



Controlling factors and effects of chronic nitrogen and sulphur deposition on methane oxidation in a temperate forest soil

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Abstract

Soil CH₄ flux rates were determined on 28 occasions between June 1996 and July 1997 in a temperate deciduous woodland in south-west England. The effects of environmental and edaphic factors on flux rates and the effects of chronic deposition of sulphuric acid, nitric acid and ammonium sulphate were investigated. The soil was a consistent net CH₄ oxidiser, with mean ($n = 10$) oxidation rates for plots exposed to ambient throughfall ranging from 44.3 to 110.6 $\mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ between samplings; net CH₄ production was not observed. The annual mean uptake rate differed by only 6% from the annual mean flux calculated from the literature for other studies of >364 d duration in temperate and boreal deciduous woodlands. The CH₄ uptake rates were correlated with soil water potential (square-root transformed), temperature and depth of organic horizon ($r^2 = 0.78, 0.30$ and 0.41 , respectively). Soil water potential was the best predictor of net CH₄ oxidation rates and when temperature was added to the regression model no improvement in the r^2 was observed. The chronic deposition of sulphuric acid stimulated net methane oxidation ($P < 0.05$), while the chronic deposition of nitric acid and ammonium sulphate had no significant effect. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Methane is an important greenhouse gas (Prinn, 1994) and increasing concentrations of the greenhouse gases are reported to be bringing about an increase in the global mean temperature of the Earth (IPCC, 1995). In addition, CH₄ plays a role in a number of additional atmospheric reactions, which may also cause environmental change (see Cicerone and Oremland, 1988; Tyler, 1991). Sinks for atmospheric CH₄ can limit these reactions and their effects, yet the only net biospheric sink for atmospheric CH₄ is consumption by soil (King, 1997). Thus, robust estimates of the soil CH₄ sink strength are required to evaluate the importance of this sink in determining atmospheric CH₄ concentrations and, thus, how soils may influence future environmental change. In addition, it is important to understand what variables affect the size of the soil atmospheric CH₄ sink in order to predict how the

sink strength will respond to anthropogenic environmental change.

A number of workers (e.g. Dobbie and Smith, 1996) have suggested that forest soils represent an important sink for atmospheric CH₄, yet few studies have enabled estimates of annual budgets of CH₄ uptake by temperate forest soils. This lack of data means great uncertainty in estimates of CH₄ sink strengths for main land use types (e.g. see Willison et al., 1995). The only way to increase the accuracy of the soil sink strength estimate for CH₄ is to carry out more medium and long-term flux studies (Born et al., 1990).

Correlations between net CH₄ oxidation, soil water status and temperature in temperate forest soils have been reported in a large number of in situ studies (e.g. Steudler et al., 1989; Crill, 1991; Bowden et al., 1993) but findings have not been consistent. For example, Ambus and Christensen (1995) observed no correlation between soil water status and CH₄ uptake, Dobbie and Smith (1996) a weak negative correlation and Castro et al. (1995) a strong negative correlation. As precipitation and temperature are predicted to change through anthropogenic activity (IPCC, 1995), it is important to understand how these variables control soil CH₄ uptake,

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Table 1
Soil characteristics for the Perridge Forest field site. Values are means \pm 1 SEM. ND: not determined

| Horizon | H | N | AE | n |
|------------------------------------|-----------------------------|----|-----------------|----|
| Depth (cm) | 10.3 \pm 0.3 ^a | 50 | ND | ND |
| Total N (%) | 1.9 \pm 0.1 | 5 | 0.3 \pm 0.0 | 5 |
| Total C (%) | 44.4 \pm 1.2 | 5 | 9.2 \pm 0.9 | 5 |
| pH | 4.2 | 8 | 4.1 | 4 |
| Bulk density (g cm ⁻³) | 0.16 \pm 0.01 | 3 | 1.16 \pm 0.01 | 3 |

^a Depth range was 4–15 cm.

so that the effects of such changes on the soil CH₄ sink strength can be reliably predicted.

Soil acidification through acid precipitation has long been recognised to have effects on forest soil systems (Abrahamson et al., 1994). However, the effects of acid precipitation on CH₄ cycling in forests have virtually been neglected in global change studies, even though S and N deposition may potentially affect CH₄ cycling in several ways (Yavitt et al., 1993). A study by Sitaula et al. (1995) showed that precipitation, acidified to pH 3 with H₂SO₄, stimulated CH₄ uptake rates in a coniferous forest soil. However, apart from Sitaula et al. (1995), little is known about S effects on CH₄ flux in temperate forests, although S is still one of the main anthropogenic components in rain (Barrett et al., 1995) and pH appears to be an important regulator of methanotrophic rate (Dunfield et al., 1993; Dedysh et al., 1998).

Since the first report of the effects of inorganic N on soil CH₄ uptake by Steudler et al. (1989), a wealth of papers have reported N effects in a range of habitat types, including forests, grasslands, agricultural soils, landfill cover soils and rice-paddies (see Hanson and Hanson, 1996). In most of these studies, large amounts of N were added at high concentrations on one or a few occasions (e.g. Castro et al., 1995) and inhibition of CH₄ oxidation was observed in response (e.g. Adamsen and King, 1993). However, such “agricultural fertilizer” type additions do not accurately mimic deposition of air-borne N compounds (NO_x and NH_x), which are deposited at significantly lower concentrations and much more frequently than fertilizer inputs. Thus, simple extrapolation of the results of N agricultural fertilizer studies to predict that soil CH₄ uptake would be inhibited by elevated atmospheric N deposition is inappropriate. However, studies conducted in areas receiving high atmospheric N deposition (Saari et al., 1997; Butterbach-Bahl et al., 1998) do suggest that soil CH₄ oxidation is inhibited by elevated N but little work has been done to simulate N deposition under experimentally controlled conditions. Such an experimental approach is required to unequivocally demonstrate that elevated atmospheric N deposition may affect net soil CH₄ oxidation.

The first of the three aims of the current work was to calculate an annual CH₄ flux for a temperate deciduous forest soil. The second was to determine the environmental

factors that regulated this flux and the third was to determine how elevated deposition of oxidised S and N and reduced N, in wet deposition, affected soil CH₄ flux.

2. Methods and materials

2.1. Site and soil description

The investigation was carried out at Perridge Forest, UK (NGR SX 869908), a temperate mixed deciduous woodland at an elevation of 180 m, consisting predominantly of mature (c. 80 y old) oak (*Quercus robur* L.). The middle storey comprised rowan (*Sorbus aucuparia* L.), beech (*Fagus sylvatica* L.) and younger oak, whilst bilberry (*Vaccinium myrtillus* L.) dominated the understorey vegetation. The site was on a gentle slope (<5°).

General soil characteristics are listed in Table 1. The soil was a freely draining, low-base status, acidic brown earth, covered by a permanent litter layer of distinguishable oak and beech litter. The H horizon, with abundant fine fibrous roots, overlaid an upper mineral AE horizon, with incipient podsolisation. The B horizon was a stronger brown colour that increased with depth, being richer in sesquioxides of Fe and Al through in situ weathering. The soil is mapped within the Denbigh 1 Association (Findlay et al., 1984) but is most accurately described as the now obsolete Dunsford series (Clayden 1964; Clayden and Hollis, 1984).

2.2. Determining in situ CH₄ flux

Methane fluxes were determined on 28 occasions between June 1996 and July 1997 using a closed chamber technique (after Goldman et al., 1995). The chamber base, a 15 cm tall grey polyvinyl chloride (PVC) pipe (111.2 cm² bore area), was cut 6 cm into the soil 60 d prior to the start of the experiment and was left in situ throughout the study. The chamber lid (10 cm tall PVC pipe) was sealed (gas-tight) to the base using a rubber sleeve. PVC sheet (3 mm thick) was PVC welded to one end of the lid and a Suba Seal (W.H. Freeman Co., Barnsley, UK), inserted through a double layer of sheet to ensure a gas-tight seal, functioned as a septum port. The PVC sheet was white to minimise chamber heating via direct solar radiation. Comparison of CH₄ concentrations in free air and immediately after capping a chamber showed that capping had no detectable effect on the initial headspace CH₄ concentration.

Headspace gas samples were taken immediately after the chamber bases were capped and after a further 30 min, using a hypodermic needle, 10 cm³ plastic syringe and 3-way tap. Capping times in excess of 30 min caused a reduction in measured CH₄ flux rate, as observed by Crill (1991).

Methane concentrations in the syringes were found to remain stable for at least 44 h but samples were always analysed within 30 h of collection. Methane concentrations were determined on a Shimadzu 14-B GC fitted with a FID operated at 120°C. Methane was separated isothermally on a

2 m Haysep-D packed glass column at 50°C, with N₂ carrier gas flowing at 40 cm³ min⁻¹. The detector response was calibrated using certified gas standards (British Oxygen Company, Special Gases, UK), nominally containing 10.2 µl l⁻¹ CH₄ in air.

2.3. Climate and soil monitoring

Air temperature, soil water potential (Ψ_{soil} ; 5–10 cm depth) and soil temperature at 0, 5, 10, 15 and 20 cm depths below the litter layer were monitored at the site. Readings from the temperature probes and the soil tensiometers were taken at 5 min intervals and hourly averages recorded on a Didcot Datataker 500 (Didcot Instruments Co. Ltd, Oxford, UK). Throughfall volume and pH were determined weekly using 10 rainfall collectors (12 cm dia.) placed randomly throughout the site at 1.45 m height. Chloride, NO₃⁻-N, PO₄³⁻-P and SO₄²⁻-S concentrations in throughfall were determined by ion chromatography using a Dionex AS4A anion column (Dionex, Sunnyvale, CA, USA) after filtration of the throughfall using Sep-pak C-18 cartridge filters. Ammonium-N concentrations were determined by the alkaline phenate/sodium nitroprusside method on a BEMAS Autoanalyser (Burkard Scientific, Uxbridge, UK).

Bulk precipitation was monitored at an open grass meadow, c. 800 m from the woodland field site, using three collectors of the same design as for throughfall sampling. A tipping bucket rain gauge (Didcot Instruments Co. Ltd, Oxford, UK), with a resolution of 0.1 mm, was used to record hourly rainfall totals.

Soil bulk density was determined by taking cores of known volume and determining the dry weight of the soil. Stone weight and volume were corrected for in the A horizon after sieving to 2 mm; the H horizon contained no stones. pH was measured following Grimshaw (1989) and organic C was determined using a modified Tinsley (titration) method (Grimshaw et al., 1989). Total N was determined by wet oxidation (Rowland and Grimshaw, 1985).

2.4. Experimental layout and treatment additions

Fifty chamber bases were placed in a randomised block design at the forest field site, with two blocks adjacent to each other at each of five elevations. Each block contained one replicate of each treatment: NA, nitric acid; SA, sulphuric acid; AS, ammonium sulphate; UT, unamended throughfall; AT, ambient throughfall (see below for fuller explanation of treatments).

Small rainfall exclusion roofs (148 cm²) were placed 12 cm above the chamber bases, except for those receiving AT treatment (absolute control). Thus, the AT treatment plots received throughfall whenever there was a precipitation event. Collected throughfall, amended with HNO₃, H₂SO₄ and (NH₄)₂SO₄ where appropriate, was added to replicate plots of the other four roofed treatments

on a weekly basis. The volume added was equal to the average throughfall for the preceding week, which was calculated from the volumes collected in the 10 throughfall collectors.

Throughfall used in treatment additions was collected in four box-shaped PVC containers (ca. 2.5 m² surface area), placed at each edge of the field site and set at 1 m height. The throughfall passed through a silicon tube into a partially-buried, blacked-out, 10 l bottle and equal aliquots from each bottle were placed into another receptacle and mixed. Treatment UT received this throughfall in unamended form (control). Treatment NA received throughfall to which HNO₃ was added to give a final concentration of 71.0 µM (assuming no HNO₃ already present in the throughfall). Similarly, treatment SA received H₂SO₄ at a concentration of 140.7 µM and treatment AS received (NH₄)₂SO₄ at a concentration of 59.6 µM, in throughfall. Ion contents of treatments were analysed using the same procedures described for throughfall. The first treatment application was made on 7 July 1996 and applications were then made weekly (when rainfall occurred in the preceding week) until 15 July 1997.

Based on bulk precipitation data for areas local to Perridge, from the 5 y previous to the current study, the treatment additions were designed to provide an enrichment of oxidised N deposition by 11 kg N ha⁻¹ y⁻¹ (NA), oxidised S deposition by 50 kg S ha⁻¹ y⁻¹ (SA) and reduced N deposition by 18.5 kg N ha⁻¹ y⁻¹ (AS). These additions were chosen after examination of data in Barrett et al. (1995) and intended to mimic medium to heavy deposition amounts of oxidised N, oxidised S and reduced N.

2.5. Statistical analysis

All data analyses and statistical comparisons were performed using SAS (SAS Institute, 1988). Repeated measures randomised block analysis of covariance were used to analyse treatment effects on field CH₄ flux. Generalised linear modelling (GLM) was used when missing values occurred and residuals of the repeated measures analyses were tested for normality using the Shapiro–Wilk test. Values of $\alpha \leq 0.1$ were taken to indicate that data or residuals were not normal; all flux data in the current study fitted a normal distribution (i.e. $\alpha > 0.1$).

Relationships between climatic and edaphic variables and CH₄ flux rate were determined using correlation and multiple-regression analysis (SAS Institute, 1988). Mean fluxes of treatment AT (the absolute control) for each sampling date were used in the regression analyses. Frequency distributions of the residuals were tested for normality, as above, and Ψ_{soil} data were square-root transformed to improve the fit of the residuals to a normal distribution. Coefficients of variation (CV) for treatment AT were calculated for each sampling date to provide a measure of the spatial heterogeneity of flux rates at the site.

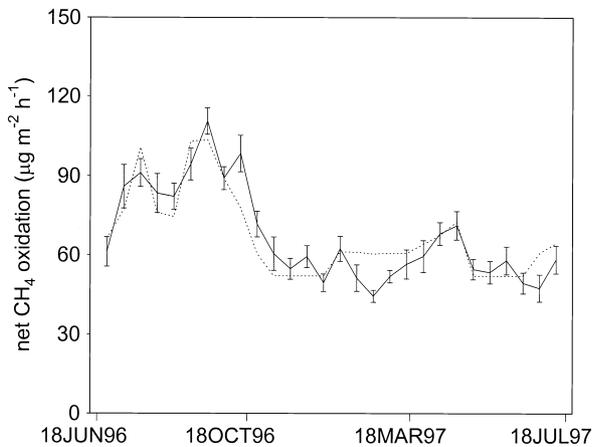


Fig. 1. Net soil CH₄ oxidation in situ at Perridge Forest for the ambient throughfall treatment (AT). For directly measured flux (—), rates are shown for 28 sampling occasions from June 1996 to July 1997 and the rates are means ± 1 SEM ($n = 10$). Also shown are flux rates determined from soil water potential data collected during CH₄ flux measurements (···). These flux values were calculated using the regression equation generated from the observed relationship between net CH₄ oxidation and soil water potential at the site.

3. Results

3.1. Methane flux and climate

The soil was a consistent net CH₄ oxidiser, with mean oxidation rates under the ambient throughfall (AT) treatment ranging from 44.3 to 110.6 $\mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ between samplings (Fig. 1). The annual mean oxidation rate was $67.1 \pm 3.4 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ and the CV values for each sampling ranged from 14.2 to 34.2%, the mean value being 23.7%. Net production of CH₄ was not observed from any replicate on any occasion.

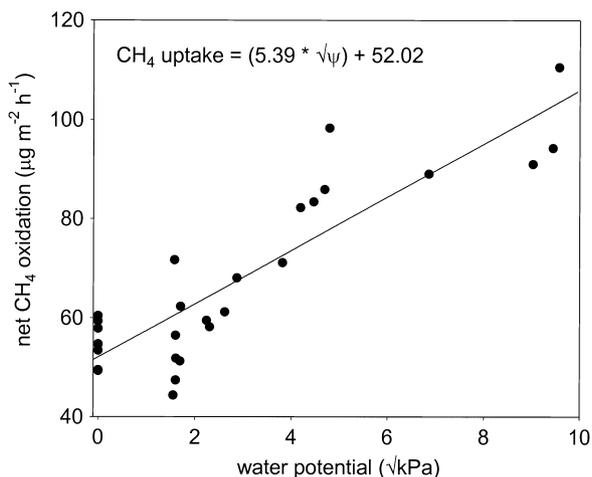


Fig. 2. Relationship between in situ net soil CH₄ oxidation and the square-root of soil water potential (5–10 cm depth) measured at the oak woodland site; $r^2 = 0.78$. Oxidation rates were determined on 28 occasions from June 1996 to July 1997 and each data point is the mean of $n = 10$. Note that as soil water content increased, net CH₄ oxidation decreased.

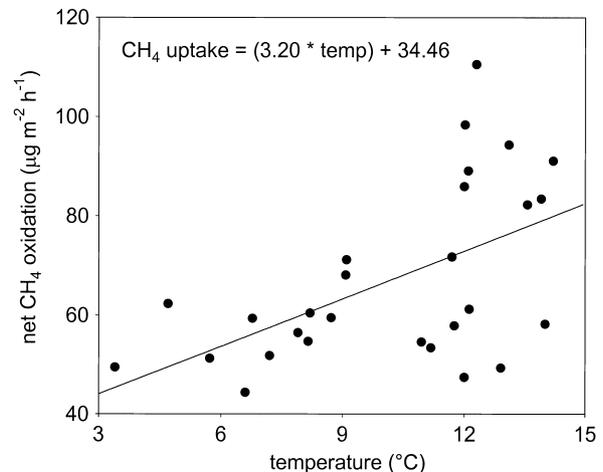


Fig. 3. Relationship between in situ net soil CH₄ oxidation and soil temperature (20 cm depth); $r^2 = 0.30$. Oxidation rates were determined on 28 occasions from June 1996 to July 1997 and each data point is the mean of $n = 10$.

Correlation analyses between CH₄ flux and other variables (soil and air temperature, Ψ_{soil} , direct precipitation and throughfall volumes) were performed to attempt to explain the observed changes in CH₄ flux over the course of the study. Of the measured variables, CH₄ uptake rates only correlated with Ψ_{soil} and temperature (at all soil depths and air); the strongest soil temperature correlation was observed with the 20 cm soil depth values. Figs. 2 and 3 show the relationship between net CH₄ oxidation rate and Ψ_{soil} and soil temperature (20 cm depth), respectively. Of the two, Ψ_{soil} most closely predicted CH₄ uptake and a square-root transform of Ψ_{soil} data improved the fit of the model, increasing the r^2 from 0.69 to 0.78. When temperatures were added to this regression model, no improvement in the r^2 was achieved.

The relationship between Ψ_{soil} and net CH₄ oxidation rates was used to estimate hourly soil CH₄ flux rates for the forest site, using the hourly Ψ_{soil} data ($n = 9262$) collected across the study period. The annual mean oxidation rate calculated using this method was $70.3 \pm 0.2 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$. The annual CH₄ sink strength for the forest site estimated from the measured flux was $4.4 \text{ kg C ha}^{-1} \text{ y}^{-1}$ and predicted from the relationship with soil water potential was $4.6 \text{ kg C ha}^{-1} \text{ y}^{-1}$. The size and temporal variation of the predicted rates for CH₄ flux closely followed the measured values (see Fig. 1).

The depth of the H horizon positively correlated ($r^2 = 0.41$, $P < 0.05$) with the yearly mean CH₄ uptake of the individual replicate plots receiving treatment AT (data not shown).

3.2. S and N deposition

The measured annual precipitation at the Perridge site was markedly lower than that predicted from regional annual rainfall totals between 1991 and 1995, with

Table 2

Total ion deposition to treatment plots receiving unamended throughfall (UT), and throughfall amended with nitric acid (NA), sulphuric acid (SA) or ammonium sulphate (AS). Total deposition values are also shown for collected bulk precipitation (BP). The median pH values are shown

| Treatment | Total deposition (kg ha ⁻¹) | | | | | | |
|-----------------|---|---------------------------------|----------------------------------|-----------------|----------------------------------|----------------|-----|
| | NH ₄ ⁺ -N | NO ₃ ⁻ -N | SO ₄ ²⁻ -S | Cl ⁻ | PO ₄ ³⁻ -P | H ⁺ | pH |
| UT | 3.8 | 1.8 | 7.9 | 97.5 | 1.2 | 0.05 | 5.2 |
| NA | 3.9 | 8.0 | 8.7 | 102.5 | 1.2 | 0.79 | 4.1 |
| SA | 3.9 | 2.0 | 31.4 | 113.0 | 1.3 | 3.30 | 3.3 |
| AS | 12.2 | 2.0 | 18.5 | 102.8 | 1.2 | 0.04 | 5.3 |
| BP ^a | 2.1 | 2.1 | 5.9 | 83.7 | 0.3 | 0.23 | 4.8 |
| BP ^b | 1.5 | 1.5 | 4.4 | 61.9 | 0.3 | 0.17 | 4.8 |

^a Quantity in bulk precipitation.

^b Corrected quantity in bulk precipitation assuming bulk volume was equivalent to throughfall volume.

745 mm falling against an average of 1109 mm. The total throughfall volume added to plots receiving treatments SA, NA, AS and UT was 551 mm. As a result, the total amounts of HNO₃, H₂SO₄ and (NH₄)₂SO₄ added to the soils were lower than targeted (Table 2).

Total deposition compared with the control (UT), of NO₃⁻ in treatment NA, of SO₄²⁻ in treatments SA and AS and NH₄⁺ in treatment AS, were c. 3, 4, 2.5 and 4.5 times, respectively (see Table 2). The increase in proton deposition was 16 and 67 times for treatments NA and SA, respectively. Similar increases in the mean ion concentrations were observed for the elevated treatments when compared to the control (Table 3). Also, at each time of measurement, despite natural temporal variation in the ion content of collected throughfall used for treatment additions, concentrations of the experimentally enriched ions were consistently higher in the relevant treatment when compared with the control (data not shown). The concentrations of Cl⁻ and PO₄³⁻-P were similar between treatments within each time of measurement, suggesting that collected throughfall used for treatment additions on a particular day had similar chemical compositions before being enriched with the treatment compounds.

Total precipitation volume in the 10 throughfall collectors ranged between 448 and 619 mm and the total ion deposition to each collector varied by as much as 50% for

some ions. Ion concentrations varied over time and between collectors and were generally higher in throughfall than bulk precipitation, except for N species and H⁺, where the input with the highest mean concentration varied over time (data not shown).

3.3. Effects of S and N deposition on CH₄ flux

Repeated measures blocked analysis of covariance revealed a significant treatment effect ($P < 0.05$) on CH₄ flux rates throughout the entire study. When the study period was split into quarters, a significant effect ($P < 0.05$) was only detected in the last quarter (see Table 4). On the seven sampling dates in this last quarter, the SA treatment had higher CH₄ uptake rates than the control (see Fig. 4) and these increases were significant ($P < 0.05$) on three occasions. In contrast, CH₄ uptake rates for treatments NA and AS in the last quarter were not consistently higher or lower than rates for treatment UT, and no significant differences from the control were observed on any occasion. Within the last quarter the cumulative fluxes of SA, NA and AS, when compared to UT, were 125, 108 and 105%, respectively, but only 98, 95 and 93%, respectively, in the first quarter (see Table 4). Treatment AT was not included in these analyses since it received a totally different volume and frequency of throughfall to the other treatments. However, there was no significant difference ($P > 0.05$) in CH₄ uptake between AT and UT throughout the study.

4. Discussion

Our study presents the first integrated annual measurement of CH₄ flux for an oak woodland in the UK. To permit objective quantitative comparisons with published studies, CH₄ flux data from the literature (Keller et al., 1983; Steudler et al., 1989; Crill, 1991; Bowden et al., 1993; Castro et al., 1993, 1994, 1995; Dörr et al., 1993; Koschorreck and Conrad, 1993; Yavitt et al., 1993; King and Schnell, 1994; Peterjohn et al., 1994; Schnell and King, 1994; Ambus and Christensen, 1995; Goldman et al., 1995; Dobbie and Smith, 1996; Nieminen et al., 1996; Gullede et al., 1997; Priemé and Christensen, 1997; Butterbach-Bahl et al., 1998; Ineson et al., 1998; Saari et al., 1998) were used to generate a frequency distribution of average CH₄ sink strengths for

Table 3

Mean ion concentrations in the unamended throughfall treatment (UT), and throughfall treatments amended with nitric acid (NA), sulphuric acid (SA) or ammonium sulphate (AS). Ion concentrations values are also shown for collected bulk precipitation (BP). Concentrations are means ± 1 SEM

| Treatment | Mean concentration ± 1 SEM (mg l ⁻¹) | | | | | |
|-----------|--|---------------------------------|----------------------------------|-----------------|----------------------------------|--------------------------------------|
| | NH ₄ ⁺ -N | NO ₃ ⁻ -N | SO ₄ ²⁻ -S | Cl ⁻ | PO ₄ ³⁻ -P | H ⁺ (μg l ⁻¹) |
| UT | 0.8 ± 0.2 | 0.3 ± 0.1 | 1.5 ± 0.2 | 17.8 ± 4.0 | 0.3 ± 0.1 | 9 ± 2 |
| NA | 0.8 ± 0.2 | 1.4 ± 0.1 | 1.6 ± 0.1 | 18.5 ± 3.8 | 0.3 ± 0.1 | 122 ± 29 |
| SA | 0.9 ± 0.2 | 0.4 ± 0.1 | 5.7 ± 0.3 | 19.5 ± 3.9 | 0.3 ± 0.1 | 556 ± 75 |
| AS | 2.3 ± 0.1 | 0.4 ± 0.1 | 3.4 ± 0.2 | 18.7 ± 3.8 | 0.3 ± 0.1 | 9 ± 2 |
| BP | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.8 ± 0.2 | 10.0 ± 2.4 | 0.1 ± 0.01 | 29 ± 18 |

Table 4

Cumulative soil CH₄ flux for plots treated with unamended throughfall (UT), and throughfall amended with nitric acid (NA), sulphuric acid (SA) or ammonium sulphate (AS). Flux measurements were made on 26 occasions between July 1996 and July 1997. There was a significant treatment effect of SA across the whole year ($P < 0.05$)

| Year period | No. of sample dates | Cumulative flux ($\Sigma(\mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1})$) | | | |
|--------------------------|---------------------|---|------|------|------|
| | | UT | NA | SA | AS |
| 07/96–09/96 | 6 | 588 | 563 | 574 | 548 |
| 10/96–12/96 | 6 | 382 | 416 | 426 | 364 |
| 01/97–03/97 | 7 | 296 | 329 | 355 | 284 |
| 04/97–06/97 ^a | 7 | 363 | 393 | 458 | 382 |
| Total | | 1628 | 1701 | 1807 | 1578 |

^a $P < 0.05$; significant treatment effect within the period.

temperate and boreal forest soils. Studies were categorised by their duration, ≤ 364 d or > 364 d (Fig. 5), and forest type (Tables 5a and b). Flux data duplicated in a later reference (e.g. Steudler et al., 1989; Castro et al., 1995) were included as one measurement. The uptake rates for the current study were clearly within the range reported for other temperate and boreal forests (Fig. 5).

Mosier (1990) reported that spatial variability of flux rates across a site is the greatest problem in using chamber techniques to estimate trace gas fluxes; he reported that CVs within a “uniform” site location typically ranged between 50 and 100%. The low CV range observed for the current study (14.2–34.2%) is attributed to the large number of replicates ($n = 10$) used and suggests that the annual CH₄ flux estimate for Perridge can be considered robust. As forests are rarely “uniform” sites, the low replicate number per sampling date used in a large number of studies, which is often as low as two (e.g. Crill, 1991; Koschorreck and Conrad, 1993; Dobbie and Smith, 1996), may produce

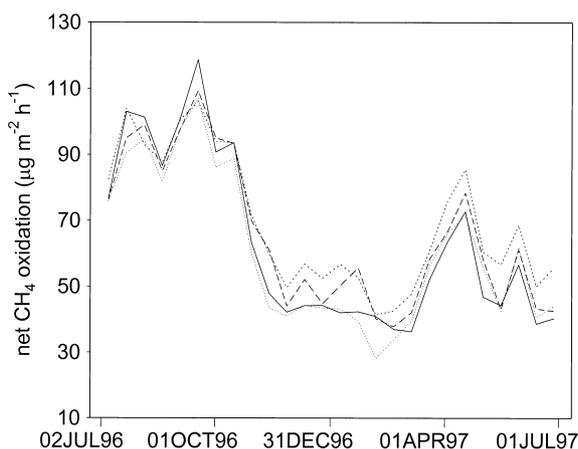


Fig. 4. In situ rates of net soil CH₄ oxidation for treatments UT (unamended throughfall; —), NA (nitric acid; - - -), SA (sulphuric acid; ---) and AS (ammonium sulphate; ···). SA rates were significantly greater than control (UT) rates across the study period ($P < 0.05$). Flux rates are means ($n = 10$); standard error bars were removed for clarity.

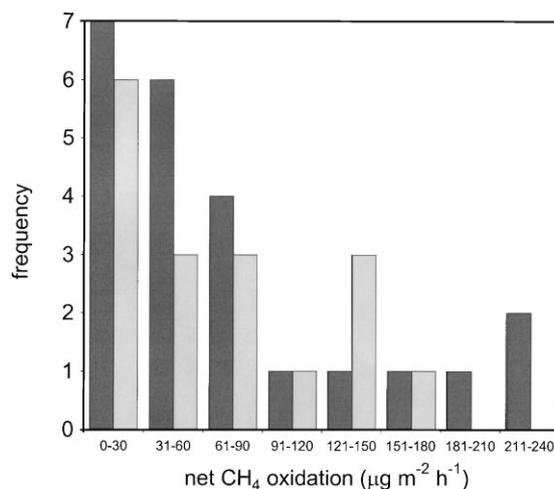


Fig. 5. Frequency distributions of mean soil CH₄ uptake in temperate and boreal forests sampled with closed system cover boxes for sampling periods of ≤ 364 d ($n = 22$; dark bars) or > 364 d ($n = 17$; light bars). The mean value for Perridge Forest and the overall literature means fall within the 61–90 category.

large errors in the prediction of mean CH₄ flux rates. Such considerations should be taken into account in future studies.

As with approximately half of the forest site studies reported in the literature (see Table 5), net CH₄ production was not observed for any replicate in the Perridge study. In the studies where net soil CH₄ production was observed, emissions were always small in comparison to the overall CH₄ uptake rates and, as a result, all studied temperate and boreal forest soils have been shown to be net sinks for atmospheric CH₄. The findings of our study support this observation.

The correlation between soil water status and net CH₄ oxidation at Perridge has also been observed in other temperate forests (e.g. Castro et al., 1995). This relationship at Perridge could be a result of changes in CH₄ production rates or soil CH₄ transport rates as soil water content varies. For soil CH₄ transport rates to be the main control of CH₄ consumption in a non-waterlogged soil, Kruse et al. (1996) stated that there must be a sub-surface maximum for CH₄ oxidation. As the Perridge soil had a low methanogenic potential and a sub-surface maximum for CH₄ oxidation (M. A. Bradford, unpub. PhD thesis, Exeter University, 1999), the control of soil water status over net CH₄ oxidation in our study is probably associated with the effect of soil water content on rate of soil CH₄ transport.

Soil water potential did not fall below -0.1 MPa and Schnell and King (1996) and Gullede and Schimel (1998) observed that a Ψ_{soil} of -0.3 to -0.2 MPa was optimal for CH₄ uptake. This suggests that the oxidation rates measured at Perridge were probably always lower than potential in situ rates. Changing soil moisture content, predicted under future anthropogenic climate change (see Kattenberg et al., 1995), would affect flux rates but could

Table 5

Summary of selected variables associated with in situ net soil CH₄ oxidation for sampling periods of (a) ≤ 364 d, or (b) > 364 d, reported in the literature for temperate and boreal forests

| Forest type | No. of sites | No. of references | Mean rate | Min. mean rate | Max. mean rate | Net production observed | Correlation with soil water | Correlation with temp. |
|-------------------------|-----------------|-------------------|---|----------------|----------------|-------------------------|-----------------------------|------------------------|
| | | | ±1 SEM | | | | | |
| | | | (μg CH ₄ m ⁻² h ⁻¹) | | | | | |
| | | | (no./total reports) | | | | | |
| a) | | | | | | | | |
| All | 22 ^a | 12 | 77 ± 14 | 13 | 225 | 9/17 | 4/11 | 4/11 |
| Coniferous ^b | 14 ^a | 6 | 56 ± 13 | 17 | 213 | 7/11 | 1/6 | 1/6 |
| Coniferous ^c | 10 | 5 | 69 ± 13 | 27 | 213 | 5/9 | 1/6 | 1/6 |
| Deciduous | 4 | 2 | 151 ± 48 | 13 | 225 | 1/1 | 0/3 | 0/3 |
| Mixed | 4 | 4 | 88 ± 19 | 47 | 125 | 1/4 | 2/2 | 2/2 |
| b) | | | | | | | | |
| All | 17 | 10 | 63 ± 13 | 6 | 160 | 6/15 | 4/8 | 6/6 |
| Coniferous | 6 | 6 | 43 ± 20 | 13 | 143 | 3/5 | 1/3 | 2/2 |
| Deciduous | 6 | 5 | 63 ± 24 | 6 | 160 | 1/5 | 2/3 | 2/2 |
| Mixed | 5 | 4 | 87 ± 20 | 33 | 147 | 2/5 | 1/2 | 2/2 |

^a One study (Nieminen et al., 1996) has been recorded twice. It was conducted over two separate years and flux measurements have not been pooled.

^b Includes peat soil sites.

^c Mineral-based soil sites only. Deciduous and mixed forests were all on mineral-based soils.

either increase or decrease the CH₄ sink strength of Perridge and similar forest soils depending on the direction of the change and the pre-disturbance soil moisture values.

Given the observed strong correlation between Ψ_{soil} and CH₄ uptake, the main advantage of using Ψ as a measure of soil water status was that continuous hourly monitoring permitted uptake rates to be predicted at a fine time resolution. The estimated annual CH₄ flux for the Perridge site from the measured flux and from the flux predicted from Ψ_{soil} were within 5%. Thus, the monitoring of Ψ_{soil} at similar sites to Perridge may be a simple and non-intensive method for estimating soil CH₄ flux, after suitable calibration of the relationship.

When monitored, temperature correlated with CH₄ uptake in all literature studies of > 364 d duration (see Table 5b) and the same was true for the current study. However, temperature did not explain any further variability in CH₄ flux within a regression model that already included Ψ_{soil} . Given the high soil water status observed in our study, this is perhaps not surprising; Crill (1991) suggested that temperature only became an important biological control when soils were dry enough not to have diffusional limitation.

Borken and Brumme (1997) and Saari et al. (1998) reported that the organic horizon acted as a diffusional barrier to CH₄ and that, when peeled away, oxidation rates increased. Thus, the positive correlation between depth of the organic horizon and net CH₄ uptake, observed in our study, is at variance with the hypothesis that control of CH₄ uptake in the Perridge soil is governed by gaseous diffusion. However, high rates of potential CH₄ oxidation occur in the lower H horizon at Perridge (M. A. Bradford, loc. cit.) and, thus, an increase in the width of the H horizon could result in a thicker band of high CH₄ oxidising activity. Varying widths of the organic horizon across the Perridge

site may explain some of the observed spatial variability in CH₄ uptake rates. In addition, the large spatial variation in throughfall ion deposition, concentration and volume, attributed to spatial heterogeneity of the forest canopy (Parker, 1983), may also explain some of the spatial variance in net CH₄ uptake at the site (see Whelan et al., 1998).

The increased mean concentration and total deposition of the majority of ions in throughfall, when compared to bulk precipitation, is a common observation (e.g. Beier and Gundersen, 1989; Whelan et al., 1998). Nevertheless, the low concentrations of the majority of ions in the Perridge throughfall and bulk precipitation suggest that Perridge is a relatively unpolluted site, as predicted from EMEP data (Barrett et al., 1995). The high Cl⁻ and SO₄²⁻ concentrations are a product of the high sea spray input to the site (see Parker, 1983), which is a characteristic of much of coastal UK. Indeed, the reduction in H⁺ deposition found under this canopy is typical of non-polluted areas, with the canopy reducing acidity of incident rainfall (Parker, 1983). Thus, the relatively unpolluted air made Perridge an excellent site for studying the effects of chronic deposition of S and N on CH₄ flux.

This is the first study to report on the effects of simulated chronic H₂SO₄ deposition on in situ CH₄ oxidation in a temperate forest soil. By the last quarter of the study, cumulative uptake rates for the SA treatment were 25% higher than for the control (see Table 4). Soil respiration (M. A. Bradford, loc. cit.) was not affected by the SA treatment, suggesting that the general soil microbial community was not adversely or positively affected by the treatment.

Our study supports the findings of Sitaula et al. (1995), who assessed the effects of collected precipitation with

different pH values (manipulated with NaOH and H₂SO₄) on soil CH₄ flux in a lysimeter study, observing significantly higher CH₄ oxidation under the most acid treatment (pH 3). The soil used in that study was an acid forest soil from beneath Scots pine (*Pinus sylvestris* L.), and not a deciduous tree species. In the Sitaula et al. (1995) study, the added treatments were at pH 3, 4 and 5.5, whilst the mean pH values for the SA and UT treatments in the Perridge study were 3.3 and 5.2, respectively. Given the similarities between our study and that of Sitaula et al. (1995), hypotheses proposed by Sitaula et al. to explain the stimulation of CH₄ uptake may also apply to our study.

Firstly, Sitaula et al. (1995) proposed that increased soil acidity would lower the NH₃-to-NH₄⁺ ratio, reducing the availability of NH₃, which can act as a competitive substrate for methane monooxygenase (Bédard and Knowles, 1989), the enzyme used to fix CH₄. Similarly, King and Schnell (1998) have suggested that elevated SO₄²⁻ deposition to soil could increase adsorption of NH₄⁺ to cation exchange sites and this would also decrease the availability of NH₃. Alternatively, Sitaula et al. (1995) proposed that increased acidity may negatively affect CH₄ production within anaerobic microsites, most methanogens being neutrophilic (Conrad, 1989), and the effect would manifest as increased net CH₄ uptake. Following a similar argument, the increased SO₄²⁻ load might be considered to stimulate competitive inhibition of CH₄ formation by active SO₄²⁻ reduction, as observed in sediments (Oremland and Polcin, 1982) and peat bogs (Nedwell and Watson, 1995). However, as Perridge soil had a low methanogenic potential (M. A. Bradford, loc. cit.), the influence of H₂SO₄ is considered to be the result of an effect on either the activity or community size of methanotrophs. The same conclusion was reached by Sitaula et al. (1995).

Further work needs to be carried out to assess the effects of chronic H₂SO₄ addition on CH₄ uptake in forest soils, to determine the ubiquity of the effect and how different S concentrations may influence the nature of the effect. Although air pollution by S compounds is becoming less significant in the developed world (emissions in the UK alone fell by c. 50% between 1970 and 1994; Fowler et al., 1997), other parts of the world, such as India and China, have a serious acid rain problem due to high S emissions (Mohan and Kumar, 1998).

The absence of a significant N effect on net CH₄ oxidation at Perridge contrasts with a number of other studies, which have reported elevated N deposition inhibits in situ CH₄ uptake in temperate forest soils (Stuedler et al., 1989; Castro et al., 1993, 1995). However, N deposition in these studies was simulated by one, or a few, heavy N applications and, as a result, the treatment applications that simulated deposition rates of between 31 and 250 kg N ha⁻¹ y⁻¹, must have been made at concentrations between 15.4 and 112.5 g N l⁻¹. These concentrations far exceed concentrations of N usually found in bulk rainfall and throughfall, even in areas of heavy air pollution. For example, Ineson et al. (1993), in a parti-

cularly extreme example of high atmospheric N deposition, detected mean concentrations of N in bulk precipitation and throughfall of 1.4 and 14.5 mg N l⁻¹, respectively. The site was a Norway spruce woodland located 1 km downwind of a pig farm, which acted as a significant point source of N, leading to a deposition of 99 kg N ha⁻¹ y⁻¹. Thus, the observed changes in CH₄ flux within “agricultural” N fertilization type studies cannot reliably predict the response of CH₄ uptake to elevated atmospheric N deposition.

Two studies (Saari et al., 1997; Butterbach-Bahl et al., 1998) have used a “field-survey” approach to assess the response of CH₄ uptake to elevated atmospheric N deposition. In contrast to the lack of response of CH₄ uptake to elevated N in our study, both studies observed that sites receiving the highest atmospheric N deposition had the lowest CH₄ uptake rates. However, the observations by Saari et al. (1997) and Butterbach-Bahl et al. (1998) could be explained by differences in climate or other factors associated with the different sites that they investigated. Such criticisms do not apply to the current experimental approach and there is a clear need for further field studies that simulate “realistic” elevated atmospheric N deposition, so that the effects on CH₄ uptake in forest soils can be unambiguously quantified.

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