Soil environmental variables affecting the flux of methane from a range of forest, moorland and agricultural Soils

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Abstract. Measurements of the net methane exchange over a range of forest, moorland, and agricultural soils in Scotland were made during the period April to June 1994 and 1995. Fluxes of CH_4 ranged from oxidation -12.3 to an emission of 6.8 ng m^{-2} s^{-1}. The balance between CH_4 oxidation and emission depended on the physical conditions of the soil, primarily soil moisture. The largest oxidation rates were found in the mineral forest soils, and CH_4 emission was observed in several peat soils. The smallest oxidation rate was observed in an agricultural soil. The relationship between CH_4 flux and soil moisture observed in peats (Flux$_{CH_4}$ = 0.023 × %H$_2$O (dry weight) $-$ 7.44, $p < 0.05$) was such that CH_4 oxidation was observed at soil moistures less than 325%(± 80%). CH_4 emission was found at soil moistures exceeding this value. A large range of CH_4 oxidation rates were observed over a small soil moisture range in the mineral soils. CH_4 oxidation in mineral soils was negatively correlated with soil bulk density (Flux$_{CH_4}$ = -37.35 × bulk density (g cm^{-3}) $+48.83$, $p < 0.05$). Increased nitrogen loading of the soil due to N fixation, atmospheric deposition of N, and fertilisation, were consistently associated with decreases in the soil sink for CH_4, typically in the range 50 to 80%, on a range of soil types and land uses.

Introduction

Methane is a greenhouse gas and currently contributes approximately 20% to the radiative forcing of global climate (IPCC 1990). The concentration of CH_4 in the atmosphere is increasing by about 1% per year (Blake & Rowland 1988), which has been attributed mainly to sources such as paddy rice cultivation, enteric fermentation, fossil fuel exploitation, and landfill (Cicerone & Oremland 1988; Khalil & Rasmussen 1990; IPCC 1994). The main sink for atmospheric CH_4 is reaction with the hydroxyl radical in the atmosphere, (Cicerone & Oremland 1988). It has been suggested that decreasing concentrations of OH, due to increasing concentrations of CH_4 and CO, may have contributed to the observed increase in atmospheric CH_4 (Khalil &

Rasmussen 1983). The only known terrestrial sink for CH_4 is oxidation by microorganisms in aerobic soils. Investigations into the dynamics of CH_4 production and consumption in soils play an important role in constraining the CH_4 budget.

The uptake of CH_4 by soil has been recognised as an important component of the global CH_4 budget (Whalen & Reeburgh 1991, Steudler et al. 1989). Fluxes have been measured in a range of environments (Whalen & Reeburgh 1990; Streigl et al. 1992; Keller et al. 1990) and although uptake rates are small relative to CH_4 emissions from terrestrial environments, the areal extent of the soil sink is large. The size of the soil sink has been estimated at between 15 and 45 Tg CH_4 y^{-1} (IPCC 1994) and is comparable with the annual increase in global atmospheric CH_4 (35–40 Tg CH_4 y^{-1} (IPCC 1994)). Any change that may have occurred in the soil sink strength could therefore have influenced the rate at which atmospheric CH_4 concentrations have increased. Ojima et al. (1993), calculated that in the absence of a sink of approximately 20 Tg y^{-1} in temperate soils the atmospheric concentration of CH_4 would be increasing at about 1.5 times the current rate.

Rates of CH_4 uptake in soils appear to be governed by soil texture (Dorr et al. 1993), soil climate (temperature, soil moisture) (Whalen et al 1990), land use (Dobbie et al. 1996), N loading (Steudler et al. 1989), balance of production versus consumption (Yavitt et al. 1990) and environmental conditions such as soil pH (Hutsch et al. 1994). Varying combinations of the above processes and difficulties in assessing the importance of each between sites, (e.g. peat vs mineral soils), requires a greater understanding of the relative importance of the different environmental parameters and processes which control the exchange of CH_4 between soils and the atmosphere.

In this paper we report measurements of CH_4 flux rates from a range of soils and environmental conditions over a comparable time period. The measurements have been analysed to investigate the relative importance of a range of environmental variables on the net exchange of CH_4 in the field.

Methods

Flux measurements

Flux measurements were made using a static chamber method. Polypropylene chambers, volume 25 l (Clayton et al. 1994), were permanently inserted into the ground to a depth of about 5 cm with as little disturbance as possible. Chambers were enclosed for periods of up to one hour using a lid made of flexible domed polyethylene. This allowed the volume of the chamber to change as the 500 ml of sample was withdrawn, therefore minimising

leakage and allowing photosynthetically active light to pass through. Samples were collected into 1 l tedlar bags and analysed using tunable doide laser spectroscopy (TDL), (Aerodyne Reasearch Mas.), within 24 hrs of collection. The TDL, using infra-red absorption spectroscopy (Zahniser et al. 1995) has a precision of typically 0.05% under the conditions of analysis, and is equivalent to ±1ppb in ambient samples of approximately 1800 ppb. Standard gas mixtures containing 2110 ppb CH_4 remained stable in the tedlar bags for at least two weeks. The flux was calculated from the change in concentration over a known time period, to the headspace volume and the area of soil enclosed.

In order to confirm the assumption that the change in headspace concentration was linear with time during the measurement period, replicate samples were withdrawn at 20, 40 and 60 minutes after enclosure into 5 ml gas tight syringes (Hamilton) and were analysed by gas chromatography fitted with an FID detector (Chrompack CP9000), the results showed the change in CH_4 concentration was linear ($r^2 = 0.997$) over the measurement period.

Three soil samples (top 10 cm), were taken and bulked, every time fluxes were measured. A subsample (2 × 10 g) was analysed for moisture content (% weight loss on drying). The soil sample was then frozen until analysis for soil available NH_4^+ and NO_3^- (15 g soil extracted with 50 ml 1M KCl) (Crooke & Simpson 1971; Henrikson & Selmer-Olsen 1970) and pH (0.01M $CaCl_2$). Soil temperature at 5cm depth was routinely measured during flux measurements. Dry bulk density was calculated from the mass of oven dry soil in a given volume and soil texture analysis was determined by dispersion and sedimentation (Rowel 1994).

An analysis of variance was used to determine the significance ($p < 0.05$) of differences between CH_4 flux rates and environmental variables between sites. The relationship between CH_4 flux rates and the environmental variables measured was analysed by simple linear regression.

Site description

Sites were selected on a range of soil types and land uses throughout Scotland to provide a broad range of the environmental parameters affecting the magnitude and direction of CH_4 flux. The effect of enhanced N loading due to increased N deposition and N cycling was investigated by selecting sites with a range of N deposition along an altitude transect, and by including measurements from a N fixing alder plot. The effects of soil moisture, texture, and land use were examined by measuring fluxes of CH_4 from agricultural, forest and moorland soils. Fluxes were measured over an area of blanket bog and forested blanket bog to quantify the scale of net CH_4 oxidation in a peatland enviroment. The measurement sites:

Glencorse (NT 241631) – an experimental field site near Edinburgh, S.E. Scotland (186m a.s.l.) which was converted from arable/pasture to forest in 1984. Sites were established in plantations of Red alder, Common birch, Sitka spruce and Rye grass. Three chambers were installed randomly in each plot and CH_4 fluxes were measured on 20/6/94 and 30/6/94 ($n = 6$ per plot). The soil was a brown forest soil of the Macmerry/ Winton series (Brown & Shipley 1982), textural class – clay loam.

Devilla (ND 065453) – a lowland Scots Pine plantation near Kincardine, Fife, E. Scotland (65m asl), planted in 1952 on a brown forest soil, with gleying, of the Rowanhill association (Brown & Shipley 1982). The soil was a sandy clay loam overlain by an organic layer of varying thickness. Three chambers were installed randomly and fluxes were measured on 23/6/94 and on 29/6/94 ($n = 6$).

North Berwick (NT 555835) – an arable agricultural field planted with oilseed rape and an adjacent shelter belt in East Lothian, S.E. Scotland (60m asl), on a brown forest soil with gleying of the Kilmarnock association (Brown & Shipley 1982). Fluxes were measured 5 times between 8/6/95 and 23/6/95. Nine chambers were installed randomly in the oilseed rape field ($n = 45$) and three in the shelter belt ($n = 15$).

East Linton (NT 613767) – an arable agricultural field in East Lothian, S.E. Scotland (50m asl), on a brown forest soil of the Winton series (Brown & Shipley 1982), textural class – sandy clay loam. Fluxes were measured seven times between 14/4/94 and 9/5/94, before and after the second application of fertiliser (43 kg NH_4NO_3-N ha^{-1}) to a winter wheat crop. On measurement days 14/4, 24/4 and 9/5 three chambers were measured, on the other days nine chambers were measured ($n = 45$).

Dunslair (NT 288436) – A mixed upland coniferous forest near Peebles, S.E. Scotland. Sites were chosen below and above the altitude which commonly experiences hill cloud, at 380m asl on a mature sitka spruce plantation on a brown forest soil and at the hill summit at 615m asl, a mature sitka spruce plantation and a heather moorland on a peaty podzol of the Ettrick association (Brown & Shipley 1982). The soils at all sites were overlain by at least 10 cm of peat. Three chambers were installed randomly in each plot and fluxes were measured on 27/4/94 and on 6/7/94 ($n = 6$ per plot).

Caithness – (ND 065453) sites included an area of blanket bog and plantations of mature sitka spruce and lodgepole pine at Loch More, Caithness, N.E. Scotland (135 m asl). Nine chambers were installed randomly in the blanket bog, fluxes were measured seven times between 30/5/94 and 10/6/94 ($n = 4$ on measurement day one, $n = 9$ on subsequent days). In the forest plots three chambers were installed randomly in each plot, flux measurements were made on four occasions between 30/5/94 and 10/6/94.

Auchencorth Moss – an area of drained blanket bog near Penicuik, Midlothian, S.E. Scotland. Three chambers were installed and measurements were made on 3/5/95 and 25/5/95 ($n = 6$).

Results

Methane fluxes and the major soil variables: moisture, temperature, bulk density, pH, NO_3-N and NH_4-N, for all sites are summarised in Table 1. Fluxes ranged from 6.8 to -12.3 ng m^{-2} s^{-1}. The largest oxidation rates were observed in the mineral forest soils at Glencorse. CH_4 emission and oxidation were observed in the peat soils with the largest emission occurring in peats with the highest soil moisture.

CH_4 fluxes from mineral soils

Glencorse

CH_4 oxidation rates ranged from -4.8 to -12.3 ng m^{-2} s^{-1} (Table 1) on the two dates measured and were found to be significantly ($p < 0.05$) lower in the alder plantation than in the other sites at Glencorse. The NO_3-N concentration in the soil from the alder plantation was twice as large (8.11 ug NO_3-N g^{-1} dry soil) as from the other plots and the soil was more acidic. Larger rates of CH_4 oxidation were observed for the sitka and birch plots than the grass plot, however differences were only significant ($p < 0.05$) between the grass and sitka plots. No significant relationship between soil bulk density and CH_4 uptake rate was found, but the lowest oxidation rate was associated with the highest soil bulk density. Differences between all other soil variables measured were not significant.

Devilla

CH_4 oxidation rates at Devilla forest averaged -9.9 ng m^{-2} s^{-1} on the two dates measured and were similar to the fluxes measured at Glencorse.

North Berwick

In the oilseed rape field CH_4 oxidation rates were significantly ($p < 0.05$) lower than those measured in the shelter belt (Figure 1). Oxidation rates ranged from -1.1 to -1.6 ng m^{-2} s^{-1} compared to -4.7 to -9.6 ng m^{-2} s^{-1} in the shelter belt. CH_4 oxidation rates increased over the measurement period and were correlated ($p < 0.05$) with decreasing soil moisture and

Table 1. Methane fluxes and soil physical and chemical characteristics.

Site	CH$_4$ flux (ng m^{-2} s^{-1})	n	Soil moisture (% dry wt.)	NO$_3$-N (ug g^{-1} dry soil)	MH$_4$-N (ug g^{-1} dry soil)	pH CaCl$_2$	Soil temp. (°C)	Soil bulk density (g cm^{-3})
Mineral soils								
Glencorse Grass	−9.8 (1.2)[1]	6	23.3	1.79	5.29	4.7	14.4	1.1
Alder	−4.8 (1.9)	6	25.9	8.11	4.48	3.3	11.1	1.13
Sitka	−12.3 (1.5)	6	19.5	2.11	3.85	4.2	10.6	1.01
Birch	−11.2 (1.6)	6	26.0	3.06	5.46	3.9	11.6	1.11
Devilla Pine	−9.9 (4.1)	6	28.9	2.54	3.47	3.1	10.2	1.0
East Linton agricultural	−0.2 (0.6)	45	23.0	11.3	8.6	6.1	11.3	1.23
North Berwick arable	−1.4 (0.2)	45	19.9	1.5	3.6	5.1	10.7	1.30
Shelter belt	−6.9 (2.0)	15	29.7	0.4	6.2	4.6	10.4	1.02
Peat soils								
Dunslair moorland	−6.8 (3.2)	6	147	1.2	6.32	3.5	7.3	nd
High altitude forest	−2.6 (1.0)	6	134	1.42	24.8	3.2	7.5	nd
Low altitude forest	−4.6 (2.3)	6	103	1.19	4.91	3.1	9.1	nd
Loch More sitka	6.8 (6.1)	9	516	nd	nd	2.6	8.1	nd
Pine 1	4.9 (3.8)	12	654	nd	nd	2.7	7.8	nd
Pine 2	−2.1 (1.9)	11	319	nd	nd	2.7	8.3	nd
Blanket peat	6.7 (10.9)	40	564	nd	nd	3.2	9.0	nd
Auchencorth Moss blanket peat	3.9 (6.9)	6	400	nd	nd	2.6	10.5	nd

[1] = mean (standard deviation)
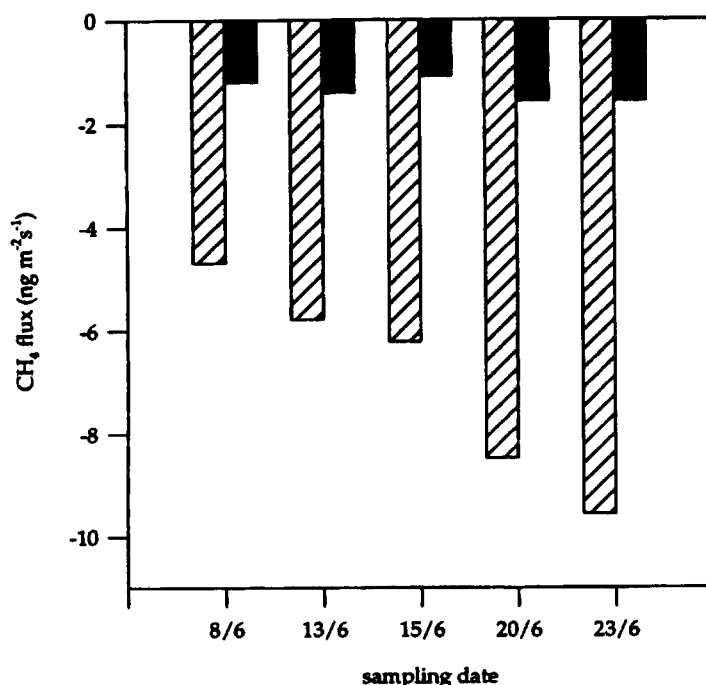n = number of measurements
nd = not determined

Figure 1. CH_4 oxidation rates from an oilseed rape field (■) and adjacent shelter belt (▨), North Berwick.

increasing soil temperature. The shelter belt soil responded more positively to changing environmental conditions, with oxidation rates increasing by over 100% compared to an $\sim 30\%$ increase in the oilseed rape field. This was despite the soil in the rape field drying out at a much higher rate. Soil moisture was larger and soil bulk density smaller in the shelter belt compared to the oilseed rape field. The soil in the shelter belt was also more acidic. Soil NO_3-N concentrations were largest in the oilseed rape field compared to soil NH_4-N concentration which were larger in the shelter belt.

East Linton

At East Linton, CH_4 fluxes were measured before and after the second application of N fertiliser (Figure 2). The largest CH_4 oxidation rates (-0.7 ng m^{-2} s^{-1}) were observed before, and until one day after, fertiliser application when high rainfall transported the fertiliser into the soil and CH_4 emission was observed (0.3 ng m^{-2} s^{-1}). Oxidation was again observed 16 days after fertiliser application, although rates were six times lower than before fertiliser application (-0.1 ng m^{-2} s^{-1}) and the soil moisture was 5% lower.
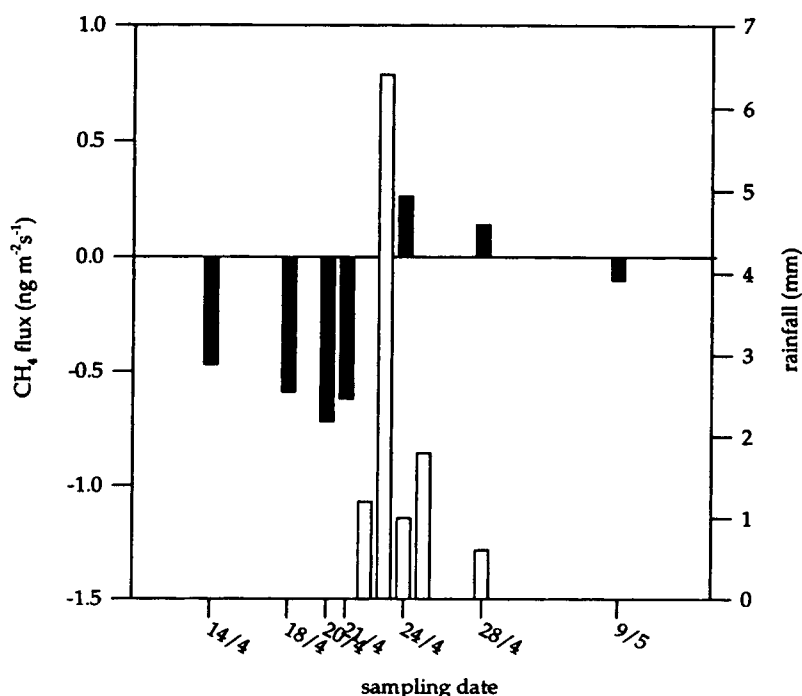
Figure 2. CH$_4$ flux and rainfall (20/4 to 29/4) from the agricultural site, East Linton, before and after the application of 43 kg NH$_4$NO$_3$-N ha^{-1} on 19/4. ■ CH$_4$ oxidation □ rainfall.

CH$_4$ fluxes from peat

Dunslair Heights

Mean CH$_4$ oxidation rates ranged from -2.6 to -6.8 ng m^{-2} s^{-1}. A similar pattern of CH$_4$ oxidation was observed on 27/4/94 and 6/7/94 with the smallest oxidation rates being observed at the high altitude forest site and the largest oxidation rates at the high altitude moor (Figure 3) despite the large differences in soil temperature and moisture content between the two sampling dates. The high altitude forest site with the smallest oxidation rate on both sampling dates, differed significantly ($p < 0.05$) on 6/7/94 (high altitude forest -2.9 ng m^{-2} s^{-1}, compared to -9.1 ng m^{-2} s^{-1} and -6.5 ng m^{-2} s^{-1} for the moor and low altitude forest sites, respectively) but not on 27/4/94. Significantly larger concentrations of soil available NH$_4$-N were found at the high altitude forest site (24.8 ug NH$_4$-N g dry soil) compared to the low altitude forest and moor sites (4.9 and 6.3 ug NH$_4$-N g dry soil respectively). Soil moisture was ~10% higher and the pH was 0.3 pH units higher at the moor site than
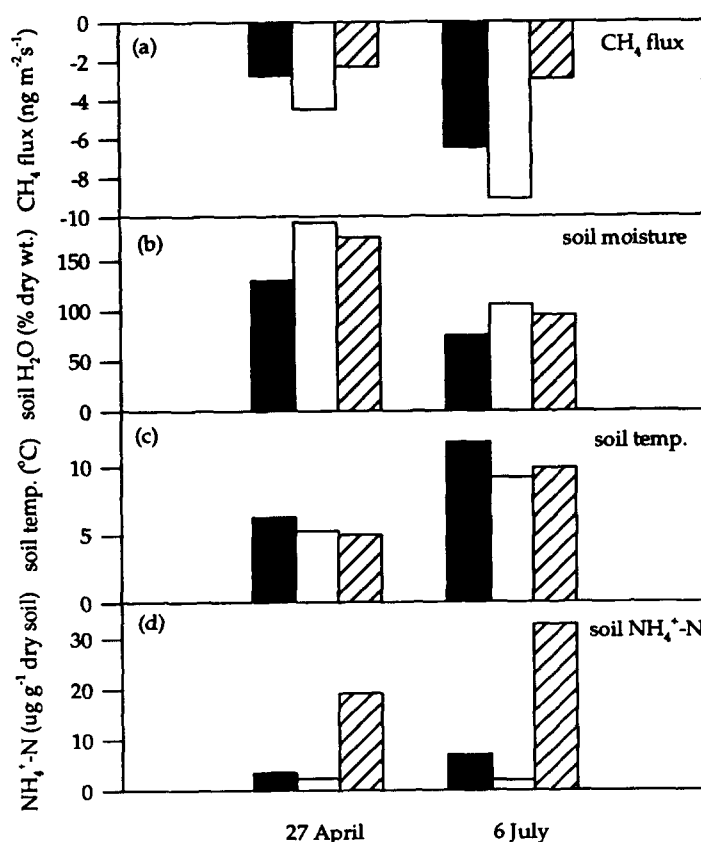
Figure 3a. CH$_4$ oxidation at Dunslair on 27/4 and 6/7, *3b* soil moisture (% dry weight), *3c* soil temperature (°C) and *3d* available NH$_4$-N (ug g^{-1}) dry soil. ■ low altitude forest □ high altitude moorland ▨ high altitude forest.

at the high altitude forest site. The low altitude forest site had the lowest soil moisture, highest soil temperature, and lowest soil N concentrations.

A large increase in CH$_4$ oxidation rate was observed between the sampling dates coinciding with an approximate 50% decrease in soil moisture and 50% increase in soil temperature. Oxidation rates at the low altitude forest site increased from -2.7 to -6.5 ng m^{-2} s^{-1} and at the moor site from -4.5 to -9.1 ng m^{-2} s^{-1}. However at the high altitude forest site only a small $\sim$0.5 ng m^{-2} s^{-1} increase was observed, despite the similar observed change in environmental conditions.
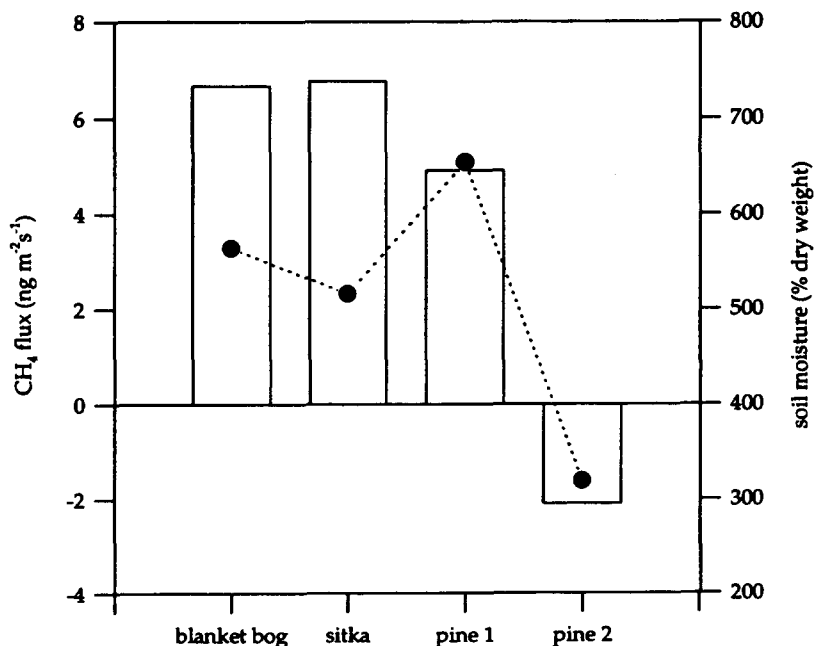
Figure 4. CH₄ flux from areas of forested and non-forested blanket bog, Loch More, Caithness. ☐ CH₄ flux ● soil moisture.

Loch More

At Loch More both emission and oxidation were observed. A mean net emission flux of 6.7 ng m^{-2} s^{-1} was measured for the blanket peat, and fluxes ranged from 6.8 to −2.1 ng m^{-2} s^{-1} in the forested plots (Figure 4). CH_4 oxidation was only observed in the driest peat. The pH of the blanket peat was significantly less acidic than at any of the forested sites (Table 1).

Auchencorth Moss

At Auchencorth Moss a mean net CH_4 emission of 3.9 ng m^{-2} s^{-1} was observed. The peat had a high moisture content and was very acidic (Table 1).

Discussion

The results of the field measurements over a range of soils provide examples of both CH_4 emission and oxidation and are within the range of fluxes reported in the literature (Crill 1991; Dorr et al. 1993). In general, the mineral forest

soils oxidised CH_4 with an average flux of -9.0 ng m^{-2} s^{-1}. In contrast, the agriculturals soil showed much smaller rates of CH_4 oxidation and at East Linton emitted CH_4 after prolonged rainfall and fertilisation. The peats showed both oxidation and emission in the range 6.8 to -6.8 ng m^{-2} s^{-1} with the net flux being regulated by soil moisture.

To illustrate the range of fluxes at each of the measured sites and sum-marise the association of CH_4 oxidation and emission fluxes with small and large N input and increasing soil moisture, the mean fluxes from each site have been plotted in order of decreasing CH_4 oxidation rates in Figure 5. Although the absolute range of fluxes is small, and for the CH_4 oxidation rates which constitute the majority of the data, the overall mean flux and standard deviation are even smaller being -6.1 ± 4.1 ng m^{-2} s^{-1}, there are clear effects of land use and N input associated with the decreased fluxes. It is convenient therefore to discuss the effects of each of the major variables on rates of CH_4 oxidation or emission in turn.

Effect of soil moisture

The response of CH_4 oxidation to soil moisture has been widely reported for laboratory studies and field observations with a clear inverse relationship between CH_4 oxidation and soil moisture (Whalen et al. 1990, 1991; Steudler et al. 1989). The range in CH_4 fluxes over peat soils, from emission of 6.8 to oxidation of -6.8 ng m^{-2} s^{-1}, span a wide range in soil moisture, 654 to 103 % dry weight. The data plotted in Figure 6 show a clear relationship between CH_4 flux and soil moisture ($r^2 = 0.836$) with a change from oxidation to emission at a soil moisture of 325% ($\pm 80\%$ from 95% confidence interval). The measurements of CH_4 oxidation in the peat soils of Dunslair showed a marked increase between sampling dates corresponding to a decrease in soil moisture and increase in soil temperature. The effects are consistent with the literature on net exchange of CH_4 over peatlands (Whalen & Reeburgh 1990) and show the competition between methanogenesis and CH_4 oxidation as soils become progressively drier. The progression from oxidation in dry soils to emission in wet soils is also closely coupled with oxygen supply and gas transport into the soil. Clearly, as gaseous diffusion becomes progressively restricted by water filled pore space the supply of oxygen is gradually limited.

Effect of bulk density

Gaseous diffusion in soils is also influenced by soil bulk density. In the measurement of CH_4 oxidation rates in the mineral soils, a negative rela-tionship with soil bulk density was observed (Figure 7). Bulk density is a likely indicator of the effect of diffusivity in the soil which influences the
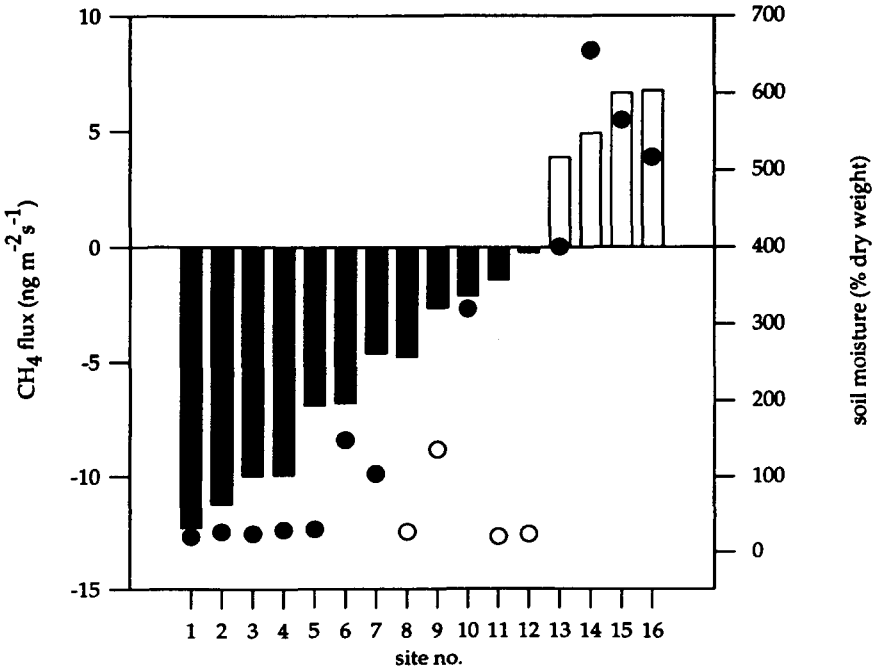
Figure 5. CH$_4$ oxidation (■) and emission (□) rates, and soil moisture (% dry weight) from low N (●) and high N (○) forest, moorland and agricultural soils. Site 1 = Glencorse Sitka, 2 = Glencorse Birch, 3 = Glencorse Grass, 4 = Devilla Pine, 5 = Dunslair moor, 6 = N. Berwick shelter belt, 7 = Glencorse Alder, 8 = Dunslair low altitude forest, 9 = Dunslair high altitude forest, 10 = Loch More Pine 2, 11 = N. Berwick arable, 12 = East Linton arable, 13 = Auchencorth Moss blanket peat, 14 = Loch More Pine 1, 15 = Loch More blanket peat and 16 = Loch More Sitka. High N sites received N through N deposition, fertilisation and fixation.

gas transport of substrate to methane oxidisers. The two smallest oxidation rates had the highest bulk densities and were found in the agricultural soils. Compaction during cultivation may increase bulk density and Hansen et al. (1993) found a 52% reduction in oxidation rates following compaction. Studies have attributed variations in CH$_4$ oxidation rates as a function of soil physical parameters, and soil diffusivity has been shown to be the controlling parameter on flux rates in several studies (Dorr 1993; Keller & Reiners 1994). Whalen & Reeburgh (1990), however, concluded that CH$_4$ oxidation was not controlled by gas diffusion in tundra soils, and Crill (1991) found a diffusional control on oxidation only during periods of most active microbial activity.
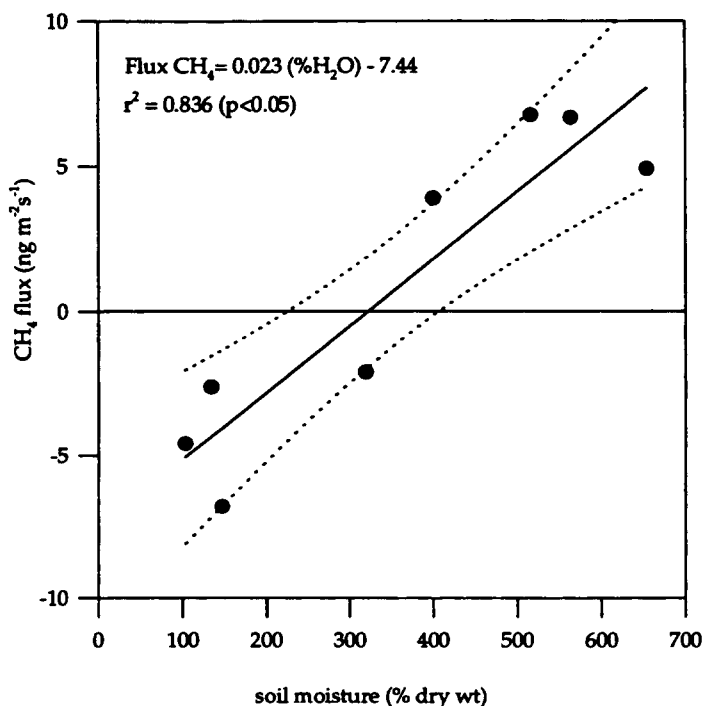
Figure 6. CH$_4$ flux from the peat soils studied correlated with soil moisture. The solid lines were fitted by linear regression, the dotted lines show the 95% confidence intervals.

Effects of N

Increased N loading due to N fixation, atmospheric deposition of N, and fertilisation were associated with decreases in the soil sink for CH$_4$ on a range of soil types and land uses. At all sites studied, the significance of the correlation between CH$_4$ flux, and soil moisture increased when the sites with high N inputs were excluded, indicating the importance on N as a mediator of CH$_4$ flux rates.

Inhibition of CH$_4$ oxidation in soils by various forms of N has been documented for many soils (Steudler et al. 1989; Adamsen & King 1993; Castro et al. 1994). Experiments on pure cultures have demonstrated the inhibitory effects of NH$_3$ on CH$_4$ oxidation, and of CH$_4$ on NH$_4^+$ oxidation (Hyman & Wood 1983; O'Neill & Wilkinson 1977). This inhibition is thought to be due to competitive inhibition for active sites on the mono-oxygenase enzyme system (O'Neill & Wilkinson 1977). However results are not always consistent with the competitive inhibition theory as the effects of the inhibition are often long term (Mosier et al. 1991), lasting long after added NH$_4^+$ has been nitrified.
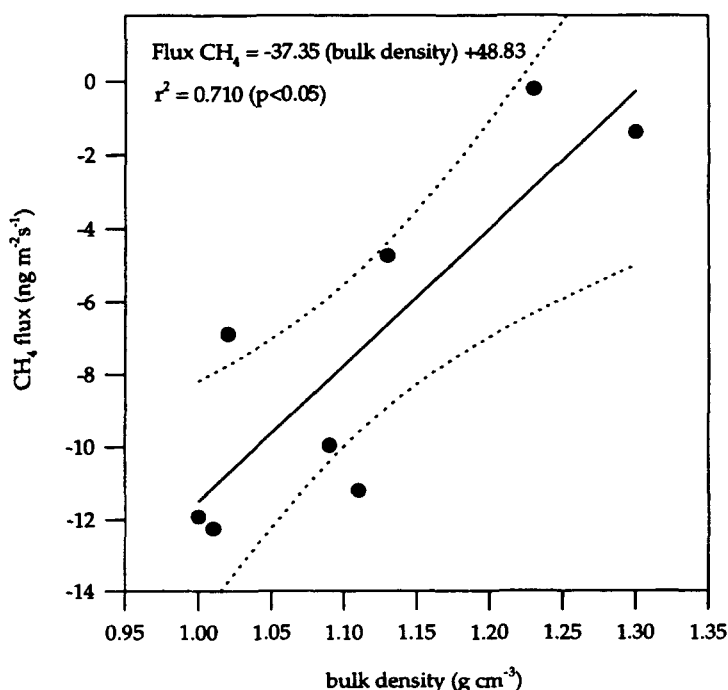
Figure 7. CH₄ oxidation rates from the mineral soils correlated with soil bulk density. The solid lines were fitted by linear regression, the dotted lines show the 95% confidence intervals.

CH_4 oxidation rates at Glencorse were found to be significantly lower in the alder plot than in the adjacent birch, sitka and grass plots. The increased available NO_3-N concentrations in the soil caused by N fixation by the actinomycete frankia in the root nodules of red alder is consistent with the low rate of CH_4 oxidation observed. However, high soil bulk density was also found at this site and would have contributed to the low oxidation rate observed. This soil was also more acidic, although no correlation between soil pH and oxidation rates was found.

At East Linton, the winter wheat field, the mean oxidation rate was only 2% of the rates observed at forest sites on similar soil types, and CH_4 emission was observed after a period of rainfall. It is possible that the effects of N fertilisation, compaction, and cultivation had decreased the capacity of this soil to oxidise CH_4 to an extent that net emission was observed. Sixteen days after fertilisation, when the soil moisture had substantially decreased, CH_4 oxidation rates were six times lower, showing the inhibitory effect of N fertilisation.

At North Berwick an 80% reduction in CH_4 oxidation rates was observed in the oilseed rape field relative to the adjacent shelter belt. Similar results have been found in other studies (Dobbie et al. 1996; Lessard et al. 1994). The observed decrease in oxidation rates as a result of cultivation is almost certainly a consequence of compaction and the inhibitory effects of N. The soil NO_3-N concentrations were $\sim$3 times larger in the oilseed rape field than in the shelter belt and the soil NH_4-N concentrations were higher in the shelter belt, suggesting lower nitrification rates in the shelter belt relative to the oilseed rape field. However the effects of N cannot be seperated from the increased bulk density, due to compaction, found at this site.

Large soil NO_3-N concentrations were associated with small CH_4 oxidation rates in several of the mineral soils studied. No correlation was found between oxidation rates and soil NH_4^+, which agrees with findings by Crill et al. (1994) and Sitaula & Bakken (1993). It has been suggested that nitrification rates rather than NH_4^+ concentrations may be responsible for the inhibition (Mosier et al. 1991; Sitaula & Bakken 1993). The high soil NO_3-N concentrations (the end product of nitrification) in this study may be indicitive of nitrification rates and therefore the inhibition of CH_4 oxidation rates could be related to N turnover. However the mechanism of the inhibition is not certain.

At Dunslair Heights, the smallest CH_4 oxidation rates were found at the forested site on the hill summit, which was the site with the largest soil available NH_4-N compared to the low altitude forest and the adjacent moor site. The hill summit is frequently in cloud and receives much larger inputs of deposited N species. The total annual deposition of N at the site increases from 6.4 kg ha^{-1} at 275m to 24.3 kg ha^{-1} at 600 m, the summit (Crossley et al. 1992). Because the trees intercept polluted cloud water, HNO_3 and NH_3 deposition rates were up to 90% larger at the afforested high altitude site (Fowler et al. 1989), resulting in the much higher soil available NH_4-N concentrations observed relative to the adjacent moorland site. The change in soil moisture and temperature that occurred over the study period did not significantly increase oxidation rates, at the high altitude forest site, indicating that N dynamics were possibly having a negative effect on the microbial population response to changes in soil moisture and temperature. Environmental variables measured such as soil moisture, temperature and pH, did not appear to correlate with the observed differences in CH_4 oxidation rates.

In contrast to the mineral soils, low rates of CH_4 oxidation at Dunslair were associated with high soil NH_4-N concentrations. NH_3 may be acting as a competitive inhibitor of CH_4 oxidation rates (O'Neill & Wilkinson 1977), however the NH_4^+ accumulation and low pH at this site suggests low nitrification rates. It also is possible that an ion toxicity mechanism due to the high

atmospheric pollution loading at this site is having an inhibitory effect on methanotrophs and nitrifiers. Several studies have identified salts (Adamsen & King 1993) and the products of NH_4^+ oxidation, hydroxylamine and nitrite, as having toxic effects on methanotrophs (Schnell & King 1994). More work is required to estimate the relative effects of deposited species on CH_4 oxidation rates.

Effects of temperature and pH

The temperature response of CH_4 oxidation has been reported for a variety of soil environments with Q_{10} values in the range 1.3 to 2.3 (Whalen et al. 1990; Dunfield et al. 1993; Adamsen & King 1993). No significant correlation with temperature was observed in this study, the temperature range in which fluxes were measured was however small, averaging $9.9 \pm 1.9\,^\circ C$.

The effect of pH on CH_4 oxidation rates is not well documented. Hutsch et al. (1994) observed an inhibitory effect of low pH on CH_4 oxidation. Dunfield et al. (1993) concluded that the microorganisms involved in CH_4 metabolism in peat soils were not well adapted to low pH values, although studies including this one have measured oxidation in soils of low pH (Castro et al. 1993). The acidifying properties of conifers is well documented (Hornung 1985) and low pH values were associated with soils under the conifer plantations at Dunslair Heights (pH 3.2) and Loch More (pH 2.7). A low pH was observed in the alder plot at Glencorse (pH 3.3), red alder is also known to accelerate soil acidification (Sheppard 1993). However, overall no correlation was observed between CH_4 oxidation rates and soil pH at the sites studied.

Effects of disturbance and cultivation

The effect of land use was well illustrated by the small fluxes found at East Linton and the large difference in the oxidation rates between the oilseed rape field and shelter belt at North Berwick. The decrease in CH_4 oxidation rates associated with cultivation and disturbances, such as the conversion of forest to agriculture, have been reported (Lessard et al. 1994; Keller et al. 1990; Dobbie et al. 1996). A number of factors may contribute to the observed decrease in CH_4 oxidation rates. N fertilisation effects have been well documented (Steudler et al. 1989; Castro et al. 1994), and increased compaction due to cultivation, leading to a decrease in soil diffusivity, has also been shown to have a negative effect on CH_4 oxidation (Hansen et al. 1993). Bender & Conrad (1994) suggested that the vertical stratification of CH_4 oxidising activity was destroyed by plowing, influencing oxidation rates.

The birch and sitka plots at Glencorse had higher CH_4 oxidation rates than the grass plot, although the difference was only significant for the sitka plot

which also had a lower soil moisture content. It would therefore be premature to speculate on the effects of afforestation on CH_4 oxidation rates at this site. Possible reasons for higher CH_4 oxidation rates under trees include a decrease in soil bulk density and formation of a stable soil structure (Brady 1990), leading to improved aeration. Keller et al. (1990) speculated that soils under the forest canopy reside in a more stable micro-climate where soil moisture and temperature are well buffered. In the grassland it is possible that the dense rhizosphere and associated high microbial activity results in competition for O_2, which leads to the formation of anaerobic microsites and hence lower oxidation rates.

Summary

Field measurements of CH_4 flux from a range of soil environments showed that soil moisture, N input and soil diffusivity strongly influence rates of CH_4 oxidation. Both CH_4 oxidation and emission were observed with fluxes ranging from -12.3 to 6.8 ng m^{-2} s^{-1}.

In the peat soils, soil moisture was found to be the most important environmental variable affecting the magnitude and direction of flux ($Flux_{CH4}$ = $0.023 \times \%H_2O$(dry weight) $- 7.44$, $p < 0.05$), with CH_4 oxidation being observed below 325% ($\pm 80\%$), and net emission occurring at soil moistures above this value. The importance of soil moisture in determining the magnitude and direction of flux from these environments demonstrates the sensitivity of peatlands to future changes in climate. Increased N loading due to atmospheric deposition, and scavenging by trees, was associated with low CH_4 oxidation rates in an upland peaty podzol. The effects of atmospheric pollution could have important mediating effects on the size of the CH_4 soil sink.

The mineral soils showed a range of oxidation rates over a small range in soil moisture. The highest rates were observed in mineral forest soils, with the exception of the red alder site where high rates of N cycling and a higher soil bulk density were correlated with lower CH_4 uptake rates. The lowest oxidation rate was observed in an agricultural soil where compaction and fertilisation resulted in high soil bulk densities and soil NO_3-N concentrations. Mineral soil oxidation rates were significantly correlated with soil bulk density ($Flux_{CH4}$ = $-37.35 \times$ bulk density (g cm^{-3}) + 48.83, $p < 0.05$), indicating the importance of soil diffusivity in determining the size of the soil sink for CH_4.

Comparing CH_4 flux rates and soil environmental parameters from a wide range of soil environments can provide an insight into the controls on CH_4

flux rates, and combined with seasonal studies, will allow CH_4 flux rates to be predicted.

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