Influence of nitrogen fertilization on methane uptake in temperate forest soils

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METHANE, a long-lived gas (8–10 years residence time), is important in the chemistry of the atmosphere and the Earth's radiation balance[1–3]. The tropospheric abundance of CH_4 has been increasing by ~1.1% yr^{-1} over the past decade[4,5]. The cause of this increase may be due to either increases in global sources or decreases in global sinks[1,6,7]. Although considerable research has focused on measuring CH_4 emissions from major biological sources[7,8], much less is known about the magnitude of, and factors controlling, biological sinks of CH_4. The largest biological sinks for methane are microorganisms in aerobic soils[7]. Here we report a study of CH_4 uptake by aerobic temperate-forest soils. We measured CH_4 consumption rates (up to 3.17 mg CH_4–C m^{-2} day^{-1}) that were higher than reported previously. Globally, soils of temperate and boreal forests may consume up to 9.3 Tg CH_4–C yr^{-1}. We also found that the CH_4 uptake rates of these soils were decreased significantly by elevated soil moisture (14%) and nitrogen additions (33%), implying that nitrogen fertilization may reduce this CH_4 sink.

In the spring of 1988, nine (25 m^2) plots were established in each of two forest stands at the Harvard Forest in central Massachusetts: a 62-year-old red pine (*Pinus resinosa* Ait.) plantation and an ~80-year-old mixed black oak/red maple (*Quercus velutina* Lam./*Acer rubrum* L.) stand. Both stands were established on Gloucester-series soils following pasture abandonment in the early 1900s. Forest-floor soils in both stands are acidic, with pH values of 3.2 and 3.3 in the pine and hardwood stands, respectively. In each stand, three plots served as controls, three received a total of 37 kg N ha^{-1} yr^{-1} (low-N plots), and three received a total of 120 kg N ha^{-1} yr^{-1} (high-N plots). Fertilizer, added as NH_4NO_3, was applied in six equal additions from April to September. The total N applied to the low-N plots was four times the amount these forests normally receive in wet deposition[9,10], but was less than or equal to the amount received by forests in polluted areas of western and central Europe[11–13].

Measurements of CH_4 fluxes between soils and the atmosphere were made using 0.065-m^2, two-piece PVC-plastic chambers to cover the soil surface. The lower half (anchor) of the chamber was permanently implanted 1 cm into the forest floor in April 1988. One anchor was established in each plot. Flux measurements were conducted simultaneously at each of the nine plots in both stands, allowing us to examine both spatial and temporal variability among the various treatments. Air and soil (0–2.5 cm and 2.5–5.0 cm) temperatures were measured during each incubation. Soil moisture was analysed gravimetrically and available soil nitrogen was determined[14].

Methane fluxes were measured six times (every four hours) over a 24-hour period by sealing the chamber top to the anchor (total chamber volume ~5.4 l) for a 30-min incubation. Gas samples (20 ml) were withdrawn from the headspace at the onset of incubation and at 10-min intervals thereafter. Chamber tops were removed at the conclusion of each incubation. A Poropak-Q column and a flame-ionization-detection gas chromatograph were used to separate and analyse methane from the headspace gas samples. Fluxes were calculated by a linear fit of concentration data as a function of the incubation time.

Methane uptake rates were measured in both stands for all treatments from May through October 1988 and the mean uptake rates observed over the sampling period were 0.13 mg CH_4–C m^{-2} h^{-1} in the hardwood control plots and 0.11 mg CH_4–C m^{-2} h^{-1} in the pine control plots. The monthly uptake rates shown in Fig. 1 are the means of rates measured from the biweekly samplings.

Observations of CH_4 consumption in temperate and boreal forests are few, but our study suggests that aerobic soils in these systems are more important than considered previously. Our uptake rates are about ten times greater than measurements in another New England temperate-forest ecosystem, where rates of 0.18 mg CH_4–C m^{-2} d^{-1} were reported[15]. Consumption rates comparable to ours have been found in the Great Dismal Swamp forest only during drought conditions, when the soils became aerobic. Some evidence from the literature indicates that dry tropical-forest soils are also CH_4 sinks[15,17,18] with rates of ~0.18–0.37 mg CH_4–C m^{-2} d^{-1}.

The amount of atmospheric CH_4 consumed by soils of tropical, temperate and boreal forests was estimated using rates from this study and ref. 15 for temperate and boreal forests and rates from refs 17 and 18 for tropical forests. The uptake rates were assigned functional periods of 365, 200 and 120 days in tropical, temperate and boreal systems, respectively, corresponding to the approximate number of frost-free days in these systems. Current estimates (1980) of the areas of tropical-, temperate- and boreal-forest ecozones were developed from ref. 19 and used with the above uptake rates to calculate the magnitude of the individual ecozone sinks.

A new finding based on this analysis is that temperate and boreal forests may play a much larger role than tropical forests

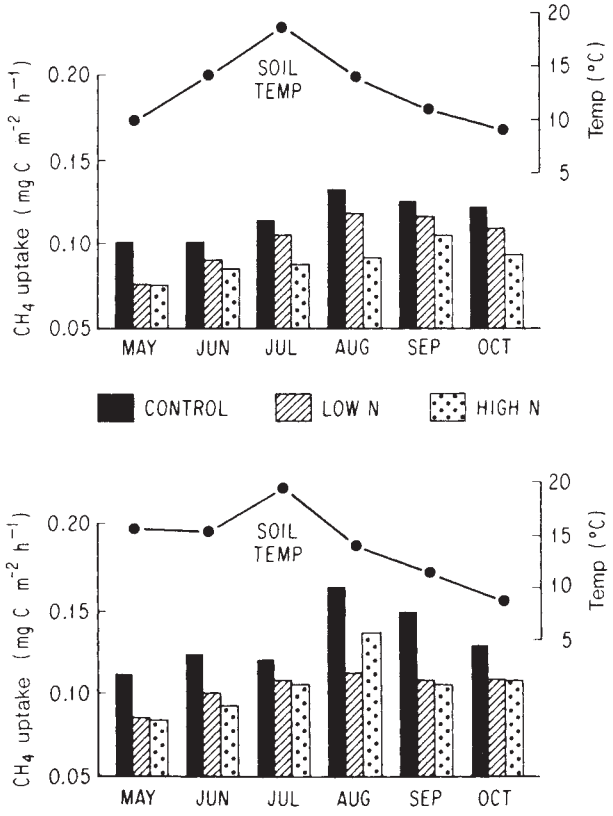

FIG. 1 Mean monthly CH_4 uptake and soil temperature (0–2.5 cm) for pine (top) and hardwood (bottom) stands at Harvard Forest. Low-nitrogen-fertilized plots received 37 kg N ha^{-1} yr^{-1} and high-nitrogen-fertilized plots received 120 kg N ha^{-1} yr^{-1}.

in the consumption of atmospheric CH_4 (Table 1). We estimate that temperate and boreal forests annually consume up to 9.3 Tg CH_4-C (Tg = 10^{12} g), an amount 3.7 times larger than the 2.5 Tg CH_4-C consumed by tropical forests. Our estimate for tropical forests is less than the 4 Tg CH_4-C yr^{-1} reported in refs 17 and 18 because we used a smaller ecozone area (18.5×10^{12} m^2) in the calculation. There is considerable uncertainty in estimating the magnitude of the CH_4 sink for these systems, however, because of the limited number of measurements in tropical forests, the lower reported rates for temperate forests[15] and the difficulty in assessing the effects of soil temperature, moisture and nitrogen status on the consumption rates in all the systems.

Methane uptake showed no correlation with the soil temperature over the sampling period May to October (Fig. 1). Linear regression analysis of consumption rates with soil temperature showed no correlations: pine $r^2 = -0.005$; hardwood $r^2 = 0.022$.

We observed that both the moisture conditions and the nitrogen status of the sites affected the magnitude of the sink. The effect of soil moisture conditions on CH_4 uptake is demonstrated by comparing the 11 July rates to the 25 July rates (Fig. 2). Lower uptake rates (paired t-tests $\alpha < 0.001$) were measured in all plots during the 25 July sampling when soil moisture was increased significantly (analysis of variance (ANOVA) $P < 0.01$). This is consistent with other observations[15,16]. The mechanism responsible for effects of moisture on CH_4 uptake has been discussed[15]. Briefly, the organisms that oxidize methane include methanotrophs[20,21] and also nitrifiers[22]. Both methane oxidizers and methane-producing bacteria (methanogens) are thought to be widespread in soils. In fact, they often exist in the same areas. Methanogens are obligate anaerobes, occupying deeper, wetter soil horizons, whereas the methane oxidizers (obligate aerobes) occupy surface, aerobic horizons. Changes in soil moisture result in changes in the net balance of methane production and consumption with wetter conditions shifting the balance towards production and/or reduced gas exchange with the atmosphere.

An important and previously unreported finding of this study is that increased soil nitrogen content resulted in lower CH_4 uptake rates (Fig. 1). After only four months of fertilization, methane consumption in the fertilized plots of both stands was reduced by up to 15% in the hardwood stand and 24% in the pine stand. Analysis of the consumption rates after six months of fertilization indicates that the difference becomes more pronounced—the consumption rates were reduced by ~33% in the high-N plots relative to the controls. We found that, over the six-month sampling period, uptake rates in the fertilized plots of both stands were reduced significantly compared to the control plots (ANOVA $P < 0.005$). The long-term trajectory of this relationship, however, is not well known.

TABLE 1 Estimates of CH_4 uptake by tropical, temperate and boreal forests

Ecozones	Area (10^{12} m^2)	CH_4 uptake range (g C $\times 10^{-4}$ m^{-2} d^{-1})	Tg* C yr^{-1} (min. -max.)
Tropical forests			
Tropical moist	10.83	1.87-3.75	0.74-1.48
Tropical seasonal	7.66	1.87-3.75	0.52-1.05
		Total tropical forests	1.26-2.53
Temperate & boreal forests			
Temperate evergreen	4.88	1.87-27.5	0.18-2.68
Temperate deciduous	4.41	1.87-31.7	0.16-2.80
Boreal	11.60	1.87-27.5	0.26-3.83
		Total temperate and boreal forests	0.60-9.31

* Tg = 10^{12} g.

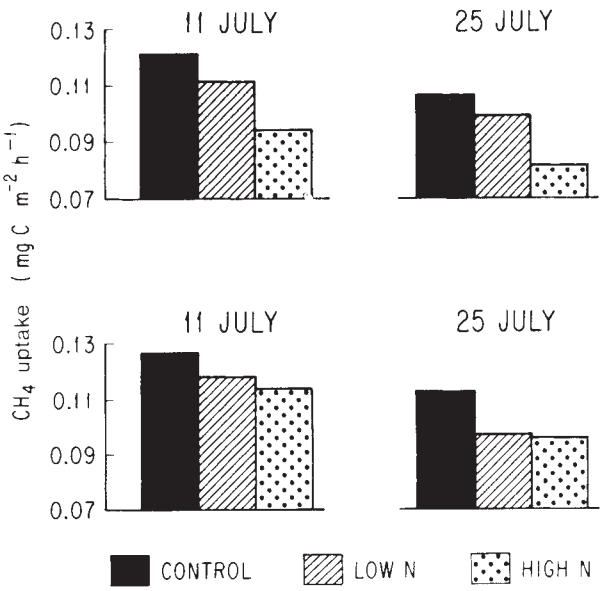

FIG. 2 Methane uptake by control and nitrogen-fertilized soils of pine and hardwood forests (top and bottom, respectively) at Harvard Forest, Massachusetts. Measurements made before (11 July 1988) and immediately after (25 July 1988) a 6-cm rain event. Soil temperatures (0-2.5 cm) ranged from 20.1 to 17.5 °C in the pine stand and 20.6 to 18.2 °C in the hardwood stand on 11 July and 25 July, respectively.

The mechanism responsible for the effect of nitrogen on CH_4 uptake is complex because it involves both methanotrophs and nitrifiers. Laboratory studies indicate that oxidation of CH_4 by a variety of methanotrophs is competitively inhibited by nitrogen, especially ammonium[20,23-25].

Nitrifying bacteria, including the dominant soil ammonium-oxidizing bacterium *Nitrosomonas europaea*, have the ability to oxidize CH_4, even at low atmospheric concentrations[26,27]. Further, laboratory cultures using *N. europaea* showed reduced CH_4 oxidation activity[26] at ammonium concentrations (15 p.p.m.) equivalent to or higher than those present in soils at our sites. The results of these laboratory studies are consistent with our field observations and suggest that CH_4 oxidation may be suppressed in systems that receive high inputs of nitrogen, such as agroecosystems and acid-rain-affected temperate and boreal forests. The identification of a link between nitrogen inputs and CH_4 uptake rates is especially important in understanding the role that aerobic soils play in the global atmospheric methane cycle. The global-scale consequences of a reduction in the CH_4 sink with nitrogen fertilization are uncertain because of the lack of data on the generality of the methane-nitrogen interaction. Further measurements in agroecosystems, pastures and in systems receiving high nitrogen inputs from deposition are necessary to clarify the nitrogen-methane interaction before extrapolation to a global basis. □

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Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems

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SEDIMENTS of aquatic systems play a critical part in controlling phosphorus loading to the water column[1]. Because P loading is an important determinant of productivity in aquatic systems, there has been keen interest in variables that influence P release from sediments. In disagreement with present theories[1,2] our data from 23 different aquatic systems indicate that sulphate concentration of waters is an extremely important variable controlling P release from sediments. The increased P release from sediments at higher sulphate concentrations may help to explain why primary production in freshwater systems (with relatively low sulphate concentrations) tends to be P limited[3], whereas in many saline systems (with high sulphate concentrations) production is often P sufficient[4]. Further, our results indicate that anthropogenically induced changes from atmospheric S inputs could, over time, alter the P cycle of aquatic systems.

To examine the controls of P release from sediments, without the possible artefacts of sediment core studies, we used an *in situ* geochemical approach[5–8] (Fig. 1, legend). Briefly, sediment P immobilization is inferred when measured P release is less than that expected from decomposition reactions. Particles reaching bottom sediments show P:C ratios that vary between 3 and 10 mmol per mol C (refs 9 and 10); when the ratio of dissolved P to dissolved inorganic carbon (DIC) release is equal to this value, the decomposition reactions alone may be adequate to explain P release from sediments. Release ratios below 3 mmol P per mol C indicate that sediment uptake is significant, whereas ratios above this value indicate that there is P release from sediments that was taken up previously by sorption, mineral formation or bacterial uptake[7,8]. The advantage of this approach is that it allows us to distinguish between two very different cases: (1) low sediment P release that is due to low availability of degradable organic materials (hence low metabolism); and (2) low sediment P release that is due to the fact that sediments have the capacity to take up P and prevent its release to overlying waters. That is, low absolute P release is not necessarily due to the capacity of sediments to immobilize P (case 1). The ratio of P release to inorganic carbon release (relative P release; RPR) is a far better indicator of the capacity of sediments to immobilize P.

Previous reports suggest that oxygen, through its control on the iron cycle, is the critical variable controlling P immobilization by sediments of aquatic systems[1,2]. The oxygen-control model states that under oxic conditions a micro-layer rich in iron oxide traps P, preventing its release into overlying waters, whereas under anoxic conditions these iron oxides are reduced chemically and previously bound P is released into solution[2]. If this model represents the dominant processes occurring in sediments, RPR would be consistently low (<3–10 mmol P per mol C) under oxic conditions and high (>3–10 mmol P mol C) under anoxic conditions[7,8]. Our results do not show any such consistent pattern. In the 23 systems examined, we found a large variation in RPR under both oxic (0.1–10 mmol P per mol C) and anoxic conditions (0.1–35 mmol P per mol C). The difference in RPR between oxic and anoxic conditions is, therefore, small in comparison with the large variation in RPR among systems.

Clearly, some variable(s) other than oxygen must have a major influence on RPR. Our preliminary data and previous reports indicate that such variable(s) are related strongly to the ionic strength of waters[5–8,11]. We therefore tested several variables thought to influence sediment P release that could be correlated with ionic strength (Table 1)[12–18]. Of these variables, sulphate concentration of surface waters was the only variable with predictive significance ($P < 0.01$) under both oxic and anoxic conditions (Table 1).

Our data show that RPR and sulphate concentration of waters are related and that a relationship exists independent of whether bottom waters are oxic or anoxic (Fig. 1). Under oxic conditions RPR increased monotonically from 0.1 to 10 mmol P per mol C over the entire range of sulphate values tested (10–30,000 μM). Anoxic RPR showed a similar pattern to oxic RPR but had a steeper initial slope and reached maximum values at sulphate concentrations of only 100–200 μM (Fig. 1). Considering the entire data set for both oxic and anoxic conditions, three patterns emerge: Group I, brackish and saline systems, with high sulphate concentrations (~3,000–30,000 μM), have high RPR values (3–10 mmol P per mol C) under both oxic and anoxic conditions. In these systems, even under oxic conditions, immobilization of sediment P is generally not large; Group II, fresh water systems with low sulphate concentrations (below about 60 μM) generally have low RPR values (less than 1 mmol P per mol C) under both oxic and anoxic conditions. In these systems, P immobilization in sediment evidently continues to be important even after bottom waters become anoxic; Group III, fresh water systems of intermediate sulphate concentration (~100–300 μM) generally have fairly low RPR under oxic conditions but tend to have very high RPR when bottom waters become anoxic. These are the only systems that correspond to the classic pattern[2] of P immobilization under oxic conditions and P release under anoxic conditions.

TABLE 1 Spearman rank-correlation coefficients between relative P release (RPR) and several variables that might be responsible for controlling P release

	Conductivity	SO_4^{2-}	pH	P:C	Sediment Fe	Chlorophyll
Oxic	0.75*	0.85*	0.57*	0.39	0.12	0.19
Anoxic	0.44	0.69*	0.41	0.34	0.20	0.38

'Oxic' refers to RPR when water above the sediments is oxygenated; 'Anoxic' refers to RPR when overlying waters are anoxic.

* Significance at the 99% level. P:C is the phosphorus-to-carbon ratio of suspended particles (seston) in surface waters. This ratio may be a reasonably good indicator of P:C ratios for freshly sedimented particles[9]. Sediment Fe is the iron content of upper 5–10 cm of the sediments. Chlorophyll represents mean surface-water value of chlorophyll *a* during the summer season. Twenty-three aquatic systems are included in this analysis; for data sources see Fig. 1. The range of values represented from these systems are: conductivity, 18–40,000 μS cm^{-1}; sulphate, 11–27,000 μM; pH, 5.5–8.5 (H^+, 0.0032–3.2 μM); sediment Fe, 0.9–4.5% dry weight; chlorophyll 1.5–60 μg l^{-1}.