Biogeochemistry **29:** 199–222, 1995.

Effect of nitrogen fertilizers and moisture content on CH_4 and N_2O fluxes in a humisol: Measurements in the field and intact soil cores

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Received 8 September 1994; accepted 24 January 1995

Abstract. Field and laboratory studies were conducted to determine effects of nitrogen fertilizers and soil water content on N_2O and CH_4 fluxes in a humisol located on the Central Experimental Farm of Agriculture Canada, Ottawa. Addition of 100 kg N ha^{-1} as either urea or $NaNO_3$ had no significant effect on soil CH_4 flux measured using chambers. Fertilization with $NaNO_3$ resulted in a significant but transitory stimulation of N_2O production. Inorganic soil N profiles and the potential nitrification rate suggested that much of the NH_4^+ from urea hydrolysis was rapidly nitrified. CH_4 fluxes measured using capped soil cores agreed well with fluxes measured using field chambers, and with fluxes calculated from soil gas concentration gradients using Fick's diffusion law. This humisol presents an ideal, unstructured, vertically homogeneous system in which to study gas diffusion, and the influence of gas-filled porosity on CH_4 uptake. In soil cores gradually saturated with H_2O, the relationship of CH_4 flux to gas-filled porosity was an exponential rise to a maximum. Steepening CH_4 concentration gradients partially compensated for the decreasing diffusion coefficient of CH_4 in soil matrix air as water content increased, and diffusion limitation of CH_4 oxidation occurred only at water contents $> 130\%$ (dry weight), or gas-filled porosities < 0.2.

Key words: diffusion limitation, humisol, methane oxidation, nitrogen fertilizers, nitrous oxide

Introduction

Nitrous oxide (N_2O) and methane (CH_4) are trace atmospheric constituents important in global warming and ozone chemistry (Duxbury & Mosier 1993). Microbial oxidation of atmospheric CH_4 occurs widely in aerobic soils, an important phenomenon in light of increasing atmospheric CH_4, and declining CH_4 oxidation by atmospheric OH^- (Ojima et al. 1993). Soil microorganisms are the major global source of N_2O, primarily through the processes of nitrification and denitrification. Denitrifiers can also consume N_2O, but soils are not considered a significant net N_2O sink (Duxbury & Mosier 1993).

Increased soil N_2O production upon addition of N fertilizers is well documented (Eichner 1990).

Conversion of natural ecosystems to cultivation has been linked to declining CH_4-oxidizing activity (Keller et al. 1990; Mosier et al. 1991; Bronson & Mosier 1993; Lessard et al. 1994). Nitrogen fertilization is often cited as a cause of this trend, but field studies show inconsistent results. Fertilization with 37 or 120 kg NH_4NO_3-N ha^{-1} over one year inhibited CH_4 oxidation in forest soils (Steudler et al. 1989), and strong inhibition resulted from 100 kg N ha^{-1} of KNO_3, NH_4Cl, or urea applied once to a drained peat (Crill et al. 1994). However, Bronson & Mosier (1993) observed no effect of up to 150 kg urea-N ha^{-1} addition on CH_4 oxidation in a clay soil under wheat, or of 218 kg N ha^{-1} on a clay loam under corn.

Study of the Broadbalk wheat experiment revealed decreased soil CH_4 oxidation potential under long-term (> 7 year) but not short term N-fertilizer addition (Hütsch et al. 1993). Nitrogen may affect CH_4 flux through long term changes in microbial populations and ecological interactions rather than direct inhibition of extant populations. Nitrogen turnover rate rather than the absolute N level may be a controlling factor (Mosier et al. 1991; Hütsch et al. 1993). On the other hand, NH_4^+ (or more correctly, NH_3) inhibits CH_4 oxidation in pure cultures of methanotrophs (Bédard & Knowles 1989), and in laboratory studies of soil and sediment (Nesbit & Breitenbeck 1992; Adamsen & King 1993; Bosse et al. 1993; Bronson & Mosier 1994). NH_3 probably inhibits CH_4 oxidation through competition with CH_4 for the active site of methane monooxygenase, and may also compete with CH_4 for ammonia monooxygenase in nitrifiers (Bédard & Knowles 1989). Nitrite and hydroxylamine produced through NH_3 oxidation are also inhibitory to methanotrophs (Hubley et al. 1975; King & Schnell 1994). Both long-term and short-term effects of fertilization therefore seem plausible.

The diffusion rate of atmospheric CH_4 into soils may limit the microbial CH_4 oxidation rate (Dörr et al. 1993). Soil texture (Dörr et al. 1993), soil compaction (Hansen et al. 1993), and soil moisture content (Steudler et al. 1989; Adamsen & King 1993; Koschorreck & Conrad 1993; Lessard et al. 1994) all affect the CH_4 oxidation rate of soils, perhaps due to restriction of CH_4 diffusion as gas-filled porosity decreases. However, controlled studies of water addition to intact soil systems are lacking.

Because of high water-holding capacity, humisols can be seasonally flooded, and present alternating anaerobic and aerobic conditions for microbial growth. Organic soils represent a unique environment of carbon and nitrogen cycling (Tate III 1982). The following paper examines effects of moisture content and nitrogen fertilizers on CH_4 and N_2O fluxes in a humisol.

Materials and methods

Field nitrogen fertilization

All studies were undertaken in 1993 on a humisol located on the Central Experimental Farm of Agriculture Canada in Ottawa, Ontario. An organic layer (loss on ignition 70.6%; pH in H_2O 7.2; density 2.43 g cm^{-3}; bulk density 0.41 g cm^{-3}) was underlain by a clay pan at 30–40 cm depth. An uncharacterized plant community dominated by perennial grasses colonized the study area. Twelve 2 m × 2 m plots in a 6 m × 8 m block were randomly assigned to three treatments: no fertilizer addition, or 100 kg N ha^{-1} of urea (soluble) or $NaNO_3$ fertilizer broadcast onto plots followed by irrigation with 10 L H_2O per plot on calendar day (CD) 195.

Each plot contained three, 0.282 m^2 acrylic chamber collars, protruding 5 cm above the soil surface. These were used as described in Lessard et al. (1994) to determine N_2O and CH_4 fluxes at one week intervals from CD 159 to CD 285 (June 8 to October 12), between 1100 h and 1500 h on each day. Soil temperature was estimated using thermistors buried to 7.5 cm depth in each chamber, and soil moisture by oven drying (50 °C) to constant weight soil from 0–15 cm depth, pooled from at least three, 2.5-cm diameter cores.

CH_4 was measured using either a Varian (4.8 m Porapak N column; oven temperature 60 °C; detector temperature 390 °C) or Shimadzu (1.2 m Porapak Q column; oven temperature 50 °C; detector temperature 110 °C) gas chromatograph with a flame ionization detector and a 0.5 mL sample loop. N_2O and O_2 were measured using a Varian or a Perkin-Elmer (1.2 m Porapak Q column; oven temperature 40 °C; detector temperature 275 °C) gas chromatograph with an electron capture detector (^{63}Ni) and a 0.5 mL sample loop. Injection ports were used in other experiments when <2 mL sample was available.

For negative CH_4 fluxes (i.e. net CH_4 consumption), rate constants from first-order regressions of ln[CH_4] versus time were used to calculate flux at 1.7 ppmv CH_4. N_2O fluxes, and positive CH_4 fluxes, were estimated by linear regression. For statistical analyses the three chambers within each plot were pooled, and Repeated Measures ANOVAs performed with fertilizer treatment as a grouping factor and sampling day as a repeat factor, using SYSTAT (SYSTAT Inc. Evanston, Illinois). Homogeneity of variance was checked using residual plots. All multivariate probabilities given are the Pillai Trace Statistic, and multiple comparisons were done by the Bonferroni method.

Three 2.5-cm diameter soil cores per plot, divided into 0–3, 3–6, 6–12, 12–18, 18–24, and 24–30 cm depth intervals, were pooled at several dates after fertilization. A portion was frozen immediately and later extracted (2.5 g fresh wt. of soil: 10 mL of 2 M KCl) for colorimetric determination of NH_4^+

and NO_3^- using an automated analysis system described previously (Megraw & Knowles 1987a). A small amount of activated charcoal was added to decolorize extracts after this was shown not to affect N recovery. Within two days of sampling on CD 215, CD 222, and CD 229, 5 g ± 0.1 g subsamples (fresh wt.) of each plot × depth were placed in 60-mL serum vials containing ambient (2 ppmv) CH_4, and CH_4 concentrations determined at 24-h intervals for 3–4 days.

Potential nitrification rate

Soil sampled from 0–20 cm depth on CD 222 (81% H_2O) and stored at 12 °C was slurried at a 1:3 weight ratio of soil : distilled deionized H_2O, and 15-mL aliquots distributed into 60-mL serum vials. NH_4Cl solutions (5 mL) were added to triplicate flasks at initial concentrations of 19 to 450 μg NH_4^+-N g $soil^{-1}$. Slurries were incubated at 25 °C under ambient (2 ppmv) CH_4 on a gyratory shaker at 250 rpm. One-mL slurry samples were removed 1.5 h and 8 h after adding NH_4Cl and frozen immediately. For analysis, samples were thawed by centrifuging 5 minutes (4 °C, 13000 g), resuspended by manual shaking, and centrifuged again for 15 minutes. NH_4^+, NO_3^- and NO_2^- in the supernatant were analyzed colorimetrically (Megraw & Knowles 1987a).

Flux estimation methods comparison

On CD 201 and CD 222 (July 20 and August 10), various methods of estimating CH_4 and N_2O fluxes in unfertilized soil were compared. These involved a) field chambers as described above, in control plots only; b) soil cores with an enclosed headspace; c) field gas concentration gradients; and d) gas concentration gradients in soil cores.

Cores were 50-cm long, 7.8-cm diameter polyvinyl chloride tubes sharpened at one end. These were driven with a sledgehammer to 40 cm depth, such that the entire organic horizon and some of the clay pan was sampled. No compaction was evident. After removing cores, 0.5-cm diameter holes previously drilled at 5-cm intervals were fitted with plug-type rubber septa (for Shimadzu gas chromatographs), so air in the soil matrix and over the soil surface (headspace) could be sampled with syringes. Core bottoms were fitted with plastic caps, and a gas-tight seal assured with Terostat sealant (Teroson GmbH, Heidelberg, Germany). Soil cores were taken from within 3 m of the experimental plots, stored at 22.5–25 °C, and gas fluxes determined within 2 (CD 201) or 5 (CD 222) days. For enclosure flux determination, core tops were capped as described above and 2-mL headspace samples removed at 30–60 minute intervals for 2–3 h. When sampling enclosed cores, 1 atm pressure was maintained by reinjecting an equal volume of air.

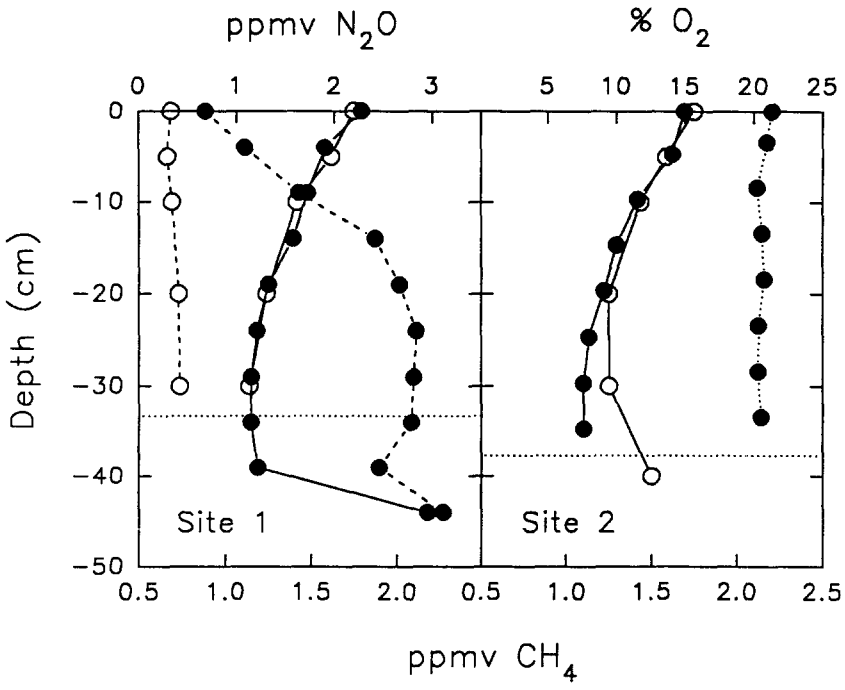

Fig. 1. Typical CH_4 (solid lines) N_2O (dashed lines) and O_2 (dotted lines) concentration gradients measured in the field (o) and in soil cores (•) at two unfertilized sites on CD 201. Horizontal dotted lines indicate the position of the clay layer.

Gas concentration gradients were determined in cores by sampling 2 mL of headspace and soil matrix air through the 5-cm spaced ports, and in the field by inserting a 1.5 mm ID stainless steel tube to 5, 10, 20, and 30-cm depths and withdrawing 10 mL of soil matrix air into syringes fitted with nylon valves. On CD 201, a field gradient was sampled within 20 cm of each coring site for direct comparison. Flux was calculated using Fick's law (Whalen et al. 1992; Koschorreck & Conrad 1993). For CH_4:

$$J = D_{CH_4soil} \times d[CH_4]/dz \quad (1)$$

where J is flux (μmol m^{-2} d^{-1}) and D_{CH_4soil} is the binary diffusion coefficient of CH_4 in soil matrix air (m^2 d^{-1}), estimated as described below. CH_4 concentration decreased linearly to 20 cm (e.g. Fig. 1), so $d[CH_4]/dz$ (μmol m^{-4}) was estimated as the slope of the concentration gradient.

To determine D_{CH_4soil} in equation (1), CH_4 oxidation in two soil cores was halted using methyl fluoride (CH_3F) (Oremland & Culbertson 1992). One mL ($\cong$ 1% of gas phase) of CH_3F (Matheson Gas Products, Ville St. Laurent, Quebec) was injected into each side port, 24 h and 2 h before injecting

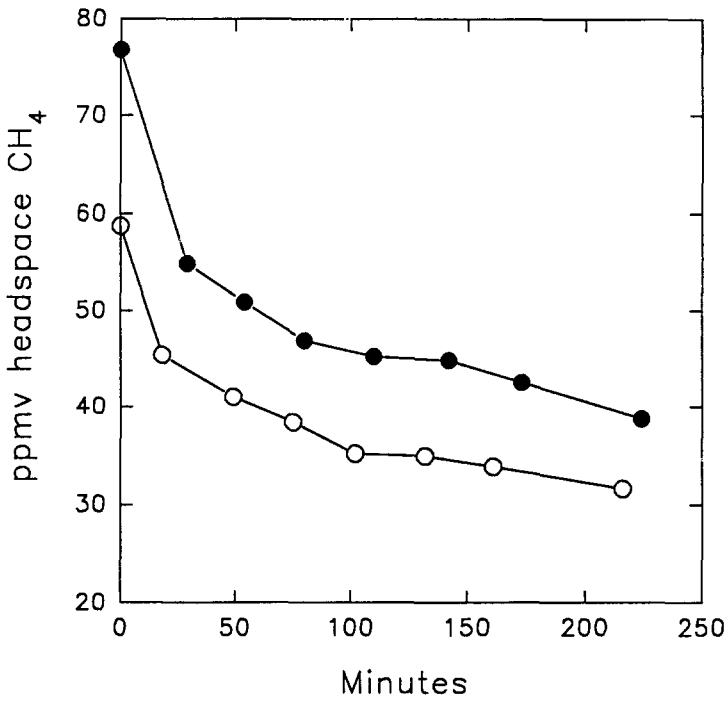

Fig. 2. Disappearance of added CH_4 from the headspace of two cores in which CH_4 oxidation was completely inhibited by CH_3F, used in the estimation of D_{CH_4soil} on CD 201.

0.05 mL (≅ 100 ppmv) CH_4 into the headspace. Addition of CH_3F to cores completely halted CH_4 oxidation 3 h later (data not shown). At 20–30 minute intervals for 3 h, 1-mL gas samples from 0–20 cm depth were taken for CH_4 determination (Fig. 2). The initial point (immediately after injecting CH_4) was omitted from calculations as $d[CH_4]/dz$ was nonlinear, and headspace CH_4 may not yet have equilibrated. CH_4 fluxes were estimated using the relaxation constant (Sparks 1989), obtained from first-order regression of $\ln([CH_4] - [CH_4]_{equilibrium})$ versus time. Flux estimation by linear regression at 20–100 min. and 100–220 min. (Fig. 2), or by difference at each time interval, gave results within 10% of the estimate by first-order regression. From J and $d[CH_4]/dz$, D_{CH_4soil} could then be estimated from equation (1) at each sampling time. D_{N_2Osoil} was calculated from D_{CH_4soil} assuming the same ratio as D_{N_2Oair}/D_{CH_4air} (0.734) (Campbell 1985; Striegl 1993).

As an alternative to the experimental determination of D_{CH_4soil}, the following estimate was used:

$$D_{CH_4soil} = D_{CH_4air} \times a\phi_g^b \qquad (2)$$

where D_{CH_4air} is 1.95 m^2 d^{-1} at 22.5 °C (Striegl 1993), ϕ_g is fractional gas-filled soil porosity, a and b are factors to compensate for soil-dependent tortuosity. Suggested average values of a = 0.9 and b = 2.3 were used (Campbell 1985).

Gas-filled porosity (ϕ_g) was determined in cores using a plastic cap fitted with a 60-mL syringe and pressure valve (0–60 mm Hg) as a gas pycnometer (Vomocil, 1965). After fitting the cap and ensuring a gas-tight seal, enough air to raise the pressure by about 30 mm Hg was injected into the core headspace. Core gas volume was determined from the constancy of pressure × volume before and after injection. Cores were later harvested to determine the depth of the clay pan, and ϕ_g corrected by assuming a clay ϕ_g of zero. This assumption was found to be valid by comparing ϕ_g in deeper, 50-cm cores containing proportionally more clay. The ϕ_g of each core was considered separately in calculations involving that core or adjacent field sites on CD 201, while an average of 0.474 was used for field gradients on CD 222. The pycnometer procedure also served as a leak test for each core, and to estimate bulk density and soil density in cores dried at 50 °C to constant weight.

The effect of H_2O on CH_4 consumption

A set of unfertilized soil cores was taken on CD 222. Three cores were kept as unwatered controls and three each were gradually saturated with H_2O in 50-mL or 150-mL increments, at 3–5 day intervals. One control and one core receiving 150-mL waterings were later discovered to be leaky and were discarded. Enclosure fluxes were measured at 5 h and 24 (± 4) h after each H_2O addition, by sampling at 0.5-h intervals for 1.5 h. Gas concentration gradients were measured after 24 (± 4) h. Water penetration was slow on the first 3–4 waterings. To force water into the soil matrix at these times, and prevent percolation down the sides of cores, a 60-mL syringe was inserted into a subsurface port and a suction created. Cores were stored at 25 °C, but flux measurements were done at room temperature varying from 23–27.5 °C. All calculations accounted for temperature variation (Striegl 1993).

In a parallel set of cores, 1 mL of CH_3F was periodically injected into each side port and allowed to diffuse slowly out of the cores. These controls were intended to distinguish between H_2O effects on CH_4 oxidation through diffusion, and H_2O effects on methanogenesis. However, methanogenesis was shown to be insignificant without the need for these (see Results). Enclosure N_2O fluxes were measured at irregular intervals. CH_3F was assumed not to affect N_2O production, but this assumption is invalid if methanotrophs or nitrifiers contributed to N_2O flux and were inhibited by CH_3F.

Results

Field nitrogen fertilization

The field was a net CH_4 source until sometime between CD 194 and CD 201, when the moisture level declined from 130% to 95% (Fig. 3). Until late in the season, average CH_4 oxidation was then nearly constant between 20–25 μmol m^{-2} d^{-1}, despite a gradual decline in water content and, to a lesser extent, temperature. A Repeated Measures ANOVA of post-fertilization CH_4 flux showed no significant effects of fertilizer treatment ($P = 0.084$), sampling day ($P = 0.21$) or sampling day $\times$ fertilizer treatment ($P = 0.55$).

N_2O fluxes were highly variable. On CD 173 and CD 186 (prior to fertilization) net fluxes were negative in 20 of 34, and 26 of 36 chambers, respectively. Although significance was not tested for each chamber, the binomial probability of obtaining 26 of 36 negative fluxes when the actual flux is nil, is only P(2-tail) = 0.0064. The mean flux on CD 186 of -6.23 μmol N_2O m^{-2} d^{-1} (SEM = 1.9), is significantly less than 0 at the $P = 0.01$ level.

N_2O fluxes were log transformed, and to avoid negative fluxes only data from CD 208 to CD 236 were used in the Repeated Measures ANOVA. N_2O flux on these days was significantly affected by treatment ($P = 0.015$), and sampling day ($P = 0.002$), but not by treatment $\times$ sampling day ($P = 0.30$). Fluxes in control versus urea plots were not significantly different ($P = 0.11$), but $NaNO_3$ plots produced significantly more N_2O than control plots ($P = 0.005$). The stimulation by $NaNO_3$ was transitory (Fig. 3), and unless large flux episodes were missed by the sampling regime, accounted for a small fraction of the added fertilizer. Based on average fluxes between CD 201 and CD 222, 1.23 mmol m^{-2} of added NO_3^--N and 0.40 mmol m^{-2} of added urea-N (not significant) were lost as N_2O, or 0.17% and 0.056%, respectively, of the amounts added.

KCl-extractable NO_3^- profiles are shown in Fig. 4. No extra NH_4^+ was detected at any depth in urea plots compared to control plots, on CD 201 or later (data not shown). This suggests that added urea, upon hydrolysis, was rapidly nitrified, volatilized, or assimilated by plants and microorganisms. Elevated NO_3^- concentrations in urea plots on CD 201 implicates nitrification as the primary factor. Why NO_3^- in plots with added urea should later decline while those in $NaNO_3$ fertilized plots did not is unclear, but may have been related to fertilization effects on plant growth and pH. Plant cover in $NaNO_3$-fertilized plots appeared chlorotic compared to other plots.

Typical depth profiles of potential CH_4 oxidation are shown in Fig. 5. A Repeated Measures ANOVA using sampling day (CD 215, CD 222, and CD 229), and depth (0–3, 3–6, and 6–12 cm) as repeat factors and fertilizer treatment as a grouping factor, showed neither significant fertilizer effects

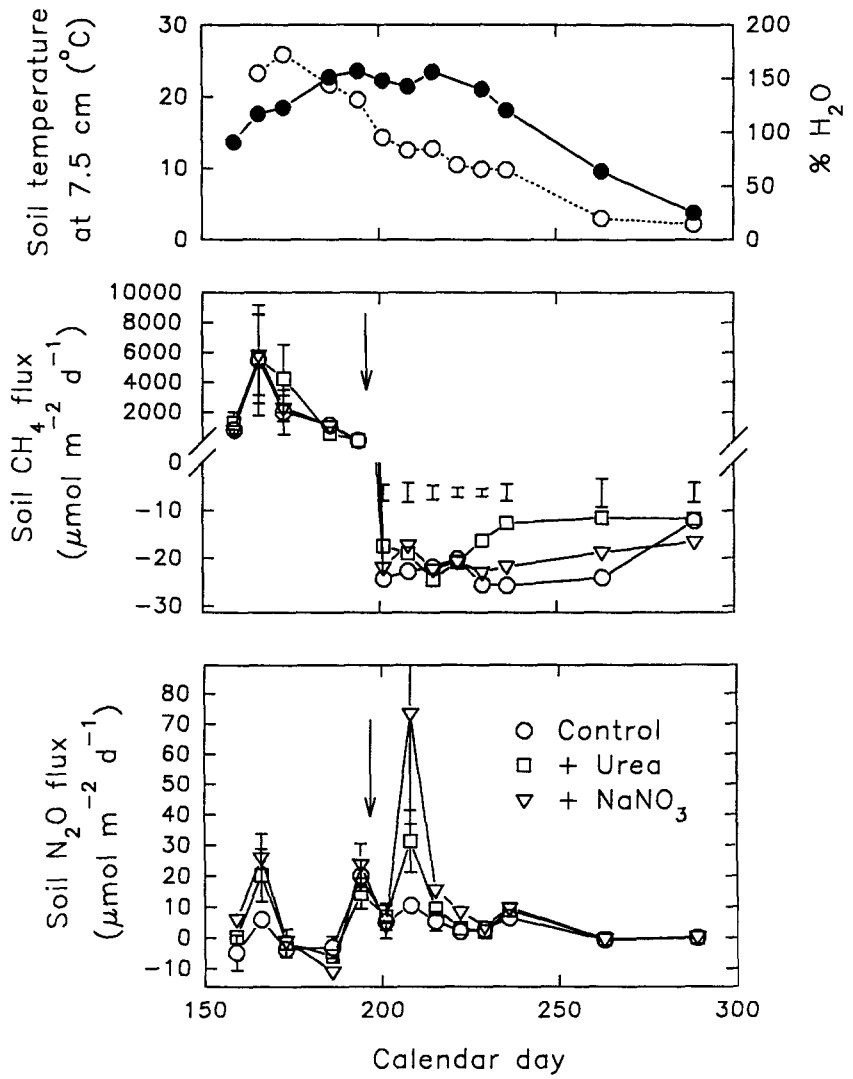

Fig. 3. Chamber CH_4 and N_2O fluxes in an Ottawa humisol from June 4 to October 16, 1994, with corresponding soil moisture (% dry weight) at 0–15 cm depth (o) and soil temperature at 7.5 cm (•). The arrow indicates the addition of 100 kg N ha^{-1} of urea or $NaNO_3$ on CD 195. Each point is the mean of four plots containing three chambers each, ±1 SEM for each treatment. CH_4-flux error bars after CD 200 represent 1 SEM pooled for each day, from the Repeated Measures ANOVA.

($P = 0.53$), nor significant interactive fertilizer effects (depth × fertilizer, $P = 0.96$; sampling day × fertilizer, $P = 0.97$; depth × day × fertilizer, $P = 0.23$). The variability of CH_4 oxidation with depth was significant ($P < 0.001$), as were sampling day ($P = 0.002$) and depth × day effects ($P = 0.046$).

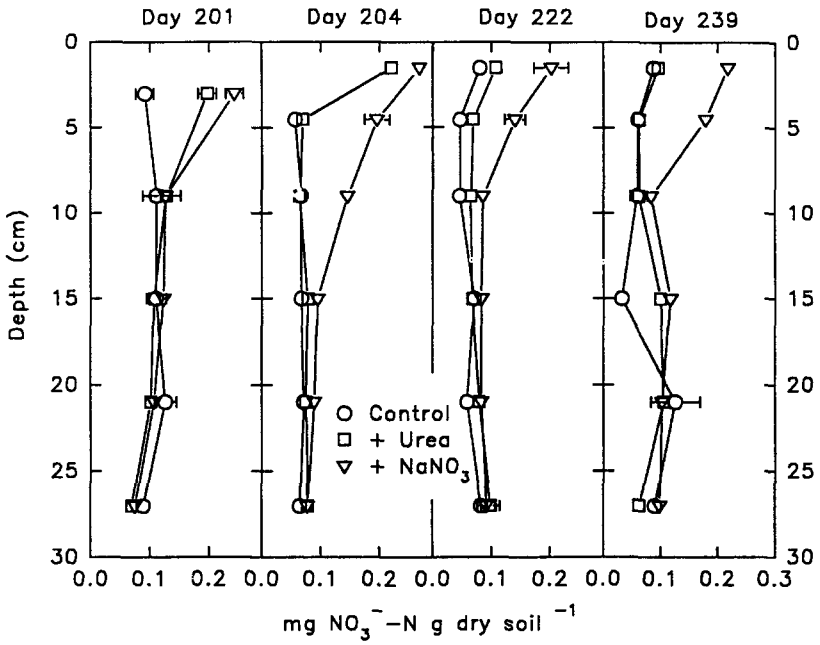

Fig. 4. 2 M KCl-extractable NO_3^--N with depth and time, in control plots and plots receiving 100 kg N ha^{-1} urea or $NaNO_3$ on CD 195. Data are means of 3 or 4 plots ± 1 SEM.

Potential nitrification

Regardless of the amount of NH_4^+ added, 60–70% was not recoverable from the liquid phase of soil slurries and was assumed to be bound to exchange sites. This bound NH_4^+ was subject to nitrification, probably as it equilibrated with the solution. Average dissolved NH_4^+ concentration (the arithmetic mean of concentrations at the beginning and end of the incubation) was 44 μM in control slurries and ranged from 91 μM to 2.1 mM in slurries with added NH_4^+. Nitrification, measured as appearance of NO_2^- and NO_3^-, was not affected by NH_4^+ concentration over 91 μM ($P = 0.065$; coefficient was a decrease of 3.6% per mM NH_4^+). The average nitrification rate in all vials with added NH_4^+ was 5.95 μmol N g dry $soil^{-1}$ d^{-1}. An average of only 3.3% appeared as NO_2^- rather than NO_3^-.

Flux estimation methods comparison

Examples of field and core gas concentration gradients on CD 201 are shown in Fig. 1. CH_4 concentration declined linearly to 20 cm, but a slight horseshoe shape in many cases indicates two CH_4 sources, the atmosphere and a deep

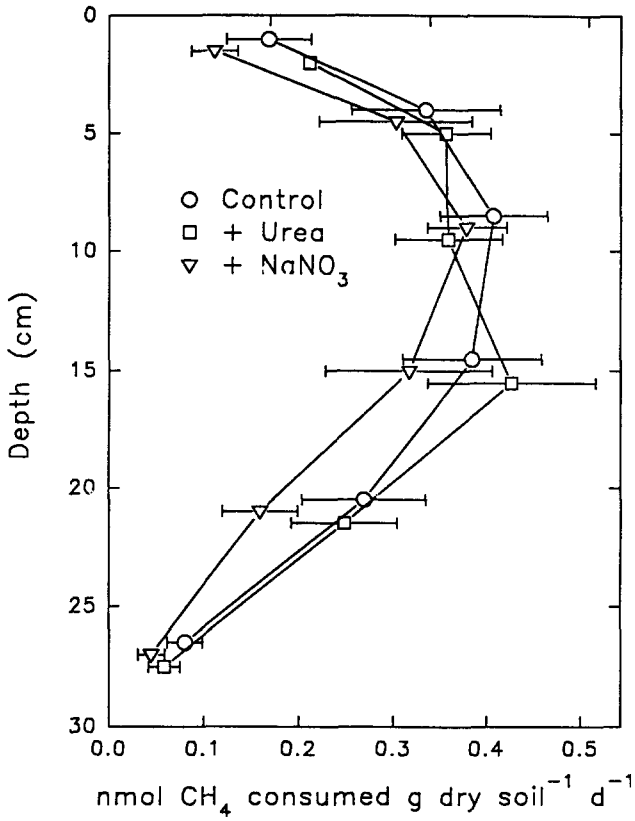

Fig. 5. Potential atmospheric (2 ppmv) CH_4 oxidation rate with depth on CD 215, of soil samples from control plots and plots receiving 100 kg N ha^{-1} urea or $NaNO_3$ fertilizer on CD 195. Points are means of four samples ±1 SEM.

(> 30 cm) soil layer. Soils were aerobic throughout the organic layer. Field and core CH_4 gradients were nearly identical at each sampling spot (e.g. Fig. 1), a fact reflected in the closeness of gradient-calculated fluxes (Table 1). N_2O concentration gradients were less consistent between the field and cores, although they were also linear to > 15 cm (Fig. 1), indicating a non-surface source of N_2O.

Average ϕ_g was 0.395 on CD 201 and 0.474 on CD 222. Good agreement of CH_4 fluxes between field chambers and cores, and between gradient and enclosure estimates were obtained on both dates (Table 1). N_2O fluxes were much more variable (Table 2). N_2O flux comparisons are complicated by the non-normal distribution, and variability from positive to negative. Using a nonparametric Kruskal-Wallis test, core flux was significantly greater than chamber flux (P = 0.003) on CD 201. However, $d[N_2O]/dz$ in cores was

Table 1. Fluxes of CH_4 (μmol m^{-2} d^{-1}) in a humisol determined by various methods on two dates, with standard errors (SEM) and coefficients of variation (CV). See text for details of methods and calculations.

Method	Calendar day 201				Calendar day 222			
	N	Flux	SEM	CV(%)	N	Flux	SEM	CV(%)
Enclosure methods								
Cores	11	−23.3	2.39	34.0	7	−28.9	2.51	22.9
Chambers	12	−23.9	4.16	60.3	12	−20.7	1.73	28.9
Gradient methods								
$D_{CH_4soil} = 0.9\ \phi_g^{2.3}\ D_{CH_4air}$								
Core gradients	11	−21.0	1.27	20.0	7	−23.2	1.79	20.4
Field gradients	11	−21.0	1.96	30.8	9	−20.2	6.28	92.6
$D_{CH_4soil} = 0.192\ m^2\ d^{-1}$								
Core gradients	11	−19.0	1.56	27.2				
Field gradients	11	−19.1	1.03	17.9				

not significantly greater than in adjacent field sites (Kruskal-Wallis test, $P = 0.076$). The disparity between core and chamber fluxes could therefore result from non-random sampling (i.e. cores were taken from outside of the experimental area), combined with the large spatial variability of N_2O production, or it could result from some disturbance effect of coring. While core CH_4 fluxes can be extrapolated to the field, the same may not be true of N_2O. Applying Fick's law to N_2O concentration gradients still agrees well with enclosure fluxes, if one considers field and core measurements separately (Table 2).

Equation (2) was used for empirical estimation of D_{CH_4soil}, due to better agreement with chamber fluxes than other adjustments (e.g. in Striegl 1993). Indeed, D_{CH_4soil} determined in CH_3F-spiked cores on CD 201 (0.192 m^2 d^{-1}) was close to the empirically estimated value from equation (2) (0.206 m^2 d^{-1}). These values are similar to those reported for other soils (Koschorreck & Conrad 1993). The relaxation constant of added CH_4 in CH_3F-containing cores was −0.578 h^{-1}.

The effect of H_2O on CH_4 consumption

CH_4 oxidation increased nonlinearly with decreasing water content, exhibiting a plateau above about ϕ_g = 0.2–0.25 (120–130% H_2O) (Fig. 6). An

Table 2. Fluxes of N_2O (μmol m^{-2} d^{-1}) in a humisol determined by various methods on calendar day 201, with standard errors (SEM) and coefficients of variation (CV).

Method	N	Flux	SEM	CV(%)
Enclosure methods				
Cores	5	43.5	9.33	47.9
Chambers	12	6.39	3.57	193
Gradient methods				
$D_{N_2Osoil} = 0.9\ \phi_g^{2.3}\ D_{N_2Oair}$				
Core gradients	5	36.4	13.3	81.9
Field gradients	5	10.3	7.35	159
$D_{N_2Osoil} = 0.141\ m^2\ d^{-1}$				
Core gradients	5	30.5	10.6	77.5
Field gradients	5	7.94	5.30	150

equation describing CH_4 oxidation as an exponential function of ϕ_g was fit to the cores watered in 50-mL increments, using the curve fit function of SigmaPlot 5.1 (Jandel Scientific, San Rafael, CA, USA). This is unbiased over the entire range of ϕ_g tested and is of the form:

$$J(\mu mol\ m^{-2}d^{-1}) = 28.3 - 46.7e^{(-7.74\phi g)} \quad (3)$$

CH_4 oxidation in the two unwatered control cores decreased during the course of the experiment, by averages of 0.33 and 0.090 μmol m^{-2} d^{-2}. Core ϕ_g was experimentally decreased over time by watering, so any decline in soil CH_4-oxidizing capacity due to factors other than water content would introduce error into the experiment. Compensating for this decline by expressing fluxes as percentages of control cores on each day, and multiplying by the average control flux over the course of the experiment (23.5 μmol m^{-2} d^{-1}), gives a similar exponential relationship, with a sharper rise to the maximum:

$$J(\mu mol\ m^{-2}d^{-1}) = 23.3 - 78.9e^{(-16.7\phi g)} \quad (4)$$

The decline does not affect the nature of the water relationship, only its magnitude.

Only cores watered in 50-mL increments were included in these calculations. In cores given 150-mL waterings, H_2O rather than gas was often

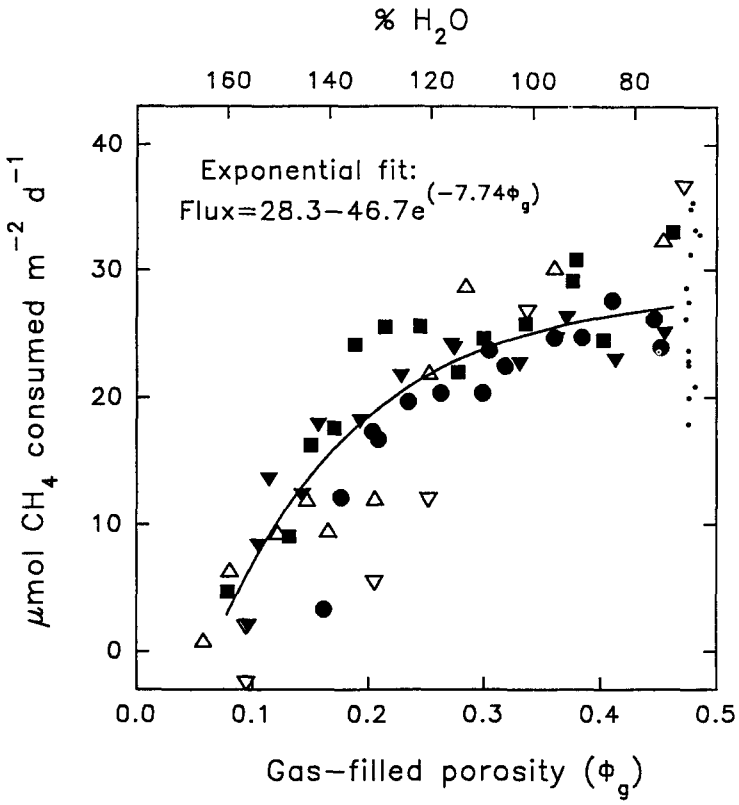

Fig. 6. Effect of H_2O content on CH_4 oxidation in soil cores. Each symbol type represents a separate core gradually saturated with H_2O in 50-mL (closed symbols) or 150-mL (open symbols) increments, at 3–5 d intervals. Fluxes are means of measurements taken 5 and 24 (±4) h after each H_2O addition. ϕ_g was estimated after each watering using a gas pycnometer; % H_2O from measurements at the start and end of the experiment only. Dots represent two cores unwatered throughout the experiment.

sampled from the upper ports, and CH_4 gradients were often nonlinear, declining steeply in a 5–10 cm deep subsurface zone. The larger water addition may have had a piston effect, a front of infiltrating H_2O acting as a diffusion barrier. To show that this was not a problem in cores receiving 50-mL water additions, soil samples from 5-cm increments were taken at the end of the experiment and dried (50 °C). There was no obvious increase or decrease of H_2O content with depth in these samples, it was constant within ± 12% throughout the soil profile (data not shown).

Decreases in $d[CH_4]/dz$ (more negative values) as water content increased (Fig. 7) compensated in part for a concurrent decrease in D_{CH_4soil}, and flux remained constant over a wide ϕ_g range. Fig. 7 also suggests that the decline

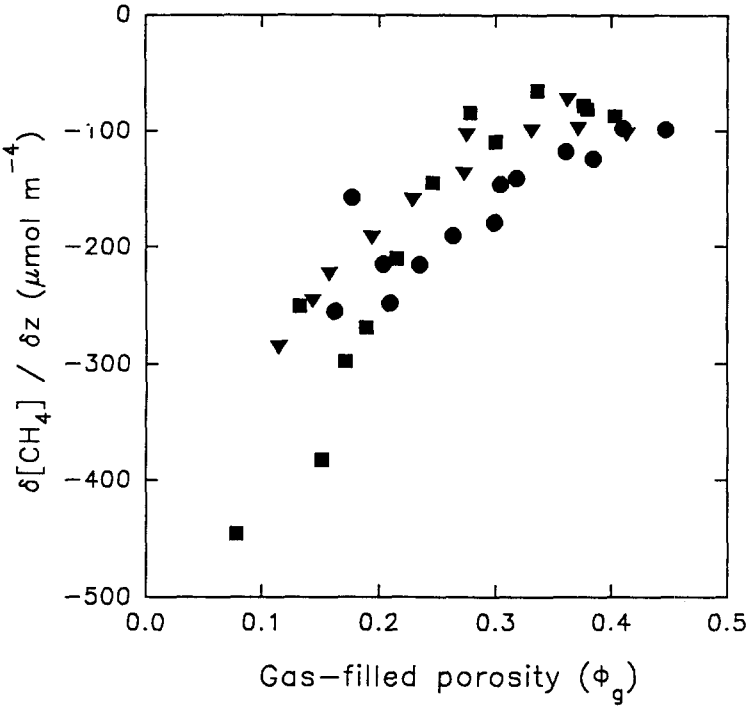

Fig. 7. Effect of gas-filled porosity (ϕ_g) on CH_4 concentration gradients with depth (0–15 cm) in soil cores. Each symbol type represents a separate core gradually saturated with H_2O in 50-mL increments. Gradients were measured 24 (±4) h after each H_2O addition.

of CH_4 oxidation at low ϕ_g resulted from diffusion limitation rather than CH_4 production. $d[CH_4]/dz$ continued to decrease as long as H_2O was added, whereas an opposite trend would be expected as CH_4 production began. Also, CH_4 oxidation in cores watered in 50-mL increments was halted at the end of the experiment ($\phi_g \cong 0.11$) by injecting 1 mL CH_3F into each of the top four ports. No CH_4 flux, positive or negative, was then evident in cores (data not shown). The cores watered in 150-mL increments, when left at $\phi_g \cong 0.1$ for several days, did begin to produce CH_4.

The coefficients a and b from equation (2) are empirical adjustments for soil tortuosity. These were estimated by fitting core enclosure flux, ϕ_g, and $d[CH_4]/dz$ to equations (1) and (2) for each 24-h sampling time of cores receiving 50-mL water additions. $d[CH_4]/dz$ was estimated for 0–15 cm, except on the last few dates when $[CH_4]$ reached a minimum before 15 cm. This gave a = 0.67 and b = 1.68, while a = 0.9 and b = 2.3 were average values suggested by Campbell (1985) and used in the methods comparison (Tables 1 and 2).

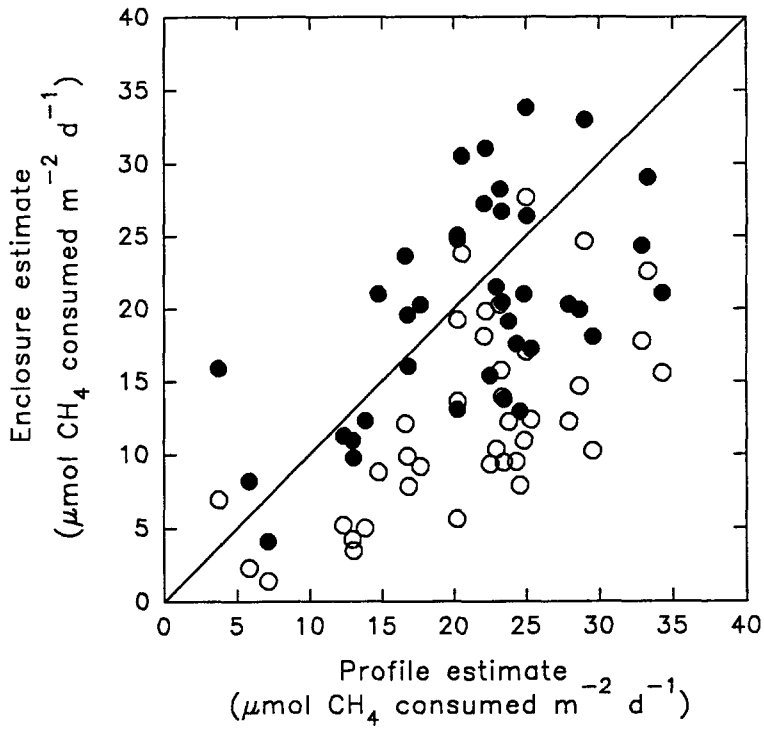

Fig. 8. Comparison of CH_4 flux in cores estimated either by measuring enclosed headspace depletion, or by applying Fick's law in the form $J = D_{CH_4air} \times a\phi_g^b \times d[CH_4]/dz$; where a = 0.67 and b = 1.68 (•). A range of ϕ_g was created by gradually saturating cores with H_2O in 50-mL increments. The line at x = y is included as a visual aid only.

Gradient-based core CH_4 fluxes determined from equations (1) and (2) are unbiased in relation to ϕ_g (Fig. 8). Although using equation (2) with a = 0.9 and b = 2.3 (Campbell 1985) underestimates core enclosure fluxes, the underestimate is consistent over the entire range of ϕ_g. Our estimates of these factors (a = 0.67, b = 1.68) may not be ideal, since not enough low-flux points are present for even weighting. Nevertheless, they are also unbiased towards ϕ_g. The exponential nature of equation (2) seems valid, introducing no skew at extremes of ϕ_g.

N_2O fluxes in cores gradually saturated with H_2O are shown in Fig. 9. Due to extreme variability, the same ϕ_g versus flux relationships could not be calculated as with CH_4. Cores often showed a burst of N_2O production after water addition, which then gradually trailed off. Absolute water content also affected flux, as revealed by the gradually increasing size of the flux bursts at each watering time.

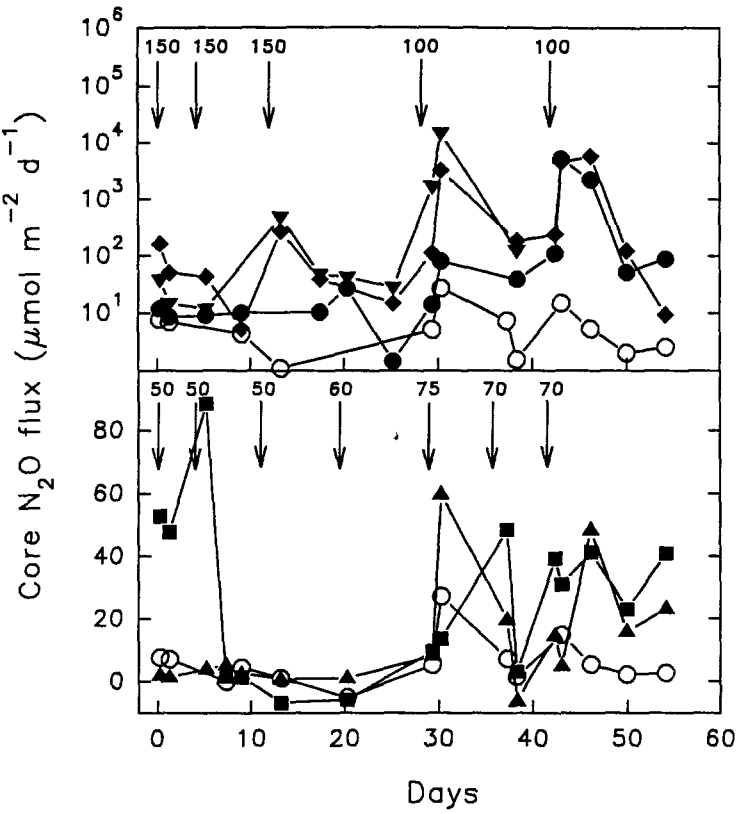

Fig. 9. Soil core N_2O flux in response to water addition. Arrows indicate the timing and amounts (mL) of H_2O additions. Each symbol type represents a separate core, except (o) which represents average flux in three cores unwatered throughout the experiment.

Discussion

Field nitrogen fertilization

Fertilization with 100 kg N ha^{-1}, or 1 mg N cm^{-2}, assuming penetration to only 5 cm depth, amounts to 0.48 mg N g dry $soil^{-1}$, about 34 mM N at 100% H_2O. This level of $NaNO_3$ inhibited CH_4 consumption in slurries by only 19% (Dunfield & Knowles, unpublished data), and such inhibition would occur in the upper 5 cm only. However, less than 500 μM NH_4Cl was needed to completely halt CH_4 oxidation in slurries (Dunfield & Knowles, unpublished data). Variations in penetration depth or moisture content have very little bearing on the conclusion that, assuming slurry studies were correct, 100 kg urea-N ha^{-1} should have inhibited field methanotrophic activity.

We suggest two hypotheses to explain the lack of such an effect in this study. 1) Most of the NH_4^+ released upon urea hydrolysis was immobilized on cation exchange sites in the upper few cm of the soil. The field showed a subsurface maximum of potential CH_4 oxidation, similar to forest soils (Adamsen & King 1993; Koschorreck & Conrad 1993), although CH_4 oxidation was evident throughout the humic layer. Since CH_4 oxidation was not diffusion limited, surface–localized NH_4^+ should have little effect on overall CH_4 flux. CH_4 oxidation would simply occur in deeper soil. However, incubations of soil at three, four, and five weeks following fertilizer application showed no inhibition of CH_4 oxidation at any depth, and no extra NH_4^+ was detectable in the upper few cm of urea-fertilized plots.

While surface-immobilization could have been a factor immediately after fertilization, a more likely explanation is: 2) NH_4^+ was rapidly oxidized, volatilized as NH_3, or assimilated as urea was hydrolysed (Gould et al. 1986). Measurements of soil nitrogen ions implicate oxidation as a major factor. In comparison to control plots, no extra KCl-extractable NH_4^+ was recovered from urea plots six days after fertilization, but NO_3^- levels were elevated. The estimated nitrification rate of 5.95 μmol N g dry soil^{-1} d^{-1}, or 83.3 μg N g dry soil^{-1} d^{-1}, even without considering the possibilities of population growth and enzyme production, could consume 100 kg NH_4^+-N ha^{-1} in 5.8 days (assuming an active depth of 5 cm). This nitrification potential is higher than in most other soils (Mahli & McGill 1982, and references therein; Megraw & Knowles 1987a). Urease activity might have been the rate-limiting step for conversion of urea to NO_3^- in the field. As a comparison, CH_4 oxidation in another drained peat soil was inhibited by urea or NH_4Cl addition three weeks after fertilization, but NH_4^+ also remained elevated at this time (Crill et al. 1994). Bronson & Mosier (1993) observed inhibition of CH_4 oxidation from 218 kg N ha^{-1} added urea only immediately after fertilization. Cessation of inhibition corresponded to loss of soil NH_4^+.

Unlike some arable soils, humisols may have considerable methanogenic potential (Megraw & Knowles 1987b; Glenn et al. 1993). Our humisol exhibited net CH_4 production early in the season when flooded, and even after becoming a net CH_4 sink, a subsurface CH_4 source was indicated by CH_4 gradients. The deep CH_4 source occurred in the clay layer or humisol-clay interface, where O_2 diffusion may be limited and reducing microsites occur. Soil CH_4 profiles were not measured throughout the year, so the dynamics of this phenomenon are unclear. An endogenous dissolved CH_4 supply, even if transitory, could help maintain soil methanotrophs. Inhibition of CH_4 oxidation through long-term fertilization might then occur as elevated NO_3^- levels raise the soil redox potential and reduce methanogenesis. The CH_4 oxidation rate in this field (20–25 μmol m^{-2} d^{-1}) is at the low end of the range

found in natural grassland and forests (Steudler et al. 1989; Born et al. 1990; Ojima et al. 1993), but similar to levels in other cultivated soils (Mosier et al. 1991; Bronson & Mosier 1993; Hansen et al. 1993; Lessard et al. 1994). The endogenous CH_4 source may or may not mitigate net CH_4 flux, depending on its magnitude and on CH_4 diffusion rates.

The negative N_2O flux on CD 186 is unusual, but not without precedent (e.g. Ryden 1983). The soil at this time was still flooded, and under these reducing conditions denitrifying organisms may have been limited by the supply of oxidised nitrogen molecules. Complete reduction of NO_3^- and NO_2^- to N_2 would therefore be advantageous (Davidson 1991), as would the ability to scavenge ambient N_2O. N_2O fluxes are strongly affected by H_2O content, as this influences availability of O_2, NO_3^-, NO_2^-, and growth substrates. Bursts of N_2O production, as observed in our cores, often follow water addition (Davidson 1992; Bronson & Mosier 1993; Hansen et al. 1993). However the presence of CH_3F in these cores may complicate the results by inhibiting nitrifiers.

About 0.17% of added NO_3^--N, and 0.056% (not significant) of added urea-N were lost as N_2O in this experiment. The NO_3^--N loss as N_2O is within the ranges found in other experiments, while the urea loss is somewhat less (Eichner 1990). Stimulation of N_2O production by $NaNO_3$ suggests a denitrification source of N_2O. However, if nitrification of urea-N did occur as predicted in less than 6 days, the sampling regime could have missed an episodic, nitrification-related N_2O burst. On the initial post-fertilization sampling date (6 days) N_2O fluxes were small. This apparent "delay" probably attests to the number of temporally variable factors controlling N_2O fluxes (Davidson 1991). The small (nonsignificant) stimulation of N_2O production by urea may have been a NO_3^- effect.

The fact that $NaNO_3$ stimulated N_2O flux even though NO_3^- concentrations were also high (> 1 mM) in control plots, suggests that the ratio of products rather than the absolute denitrification rate was altered by fertilization. With more NO_3^- available, and perhaps limiting energy sources, reduction of N_2O would become less advantageous for denitrifiers. Inhibition of soil N_2O-reducing activity has been shown to result from NO_3^- addition (Blackmer & Bremner 1978). The transitory nature of N_2O production from $NaNO_3$, even while NO_3^- levels remained elevated, could have resulted from increasing aeration as water content declined. N_2O profiles late in the season indicated a subsurface N_2O source, perhaps because denitrification at this time was confined to anaerobic microsites in deep soil.

Diffusion

Application of Fick's law to concentration gradients produced similar flux estimates as enclosure methods, over a wide range of ϕ_g. The usefulness of diffusion-based CH_4 flux estimation has been previously demonstrated by Koschorreck & Conrad (1993), using experimentally determined soil diffusion coefficients. Whalen et al. (1992) bypassed estimation of the diffusion coefficient in a forest soil by applying equation (2), but with less success. Vertical zonation and horizon structure introduce problems, although not with the humisol used in our study. Whalen et al. (1992) also pointed to the difficulty in applying average tortuosity adjustment values of a = 0.9 and b = 2.3 (Campbell 1985) to different soils. Accounting for tortuosity is a problem in any such study, and several correction factors have been suggested (Striegl 1993). Equation (2) worked well here, giving a D_{CH_4soil} estimate similar to that determined in cores containing CH_3F, and causing no skew in flux estimation at extremes of ϕ_g. The suggested average values a = 0.9 and b = 2.3 were very close to those calculated from cores.

The use of soil cores for further study was justified by the agreement of field and core-derived CH_4 fluxes, whether by enclosure or diffusion-based estimates. Compared to chambers, the small surface area of cores and the restriction of lateral gas diffusion should result in higher variability, but this was not evident. Longer core incubation times (2–3 h versus 30 min.) may have compensated by allowing more precise measurements. Cores certainly are not perfect mimics of the field. The temperature variability with depth is much less, for example. However, other studies stress a relatively minor influence of temperature on CH_4 oxidation (Steudler et al. 1989; Born et al. 1990; Dörr et al. 1993; Dunfield et al. 1993; Koschorreck & Conrad 1993; Crill et al. 1994).

Since CH_4 relaxation constants are much larger than first-order rate constants for CH_4 consumption in tundra soil, movement of CH_4 through soil matrix air should not limit CH_4 oxidization (Whalen & Reeburgh 1990). However, diffusion in our humisol was much slower, perhaps due to small particle size and lack of macropores. In cores, the average relaxation constant on CD 201 (ϕ_g = 0.4) was $-0.58\ h^{-1}$, and the average first-order rate constant for CH_4 consumption was $-0.11\ h^{-1}$. Although diffusion is the faster process, the figures are in the same order of magnitude. Gas transport could be a limiting factor in this soil, especially at higher water content.

The relationship between CH_4 oxidation and ϕ_g in soil cores was an exponential rise to a maximum. The exponential nature of the relationship is expected from the theoretical exponential dependence of the diffusion coefficient on ϕ_g (Campbell, 1985). At ϕ_g values above 0.2 (< 130% H_2O) the plateau region of the relationship is reached, where the diffusion rate is very

fast in relation to the microbial oxidation rate. Further increases in ϕ_g above 0.2 had little effect on CH_4 oxidation, either in cores or in the field. Soil CH_4 consumption acts as its own buffer, causing decreases in $d[CH_4]/dz$ (i.e. steeper concentration gradients) which partially compensate for decreasing D_{CH_4soil} as ϕ_g decreases. Microbial CH_4 consumption is concentration dependent, but at high ϕ_g, CH_4 gradients are shallow (CH_4 declined by < 0.3 ppmv over 15 cm at $\phi_g > 0.4$), and relatively large changes in $d[CH_4]/dz$ can arise with small changes in absolute soil CH_4 concentration.

Diffusion of CH_4 in soil water rather than soil air may limit methanotrophic activity, and explain the commonly observed dependence of CH_4 consumption on moisture content (Koschorreck & Conrad 1993). However this hypothesis is not consistent with our data. Even as CH_4 oxidation in the humisol declined with H_2O contents above 130%, $d[CH_4]/dz$ (of soil matrix air) continued to steepen. If CH_4 diffusion through water films from gas-filled pores to methanotrophs was limiting, such a trend should not occur. In fact, the opposite would be expected. Rather, our data are consistent with the idea that at high H_2O content, CH_4 delivery from the atmosphere to subsurface methanotrophs is limited by its diffusion rate through soil matrix air. As diffusion rates decline in relation to CH_4 oxidation rates, subsurface CH_4 concentrations decrease and, since it is a first-order process, so does CH_4 oxidation. Another important point is that, although our humisol was diffusion limited only at extremely high H_2O contents, limitation would occur over a greater range of H_2O content if potential CH_4 oxidation was much higher. Therefore, in soils with similar diffusion characteristics but higher CH_4 oxidation potentials (e.g. fine-textured forest soils), diffusion limitation of CH_4 oxidation could be evident at commonly occurring moisture contents.

Soil cores wetted in 50-mL increments had constant moisture content with depth, and no methanogenic activity, so this was purely a study of diffusion control. In the field, of course, this is not always the case. The exponential relationship did not hold in cores watered in 150-mL increments (equivalent to 3 cm rainfall), as diffusion in these cores may have been limited by a penetrating water front. Adamsen & King (1993) also noted an effect of the amount of water added to cores. In our humisol cores receiving 150-mL H_2O additions, methanogenesis began at $\phi_g \cong 0.1$, after a lag phase (data not shown). Methanogenesis as a control of flux was not investigated thoroughly here, but is probably a complex relationship involving total soil moisture, the timing and amount of rainfall events, and substrate availability.

That immediate inhibition of methanotrophs and methane monooxygenase from nitrogen fertilization can occur is well proven by laboratory soil studies (Nesbit & Breitenbeck 1992; Adamsen & King 1993; Bosse et al. 1993; Bronson & Mosier 1994). However the extent to which this potential inhibition

manifests itself in the field will be mitigated by the four-dimensional nature of soil. Temporal changes in soil nitrogen through processes such as nitrification may be critical. Physical soil factors controlling the downward movement of fertilizer must be considered in relation to the depth at which CH_4 oxidation does or can occur, and to soil porosity and water content as determining the severity of diffusion limitation.

Acknowledgements

This work was supported by an Agriculture Canada Green Plan contract to RK. PD was supported in part by a fellowship from the Canadian Eco-Research Council. Thanks to P. Rochette for chambers, and to R. Carrier, M. Kuhl, and C. Tauchner for laboratory assistance.

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