
The Effect of Agriculture on Methane Oxidation in Soil [and Discussion]

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The effect of agriculture on methane oxidation in soil

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Aerobic soils are an important sink for methane (CH₄), contributing up to 15% of global CH₄ destruction. However, the sink strength is significantly affected by land management, nitrogen (N) fertilizers and acidity. We tested these effects on samples taken from the Broadbalk Continuous Wheat, Park Grass permanent grassland and Broadbalk and Geescroft Wilderness Experiments at Rothamsted. The rates of uptake from the atmosphere of both enhanced (10 ppmv) and ambient (2 ppmv) concentrations of CH₄ were measured in laboratory incubations of soil cores under controlled conditions.

The most rapid rates of uptake were measured in soil from deciduous woodland at pH 7 (measured in water); acidic (pH 4) woodland soil showed no net CH₄ oxidation. While disturbance of the cores used in the experiments did not affect the rate of CH₄ uptake, extended (150 years) cultivation of land for arable crops reduced uptake rate by 85% compared to that in the soil under calcareous woodland. The long-term application of ammonium (NH₄)-based fertilizer, but not nitrate (NO₃)-based fertilizer, completely inhibited CH₄ uptake, but the application for the same period of farmyard manure that contained more N than the fertilizer had no inhibitory effect.

Autoclaving showed that the uptake of CH₄ was microbially mediated. The most likely causes of the inhibitory effects seen are (i) insufficient concentrations of CH₄ *in situ* to activate methane monooxygenase; (ii) the direct inhibition of CH₄ oxidation by NH₄⁺ ions as the methanotrophs become adapted to oxidizing NH₄⁺ ions; (iii) the suppression of methanotrophs by NH₄-based fertilizers and acidity; (iv) the requirement of methanotrophs for a stable soil architecture which is incompatible with the disturbance caused by regular arable cultivation. These explanations are not mutually exclusive; several may operate concurrently.

1. Introduction

Methane (CH₄) is a radiatively active (greenhouse) gas. The WMO/UNEP (1990) estimated that CH₄ contributed 15% of the change in radiative forcing that occurred between 1980 and 1990. Its current global average atmospheric concentration is 1.72 ppmv (parts per million by volume). For several decades the concentration was increasing rapidly by *ca.* 20 ppbv a⁻¹ (about 1% per year),

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but the rate of increase has declined markedly in the last few years to about 10 ppbv a⁻¹ (Dlugokencky *et al.* 1994) for reasons that are not yet clear. The causes of the increase are not well identified either, but are thought to include increased production from ruminants and paddy rice cultivation and the exploitation of natural CH₄ deposits. There are also suggestions that the natural sinks may have decreased in strength.

The soil is an important source of CH₄ when under anaerobic conditions, such as in natural wetlands or flooded rice but aerobic soil is an important sink where CH₄ is oxidized to CO₂ or assimilated into the microbial biomass. Oxidation is environmentally beneficial because each molecule of CH₄ is 21 times more radiatively active than one of CO₂ (WMO/UNEP 1990). Estimates of the total sink strength of the soil vary between 10% (Duxbury & Mosier 1993) and 15% (Born *et al.* 1990) of global CH₄ destruction. Methane uptake has been observed in tropical soils (Seiler *et al.* 1984), peat soils (Yavitt *et al.* 1990), temperate forest soils (Steudler *et al.* 1989; Born *et al.* 1990), grasslands (Mosier *et al.* 1991) and desert soils (Striegl *et al.* 1992).

Net CH₄ flux is determined by the balance between production and consumption. Both may occur in some units of soil, e.g. production in an anaerobic zone below the water table or in a microsite, and consumption in an aerobic (surface) layer. Much of the CH₄ generated in soil is oxidized before it reaches the atmosphere. Galchenko *et al.* (1989) estimated that 39–92%, 78–95% and 60–90% of the CH₄ produced in rice paddy, swamps and lakes, and seas, respectively, was oxidized in aerobic layers before the CH₄ could escape to the atmosphere.

Recent measurements of CH₄ uptake by predominantly aerobic soil have shown significant variations that appear to be caused by land management and nitrogen (N) deposition from the atmosphere (for the latter see Melillo *et al.* 1989). Nesbit & Breitenbeck (1992) found that cultivated soils took up CH₄ when exposed to large concentrations (greater than 1000 ppmv), but not when exposed to ambient concentrations. Dobbie & Smith (1994) found that forest soils took up CH₄, on average, at three to four times the rate at which it was taken up by agricultural soils. Mosier & Schimel (1991) and Mosier *et al.* (1991) reported that arable soil absorbed less CH₄ than pasture, and that the application of N fertilizer and irrigation reduced the rate of uptake further. An annual application of fertilizer equivalent to only 22 kg N ha⁻¹ a⁻¹ for 15 years as ammonium nitrate (NH₄NO₃) reduced CH₄ uptake by 41% compared with adjoining unfertilized pasture; table 1 summarizes the results. Bronsen & Mosier (1994) found that ammonium chloride, and also the nitrification inhibitor nitrapyrin and the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT), had similar inhibitory effects. In addition Steudler *et al.* (1989) measured a reduction of CH₄ uptake by temperate forest soil when a total of 37 or 120 kg N ha⁻¹ was applied in six equal monthly doses; the effect increased between the fourth and sixth doses, indicating a cumulative effect of N. These changes are significant because, without the soil sink for CH₄, the atmospheric concentration would be increasing at 1.5 times the current rate (Duxbury & Mosier 1993; Ojima *et al.* 1993).

Research to date has found it difficult to separate the effects on CH₄ uptake of land use (arable, pasture, woodland), N rate and form, and soil acidity (which results from the application of NH₄-based fertilizers unless soil is limed). The Classical Experiments at Rothamsted Experimental Station, begun in the 1840s and 1850s, compare the effects of NH₄- and NO₃-based fertilizers on the growth

Table 1. *Effects of land use and nitrogen fertilizer on methane oxidation by soil*
(Adapted from Mosier & Schimel (1991).)

land use	methane oxidation (mg CH ₄ m ⁻² d ⁻¹)
pasture:	
fertilized	0.55
unfertilized	0.84
wheat (unfertilized)	0.20
irrigated wheat:	
control	0.11
+ urea	0.12

of permanent grassland and arable crops, and examine the natural regeneration of woodland over 100 years on neutral soil buffered with lime or unbuffered soil that is now very acid. These unique experiments are being used to unravel the complex interactions between land use and fluxes of trace gases, initially CH₄.

2. Experimental methods used in trace gas flux studies

Soil is a heterogeneous material. Its physical, chemical and, especially biological properties vary spatially and temporally. Because of this, measuring and understanding elemental cycling processes such as CH₄ uptake is complex and tedious, requiring large samples and/or many replicates if large errors are to be avoided. While measurements integrated over a large scale are required for best estimates of fluxes over landscapes, the elucidation of processes and the factors controlling them require rigorously controlled studies. Techniques have therefore centred on cover boxes in the field or the incubation of small cores of soil in the laboratory; Mosier (1989) made a useful review of these small-scale techniques. Some of the techniques used in the field are now very sophisticated: Butterbach-Bahl *et al.* (1994) described the continuous (five samples per hour) measurement of fluxes of CH₄, NO, N₂O and NO₂ in a forest in Bavaria and the correlation of these fluxes to meteorological events, and Hargreaves *et al.* (1994) reported the use of a tuneable diode laser system to measure CH₄ fluxes from peatlands.

Studies at Rothamsted have utilized the incubation of small cores in the laboratory. This facilitated the control of environmental conditions (temperature and moisture), the manipulation of factors such as applications of fresh N fertilizer, and the minimizing of errors to enable the detection of differences in CH₄ uptake with a manageable number of soil cores. Full details of experimental methods were given by Hütsch *et al.* (1993, 1994).

The measurement of CH₄ uptake from ambient concentrations is not easy, so early work at Rothamsted used enhanced concentrations of *ca.* 10 ppmv to aid detection. All early measurements made with enhanced concentrations have now been repeated at ambient concentrations; rates of uptake are not significantly different, so the uptake at 10 ppmv is not an artefact of adding extra CH₄. For the work with enhanced concentrations of CH₄, usually four replicate cores were used, with two gas samples analysed at each sampling time from each core; eight

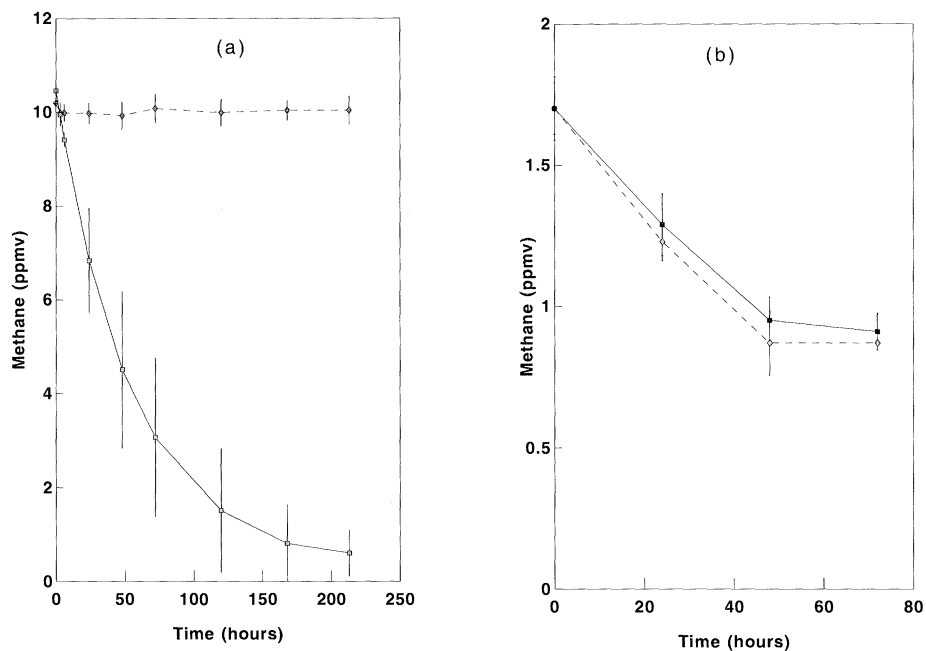


Figure 1. Effects of (a) autoclaving and (b) physical disturbance on the oxidation of CH_4 by soil. (a) —□—, without autoclaving; —◇—, with autoclaving. (b) —■—, intact core; —◇—, broken core.

replicate cores were used for woodland soil because of its expected greater spatial variability. For the later work with ambient concentrations of CH_4 , eight replicate cores were always used.

Autoclaving of cores was used to confirm that the uptake of CH_4 was biologically mediated. Cores were autoclaved at 123°C (30 min sterilizing time, 10 min purge time) and then CH_4 uptake and carbon dioxide (CO_2) production measured; the physical structure of the cores remained intact; no water was lost. Figure 1a shows the result of one of these experiments. Clearly no CH_4 was taken up by the soil after autoclaving, establishing that the process is biological. However, the physical integrity of soil cores can be very important in biologically mediated reactions, especially where diffusion rates and gas gradients are involved. Further tests were therefore made on this effect. Figure 1b shows CH_4 uptake by intact and roughly broken cores; there is no significant difference between them, indicating that breaking/disrupting cores does not produce artefacts in CH_4 uptake.

3. Results

(a) Effects of land use and management

Figure 2 shows the uptake of CH_4 by soil under arable land (Broadbalk Continuous Wheat), cut grass (Park Grass) and grazed grass (Broadbalk Wilderness, grazed section) and woodland (Broadbalk Wilderness, wooded section); the soils

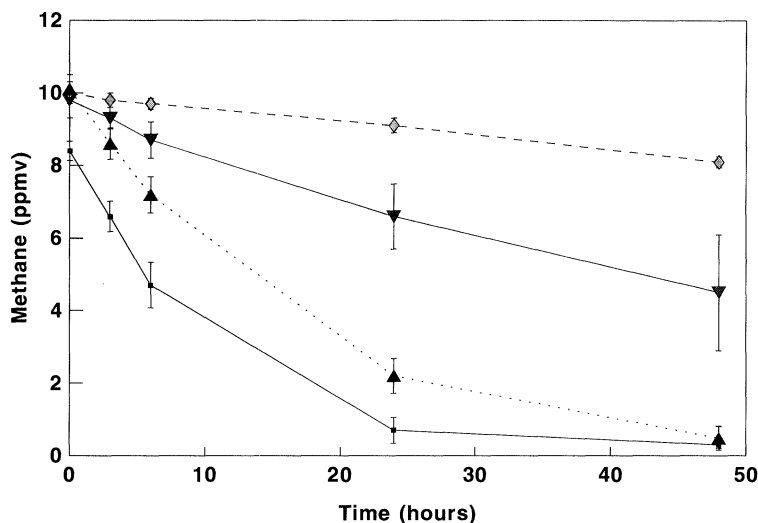


Figure 2. Effect of land use on the oxidation of CH_4 by soil. Data from the Broadbalk Continuous Wheat, Broadbalk Wilderness (woodland and grazed grass), and Park Grass Permanent (cut) Grass Experiments at Rothamsted Experimental Station. In no case was N fertilizer applied. —■—, woodland; ···▲···, cut grass; —▼—, grazed grass; - -◇- -, arable.

have pH values between 5.9 (grazed Wilderness) and 7.5 (Broadbalk arable) and receive no N other than from the atmosphere, or from animal returns in the case of the grazed grass; atmospheric inputs total $40\text{--}50 \text{ kg ha}^{-1} \text{ a}^{-1}$ to arable and grassland, perhaps $60\text{--}70 \text{ kg ha}^{-1} \text{ a}^{-1}$ to woodland (Goulding 1990). The effect of cultivation is immediately apparent. Growing grass cut for hay caused only a small reduction in the rate of uptake of CH_4 over that in undisturbed woodland soil, but 150 years of arable cultivation has caused an 80% reduction in the rate of CH_4 uptake. This has to be compared with the result of figure 1*b*, which shows that simply disturbing or breaking soil does not immediately reduce the rate of CH_4 uptake. The soil under the grazed grass absorbs CH_4 at a much slower rate than that under the cut grass. This may be due to an effect of N excreted from the sheep as urine and faeces, which contains much $\text{NH}_4\text{-N}$ (see below).

(b) Effect of nitrogen fertilizer

The Broadbalk Experiment permits the truly long-term effects of fertilizer on environmental emissions to be assessed. All plots are at pH 7.5 and are managed in exactly the same way, except for fertilizer applications. All have grown winter wheat, with conventional cultivation, every year since 1843 except for the period from 1926 to 1967 when they were fallowed one year in every five to control weeds. Figure 3 shows that the continued application for 150 years of $144 \text{ kg ha}^{-1} \text{ N}$ fertilizer has significantly reduced CH_4 uptake by about 50% compared with soil receiving no fertilizer; the reduction increases with the amount of fertilizer applied (Hütsch *et al.* 1993).

The effects we observed appear to be caused by NH_4^+ rather than by inorganic N because we found no effect of NO_3^- . Figure 4 shows uptake rates of CH_4 by soil from plots of the Park Grass Experiment that are at pH 6.1–6.3 and receive

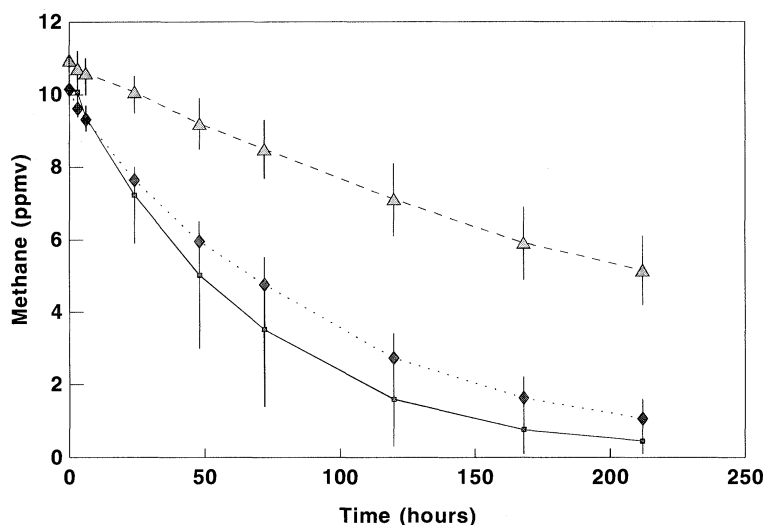


Figure 3. Effect of long-term applications of fertilizer and farmyard manure on the oxidation of CH_4 by soil. Data from the Broadbalk Continuous Wheat Experiment at Rothamsted. Fertilizer applied as ammonium sulphate from 1843 to 1968; thereafter as ammonium nitrate. Farmyard manure contains *ca.* 240 kg N ha^{-1} . All plots at *ca.* pH 7.5. —□—, Farmyard manure; $\cdots \blacklozenge \cdots$, no fertilizer; —△—, 144 kg N ha^{-1} .

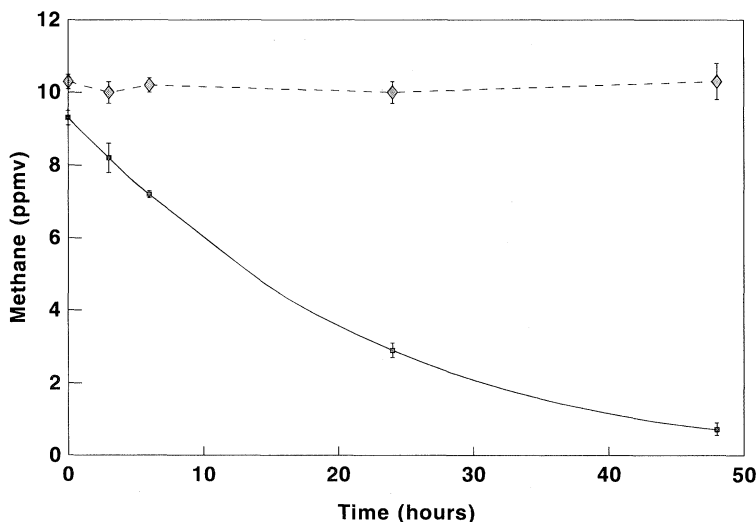


Figure 4. A comparison of the effects of ammonium-based and nitrate-based fertilizer on the oxidation of CH_4 by soil. Data from the Park Grass Experiment at Rothamsted. Plot 9/2 a ($-\diamond-$) has received 96 kg N ha^{-1} annually as ammonium sulphate since 1856; Plot 14/2 a ($-\square-$) has received 96 kg N ha^{-1} annually as sodium nitrate since 1856.

$96 \text{ kg N ha}^{-1} \text{ a}^{-1}$, but Plot 14/2 receives NaNO_3 and Plot 9/2 $(\text{NH}_4)_2\text{SO}_4$. There is no uptake of CH_4 by the soil that has received $\text{NH}_4\text{-N}$ for 140 years, whereas CH_4 uptake in the $\text{NO}_3\text{-treated}$ plot is the same as that on an unfertilized plot at the same pH. The form of the N applied therefore has a significant effect on CH_4

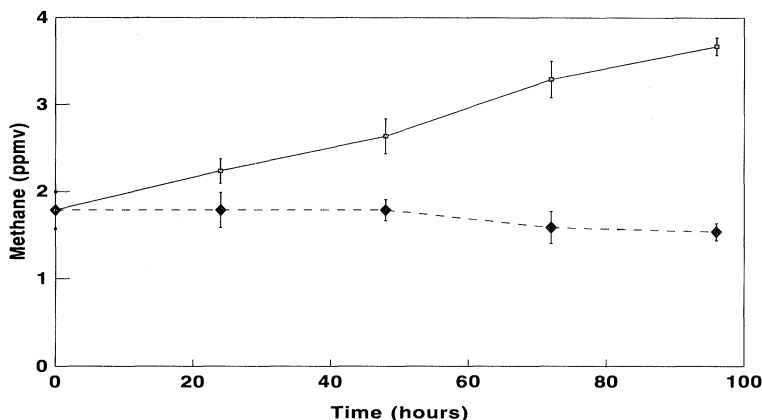


Figure 5. The immediate effect on CH_4 oxidation in soil of applying water or a solution of NH_4^+ ions; the data suggest rapid inhibition of CH_4 oxidation and the simultaneous production and consumption of CH_4 (see text). Soil taken from the farmyard manure plot on the Broadbalk Continuous Wheat Experiment at Rothamsted. —□—, with ammonium-N added; -◆-, with water added.

metabolism. Some other research supports the idea that only NH_4^+ inhibits CH_4 oxidation. For example, Nesbit & Breitenbeck (1992) found that an addition of $\text{NH}_4\text{-N}$ to a culture of methanotrophs ($7 \mu\text{mol g}^{-1}$, *ca.* 340 kg N ha^{-1} to the topsoil to 23 cm) inhibited CH_4 uptake, but the same application of $\text{NO}_3\text{-N}$ increased CH_4 uptake. However, much larger applications of $\text{NO}_3\text{-N}$ (*ca.* $1700 \text{ kg N ha}^{-1}$) reduced CH_4 uptake over that of controls, and Prieme (1994) also found an inhibitory effect of NO_3^- , so the exclusive inhibitory effect of NH_4^+ is by no means proven.

We have evidence, too, that $\text{NH}_4\text{-N}$ has an immediate, ie short-term, effect as well as a long-term effect, and that simultaneous production and consumption of CH_4 can occur: figure 5 shows no net change in CH_4 concentration in soil to which only water was added, but net CH_4 production in soil receiving the same volume of NH_4^+ solution. This can only be explained if the treatment with water alone was producing CH_4 at the same rate as the 'water + NH_4 ' treatment; the difference in observed CH_4 production rates occurred because the treatment receiving only water was also consuming CH_4 at about the same rate as it was being produced. The short-term suppression of CH_4 oxidation by NH_4^+ is in contradiction to the observations of Hütsch *et al.* (1993). This may be because they injected a small volume of NH_4^+ into intact cores and then incubated them, whereas we sieved and thoroughly mixed the soil with the NH_4^+ .

The continued application of $35 \text{ t farmyard manure ha}^{-1} \text{ a}^{-1}$ appears to have had no effect on CH_4 uptake (figure 3). This is despite the fact that the manure contains more N ($240 \text{ kg N ha}^{-1} \text{ a}^{-1}$, much of which is in the NH_4^+ form) than that applied as fertilizer. Possible reasons for the lack of effect are: (i) the manured plot has a much better structure that permits methanotrophs to survive despite the inhibitory effects of $\text{NH}_4\text{-N}$; (ii) the much larger microbial biomass (Jenkinson & Powlson 1976) and, perhaps, nitrifier population (but see Meiklejohn 1969) on the manured plot rapidly removes any NH_4^+ ; (iii) a change in the ratio of nitrifiers to methanotrophs is less detrimental to CH_4 oxidation in

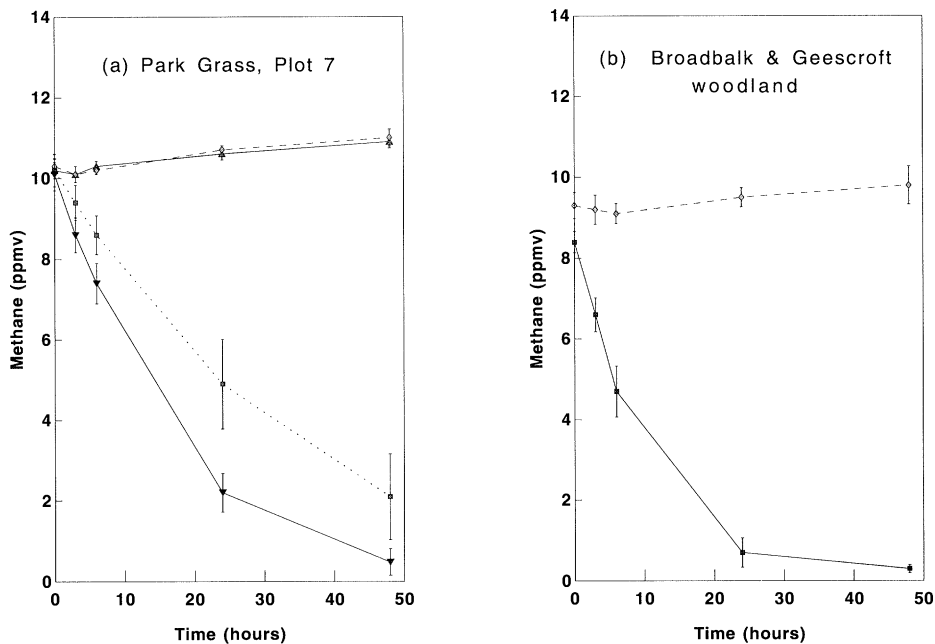


Figure 6. A comparison of the effects of soil pH on the oxidation of CH₄ by soil. Data from (a) the Park Grass Experiment at Rothamsted, and (b) the Broadbalk and Geescroft Wilderness (woodland) Experiments. Plot 7 of Park Grass receives no nitrogen fertilizer. (a) —▼—, Section A, pH 6.2; ···■···, Section B, pH 5.6; -◇-, Section C, pH 5.1; —△—, Section D, pH 4.8. (b) —■—, Broadbalk Wilderness, pH 7.5; -◇-, Geescroft Wilderness, pH 4.1.

this soil because of the much greater total bacterial population; (iv) greater O₂ demand by the farmyard manure treatment during wet weather results in short periods of CH₄ production which stimulates methanotrophs; (v) NH₄⁺ is released slowly from farmyard manure compared with the instantaneous addition of NH₄⁺ from inorganic fertilizer.

(c) Effect of soil pH

The Park Grass experiment permits the comparison of the effects of a stable soil pH (the experiment began in 1856) on CH₄ uptake by soil without the complicating effects of fertilizer or management. Figure 6a shows CH₄ uptake by soil taken from the four sections of Plot 7 of the experiment. This plot receives no N fertilizer and its sections are limed for target pH values of 7, 6 and 5, with Section 'd' unlimed and allowed to reach equilibrium with atmospheric inputs. Acidity has a marked effect on CH₄ oxidation. A reduction in soil pH from 6.2 to 5.6 reduces uptake rate considerably, and at pH values below 5.1 no CH₄ is oxidized. In fact there is a slow production of CH₄ from the soil.

Figure 6b shows the effect of acidity on CH₄ uptake in a woodland soil. The neutral soil under Broadbalk Wilderness absorbs CH₄ rapidly; its rate of uptake is the fastest measured in any of the sites at Rothamsted. By contrast, the soil under Geescroft Wilderness that has acidified to pH 4.1 in the surface through inputs of acid deposition, emits rather than absorbs CH₄.

The effects of acidity in these experiments could be indirect, caused by the build-up of organic material at the surface of the acid soils. The most acid sections of the Park Grass Experiment have a mat of undecomposed organic material, the thickness of which increases with the acidity, and Geescroft Wilderness has a surface layer of undecomposed leaf litter. This peat-like material could well be a net CH_4 producer. Alternatively, there may be a direct inhibiting effect of acidity on methanotrophs.

The inhibition of CH_4 uptake in acid soil is not always found. We have measured small but significant uptake rates of CH_4 in soil cores taken from a Norway spruce forest at pH 4.7 and there have been other reports of CH_4 uptake in acidic forest soils (Yavitt *et al.* 1993). We discuss the possible effects of soil acidity and their interaction with NH_4^+ below.

4. Discussion

The sink strength of soil for CH_4 is determined by the relative rates of production and oxidation. These are determined by the population and activity of three groups of bacteria: methanotrophs and nitrifiers, which can both mediate oxidation, and methanogens which are responsible for its formation. Methanotrophs are widely distributed in soil, and their numbers may be stimulated by large concentrations of CH_4 . Harriss *et al.* (1982) found that a swamp soil was particularly effective at oxidizing CH_4 after it had dried. Thus rapid CH_4 uptake may be the result of previous periods of CH_4 production.

There are at least four possible causes of the reductions in CH_4 uptake that we observed.

1. The enzymes that oxidize CH_4 , ammonia monooxygenase and methane monooxygenase, require a minimum (threshold) concentration of substrate to trigger activity. This concentration will vary between species but, generally, appears to be greater than ambient (Nesbit & Breitenbeck 1992). Thus the microbes in cultivated and therefore well-aerated soils, do not experience sufficient CH_4 production to trigger CH_4 oxidation. However, the greater oxygen demand of the farmyard manure plot on Broadbalk will increase the possibility of periods of CH_4 production during wet weather and thus of achieving sufficiently large CH_4 concentrations to trigger CH_4 oxidation.

2. Ammonia monooxygenase and methane monooxygenase can use either NH_4^+ or CH_4 as a substrate. Under certain circumstances, a prevalence of NH_4^+ may result in an adaptation of methanotrophs to favour oxidation of NH_4^+ .

3. Ammonium ions may suppress methanotrophs directly, or have an indirect effect through acidification of the rhizosphere, resulting from H^+ excretion by plant roots as NH_4^+ is taken up.

4. Physical, chemical and biological parameters define the ecological niche of individual species. Different land management practices may limit or prevent the formation of niches of one group, e.g. nitrifiers or methanotrophs.

The effect of NH_4^+ ions seems to be universal and without doubt. The effect of acidity varies, suggesting that it is not the acidity itself that affects methanotrophs but some other change that sometimes accompanies acidification; this could be the release of toxic ions such as aluminium. The effect of NH_4^+ could possibly be indirect, its uptake by plant roots leading to the excretion of H^+ ions and acidification of the rhizosphere. However, most of our measurements of CH_4

Table 2. Rates of oxidation of methane measured over a range of soils, land use types and countries

source	methane oxidation rate/(mg CH ₄ m ⁻² d ⁻¹)		
	arable	grassland	woodland
Rothamsted, U.K.	0–0.13	0.00–0.19	0.00–0.24
Mosier & Schimel (1991), U.S.A.	0.03–0.20	0.35–0.84	–
Dobbie & Smith (1994):			
U.K.	0.30–1.30	–	0.80–2.40
Denmark	0.08–0.20	–	0.40–0.70
Prieme (1994), Denmark	–	–	0.87–1.60

oxidation have been made 9–12 months after the last N application. It seems unlikely that the localized effect of H⁺ excretion will persist for this length of time. Also, for the Park Grass Experiment, most of the soil studied in the experiments is rhizosphere soil, the top 12 cm soil being full of grass roots. It seems unlikely that unmeasured acidification of the rhizosphere has occurred in this soil.

Table 2 compares rates of CH₄ oxidation measured in Rothamsted long-term experiments (this work and Hütsch *et al.* 1993, 1994) with rates measured over a range of countries, soils, land use types and managements, and using a range of sizes of cover boxes, micrometeorological techniques and tuneable diode lasers. The rates we observe are of the same order as those observed by other groups, but among the slowest. Our data would, therefore, seem representative of field rates. However, a true comparison of sites and factors requires standardized techniques and an understanding of the effects of factors that vary between sites, such as temperature and moisture. It is possible that rates of CH₄ oxidation are genuinely slower in south east England because of the long history of farming of agricultural land, and because of the large deposition of atmospheric N to woodland and forest. However, we may find faster rates of oxidation under certain conditions when we extend measurements through the year.

5. Conclusions

The way in which land is managed greatly influences the ability of soil to oxidize CH₄. Thus land management will have an indirect impact on the build-up of CH₄ in the atmosphere as well as a direct effect in some situations (wetlands). It would be wrong merely to blame intensive agriculture as is so often done. Methane uptake is inhibited by all forms of agriculture, even 'rough' grazing, and probably by forestry through increased atmospheric N inputs and, perhaps, acidification.

The research suggests that NH₄⁺ ions, and therefore NH₄-based fertilizers, but not NO₃-based fertilizers, inhibit CH₄ uptake by soil. The reasons for this are not yet clear, but involve the complex relationship between nitrifiers and methanotrophs, and possibly methanogens as well. Soil acidity is also an important factor in determining the rate of uptake of CH₄, but the relationship is not simple: some acid soils rapidly oxidize CH₄, others produce CH₄. However, the factors that af-

fect CH₄ uptake also affect the production and consumption of other greenhouse gases by soil. One should not consider one gas in isolation when developing policy on land use and greenhouse gases.

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Discussion

R. S. CLYMO (*School of Biological Sciences, QMC, London, U.K.*). In the experiment comparing autoclaved with non-autoclaved soil, no uptake of CH₄ by the autoclaved soil was observed. I find this surprising. Should not a small amount, perhaps 5–10%, of the CH₄ have diffused into the pore space of the autoclaved soil core?

K. W. T. GOULDING. We think that there may well have been some diffusion of CH₄ into the pore space of the autoclaved soil. However, after the CH₄ was introduced into the jars they were allowed to stand for 15 min to permit complete equilibration of the added CH₄ (Hürsch *et al.* 1993). Thus t_0 was not 0 but 15 min. The soil moisture content of the cores was 16–17% w/w, and so the soil was sufficiently permeable for the CH₄ to diffuse rapidly and unmeasured during this time. This would not have affected subsequent measurements of the rate of any uptake and oxidation of CH₄ by the organisms in the soil.

K. A. SMITH (*Soil Science Department, SAC, Edinburgh, U.K.*). The effect of land use change from natural forest to agricultural land may be greater than the effect of fertilizer addition, in reducing the soil sink for methane, judging by recent results obtained in Edinburgh and Copenhagen.

The rate of land use change, and the rate of change of fertilizer use is, surely, too slow to account for the sudden levelling off of the rate of increase of the concentration of methane in the atmosphere.

M. G. R. CANNELL (*Institute of Terrestrial Ecology, Edinburgh, U.K.*). Are changes in land use and management playing a significant role in the current slowing in the rate of increase in atmospheric methane concentrations?

K. W. T. GOULDING. Our results agree with Dr Smith's observations. Con-

version from unfertilized woodland to unfertilized arable land caused a greater reduction in the rate of CH_4 consumption than was caused by applying nitrogen fertilizer to the arable land. However, we must not forget that agriculture is an essential industry. For agricultural land, our data show the major reduction in the rate of CH_4 uptake to be associated with ammonium-fertilized and grazed agricultural land, not with cut or unfertilized grass or with organically manured land. We would also add that changes in land use have been occurring throughout the world for thousands of years. In the developed world, major changes in land use – e.g. from forest to agriculture – were made at least several centuries ago. These cannot account for the recent increases in atmospheric CH_4 . However, the past 50 years have seen significant increases in the area of arable land through the ploughing of permanent grassland and an intensification of agriculture, particularly the greatly increased use of fertilizers and large increases in stocking density of grazing animals. We cannot quantify the contribution that these changes would have made to CH_4 uptake by land, and thus to the increase in CH_4 in the atmosphere, but they must have been significant.

Regarding the recent decrease in the rate of increase of atmospheric CH_4 concentrations, we agree that changes in the use of land and the application of fertilizers and manures are unlikely to have been the cause. Rumours of repairs to leaking natural gas pipelines in the former Soviet Union, and the industrial recession generally, may be a more likely cause.