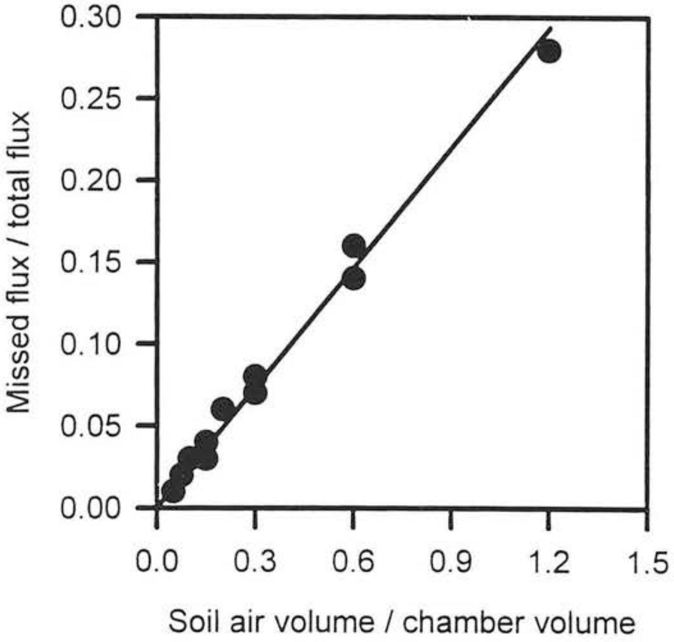


Figure 4: *Relationship between under-estimation of true flux and the ratio of total soil air volume to chamber volume, based on the results shown in Table 1. A linear regression has been fitted, with the intercept set at 0; the equation of the line is* $y = 0.24x$, *where* y *is the proportion of the flux missed and* x *is the ratio of soil air volume to chamber volume (*r^2 *for the regression is 0.9901).*

The fact that chamber concentrations were found to increase in excess of concentrations in the soil at the bottom of the core (Figure 3c) suggests that the source of N_2O must have been close to the surface. This accords with the results of Luo *et al.* (1998), who found N_2O production in pasture soil to occur mainly in the top 5 cm. Since the exact depth of N_2O production within the soil core was not determined, it would need further assumptions to compare model predictions and experimental findings in detail. This would doubtless over-stretch the outcome of the experiment, which was designed in such a way that it could be used only to test in principle the conclusions of the model.

In spite of the presented observations (and the others cited in the Introduction) of virtually linear increases in chamber concentration, non-linear accumulations have clearly been observed in some studies, and these need an alternative explanation. If the apparent emission rate of N_2O or CO_2, for example, increases with time after closure, this is most probably due to the soil's warming (Denmead, 1979) and a consequent increase in microbial activity. If the apparent rate decreases with time the possible explanations include soil cooling (Denmead, 1979), and increased diffusive escape from the chamber to the outside atmosphere, as the concentration difference increases. There are three likely pathways for such an escape: a leak in the chamber itself; an inadequate seal between the chamber wall and the soil; and diffusion through the topsoil and under the chamber wall (which is commonly inserted to ca 5 cm depth). The first two pathways should always be avoidable with sufficient care; the third is unlikely to be important in moist soils of medium to fine texture, but if the bottom of the chamber wall is within a dry sandy horizon of high diffusivity, a significant loss could occur by diffusion through the soil. Anthony *et al.* (1995) reported that half of all chamber measurements in a large study on a 'very sandy soil' in Texas showed an emission rate that decreased in the second sampling interval after closure, compared with the first; loss through the soil could well have been responsible. Where such soil conditions prevail, it is desirable to make the chamber as large in area as possible, to maximise the ratio of emitting surface to wall circumference, and to maximise the height above the soil surface (consistent with analytical sensitivity), to avoid an excessive concentration difference between the chamber and the outside atmosphere. In any study it is prudent to carry out checks on linearity of gas accumulation in the local conditions before deciding whether single sampling at the end of a closure period will suffice, or whether multiple sampling times are needed within every closure period.

Finally, it should be noted that in relation to the effects of chamber closure on gas concentrations in the soil profile there is a major difference, which Gao and Yates (1998) ignored, between, on the one hand, those gases that are produced *in situ* (e.g. CO_2, N_2O, ^{222}Rn) and, on the other, a gas such as the fumigant methyl bromide which is injected into the soil in a single operation (Gao and Yates 1998) . For the latter, the concentration may change little over a short period when emissions are being measured with a closed chamber, but as explained above this is not true for the other gases.

5 Conclusions

There is a direct feedback effect of the headspace concentration in a closed chamber on the concentration at the source of gas production within the soil beneath it. This feedback is immediate and it is desirable to take account of it, rather than assume a constant soil gas concentration during the period of chamber deployment. The increase in soil gas concentration is also responsible for the departure from linearity of the flux increase under a closed chamber being much less than previously predicted. However, some proportion of the produced gas is stored within the soil profile while a closed chamber is in place. This leads to an under-estimation of the real fluxes by the closed-chamber technique. One way to minimize this error is to maximize the chamber's height, provided there is sufficient analytical sensitivity to cope with the consequent dilution of the emitted gas. Another possibility is to estimate total volume of air in the soil underneath the chamber and to calculate the proportion of missed flux. Taking account of under-estimation of fluxes is especially necessary on deep soils with a large air-filled porosity.

CHAPTER IV

Predicting N_2O emissions from agricultural land through related soil parameters

(A version of this chapter is in press in Global Change Biology)

1 Introduction

The atmospheric concentration of nitrous oxide (N_2O) has been increasing over the last few decades at an accelerated rate. Its contribution to radiative forcing (Prather *et al.* 1995) and its influence on atmospheric ozone (Crutzen 1974) have raised interest in evaluating its sources and sinks. Under the 1997 Kyoto Protocol of the United Nations Framework Convention on Climate Change, over 170 nations agreed to develop, periodically update and publish national inventories of anthropogenic emissions of several greenhouse gases, including N_2O, and the industrialised countries agreed to reduce future emissions below 1990 levels.

The current IPCC "Phase II methodology" for producing national inventories of N_2O from agricultural land assumes a default emission factor of 1.25% of all the nitrogen added to the soil (IPCC 1997), based on a study by Bouwman (1996). This procedure does not account for climate, management practice, irrigation, soils, crop types and other variables that have been found to influence N_2O emissions. For example, a 20-fold variation in annual N_2O emissions between 1992 and 1998 has been reported for one grassland site in Scotland, despite it having received similar amounts of N each year (Dobbie *et al.* 1999). Efforts are currently underway to develop improved methodologies for estimating N_2O emissions from agricultural soils, taking account of regional and seasonal variations (Smith *et al.* 1999).

These efforts will inevitably involve modelling approaches. One initiative in this direction is the US Trace Gas Network (TRAGNET), which recently supported the comparison of four existing process models (Frolking *et al.* 1998). However, because of the nature and relatively large amount of required input data, it is questionable whether such models will be applied on a large scale or in many countries. Another approach is the use of empirical models. In terms of complexity, these are somewhere between the current IPCC emission factor approach, and the complex process models described by Frolking *et al.* (1998). In a process model, relevant soil parameters would be predicted and the predictions used in a submodel for calculating N_2O fluxes. An empirical model may be considered to be such a submodel, but one that is based on the direct measurement of relevant soil parameters. Direct measurement of soil parameters instead of their prediction makes the empirical model less complex. Nevertheless, an empirical submodel can still be used as part of a more complex process model.

Developing a number of different empirical models for specific regions is probably superior to a single general or global approach. To take one example, Flessa *et al.* (1995) found that in southern Germany about half of the annual N_2O emissions occurred during freeze-thaw cycles in winter. This feature was not reproduced by any of the process models used in the first TRAGNET exercise (Frolking *et al.* 1998), whereas in a regional, empirical model such a characteristic would probably have been represented, allowing for a more accurate emission estimate. Another specifically regional factor is the nature of the soil microbial population. For an English soil, for example, the lower threshold for denitrification, the main process of N_2O production in soils, has been found to be just above 5°C, whereas for a Queensland soil it was somewhere between 10°C and 15°C (Powlson *et al.* 1988). Apart from these known specific examples, there are possibly many other factors that strongly influence N_2O emissions from soils in certain regions or agricultural systems, of which we are not yet aware. Therefore, it seems justified to continue the development of more empirical models, based on identified main driving variables for particular systems before eventually aiming at the creation of a universally applicable model, covering all possible conditions.

In the present study, the development and verification of such an empirical model is described for N_2O emissions from intensive agricultural systems in a temperate climate. It has been developed on the basis of a two-year data set from one grassland site in Scotland, and tested against data from the same site, from other grassland sites elsewhere in Scotland, and from small grain and vegetable crops in the same region.

2 Model development

Most of the N_2O emission and soil data used in this study were collected in the context of other studies between 1992 and 1998 (Clayton *et al.* 1997; Dobbie *et al.* 1999) on different grassland and arable sites in Scotland. Data from one grassland site (Glencorse Mains) in 1992 and 1993 were analysed in order to derive criteria for the determination of emission rates based on measured soil parameters. These criteria were then applied to independent data-sets obtained in 1996-98, from the same field site, from two other grassland sites differing in soil type, and from sites with four different arable crops. Each data-set covers either one or two cropping seasons (Table 1). As baseline data, a part of the data was used that has been presented earlier by Clayton *et al.* (1997) in their study on the effect of five different types of fertiliser on N_2O emissions in 1992-94. To enable comparisons to be made with later sets of data, only the results for two of the fertiliser treatments (urea and ammonium nitrate) were used in the present study. These are also the most common types of commercial N fertiliser in use in the UK, and were the only ones used in the later experiments. It was recognised that there is a conflict between the pursuit of detail and the number of data points available, as well as the error attached to each of these points. For example, the average values for N_2O emission rates were calculated from six replicate chambers per fertiliser treatment. Coefficients of variation of flux measurements with the chambers used in these studies are of the order of 70-80 % (Dobbie *et al.* 1999); therefore, to get a more robust set of data, it was decided to pool both fertiliser treatments together by averaging their mean values. This was not only done for the N_2O values but also for the values for soil water content. Soil NH_4^+-N and NO_3^--N were pooled together to give a total topsoil mineral N content, $N_{mineral}$, and the latter values were also averaged over the two fertiliser treatments.

Table 1: *Crops and field sites from which data for N_2O modelling were obtained*

Crop/Site/Grid reference	Year	Soil Series	Soil Texture
Grassland			
Glencorse Mains (Edinburgh area), NT 238628	1992-93, 1997-98	Winton Series; imperfectly drained gley	clay loam
SE Scotland (E. Lothian), NT 598846	1997, 1998	Kilmarnock Series; imperfectly drained brown forest soil	sandy loam
SW Scotland (Ayrshire), NS 383225	1997, 1998	Bargour Series; imperfectly drained brown forest soil	sandy clay loam
Arable			
Winter wheat, Bush Estate (Edinburgh area), NT 247648	1996	unnamed alluvium	loam
Winter wheat, Bush Estate, NT 253649	1997	Easter Bush Series; imperfectly drained brown forest soil	sandy clay loam
Potatoes, Bush Estate, NT 247650	1996	unnamed alluvium	loam
Potatoes, Bush Estate, NT 248656	1997	Darvel Series; freely drained brown forest soil	sandy clay loam
Broccoli, E. Lothian, NT 532847	1997	Kilmarnock Series; imperfectly drained brown forest soil	sandy loam
Oilseed rape, Bush Estate, NT 246653	1998	Macmerry Series; imperfectly drained brown forest soil	sandy clay loam

The model is basically a boundary line approach. A boundary line describes the upper limit of a response that can be expected over a range of values for a driving parameter when no other parameters are limiting. The principles have been described by Webb (1972). In this model, the "response" is N_2O emission, and the model takes into account as driving parameters soil water-filled pore space (WFPS), soil temperature, and the mineral nitrogen content in the topsoil ($N_{mineral}$). In earlier studies, these three parameters have individually been found to correlate with N_2O emission rates. Initial analysis of these parameters revealed only poor correlation with N_2O emissions, and different parameters were limiting at different times. However, when only the sampling occasions on which two out of these three parameters were apparently not limiting were included, the correlation of the third parameter with N_2O emissions became significant (Smith *et al.* 1998a,b). The conventional method of developing a boundary line model would be to define a function for the boundary line of each parameter and to combine them into one over-all function. This approach departs from the conventional method by using boundary lines to define conditions for lower and upper limits of flux ranges. Instead of a discrete value, a range is defined within which the flux is expected to be. Emissions of N_2O are categorised into "low" (1-10 g), "medium" (10-100 g), and "high" (100-1000 g N_2O-N ha^{-1} day^{-1}) emission ranges. These values are considered to best represent most of the observations in intensive agriculture in Scotland. During most days of the year, emissions tend to be within the "low" range, increasing to "medium" or "high" only after fertiliser applications, depending on temperature or WFPS limitations.

While a low mineral N content is generally associated with a small N_2O flux, large mineral N contents can result in large fluxes, if other factors are not limiting. It has been found that N_2O flux tends to be small, as long as NO_3^--N concentrations remain less than 5 mg kg^{-1} soil (Ryden 1983; Goulding *et al.* 1993). However, at higher mineral N concentrations, for example after fertiliser application, other factors play a greater part in controlling the N_2O flux (de Klein and van Logtestijn 1996). To determine the threshold above which $N_{mineral}$ is no longer limiting, a scatter plot of

N_2O against $N_{mineral}$ was made for the pooled baseline data (Fig. 1). It indicated that below 10 mg $N_{mineral}$ kg^{-1} soil, N_2O fluxes are in the "low" range (< 10g N_2O-N ha^{-1} day^{-1}), whereas above 10 mg kg^{-1} $N_{mineral}$ no longer seems to be limiting.

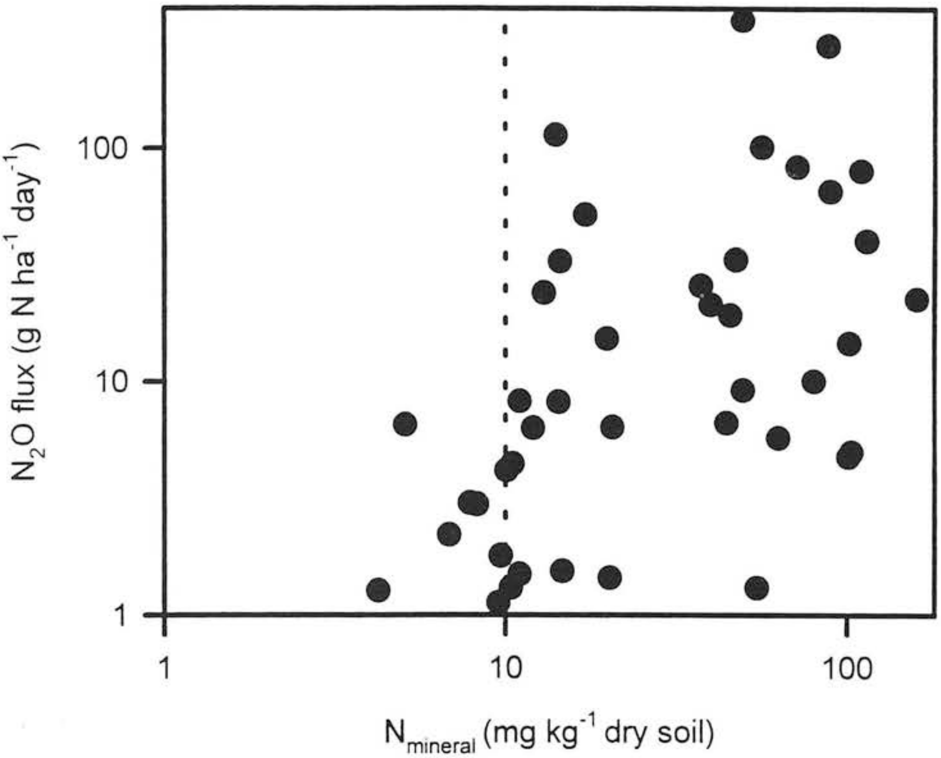


Figure 1: *Determination of threshold value (indicated by vertical dotted line) below which $N_{mineral}$ limits N_2O flux to values <10 g N_2O-N ha^{-1} day^{-1}.*

To evaluate the limiting conditions for all data with $N_{mineral}$ values above 10 mg kg^{-1} soil, they were sorted them into the three N_2O flux ranges (1-10, 10-100 and 100-1000 g N ha^{-1} day^{-1}). In Fig. 2, WFPS is plotted against soil temperature, using different symbols for each flux range.

Lower boundary lines of WFPS/soil temperature combinations for the upper flux ranges were determined by linking the points with the lowest WFPS/soil temperature combinations of each flux range. The boundary line below which N_2O flux is limited to values below 10 g N_2O-N ha^{-1} day^{-1} is given by

$$[\% \text{ WFPS}] + 2\,[\text{temp in } ^{\circ}\text{C}] = 90; \qquad (1)$$

and the boundary line for N_2O flux to exceed 100 g N_2O-N ha^{-1} day^{-1} is given by

$$[\% \text{ WFPS}] + 2\,[\text{temp in } ^{\circ}\text{C}] = 105. \qquad (2)$$

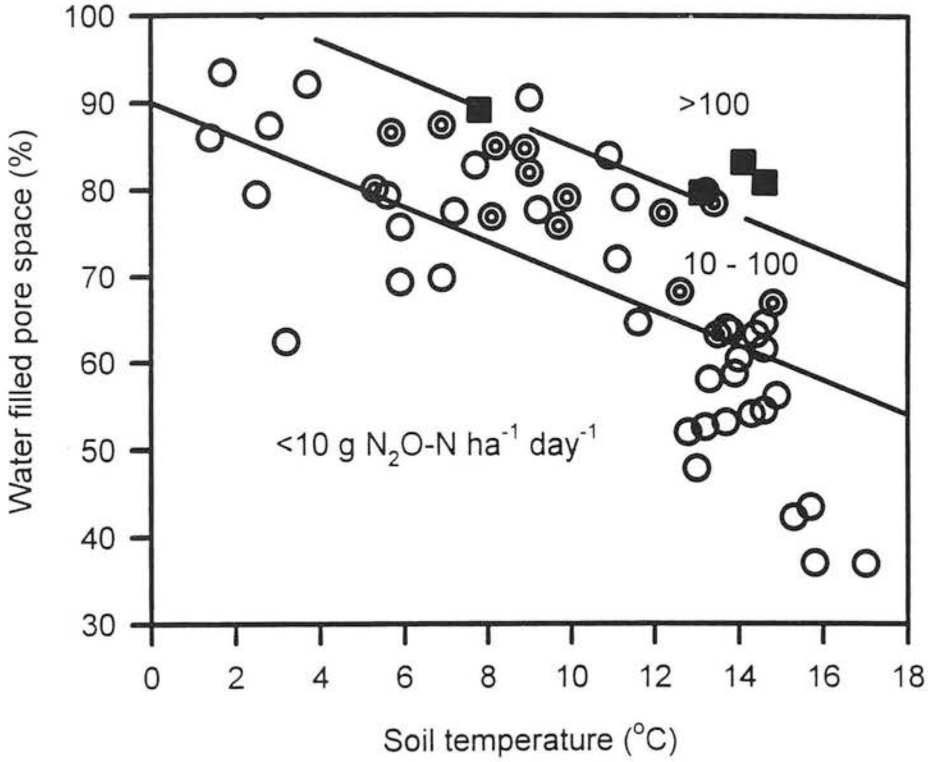


Figure 2: *Defining lower limits to WFPS and soil temperature conditions, below which N_2O flux is limited to values <10 (continuous line) or <100 g N_2O-N ha^{-1} day^{-1} (dashed line). Symbols indicate WFPS/soil temperature combinations at which observed N_2O flux was <10 (O), 10-100 (⊙), and >100 g N_2O-N ha^{-1} day^{-1} (□), when $N_{mineral}$ was not limiting.*

In accordance with Powlson *et al.* (1988), temperatures below 5°C were assumed to limit N_2O flux to values in the "low" range. Therefore, the criteria established for the three flux ranges are as given in Table 2. In all the following discussion, the background emission is considered to be 1 g N_2O-N ha^{-1} day^{-1}, and the maximum emission is considered to be 1000 g N_2O-N ha^{-1} day^{-1}.

To validate the model, a comparison was made between the directly measured N_2O emissions at the Glencorse mains site with model predictions (Fig. 3). These predictions (shown as vertical bars in Fig 3) were obtained by applying the criteria described above to directly measured values of $N_{mineral}$, WFPS, and soil temperature at the site. Total N_2O emissions per season were calculated by integrating all data obtained on those dates when all the other parameters were measured, over a particular season. Values for days without such measurements were derived by linear interpolation between neighbouring points. To estimate the total seasonal emission from the model, geometric means of the predicted flux ranges were used, and again linear interpolation between successive values was used (Fig 3), followed by integration under the curve.

Table 2: *Criteria for prediction of N_2O flux ranges*

Flux range (g N_2O-N ha^{-1} day^{-1})	$N_{mineral}$ (mg kg^{-1} soil)	Soil temp. (°C)		[% WFPS] + 2 [temp in °C] (dimensionless value)
1-10	< 10	< 5	and/or	< 90
10-100	> 10	> 5	and	90-105
100-1000	> 10	> 5	and	> 105

WFPS: soil water-filled pore space

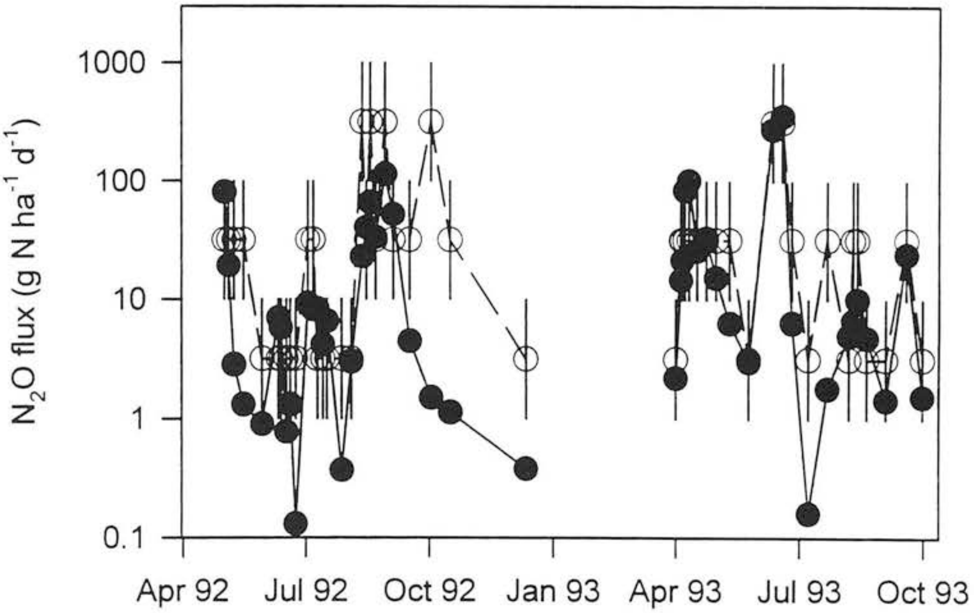


Figure 3: *Measured and predicted N_2O fluxes at the grassland site at Glencorse Mains in 1992 and 1993. Vertical bars indicate the predicted flux range, open circles the corresponding log-mean values, and solid circles the directly measured values.*

The predicted and measured emissions for the period of observation in 1992 are shown in Table 3. The predicted value was much greater than that estimated from integration of the measured values shown in Fig. 3. The latter agreed well, however, with the estimate based on integration of all the flux measurements, including those made when soil mineral N etc were not determined (data of Clayton *et al.* 1997) (Table 1). Much of the discrepancy between predicted and measured fluxes related to results late in the season, when warm, wet soil conditions and high mineral N content led to predicted flux levels that were much higher than those observed. It was noted that the proportion of the soil mineral N occurring as nitrate during this period was low. (This aspect is considered further in the Discussion section below.)

The agreement between predicted and corresponding measured seasonal fluxes was much closer for the 1993 data (Table 3), although the measured value was 70% higher than the integrated value obtained from all flux measurements (Table 3; data of Clayton *et al.* 1997). More than half of the overestimation resulted from interpolation over a period of just over 2 weeks without measurements of soil mineral N etc, prior to the June fertilisation. The implications of this for the modelling approach are considered in the Discussion below.

The procedure described above was then applied to the data sets for other years at Glencorse Mains, and those for the other sites, without modification.

3 Results

3.1 *Grassland sites*

The predictions based on data obtained by Dobbie *et al.* (1999) for Glencorse Mains in 1997 and 1998 are compared in Fig. 4a with the directly measured N_2O data. About half of the direct observations were within the predicted range; the remainder were mainly below it. Thus a large observed emission peak in June and July 1997 decreased faster than predicted, and another peak in spring 1998 was lower than predicted. However, in general, the variation in flux over time was reasonably captured by the model. The total emission given by the model for 1997 was 87% of the flux estimated by integrating those measurements made on dates when other parameters were also measured. The corresponding value was 127 % in 1998. The model gave somewhat greater discrepancies from the seasonal fluxes obtained by integrating over all flux measurements, overestimating the observed emissions by 34 and 63 % in the two years. Model predictions also agreed very closely with the measured fluxes at the site in SE Scotland in 1997 and 1998 (Fig. 4b, Table 3), even though the soil at this site had a lighter texture (sandy loam) than at Glencorse Mains (clay loam), and a higher bulk density (1.50 as compared to 1.12 Mg m^{-3}). However, as for Glencorse Mains, there was an overestimation compared with the value obtained from all the flux measurements (Table 3).

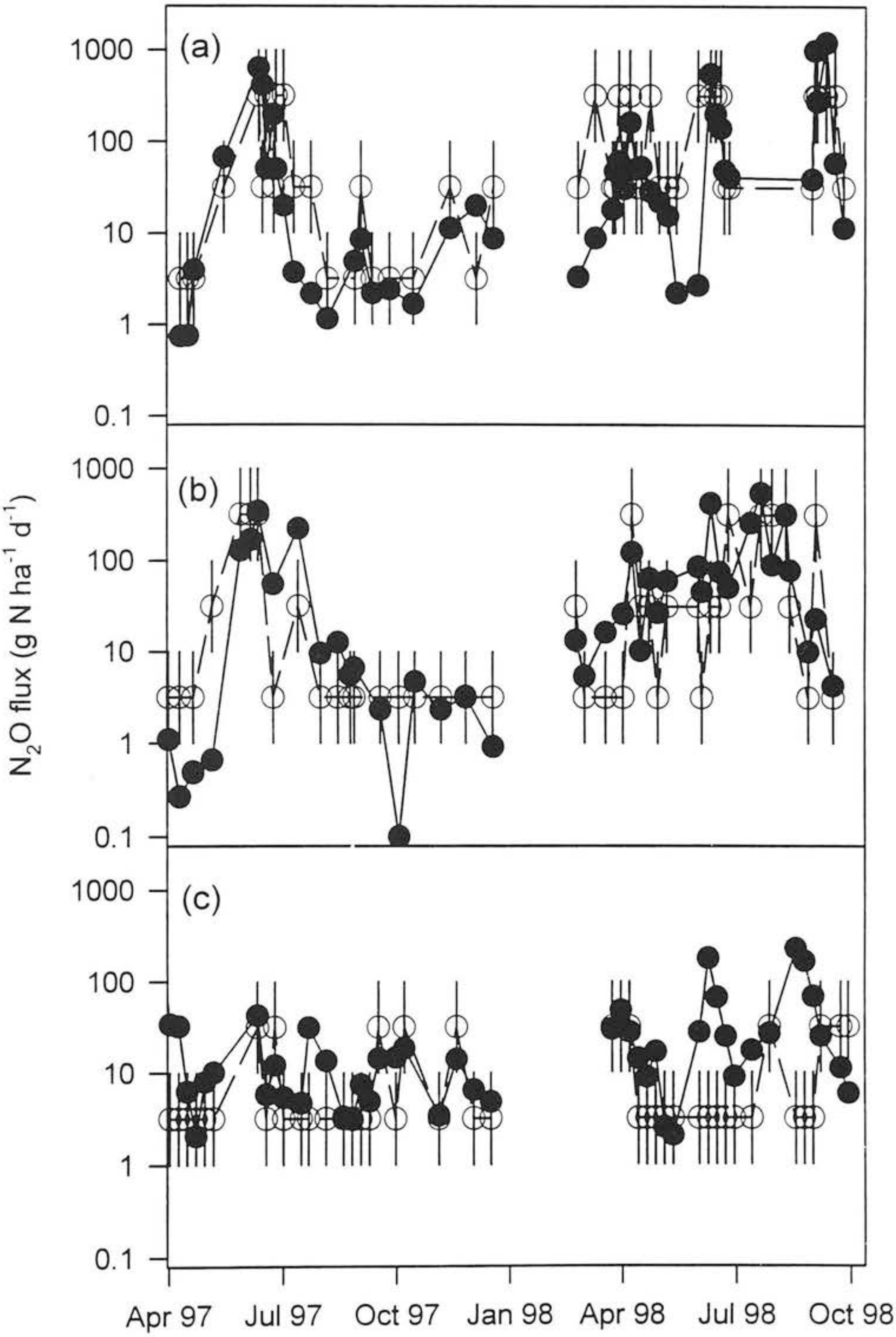


Figure 4: *Measured and predicted N_2O fluxes from grassland: (a) Glencorse Mains, (b) SE Scotland, and (c) SW Scotland. Symbols as in Fig. 3.*

Table 3: *Modelled and measured seasonal N_2O fluxes*

		Seasonal N_2O flux (kg N_2O-N ha^{-1})		
Crop/Site	Year	Predicted	Measured (based on soil sampling dates only)	Measured (all flux measurements included)
Grassland				
Glencorse Mains	1992	13.0	2.6	2.2
	1993	9.3	8.0	4.7
	1997	13.3	15.3	9.9
	1998	28.9	22.8	17.7
SE Scotland	1997	12.3	12.1	7.5
	1998	20.3	21.1	17.9
SW Scotland	1997	2.8	3.9	3.1
	1998	2.3	9.2	7.6
Arable				
Winter wheat	1996	0.70	0.32	0.42
	1997	0.82	0.95	0.86
Potatoes	1996	0.64	3.4	2.9
	1997	0.92	4.4	4.5
Broccoli	1997	3.1	11.4	10.7
Oilseed rape	1998	0.43	0.66	0.66

At the SW Scotland site (sandy clay loam, bulk density 0.96 Mg m^{-3}), measured emissions were higher than predicted during some periods, especially in the summer of 1998 (Fig. 4c). While $N_{mineral}$ was not limiting during these periods, and temperatures were relatively high, low WFPS values resulted in low predictions. The seasonal estimates were thus underestimated by 28% in 1997, and by 75% in 1998 (Table 3).

3.2 Winter wheat and oilseed rape

The model was also tested against data for winter wheat crops in 1996 and 1997 and oilseed rape in 1998, at the Bush Estate, 10 km south of Edinburgh (from Dobbie *et al.* 1999). Both sets of data for the wheat were from neighbouring fields with loam (1996) and sandy clay loam (1997) texture. The oilseed rape crop was also on a sandy clay loam. N_2O emissions from these crops were much lower than from grassland. They rarely exceeded 10 g N_2O-N $ha^{-1}d^{-1}$ and were never found to be above 100 g N_2O-N ha^{-1} day^{-1}. The model also predicted low fluxes (Fig. 5, Table 3). Predictions were always in the range of 1-10 g N_2O-N ha^{-1} day^{-1}, except for one day for the winter wheat in 1996 and one day for the oilseed rape, where fluxes were wrongly predicted to be between 10 and 100 g N_2O-N ha^{-1} day^{-1}. Observed small fluctuations were not reflected in the predictions, as they mainly occurred within the lowest flux range. Measured fluxes were sometimes even below the assumed background of 1 g N_2O-N ha^{-1} day^{-1}. While $N_{mineral}$ was seldom limiting, N_2O flux was usually low because of low WFPS/soil temperature combinations (Fig. 6). For the winter wheat, total emissions were overestimated by 119% in 1996, whereas in 1997 they were underestimated by 14%. The large relative overestimation of the winter wheat in 1996, however, represents a relatively small absolute value of 0.38 kg N_2O-N ha^{-1}. Emissions from the oilseed rape were underestimated by 35%, or 0.23 kg N_2O-N ha^{-1}.

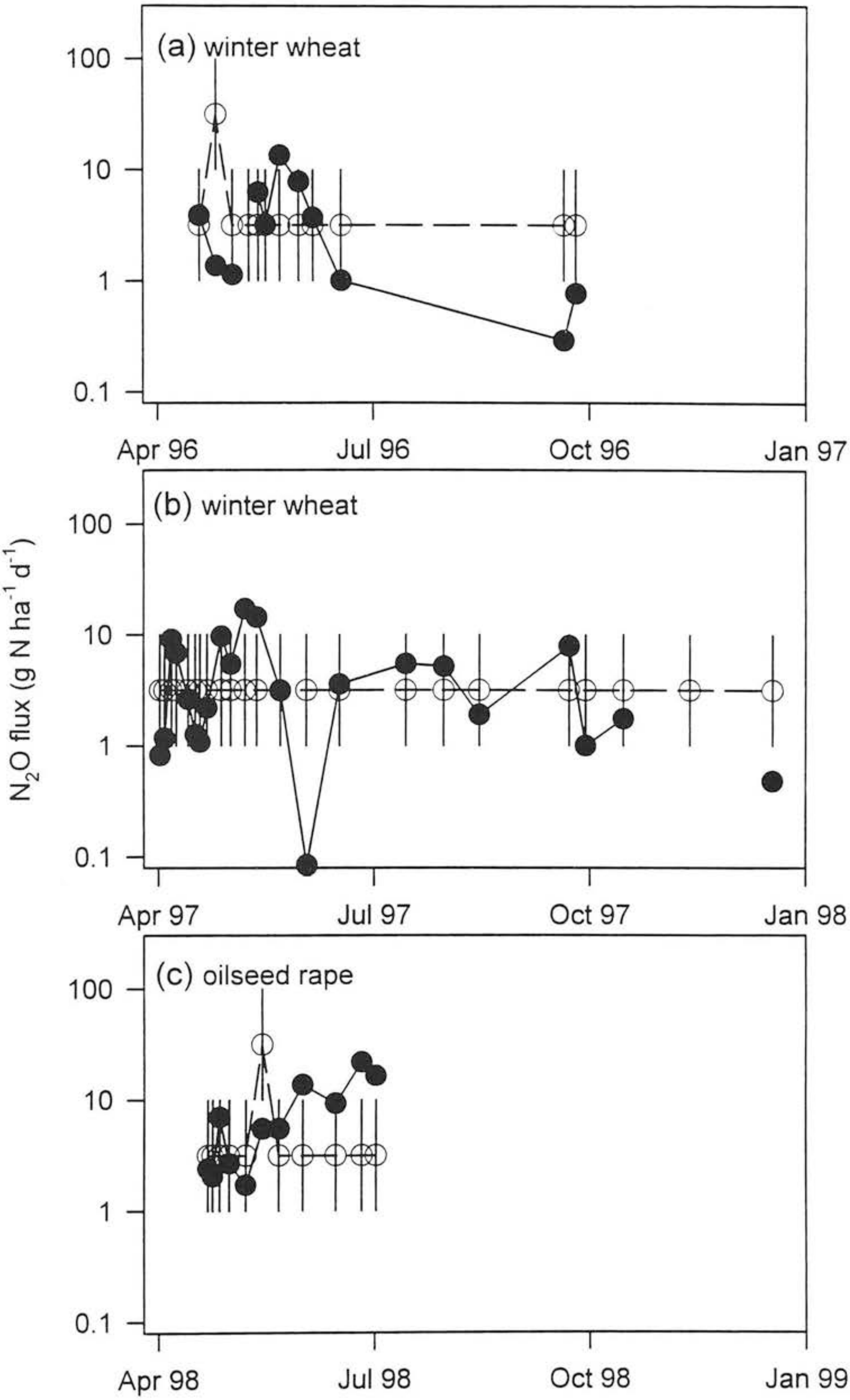


Figure 5: *Measured and predicted N_2O fluxes from (a) winter wheat, 1996, (b) winter wheat, 1997, (c) oilseed rape, 1998. Symbols as in Fig. 3.*

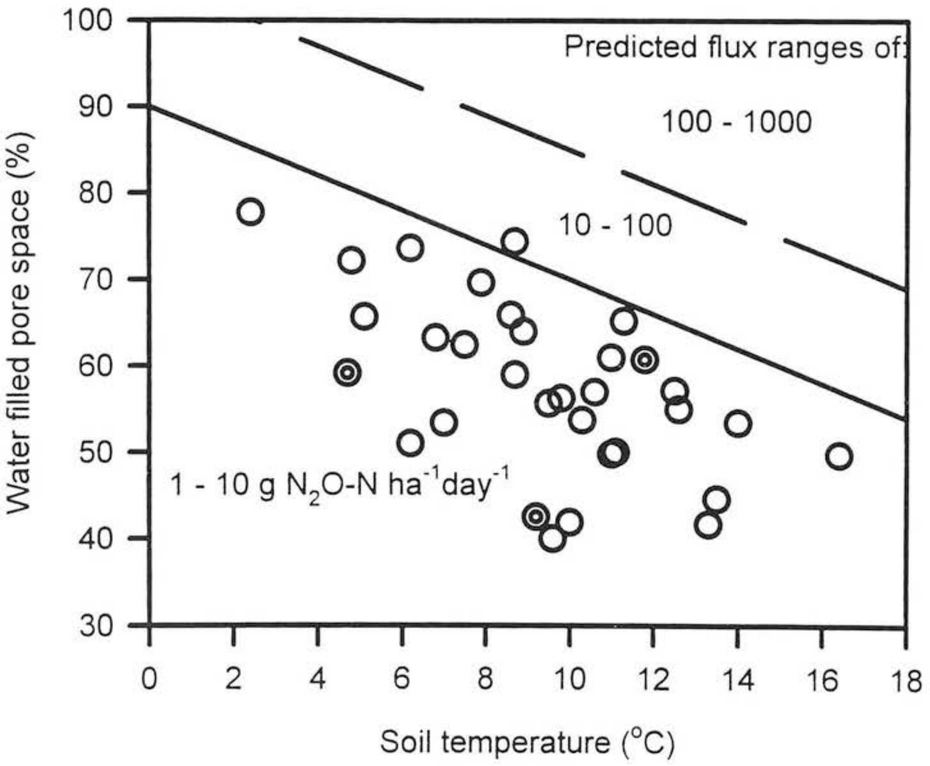


Figure 6: *Combinations of WFPS and soil temperature observed at the winter wheat sites in 1996 and 1997, when observed N_2O flux was <10 (O), or 10-100 g N_2O-N ha^{-1} day^{-1} (⊙). Values are concentrated in the region where the model predicts N_2O fluxes of 1-10 g N_2O-N ha^{-1} day^{-1}. Boundary lines are as in Fig. 2.*

3.3 Potatoes and broccoli

The model was finally applied to N_2O emission and soil data from two potato crops on different fields on Bush Estate in 1996 and 1997 (loam and sandy clay loam, respectively) and from a broccoli field (sandy loam) at the SE Scotland site in 1997. In these crops, the model failed almost completely to reproduce large observed peaks in N_2O emissions (Fig. 7). Predictions tended to be low because of low WFPS/ soil temperature combinations. In 1996, they were only 19%, and in 1997 only 21%, of the measured values (Table 3). Similarly, the predicted emissions from broccoli were only 27% of the measured value.

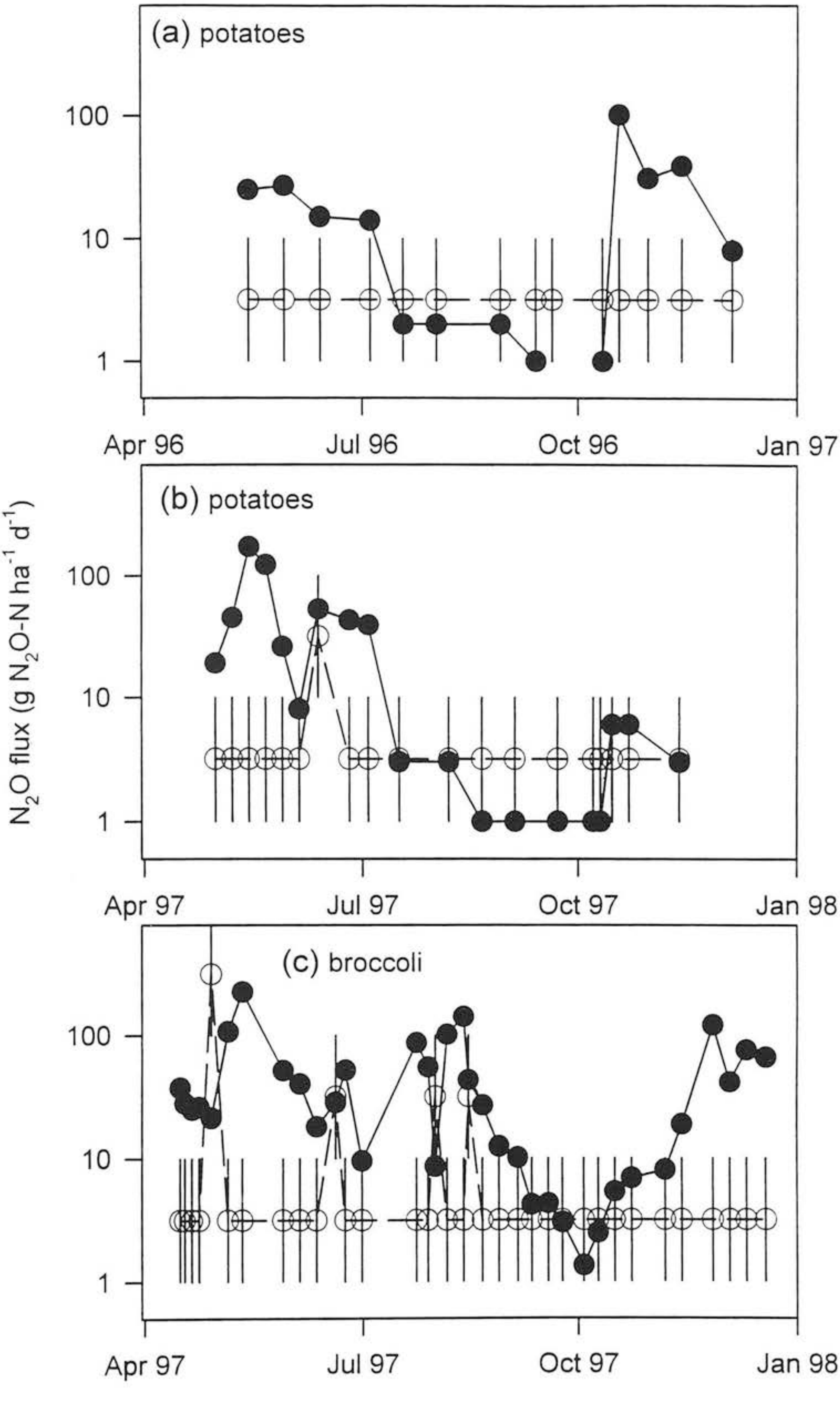


Figure 7: *Measured and predicted N_2O fluxes from (a) potatoes, 1996 (b) potatoes, 1997, (c) broccoli, 1998. Symbols as in Fig. 3.*

4 Discussion and conclusions

The dataset from which the model was developed (from Clayton *et al.* 1997 and McTaggart *et al.* 1997) was not obtained with the present purpose in mind, and was less than ideal for the purpose. The N_2O flux measurements were adequate. They had been made on a daily basis immediately after each N fertiliser application, with a gradual reduction in frequency as the measured N_2O fluxes diminished, and so they documented the "peak and tail" patterns of emission very satisfactorily. Soil temperatures were also measured on each flux measurement occasion. However, soil sampling for water content (and thus WFPS calculation) and $N_{mineral}$ content was less frequent, and there were some prolonged intervals without sampling immediately prior to fertiliser applications. Because measured or modelled flux data had to be restricted to those dates that were coincident with the soil sampling, interpolation of flux values over such periods gave substantial increases in the calculated cumulative flux, which the additional flux measurements that were actually carried out demonstrated were not real.

In spite of this weakness, the model predicted emissions reasonably well on the same site in later years, when total seasonal emissions were several times larger (Table 3). It also performed well on another grassland site with a lighter soil. On a third grassland site, in SW Scotland, predictions were less accurate, however. The underestimation of large measured fluxes at this site indicate the possible involvement of other factors that have not been included in the model. For example, soil aggregate size, and the respiration rate within the aggregates, could be important. They influence the anaerobic volume in the centre of aggregates in otherwise aerobic soil (Smith 1980) and therefore the denitrification potential. However, no experimental investigation has yet been made of aggregate size and respiration rate at this site.

Another possible explanation of why the observed fluxes were higher than predicted at this site is a different pore space distribution, as compared with the soils at the two other grassland sites. Although it has not been systematically studied yet, the relatively low bulk density (0.96 Mg m^3) found at the SW Scotland site suggests a large proportion of macropores. Assuming that denitrification occurs only within soil aggregates and not in the inter-aggregate macropores, it might be appropriate to consider only the intra-aggregate WFPS as important for denitrification, ignoring the pore space between the aggregates. Macropores drain much faster than intra-aggregate pores and could be air-filled when the aggregates themselves are still wet. Anaerobic and denitrifying microsites could therefore still exist, even when the WFPS seems to be low because of a large proportion of air-filled macropores in the total soil volume.

It might also be argued that the large observed N_2O peaks under dry conditions were a result of nitrification. Davidson (1991) concluded that nitrification is the main source of N_2O at WFPS < 60%. However, it seems unlikely that this process could have produced the observed emissions of more than 100 g N_2O-N ha^{-1} day^{-1}, which generally required much higher WFPS values at the prevailing temperatures (Fig. 2). During the nitrification process, N_2O is not a compulsory intermediate but only a possible by-product, and peak fluxes reported from drier grassland systems (Mosier *et al.* 1996), where nitrification is accepted as being the dominant process in N_2O production, tend to be an order of magnitude smaller than the peaks observed in SW Scotland, when WFPS was low.

The model was conceived as a relatively simple tool to apply to soil data commonly acquired in conventional studies of crop response to N fertilisers, to estimate the likely scale of associated N_2O emissions. A simple criterion of N availability for N_2O production was used, namely the sum of the NO_3^--N and NH_4^+-N in the uppermost 10 cm of the soil. The nitrate represents a direct source of N_2O via denitrification, while the ammonium represents a source via nitrification and a second denitrification source via the nitrate produced by the nitrification process. Rather than trying to differentiate between the contributions of the different processes and substrates, we added the substrate concentrations, so that the model was made independent of the type of N fertiliser used. In the event, the observed fluxes in the autumn of 1992 were much lower than predicted, and this was associated with low nitrate-N concentrations (1-5 mg kg^{-1} soil) but substantially higher ammonium-N concentrations (8-20 mg kg^{-1} soil). Had other threshold criteria been applied to predict high fluxes, e.g. that the 10 mg $N_{mineral}$ kg^{-1} threshold must include 5 mg NO_3^- -N kg^{-1}, then the predicted emission over this period (and the seasonal cumulative emission) would have been much reduced. Further refinement of the criteria, with the exploration of additional combinations, is planned for future work.

The generally low N_2O fluxes from winter wheat and oilseed rape were predicted only roughly. The flux ranges of the model were not narrow enough to account for the relatively small fluctuations. In these crops, low WFPS, especially at higher temperatures, seems to be the main reason for consistently low emissions (Fig. 6). Possible explanations for the low WFPS under these crops include increased evapotranspiration as compared to grassland, improved drainage of the topsoil under the arable crops, both through cultivation and artificial drainage, and lower available soil carbon concentrations that drive respiration in microsites and thus promote denitrification.

For the grassland, wheat and oilseed rape data combined, there was virtually a 1:1 relationship between predicted and measured total seasonal emissions (Fig. 8). This correlation is similar to the results of another empirical model for N_2O from grassland on peat soil, described by Velthof *et al.* (1996). However, whereas these authors considered empirical models to be site-specific by definition, our results indicate that an empirical model can, in a limited way, successfully be applied to other sites and also crops. The accuracy of the prediction is also comparable to more sophisticated models such as those described by Li *et al.* (1992), Engel & Priesack (1993), Parton *et al.* (1996) and Potter *et al.* (1997), as indicated by the model inter-comparison carried out by Frolking *et al.* (1998).

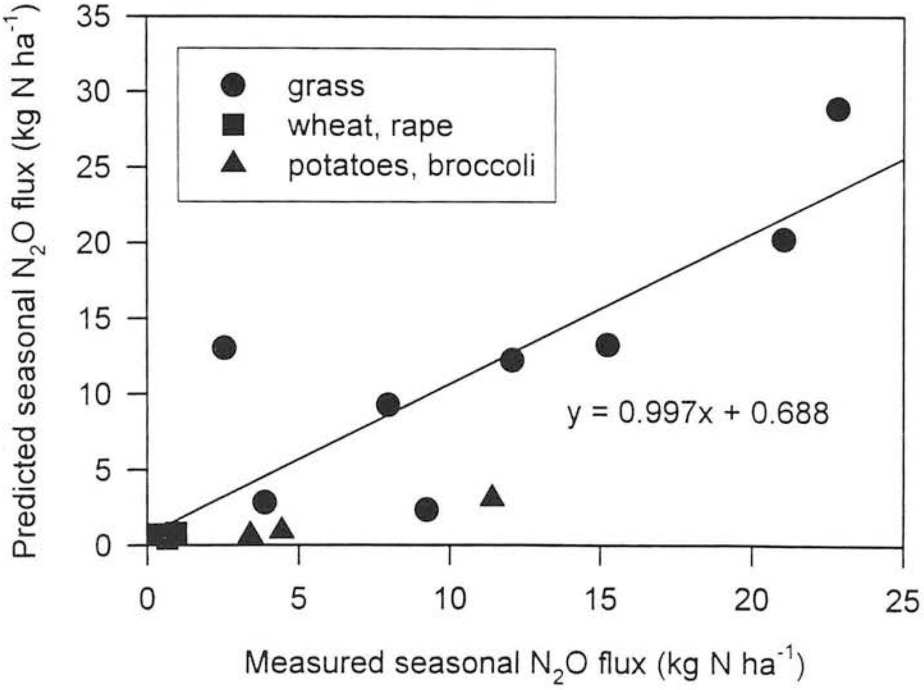


Figure 8: *Comparison of predicted and measured seasonal emissions from different crops and sites in Scotland (using only the flux measurements made on dates when soil parameters determined). Points for potatoes and broccoli excluded from regression, for which* $r^2 = 0.714$ ($p<0.01$).

However, the applicability of the developed model seems to be limited to grassland and crops such as small-grain cereals and oilseed rape. It does not extend to vegetable crops such as potatoes and broccoli. Large emissions observed in these crops were consistently underestimated by a factor of 4 or 5 (Table 3, Fig. 8). This suggests other, or additional, factors of importance. Increased availability of labile organic matter after harvest has been assumed by Smith *et al.* (1998b) to be responsible for an observed increase in N_2O emissions after potato harvest. In laboratory experiments, Weier *et al.* (1993) found that the addition of available carbon greatly increased denitrification, whereas the addition of N alone had only a small effect. A generally low C:N ratio in vegetable crop residues (Jackson *et al.* 1994) is likely to favour rapid decomposition and, therefore, carbon availability. Sheep grazing on the residues of the broccoli apparently accelerated this process, inducing a large winter peak.

There were other major differences in the management of the vegetable crops. Whereas grass, winter wheat and oilseed rape in South Scotland cover the soil throughout the winter, vegetables are planted in bare soil in spring. Their initially poor root systems are slower in taking up N that has been mineralised over winter or has been applied as mineral fertiliser. Therefore, $N_{mineral}$ contents in spring tended to exceed concentrations found on the grassland, winter wheat, and oilseed rape sites, even immediately after fertiliser application (data not shown). High concentrations of NO_3^- have been found to inhibit the conversion of N_2O to N_2 (Weier *et al.* 1993). To extend the model, it might therefore be necessary to re-evaluate the $N_{mineral}$ threshold. Instead of considering it as either a limiting or a non-limiting factor, it might be necessary to introduce a category for high $N_{mineral}$ values, where they are seen to make large N_2O emissions possible, even at lower WFPS/ temperature combinations. Another potential improvement is in the depth of sampling for $N_{mineral}$. Although the shallow sampling (to 10 cm) has proved adequate for grassland and small grain crops, it may well be that deeper sampling would have produced better results for these other crops. In addition, more soil cores per plot might be needed if the distribution of $N_{mineral}$ turns out to be more heterogeneous than under grass or cereals. These aspects, too, are intended to be the subject of further work.

The largest emissions of N_2O derived from Scottish agriculture are from grassland, while consistently low emissions are observed from cereals (Dobbie *et al.* 1999). Since vegetable crops are only a marginal proportion of the total agricultural land, it is unlikely that the current failure of the model to predict their emissions would have much impact on the accuracy of an overall regional estimate.

The soil datasets on which the model was based were less than ideal for the purpose, not having been collected with this particular application in mind. There were longer intervals between soil sampling occasions than between the dates when just flux measurements were made, and this affected the quality of the flux integration over the whole season based on "soil sampling dates" alone. The same problem applied, of course, to the modelled points and their integration. Nevertheless, the match between predicted and measured values shown in Fig. 8 was generally satisfactory. When the measurements of seasonal total flux obtained using the less detailed dataset were plotted against the corresponding values obtained with the full flux dataset, a very good correlation was obtained (Fig. 9), but the less frequent measurements gave, on average, a 25 % larger total flux.

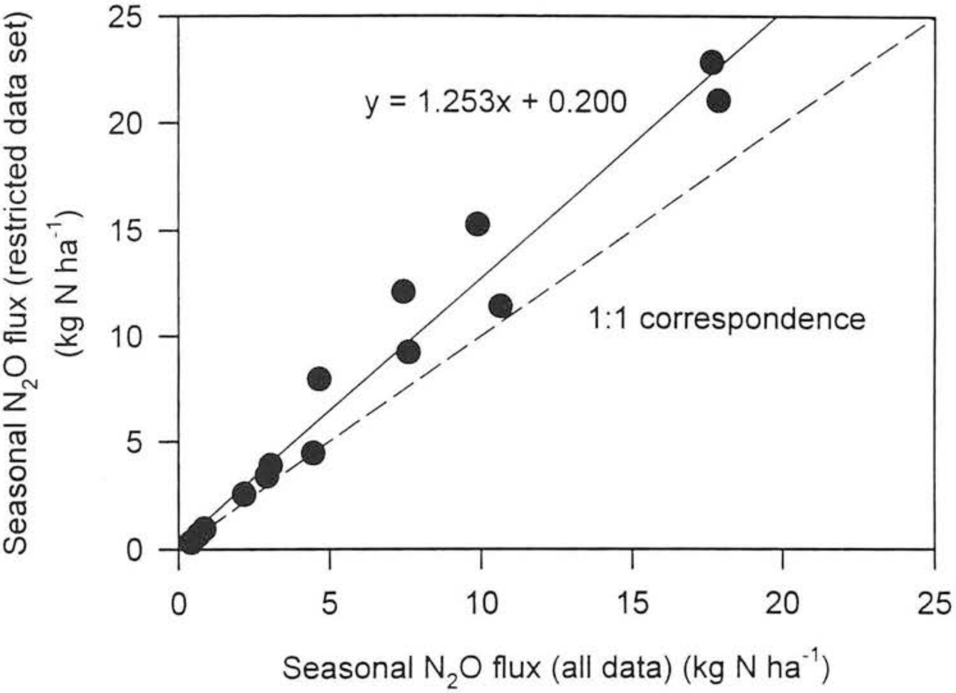


Figure 9: *Comparison of seasonal N_2O flux determined from all flux measurements, and seasonal flux determined from measurements made on dates when soil parameters determined.* $r^2 = 0.962$ $(p<0.01)$.

Taking the results shown in Figs. 8 and 9 together, it seems very likely that more frequent measurement of WFPS, soil temperature and soil mineral N content would have given an even better prediction of fluxes from these agricultural systems. This raises the prospect of being able to make flux predictions for many more sites and seasons than would be possible by conventional direct flux measurement, by much simpler procedures, i.e. logging soil temperatures and making frequent measurements of soil mineral N and water content (and then deriving WFPS from the latter with the aid of a bulk density measurement).

CHAPTER V

Measurement of CH_4 emissions from Italian rice paddies over two seasons

1 Introduction

Measurements of total CH_4 emissions over entire cropping seasons and determinations of diurnal and seasonal variability have already been carried out before by other working groups at the same Institute in Vercelli, Italy (Holzapfel-Pschorrn and Seiler, 1986; Schütz *et al.*, 1989; Butterbach-Bahl, 1993; Butterbach-Bahl *et al.* 1997) where this study was carried out. The focus of the previous studies was mainly on the effect of fertilizer type and rice variety on CH_4 emission. Within the RICEOTOPES project, the main aim was to establish a link between CH_4 flux intensity and the isotopic signature of the emitted CH_4. There were a total of six partner institutes involved in the project. The work carried out and discussed within the framework of this thesis was only a small part of the entire project. Its main objective was to provide a baseline of CH_4 flux values over two seasons, which would then be used in the interpretation of results from experiments done by the partner institutes. In general, the findings of this particular part of the project are comparable to what has been found before. Therefore, the focus of this chapter is on the aspect of variations in ebullition of CH_4, and how this might help to explain inter-seasonal changes in total CH_4 emissions. This might be of particular interest for the interpretation of isotopic signals.

2 Measurements and methods

2.1 *Field site and management*

A co-operation agreement was made with the Istituto Sperimentale per la Risicoltura, Sezione Spezzialisata per la Risicoltura, at Vercelli (45°20'N, 08°25'W) , to use one of their fields and part of their laboratory space for the project work. The requirements of parallel micrometeorological measurement methods led to the selection of a field site that consisted of two neighbouring fields of about 1 ha each. Together with two other fields they formed one unit in the irrigation system and were subject to the same agricultural management. The management of the fields was the same in both years. However, as usual in agricultural practice, there were variations to the exact timing of field operations. Details of the field operations relevant to CH_4 emissions are given in Table 1.

Table 1: *Timing of field operations relevant to CH_4 emissions*

	Year	
Operation	1998	1999
1st fertilization	12-May	23-Apr
harrowing	14-May	30-Apr
flooding of fields	15-May	03-May
sowing	19-May	05-May
drainage (start)	01-Jun	21-May
drainage (end)	12-Jun	01-Jun
2nd drainage (for 3 days)		16-Jun
2nd fertiliser application	22-Jul	13-Jul
field drained (water level 0 cm)	30-Aug	07-Sep
harvest	10-Oct	30-Sep

The location of the fields is indicated in Figure 1. Also, the location of the chambers, sampling masts and other equipment described in following chapters is shown on this map. The fields were used for the multiplication of seed-base material for the variety Koral. This variety has been developed at the Istituto Sperimentale in recent years. It is a relatively tall variety, averaging 105 cm. The soil at the site is a sandy loam with 62% sand, 26% silt, and 12% clay. Organic carbon content was 2.5%, pH increased from about 6 to 7.2 during the vegetation period. Unlike the usual practice of burning the fields after harvest, straw and stubbles from the previous season were ploughed under in early April. Before ploughing, 26 kg N ha^{-1} were applied as calcium cyanamide. About 4 weeks later, the fields were harrowed several times and fertiliser was applied and worked into the upper layer of soil. Application rates per hectare were 97.7 N as urea, 33.8 kg P_2O_5 as Thomas-phosphate, and 156 K_2O_5 as potassium chloride. Then, water was applied through a gravity flow system. The flow rate throughout the season was about 5 m^3 ha^{-1} h^{-1} and the water table was maintained at 5-10 cm. Pre-germinated rice seeds were broadcast with a disc spreader directly into the water. Competition of algae with the crop made it necessary to drain the field once in 1998. At the end of the drainage, herbicides were applied. In 1999, there was a brief second drainage for this latter operation because it could not be done at the end of the algae-related drainage. Although it has not been systematically quantified, weed coverage seemed to be more intense at the beginning of the 1999 season. The main weeds were *Heteranthera spp.*, an import from South America. A second application of a small amount of fertiliser (36 kg N as urea, and 63.4 kg K_2O_5 as potassium chloride) was made shortly before flowering. The main water supplying canals were closed in the last week of August, in both years; and the fields dried out during the first week of September in 1998, but due to heavy rains, the drying was delayed for about 1 week in 1999. Harvest followed a few weeks later (end of September / beginning of October).

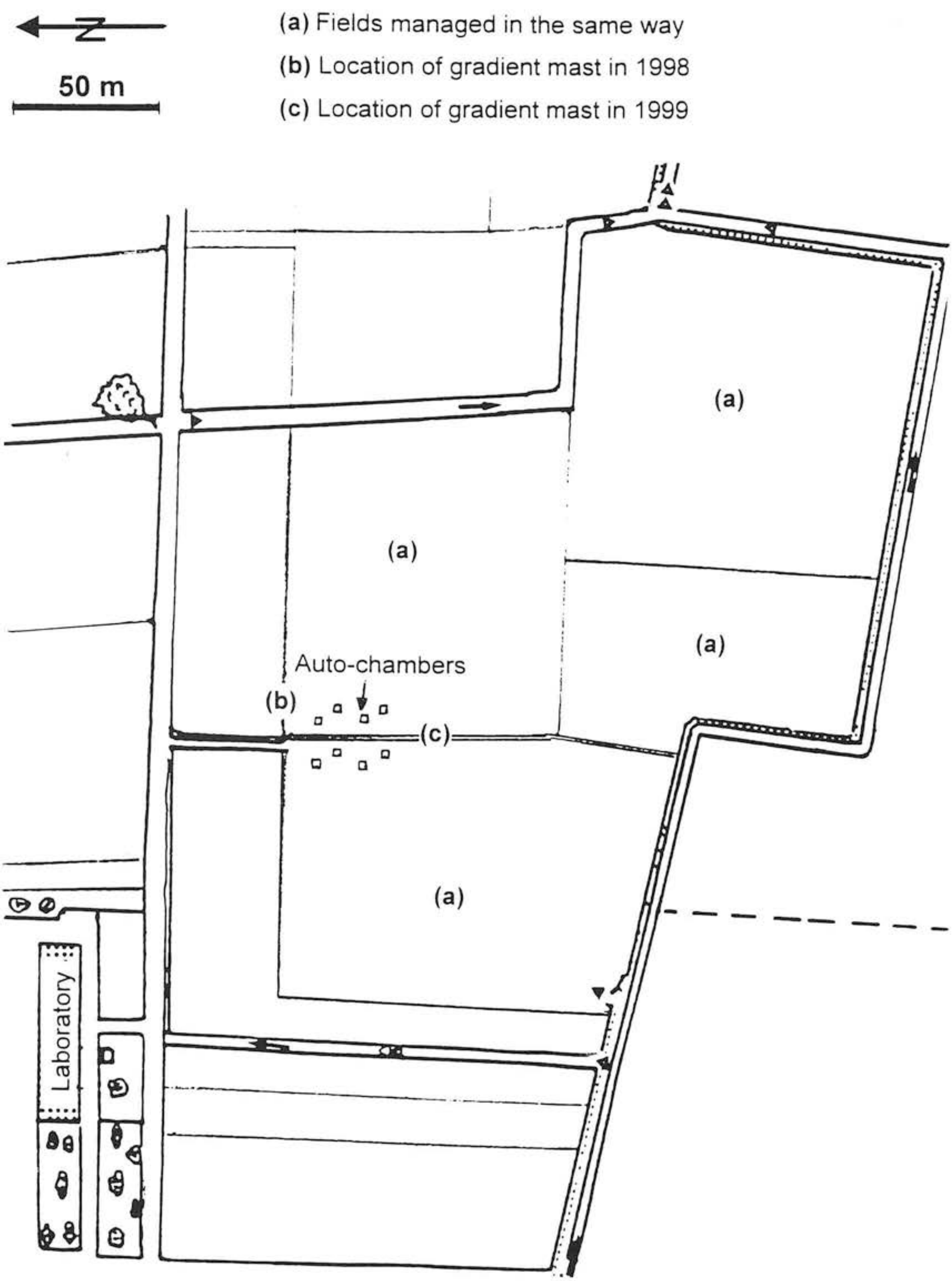


Figure 1: *Map of field site at the Istituto Sperimentale per la Cerealicoltura in Vercelli.*

2.2 *CH_4 sampling and analysis system*

Eight chambers were placed into two adjacent small fields immediately after sowing. The geometry of the set-up was the same in both years and is shown in Figure 1. Access to each chamber was over the narrow dam (~1.2 m wide) which divided the field, and then via wooden footpaths which went off perpendicularily to the left and to the right after 10 m, 18 m, 26 m, and 34 m into the fields. On each side of the dam, 4 chambers were located. They were placed alternately either 4 m, or 8 m, into the field. Thus, the total area covered by this set-up was about 25 m by 13 m. The chambers had dimensions of 0.8 m by 0.8 m and were 1.0 m high. They were made similar to those described by Butterbach-Bahl (1993). Each structure consisted of a painted metal frame, holding together 4 mm Perspex sheets, and a hinged Perspex lid. Joints were made with commercial plastic profiles and sealed with silicone-gel. Foam rubber draught excluder was used as a gas seal between the lid and the top frame. The chambers rested on 25 cm long iron spirals with a diameter of 7 cm, that had been screwed into the ground beforehand. Small gaps between the lower rim of the chambers and the soil allowed for water exchange, while the flood water provided a gas seal. During drainage, the chambers were lowered to the ground to be gas tight. Opening and closing of the chambers was done with two pneumatic, double-acting cylinders (Festo Ltd., Mod. DSNU-20-320P-A). The cylinders were adjusted to provide a positive downward tension on the lid during closure, to ensure a good gas seal. The power supply to the valve also operated a small fan (RS, stock no. 250-1577, flow rate: ~1 m^3 min^{-1}) inside the chamber that was started at the same time as the chamber closed and stopped as it opened. The cylinder action was controlled by a 3-way solenoid valve (Festo Ltd., Mod. MFH-5-1/8 B). Compressed air was supplied by an air compressor (Compair, Mod. H 8-25) located in an equipment cupboard in the field. The compressor had to be replaced three times due to faults in the electric motor, probably due to the high air humidity. One compressor burned out because a snake had entered into the casing and blocked the movements. For several weeks after this, the compressed air was supplied by gas cylinders.

Gas samples were drawn from the chambers into a laboratory on the second floor of the Institute building by a vacuum pump (Charles Austen Pumps Ltd, Mod. Capex B-2) at a flow rate of 300 ml min^{-1}. The first part of the sampling line consisted of a 2 mm i.d. Rilsan tube, 42 m long leading from each chamber to a central 12 port rotary valve (Scanivalve Corp., Mod 1P-12T) sitting in the cupboard in the field. This valve was driven by a stepping motor and selected the chamber to be sampled, by connecting the tube from the respective chamber to one common outlet tube. This common tube was 160 m long (Rilsan, 2 mm i.d.), and, resting on 4 m high poles, bridged the distance between the field cupboard and the laboratory. The entire sampling line was flushed about 3 times (i.e. 6.5 min.) before a 2 ml sampling loop was flushed with sample at a rate of 4 ml s^{-1} for 29 s. After pressure in the sampling loop was allowed to equilibrate for 5 s with the outside air, the sample was injected into a GC/FID system (Hewlett Packard, Mod. 5890 series II) with an external integrator (Hewlett Packard, Mod. 3395). The sample loop was connected to a 6-port, two-position rotary valve (Valco Instruments Co. Inc., Mod. E60-230). Loading and injection were the same as described by Arah *et al.* (1994). The flow paths during flushing of the sampling line and filling of the sample loop is shown in Figure 2. The GC settings for gas pressures were: air: 250 kPa; H_2: 125 kPa, N_2: 400 kPa, column head pressure: 100 kPa. Operating temperatures were: oven: 50°C, detector: 250°C. Calibration was carried out at the beginning of each sampling sequence by two samples of a 50 ppm CH_4 standard (Air Liquide, Torino) loaded and injected as shown in Figure 2. To reduce the flushing time, it was necessary to by-pass the resistance of the sample loop as long as no sample was to be loaded. Tests with standards of 50 ppm, and 2 ppm CH_4, in 5 l Tedlar bags connected alternately to the sample inlets in the chambers, were carried out to estimate carry-over effects. It was found that after flushing the entire line about 3 times, the result was within ± 2 % of that obtained when the standards were injected directly into the GC. The performance of the sampling line was also tested several times during the season by taking manual samples directly from the chambers with syringes and comparing the measured concentrations with those of simultaneous samples that had been travelling through the sampling line. The entire sampling and injection procedure took 7 min. per sample. Therefore, the closing of the chambers was also staggered at 7 min intervals, with chamber 1 being closed first and chamber 8 last.

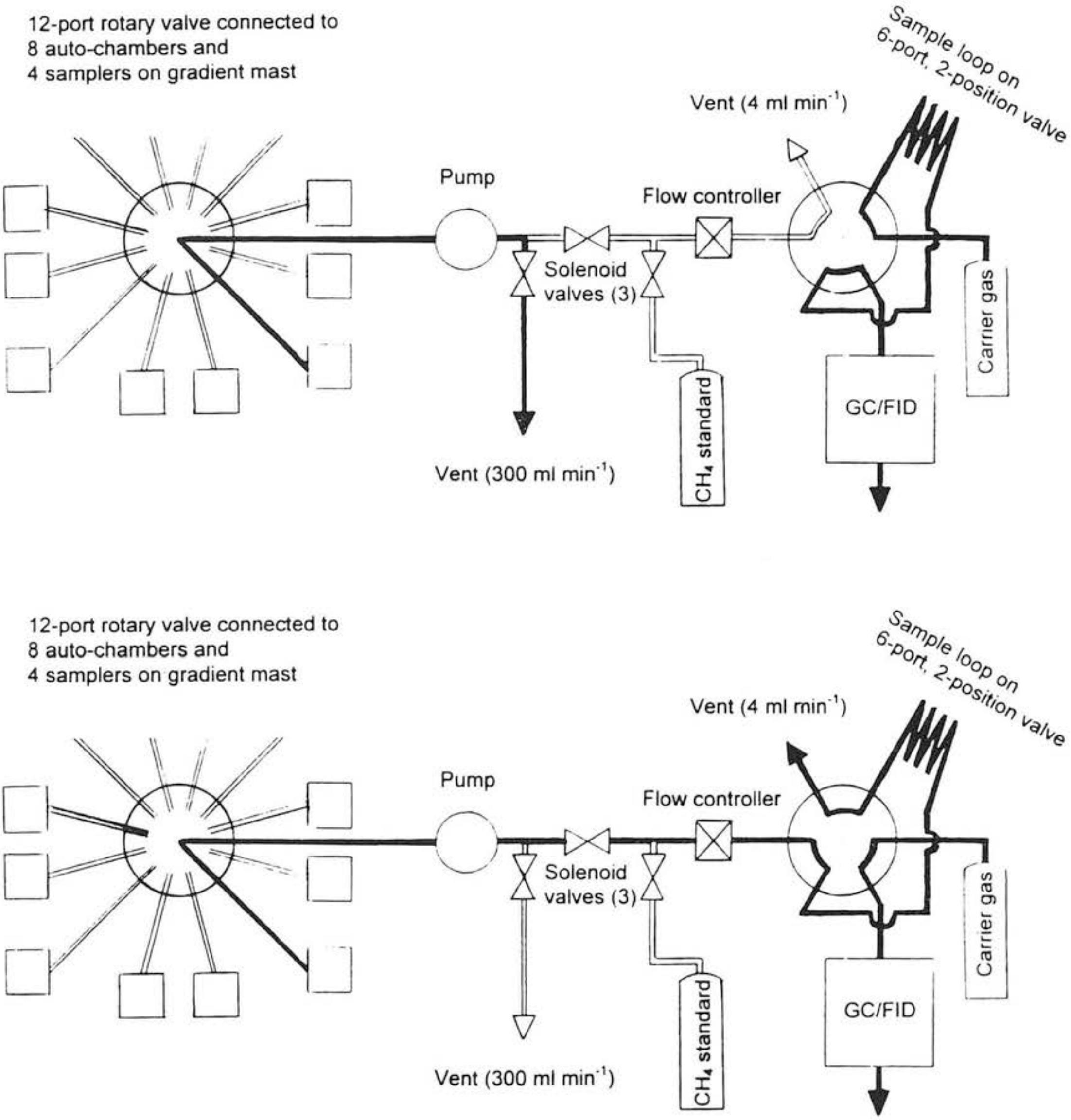


Figure 2: *Schematic diagram of sampling and injection system; (a) injection of sample and flushing of sampling line with sample from the following chamber, (b) loading of sample; (black lines indicate gas flow, white lines indicate no gas flow).*

The closing period of each chamber was 31 min., leading to a 87 min.-sequence for all 8 chambers to be sampled. The background concentration was determined when four chambers had been closed by taking two ambient samples through a 10 m long Rilsan tube connected to one of the free ports of the Scanivalve in the field cupboard. The inlet of this tube was located in the field at 0.8 m above the ground. The concentration in the chambers was determined at the end of the closing period and flux was calculated from the concentration increase above the background concentration and the closing time. The gas density was assumed to be 25 litres mol^{-1}, and the concentration increase was assumed to be linear. This assumption was tested in both seasons and was found to be valid. Taking more samples over the period of closure would have been desirable (to check linearity continuously). However, the distance between the field site and the laboratory, and the resulting long period between successive samplings, would have extended the closure periods of all eight chambers beyond an acceptable limit. After considering possible effects of longer closure on temperatures within the chamber and possible plant physiological effects, this option was rejected. Depending on the requirements of other parallel measurements and the performance of the system, 2-8 complete closure/sampling sequences were carried out per day. When only two sequences were carried out, they were timed so that they would cover the time of the lowest and the highest diurnal emissions.

The entire system was controlled by a computer driven control unit. This unit consisted of two boxes containing mainly relays that controlled the power supply to the respective valves or other operational devices. One of these boxes was located in the field cupboard and controlled the solenoid valves operating the pressure cylinders on the chambers and the stepping motor of the Scanivalve for sample selection. The second box was located in the laboratory and controlled the valves determining sample flow and injection as well as the pump and the integrator. Signals were sent from a laptop computer (Dell, Mod. XPICDM 166ST) to the box in the laboratory, and from there via a telephone cable, resting on the same poles as the sample line, to the box in the field. This system, including the software for writing the operation protocols, had been bought commercially (Spectra Elettronica, Milan, Mod. RS422).

Frequent break-downs of the system was experienced during thunderstorms. Usually it was possible to restore it by one's own means within one day. However, towards the end of the first season it needed attention by the manufacturer and was not ready for use again until the beginning of the second season. In the meantime, chamber closure, sampling and analysis were done manually. For the second season, an optical coupling had been built into the signal transmission line as a protection; however, this was without much success. Therefore, after a second major burn-out during the 1999 season, a completely new system was built by our partners at the Max-Planck-Institute at Mainz. This system had an optical signal transmission between the laboratory and the field and was not affected by lightning striking nearby. It was run by software written by Thomas Marik, Max-Planck-Institute, Mainz, in Visual Basic (Microsoft Windows).

The entire set-up provided flux data for various studies. These include the study on variations in CH_4 pathways discussed in this chapter as well as work involving static and dynamic gradient methods described in the two following chapters.

2.3 *Measurement of ebullition*

Measurements to determine the contribution of gas bubbles to the total CH_4 were carried out in 1998 and 1999 at the tillering and flowering stages of the rice crop. At each of the two growth stages in 1998 and 1999, four replicate measurements were made in the morning and in the afternoon, respectively. In 1998, these measurements were made in the periods 18-26 June and 10-14 August. In 1999, the fields had been drained between the 16 and 19 June. Therefore the sampling periods in 1999 were delayed until 5-9 July and 16-21 August 1999.

The emission rate via gas bubbles was determined by placing next to each chamber two inverted plastic funnels (Merck, cat. no. 237/0238/04, diameter 14 cm) extending at the narrow end into the cylinder of a 60 ml syringe (Merck, SZR-150-071V), fitted with a 3-way stop-cock. These sampling devices were filled with water by evacuating with a 3-way stop-cock. These sampling devices were filled with water by evacuating the air through the opened stop-cock. After 1.5 to 2.5 hours, gas bubbles that had collected in the headspace of the cylinder were sampled with 2 ml glass syringes, also fitted with a stop-cock. The sample volume was recorded and the samples diluted (1:100) by injecting 0.5 ml into 60 ml plastic syringes, which were then filled up to 50 ml with ambient air. When too little sample volume was available for this procedure, the entire sample was taken and the quantity of air added to the syringe was also correspondingly reduced, to maintain the 1:100 dilution factor. The diluted sample was then flushed through a 0.5 ml injection loop and injected manually into the GC. The emission rate for each sampling location was calculated from the volume of the collected gas bubbles and the measured CH_4 concentration. Because of various problems, such as funnels tipping over due to placement in soft unstable sediment, or stop cocks becoming detached during handling, the number of samples available for analysis on some occasions was reduced from 16, to 13 to 15. Diffusion through the water column was ignored as a pathway in the calculation of the flux. This seemed justified as it has been estimated that only about 2% of the total CH_4 is emitted in this way (Butterbach-Bahl, 1993). Student's t-test (unequal variances, two-tail) was applied to analyse differences between various sub-sets of data.

3 Results

3.1 Seasonal flux trends

Despite the same management and similar weather conditions in both seasons, marked differences in the CH_4 flux were observed (Figure 3). In 1998, average daily emissions were 21.5 mg CH_4 $m^{-2}h^{-1}$ (standard variation = 10.1) and total seasonal emissions reached 58 g CH_4 m^{-2} (standard error = 6.3 g). In 1999, average daily emission values were smaller (average = 17.9 mg CH_4 m^{-2} h^{-1}, standard variation = 4.0). However, due to the season starting earlier and ending later in 1999 (9 additional days of CH_4 flux measurement), total seasonal emissions were only 14 % smaller in 1999 (average = 50.1 g CH_4 m^{-2}, standard error = 11.6). As shown in increase in flux values followed by a rapid decrease, probably after CH_4 stored in the soil had been released. This feature was more strongly expressed in 1998 than in 1999. After the fields were flooded again, flux increased rapidly in 1998 before continuing to fluctuate around 30 mg CH_4 m^{-2} h^{-1} until the middle of August. In 1999, this increase after re-flooding was less expressed and was possibly interrupted by the second brief drainage in this season. Flux values throughout the middle of the season fluctuated around 20 mg CH_4 m^{-2} h^{-1} before declining towards the end of August. In both seasons, a brief and sudden spike in emissions was observed after the final drainage at the beginning of September. Similar to the drainage situation in spring, this was more evident in 1998 than in 1999. After this sudden release of CH_4, fluxes decreased within a few days to very low values. In 1998, there was a significant linear correlation between average daily air temperature and average daily CH_4 flux ($p < 0.01$), with the flux increasing by 0.2 mg CH_4 m^{-2} h^{-1} with each 1°C-increase in air temperature. For 1999, no such correlation was observed.

There was a considerable difference in flux variation among the 8 chambers between 1998 and 1999. During the first part of the 1998 season, the CH_4 flux from the highest emitting chamber was about 2.5 times that from the lowest emitting chamber. The chambers had to be relocated after a failure of the air compressor during the first week of July that had left the chambers closed for 3 days and caused visible plant damage. After the relocation, the average flux values for the rest of the season showed a smaller inter-chamber variation. In 1999, 7 of the 8 chambers again gave a spread of values similar to those seen in 1998. However, one chamber emitted on average over the season about 4 times as much CH_4 as the lowest emitting chamber, and more than twice as much as the second highest emitting chamber. On examining the underlying soil at the end of the experiment, it was found that this chamber had been located above a dense mat of straw, about 4 cm thick, buried at about 19 cm depth. Remains of straw were also found underneath other chambers. However, these were only individual stalks or stubbles and not densely packed mats.

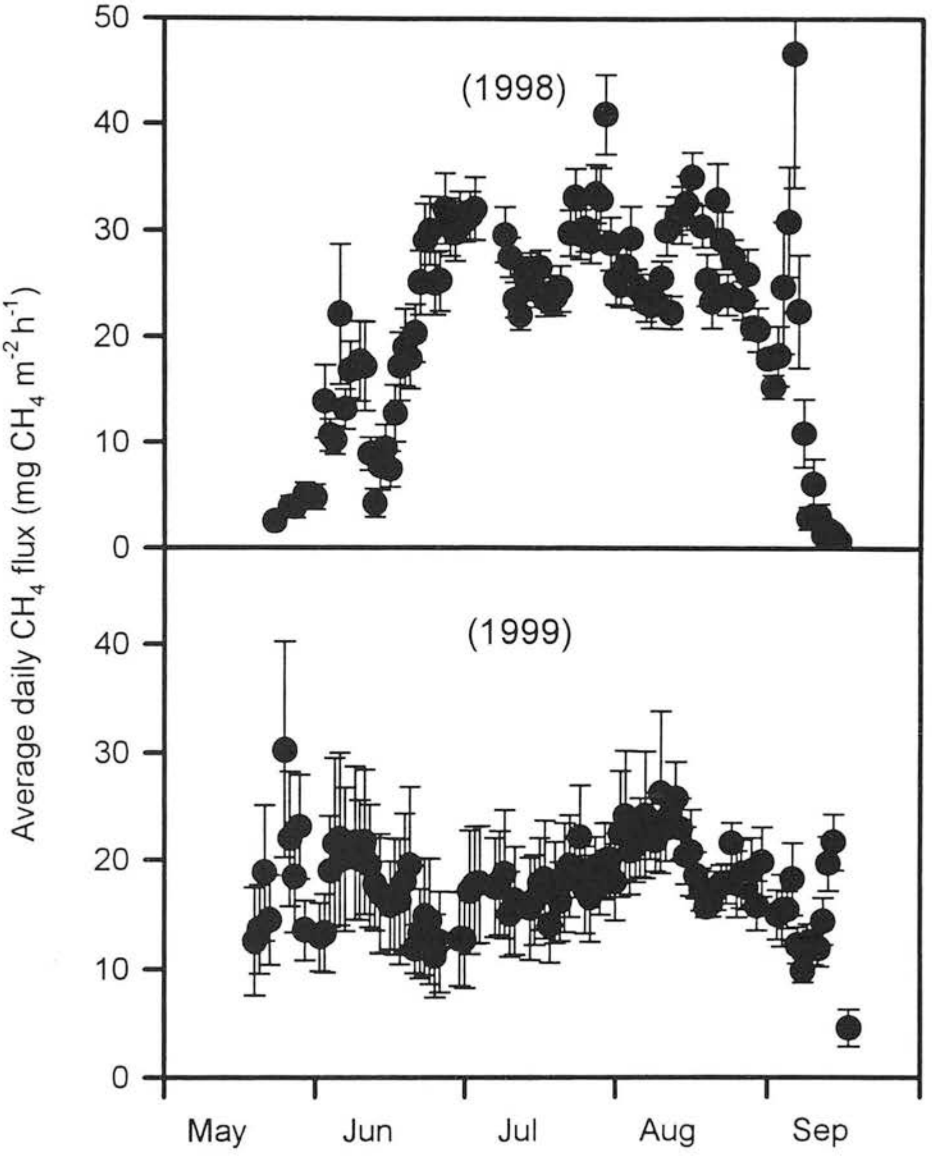


Figure 3: *Seasonal flux trends in* CH_4 *emissions in 1998 and 1999. Error bars indicate ± 1 standard error.*

Such a feature might not be uncommon in agricultural fields. Combine harvesters do not always discharge the straw continuously. Internal blockage of the flow can cause straw to be accumulated over tens of metres before it is being discharged over a much shorter distance, leading to an uneven distribution.

3.2 *Variation in emission pathways*

The relative importance of the two main pathways was subject to diurnal, seasonal and inter-seasonal variations. In general, the proportion of CH_4 emitted via gas bubbles was greater in the afternoon than in the morning. This tendency applied to both seasons and both growing stages (Table 2). During tillering in 1998, the proportion of bubble flux was significantly smaller in the morning than in the afternoon ($p < 0.01$). Large variations between measurements from individual days in one and the same measurement series (i.e. "Tillering 1999") led to the differences being identified as non-significant despite tendencies towards larger proportions of bubble flux during the afternoons during flowering in 1998 and tillering stage in 1999. During the flowering stage in 1999, differences were marginal.

Table 2: *Diurnal variation in the proportion of CH_4 emitted via gas bubbles.*

	Bubble flux/total flux		
Growth stage, year	morning	afternoon	p (morning < afternoon)
Tillering 1998	0.19	0.49	0.004
Tillering 1999	0.10	0.18	0.41
Flowering 1998	0.16	0.24	0.35
Flowering 1999	0.097	0.104	0.82

Apart from the diurnal variation, there was an observed seasonal variation with a tendency towards smaller proportions of CH_4 emitted as gas bubbles as the plants developed from tillering to flowering stage (Table 3). In both seasons, the proportion of total CH_4 emitted via bubbles decreased by about one third in the later growth stage. However, this tendency was not statistically significant.

Table 3: *Seasonal and inter-seasonal variation in the proportion of CH_4 emitted via bubbles.*

	Proportion		
Growth stage	1998	1999	p (1998 > 1999)
Tillering	0.34	0.14	0.025
Flowering	0.20	0.10	0.04

Total CH_4 flux strength in 1999 was found to be smaller than in 1998. Interestingly, the proportion of CH_4 emitted via bubbles was also found to have decreased in 1999. At both growing stages, the proportion of bubble flux was only about half of what it had been in 1998. This difference was significant ($p < 0.05$) at both growing stages (Table 3).

Apart from the variation in the relative importance of the gas bubble flux, there were also variations observed in the concentration of CH_4 in the gas bubbles. Concentrations in those gas bubbles reaching the water surface were found to be significantly higher during the flowering stage than at the tillering stage (Table 4). This difference was significant in 1998 ($p < 0.01$) and in 1999 ($p < 0.001$).

Table 4: *CH_4 concentration (%) in gas bubbles reaching the water surface, at different growth stages.*

	CH_4 (m^3 m^{-3})		
Year	tillering	flowering	p (tillering<flowering)
1998	0.11	0.15	0.0014
1999	0.025	0.069	0.00004

In 1999, when the proportion of CH_4 emitted via bubbles was smaller, the CH_4 concentration in the gas bubbles was also significantly smaller at both growing stages ($p < 0.001$).

Comparing total CH_4 fluxes at the different growth stages in 1998 and 1999, it was found that additional gas bubble flux accounted for 69 % of the additional total flux during the tillering stage in 1998. At the flowering stage, transport via gas bubbles accounted for 34 % of the additional CH_4 emitted in 1998.

4 Discussion and conclusions

Inter-seasonal variations in CH_4 emissions have been found in earlier studies. At the same site, but on a different field, Schütz *et al.* (1989) had previously reported total seasonal CH_4 flux to vary by a factor of 2.5 between 1983 and 1985. Butterbach-Bahl *et al.* (1997) had found at the same site a doubling of average diurnal CH_4 flux from the 1990 to the 1991 season. They assumed this increase was due to an application of straw after the first season. Inter-seasonal variations of the same order were also reported by Khalil *et al.* (1998) from rice fields in China. No apparent cause for these fluctuations was found in that case. The differences in average daily CH_4 emissions between the two seasons found in this study can probably not be allocated to one specific factor. As mentioned before, the management of the fields had been generally the same in 1998 and 1999 as in the previous years, according to the field manager. However, identified differences between the seasons include the earlier sowing date in 1999 and the additional but brief second drainage event the same year. Another possible difference that has not been directly quantified could be the spatial distribution of straw ploughed into the soil. Straw has been identified in several studies as leading to increased CH_4 emissions by providing substrate for methanogenesis (Bronson *et al.*, 1997; Yagi & Minami, 1990; Sass *et al.*, 1990). If the chambers did not cover a representative combination of areas with enhanced and low straw accumulations, it could have led to an under- or overestimation of the real emissions from this field. This seems to have been more likely in 1999 when average flux showed wider differences between the chambers than in 1998.

In 1999, CH_4 concentrations in gas bubbles reaching the water surface were several times smaller than in 1998. Also, the proportion of CH_4 emitted via this pathway was more than halved in 1999. The proportion of gas bubble flux in both years was within the range of values reported for the 1991 season in Vercelli by Butterbach-Bahl *et al.* (1997). Nevertheless, statistically significant differences were observed between the two seasons. It could be argued that CH_4 produced from root exudates is more likely to get emitted via plants because of the spatial proximity of the process to the plant roots, whereas CH_4 produced from decomposing straw might be more likely to find its way to the atmosphere in form of gas bubbles. In addition, straw amendment seems to favour the formation of gas bubbles. Nouchi *et al.* (1994) found almost no gas bubble formation in mineral fertiliser plots, whereas bubbles were abundant in rice straw plots. Therefore, an explanation for smaller emissions in 1999 could be smaller amounts of straw, or that incorporated straw had been generally better decomposed before flooding in 1999 (with the exception of the abnormal accumulation at the location of chamber 1). While about two thirds of the additional flux measured at the tillering stage in 1998 as compared to 1999 could be explained by additional bubble flux, this proportion was only one third at the flowering stage. This does not necessarily imply smaller proportions of CH_4 emerging from decomposing straw at this stage. Some gas bubbles might actually find their way into the root and stem base before being emitted via the plant aerenchyma (Hosono & Nouchi, 1997). This pathway would be more effective at the flowering stage when this part of the plants is more developed than at the tillering stage. An under-estimation of gas bubble formation, or CH_4 that would have been emitted as bubbles, might be the consequence at the later growing stage.

The effect of the second brief drainage in 1999 on CH_4 fluxes is difficult to quantify. In general, intermittent drainage has been found to considerably reduce CH_4 emissions (Sass *et al.*, 1992; Yagi *et al.*, 1996). However, since this question was not part of this study and thus has not been experimentally explored, the possible effect of the second drainage on reducing fluxes in 1999 is only speculative.

It is intended to use the results of this chapter, and the hypotheses formulated in the discussion, in the interpretation and modelling of isotopic signals measured by other partners in the RICEOTOPES project.

CHAPTER VI

CH_4 measurements above paddy rice by the aerodynamic gradient method

1 Introduction

In the previous chapter (V), an example for the measurement of CH_4 by the closed chamber technique was given. Fluxes of CH_4 from paddy fields are relatively large compared to N_2O fluxes from intensive agriculture. In terms of molecules per unit area and time, average CH_4 fluxes measured in rice paddies (~ 300 mol ha^{-1} d^{-1}, or 4800 g CH_4 ha^{-1} d^{-1}) are about an order of magnitude larger than peak N_2O fluxes (~ 36 mol ha^{-1} d^{-1}, or ~ 1000 g N_2O-N ha^{-1} d^{-1}). Large fluxes lend themselves to the application of micrometeorological measurement techniques since analytical precision is less likely to be a limitation. In this chapter, the application of the aerodynamic technique to CH_4 flux from paddy rice is discussed. The aerodynamic gradient method for measuring trace gas fluxes between the land surface and the atmosphere is a micrometeorological method that has the advantage of using simple instrumentation but is difficult to apply when scalar gradients are small (Moncrieff *et al.*, 1997), e.g. over forest canopies. Nevertheless, it has been successfully applied to the measurement of fluxes of ammonia (Sutton *et al.*, 1993) and sulphur dioxide (Fowler and Unsworth, 1979). The method has been described by Monteith and Unsworth (1990). It is based on the assumption of all scalars are transported with the same efficiency and, when the exchange coefficient of momentum is known through anemometry, the flux of a trace gas of interest can be calculated from its concentrations at different heights. In this study, which sought to apply the method to CH_4 emissions from a rice paddy, the exchange coefficient was derived from values of the friction velocity (u_*) measured with a sonic anemometer located about 30 m from the gas sampling mast at the Vercelli field site. This anemometer was part of an eddy covariance system operated by the Institute of Terrestrial Ecology, Edinburgh.

The main purpose for using the gradient method in this context was to obtain flux values from a larger area than that covered by the closed chambers, for comparison with the closed chamber measurements, described in Chapter IV. It was argued that the chambers might be located in parts of the field with unrepresentatively high emissions and an intercomparison with another method would help resolve the issue of spatial averaging of the surface flux of CH_4.

2 Material and methods

The location of the sampling mast is indicated in Figure 1 in Chapter V. Air samples were collected through sample tubes of 15 m length made of 2 mm i.d. Rilsan tubing at 1.5 m, 2.5 m, and 4.5 m above ground level. At the lowest sampling height (1.5 m above ground) duplicate inlets were used, one located 10 m from the mast into the eastern part of the field, the other 10 m into the western part of the field. This was done in order to increase the flux footprint at this sampling height. For a typical situation with a value for u_* of 0.15 m s^{-1}, 80 % of the flux signal at 1.5 m height would come from within 26 m of the sampler, according to the model of Schuepp *et al.* (1990). This is a relatively small footprint compared to the one for the sampler at 2.5 m (80 % from within 95 m) or 4.5 m (80 % from within about 270 m). Gas samples were drawn at a constant rate, (usually) for 30 min, by small membrane pumps (flow rate 100 ml min^{-1}) into 3 l Tedlar® bags. Sub-samples were taken from these bags with plastic syringes and analysed immediately on the GC/FID system described in Chapter V.

The surface flux of CH_4 was calculated as in Equation 1:

$$F = -u_* \chi^* \quad , \qquad (1)$$

where F is the flux of CH_4, u^* is the friction velocity and χ^* is the friction concentration, or the von Kárman constant (k) multiplied by the slope of CH_4 concentration over $\ln(z\text{-}d)$, the logarithm of height (z) minus the zero plane displacement (d) (Sutton *et al.*, 1992).

A value of 0.41 was used for k. The zero plane displacement (*d*) was assumed to be 0.75 m. The *d*-value chosen was relatively high for the 1 m tall crop because of the density of its canopy and the smooth surface provided by the inclined and overlapping flag leaves and ears. Usually, *d* is somewhere between 0.6 and 0.7 times the crop height.

In its simplest form, Equation (1) applies only to neutral conditions, i.e. when temperature is the same at all measuring heights and gas exchange is driven exclusively by wind. When potential temperatures decrease with increasing height, the situation is unstable and a parcel of air from close to the ground surface can partly be moved upwards due to its greater buoyancy at greater height. This was the case on six out of seven measurement occasions. In these cases, it was necessary to numerically adjust the height axis in the determination of χ^* by subtracting from $\ln(z-d)$ the expression $2\cdot\ln((1+x^2)/2)$, where x equals $(1-16(z-d)/L)^{0.25}$, and L is the Monin-Obukhov length (Sutton *et al.*, 1993). The parameter L was obtained from a sonic anemometer operated on site by Ken Hargreaves, ITE Edinburgh. When temperatures increase with increasing height, gas exchange is partly suppressed by the lower buoyancy of air parcels close to the surface. In this case, the situation is stable and the height axis for calculating χ^* was numerically adjusted by adding to $\ln(z-d)$ the expression $5.2\cdot(z-d)\cdot L^{-1}$ (Sutton *et al.*, 1993). This applied to one measurement occasion within this experiment.

3 Results and discussion

Relatively low wind speeds, combined with large CH_4 fluxes from the rice paddy, resulted in CH_4 concentration gradients between the lowest (1.5 m) and the highest sampling height (4.5 m) that were easily detectable by the GC/FID system. The smallest differences were around 70 ppb, or about 10 times the noise level of the system (+/- 5 ppb). The flux values obtained by the gradient tended to be smaller than those measured with the array of the eight closed chambers (Table 1). Only in 2 out of 7 comparisons did the gradient method give slightly larger values. A paired t-test showed that the differences between gradient method and chamber method were nevertheless significant over the period from 13-22 August ($p < 0.05$).

Table 1: *Comparison of CH_4 flux values measured with different methods.*

		CH_4 flux (mg CH_4 m^{-2} h^{-1})					
		average		error (*)		wind	
date	time	gradient method	chamber method	gradient method	chamber method	speed at 11 m ($m\ s^{-1}$)	main direction
13/8/99	17:08-17:23	17.9	21.5	1.88	4.12	3.3	S
16/8/99	15:20-15:50	16.1	15.9	0.64	1.17	2.3	E
17/8/99	12:05-12:35	14.1	13.1	1.87	0.97	1.4	W
18/8/99	16:25-16:53	13.9	19.7	1.34	1.67	1.0	S-W
19/8/99	12:15-12:40	11.4	13.8	1.53	0.71	1.5	S
21/8/99	13:20-13:50	17.5	22.8	2.11	2.54	1.8	S-E
22/8/99	12:45-13:15	15.9	20.2	2.09	4.43	3.5	N-E

(*) The error for the gradient method indicates the maximum error due to analytical limitations of the GC/FID gas analysis system. The error value for the chamber method is the standard error for 8 replicate chambers.

The hypothesis that the chambers were placed in locations with relatively high emissions can neither be clearly rejected, nor can it be accepted. On a neighbouring field, on a plot to the east of the main site, which lay about 100 m from the sampling mast, lower fluxes were found. A different management technique, the so-called direct drilling and delayed flooding method, had been applied there. Measurements with manual chambers once a week showed flux values to be about 50 % of those in the main field. The neighbouring fields to the west and the north were not directly monitored but are likely to have exhibited the same difference in flux as they were also directly drilled and flooded after a delay of several weeks. The proportion of the flux footprint extending into these fields gets larger with increasing sampling height.

There are two ways of interpreting these results, each coming to a different conclusion. On the one hand, lower emissions at greater distances from the sampling location might have contributed to reducing CH_4 concentration at greater sampling heights, as the flux footprint increased and included larger proportions of the lower-emitting area. In other words, it might possibly increase the concentration gradient between the sampling heights and, therefore, lead to an overestimation of the flux signal by the gradient method. This would make the difference from the chamber values even larger and it could be concluded that the chambers were placed in locations with unrepresentatively high emissions.

On the other hand, one can investigate the issue of the flux footprint by using the available data. For this reason, fluxes were calculated on the basis of the concentration differences between the two lowest and, respectively, the two highest sampling heights only, instead of all three sampling heights as in Table 1. Using only two sampling heights is not necessarily enough for a reliable measurement. However, it might provide some information on the effect of a non-homogenous flux footprint on the overall result and therefore seemed justified in this context.

The average flux values and standard deviations obtained from the gradient and the chamber method between 13 and 22 August, and the gradient method based on only two sampling heights, are shown in Table 2. The standard deviations in this context are partly a result of the temporal fluctuations in CH_4 emissions during the 10 days of observation, and partly caused by measurement errors. Since both methods were applied to the same experimental unit (same field and time), it is possible to apply a paired-sample t-test to detect potentially significant differences between the methods. This test analyses the differences within the sample-pairs (gradient method on day 1 - chamber method on day 1, gradient method on day 2 - chamber method on day 2, ... , gradient method on day n - chamber method on day n). It therefore cancels out differences caused by temporal fluctuations in CH_4 emissions during the observation period.

As shown in Table 2, the smaller flux footprint (sampling heights: 1.5 m, 2.5 m) was associated with larger fluxes. On average, they were even slightly larger than the fluxes measured by the chamber method. However, the difference was not significant. From the larger flux footprint, i.e. into the neighbouring fields (sampling heights: 2.5 m, 4.5 m), average flux was significantly smaller than the chamber flux (Table 2). The flux calculated on the basis of all three sampling heights provided a value close to the average of the values from the small and the large flux footprints. From this analysis, it is concluded that the chambers were giving flux values representative of the main field site.

Table 2: *Comparison of flux values obtained by the gradient method, based on different sampling heights, and the chamber method.*

		CH_4 flux 13-22 Aug ($mg\ m^{-2}\ h^{-1}$)		
Method	sampling heights	average	standard deviation (1)	Grouping (2)
Gradient method	1,5 m, 2.5 m, 4.5 m	15.25	2.28	a
	1.5 m, 2.5 m	19.20	6.12	ab
	2.5 m, 4.5 m	10.35	6.42	a
Chambers		18.13	3.86	b

(1) Including measurement errors and temporal variations in flux during the measurement period of 10 days.
(2) A paired-sample t-test has been applied, cancelling out temporal variations; same letters indicate no significant difference ($p < 0.05$).

The two conclusions are obviously in contradiction to each other. No straightforward explanation for the factors leading to the second conclusion, based on observed evidence, could be given. Flux estimates based on two sampling heights are more variable than those based on more sampling heights. This is reflected by the large standard deviation for the measurements based on two heights. Despite the fact that the mean flux based on the greater heights (2.5 m, 4.5 m) was only about half of the flux based on the lower heights (1.5 m, 2.5 m), the difference was not found to be significant. This is a weak point of the second conclusion. Nevertheless, there is no experimental evidence to support the reasoning leading to the first conclusion. Therefore, it probably has to remain an open question whether the flux measured with the chambers was representative for the entire field, or not. The issue of large-scale spatial inhomogenety on fluxes measured by the gradient method certainly merits further investigation, beyond the scope of this thesis.

Keeping in mind the relatively small area covered by the chambers (Figure 1 in Chapter V), the much larger footprint of the gradient method and the changing wind directions, the agreement between both methods is still surprisingly good. It could be an indication for a relatively low spatial heterogenity of CH_4 fluxes in this area. Since the area is a large floodplain that had formed before the last ice-age and where meandering rivers (Po, Sesia) have mixed the sediment for thousands of years until the first agricultural fields were laid out some 400 years ago and planted with rice, which is still the only crop today apart from the occasional soja-bean or maize field, then it is certainly not the most unlikely of assumptions that the soil and ecosystem of this area exhibits a high degree of homogenity that might be reflected by very similar fluxes of CH_4 over large distances.

CHAPTER VII

Estimating CH_4 flux by a gradient accumulation method

1 Introduction

During the measurement period at Vercelli reported in this thesis it was regularily observed that low wind speeds ($u<1$ m s^{-1}) were not unusual during late evening and night-time periods. Under such conditions, the measurement of surface fluxes by the aerodynamic gradient method has been shown to be problematic (Holtslag, 1984). In addition, dew-formation on plants and equipment could often be observed around sunset, indicating radiative cooling of the air close to the surface. This is likely to lead to the development of a temperature inversion close to the ground, conditions which limit turbulent transfer (Fleagle and Businger, 1980) and which results in a stable boundary layer. Within this layer, large concentrations of contaminants may build up close to the surface and numerical transfer models are no longer applicable (Mahrt, 1998) because assumptions they are built on are no longer valid. One possibility for estimating trace gas fluxes under such conditions could be a budget approach. The budget approach relies on the assumption that there is little or no gas exchange between the stable boundary layer and the air above it. The temperature inversion is comparable to a lid on a closed chamber of indefinite area. Fluxes are calculated from knowing the height of the inversion and the increase in concentration of the gas below it.

Two examples of the budget approach cited in the literature show how it can be applied on the a landscape scale: CH_4 emissions from a wetland area in North Scotland (Gallagher *et al.*, 1994); and a study of nocturnal O_3 depletion in the Upper Rhine Valley (Güsten *et al.*, 1998). Before describing and discussing the

Vercelli experiment, a short summary is given of the development of a surface-based inversion and the accumulation of trace gases below it.

1.1 Development of a surface inversion layer

The development of a stable boundary inversion layer is the product of several factors, but mainly a combination of low wind speed and radiative cooling of the earth's surface after sunset (Mahrt, 1998). The latter phenomenon attracted early attention from meteorologists who were attempting to predict nocturnal ground frost (Brunt, 1932; Groen, 1946). In a simple form, Groen (1946) wrote the energy balance at the earth's surface as

$$G = Rn - H - \lambda E \tag{1}$$

where G is the heat flux density in the ground, Rn is the net radiation flux at the earth's surface, H is the sensible heat flux, and λE is the latent heat flux at the earth's surface.

According to Melgarejo and Deardorff (1974), the height of the nocturnal surface inversion is the height to which significant radiative cooling has occurred. Several experiments have been undertaken to determine this height and the development of the inversion. In a broad shallow river valley near Bedford, England, Grant (1997) found cooling rates to be significantly greater at 2 m height than at 16 m height for the first 1.5 hours after the sensible heat flux changed sign. Cooling rates at 16 m were the same as at 30 m. The different cooling rates at different heights establish the gradients in the near surface layer. This indicates an initially very shallow inversion, probably somewhere below 16 m. The nocturnal surface inversion grows in height as surface temperatures continue to decline as the air continues to lose energy due to longwave radiation (Yamada, 1979). Following the development over longer time periods, Surridge and Swanepoel (1987) observed the height of the inversion to grow relatively fast during about the first hour or so, and at a slower rate later on. They assumed that the presence of a nearby river and a water reservoir had a delaying effect on the growth rate at two of their sites. At a third site, exhibiting the dry features of the central southern African regions, they found the boundary layer to grow faster.

While the inversion layer starts growing from the ground and thus, is initially very shallow, it is mainly the well-developed boundary layer of 50 to 500 m height that has attracted attention so far. For the purpose of measuring trace gas emissions, the initially shallow boundary-layer might be of greater interest than the well-developed one. Practically, it allows measurements to be made using a mast, or a tower, instead of a tethered balloon or an aircraft. The advantage of this is that it allows for the automation of the monitoring of gas concentrations and other parameters at different heights at significantly lower cost and complexity. Also, terrain effects during the early development of the boundary-layer appear to be smaller than in the later steady state layer. Grant (1997) noted: "It is curious that the structure of the transition boundary-layer may be more universal than the structure of the steady state nocturnal boundary-layer." This could be another reason to concentrate more on the transition boundary-layer, when attempting to determine soil gas emissions. It might also indicate the possibility of applying the budget method in more complex terrain.

1.2 *Accumulation of trace gases*

While experiments on the height of the boundary-layer rarely include information on mixing ratios of contaminants, experiments on mixing ratios of contaminants rarely include information on the height of the boundary layer. Studying ^{222}Rn concentrations above grass and wheat fields, Butterweck (1991) detected up to 6-fold increases in concentration during calm nights. Around sunrise, when the nocturnal boundary-layer breaks up, the mixing ratios declined rapidly. If the relatively constant escape rate of ^{222}Rn from the soil is known, it can be used as a natural tracer for other gases, assuming similar transport and storage characteristics. This approach had been successfully applied by Kuhlmann *et al.* (1998) to determine CH_4 emissions from a wetland region in the Hudson Bay Lowlands. They calculated CH_4 flux as

$$F_c = \frac{\Delta C_{\mathrm{CH4}}}{\Delta C_{\mathrm{Rn}}} F_{\mathrm{Rn}} \tag{2}$$

where F_c is the CH_4 flux, ΔC_{CH4} and ΔC_{Rn} are the relative increases in CH_4 and ^{222}Rn mixing ratios over the observation period, and F_{Rn} is the ^{222}Rn flux over the same period.

Using a natural tracer such as ^{222}Rn makes the determination of the inversion height superfluous. Trumbore *et al.* (1990) and Ussler *et al.* (1994) made use of this technique to determine CO_2 exchange rates in forests. However, since ^{222}Rn is highly soluble in water, this technique is unlikely to be useful in flooded environments like rice paddies, however.

Another example of trace gas accumulation in the nocturnal boundary-layer is given by Hurst *et al.* (1997). In this study over 15 months, mixing ratios of CO, CH_4, N_2O, and eight halogenated trace gases were monitored at three heights (51 m , 123 m, and 496 m) on a television tower in eastern North Carolina. Differences in the daily concentration at 51 m and 496 m were observed for some of the gases. For CH_4, the daily concentration at 496 m was smaller and out of phase with the daily cycle at 51 m. While mixing ratios at 496 m were lower than at 51 m and remained constant during the night, they increased during the night at 51 m until the early morning hours. This assumes a nocturnal boundary-layer height somewhere between 51 and 496 m. In the late morning, concentrations decreased at 51 m and increased at 496 m as CH_4 stored at the lower height was mixed upward during the break-up of the nocturnal boundary-layer. During the day, mixing ratios were the same at both heights and decreased slowly and simultaneously before they increased again in the evening at 51 m, while remaining constant at 496 m.

At the field site in Vercelli, CO_2 accumulation was monitored automatically by Thomas Marik from the Max-Planck-Institute, Mainz, for a number of nights at 1.5 m, 3 m, 5 m, and 9 m above the ground. An example of CO_2 accumulation in the near surface layer between 19:00 and 21:30 local time on 01.08.1999 is shown in Figure 1. During the daytime, the rice plants assimilate with lower concentrations at lower heights. At about 20:10, half an hour before sunset, CO_2 respiration exceeded assimilation and the CO_2 concentration at 1.5 m increased above the concentration measured at greater heights. Concentrations at the greater sampling heights also started to increase but with some delay. Air temperatures at 1.2 m above ground decreased from about 27°C at 20:00 to 23.5°C at 21:00 (data from T. Marik, MPI Mainz).

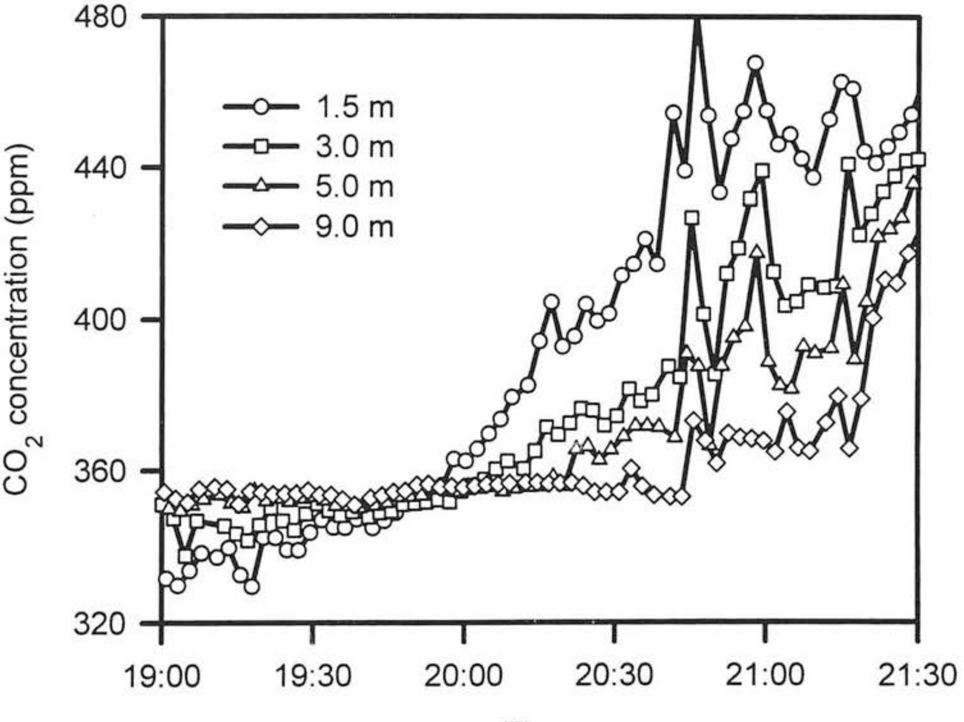


Figure 1: *Development of CO_2 concentrations at different heights in the near surface boundary layer on 01 August 1999; wind speeds at a height of 11 m were around* $1\ m\ s^{-1}$ *(Data of T. Marik, MPI Mainz).*

Only at about 20:45, did concentrations start to increase at 9 m height (Thomas Marik, Max-Planck-Institute für Chemie, Mainz, personal communication). The successive increase from lower to higher levels may have been an indication of the growth of a nocturnal near-surface inversion layer.

2 Material and Methods

2.1 *Sampling and analysis*

In 1998, a sampling mast with 4 inlets (0.8 m, 1.6 m, 3.2 m and 6.4 m above ground) was installed at the field site (Figure 1 in Chapter V). Samples were taken through the remaining 4 inlets of the 12-port rotary valve in the field. They were transported and analysed the same way as the samples taken from the automated chambers (Chapter V, Materials and methods). Starting with the lowest height, successive heights were sampled at 5 minute intervals. In this way, 9 full gradients were sampled and analysed within 3 hours. Before and after such a sequence, CH_4 flux was measured by the closed chamber technique described in Chapter V. Flux values obtained by the gradient accumulation technique were compared against the average of these two chamber measurements.

In 1999, a higher mast was installed on the dam between the two fields (Figure 1 in Chapter V) with inlets at 3 m, 5 m, 7 m, 9 m, and 11 m above ground. Additionally, two replicate sets of sample inlets were installed at 0.5 m and 1.5 m above ground, one 10 m to the east, and one 10 m to the west of the main sampling mast. This was considered necessary because of the larger variability in CH_4 concentrations closer to the ground and in order to avoid any effect of the 1.2 m wide dam on concentrations at the lower heights. Samples from the same height were averaged for further calculations. With a total of 9 sample inlets it was no longer possible to automatically sample and analyse within a reasonable time-span. Therefore, a small table was installed about 8 m from the mast. This table was fitted with 9 holders for 60 ml plastic syringes, which could be simultaneously filled by hand. All sample lines were

15 m long and consisted of 2 mm i.d. Rilsan tubing. The sampling procedure consisted of replacing the dead volume of the sample tube with an air sample by drawing about 50 ml of air within 30 s through the tube into the syringes. The syringes were then emptied through a 3-way stop-cock and the procedure was repeated. With the third filling of the syringes, the second set of air samples that were stored in the tubes (volume 45 ml) were drawn into the syringes. Tests with different CH_4 standards had shown that the carry-over effects from previously higher, or lower, concentrations were negligible in this procedure. About 10 ml of each sample were then used to manually flush a 2 ml sample loop which was then injected into the GC/FID described in Chapter V. Sample analysis was done the same evening, immediately after sampling.

On 26 July 1999, a sampling tube (6 mm i.d.) was moved upwards with a tethered He-filled balloon (2 m^3, "Giant 72'", Everts International Ltd, Scunthorpe, England) in 15 s steps from 1 m to 2 m, 4 m, 8 m, 12 m, 16 m and 20 m and the same downwards. Between 21:16 and 22:18 a total of 15 ascents and descents were made. Sample air was continuously drawn into the sample tube at a rate of 5 l s^{-1} and analysed on line by a tuneable diode laser (TDL) system (Aerodyne®), operated by colleagues from the EC Joint Research Centre (JRC) in Ispra. Tests with the set up showed that concentration changes at the inlet of the sampling tube were detected by the TDL within less than 2 s. The TDL system was otherwise used for measuring CH_4 flux by the eddy covariance method by the JRC group. Readings of CH_4 concentration were taken virtually instantaneously, i.e. they were averaged only over a very short time (~ 1 s).

2.2 *Calculation of flux*

Flux values were calculated only for situations when there was a significant concentration increase at the lower heights but no (or only little) change at the top height.

In 1998, this applied to 6 out of 101 intervals of 35 min between successive gradients that were sampled between 22 and 30 July. Concentration increase between different sampling heights was assumed to be linear. Concentrations at ground level were obtained by linear extrapolation downward from the two lowest sampling heights. The height at which concentration remained constant was estimated by linear extrapolation from concentration changes at the two uppermost sampling points. This height was always below 8.6 m. An example is given in Figure 2. Flux was calculated as the concentration increase integrated over height and divided by the time over which the increase had occurred.

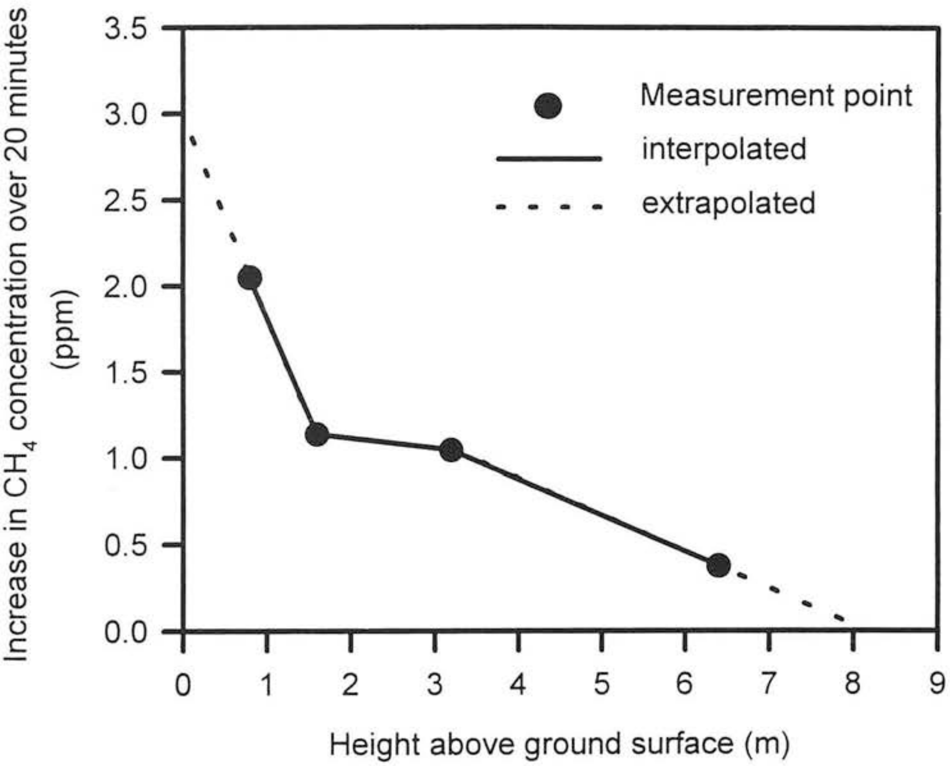


Figure 2: *Accumulation of* CH_4 *in the evening of 29 July 1998. Flux can be calculated as the area underneath the line (interpolated and extrapolated) divided by the time interval between two successive measurements at one height (20 minutes).*

Calculations for the 1999 data were done the same way, with the only difference that no extrapolation was done in the upward direction. Instead, 11 m was assumed to be either the limit, or above the limit of the inversion height. Concentrations at the two uppermost sampling heights were usually very similar and would otherwise have led to large errors had the same type of extrapolation been applied as in 1998.

On one occasion (25.08.1999), and for the data obtained with the balloon/TDL set-up, flux was calculated as the slope of the linear regression through the total CH_4 stored within the sampled profile (11 m for the mast, 20 m for the balloon) over time.

3 Results

3.1 Gradient mast 1998

On six occasions around sunset, considerable increases in CH_4 concentration near the ground were observed, whereas at the top sampling height concentrations changed only slightly (Table 1). On 4 occasions, the largest increase in CH_4 concentration was observed at the lowest sampling height on one occasion at the second lowest height (1.6 m) and once at 3.2 m. Whereas concentrations increased within 20 minutes by up to 5 ppm in the lower heights, they only tended to slightly increase at 6.4 m. Nevertheless, absolute concentrations at 6.4 m were well above the 2 ppm background concentration measured during the day.

Table 1: *Increase in CH_4 concentration at different heights above ground over 20 min intervals between two samplings at the same height (The start time indicates when the first sample was taken; entire sampling time was 35 min.)*

		Concentration increase (ppm)			
Date	Time	0.8 m	1.6 m	3.2 m	6.4 m
22/07/98	20:45-21:20	3.70	5.00	1.61	0.09
23/07/98	22:00-22:35	3.90	3.15	0.88	0.36
24/07/98	20:30-21:05	3.72	3.21	3.15	0.79
26/07/98	20:30-21:05	1.83	1.83	1.78	0.65
29/07/98	19:50-20:25	2.05	1.14	1.05	0.38
30/07/98	19:10-19:45	0.81	1.33	1.91	0.28

They tended to be around 4.7 ppm during the sampling time (standard deviation = 1.5 ppm), indicating that the observed accumulation was an intermediary step in the formation of a boundary layer that had begun to develop already at an earlier time and was breaking up from time to time. An example of the development and decay of a near surface CH_4 accumulation is indicated in Figure 3.

Compared to the flux measured by the closed chamber technique, flux measurements by gradient accumulation tended to be lower (Table 2). The gradient method only once yielded a slightly larger flux value than the chamber technique.

Table: 2: *Comparison of CH_4 fluxes (mg CH_4 m^{-2} h^{-1}) measured by the closed chamber technique and the gradient accumulation method.*

		CH_4 flux (mg m^{-2} h^{-1})	
Date	Start time	Gradient	Chambers
22/07/98	20:45	29.94	30.50
23/07/98	22:00	22.51	33.20
24/07/98	20:30	34.71	34.00
26/07/98	20:30	20.56	34.50
29/07/98	19:50	13.80	29.00
30/07/98	19:10	15.76	29.00
	Average	22.88	31.70
	Stdev.	8.11	2.51

3.2 Gradient mast 1999

The set-up and sampling procedure in 1999 enabled measurements to be made at higher resolutions in time and space. Thus it became possible to monitor the accumulation of CH_4 in the near-surface layer in more detail. An example of an unsteadily developing concentration profile on the evening of the 28.06.1999 is shown in Figure 3. At 22:26, concentrations above 7 m were about the same as they have been during the day (2.2 ppm). Below this height, they increased exponentially with decreasing height. At 0.5 m above the ground, concentrations were close to 4 ppm. Within the following 13 minutes, CH_4 which had been trapped in the lower 1.5 m was mixed upward, leading to a decrease in concentration at 0.5 m and to an increase at all greater heights, up to at least 11 m. During the next 9 minutes, concentrations increased mainly within the lower 7 m. At 22:56, the concentration at 11 m was only slightly above (0.16 ppm) that which it had been when the first measurement was taken 30 minutes previously. However, concentrations at all other sampling heights below had increased in average by 0.56 ppm.

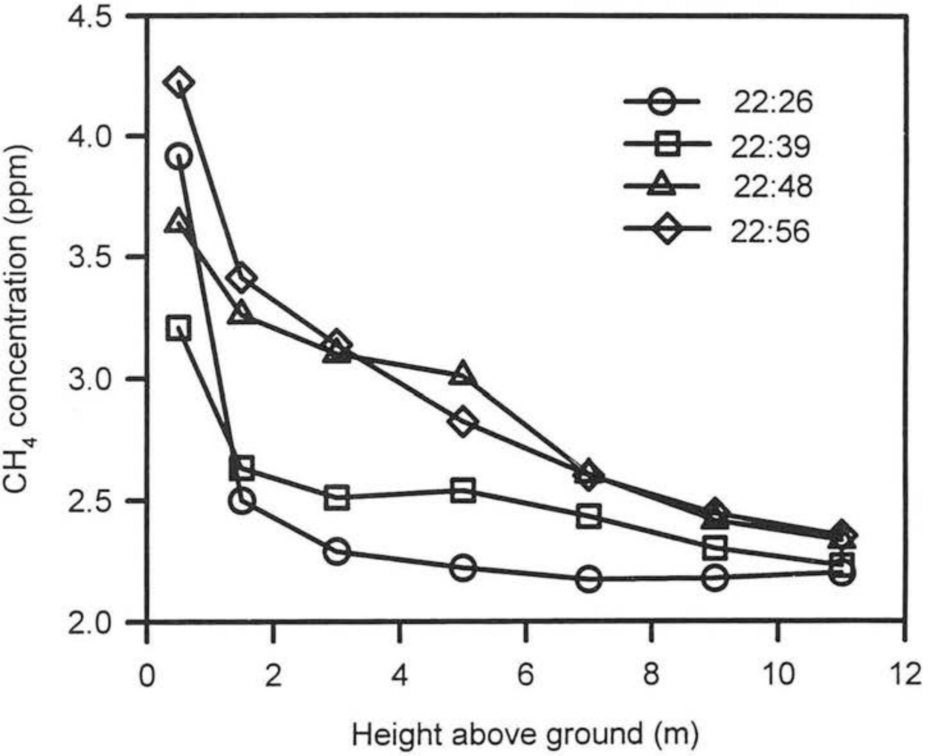


Figure 3: *CH_4 concentrations at different heights and times in the evening of the 26.06.1999.*

The flux calculated from the accumulation of CH_4 within the lower 11 m over 30 minutes was 4.7 mg CH_4 m^{-2} h^{-1}, or only 0.3 times the value obtained by the parallel closed chamber measurement. A part of the emitted CH_4 might have been mixed into the layers above 11 m. No calculations of the loss into layers above 11 m could be made from the available data. A steady and almost linear increase (6 ppb min^{-1}, r^2 = 0.91) in CH_4 concentration at 11 m confirmed the presence of upward mixing.

A different situation was observed on 25 August 1999 between 19:21 and 19:46. Wind velocity at 11 m height was at, or below, the detection limit of our anemometer (0.25 m s^{-1}). During the measurement period, the situation was stable, u* was in the range of 0.01 to 0.02 m s^{-1}; both sensible and latent fluxes were close to zero; temperature was decreasing and around 17 °C; humidity was close to saturation (Stan Cieslik, JRC-Ispra, personal communication). This means that an inversion layer was probably forming and that turbulence was very reduced. At 19:21, CH_4 concentration was almost the same between 3 m and 11 m (2.5–2.8 ppm) and still similar to the daytime values. Below 3 m they had already significantly increased to 7.8 ppm at 1.5 m and 12.8 ppm at 0.5 m above ground.

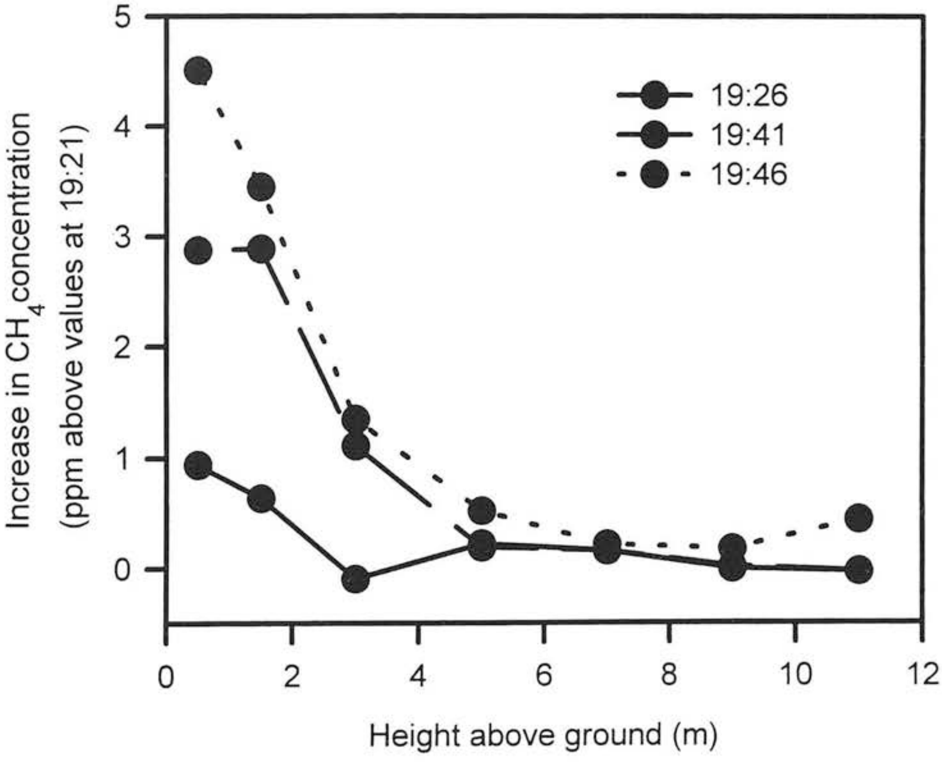


Figure 4 a: *Increase in CH_4 concentrations in three time steps above concentrations measured at 19:21 on 25.08.1999.*

During the following 25 minutes, the CH_4 concentrations below about 5 m increased continuously, while it remained about the same at heights above 5 m. After the initial measurement, three more gradients had been sampled. The relative increases in concentrations above the initial gradient at 19:21 are shown in Figure 4 a.

The total CH_4 stored within the first 11 m above ground was plotted against time (Figure 4 b) and a linear regression was fitted to the data ($r^2 = 0.97$). The slope of the regression line indicated a flux of 12.1 mg CH_4 m^{-2} h^{-1}, or about 0.53 times the flux value yielded from the parallel chamber measurement.

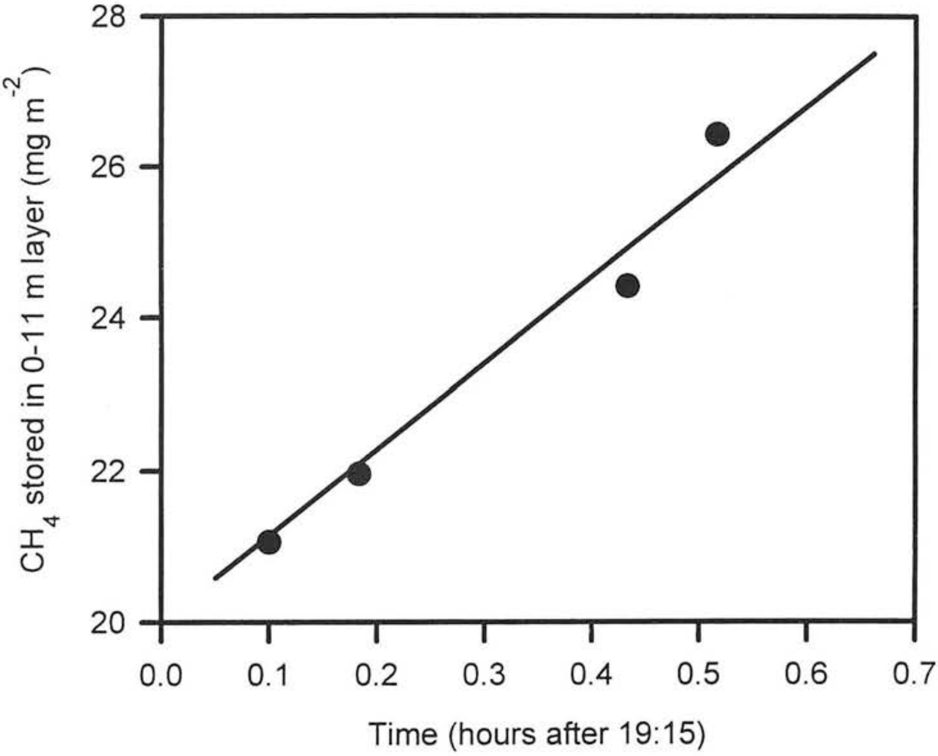


Figure 4 b: *Accumulation of CH_4 in the 0-11 m layer between 19:21 and 19:46 on 25 August 1999.*

3.3 Balloon 1999

The balloon experiment was also carried out under very stable conditions on 26 July 1999 between 20:16 and 21:18. The average wind speed at 2.5 m height during the 1 hour experiment was 0.61 m s^{-1}, u* was about 0.02 m s^{-1}, and the sensible heat flux was slightly negative (Ken Hargreaves, ITE-Edinburgh, personal communication). The observed CH_4 accumulation occurred mainly in the lower 5 m above ground with virtually no change at greater heights. The largest CH_4 concentrations found at 1 m height were around 14 ppm towards the end of the experiment. At around 21:35, CH_4-enriched air seems to have travelled across the sampling location, increasing concentrations briefly at all heights by about 0.5 ppm (Figure 5 a). This air might have come from a location where CH_4 had been accumulating for longer and where it was now being mixed into the boundary layer. This event was not included in further analysis.

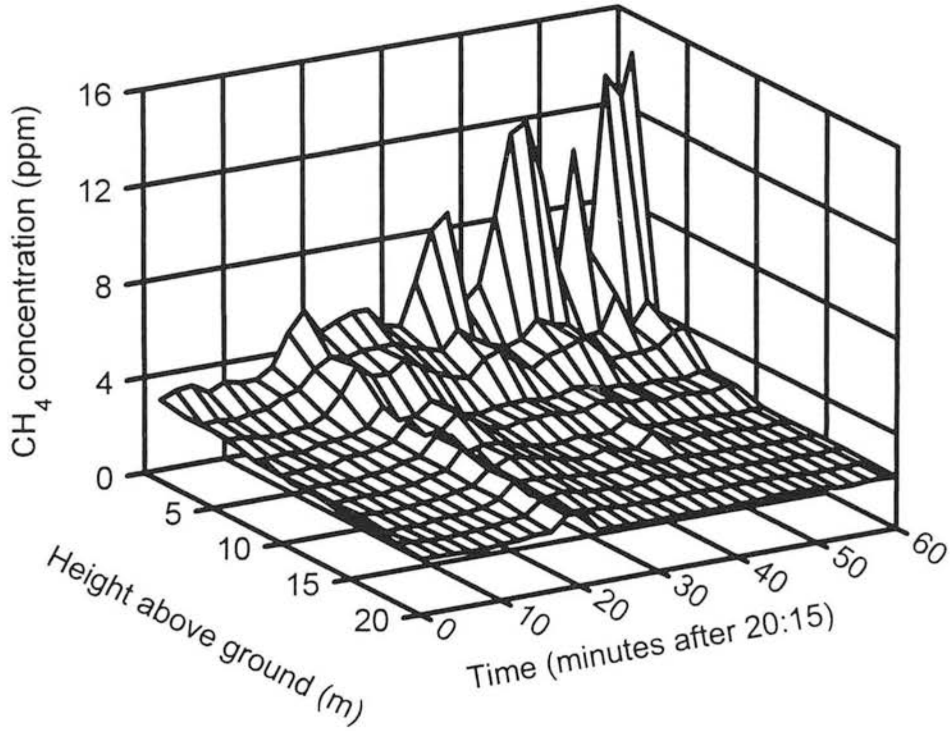


Figure 5 a: *Development of CH_4 concentrations in the 0-20 m layer as observed with a tethered balloon on 26 July1999 between 20:16 and 21:18.*

When total CH_4 stored within the lower 20 m was plotted over time, accumulation is shown to have been unsteady (Figure 5b). This might partly be explained by the very short integration time for the individual measurements at one height (~ 1 s) and partly by disturbances caused by the movement of the balloon. A linear regression through the total CH_4 stored below 20 m over time gave an r^2 value of 0.53 ($p < 0.01$) (Figure 5b). The flux value obtained from the slope of this regression was 9.2 mg CH_4 m^{-2} h^{-1}, or 0.39 times the value of the parallel chamber measurement.

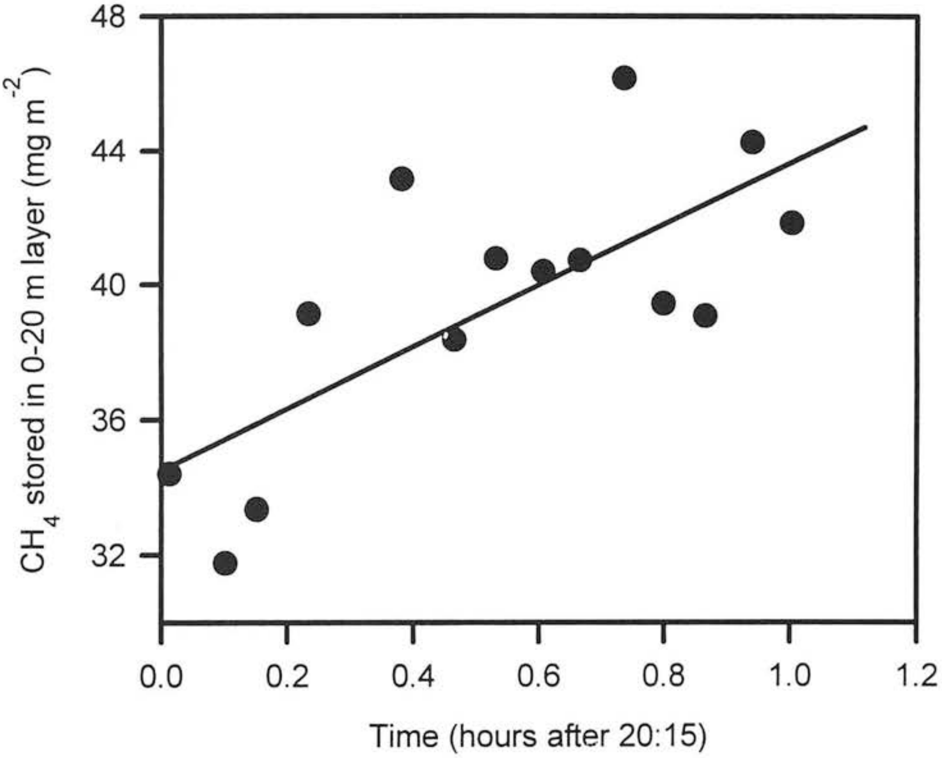


Figure 5 b: *Accumulation of CH_4 in the 0-20 m layer between 20:16 and 21:18 on 26 July1999.*

4 Discussion and conclusions

The results described above resulted from a somewhat serendipitous observation during the main experiment at Vercelli. It would have certainly have been useful to do additional temperature, wind, and humidity profiles in parallel to the CH_4 profiles to monitor better the development of near surface inversion layers. However, the idea for this particular experiment had evolved only during the course of the RICEOTOPES project and no funds were available for the additional resources needed for such work. Nevertheless, the experiment yielded interesting results on trace gas accumulation in the near surface air layer during the likely formation of a surface inversion around sunset. The experiment showed that substantial proportions of CH_4 emitted from rice paddies (as determined by chamber measurements) can accumulate in the atmosphere within the first few metres above the ground. Flux values calculated under the assumption of no exchange between the shallow near-surface accumulation layer, and the air above it, usually yielded lower values than parallel closed chamber measurements. This could be an indication of the inadequacy of our assumption of no CH_4-loss from the inversion layer under the observed circumstances. It could also be that the flux values from the chambers are an over-estimate, either because the chambers are covering unrepresentatively high-emitting sites, or because they introduce artefacts causing an over-estimation. In 1998, chamber-derived fluxes were found to be about 1.7 times as high as parallel eddy-covariance measurements at the same time and site (Werle, 1999). In 1999, eddy-covariance measurements with a different system produced flux values about 1.5 times those of obtained by chamber measurement (Ken Hargreaves, ITE-Edinburgh, personal communication).

An important and problematic point in our approach is the issue of convection of CH_4-enriched air. The experiment with the balloon/TDL system revealed the occurrence of substantial rapid concentration increases which are likely to be caused by enriched air passing the sampling location. While the relatively high time resolution during the balloon experiment allowed for the detection of such a feature, it would have not been detected as such by the 1998 set-up. Therefore, it is difficult to say how far the results in 1998 might have been influenced by convective increase in CH_4.

Another problematic issue is the question of the 'flux footprint'. Applying the model of Schuepp *et al.* (1990) to conditions similar to those observed during the measurements, it was found that 'flux footprints' are relatively large. At the sampling height of 1.5 m, 94 % of the flux is derived from within 100 m of the sampler. However, this proportion decreases with height. At 5 m it is only 49 %, and at 11 m only 11 % of the flux signal comes from within 100 m of the sampling mast. In contrast to these predictions are those of a different model by Baldocchi (1997), which was specifically designed to predict 'flux footprints' under forest canopies, i.e. conditions of low wind speed. It predicts much contracted 'flux footprints' only of a few metres. From the current understanding it is not clear which of the models is more applicable to the situation of a stable nocturnal boundary layer.

The present study differs slightly in its approach to that of Gallagher *et al.* (1994), who also measured CH_4 flux from a wetland by its accumulation in the nocturnal boundary layer. Instead of measuring CH_4 concentrations at different heights in order to determine the accumulation profiles, they measured the boundary layer height with a SODAR instrument and determined the CH_4 concentration at one height only. The boundary layer was assumed to be well mixed. This seems justified under the conditions in North Scotland where the experiment was conducted, and where u* values were about an order of magnitude larger than at the site in Vercelli. Another difference is that Gallagher *et al.* concentrated on the well-developed boundary-layer at a height around 100-150 m, whereas our study concentrated on the much lower, developing, or transition, boundary layer. In contrast to the discrepancies in the results found between our accumulation and chamber method, Gallagher *et al.* found good agreement between the nocturnal accumulation method and the aerodynamic method they used during the daytime. The dynamic gradient technique also averages flux over a larger area and is therefore may be more comparable to the accumulation method than the closed chamber technique.

Güsten *et al.* (1998) used the assumption that the nocturnal boundary layer acted like a closed chamber to the measurement of dry deposition of O_3 in the Upper Rhine

Valley. Similarly to our approach, they measured O_3 concentrations at different heights (up to 700 m). Strong O_3 gradients were found up to heights between 30 and 90 m. Ozone deposition calculated from the nocturnal profiles was 2-5 times as large as deposition rates measured in parallel by a ground based eddy-covariance system. This discrepancy might be due to a possible reaction of O_3 with atmospheric pollutants, a process that might compete with the deposition of O_3. But also the performance of the eddy correlation method under conditions of weak turbulence has been questioned (Güsten *et al.* 1998). This indicates the complementary nature of the accumulation method. It does not seem to be a perfect method, but neither are other methods for the measurement of gas fluxes on a larger scale essentially in stable conditions at night. However, for the conditions found during the day-night transition period the accumulation method may well be the most appropriate one and is certainly worth of further study.

General Discussion and Conclusions

Measurement and modelling of N_2O and CH_4 emissions from soils are a wide field. Many issues have been explored, discussed and clarified in previous studies. This thesis has looked into areas that were, and some still are, surrounded by large uncertainties. It has shed some light onto the functioning of closed chambers for measuring trace gas exchange between soils and the atmosphere. The outcome of this part of the thesis is generally applicable to biogenic trace gases produced in soils and not limited to N_2O or CH_4.

Combining the results from Chapters II and III, one can reach the conclusion that the issue of turbulence-induced pressure fluctuations accelerating gas exchange between soil and the atmosphere is questionable under certain circumstances. In the experiment on which this theory is based, Kimball and Lemon (1971) used a constant concentration gas-source (liquid heptane on a heated tray). Biologically produced trace gases, such as N_2O or CO_2, are more likely to emerge from constant production sources (or more precisely, sources that are fairly constant in their rate of production over the period of measurement). For a constant production source, it has been shown in Chapter III that an increase in gas concentration within the chamber induces an immediate increase of the gas concentration within the soil profile. A decrease in diffusivity at the soil surface, due to the exclusion of pressure fluctuations at the soil surface, would in the same way result in an increased gas concentration near the soil surface. The resulting increased concentration gradient would restore the flux to the same level as it was before the diffusivity decreased. This change in concentration gradient would lead to only an initial flux loss at the surface through additional storage of trace gas within the profile. This is different from the storage of trace gas in the soil profile due to the build up of concentration within the chamber that continues as long as the chamber is closed and thus has a larger effect.

The overall effect of the suppression of pressure fluctuations on the measured flux is probably very small, when integrated over the entire closure period. The situation might be different if there is a sink for the trace gas of interest between the source and the atmosphere. Suppression of pressure fluctuations might prolong the residence time of the gas within the profile, leading to a larger proportion of the produced gas being lost on the way to the atmosphere and therefore, in a lower flux estimate.

Modelling in Chapter III has shown that flux can be significantly underestimated by closed chambers, especially, if they are shallow and on soils with large air-filled porosity. The scale of the underestimation might seem relatively small considering uncertainties due to spatial variability as discussed for example by Dobbie *et al.* (1999). Also, when comparing, for example, different fertiliser types, the absolute flux values might be of lesser importance than the relative values, and applying the correction proposed in Chapter III might seem unnecessary. Nevertheless, when the focus is on monitoring N_2O flux for the purpose of contributing to large-scale estimates of N_2O emissions, it would lead to an underestimation, if no such correction were applied. This would be undesirable because the error would be systematic, and not random, as it is for spatial variability.

All the considerations in Chapters II and III are of little importance to the measurement of CH_4 from flooded soils, such as in rice paddies. In this environment there are no continuous air-filled pores connecting the inside of a chamber with the outside. Thus, mass flow due to depressurisation is impossible to occur. Exceptions could be natural wetlands with *Phragmites* or similar plants that produce offshoots through rhizomes. Here, continuous pores and mass flow due to depressurisation of parts of the plant system has been demonstrated by Armstrong *et al.* (1991).

Chambers tend to be tall in rice paddies. They are usually at least as high as the crop, i.e. about 1 m. In combination with the very low soil air porosity, even if one includes the air-spaces within the plants, this results in negligible correction factors for flux loss due to storage within the soil profile or the plant aerenchyma. The only conclusion from Chapters II and III relevant to CH_4 measurements from wetlands is that the increase in gas concentrations within the chamber is expected to be linear. This has been confirmed in the course of the experiments described in Chapter V (data not shown). A shift in the concentration gradient driving the flux is not expected, if CH_4 is evolving from a constant production source (constant during the time of chamber closure). If, nevertheless, concentrations do not increase linearily, it is likely that other factors are responsible. These could be changes in the parameters controlling CH_4 production, or the fact that the chamber is not completely gas-tight.

The accuracy of field measurements of trace gas fluxes is an important condition for the development of generally applicable predictive models. This is especially relevant if models are validated against data that has been collected with one method, and are applied to data obtained by a different method. Systematic errors in one of the methods might render it impossible to apply the respective model. Also, it has been shown that a model might be only transferable in a limited way to another system from that against which it was validated. The empirical model developed in Chapter IV on the basis of data from grassland was able to predict total annual emissions from the same type of land use on different fields. It also predicted reasonably well emissions from small-grain crops. However, it underestimated emissions from vegetable fields several-fold. Similarly, the more complex model by Parton *et al.* (1996) only performed well on the low input and dry grassland system it was based on; it failed to predict the much larger fluxes from an intensively managed grassland in Scotland, or from two intensively managed arable plots in Germany (Frolking *et al.*, 1998). This seems to suggest that models are unlikely to predict emissions from systems they have not been validated against. They can certainly not substitute for field measurements in areas or systems where no intensive measurements have taken place so far.

Considering N_2O emissions from agricultural soils, there are a large number of areas and systems that have not been monitored over entire seasons. These include the intensively managed *Chernozem* soils in Russia and the Ukraine, as well as many tropical areas and their highly diverse land use systems (e.g., inter-cropping and agro-forestry). Lack of resources is likely to limit the number of measurements that can be carried out in such areas. Thus, it would be desirable to have methods for the measurement of trace gas fluxes that have low requirements in terms of equipment and expert labour.

Two methods which integrate over larger areas and have the advantage of using simple instrumentation were applied to measuring CH_4 flux from a rice paddy. One was the aerodynamic gradient method for measuring trace gas fluxes between the land surface and the atmosphere, as described by Monteith and Unsworth (1990). The results from this method were similar to those obtained with an array of 8 closed chambers (Chapter VI). The second method applied was the gradient accumulation, or boundary layer budget method (Chapter VII). This had been applied earlier to measure CH_4 from a wetland (Gallagher *et al.*, 1994) and to measure the dry deposition of O_3 in the Upper Rhine valley (Güsten *et al.*, 1998). The novel aspect in the present study was to make use of the initially very shallow transition boundary layer as described by Grant (1997). This has the advantage of faster concentration increases and lower sampling heights. The results from this method tended to be considerably lower than those from the closed chamber method. Performance of this method would probably be better in a drier environment, where condensation of moist air in the evening which induces turbulence near the ground is less likely to occur. One problem to be solved relating to the gradient accumulation method is the 'flux footprint' analysis. It is not clear whether the 'flux footprint' is very large at low wind speeds (Schuepp et al., 1990), or very small (Baldocchi, 1997).

Apart from the question of 'flux footprint', the most important limitation to both methods is their dependence on certain meteorological conditions. The dynamic wind gradient is applicable only at wind speeds above 1 m s^{-1} (Holtslag, 1984; Mahrt, 1998). With increasing wind speeds, concentration gradients decrease and the application of the method again becomes difficult. The accumulation gradient method relies on the assumption that turbulent exchange between the near-surface inversion layer and the above atmosphere is completely suppressed. This condition is only approached at very low wind speeds when there is also a strong temperature inversion due to radiative cooling at the soil surface (Mahrt, 1998). Both techniques are therefore not applicable on a continuous basis, unlike, for example, the closed chamber technique. In measuring CH_4 from wetlands, this might be of lesser importance than in measuring N_2O emissions. Daily average CH_4 emissions have been reported to change only little over short time periods, such as days or weeks (e.g. Schütz *et al.* 1989; Walter *et al.*; 1996; Khalil *et al.*, 1998). This finding was confirmed in this thesis, Chapter V. Therefore, good seasonal estimates might also be achievable with lower sampling frequencies (Buenida *et al.*, 1998; Khalil *et al.*, 1998b). Fluxes of N_2O from intensive agriculture are much more variable over the season, changing by orders of magnitude within a few days (i.e. Ryden and Lund, 1980; Davidson *et al.*, 1996; Smith *et al.*, 1998). This requires higher sampling frequencies at certain times, especially after fertiliser application on wet soil, or when fertilisation is followed by rainfall, inducing most of the N_2O flux for the season within brief periods (Dobbie *et al.*, 1999).

An interesting method that has not been investigated in this thesis is the so-called ^{222}Rn tracer technique. Using this natural tracer makes the determination of the inversion height superfluous. The technique is based on the measurement of enhancements in ^{222}Rn and the trace gas of interest a few metres above ground during evenings and night times, together with the determination of the flux of ^{222}Rn at the soil surface by, for example, the closed chamber technique. Since ^{222}Rn emission is relatively constant over long periods of time (Dörr and Münnich, 1990), it needs to be monitored at a very low frequency only. Thus a system involving this technique could be automated for most of the time. Trumbore *et al.* (1990) and Ussler *et al.* (1994) made use of this technique (without automation) to determine CO_2 exchange rates in forests. The technique has also been successfully applied by Kuhlmann *et al.* (1998) to determine CH_4 emissions from a wetland region in the Hudson Bay Lowlands of Canada. The recent availability of commercial ^{222}Rn monitors with a high sensitivity and low maintenance requirements, as used for example by Lehmann *et al.* (1999), might offer the possibility of a wider application of this technique.

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