FINAL REPORT

Methane Production and Consumption in Grassland and Boreal Ecosystems

NAGW-1828

Principal Investigators: David S. Schimel
Ingrid C. Burke
Carol Johnston
John Pastor

OVERVIEW

The objectives of the this project were to develop a mechanistic understanding of methane production and oxidation suitable for incorporation into spatially explicit models for spatial extrapolation. Field studies were undertaken in Minnesota, Canada and Colorado to explore the process controls over the two microbial mediated methane transformation in a range of environments. Field measurements were done in conjunction with ongoing studies in Canada (the Canadian Northern Wetlands Projects: NOWES) and in Colorado (The Shortgrass Steppe Long Term Ecological Research Project: LTER). One of the central hypotheses of the proposal was that methane production should be substrate limited, as well as being controlled by physical variables influencing microbial activity (temperature, oxidation status, pH). Laboratory studies of peats from Canada and Minnesota (Northern and Southern Boreal) were conducted with amendments of a methanogenic substrate, at multiple temperatures and at multiple pHs (the latter by titrating samples). The studies showed control by substrate, pH and temperature, in order in anaerobic samples. Field and laboratory manipulations of natural plant litter, rather than an acetogenic substrate, showed similarly large effects. The studies concluded that substrate is an important control over methanogenesis, that substrate availability in the field is closely coupled to the chemistry of the dominant vegetation influencing its decomposition rate, that most methane is produced from recent plant litter and that landscape changes in pH are an important control, highly correlated with vegetation.

The results are published in the Journal of Geophysical Research-Atmospheres (Valentine D., E.A. Holland and D.S. Schimel 1993. Ecosystem and physiological controls over methane production in northern wetlands). The paper is attached.

Field studies on methane oxidation in Colorado utilized landscape gradients and existing field experiments at the LTER. Studies took advantage of long-term measurements and were complementary to studies initiated in the early 1980s. Measurements were made of soil inorganic N, methane oxidation in soils, and the production of nitrous oxide. Key results were that: (1) land use change dramatically lowered methane oxidation, (2) rates of methane oxidation and nitrous oxide production were negatively correlated, (3) increasing soil N tended to reduce rates of methane oxidation and, (4) preliminary evidence suggested that methane oxidation was principally limited by the diffusion rate of methane into soils, and secondarily limited by soil nitrogen. The effects of land use change (grassland to cropland) may act through these or other mechanisms. As the principal zone of methane oxidation appears to be about 10-30 cm deep in soils, in contrast to most microbial processes which occur within the top 10 cm of soils, disruption of this layer by tillage is implicated.

Results from this study were published in Nature (Mosier et al. 1991. Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands. Nature 350:330-332), and Chemosphere (Ojima et al. 1993. Effect of land use change on methane oxidation in temperate forest and grassland soils. Chemosphere 26:675-685). These papers are likewise attached.

Ecosystem and physiological controls over methane production in northern wetlands

David W. Valentine

Natural Resource Ecology Laboratory, Colorado State University, Boulder, Colorado

Elisabeth A. Holland and David S. Schimel[1]

National Center for Atmospheric Research, Boulder, Colorado

Peat chemistry appears to exert primary control over methane production rates in the Canadian Northern Wetlands Study (NOWES) area. We determined laboratory methane production rate potentials in anaerobic slurries of samples collected from a transect of sites through the NOWES study area. We related methane production rates to indicators of resistance to microbial decay (peat C:N and lignin:N ratios) and experimentally manipulated substrate availability for methanogenesis using ethanol (EtOH) and plant litter. We also determined responses of methane production to pH and temperature. Methane production potentials declined along the gradient of sites from high rates in the coastal fens to low rates in the interior bogs and were generally highest in surface layers. Strong relationships between CH_4 production potentials and peat chemistry suggested that methanogenesis was limited by fermentation rates. Methane production at ambient pH responded strongly to substrate additions in the circumneutral fens with narrow lignin:N and C:N ratios ($\partial CH_4/\partial EtOH$ = 0.9–2.3mg g^{-1}) and weakly in the acidic bogs with wide C:N and lignin:N ratios ($\partial CH_4/\partial EtOH$ = -0.04–0.02 mg g^{-1}). Observed Q_{10} values ranged from 1.7 to 4.7 and generally increased with increasing substrate availability, suggesting that fermentation rates were limiting. Titration experiments generally demonstrated inhibition of methanogenesis by low pH. Our results suggest that the low rates of methane emission observed in interior bogs during NOWES likely resulted from pH and substrate quality limitation of the fermentation step in methane production and thus reflect intrinsically low methane production potentials. Low methane emission rates observed during NOWES will likely be observed in other northern wetland regions with similar vegetation chemistry.

INTRODUCTION

Uncertainty in the global methane budget arises from the scarcity of source measurements, especially integrated over large areas [*Aselmann and Crutzen*, 1989; *Fung et al.*, 1991], from uncertainty about the atmospheric destruction rate [*Vaghjiani and Ravishankara* , 1991] and from new information suggesting a larger soil sink [*Steudler et al.*, 1989; *Mosier et al.*, 1991). Three-dimensional global analyses of atmospheric methane concentrations [*Fung et al.*, 1991] and isotopic composition [*Tyler*, 1986, 1989, 1991; *Quay et al.*, 1991] are the most powerful techniques for analyzing current sources and sinks, and provide hints as to controls over emissions. These analyses and other studies have suggested an important but highly uncertain methane source from northern wetlands. The Canadian Northern Wetlands Study (NOWES) and two American Atmospheric Boundary Layer Experiments (ABLE 3A and 3B) constrain bounds on that uncertainty.

In addition, no predictive or diagnostic models of methane biogeochemistry now exist for any ecosystem type. Process models of microbial transformations and relevant transport processes have not been widely used in methane biogeochemistry

but would complement global analyses by linking edaphic, biological, and climatic controls to flux rates and provide a mechanistic basis both for spatial analysis and for projection of future changes. Process models, when coupled with data describing paleowetland extent, also provide a basis for understanding past changes in methane fluxes.

Methane production is carried out by methanogenic bacteria, which are obligate anaerobes capable of using a limited number of relatively simple substrates supplied by fermentation processes. Several reviews of the mechanisms of methanogenesis recently have been compiled [*Oremland*, 1988; *Conrad*, 1989; *Knowles*, 1993]. *Conrad* [1989] enumerated the controls over methanogenesis as (1) substrate availability, (2) temperature, (3) pH, and (4) competitive electron acceptors. He argued that population size of methanogens was not likely a major control over methane production rate. While the controls over methane production at the microbial level are reasonably well known, the relative quantitative importance of the different factors is not well known, especially under field conditions. In this paper we analyze the controls over methane production from a series of sites in northern wetland ecosystems and present results from experimental manipulations of several factors. The sites chosen contrasted in plant species composition, productivity, hydrology, and pH [*Klinger et al.*, this issue].

Controls over methane production fall into two classes that must be considered together in predictive models of methane production: (1) controls over substrate availability (i.e., fermentation rate as affected by temperature, litter input, and litter decomposition rate); and (2) physiological controls over methanogenic activity (pH and redox potential) from a given supply rate of substrate.

[1] Also at Natural Resource Ecology Laboratory, Colorado State University, Fort Collins.

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The principal substrates for methanogenesis are CO_2+H_2 and acetate [Oremland, 1988; Conrad, 1989; Knowles, 1993]. Substrate abundance is constrained by the slowest link in a chain of events starting with inputs of detrital organic matter and including several decomposition and fermentation steps resulting in methanogenic substrates. While many studies identify the importance of substrate limitation as a control over methane production [Aselmann and Crutzen, 1989; Conrad, 1989], few have systematically analyzed its importance [Yavitt and Lang, 1990]. If most methane is produced largely from recent organic matter, as ^{14}C results suggest [Jeris and McCarty, 1965; Wahlen et al., 1987], then methane production should ultimately be closely coupled to terrestrial primary production and decomposition rates. NOWES provides a foundation for modeling the linkage of methane production to ecosystem change (through changing plant production and chemistry) as well as to climate change.

Temperature directly affects methanogenesis rates as well as decomposition and fermentation rates, but Westermann et al. [1989] reported that the effect of increasing temperature on the rate of methane production is largely offset by a corresponding increase in K_m (decreased substrate affinity) of methanogenic enzyme systems. Thus the observed effect of temperature will likely be manifested only through increased availability of methanogenic substrate as long as readily decomposable reduced carbon compounds are available. These interactions are important because they could lead to unexpected results, e.g., temperature increases could lead to increased instantaneous rates of methanogenesis via enhanced fermentation, but these higher rates could outstrip supply rates of readily fermentable compounds and ultimately lead to reduced methane production rates.

Appropriate redox potentials for methanogenesis require saturated or nearly saturated soil conditions and the absence of competing, more electronegative electron acceptors (NO_3^-, SO_4^{2-}, Fe^{3+}). Water table fluctuations influence not only the thickness of the aerobic zone in which CH_4 oxidation can occur but also the portion of the soil or peat profile in which methanogenesis is possible. Conversely, redox potential also may limit substrate production because very low redox potentials tend to retard decomposition. Since organic matter chemistry varies with depth in most profiles, water table depth will influence both the quantity of organic matter for methanogens and the maximum rate at which that organic matter may be processed. We considered this interaction only to the extent that we surveyed methane production potentials by depth and amended samples from the upper two peat depths.

In the field, methane emission is influenced by production but is modulated by transmission to the atmosphere which occurs via diffusion, solution transport, bubbles or vascular transport in plants [Keller et al., 1986; Conrad, 1989; Chanton and Dacey, 1991; Fechner and Hemond, 1992]. Transport, oxidation and water table depth were considered by other investigators in NOWES [Klinger et al., this issue; Roulet et al., this issue].

Detailed process studies of the sort described in this paper are an important complement to field experiments not only because they aid in model development but also because they aid in interpreting field observations. Methane flux rates observed in NOWES were much lower than expected [Roulet et al., this issue] and our process studies help explain why. Our studies help establish whether fluxes were low because of intrinsically low rates of methane production (determined from maximal laboratory methane production rates). This will be of importance in extrapolating NOWES results to other regions.

METHODS

Study Site

The four study sites were located in the Hudson Bay lowlands along a 95-km transect southwest of Moosonee, Ontario, Canada (Figure 1). The region has been gradually exposed by the receding Hudson Bay during isostatic rebound since the last glacial maximum [Webber et al., 1970], giving an age sequence along the transect extending back approximately 4000 years [Klinger et al., this issue]. From youngest (closest to James Bay) to oldest the four sites studied were the coastal fen, interior fen, Carling Lake, and Kinosheo Lake. The older two sites were ombrotrophic Sphagnum bogs while the younger two were sedge-dominated minerotrophic fens.

The vegetation and peat characteristics of the sites are described in detail by Klinger et al. [this issue] so we present only a summary here (Table 1). The relative covers of sedges, non-Sphagnum bryophytes, deciduous shrubs, and pteridophytes are highest in the interior fen, decreasing slightly in the coastal fen and are very low or absent in both of the bog sites. Conversely, the relative covers of sphagnum, ericaceous shrubs, and lichens are much higher in the bog sites (especially Kinosheo Lake) than in the fen sites. The covers of forbs and coniferous shrubs and trees were fairly constant across sites. Peat depth increased approximately monotonically from about 0.7 m in the coastal fen site to about 2.9 m at Kinosheo Lake.

Procedures

Intact cores were taken during July 1990 using a 10.2-cm^2 box corer from each of the four sites. Four cores were taken from the coastal fen site, three from the interior fen, and two each from Carling Lake and Kinosheo Lake. In addition, we sampled the top 1 m of peat from the side of a peat pit in 0.1-m increments at both bog sites. All samples were vacuum sealed in 0.13-mm-thick
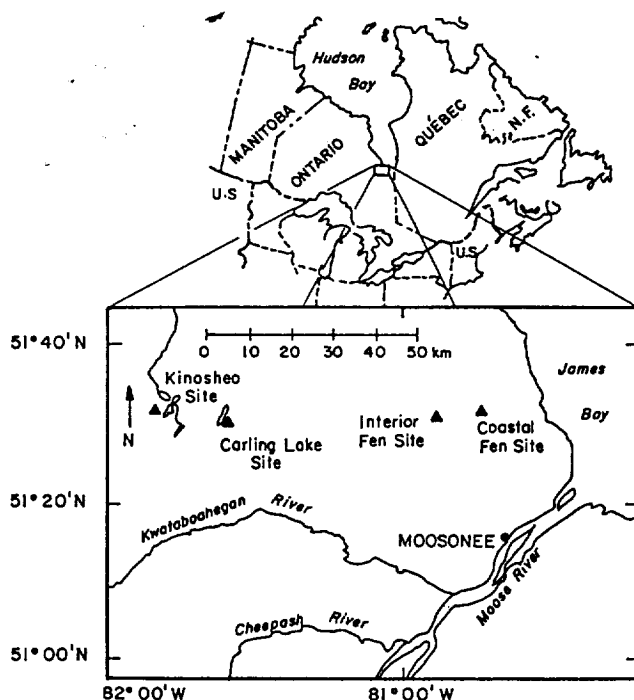

Fig. 1. Location of study sites. The two end-point sites; coastal fen and Kinosheo Lake were used for detailed methane process studies.

TABLE 1. Summary of Site Characteristics for Sites Used in Regional Survey of Methane Production Potentials

Site	Latitude and Longitude	Distance From Coast, (km)	Water Table Depth,* (m)	Soil water pH*	Peat Depth,* (m)	Basal Peat Age,* (y)
Coastal fen	51°28.2' N 80°37' W	18	0.14	6.86	0.71	1090
Interior fen	51°30.7' N 80°52.8' W	33	0.35	6.48	1.03	1960
Carling Lake	51°29.8' N 81°45.7' W	99	0.17	4.11	2.48	4110
Kinosheo Lake	51°33' N 81°49.5' W	113	0.26	4.15	2.56	4110

*From *Klinger et al.* [this issue].

polyethylene bags, then kept at 4°C until analysis. The peat horizons were classified using the von Post scale of peat humification [*Bélanger et al.,* 1988] (Table 2). Moisture content was determined gravimetrically by drying to constant weight at 70°C. Total carbon and nitrogen concentrations were determined on dried and ground samples at 10 cm increments on a Carlo Erba NA 1500 CN analyzer. Lignin and cellulose contents were determined at 10-cm intervals using the Goering-Van Soest procedure [*Goering and Van Soest,* 1970; *Kirk and Obst,* 1988].

Methane production potentials in slurried incubations were assessed for all cores at 10-cm intervals at 20°C. Incubations were performed in slurries of 20 g (fresh weight) subsamples of well-mixed peat. The peat and enough deionized water (to 100 mL) were added to a 250-mL Erlenmeyer flask under a nitrogen atmosphere. The flasks were stoppered with silicone stoppers fitted with a stopcock, septum, and in a subset of replicates, redox (platinum) and pH electrodes. These allowed monitoring of redox potentials to ensure that conditions sufficiently reduced for methanogenesis prevailed in the flasks. Slurries initially were sparged with ultrahigh pure (UHP) N_2 for 2 minutes and then continuously shaken on an orbital shaker in refrigerated incubators throughout the incubation period. Samples were subsequently allowed to preincubate for 2 weeks before measurement to allow exhaustion of initially high volatile fatty acid levels, after which incubations lasted 4-6 weeks. During the incubation period, redox potentials remained very low (-300 mV) and pH generally changed less than 0.2 units.

Flask headspaces were sampled weekly during the incubation period. Before sampling, each flask was sparged with UHP He by vigorously bubbling the slurry for 2 minutes. This procedure reduces but does not eliminate degassing problems during the assay period [*Kiene and Capone,* 1985], minimizes problems of pressure variation among flasks due to CO_2 and CH_4 accumulation, establishes similar bicarbonate equilibria among sampling periods, and lessens concentration gradients driving diffusive losses across the silicone stoppers during the assay period. The assay period following sparging varied between 0.25 and 2 hours, depending on rates of CH_4 production. At the end of the assay period we used 35-mL polypropylene syringes fitted with nylon stopcocks to sample 12 mL of the headspace. If two samples were required, as when CO_2 production rates were more rapid than CH_4 rates, then 12 mL of UHP N_2 was added as a makeup gas following the first sampling.

Gas samples were analyzed within 3 hours following sampling on a Shimadzu GC-8 gas chromatograph fitted with a flame ionization detector (FID) for CH_4 and a Carle Instruments thermal conductivity detector (TCD) for CO_2. We used a 3.175-mm OD Ni column packed with HayeSep D in an 60°C oven with a carrier gas (He) flow rate of 35 cm^3 min^{-1}. The FID was kept at 200°C and the TCD at 60°C. Concentrations were corrected for trace quantities of CH_4 (generally 0.2 parts per million by volume (ppmv)) contained in the UHP N_2 used for the headspace.

During the incubation period, production potentials generally increased for the first several weeks, after which they declined modestly in most slurries. No initial rapid methane production rates were observed, suggesting that disturbance-enhanced concentrations of volatile fatty acids were not reflected in our data.

We also assessed process controls over CH_4 production in the top two von Post horizons of Coastal fen and Kinosheo Lake peats. Temperature effects were analyzed on slurries at 10°C and 20°C. Degree of substrate limitation was assessed by adding 1.64 or 8.22 mmol ethanol (39.4 mg or 197.3 mg C equivalent, respectively) as an acetate and hydrogen source [*Bryant et al.* 1967; *Large,* 1983; *Svensson,* 1984]. Although ethanol cannot be used directly by methanogens, it is easily converted to hydrogen and acetate by other organisms [*Bryant et al.,* 1967; *Svensson,* 1984]. For our experiments, ethanol also presented two advantages over acetate: first, protonated acetic acid is toxic to microbial populations, implying that only very small amounts of acetate could be added at low pH; second, ethanol would provide a prolonged supply of substrate during the incubation. Because

TABLE 2. Depths and Von Post Indices (VPI) for Peats Used in Amended Incubations

Peat Horizon	Coastal Fen		Kinosheo Lake	
	Von Post Index	Depth, cm	Von Post Index	Depth, cm
Surface	2-3	0-10.5	1	12
Subsurface	3-5	10.5-19	2-3	12-15.5

Peats were sampled by Von Post Index, and the top two uniform VPI horizons were used in experimental studies. Full descriptions of peat profiles are in the work of *Klinger et al.* [this issue]. Chemical characteristics of peat profiles are shown in Table 3.

acetic acid is a weak acid, moreover, a significant fraction of added acetate salts would protonate and raise pH in the low pH slurries. Substrate limitation to fermenting populations was also assessed by adding 0.5 g of dried and ground plant litter samples collected on site. Effects of pH on production potentials were assessed by lowering the pH of coastal fen slurries to ~5.5 or ~4 with H_3PO_4 and raising the pH of Kinosheo Lake slurries to ~5.5 or ~7 with KOH. We also tested the response of Kinosheo Lake slurries to direct H_2 enhancements. Additions of 10 mL of H_2 brought headspace partial pressures to 0.05 atm., but no CH_4 production response occurred (12.1 versus 19.2 and 13.4 versus 8.3 µg/g for surface and subsurface layers, respectively). Because of the lack of response we dropped H_2 treatments thereafter in favor of ethanol amendments.

Statistical significance of experimental results were determined using analysis of variance.

RESULTS AND DISCUSSION

Landscape Patterns in CH_4 and CO_2 Production

Methane production potentials were highest in Coastal fen slurries and dropped rapidly with distance inland to the bogs at Carling Lake and Kinosheo Lake (p<0.01, Figure 2). This trend corresponded to patterns of soil solution pH (highest at the coast), NPP (highest at the coast), and plant community composition (sedges and bryophytes in the coastal and interior fen sites, Sphagnum moss, and ericaceous shrubs in the inland bog sites)
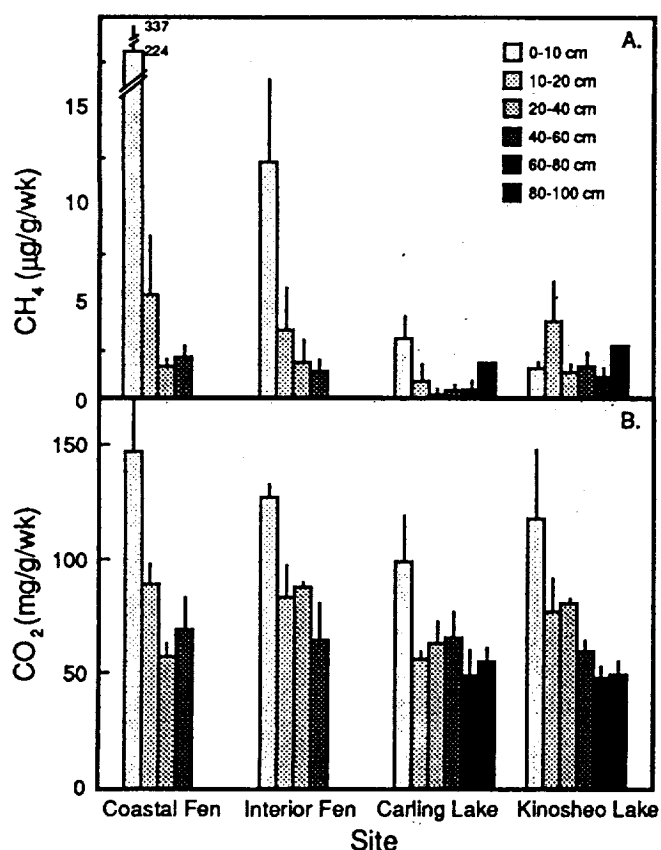

Fig. 2. (a) Methane and (b) CO_2 production potentials under unamended conditions for all sites along the regional transect and as a function of depth. Error bars are standard errors of the mean (n=4 for CF, 2 for IF, 3 for CL, 3 for KL).

[Klinger et al., this issue]. The trend also agreed with in situ measurements of CH_4 emissions, except for anomalously low emissions from the interior fen [Klinger et al., this issue] compared to the production potentials (Figure 2). This discrepancy probably resulted from CH_4 oxidation due to the low water table and deep aerobic zone (Table 1).

In the coastal and interior fens, methane production potentials were highest in the surface peats and declined with depth to a plateau below 0.2 m (p<0.0.05, Figure 2). The depth pattern was less clear in the bog sites; low CH_4 production potentials occurred at all depths. Surface peats from the bog sites, Carling Lake, and Kinosheo Lake had slightly higher production potentials, however, than did intermediate depths. Similar depth patterns of CH_4 production have also been observed in spruce-peatlands in west central Alberta [Hogg et al., 1992].

Rates of CO_2 production exhibited the same spatial pattern as methane, supporting the argument that methane production is linked to carbon substrate available for decomposition (see below) (Figure 2b). Decreases in surface peat CO_2 production potentials from coastal to inland sites were less marked than for methane, though significant. Subsurface peats had similar and low rates along the entire transect, as with methane. More methane was produced per unit CO_2 produced in the coastal than in the inland sites (p<0.005), perhaps because of more favorable physiological conditions for methanogen activity and population growth in the neutral coastal peats.

Process Controls

Organic matter quantity and quality. Methane production potentials along the transect and with depth corresponded to changes in peat chemistry and its influence on decomposition and fermentation rates. Rates of methanogenesis depend on rates of substrate supply from fermentation, and rates of fermentation depend on the amount and decomposability of organic matter [Conrad 1989; Sass et al., 1990, 1991; Svensson, 1976, 1980; Svensson and Rosswall, 1980; Taylor et al., 1991]. Decomposition of peat is slow under unperturbed conditions, and substrate for heterotrophic processes is usually limiting [Svensson, 1980]. Several investigators have found that methane production or emission was highest at sites where NPP, plant density, or biomass was highest [Klinger et al., this issue; Morrissey and Livingston, 1992; Svensson, 1976, 1980; Whiting and Chanton, 1992]. The role of NPP is clearly through the annual supply of relatively labile fractions of plant debris, though vascular transport plays a role at some sites as well.

The decomposability of the litter produced influences rates of decomposition, fermentation, and methanogensis. The chemical availability of carbon for decomposition is usually quantified by two indices of decomposability: C:N and lignin:N ratios of the material to be decomposed [Parnas, 1975, Melillo et al., 1982; Bosatta and Berendse 1984; Ågren and Bosatta, 1987; Berendse et al., 1987]. The indices have been used frequently to describe the substrate quality of litter. We use them here to describe the decomposability of peat, which is partly decomposed plant litter. We also measured cellulose content of peats, as cellulose is a relatively available C fraction, routinely measured as part of the lignin determination. Three results from this study emphasize the importance of substrate supply in controlling spatial patterns of methanogenesis: (1) CH_4 production potentials uniformly increased with substrate addition, including both EtOH and litter amendments (Figure 3); (2) CH_4 production potentials increased with increasing substrate quality (decreasing lignin:N ratios and increasing cellulose) (Table 3); (3) CH_4 production potentials
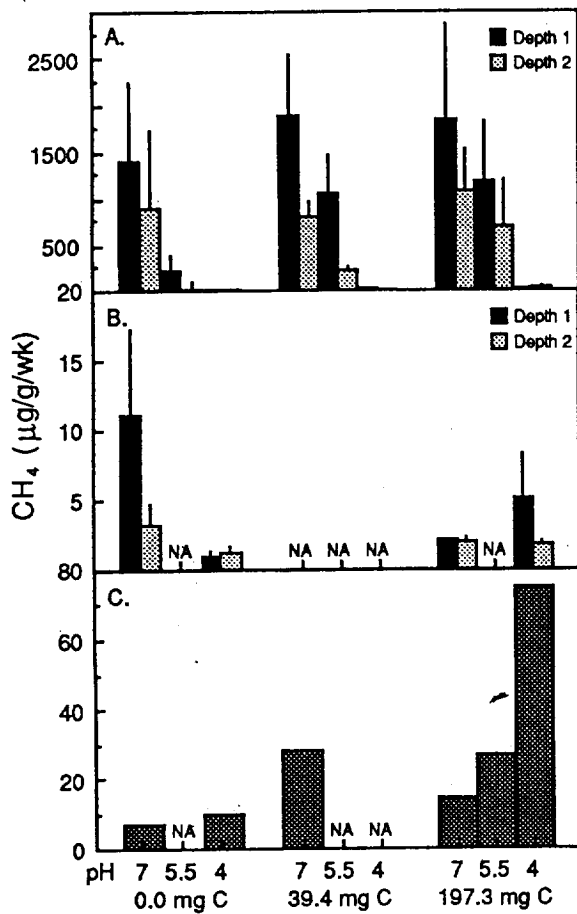
Fig. 3. The response of methane production to added EtOH and pH at two depths (see Table 2 for horizon depths and descriptions) are shown for (a) neutral coastal fen peat (n=3), (b) acid Kinosheo Lake peat (n=3), and (c) Kinosheo Lake degradational feature ("black hole") peat (low sample availability prohibited replication). "NA" indicates that a given treatment combination was not carried out, due to insufficient remaining sample. Error bars are standard errors of the mean.

increased with increasing NPP of the peat collection site (Figure 1 and *Klinger et al.* [this issue]. Both the C:N and the lignin:N ratios of surface peat increase and, presumably, substrate decomposability declines, with distance inland (Table 3). Strongly decreasing N contents inland raised the C:N ratio at Kinosheo Lake to nearly triple that of the coastal fen. Lignin:N ratios only doubled along the same transect because of partially offsetting decreases in lignin content inland. The C:N and lignin:N ratios suggest that carbon is more available for fermentation and subsequent methanogenesis at the coastal sites than at the inland sites. Higher CH_4 and CO_2 production potentials for the coastal compared to the inland sites support this.

The highest CH_4 and CO_2 production potentials always occurred in surface peats ($p<0.05$) and declined with depth. The low but nonzero CH_4 production potentials at lower depths in all sites indicate that these layers can serve as important, long term contributors to CH_4 stored in pore water and episodically released during water table fluctuations [*Roulet et al.*, this issue].

The surface peat layer receives all of the aboveground litter inputs as well as most of the inputs of fresh organic matter from root turnover and most closely reflects the chemistry of the existing vegetation. Changes in peat chemistry with depth result from historic microbial transformations and the chemistry of the vegetation from which the peat formed. As indicated by the

TABLE 3. Chemical Characteristics of Peats From Each of the Sites Along the Chromosequence Sampled During the NOWES Experiment

| Site | Depth, cm | Percent | | | | C:N | Lignin:N | pH | Bulk Density, g cm⁻³ |
		Carbon	Lignin	Cellulose	Nitrogen				
Coastal fen	0-10	46.2 (0.6)	33.2 (1.9)	23.5 (2.1)	1.9 (0.1)	25.1 (1.5)	17.8 (0.7)	6.56	0.08
	10-20	48.7 (0.4)	42.3 (1.8)	19.6 (1.4)	2.1 (0.1)	24.0 (0.6)	19.7 (0.9)	5.80	0.07
	20-80	46.9 (1.8)	46.0 (6.4)	15.6 (2.1)	2.3 (0.3)	20.6 (0.8)	20.1 (1.0)		0.13
Interior fen	0-10	45.8 (1.1)	35.2 (2.9)	23.8 (2.7)	1.8 (0.3)	26.3 (3.6)	19.4 (4.9)	5.68	0.05
	10-20	45.5 (1.5)	40.4 (5.1)	18.2 (0.8)	1.9 (0.4)	20.6 (0.7)	17.5 (2.9)	5.59	0.07
	20-80	45.8 (1.4)	38.5 (0.5)	19.0 (2.6)	2.3 (0.2)	21.2 (0.5)	17.5 (0.1)		0.12
Carling Lake	0-10	47.6 (0.8)	28.0 (1.8)	28.7 (0.4)	0.8 (0.2)	49.8 (3.5)	26.0 (0.4)	4.29	0.04
	10-20	47.9 (1.2)	29.4 (1.1)	32.8 (0.6)	0.9 (0.1)	59.3 (9.1)	28.4 (0.7)	4.27	0.04
	20-80	50.5 (0.5)	34.6 (0.5)	32.3 (1.3)	0.9 (0.1)	59.6 (3.9)	40.5 (3.6)		0.08
Kinosheo Lake	0-10	46.5 (0.5)	23.5 (2.2)	35.3 (5.7)	0.8 (0.1)	63.2 (13.5)	31.4 (6.2)	4.14	0.12
	10-20	48.0 (0.4)	19.5 (1.0)	38.5 (3.8)	0.9 (0.1)	56.7 (7.0)	23.0 (3.1)	3.97	0.13
	20-80	49.8 (0.4)	20.1 (3.1)	37.7 (4.0)	0.6 (0.1)	101.1 (9.9)	56.9 (2.0)		0.10

NOWES, Northern Wetlands Study. Characteristics are shown by depth, and standard errors of the mean are in parentheses.

pattern of CH_4 and CO_2 production rates, decomposability of organic matter also decreases with depth. In the bog sites, production potentials decreased with depth, paralleling strong increases in C:N and lignin:N ratios with depth that may have served to restrict decomposition rates. Neither the C:N nor the lignin:N ratio reflected the depth trend in the fen sites, however. A similar lack of pattern in different sites led *Hogg et al.* [1992] to suggest that other factors, such as higher P, K, and carbohydrate contents in recently dead organic matter, controlled decomposability within the peat column. The positive correlation between CH_4 production potentials and cellulose content in the fen sites seem to support this idea.

This overall landscape pattern suggests that two different sets of controls over decomposition and methane production may dominate at the two site types. The recalcitrant chemistry of organic matter, low pH, and likely low nutrient levels severely restrict microbial activities in the bog sites, resulting in the very low overall CH_4 and CO_2 production potentials. The more favorable peat chemistry, high pH, and likely higher nutrient levels at the fen sites remove this physiological restriction on microbial activity, allowing the rapid decomposition and methanogenesis rates to be limited only by the supply of substrate.

Fermentation controls the rate of substrate supply, which in turn limits methanogenic rates. Our experimental ethanol additions indicated that substrate availability limited methane production rates under certain conditions. In coastal fen surface peat slurries, methane production rates increased (Figure 3a) and carbon dioxide production rates decreased in the presence of ethanol, although neither response was significant (p>0.1). However, the proportion of respired carbon evolving as methane (i.e., CH_4/CO_2) increased strongly and significantly (p<0.005) with added ethanol. Little or no response occurred from subsurface samples (Figure 3a). The same qualitative pattern occurred (although at much lower methane production rates) in most Kinosheo Lake slurries: an 80% increase in methane production from the surface peats, with no response from the subsurface samples (Figure 3b).

Methane production increased eightfold from ethanol-treated Kinosheo Lake "black hole" slurries (p<0.05; Figure 3c). This responsiveness to substrate amendments suggests that in the field, methanogenic processes might outstrip fermentation rates. In the black holes, fermentation and methanogensis may occur at different depths. The dark color, low albedo, and lack of vegetation cover all contribute to unusually warm surface temperatures of these features [*Klinger et al.*, this issue], which accelerate decomposition. The close proximity of the water table to the surface in these depressions minimizes the distance substrate must descend to reach methanogenic populations and also minimizes the oxidizing zone through which CH_4 must ascend to reach the atmosphere. Downward transport of labile organic matter can explain how these peats could serve as such strong CH_4 sources in the field, despite low unamended methane production potentials in lab incubations.

Temperature. Many studies have demonstrated that temperature can be an important control over methane production, yet correlations between methane flux and temperature are typically weak [*Williams and Crawford*, 1985; *Crill et al.*, 1988; *Conrad*, 1989; *Moore et al.*, 1990; *Moore and Knowles*, 1990; *Whalen and Reeburgh*, 1990; *Klinger et al.*, this issue]. We found that temperature had a greater effect on methane production potentials in sites where substrate quality was higher (Figure 4). Values of Q_{10} (the ratio of methane production at T/methane production at T-10) for the coastal fen were 4.7 and 1.7 for surface and subsurface peats, respectively (Figure 4a). At Kinosheo lake,
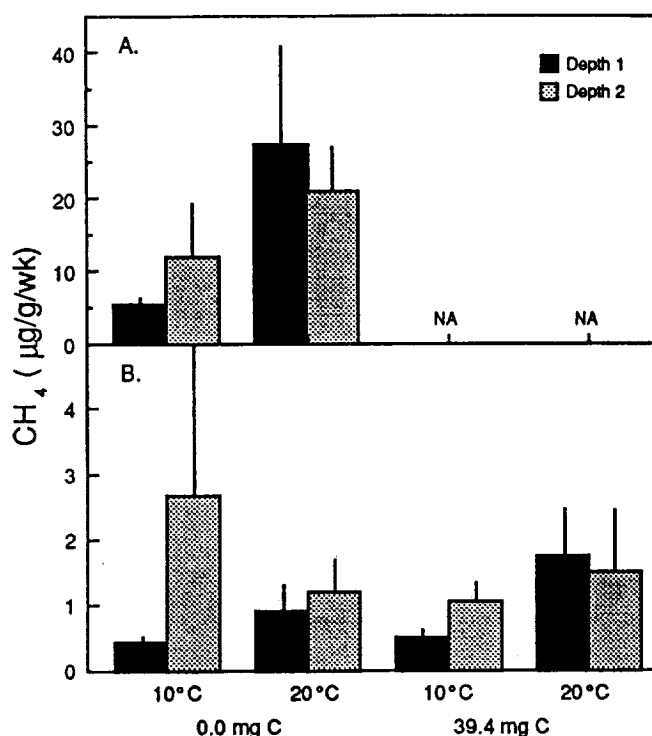

Fig. 4. Response of methane production at two depths (see Table 2 for horizon depths and descriptions) to (a) temperature in the coastal fen peats and (b) temperature and substrate (as EtOH) in Kinosheo Lake peats.

apparent Q_{10} values were 2 and -2.1 for surface and subsurface peats. The apparent decline in methane production potentials from Kinosheo Lake subsurface peats was not significant (p>0.1) but, if real, may have resulted from rapid depletion of an initially small pool of available carbon when microbial activity was enhanced by the warmer temperature. An additional experiment examined interactions between substrate amendment and temperature in Kinosheo Lake peats. Apparent Q_{10} values increased slightly from 2 to 3 in surface peat slurries, and from -2.1 to 1.4 in subsurface peat slurries--when 39.4 mg of carbon (as ethanol) was added (Figure 4b), although the CH_4 production response to both the temperature change and the ethanol were not significant (p>0.1).

Similar patterns have been observed in pure cultures of *Methanosarcina barkeri*, in which *Westermann et al.* [1989] found that temperature had little net effect on the conversion of acetate to methane. An offsetting increase in K_m apparently cancels out nearly all of the increased methanogenic enzyme activity with increasing temperature. Following this argument, apparent temperature responses of methane production are instead responses to increased substrate availability from temperature-enhanced rates of fermentation.

Responses to pH. The response of CH_4 production potentials to pH changes is important to understanding spatial variations in CH_4 production because wetlands tend to become more acidic as their species composition and hydrology change through vegetation succession over time. Site differences in successional status are a major source of landscape variability in wetlands [*Klinger et al.*, 1990; *Klinger et al.*, this issue]. Methanogenesis tends to be most rapid in the circumneutral pH range [*Conrad*, 1989; *Conrad and Schütz*, 1988], although acid tolerant [*Williams and Crawford*, 1985; *Patel et al.*, 1990] and moderately acidophilic [*Maestrojuán and Boone*, 1991] strains of methanogenic bacteria have been isolated. *Conrad* [1989]

suggested that pH limitation may also be important in the fermentation steps supplying substrate for methanogenesis.

Our pH manipulation experiments generally suggested that neutrophilic methanogen populations dominate in northern wetland peats. Methane production generally increased with increasing pH, even in acidic peats. The pH of the peats ranged from 6.5-7 in the fen sites down to almost 4 in the bog sites (Tables 1 and 3), correlating well with CH_4 production potentials. Lowering the pH of coastal fen surface peat slurries from 7 to circa 5.5 cut CH_4 production potentials almost sevenfold ($p<0.05$) from 1376 to 208 μg g^{-1} week^{-1}, and further lowering pH to 4 cut CH_4 production potentials to 5 μg g^{-1} week^{-1} (Figure 3a). Similar patterns also occurred with subsurface peat slurries. Raising the pH of Kinosheo Lake surface peat slurries from 4 to nearly 7 increased ($p<0.05$) CH_4 production potentials 20-fold from 0.5 to 11 μg g^{-1} week^{-1}, while a similar pH change in subsurface peat slurries increased CH_4 potentials from 1.3 to 3.2 μg g^{-1} week^{-1} (Figure 3b). Although Kinosheo Lake slurries produced more methane in response to both increased pH and ethanol additions individually, the combined treatment typically produced less CH_4 than the ethanol treatment alone (Figure 3b). The weaker landscape gradient in CO_2 compared to CH_4 production suggests an additive effect of pH above the substrate availability constraint.

The exception to the overall neutrophilic methanogenesis pattern occurred with peats sampled from dark-colored degradational features ("black holes") at Kinosheo Lake. These black holes were strong local methane sources in situ [Klinger et al., this issue; Roulet et al., this issue], but untreated slurries of these peats produced little more CH_4 than other Kinosheo Lake peats. Methane production from black hole slurries not only failed to increase with increased pH but actually decreased slightly ($p<0.05$, Figure 3c). Similarly, the strong ethanol response observed in these slurries was almost completely offset when pH was increased (interaction significant at $p<0.05$). This pattern suggests the presence of moderately acidophilic methanogens but also may have resulted from toxic effects of ethanol or the neutralizing titrant (KOH).

CONCLUSIONS

We hypothesized that rates of methane production should be constrained by substrate availability and regulated by temperature, redox potential, and pH. Results from sites other than the

Kinosheo "black holes" showed consistent patterns of response to substrate and pH, but quantitative responses varied with initial peat chemistry.

The positive response of methane production with respect to substrate amendment addition at ambient pH ($\partial CH_4/\partial EtOH$; Table 4) suggests that substrate availability plays a key role in regulating methane production. Sites with more decomposable peat due to narrower lignin:N ratios (coastal fen) could more readily respond to substrate additions, perhaps because of differences in population size or maximal growth rate.

Methane production with respect to pH at ambient substrate ($\partial CH_4/\partial p$H) was typically strong and positive (Table 4). The $\partial CH_4/\partial p$H at the acidic Kinosheo Lake site was much smaller than at the circumneutral coastal fen site. Similarly, $\partial CH_4/\partial T$ was larger in the coastal fen than in the inland sites (Table 4). Thus the ability of the substrate-limited site to respond to an improvement in the physiological environment (pH or temperature) for methanogenesis was limited by the low rate of substrate supply.

Litter chemistry and pH play important roles in controlling spatial and temporal variations in methane production rates. Spatially, peat chemistry reflects the chemistry of the peatland plant community, with changes in lignin:N ratio reflecting the shift in vegetation from the high N graminoids of the coastal fen community to the low N sphagnum species of the interior bogs. With increasingly acidic and nutrient deficient conditions along that successional gradient, species are favored which are acid tolerant (e.g., mosses) and which have high nutrient use efficiency, though low intrinsic growth rates [Klinger, 1990; Chapin et al., 1987; Van Cleve and Vierek, 1981; Van Cleve et al., 1991]. This results in a positive feedback, further reducing nutrient availability through immobilization into the slowly decomposing peat. As noted above, these changes in peat chemistry (lignin:N) and pH have coordinated and interactive effects on methane production, linking methane production to succession through changes in plant chemistry.

Substrate limitation of methanogenesis in northern wetland ecosystems may also contribute to seasonal variations in methane emissions. It is likely that much methane production is produced from recently produced carbon (Figure 5) [Klinger et al., this issue]. The availability of fresh litter will vary seasonally with timing of NPP and senescence and with decomposition rates. Thus seasonal variations in methane production and emission rates

TABLE 4. The Response of Methane Emission to Manipulation of Substrate, pH, or Temperature as a Function of Initial Lignin or pH While Holding Other Factors Constant

Site	Depth	Lignin:N	$\partial CH_4/\partial EtOH$	Standard Error
Coastal fen	1	17.8	47,985	27,173
Coastal fen	2	19.7	25,399	8855
Kinosheo Lake	1	31.4	32.6	54
Kinosheo Lake	2	23	54.9	8.9
	Depth	Initial pH	$\partial CH_4/\partial p$H	Standard Error
Coastal fen	1	6.56	941	960
Coastal fen	2	5.8	29.2	7.3
Kinosheo Lake	1	4.14	3.85	2.31
Kinosheo Lake	2	3.97	0.7	0.36
	Depth	Lignin:N	$\partial CH_4/\partial T$	Standard Error
Coastal fen	1	17.8	2.2	1.34
Coastal fen	2	19.7	0.89	0.44
Kinosheo Lake	1	31.4	0.05	0.06
Kinosheo Lake	2	23	0.11	0.24

Units are μg CH_4 (g peat)$^{-1}$ per g EtOH-C, °C, or pH unit as appropriate.
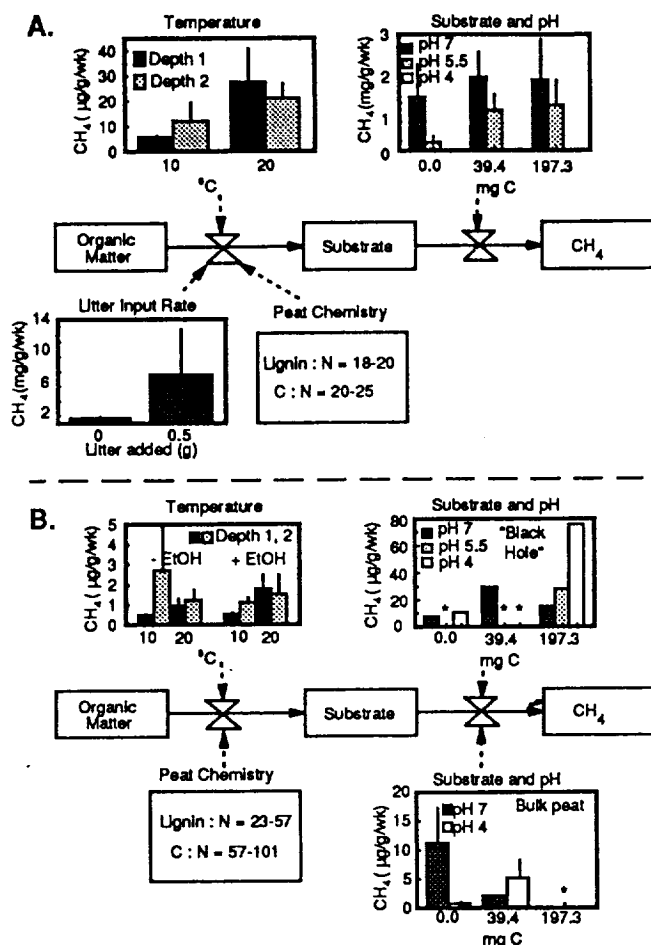
Fig. 5. Processes controlling methane production for the low N, low pH Kinosheo Lake, and the high N, neutral coastal fen site. The pathway of methane production is shown with experimental estimates of control functions adjacent. Solid lines indicate the flow of carbon through the methane pathway. Dashed lines indicate the point of influence of a control function. Asterisk indicates treatments not included because of insufficient sample.

will reflect not only microclimatic controls over methanogens and fermenters (temperature and water table fluctuations) but also variations in substrate supply. These variations, in addition to changes in porewater methane content and methane oxidation rates, lead to the common failure of simple correlations of methane emission rates with temperature, water table, and other microclimatic indicators [Crill et al., 1988; Roulet et al., 1992].

Our study has established quantitative relationships between ecosystem and physiological factors and methane production rates in controlled laboratory conditions. These results form the basis for our overall model of methane production (Figure 5). Temperature, organic matter quality, and supply rate act to control fermentation and hence substrate supply rates to methanogens. Substrate supply rate and pH, in turn, control methanogenic rates.

Thus we view methane production as an ecosystem process coupled to plant species composition, primary production, and overall heterotrophic metabolism. Spatial patterns in methane production also reflect plant physiological responses to successional and resource gradients that, in addition to climate and hydrology, influence the decomposition of peat and litter. The observed interacting effects of substrate supply rate and temperature on methane production rates will require validation through field studies in order to confirm their importance in

controlling methane emission rates. The importance of other factors not examined here, such as competitive electron acceptors (e.g., SO_4^{2-}), nutrient availability, water table fluctuations, methane transport, and methane oxidation rates, will also need to be included in future process level methane emission studies.

Finally, our results may provide a partial explanation for the low rates of methane emissions from interior bogs observed during the NOWES study [Klinger et al., this issue; Roulet et al., this issue]. Methane production rates in these sites are severely restricted at the fermentation step by poor substrate quality and at the methanogenic step by very low pH. This suggests that similar low emission rates will also be observed in other northern wetland regions with similar vegetation floristics and chemistry.

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E.A. Holland and D.S. Schimel, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307.

D. Valentine, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523.

from the mechanism outlined above. In the Antarctic Peninsula, the northern ice fronts of George VI and Larsen ice shelves have a history of recession over the past fifty years[19] and are still retreating. Another at risk is Wilkins Ice Shelf. Snow temperatures indicate that this region is at most 1-2 °C colder than the Wordie[20] and radio echo measurements show that large areas are infiltrated by brine. If the warming trend continues for another decade, this may be the next ice shelf to start receding. □

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Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands

A. Mosier*, D. Schimel†, D. Valentine†, K. Bronson* & W. Parton†

* United States Department of Agriculture, Agricultural Research Service, PO Box E, Ft Collins, Colorado 80522, USA
† Natural Resource Ecology Laboratory, Colorado State University, Ft Collins, Colorado 80523, USA

METHANE and nitrous oxide are long-lived, radiatively active trace gases that account for ~20% of the total anticipated atmospheric warming[1]. The atmospheric concentrations of both gases have increased dramatically over the past few decades, and continue to increase at a rate of ~1.1 and 0.25% yr^{-1} for CH_4 (ref. 2) and N_2O (ref. 3) respectively. Increased biospheric production is generally suggested as the reason for the increases, but decreases in global sinks may also be important. It has been suggested, for example, that nitrogen fertilization may decrease the rate at which tropical[4,5] and temperate forest soils[6] take up methane from the atmosphere. Furthermore, the recent extensive changes in land management and cultivation could be contributing to the observed increases in both atmospheric CH_4 and N_2O, as has been suggested for tropical soils[7]. Little information exists on CH_4 uptake in temperate grasslands (which currently occupy ~8% of the Earth's surface), its relation to N_2O production, or the effect of land management or cultivation[8,9]. Here we report measurements of CH_4 uptake and N_2O emissions in native, nitrogen-fertilized and wheat-growing prairie soils from spring to late autumn, 1990. We found that nitrogen fertilization and cultivation can both decrease CH_4 uptake and increase N_2O production, thereby contributing to the increasing atmospheric concentrations of these gases.

We established three sets of sites in the Colorado shortgrass steppe during late winter and spring, 1990. One set was established along a toposequence (catena) to determine whether the landscape position—sandy loam upland (midslope) versus sandy clay loam lowland (swale)—in the native prairie (catena site[10]) affected CH_4 uptake. Previous investigations[10,11] had found that ammonia and N_2O fluxes differed markedly with landscape position. A second set of sites was established in unamended and annually nitrogen-fertilized native grass pastures. The third set was established in a pair of wheat fields, cropped in alternating years (wheat-fallow system), and in an adjacent native grassland for comparison. All sites were in or near the United States Department of Agriculture-Agricultural Research Service Central Plains Experimental Range located north of Nunn, Colorado (latitude 40° 48' 23" N, longitude 104° 45' 15" W). Table 1 summarizes the soil characteristics.

On the catena, the fertilized midslope site was treated with 45 g m^{-2} of urea-N in July 1981, and the fertilized swale site was similarly treated in May 1982 (ref. 11). Four replicate, permanent plots for gas flux measurement were established in the fertilized and unfertilized midslope and swale sites by driving 20.3-cm diameter PVC pipes into the soil to a depth of 8 cm. Cattle have been excluded from the catena site since 1980. Weather and soil temperature data were continuously collected ~200 m from the site.

The annual fertilization experiment was ~1 km north of the catena site. We established six replicate plots in both nitrogen-fertilized and control grazed pastures, hereafter called AFS (annual fertilized) and CAFS (control annual fertilized) sites. The terrain in these two pastures is essentially flat, and the soil is similar to the catena midslope (Table 1). The AFS received 2.2 g N m^{-2} of ammonium nitrate annually from 1976 to 1989.

Finally, we established six plots in each of three adjacent sites—wheat, fallow, and native grassland—6 km east of the Central Plains Experimental Range. The wheat and fallow sites had been in continuous cultivation without irrigation or application of nitrogen fertilizer, pesticides or herbicides since the native prairie was ploughed in 1981. Winter wheat was planted in September 1989, and the fallow site was kept weed-free by cultivation following harvest in July 1989. The crop was harvested in July 1990, and the fallow site was planted with wheat in September 1990. The native grassland is 200 m east of the wheat-fallow field.

We measured methane and nitrous oxide fluxes by placing a closed chamber[12] over the established plots and taking gas samples from inside the chambers with 50-ml polypropylene syringes fitted with nylon stopcocks, usually 0, 15 and 30 minutes after the chambers were installed. We analysed the samples within six hours by gas chromatography using a Porapak N column and flame ionization detector for CH_4, and Porapak Q and electron capture detector[13] for N_2O from the same syringe. Flux measurements were made mid-morning on each sampling day, generally weekly at each site. We tested sampling time periods ranging from 10 to 60 minutes and taken at 2 or 3 time intervals, and in all cases CH_4 uptake was greater during the first sampling period than in subsequent periods. We therefore calculated CH_4 uptake rates assuming first-order kinetics rather than linear decay as had been suggested[6]. Measurements of CH_4 and N_2O fluxes were made at 6:00, 12:00 and 18:00 on several days. Over a 24-hour period, changes in CH_4 uptake averaged 10% or less of the mean, whereas the spatial and temporal variation in N_2O emissions was much higher[14].

We collected soil samples (0-15 cm) at the time of each gas flux measurement. The soils were analysed gravimetrically for soil water content and extracted with 2M KCl, and the extracts analysed colorimetrically for ammonium and nitrate content. We analysed soils from each site for total carbon and nitrogen content with a combustion C/N analyser. From July, we measured the soil temperature at a depth of 2.5 cm at each site to supplement the continuous soil temperature readings being made near the catena.

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TABLE 1 Physical and chemical properties of soils and flux rates of CH_4 and N_2O from each site

		Soil analysis[*]				Gas flux rates[§]				
				NO_3^-	NH_4^-	CH_4 uptake			N_2O emission	
		Total N	Total C	mg N	mg N	$\bar{X}$	s.d.		$\bar{X}$	s.d.
Site	pH	(%)		per kg	per kg	n	(g C ha^{-1} d^{-1})		n	(g C ha^{-1} d^{-1})	
Swale[†]											
Fertilized	5.6	0.223	2.215	5.1	0.7	128	3.6	1.6	108	6.2	15.5
Unfertilized	6.0	0.189	1.841	1.6	0.9	136	3.6	1.3	116	3.0	3.7
Midslope[‡]											
Fertilized	5.6	0.138	1.216	1.3	0.9	124	4.1	1.4	112	3.1	4.0
Unfertilized	6.5	0.141	1.245	1.1	0.9	132	6.3	2.1	120	1.8	1.7
Pasture[‡]											
Fertilized	5.6	0.138	1.177	6.4	20.3	180	3.8	1.8	162	6.1	10.7
Unfertilized	6.2	0.120	1.066	1.0	1.5	180	5.8	1.9	162	2.5	2.4
Wheat[‡]	5.8	0.116	0.955	1.1	1.4	162	1.3	0.6	162	2.6	2.7
Fallow[‡]	6.0	0.111	0.850	10.1	1.9	162	1.8	0.8	162	4.5	6.7
Grass[‡]	6.4	0.104	0.841	0.6	1.3	162	2.6	1.1	162	3.5	5.6

[*] Data are means for soil samples (0–15 cm) collected on each gas sampling day.
[†] The swale is a sandy clay loam soil classified as a Pachic argiustoll.
[‡] These are sandy loam soils classified as Ustollic haplargids.
[§] n, number of samples; $\bar{X}$, mean; s.d., standard deviation.

Methane uptake rates in the unfertilized grassland averaged 3.6, 5.8 and 6.3 g carbon per hectare day (g C ha^{-1} d^{-1}) in the swale, CAFS and midslope sites, respectively, between March and December 1990 (Fig. 1 and Table 1). Methane uptake at the swale was significantly less ($P < 0.01$) than at the CAFS and midslope sites. The midslope and CAFS soils were similar in texture and N content, whereas the swale site had finer texture and higher total N content (Table 1). The soil nitrate and ammonium contents of the three unfertilized soils were similar ($P > 0.05$). Annual in situ N mineralization at the midslope is, however, substantially less than in the swale[10] (41 compared with 55 kg N ha^{-1} yr^{-1}), suggesting that it is the N turnover (mineralization and nitrification)[15], rather than the mineral N content, which directly influences the CH_4 uptake.

Nitrous oxide efflux from the soils was inversely related to methane uptake (Fig. 1), averaging 3.0 and 1.8 g N ha^{-1} d^{-1} in unfertilized swale and midslope sites, respectively, compared to 3.6 and 6.3 g C ha^{-1} d^{-1}. The nitrous oxide flux from all sites was highest immediately following precipitation, when CH_4 uptake was lowest. If the fluxes of N_2O (ref. 11) and CH_4 (ref. 16) were both largely mediated by ammonium-oxidizing bac-

teria, then CH_4 uptake may have begun when the soil moisture declined to the point where slowed ammonium diffusion limited nitrification, although our data do not preclude other explanations. Under very dry conditions, both CH_4 uptake and N_2O emissions declined, and they remained low until soil water content increased.

Nitrogen fertilization decreased CH_4 uptake (Fig. 1), as was found for temperate forest soils[6]. In the AFS plots, annual N applications caused the CH_4 uptake to decrease by an average of 41% ($P < 0.01$). Methane uptake by the midslope site decreased from 6.3 to 4.1 g C ha^{-1} d^{-1} (Fig. 1) as a result of applying 45 g m^{-2} of urea-N in 1981 ($P < 0.01$). A similar N application to the more fertile swale soil in 1982 did not alter CH_4 uptake, which averaged 3.6 g C ha^{-1} d^{-1}. These data suggest that high N turnover, whether native or due to fertilization, suppresses CH_4 uptake.

Nitrogen fertilization increased N_2O emissions by a factor of 2–3 at all sites ($P < 0.05$), as had been found earlier[11]. Overall, N_2O emissions from the midslope and swale sites were 2–4 times greater in 1990 than in 1981 or 1982 (ref. 11), possibly due to wetter conditions in 1990. The inverse relationship between N_2O

FIG. 1 Effect of landscape position and nitrogen-fertilization on CH_4 uptake and N_2O emission in shortgrass prairie soils. Soil temperatures and water contents were measured in unfertilized soils.
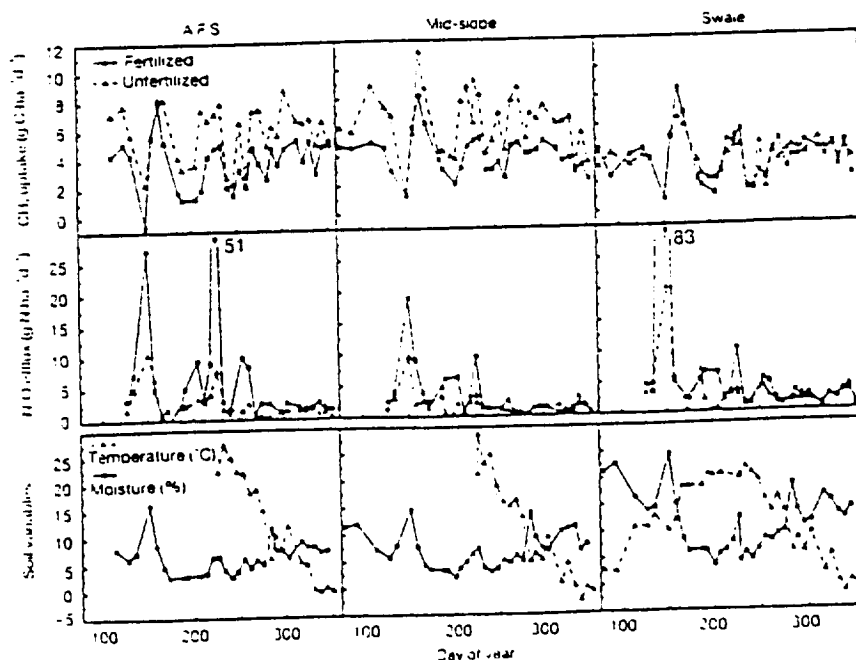
flux and CH_4 uptake was apparent with or without nitrogen fertilization. The influence of nitrogen fertilization on N_2O flux was most evident in moist soils, whereas its influence on CH_4 uptake was most evident as soils began to dry after rain (Fig. 1).

To determine whether cultivation affects CH_4 uptake in grassland soils, as observed in tropical soils[7], we began monitoring CH_4 uptake in the wheat-fallow system. During 6 months of weekly measurements, CH_4 uptake averaged 2.6, 1.8 and 1.3 g C ha^{-1} d^{-1} in native grassland, fallow and wheat sites, respectively (Fig. 2). These data indicate that disturbing the natural grassland decreased CH_4 uptake ($P < 0.01$). Soil moisture contents averaged 8.6, 11.1 and 12.9% in grassland, fallow and wheat, respectively. Soil ammonium content did not differ among the three sites but soil nitrate was on average ~10 times higher in the fallow soil than in the other two sites. Long-term experimentation and frequent flux measurements are needed to understand the reasons for differing CH_4 uptake rates in different soils and crop pastures.

Our data indicate that the semi-arid grasslands represent a significant global sink for CH_4 (ref. 8). Methane uptake in the grassland ranged from 6 to 61 μg CH_4 m^{-2} h^{-1}, compared with uptake rates of 6–24, 52, 0–112, and 10–160 μg CH_4 m^{-2} h^{-1} in tropical forest[17], subtropical broad-leafed savannah[18], tundra[19] and temperate forest soils[6,8], respectively. If our measurements are representative of CH_4 uptake by these grasslands globally, then 0.5 to 5.6 Tg of CH_4 are removed from the atmosphere in these grasslands each year.

Out data suggest that nitrogen fertilization in natural ecosystems increases N_2O emissions and decreases CH_4 uptake[6]. These data also indicate that recent changes in use or management of grasslands, such as cultivation, have decreased CH_4 uptake from and increased N_2O efflux to the atmosphere. In addition to increased production from rice paddies, ruminants and other sources[20], decreased consumption by soils may contribute to increasing atmospheric methane. □

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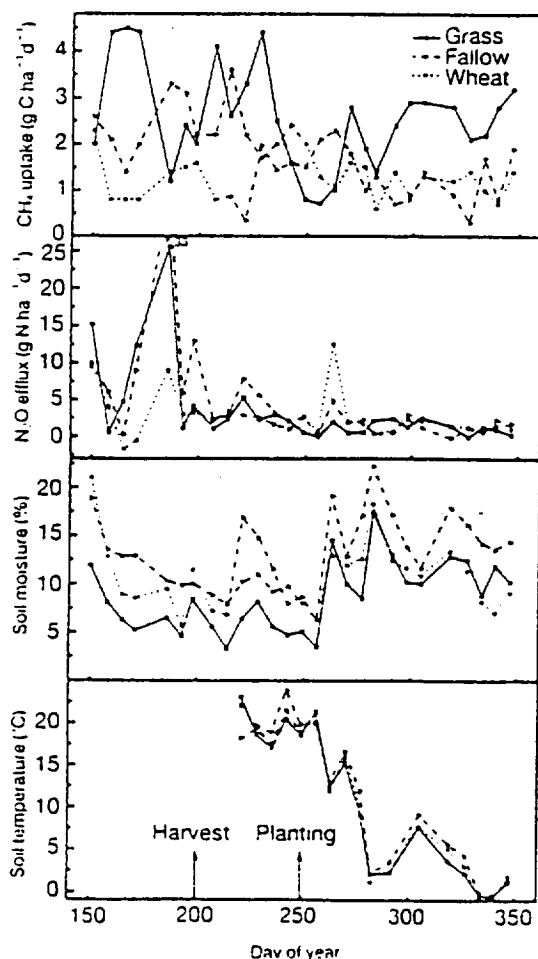20. Aselman, I. & Crutzen, P. J. J. atmos. Chem. 8, 307-358 (1989).

FIG. 2 Effects of wheat cropping on CH_4 uptake and N_2O emissions in shortgrass prairie soils. Arrows indicate approximate dates of harvest and planting, when the wheat and fallow designations switch.

Phases and electrical conductivity of a hydrous silicate assemblage at lower-mantle conditions

Xiaoyuan Li* & Raymond Jeanloz

Department of Geology and Geophysics, University of California, Berkeley, California 94720, USA

THE presence of a small amount of water in the lower mantle might affect in a significant way the geophysical and geochemical properties of its host mineral assemblage[1-5]. Here we present experimental observations of the phase behaviour and the electrical conductivity of a hydrous silicate assemblage synthesized from a mixture of $(Mg_{0.88}Fe_{0.12})SiO_3$ pyroxene and water under the pressure and temperature conditions of the lower mantle. Previous studies have shown that anhydrous $(Mg, Fe)SiO_3$ pyroxene transforms to a perovskite structure under these conditions[6-9]. We find that, although the hydrous assemblage is also dominated by the $(Mg, Fe)SiO_3$ perovskite phase, it coexists with the so-called hydrous phase D, of estimated composition $(Mg, Fe)SiH_2O_4$. Our measurements show that the inclusion of small amounts of water in the silicates can enhance the electrical conductivity of the lower-mantle assemblage by more than three orders of magnitude at these temperatures and pressures.

Our starting material was prepared by homogeneously mixing a $(Mg_{0.88}Fe_{0.12})SiO_3$ pyroxene with 4($\pm$2)% by weight of distilled water, giving a $(Mg_{0.88}Fe_{0.12})SiO_3/H_2O$ molar ratio of 4/1. The pyroxene was a natural enstatite from Bamble, Norway, which was ground to a grain size ≤ 1 μm before mixing. The high-pressure perovskite phase synthesized from anhydrous Bamble enstatite has been carefully documented in previous studies (for example, refs 4, 7, 10).

* Present address: Hawaii Institute of Geophysics, University of Hawaii, Honolulu, Hawaii 96822, USA

N 15

EFFECT OF LAND USE CHANGE ON METHANE OXIDATION IN TEMPERATE FOREST AND GRASSLAND SOILS

D.S. Ojima[1*], D.W. Valentine[1,2], A.R. Mosier[2], W.J. Parton[1], and D.S. Schimel[1,3]

[1]Natural Resource Ecology Laboratory,
Colorado State University,
Fort Collins, CO 80523, USA
[2]USDA/ARS,
P.O. Box E,
Fort Collins, CO 80522, USA
[3]Climate System Modeling Program,
University Corporation for Atmospheric Research,
P.O. Box 3000,
Boulder, CO 80307-3000, USA

ABSTRACT

Evidence is accumulating that land use changes and other human activity during the past 100 to 200 years have contributed to decreased CH_4 oxidation in the soil. Recent studies have documented the effect of land use change on CH_4 oxidation in a variety of ecosystems. Increased N additions to temperate forest soils in the northeastern United States decreased CH_4 uptake by 30 to 60%, and increased N fertilization and conversion to cropland in temperate grasslands decreased CH_4 uptake by 30 to 75%.

Using these data, we made a series of calculations to estimate the impact of land use and management changes which have altered soil the CH_4 sink in temperate forest and grassland ecosystems. Our study indicates that as the atmospheric mixing ratio of CH_4 has increased during the past 150 y, the temperate CH_4 sink has risen from approximately 8 Tg y^{-1} to 27 Tg y^{-1}, assuming no loss of land cover to cropland conversion. The net effect of intensive land cover changes and extensive chronic disturbance (i.e., increased atmospheric N deposition) to these ecosystems have resulted in about 30% reduction in the CH_4 sink relative to the soil sink assuming no disturbance to any of the temperate ecosystems. This will impact the global CH_4 budget even more as atmospheric CH_4 concentrations increase and as a result of further disturbance to other biomes. Determining the reasons for the decreased CH_4 uptake due to land disturbance is necessary to understand the role of CH_4 uptake in conjunction with the increasing atmospheric CH_4 concentrations. Without accounting for this approximately 20 Tg y^{-1} temperate soil sink, the atmospheric CH_4 concentration would be increasing about 1.5 times the current rate.

INTRODUCTION

During the past century, global methane (CH_4) concentrations have more than doubled and during the last 30 y have increased at an annual rate of about 1% (Rasmussen and Khalil, 1981; Bolle et al., 1986; Steele et al., 1987; Khalil et al., 1989). Although atmospheric CH_4 concentration is about 200 times less than CO_2, it contributes approximately 15% to current "greenhouse" forcing in the atmosphere (Hansen et al., 1989). This is because CH_4 is about 30 times more effective as CO_2 in absorbing IR radiation (Wuebbles and Edmonds,

1991), and is about 45 times more effective as a greenhouse gas overall than CO_2 when the longer atmospheric residence time of CH_4 is taken into account (Rodhe, 1990). This increase in CH_4 has been attributed to increasing sources such as rice paddy cultivation, landfill operations, fossil fuel processing and distribution, and livestock management (Khalil and Rasmussen, 1983; Seiler et al., 1984; Crutzen et al., 1986; Cicerone and Oremland, 1988; Aselmann and Crutzen, 1989). Current estimates of global annual CH_4 atmospheric loading are 400 to 600 Tg.

Methane emission is offset by oxidation that largely takes place in the atmosphere through reaction with the OH radical (Crutzen and Gidel, 1983; Khalil and Rasmussen, 1983; Cicerone and Oremland, 1988). The current increases in atmospheric concentrations of CO and CH_4 are expected to result in a decline in the OH radical over the next 50 years (Thompson and Cicerone, 1986; Vaghjiani and Ravishankara, 1991). Thompson and Cicerone (1986) estimate an increase in atmopsheric CH_4 from 1.6 to 2.9 ppmv would occur from 1985 to 2035, based on their photochemical model experiments. Given the magnitude of CH_4 increases and OH losses, it is estimated that approximately 50% of the methane increase will be due to an increased lifetime of methane resulting from a smaller OH sink, with the rest due to increased emissions of methane (Thompson and Cicerone, 1986).

An additional CH_4 sink exists, observations that aerobic soils also serve as sinks for atmospheric CH_4 (Keller et al., 1983; Seiler et al., 1984) and the confirmation that the phenomenon is widespread (Born et al., 1989; Steudler et al., 1989; Striegl and Ishii, 1989; Keller et al., 1990; Whalen and Reeburgh, 1990; Mosier et al., 1991) suggest that the dynamics of the soil sink term needs to be criticaly evaluated in estimating the global budget. Current estimates of the terrestrial soil sink for CH_4 ranges between 40 to 60 Tg y^{-1} (Cicerone and Oremland, 1988; Schutz et al., 1990). Whalen et al. (1990 and 1991) suggested that CH_4 oxidation in tundra and taiga soils not only accounts for consumption of CH_4 produced in these soils but also consumes atmospheric CH_4. They concluded that soil CH_4 oxidation could provide a negative feedback to atmospheric CH_4 increases, and if soils dry out with climate change, the soil oxidation sink would become more pronounced. A number of factors influence the magnitude of the soil sink for methane, including soil water status, soil temperature, nitrogen dynamics, and microbial population, but quantification of these factors on the dynamics of methane uptake is still poor. In addition, little is known about how CH_4 oxidation proceeds in the major croplands that cover approximately 1500 10^6 ha or approximately 10% of the global land surface (Houghton et al., 1983).

The objective of this paper is to assess the role of temperate forest and grassland conversion and the interaction between land cover conversion and changes in atmospheric CH_4 on soil CH4 uptake from 1850 to the present. This assessment takes into account the change in sink strength relative to estimated changes in atmospheric concentration of CH_4 during this period and changes in atmospheric deposition of N over temperate regions of the Earth.

LAND USE IMPACT ON THE SOIL SINK FOR METHANE

Land use changes can affect key biogeochemical rates, leading to changes in N_2O fluxes from land clearing in forests (Luizao et al., 1989); increased N_2O fluxes due to fertilization (Mosier et al., 1986); decreased CH_4 uptake by soils fertilized with N (Steudler et al., 1989, Mosier et al., 1991); and increased CH_4 flux due to cattle and paddy rice cultivation (Crutzen et al., 1986; Cicerone and Oremland, 1988; Aselmann and Crutzen, 1989). These impacts are locally driven, but aggregated they have an impact on the regional and global flux of key biogenic trace gases, such as CH_4 and N_2O.

The oxidation of CH_4 has been observed in temperate forest soils (Keller et al., 1983, 1986; Steudler et al., 1989; Yavitt et al., 1990), and tropical forest soils (Keller et al., 1986, Steudler et al., 1991). Methane uptake values for temperate deciduous forests ranged between 0.5 to 5.5 kg CH_4 ha^{-1} y^{-1} (Keller et al., 1983; Steudler et al., 1989). In relatively undisturbed tropical ecosystems, CH_4 uptake in forests ranged from 0.5 to 2.9 kg CH_4 ha^{-1} y^{-1} (Keller et al., 1983, 1986, 1990; Seiler et al., 1984) and in more arid savanna and woodlands was 4.6 kg CH_4 ha^{-1} y^{-1} (Seiler et al., 1984). And Striegl, pers. comm., estimated uptake of 2.4 kg CH_4 ha^{-1} y^{-1} for Mojave Desert/Southern Great Basin soil. It should be noted that most of these estimates may not represent the annual uptake of CH_4 since measurements were not taken throughout the year.

A recent study showed that semiarid grasslands are an important methane sink and conversion of these grasslands to croplands significantly reduces oxidation of CH_4 in these soils (Mosier et al., 1991). Chamber measurements of CH_4 uptake and N_2O fluxes were made from a native shortgrass steppe, an annually fertilized shortgrass steppe, a previously cultivated site that was put back into grassland in 1939 ("go-back", visually indistinguishable from the native shortgrass steppe), and a cultivated dryland wheat-fallow site (Mosier et al. 1991).

Estimates of annual methane uptake in the dryland wheat field showed 75% less CH_4 uptake relative to the undisturbed grassland site (Figure 1). Cultivation appeared to have a long-term impact on the uptake potential of temperate grasslands. The "go-back" plot consumed less than 40% of the CH_4 in the undisturbed soils. Nitrogen additions of 22 kg ammonium-nitrate ha^{-1} y^{-1} for 15 years to these grasslands also depressed methane uptake. The amount of organic matter present, the fertility of the soil, and other factors such as changes in soil physical properties and soil microbiological properties appear to play an important role in CH_4 oxidation (Mosier et al. 1991).

The mechanisms by which CH_4 oxidation potential is reduced following conversion to cropland or change in N dynamics are not yet clear. Factors such as water availability, fertilizer applications, atmospheric N deposition, soil structural changes, and cropping management contribute to modifications of the soil CH_4 uptake. In particular, simultaneous measurements of N_2O and CH_4 fluxes in a semiarid grassland steppe indicated an inverse relationship between N_2O emissions and CH_4 uptake under conditions of varying soil moisture (Mosier et al. 1991). The pattern of N_2O efflux relative to rainfall is similar to the pattern of N-mineralization in grassland ecosystems (Parton et al., 1988; Schimel et al., 1988) and conforms with the observed role N-fertilizers plays on reducing CH_4 uptake by soils (Steudler et al., 1989).
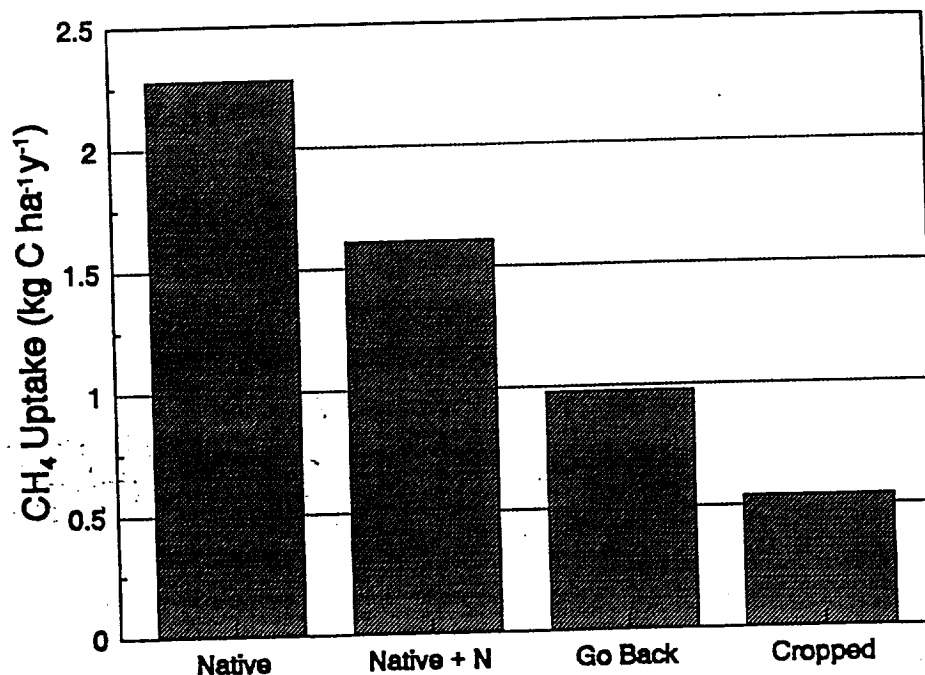
Figure 1. Effect of N-fertilization ("Native+N"), past cultivation ("Go Back" returned to grass in 1939), and current cropping ("Cropped") on uptake of atmospheric methane in shortgrass steppe soils ("Native").

GLOBAL PERSPECTIVE ON THE SOIL SINK FOR CH₄

Estimates indicate that the global oxidation of CH_4 is exceeded by production by about 50 Tg each year, or approximately 10% of the total source. Because 80 to 90% of this oxidation of CH_4 occurs in the atmosphere, what is the role of soils in the global CH_4 budget? Measurement and modeling of the two-dimensional distribution of CH_4 concentration in an unsaturated zone near buried waste (Striegl and Ishii, 1989) demonstrated that *in situ* rates of CH_4 consumption increase in response to elevated CH_4 concentrations in the soil atmosphere. Laboratory measurements of the concentration dependence of oxidation rates indicate that potential microbial CH_4 consumption far exceed potential CH_4 diffusion rates (Whalen and Reeburgh, 1990; Bender and Conrad, this issue; Striegl, this issue), and soil temperature has a minor effect on soil uptake of atmospheric CH_4 (Born et al., 1990, Mosier et al., 1991, Whalen and Reeburgh, 1990). Assuming that soil oxidation rates are CH_4 concentration dependent, as these studies suggest, then the soil CH_4 uptake has probably been increasing with the sharp rise of the atmospheric CH_4 since 1850.

In our analysis we assumed (after Striegl and Ishii, 1989; Fung et al., 1991) that current CH_4 uptake occurs by ordinary diffusion and its rate is proportional to the difference between CH_4 mixing ratios above and below the soil surface, i.e.,

$$Annual\ CH_4\ Uptake = k \times \Delta[CH_4]$$

[1]

Minimum soil CH_4 concentrations are clearly variable, but measurements in several ecosystems suggest that a reasonable minimum soil CH_4 concentration would be 0.4 ppmv (Striegl, 1988; Striegl and Ishii, 1989). Because diffusion is proportional to [air-filled porosity]$^{1/3}$, we also assumed that broad patterns of soil moisture in 1850 were not different from current patterns. We solved for k for each of the land cover types identified in Table 1, based on the current atmospheric CH_4 concentration and observed annual uptake rates. Using the calculated k's, estimates for land-cover-specific CH_4 uptake at atmospheric CH_4 levels in 1850, 1900, 1950, and 1980 were made.

During the past 150 y, rapid changes to land cover due to conversion of natural areas to croplands and for fuel wood extraction has occurred. Using data derived from the World Resources 1987 Report (WRI 1987), we estimated land-cover changes in the mid-latitudes during the past century from North Africa and Middle East, North America, China, South Asia, Europe, and the former USSR (Table 1). New croplands between 1850 and 1950 in these temperate regions were derived primarily from grassland conversion. In the USSR and China during this time, forest conversion was also a significant contributor to cropland expansion. In North America and Europe, reversion of cropland back into forest and grassland has occurred during the past 80 y, and over the whole temperate region the amount of land cover change was approximately 1000 10^6 ha or about 14% of the temperate forest and grassland area being considered in these six regions.

In order to assess the effect of changing atmospheric concentrations on the soil sink in combination with land cover changes, we made a retrospective analysis of CH_4 uptake in temperate soils since 1850 under three land cover scenarios. These scenarios are a "no-disturbance" (i.e., area of land cover have maximal consumption rates of undisturbed ecosystems), "intensive" disturbance by land cover change only (i.e., consumption rates are reduced in areas that are under a different land cover class due to cropland conversion), and a combined "intensive plus extensive" disturbance which includes land use changes as well as anthropogenic changes in N deposition. This last scenario probably best represents actual changes in CH_4 uptake since 1850.

For the "no-disturbance" scenario, we assumed that pristine forests and grasslands would take up CH_4 at or near the maximum rates currently observed in these systems, and that land cover changes from the pristine condition had not occurred. Uptake rates were calculated as

$$CH_4 \ Uptake_u = k_u \times \Delta[CH_4] \times Area_u \qquad [2]$$

where k_u equals current "undisturbed" uptake relative to current $\Delta[CH_4]$. Assumptions for the "intensive" land cover change scenario were similar except that land cover changes (derived from WRI 1987) decreased CH_4 uptake rates in affected areas, and uptake rates were calculated as

$$CH_4 \ Uptake_i = CH_4 Uptake_u - (k_u - k_i) \times \Delta[CH_4] \times \Delta Area_i \qquad [3]$$

Table 1. Estimates of historic CH_4 mixing ratios (Houghton et al. 1990), temperate forest and grassland cover patterns (WRI 1987), area impacted by chronic N deposition (based on Melillo et al. 1989), and consequent CH_4 uptake rates.

Biome	Year	CH_4 mixing ratio	Land cover area	Extensive impact area	CH_4 uptake coefficients			Annual CH_4 uptake		
		(ppmv)	(10^6 ha)		k_u	k_i	k_e	(kg CH_4 ha^{-1})	Intensive	Extensive
								Undisturbed		
Temperate Forest	1850	0.8	2645	0				1.69	0.68	1.14
	1900	0.9	2537	265	4.24	1.69	2.85	2.12	0.85	1.42
	1950	1.1	2383	529				2.96	1.18	1.99
	1980	1.7	2302	1323				5.50	2.20	3.70
Temperate Grassland	1850	0.8	3906	0				0.95	0.38	0.64
	1900	0.9	3825	391	2.38	0.95	1.60	1.19	0.48	0.80
	1950	1.1	3732	781				1.67	0.67	1.12
	1980	1.7	3675	1953				3.10	1.24	2.09

where k_i is 0.4 k_u and area$_i$ is the area that underwent cropland conversion. The k_i value is based on estimates of cultivation effects in a grassland region which reduced CH_4 uptake rates to 25 to 40% of the non-cultivated soils (i.e., "native" grassland soil, Figure 1, Mosier et al., 1991) and we assumed the less severe impact. Finally, we assumed in the combined scenario that half of the "native" temperate forests and grasslands were in fact not pristine and therefore were taking up CH_4 at rates near the minimum rates reported. This was based on Melillo *et al.*'s (1989) estimate that half of the temperate land area receives 80% of the N burden and has reduced CH_4 uptake of these soils by 33% (Stuedler et al., 1989). This uptake rate was calculated as

$$CH_4 \ Uptake_{i \rightarrow} = CH_4 Uptake_i - (k_u - k_e) \times \Delta[CH_4] \times \Delta Area, \qquad [4]$$

where k_e is 0.67 k_u.

This analysis indicates that the magnitude of the soil sink since 1850 has tripled (Figure 2). This increase in soil uptake has resulted from the increase in atmospheric CH_4 during this period. Also, during the past 150 years, areas have undergone intensive land cover changes due to forest or grassland conversion to cropland or pasture. This cropland conversion is estimated to have resulted in a reduction of approximately 2 Tg y^{-1} in the soil CH_4 sink (Figure 2).

In addition to the conversion of native land cover types to croplands, extensive changes have also occurred that are not reflected in data on land cover changes alone. These include increased N deposition in eastern North America, Europe, and China, as well as changes in forestry practices involving disturbance by compaction, disking (plowing), biomass burning, and N fertilization. The impact of these extensive changes would lower the soil sink even more during the past 150 years. The net effect of intensive land cover disturbance and extensive chronic disturbance to terrestrial ecosystems resulted in a 7 Tg y^{-1} reduction from the "no-disturbance" CH_4 sink to 20 Tg y^{-1} (Figure 2). These reductions in soil sink strength will diminish the capacity of soils to act as a negative feedback mitigating future increases in atmospheric CH_4 concentration.

SUMMARY

The global CH_4 budget is affected by processes controlling both the production and consumption of CH_4. Much attention has been focussed on the factors related to land cover and land use changes affecting CH_4 production (Cicerone and Oremland, 1988; Aselmann and Crutzen, 1989) and on factors related to atmospheric oxidation of CH_4 (Crutzen and Gidel, 1983; Vaghjiani and Ravishankara, 1991). However, recent studies have documented the widespread nature of soil CH_4 consumption and have begun to question the validity of the current global CH_4 budgets.

A severe constraint on regional or global assessments of the terrestrial CH_4 sink is the paucity of measurement sites and the infrequency of measurements from which to base CH_4 budgets. The measurements used for annual estimates from particular ecosystems are rarely collected over a sufficient period of time or area to capture spatial or seasonal variability of gas efflux or uptake from a particular area. The interaction of climate variability, microbial community and ecosystem dynamics, and land surface characteristics make
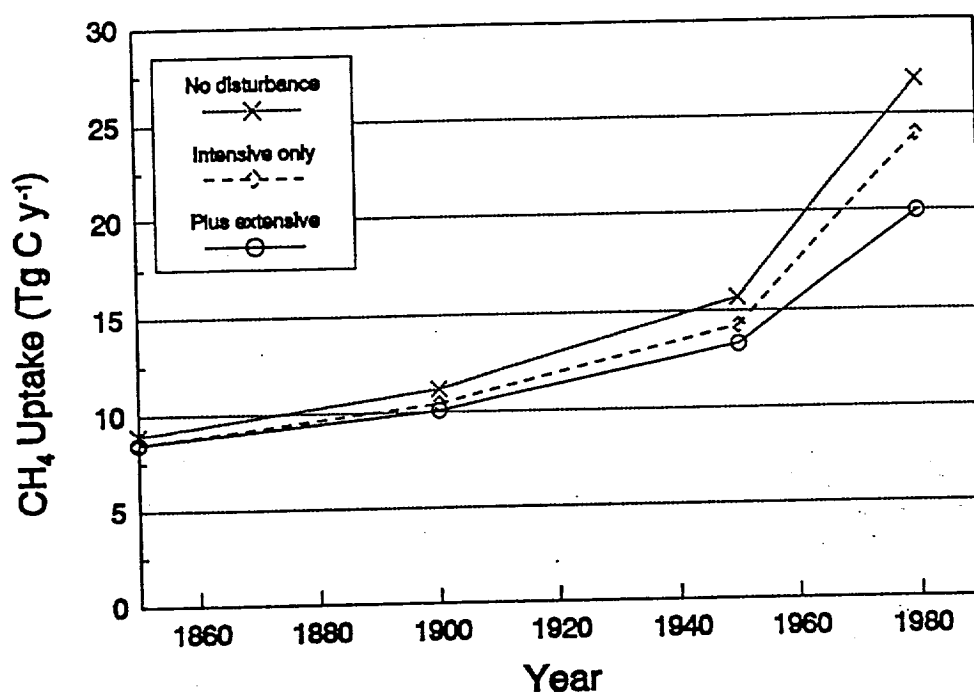
Figure 2. A retrospective estimate of the global CH_4 soil sink relative to changes in atmospheric methane from 1850 to 1980. The "No disturbance" line indicates estimated soil CH_4 uptake assuming that no major land cover changes have taken place and that uptake rates were near maximal. The "Intensive" line represents estimated soil CH_4 uptake assuming that soil CH_4 uptake was altered by land cover changes resulting from forest or grassland conversion to cropland or pasture. The "plus extensive" line represents the added change in CH_4 uptake due to increased atmospheric inputs of N over large areas of the world.

quantitative estimation of the flux of trace gases very difficult. Further, the processes resulting in change over time in soil CH_4 oxidation are not well known. Yet, as with many trace gas species, only scanty data are available to extrapolate fluxes over large areas and to estimate how they may change in time. While this extrapolation is prone to large estimation errors, cross-checks between surface flux inventories and inverse calculations provide bounds on uncertainties and serve to guide future studies.

In this study, we have assessed the potential CH_4 sink from temperate soils. The magnitude of this sink in the temperate region considered is approximately 27 Tg y^{-1}. However, with changes in land use and other factors affecting biogeochemical rates in these systems, we estimate that this sink has been reduced by human-induced changes by 1.5 to 6 Tg y^{-1}, depending on the nature and the extent of the disturbance. The most reasonable estimate of the current temperate soil sink is 20 Tg y^{-1}, which is approximately 30 to 50% of the global soil sink for CH_4. And without this CH_4 sink, atmospheric CH_4 concentrations would be increasing about 1.5 times the current rate.

These changes in soil consumption of CH_4 are not only occurring in the temperate region, but have been noted in other regions as well. For instance, in a tropical forested area, Keller et al., (1990) observed a 75% decrease in methane uptake rates in pastures and tropical agricultural sites compared to forest sites. In a tropical forest recovering from a hurricane, Steudler (pers. commun., 1991) observed a 50% decrease in methane uptake during the initial stage of recovery and has related this to the accelerated N cycling. Some tundra (Whalen and Reeburgh, 1990) and taiga (Whalen et al., 1991) ecosystems may also be significant CH_4 sinks, but the magnitude of this sink is uncertain due to the role of human and climate change impacts on the biogeochemical processes controlling CH_4 production and consumption. The potential influence of these extensive changes in land cover in the tropics during the past century on the global CH_4 budget needs further study.

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