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Oxidation of methane in boreal forest soils: a comparison of seven measures

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Abstract. Methane oxidation rates were measured in boreal forest soils using seven techniques that provide a range of information on soil CH_4 oxidation. These include: (a) short-term static chamber experiments with a free-air (1.7 ppm CH_4) headspace, (b) estimating CH_4 oxidation rates from soil CH_4 distributions and (c) ^{222}Rn-calibrated flux measurements, (d) day-long static chamber experiments with free-air and amended (+20 to 2000 ppm CH_4) headspaces, (e) jar experiments on soil core sections using free-air and (f) amended (+500 ppm CH_4) headspaces, and (g) jar experiments on core sections involving tracer additions of $^{14}CH_4$. Short-term unamended chamber measurements, ^{222}Rn-calibrated flux measurements, and soil CH_4 distributions show independently that the soils are capable of oxidizing atmospheric CH_4 at rates ranging to < 2 mg m^{-2} d^{-1}. Jar experiments with free-air headspaces and soil CH_4 profiles show that CH_4 oxidation occurs to a soil depth of 60 cm and is maximum in the 10 to 20 cm zone. Jar experiments and chamber measurements with free-air headspaces show that CH_4 oxidation occurs at low (< 0.9 ppm) thresholds. The $^{14}CH_4$-amended jar experiments show the distribution of end products of CH_4 oxidation; 60% is transformed to CO_2 and the remainder is incorporated in biomass. Chamber and jar experiments under amended atmospheres show that these soils have a high capacity for CH_4 oxidation and indicate potential CH_4 oxidation rates as high as 867 mg m^{-2} d^{-1}. Methane oxidation in moist soils modulates CH_4 emission and can serve as a negative feedback on atmospheric CH_4 increases.

Introduction

Many regional estimates of emission of CH_4 to the atmosphere derive from "scaling up" results of enclosure experiments (Harriss 1989), where flux is estimated by changes in headspace CH_4 concentration over time in open-bottom chambers placed over the soil. Static chamber (no forced air circulation) flux determinations are inexpensive and require minimal equipment, but they have been criticized for disturbing conditions (advection, temperature, concentration gradients) at the soil surface (Schutz & Seiler 1989; Mosier 1990). Accurate regional estimates of soil CH_4 fluxes

therefore depend on the validity of the commonly used static chamber method. Validation is lacking or indirect, usually involving comparison with micrometeorological flux estimates (e.g., Bartlett et al. 1991). However, similarity between gas flux estimates made by chamber and indirect techniques may be coincidental (Mosier 1989).

A recently introduced technique (Dörr & Münnich 1987) employs the noble gas ^{222}Rn as a conservative internal standard to provide an independent, point source flux for comparison with static chambers. Soil ^{222}Rn is produced by radioactive decay of ^{226}Ra and is removed only by diffusion to the atmosphere and radioactive decay. Soil-atmosphere exchange of any gas can be calculated from the rate of ^{222}Rn accumulation in a chamber and the ratios of molecular diffusivities and soil concentration gradients for the two gases. Disturbance of the soil ^{222}Rn concentration gradient during flux measurement is negligible in soils where ^{222}Rn has a comparatively large diffusional path length before decay. "Rn-calibrated" CH_4 fluxes could be more accurate than direct, static chamber CH_4 flux determinations for these soils (Dörr & Münnich 1990).

Static chamber experiments estimate net atmospheric CH_4 flux and give no information concerning methanogenesis and CH_4 oxidation, the soil microbial processes that influence flux. Microbial CH_4 oxidation is an important modulator of CH_4 flux, with global CH_4 consumption slightly in excess of emission (Reeburgh et al., submitted). Moist or dry soils from the tropics to arctic tundra show net CH_4 consumption (Harriss et al. 1982; Seiler et al. 1984; Steudler et al. 1989; Born et al. 1990; Keller et al. 1990; Whalen & Reeburgh 1990b; Yavitt et al. 1990a; Whalen et al. 1991), which is indicated by a decrease in chamber headspace CH_4 concentration. Inundated tundra soils that experience a reduced summer water table may become a sink for atmospheric CH_4, due partly to increased CH_4 oxidation (Whalen et al. 1991). Loci, controls and *in situ* and potential rates of CH_4 oxidation are well-characterized for aquatic environments (reviewed by Rudd & Taylor 1980; Kiene 1991), but similar, detailed terrestrial data are available only for a cultivated humisol (Megraw & Knowles 1987), moist tundra (Whalen & Reeburgh 1990b) and landfill soils (Whalen et al. 1990). The fate of oxidized CH_4 is important for models of climate change, as CH_4 is 3.7-(Lashoff & Ahuja 1990) to 30-fold (Blake & Rowland 1988) more effective as a greenhouse gas than CO_2. Clearly, an improved understanding of the controls on soil CH_4 oxidation is essential to predict the impact of climate change on the atmospheric CH_4 budget. Experiments must extend beyond chamber determinations of net flux and should involve discrete soil samples.

We have measured net CH_4 flux at permanent sampling stations in moist taiga (boreal forest) soils for two years using a static chamber

technique (Whalen et al. 1991). These soils consistently consume atmospheric CH_4 and show no evidence of methanogenesis throughout the thaw season, so that chamber determinations of net CH_4 flux are equivalent to depth-integrated rates of CH_4 oxidation. The aim of the present two-day field and one-week laboratory study was to confirm our chamber flux determinations and to explore the controls on the capacity of CH_4 oxidation in taiga soils.

We addressed these objectives by using seven techniques to directly or indirectly estimate rates of CH_4 oxidation in representative moist taiga soils. These methods included: (a) experiments monitoring the change in headspace CH_4 concentration over 0.75 h with static chambers initially equilibrated with a free-air atmosphere (1.7 ppm CH_4); (b) soil gradient measurements, where CH_4 fluxes were estimated from soil CH_4 distributions; (c) static chamber experiments estimating CH_4 flux from soil distributions of ^{222}Rn and CH_4 and the change in headspace ^{222}Rn activity over time; (d) experiments assessing the change in headspace CH_4 concentration over 24 h in static chambers initially equilibrated with amended (+20 to 2000 ppm CH_4) and free-air atmospheres; (e) jar experiments exposing soil core sections to atmospheric CH_4 concentrations (1.7 ppm); (f) jar experiments involving soil core sections under amended atmospheres (+500 ppm CH_4); and (g) jar experiments exposing soil core sections to $^{14}CH_4$. We expected these experiments to give area-based estimates of *in situ* and potential rates of CH_4 oxidation, thresholds and capacities for CH_4 oxidation, soil distributions of CH_4 and CH_4-oxidizing activity and the distribution of end products of CH_4 oxidation. This study is not a comparison of measurements of *in situ* CH_4 oxidation by seven methods. Rather, we use these seven measures because of the unique insight each provides concerning rates and controls on CH_4 oxidation in taiga soils.

Methods

Field sites

This study was conducted in the Bonanza Creek Experimental Forest (64°45′N, 148°18′W, a 5045-ha research area located 20 km west of Fairbanks, Alaska. The mean annual and July air temperatures in the Fairbanks area are −3 °C and 17 °C, respectively, and the average frost-free period is about 100 d. Precipitation averages 285 mm annually; 65% is rain. Topography is gently rolling and upland soils are well-drained. Permafrost is discontinuous and usually confined to north-facing slopes

with a black spruce (*Picea mariana*) overstory. Upland soils are stone-free and have slight morphological development. The parent material is a micaceous loess deposited during the most recent Pleistocene glaciation. The physiography of interior Alaskan taiga, including this study area, is given in Van Cleve & Dyrness (1983), Viereck et al. (1983) and Van Cleve et al. (1991).

Four upland sites were selected for study. Intermediate successional stages were represented by south-facing aspen (*Populus tremuloides*; site AS2) and north-facing birch (*Betula papyrifera*; site NB2) communities, whereas advanced successional stages were represented by north-facing black spruce (BS2) and south facing white spruce (*Picea glauca*; site UP3A) stands. The deciduous sites have a heavy ground cover of leaf litter and an insignificant understory of shrubs and herbs. The coniferous sites show a continuous ground cover of feather mosses (predominately *Pleurozium* sp. and *Hylocomium* sp.). These are invaded by lowbush cranberry (*Vaccinium vitis-idaea*) and lichens at BS2.

Field sampling

Except where noted, all measurements at sites AS2 and NB2 were taken on 9 October 1990 and measurements at sites BS2 and UP3A were taken on 11 October 1990.

Static chamber determinations of ^{222}Rn and CH_4 flux were made at stations that had been sampled regularly during the thaw season. Each chamber consisted of a skirted aluminum base permanently seated in the soil and lucite vertical sections and lids that utilize a water-filled channel for a seal (Whalen & Reeburgh 1988). Samples for CH_4 analysis were collected over a 0.75 h period from one chamber whose lid was equipped with a septum for syringe sampling of headspace gas. A second, similar chamber located within a few meters of the first chamber was used for ^{222}Rn flux determinations. Evacuated counting cells (Lucas 1957) were filled directly from the chamber lid with a quick-connect fitting.

Soil gas samples were obtained by inserting a perforated stainless steel tube to known depths and using a battery-powered diaphragm pump to fill 0.5 L Tedlar bags (Born et al. 1990). The bags were sampled by syringe and evacuated counting cell for CH_4 and ^{222}Rn analyses, respectively. Depth distributions for soil temperature were determined at each site with a portable thermistor probe.

Duplicate 30 cm soil cores were collected from each site with a 15 cm diameter stainless steel coring apparatus. Cores were then cut horizontally into three 10 cm sections. The centers of the soil cores were sub-cored using a 6.7 cm ID × 10 cm long plastic tube. Additional 10 cm long core

sections were obtained from 30 to 60 cm below the soil surface by inserting a 6.7 cm ID plastic tube into the hole created by removal of the initial 30 cm core. Bedrock limited core collection to the upper 40 cm of soil at BS2. All core sections were extruded into 1 liter Mason jars fitted with a septum for syringe sampling of headspace gas. It was impossible to maintain the integrity of the soil matrix during extrusion. Soils were returned to the laboratory and stored at 5 °C.

Methane consumption thresholds and capacities were studied using three static chambers reserved for these experiments at each site. Disappearance of CH_4 in each chamber was monitored following equilibration of the headspace with a free-air atmospheres (~ 1.7 ppm CH_4). The same chambers were used several days later in amended atmosphere experiments where headspaces were initially adjusted to about 20, 200 or 2000 ppm CH_4 (one chamber, each concentration). These additions increased the initial CH_4 concentration 10 to 1000-fold above ambient. Headspace CH_4 was sampled 7 or 8 times over a 24 h period in all experiments. The first sample (t_0) in amended atmosphere experiments was taken 0.5 h after CH_4 addition to allow equilibration of headspace gas.

Permanent sampling stations for all chamber flux studies described above were clustered within a ~ 25-m^2 area at each site to minimize natural variability; soil cores, gas samples and temperature measurements were also taken within this plot.

Laboratory studies

Laboratory studies of microbial CH_4 oxidation in soil samples were conducted in Mason jars (unless otherwise noted) at 10 °C and were completed within one week of sample collection. Two time-course experiments with periodic sampling for CH_4 consumption were conducted on all 10-cm core sections that were extruded into Mason jars from each 40 or 60 cm core. The first experiment lasted 24 h during which the decrease in CH_4 concentration was monitored after initial equilibration with the atmosphere. The second experiment was 12 h in length and initial atmospheres were adjusted to ~ 500 ppm CH_4. We also studied $^{14}CH_4$ oxidation using 25 to 100 g aliquots of homogenized soil from each 10-cm section of a single 40 or 60 cm core. Soil samples in 0.25-liter jars were equilibrated with a free-air atmosphere and amended with microliter quantities of microbially-produced $^{14}CH_4$ (Daniels & Zeikus 1983) tracer (3.5 kBq; specific activity 2005 MBq $mmol^{-1}$). Tracer addition increased the headspace CH_4 concentration by about 8%. Methane oxidation was terminated after 12 h by adding 0.2 cm^3 C_2H_2 (Bédard & Knowles 1989) and the jars plus contents were frozen until tracer recovery. Samples were

thawed and jar headspaces were flushed with He into a stripping/oxidation line (Whalen et al. 1990) where $^{14}CO_2$ was trapped directly and $^{14}CH_4$ was trapped as $^{14}CO_2$ after combustion. Soils were freeze-dried and assayed by dry combustion for ^{14}C incorporated in microbial biomass (Whalen et al. 1990)

Physical and chemical properties of the soil cores were determined at the end of these studies. Soil pH was measured potentiometrically according to McLean (1982). Soil moisture was determined gravimetrically and is expressed as percent of oven-dried (105 °C) mass. Organic content was determined by loss on ignition (550 °C) of oven-dried samples, and particle density was measured pycnometrically. Soil bulk density was computed as the quotient, over-dried mass divided by the field volume. Air-filled porosity was computed as the field volume minus the liquid and solid volumes. Determination of soil physical properties and calculations follow Klute (1986).

Methane determinations were made by flame ionization detection gas chromatography with a precision of $<1\%$ (Whalen & Reeburgh 1988); calibration gases are relatable to standards from the National Institute for Technology and Standards. Sample analysis for CH_4 was completed within a few hours of collection for field samples and immediately upon sampling in laboratory experiments.

Radon-222 activity was determined by scintillation counting of gas samples contained in Lucas cells. Counting was done in either a dual channel alpha scintillation counter (Applied Techniques) or a portable radon monitor (Pylon Model AB-5), both of which accomodated our counting cells. Counting cells were constructed of pyrex or quartz bulbs (~ 100 cc volume) equipped with a Swagelok quick-connect fitting to permit evacuation and introduction of soil gas samples. The interiors of the cells were coated with silver-activated ZnS (Lucas 1957), which was supported by either a thin coating of stopcock grease or a layer of clear Krylon paint. Cell backgrounds and efficiencies were monitored continuously. Backgrounds averaged 0.39 cpm. Counting cell efficiencies (75%) were determined by counting air from a sealed glass tube containing a ^{226}Ra standard supported on moist Mn-coated acrylic fibers (Butts et al. 1988). The counting cells were equilibrated for at least 3.5 h so that measured counts are the sum of alpha decay from ^{222}Rn and its short-lived daughters, ^{218}Po and ^{214}Po. All ^{222}Rn data were decay-corrected to the time of sampling. The precision of a ^{222}Rn standard (228 dpm) determination is 3%.

Results and discussion

Soil properties

A litter layer was characteristic of all sites, but the overlying moss carpet at BS2 and UP3A resulted in lower mean soil temperatures to 60 cm at BS2 (1.5 °C) and UP3A (2.7 °C) than at AS2 (4.5 °C) and NB2 (4.1 °C). Soil temperatures showed little variation with depth at any station, ranging about 2 °C from the surface to 60 cm (Fig 1). The dark surface, organic zone graded into a tan mineral horizon below about 7 and 15 cm at UP3A and BS2, respectively, while the transition began at about 4 cm at the deciduous sites. Bulk density (ρ_b) was lower and soil organic content, moisture content and gas-filled porosity (ϕ_g) were higher in the 0 to 10 cm and 10 to 20 cm zones at the spruce sites (particularly BS2) than at the hardwood sites (Table 1). Soils were almost entirely mineral below 30 cm at BS2 and below 20 cm at all other sites. Soil physical properties varied little below these depths. Soils were neutral or acidic with pH values varying from 4.9 to 7.4 (Table 1). Lowest soil pH was observed at coniferous sites, and pH increased with depth at all sites. Data given here for differences in pH, moisture, temperature and organic content of deciduous and coniferous taiga soils are consistent with similar reports for soils in this biome (Flanagan & Van Cleve 1983; Viereck et al. 1983; Bonan & Shugart 1989; Van Cleve et al. 1991).

Soil CH_4 distributions

Soil CH_4 concentrations decreased with depth at all four study sites (Fig. 2). Surface soil CH_4 concentrations were about 1.75 ppm, reflecting the ambient atmospheric concentration. Soil CH_4 concentrations at BS2 decreased rapidly with increasing depth to 0.14 ppm at 60 cm (Fig. 2a). Soil CH_4 concentrations at the remaining sites also showed a sharp decrease with increasing depth; however, CH_4 concentrations reached a minimum of about 0.10 ppm at a depth of 30 or 40 cm and remained constant at that concentration to 60 cm (Fig. 2b—d).

Soil CH_4 distributions in Fig. 2 suggest an extensive zone of CH_4 oxidation, no zone of CH_4 production and an atmospheric source of CH_4 for soil methanotrophs. In agreement with our data, Central Panamanian forest and agricultural soils had CH_4 concentrations at 20 and 40 cm that were less than half the atmospheric value (Keller et al. 1990), while monthly averaged soil CH_4 profiles in a mixed hardwood forest showed a continuous decrease from near-atmospheric values at 2 cm to < 0.25 ppm at 15 cm (Crill 1991). German forest and Canary Island volcanic soils had

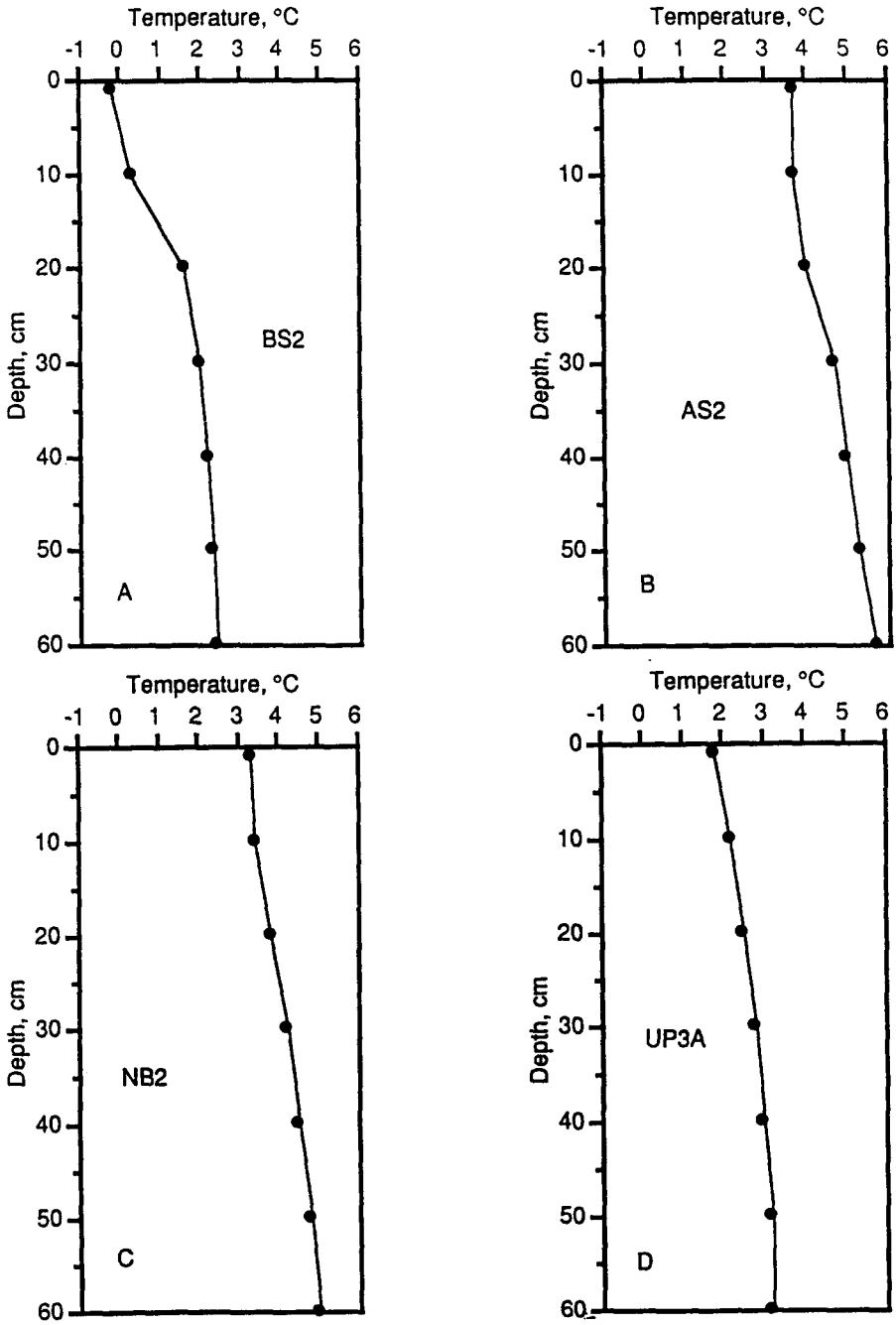

Fig. 1. Soil temperature distributions at experimental sites. A-BS2 (black spruce), B-AS2 (south-facing aspen), C-NB2 (north-facing birch), D-UP3A (white spruce). AS2 and NB2 were sampled on 9 October 1990; BS2 and UP3A were sampled on 11 October 1990.

Table 1. Soil properties at four sites in the Bonanza Creek Experimental Forest.

Depth	% Organic matter[a]				% Soil moisture[b]				ρ_b Bulk density[c]				Φ_g Gas-filled porosity[d]				pH			
cm	BS2	AS2	NB2	UP3A	BS2	AS2	NB2	UP3A	BS2	AS2	NB2	UP3A	BS2	AS2	NB2	UP3A	BS2	AS2	NB2	UP3A
0—10	91	16	24	50	491	56	69	139	0.04	0.39	0.45	0.25	0.84	0.64	0.53	0.73	5.0	6.4	5.9	4.9
10—20	13	2.5	3.8	4.1	66	28	30	30	0.13	0.88	0.78	1.21	0.77	0.43	0.48	0.41	5.0	6.3	6.3	5.4
20—30	5.4	2.0	2.2	2.4	42	23	23	27	0.91	1.26	1.43	1.57					5.6	6.4	6.6	5.9
30—40	4.0	1.8	1.9	2.0	35	17	23	26	1.84	1.32	1.73	1.31	0.12[e]	—	—	—	6.1	6.6	6.8	6.0
40—50	—	1.3	1.4	2.2	—	14	23	26	—	1.43	1.84	1.65						6.9	7.2	6.0
50—60	—	1.3	1.2	1.7	—	14	18	25	—	1.54	2.01	2.00	—	0.21[f]	0.14	0.15		7.0	7.4	6.2

[a] loss on ignition at 550 °C
[b] (w/w) on dry mass basis
[c] $g\ cm^{-3}$
[d] $cm^{-3}\ cm^{-3}$
[e] 20—40 cm depth interval
[f] 20—60 cm depth interval

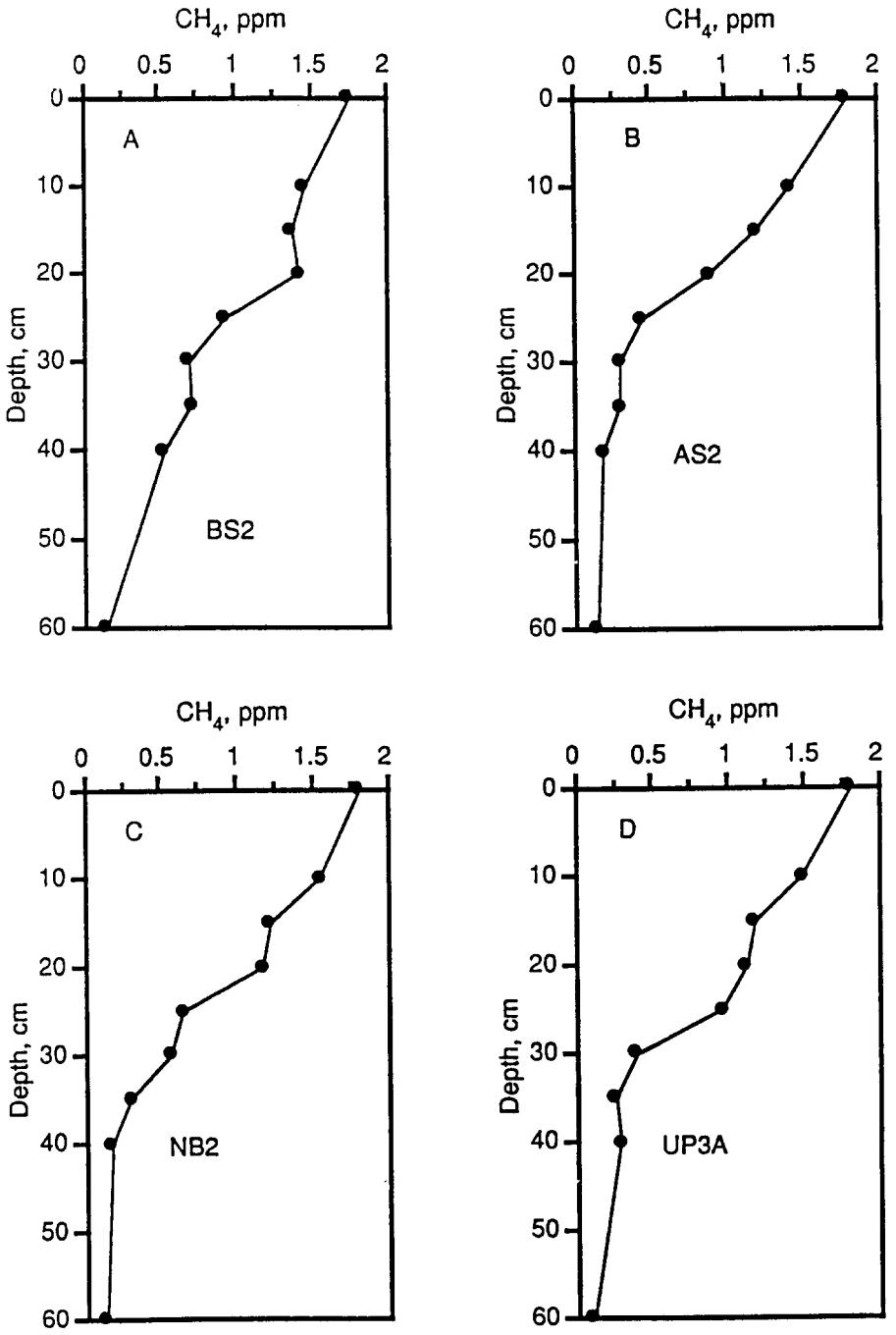

Fig. 2. Soil CH_4 distributions at experimental sites. Sites and sampling dates as in Fig. 1.

CH_4 profiles to 70 cm (Born et al. 1990) that were remarkably similar to CH_4 distributions in Fig. 2. In contrast, soil CH_4 profiles to 20 or 50 cm in mixed mesophytic and spruce forests showed zones where CH_4 was depleted and enhanced relative to atmospheric values, indicating both production and consumption of CH_4 (Yavitt et al. 1990a).

Soil CH_4 profiles and the following modification of Fick's first law (Campbell 1985) were used to estimate area-based rates of CH_4 oxidation:

$$J_{CH_4} = D_{CH_4}(0.9)\phi_g^{2.3}\,\Delta C_{CH_4} \quad (1)$$

where J_{CH_4} is the CH_4 flux (g m^{-2} s^{-1}), D_{CH_4} is the binary diffusion coefficient of CH_4 in air (0.194 cm^2 s^{-1} at 5 °C; Lerman 1979), ΔC_{CH_4} is the CH_4 concentration gradient at the air-soil interface determined by linear regression of the decrease in soil CH_4 with depth to 20 cm (g CH_4 cm^{-3} cm^{-1}), ϕ_g is fractional air-filled porosity (0 to 10 cm) and the constants 0.9 and 2.3 are recommended average values to account for tortuosity. Calculated rates of CH_4 oxidation at the four sites varied from 0.77 to 1.78 mg m^{-2} d^{-1} (Table 2). Yavitt et al. (1990a) used soil CH_4 distributions to estimate a CH_4 oxidation rate of 2 mg m^{-2} d^{-1} in a mixed mesophytic forest soil.

Table 2. Taiga soil CH_4 consumption rate summary.

Method	CH_4 Consumption, mg m^{-2} d^{-1}			
	AS2	NB2	BS2	UP3A
Static chamber[a]	0.55	0.22	0.62	0.55
Soil CH_4 profile	1.44	0.77	1.78	1.45
$^{14}CH_4$	2.32	1.57	1.52	0.87
^{222}Rn[b]	0.35	0.26	1.31	1.20
Jar, *in situ* CH_4[c]	0.10 ± 0.03	0.04 ± 0.01	1.51 ± 0.75	0.19 ± 0.16
Jar, +500 ppm CH_4[c]	71 ± 24	116 ± 22	110 ± 7	59 ± 8
Static Chamber[d] (+2000 ppm CH_4)	698	638	741	867

[a] Fluxes measured at station-CT1
[b] Fluxes measured at station-CT2
[c] Data ± standard error of mean (n = 2)
[d] Fluxes measured at station-CT3, -CT4, or -CT5

Chamber CH_4 time-course experiments

Headspace CH_4 decreased continuously from an initial concentration of about 1.8 ppm to a final concentration of 1.20 to 1.57 ppm in all 0.75 h

static chamber time-course experiments (Fig. 3). Methane oxidation rates were calculated from chamber geometry and regression analysis of headspace CH_4 concentration versus time (Whalen & Reeburgh 1988). Most studies using static chamber experiments to assess rates of CH_4 oxidation in soils have fit a linear function to the concentration versus time data (e.g. Steudler et al. 1989), although an exponential model has also been used (Keller et al. 1990; Mosier et al. 1991). We employed a linear function because the goodness of fit ($r^2 = -0.96$ to -0.98) was not significantly improved by use of an exponential model.

Methane oxidation rates in static chamber experiments varied from 0.22 to 0.62 mg m^{-2} d^{-1} (Table 2), in close agreement with the May through September 1990 median CH_4 oxidation rates of 0.26 to 0.56 mg m^{-2} d^{-1} reported for these same sites (Whalen et al. 1991). These CH_4 oxidation rates fall toward the low end of net CH_4 oxidation rates reported from other studies using static chamber techniques in non-waterlogged soils. Temperate evergreen and deciduous forests showed mean CH_4 oxidation rates of 0.4 to 4.15 mg m^{-2} d^{-1} (Keller et al. 1983; Steudler et al. 1989; Crill 1991), while tropical forest soils had average CH_4 oxidation rates of 0.14 to 0.8 mg m^{-2} d^{-1} (Keller et al. 1986; Goreau & de Mello 1988; Keller et al. 1990). Net CH_4 oxidation rates ranged to 2.7 mg m^{-2} d^{-1} in moist tundra (King et al. 1989; Whalen & Reeburgh 1990a, b; Barlett et al. 1992), varied from 0.14 to 1.46 mg m^{-2} d^{-1} in semiarid grasslands (Mosier et al. 1991) and averaged 1.25 mg m^{-2} d^{-1} in broadleafed savannah (Seiler et al. 1984).

Results of the 24 h time-course experiments in a free-air atmosphere indicated that soil microbes at all sites could consume CH_4 to threshold concentrations ranging from <0.10 to 0.87 ppm (Table 3). A low threshold for CH_4 oxidation is not clearly correlated with a high *in situ* rate of CH_4 oxidation. Station NB2 had the lowest rate of CH_4 oxidation in static chamber experiments (Table 1), but three additional stations at NB2 showed the lowest thresholds for CH_4 oxidation (Table 3). Stations at UP3A demonstrated high thresholds for CH_4 oxidation (Table 3), but weekly May through September sampling of four other permanent stations within each site type (Whalen et al. 1991) showed a significantly higher median rate of CH_4 oxidation at UP3A (0.40 mg m^{-2} d^{-1}) than at NB2 (0.26 mg m^{-2} d^{-1}). The lack of a negative relationship between CH_4 oxidation thresholds and rates may result from a small sample size, local spatial variability in soil physical and biological characteristics and the small range in low rates of CH_4 oxidation. Overall, these data are consistent with results of similar chamber and jar experiments in moist tundra and landfill soils, which showed median thresholds for CH_4 oxidation ranging from 0.23 to 0.37 ppm (Whalen et al. 1992).

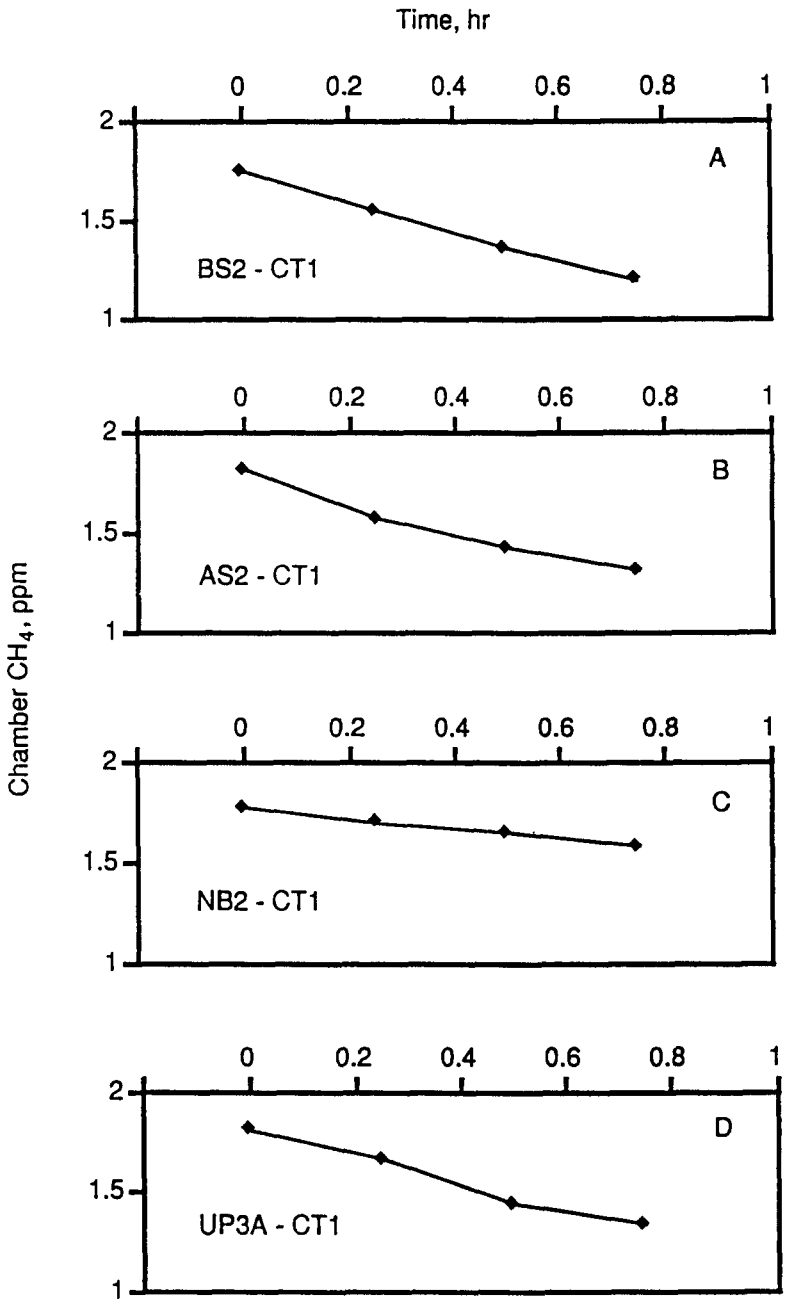

Fig. 3. Static chamber CH_4 time-course measurements at experimental sites. Station 1 (CT1) was sampled at each site. Sites and sampling dates as in Fig. 1.

Table 3. Methane oxidation threshold and capacity experiments.

	Headspace CH_4 Concentration, ppm					
	Free-air atmosphere			Amended atmosphere		
Station	Date	t_0	t_f	Date	t_0	t_f
AS2-CT3	8 Jun	1.86	0.51	14 Jun	22.2	0.60
AS2-CT4		1.88	0.26		133	0.78
AS2-CT5		1.85	0.54		1403	9.69
NB2-CT3	27 Jul	1.67	BD	10 Aug	2829	18.51
NB2-CT4		1.73	0.10		160	12.52
NB2-CT5		1.75	0.17		21.0	1.08
UP3A-4	22 Jun	1.78	0.81	2 Jul	21.0	0.75
UP3A-5		1.80	0.87		166	0.90
UP3A-6		1.82	0.84		1879	0.84
BS2-CT3	2 Jul	1.84	BD	5 Jul	20.4	BD
BS2-CT4		1.75	0.12		141	BD
BS2-CT5		1.76	0.46		1657	0.56

BD = below detection limit (0.10 ppm). Initial (t_0) and final (t_f) headspace CH_4 concentrations in static chamber experiments. Chambers were initially equilibrated with a free-air atmosphere in CH_4 oxidation threshold experiments. Chamber headspace CH_4 concentrations were adjusted to ~20, 200 and 2000 ppm in oxidation potential experiments. Data for t_f were taken after 24 h.

Results of amended atmosphere experiments suggest that these soils have a high CH_4 oxidation capacity (Table 3). Methane concentrations in chamber headspaces were sub-atmospheric within 24 h following CH_4 addition in all but three experiments, despite adjustment of initial concentrations to levels ~10^3-fold above ambient in some cases. Previous chamber and jar experiments on tundra and landfill cover soils (Whalen & Reeburgh, 1990b; Whalen et al. 1990) show an immediate response to CH_4 amendments, and undetectable changes in response for periods up to a week. These observations suggests that CH_4-oxidizing activity is present continously and that induction of activity is not important. The final headspace CH_4 concentration was higher than expected at NB2-CT3 and NB2-CT4, based on the results of experiments involving free-air atmospheres. Soil moisture content (0 to 10 cm) and temperature (mean to 13 cm) were similar at about 60% (w/w) and 13 °C in nearby sites on 27 July and 10 August, suggesting that differences in microbial population size or structure between dates rather than physical variables account for the observed patterns of CH_4 utilization.

Headspace CH_4 concentrations at t_1 and t_2 (between 1 and 2 h after

CH_4 addition) in amended atmosphere experiments (+ ~ 2000 ppm) were used to estimate potential CH_4 oxidation rates varying from 638 to 867 mg m^{-2} d^{-1} for these sites (Table 2).

Laboratory time-courses under a free-air atmosphere

Headspace CH_4 concentrations decreased in most laboratory experiments involving 10-cm core sections initially equilibrated with a free-air atmosphere. First order rate constants, k(d^{-1}), were determined from a least squares fit of ln[CH_4] versus time. Slopes were highly significant for 41 of the 44 core sections ($p < 0.05$; $n = 5$ or 6), indicating that most soil samples were capable of CH_4 oxidation to 60 cm. Methane oxidation rate constants were generally around −0.3 to −1.5 d^{-1}, although values as high as −25 d^{-1} were found for some core sections at BS2. The highest (most negative) rate constants were generally observed for 10 to 20 cm or 20 to 30 cm core sections at all sites; no other pattern was noted.

Only a few soil CH_4 oxidation rate profiles have been reported. Methane consumption increased with increasing depth to 30 cm in generally waterlogged, moss-derived peats (Yavitt et al. 1990b) but showed no depth-dependence in peat pore water to 30 cm (Yavitt et al. 1988). Methane oxidation was observed in core sections from the <10 cm organic horizon in well-drained tundra soil (Whalen & Reeburgh 1990b), to the water table (12 cm) in arctic hummocks (Whalen et al. 1992) and to 8 cm in the inorganic cover soil of a retired landfill (Whalen et al. 1990).

The mass of CH_4 in each 10 cm soil zone was calculated from ϕ_g (Table 1), the soil CH_4 profiles (Fig. 2) and the core volume. The *in situ* rate of CH_4 oxidation was calculated as the product of the first-order rate constant and the mass of soil CH_4. Rates are normalized to soil mass and show a maximum in the 10 to 20 cm mineral zone at all sites except NB2 (Fig. 4). When data for each core segment are expressed on a volume basis, this subsurface maximum in the CH_4 oxidation rate is even more pronounced at BS2, AS2 and UP3A, and is evident at NB2 as well. This results from the relatively low surface ρ_b (Table 1). Overall, the results indicate that CH_4 oxidation occurs to about 30 (Fig. 4a-c) or 50 cm (Fig. 4d) in these soils, and below that depth the process is limited by substrate availability (Fig. 2).

Methane oxidation rates for each 10 cm core section were summed to give area-based rates for each site. Methane oxidation rates varied from 0.04 to 1.51 mg m^{-2} d^{-1} (Table 2), with highest area-based rates occurring at BS2 due to the exceptional rate of CH_4 oxidation in the 10 to 20 cm soil zone (Fig. 4a).

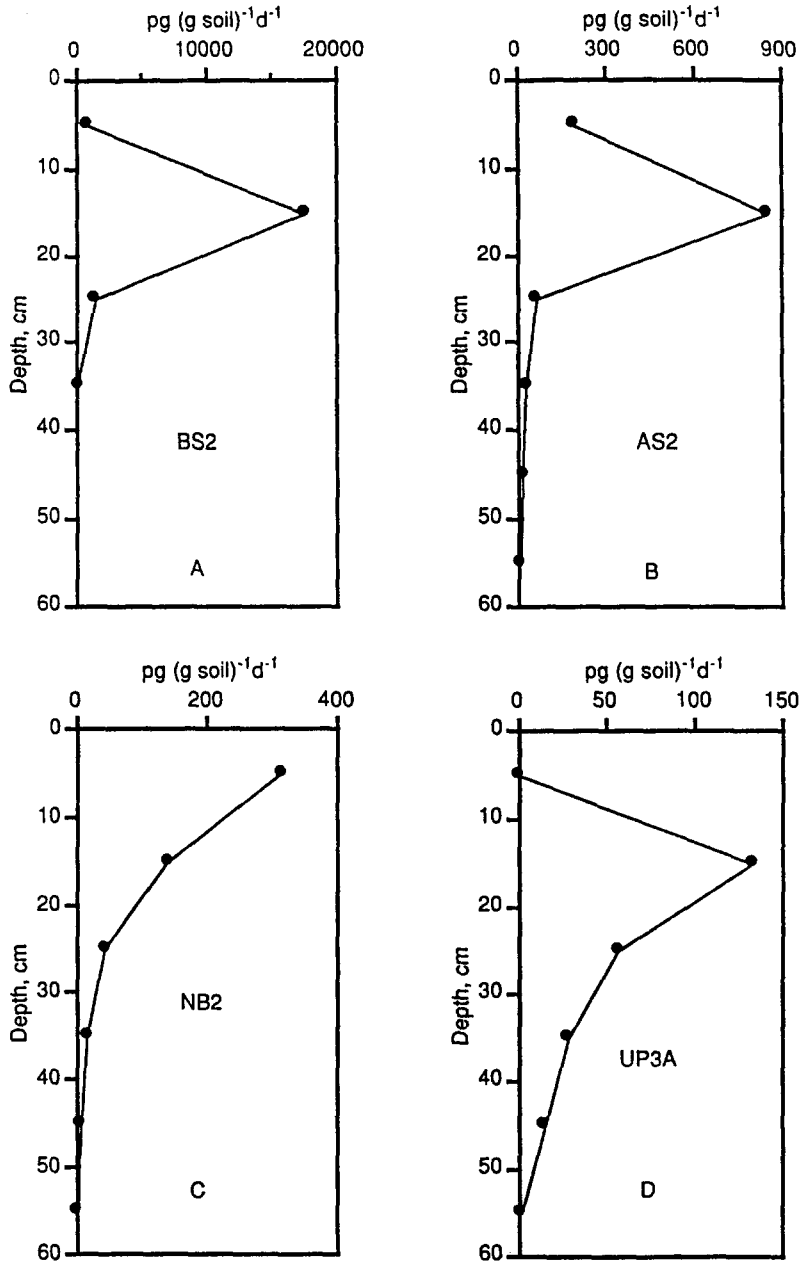

Fig. 4. Methane oxidation rates derived from jar experiments on 10 cm core segments from experimental sites. Each segment was exposed to a free-air atmosphere. Rates were corrected to *in situ* CH_4 concentrations and are plotted at the midpoint of each depth interval. Sites and sampling dates as in Fig. 1.

Laboratory time-courses under an amended atmosphere

Most laboratory experiments involving 10 cm core sections amended with ~ 500 ppm CH_4 showed a decrease in headspace CH_4 concentration over a 12 h period. A linear decrease in headspace CH_4 concentration indicated zero order consumption, that is, oxidation rates were maximum and independent of CH_4 concentration. Regression analysis gave significant slopes for 43 of 44 core sections ($p < 0.05$; $n = 4$). High slopes (k values) in free-air experiments were not always associated with high slopes in amended atmosphere experiments; coefficients of correlation (Kendall's τ) were significant ($n = 8$ or 12; $p < 0.05$) only for BS2 and NB2 when data within each site type were compared. The lack of correlation between these variables at the other two sites likely reflects the small sample size coupled with the small range in data. However, we cannot discount the possible adverse effect of repeated sample handling or the possibility that genuine depth-dependent differences exist in the microbial consortium and its response to *in situ* and elevated substrate levels.

Maximum or potential rates of CH_4 oxidation for each core section were calculated from the soil mass, jar headspace volume, and slope of the linear regression of CH_4 concentration versus time. Potential CH_4 oxidation rates normalized to soil mass show a maximum in the 10 to 20 cm zone at BS2 only (Fig. 5), in contrast to calculated *in situ* CH_4 oxidation rates normalized to soil mass for these same core sections (Fig. 4). Volume-based potential rates of CH_4 oxidation were maximum in the 10 to 20 cm soil zone for all cores, in agreement with data for volume-based *in situ* rates of CH_4 oxidation for these cores. The data indicate that all soil intervals except the 0 to 10 and 30 to 40 cm sections at BS2 (Fig. 5a) and the 50 to 60 cm section at NB2 (Fig. 5c) are capable of rapid CH_4 oxidation if substrate is available.

Potential rates of CH_4 oxidation varied from 0 to 1350 ng (g soil)$^{-1}$ d^{-1} (Fig. 5) and depended on both the size of the CH_4-oxidizing microbial population and soil physical characteristics. The average oxidation rate of about 140 ng CH_4 (g soil)$^{-1}$ d^{-1} is roughly 10^3-fold lower than the rate of 130 to 280 μg CH_4 (g soil)$^{-1}$ d^{-1} we calculate from data given by Megraw & Knowles (1987) for humisol soil not previously exposed to exogenous CH_4 and is 10^2-fold lower than the V_m (maximum oxidation rate) of 60 μg CH_4 (g soil)$^{-1}$ d^{-1} determined by kinetic analysis of CH_4 utilization by composites of a landfill cover soil (Whalen et al. 1990). Data from all 10 cm depth intervals were summed to estimate area-based potential CH_4 oxidation rates at each site. Rates varied from 59 to 116 mg CH_4 m^{-2} d^{-1} (Table 2).

The subsurface maximum in volume-based rates of *in situ* and potential

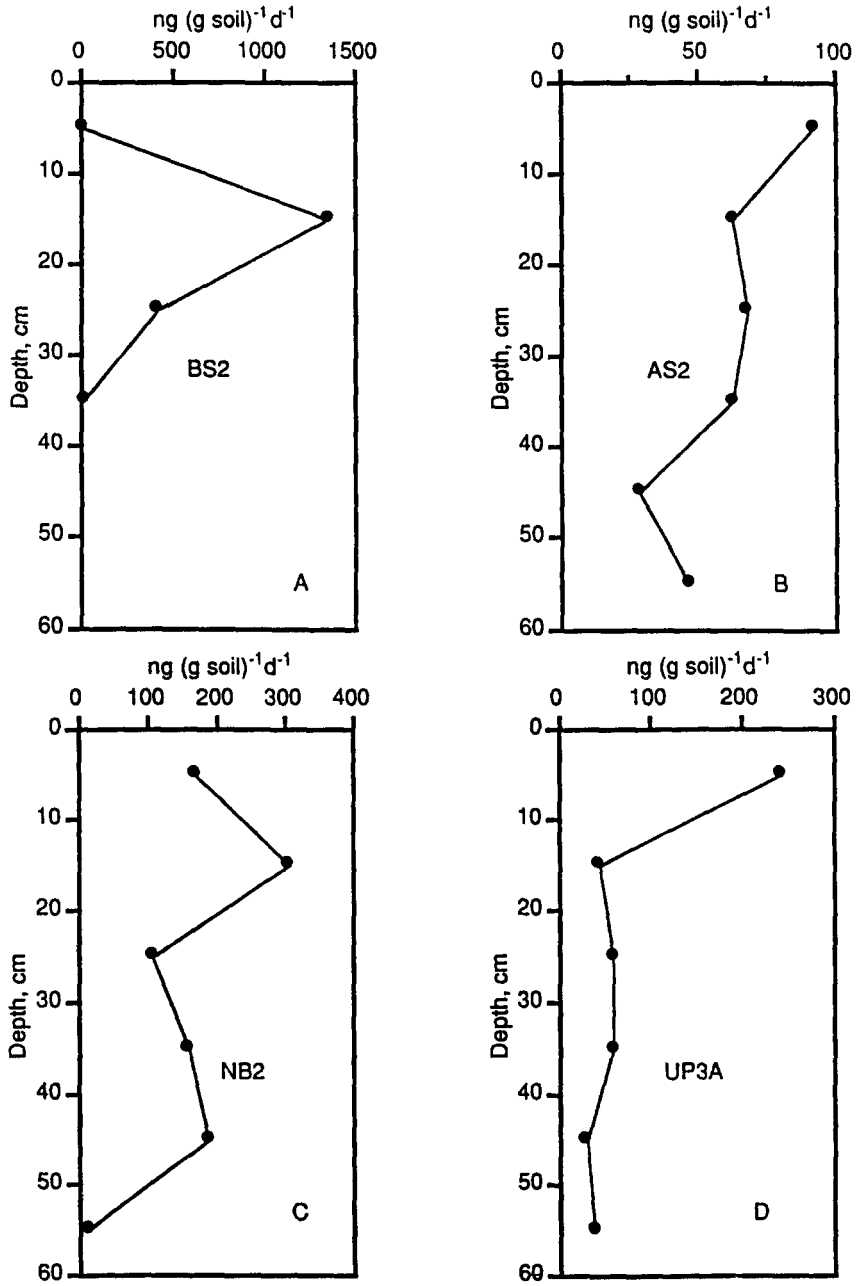

Fig. 5. Potential methane oxidation rates derived from jar experiments on 10 cm core segments from experimental sites. Each segment was exposed to an amended (+500 ppm CH_4) atmosphere. Rates are plotted at the midpoint of each depth interval. Sites and sampling dates as in Fig. 1.

CH_4 oxidation is surprising. It may result from the large surface area in the less porous mineral soil (Table 1) or soil moisture. We found little or no CH_4 oxidation in the 0 to 2 cm horizon in well-drained tundra (Whalen & Reeburgh 1990b) and landfill cover soils (Whalen et al. 1990), regardless of organic content. A reduction in soil moisture content from the ambient level of 11% to 6% severely reduced CH_4 oxidation in a landfill cover soil (Whalen et al. 1990), suggesting a high sensitivity to drying. Soils adjacent to the atmosphere experience wide fluctuations in moisture, which may prevent establishment of a vigorous community of methanotrophs. Atmospheric CH_4 (the source of energy, reducing equivalents, and cell carbon for soil methanotrophs) is available below the surface organic soil horizon. This zone may function as a highly permeable buffer to variations in subsurface soil moisture.

Laboratory experiments on $^{14}CH_4$ oxidation

All 10 cm core segments exposed to $^{14}CH_4$ except the two deepest (40 to 60 cm) at NB2 showed CH_4 oxidation, as evidenced by the appearance of $^{14}CO_2$ and ^{14}C-labeled biomass (Fig. 6). These data confirm that decreases in headspace CH_4 resulted from microbial CH_4 oxidation in free-air (Fig. 4) and amended atmosphere (Fig. 5) time-course experiments involving core sections to 60 cm. An average (± 1 S.D.) of 39 $\pm$ 30% of the added label was used and 101 $\pm$ 7% was recovered in these experiments. Data from each site were summed to give area-based CH_4 oxidation rates that varied from 0.87 to 2.32 mg m^{-2} d^{-1} (Table 2).

The fraction of oxidized CH_4 that was incorporated into microbial biomass (m^2 basis) was similar among sites, ranging from 34 to 43%, with the balance respired as $^{14}CO_2$. There were no depth-dependent differences in the partitioning of label between ^{14}C-biomass and $^{14}CO_2$ (Fig. 6). No pattern is evident for other studies examining the distribution of end products of $^{14}CH_4$ oxidation in soils, and our data are well within the range of results given in earlier investigations. For example, the fraction of oxidized $^{14}CH_4$ that was converted into biomass was 15 to 22% and 50 to 68% for peat (Yavitt et al. 1988; 1990b) and forest soils (Yavitt et al. 1990a) in Appalachia. In addition, 54%, 69% and $>70\%$ of the $^{14}CH_4$ oxidized in tundra (Whalen & Reeburgh 1990b), landfill (Whalen et al. 1990) and cultivated humisol (Megraw & Knowles 1987) soils, respectively, was recovered as ^{14}C-biomass.

The CH_4 relaxation depth, ξ, is the order of magnitude of the projected path length in the soil for a CH_4 atom before oxidation (Søgaard-Hansen & Damkjaer 1987). Methane relaxation depths at each site were calculated from soil CH_4 distributions (Fig. 2) and the relationship $C_z = C_0$

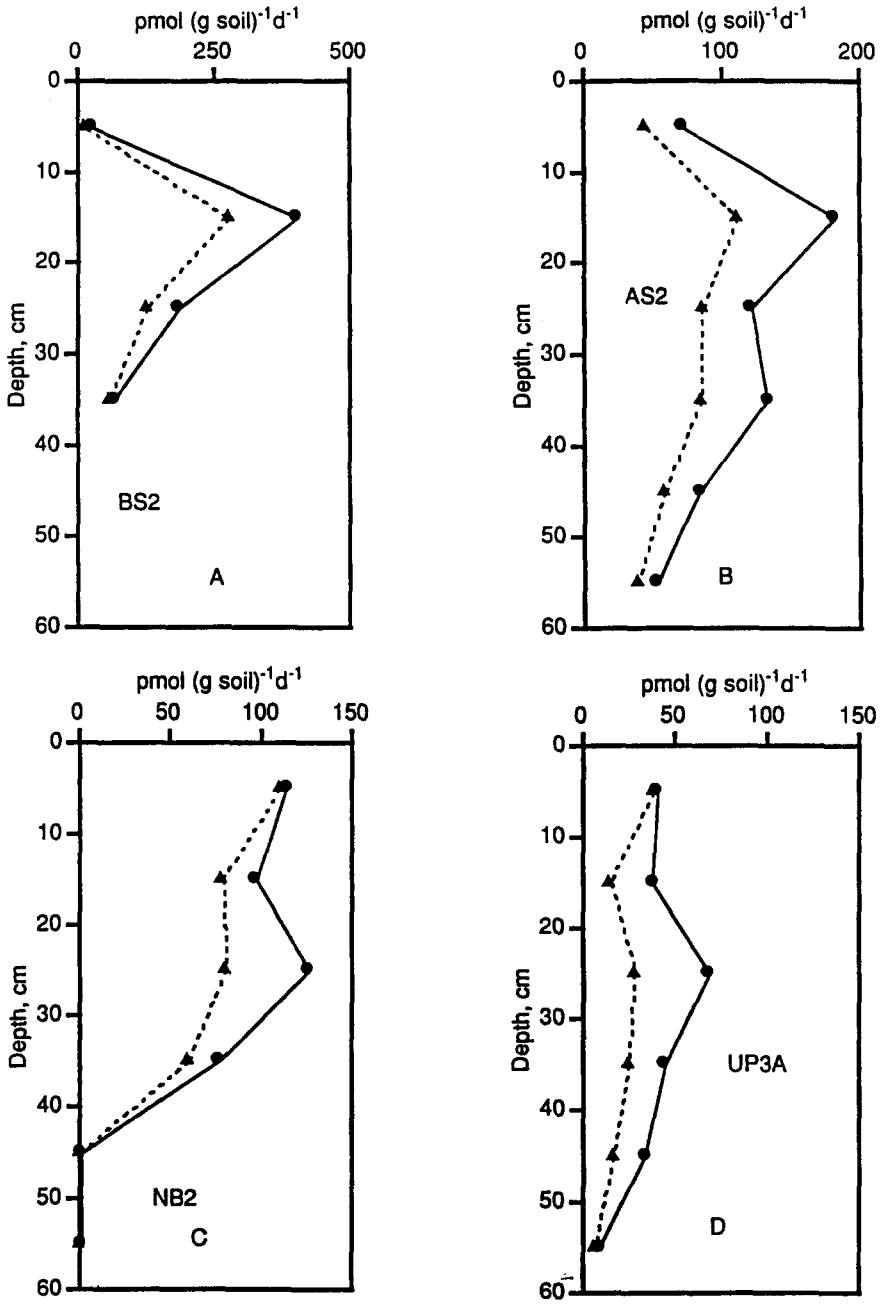

Fig. 6. Results from $^{14}CH_4$ addition experiments on core sections from experimental sites. Solid line is $^{14}CO_2$ production rate; Dashed line is ^{14}C-biomass production rate. Sites and sampling dates as in Fig. 1.

exp($-z/\xi$) given by Born et al. (1990), where C_z and C_0 are CH_4 concentrations at depth z and in the atmosphere. Values of ξ ranged from 23 to 39 cm, so we expected little or no CH_4 oxidation below this depth.

However, amended atmosphere and radiocarbon jar experiment indicated that many soils were capable of significant CH_4 oxidation to 60 cm (Fig. 5b—d and Fig. 6b, d). Addition of substrate to resting microbial cells can stimulate metabolic activity (Roszak & Colwell 1987), which may account for the CH_4 oxidation observed in core segments taken below ξ. Another possible explanation for the high CH_4 oxidizing potential at depth is fortuitous metabolism by nitrifying bacteria. Nitrifiers exist in soils and marine nitrifiers have been demonstrated to oxidize CH_4 (Ward 1987, 1990). Diffusion and percolation may supply sufficient NH_3, O_2, and CO_2 to support chemoautotrophic NH_3 oxidation deep within the soil. Addition of CH_4 to soil cores in jar experiments may provide a competing substrate for ammonia monooxygenase, which has a wide specificity (Bédard & Knowles 1989).

^{222}Rn-calibrated CH_4 fluxes

Static chamber experiments assessing soil ^{222}Rn flux showed a continuous increase in headspace ^{222}Rn over the 0.5 h time-course (Fig. 7), in contrast to similar experiments measuring CH_4 flux (Fig. 2). Rn-222 fluxes varied from 0.14 to 0.45 atom cm^{-2} s^{-1} and averaged ($\pm$1 S.D.) 0.35 $\pm$ 0.14 atom cm^{-2} s^{-1}. The mean ^{222}Rn emission rate agrees with the average flux of 0.35 atom cm^{-2} s^{-1} reported for tropical forest soils (Trumbore et al. 1990) and lies between the mean fluxes of 0.22 and 1.07 atom cm^{-2} s^{-1} found in sandy and clayey temperate forest soils (Dörr & Münnich 1990). These studies also used static chambers to determine ^{222}Rn fluxes.

Soil ^{222}Rn activity increased with depth (Fig. 8), consistent with the observed flux (emission to the atmosphere). The positive slopes associated with time-courses for soil ^{222}Rn fluxes (Fig. 7) and depth distributions of soil ^{222}Rn (Fig. 8; z positive downward from soil surface) as well as the negative slopes observed for soil CH_4 profiles (Fig. 2) were also reported for German soils showing net CH_4 consumption (Born et al. 1990; Dörr & Münnich 1990). However, our ^{222}Rn profiles, derived from limited data, deviate from a theoretical steady state profile that decreases exponentially to the soil surface from a constant value at depth (Dörr & Münnich 1987). Rn-222 profiles similar to those in Fig. 8 have also been reported for stratified tropical forest soils (Trumbore et al. 1990).

Soil gas (^{222}Rn and CH_4) profiles and ^{222}Rn chamber experiments were used to calculate ^{222}Rn transport-corrected rates of area-based CH_4 oxidation according to Dörr & Münnich (1987):

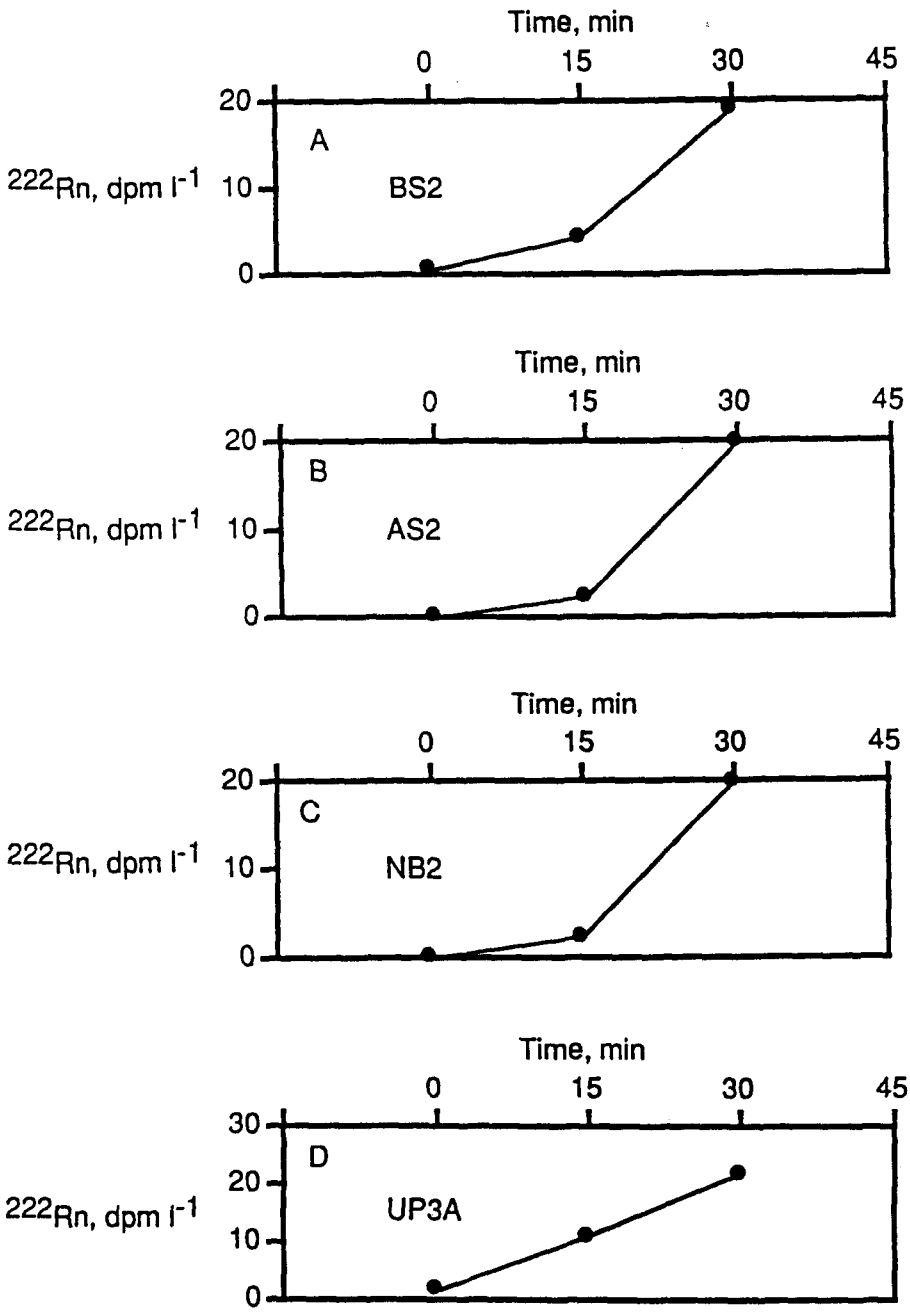

Fig. 7. Static chamber ^{222}Rn time-course measurements at experimental sites. Station 2 (CT2) was sampled at each site. Sites and sampling dates as in Fig. 1.

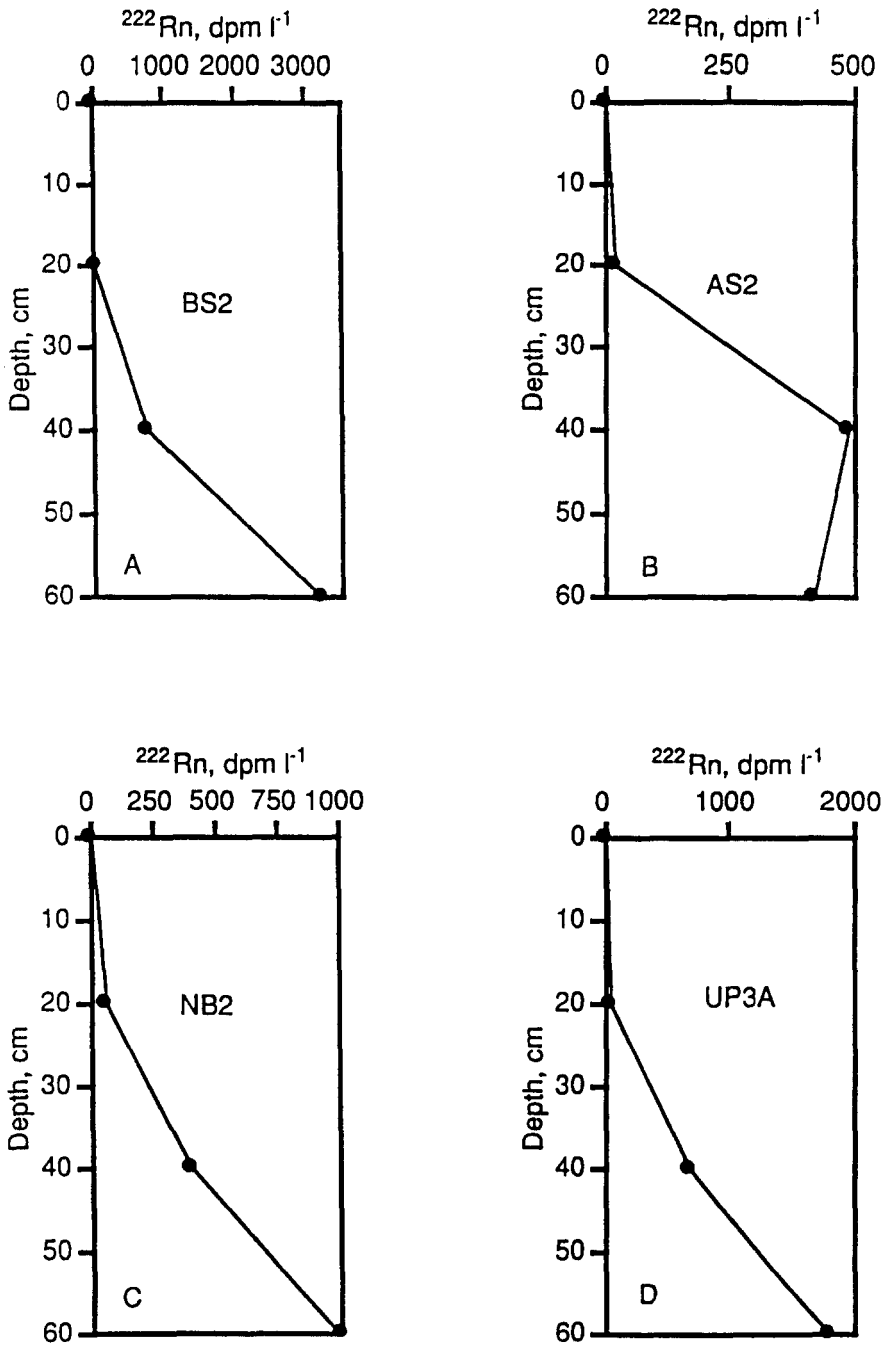

Fig. 8. Soil ^{222}Rn distributions at experimental sites. Sites and sampling dates as in Fig. 1.

$$J_{CH_4} = J_{Rn} (D_{CH_4}/D_{Rn}) (\Delta C_{CH_4}/\Delta C_{Rn}) \quad (2)$$

where J's are fluxes of CH_4 (mg m^{-2} d^{-1}) and ^{222}Rn (dpm m^{-2} d^{-1}), D's are binary diffusion coefficients of CH_4 (0.194 cm^2 s^{-1}; Lerman 1979) and Rn (0.1 cm^2 s^{-1}; Tanner 1964) in air and ΔC's are soil concentration gradients of ^{222}Rn (dpm cm^{-3} cm^{-1}) and CH_4 (mg cm^{-3} cm^{-1}). Radon-222 fluxes were determined by linear regression of the ^{222}Rn increase in the chamber headspace. Soil CH_4 concentration gradients were determined for Equation 1 above and soil ^{222}Rn concentration gradients were calculated as the difference between ^{222}Rn activities at 20 and 0 cm. Trumbore et al. (1990) calculated ΔC_{Rn} from a third order polynomial fit to ^{222}Rn distributions in stratified soils similar to those in Fig. 8, but noted that the derivative was approximately equal to the slope of a linear fit to data in the 0 to 20 cm soil zone. Methane oxidation rate estimates from the ^{222}Rn method varied from 0.19 to 1.60 mg m^{-2} d^{-1} (Table 2).

Comparison of information from each measure

The ^{222}Rn technique provides an independent, indirect check on chamber CH_4 flux determinations. Both methods are nondestructive, so permanent sampling stations can be visited repeatedly. The ^{222}Rn method gave CH_4 oxidation rate estimates that were 65 to 220% of the static chamber-derived estimates (Table 2). The methods appear to compare poorly when data are cast as percent difference, but we feel that agreement is satisfactory for two reasons.

First, both methods clearly indicate that CH_4 fluxes are low, but both methods also have the potential for large errors. An error in determining a small concentration change with time at sub-atmospheric CH_4 concentrations in static chamber experiments results in a relatively large error in the flux estimate. A 0.1 ppm error in CH_4 concentration determination at t_0 or t_f in a static chamber flux experiment will bias the slope of the regression equation used to calculate flux, and will reduce the CH_4 oxidation rate estimate, for example, for AS2. The rate would drop from 0.55 (Table 2) to 0.45 mg m^{-2} d^{-1}, or 20%. The largest source of error in our ^{222}Rn technique probably results from determining ΔC_{Rn} in Equation 2 using two points (0 and 20 cm) in a heterogeneous soil zone (Table 1). A 20% error here is not unreasonable and could increase the CH_4 flux estimate at AS2 from 0.35 (Table 2) to 0.44 mg m^{-2} d^{-1}. Steps were taken in the 1991 field season to reduce both sources of error. The number of gas samples collected in the 0 to 20 cm soil zone was increased to better estimate ΔC_{Rn}, and the sampling interval was decreased in 0.75-h static

chamber CH_4 flux determinations to add observations and reduce the influence of outliers.

The second indication that the two techniques did not yield appreciably different CH_4 oxidation rate estimates relates to spatial heterogeneity in microbial activity. Experiments at each site were conducted simultaneously, but at different stations. Hence, differences in rate estimates may simply reflect local variability. The ^{222}Rn flux estimates in Table 2 lie well within the range of estimates determined by weekly 0.75-h time-courses for chamber CH_4 fluxes at these same stations in 1990 and 1991 (Whalen et al. 1991 and unpublished). A better experimental design involves use of a single station to determine CH_4 and ^{222}Rn fluxes simultaneously with a static chamber. Dörr and Münnich (1990) found that the annual mean ^{222}Rn-calibrated CH_4 flux exceeded the direct static chamber flux by a factor of 4 with this approach. The difference was attributed to a reduction in the concentration gradient for soil CH_4 during static chamber experiments.

Rn-222 flux and profile measurements also give information on the effective soil diffusivity of the gas under investigation. The effective diffusivity for CH_4 (P_{CH_4}) is calculated (Born et al. 1990) as:

$$P_{CH_4} = (D_{CH_4}/D_{Rn})\,(J_{Rn}/\Delta C_{Rn}) \qquad (3)$$

Values of P_{CH_4} were 0.012, 0.013, 0.053 and 0.078 $cm^2\ s^{-1}$ for NB2, AS2, UP3A and BS2. This rank order is consistent with the expected order based on ϕ_g and ρ_b (Table 1). Effective diffusivities in these soils were lower than D_{CH_4} (0.194 $cm^2\ s^{-1}$) by a factor of 2 to 16, in reasonable agreement with the expected reduction (factor of 2 to 10) of free-air diffusivities of gases in unconsolidated porous media (Lerman 1979). Values of P_{CH_4} for deciduous sites are within the range reported by Born et al. (1990) for various European soils ($\sim$0.001 to 0.03 $cm^2\ s^{-1}$), whereas values for coniferous sites are higher. Effective diffusivities derived from ^{222}Rn studies (Equation 3) for all sites under a range of moisture and temperature regimes can be used to estimate CH_4 oxidation rates from Fick's first law ($J_{CH_4} = P_{CH_4}\,\Delta C_{CH_4}$) and soil CH_4 profiles. Calculation of P_{CH_4} for a wide range of soils provides a useful index of the ability of moist soils to consume atmospheric CH_4; P_{CH_4} limits CH_4 oxidation in nonwaterlogged soils where the atmosphere is the sole CH_4 source for soil methanotrophs.

Methane oxidation rates calculated from soil CH_4 profiles and Equation 1 were consistently 1.5 to 3.5-fold higher than estimates from static chambers (Table 2). This is a nondestructive (non-jar) technique that gives a rough estimate of *in situ* CH_4 oxidation rates. However, this estimate requires no information beyond that needed for other CH_4 oxidation rate

estimates, as ϕ_g and ΔC_{CH_4} are necessary components of CH_4 oxidation rate estimates from jar and ^{222}Rn experiments, respectively. Sources of error in Equation 1 may stem from the determination of ϕ_g in the stratified 0 to 10 cm soil zone or the application of "average" coefficients to correct D_{CH_4} for tortuosity. Values of $D_{CH_4}(0.9)\phi_g^{2.3}$ in Equation 1 vary from 0.041 to 0.117 $cm^2\ s^{-1}$ and overestimate P_{CH_4} if ϕ_g is accurately determined. We feel that the error lies in the coefficients used to adjust D_{CH_4}. These depend on both soil structure and moisture; Currie (1984) demonstrated that for a single soil type of varying moisture content no single relationship was satisfactory. In contrast, we are confident in our estimates for ΔC_{CH_4} in Equation 1 because soil CH_4 distributions similar to those in Fig. 2 were observed throughout the 1990 and 1991 thaw seasons.

Rates of *in situ* CH_4 oxidation estimated from jar experiments were lower than chamber-derived estimates at all sites except BS2 (Table 2), in contrast to the consistently high CH_4 oxidation rates estimated from soil CH_4 profiles. Decreased CH_4 oxidation rates in jar experiments relative to chamber-derived estimates are probably a consequence of disturbance of the soil during sample collection. The effects of sample collection, transport, and confinement on rates of microbial activity are well-documented, but totally unpredictable (Karl 1986). This method does not allow repeated sampling at a fixed station, unlike chamber methods. However, this method identifies soil zones of microbial activity, important information for modeling the response of soil methanotrophs to climate change.

The elevated rate of *in situ* CH_4 oxidation in the jar *vs.* chamber experiment at BS2 (Table 2) is consistent with our suggestion that sample handling reduced microbial activity. The high CH_4 oxidation rate estimate in the jar experiment clearly results from a substance "hotspot" (Fig. 5a). The soil CH_4 profile taken in the same area provides further evidence that this hotspot is a localized phenomenon; a more rapid decline in soil CH_4 concentration is not apparent in the 10 to 20 cm zone (Fig. 2a). Localized zones of enhanced microbial activity have frequently been found for soil denitrification (e.g. Parkin 1987), but we are unaware of similar reports for soil CH_4 oxidation.

Chamber experiments involving amended atmospheres are a nondestructure method of estimating potential CH_4 oxidation rates. Although results of these experiments suggest a high capacity for CH_4 oxidation in soils at all sites (Table 3), we cannot dismiss these potential rates (Table 2) as overestimates for two reasons. First, equilibration as well as microbial oxidation decreases the headspace CH_4 concentration immediately after chamber amendment. Added CH_4 can be expected to equilibrate with gases in the chamber headspace and air-filled pore space in surface, organic soil within a few minutes (Whalen & Reeburgh 1990b), but we

have no information concerning rates of equilibration with the more firmly packed subsurface mineral horizon. Therefore, we conservatively used time points >1 h after CH_4 addition to the chamber when calculating potential CH_4 oxidation rates. Second, lateral diffusion beneath soil collars may have allowed added CH_4 to escape the chambers. Relaxation depths ranged from 23 to 39 cm. Chamber collars extended to a soil depth of 15 or 20 cm, so loss of chamber CH_4 by diffusion was possible. We feel these losses were minimal. Chamber bases were firmly placed well into mineral soils of low ϕ_g (Table 1) and final headspace CH_4 concentrations (t_f) in all free-air and most amended atmosphere chamber experiments were well below atmospheric concentrations (Table 3).

Amended atmosphere jar experiments give an additional, conservative estimate of potential rates of CH_4 oxidation. The technique is destructive and sample handling may reduce rates of microbial activity, but confinement insures retention of added headspace CH_4. Jar experiments gave potential CH_4 oxidation rates that were only 7 to 18% of rates estimated from chamber experiments (Table 2). Nonetheless, these CH_4 oxidation rates of 59 to 116 mg m^{-2} d^{-1} were at least 10^2-fold higher than chamber estimates under a free-air atmosphere, providing convincing evidence for a high potential for CH_4 oxidation at all sites. We consider potential rates to be an intensive property of the system, while capacity is an extensive property.

The $^{14}CH_4$ experiment is also destructive, but it is the only technique capable of assessing the end products of CH_4 oxidation. Moreover, it unequivocally demonstrates that microbial CH_4 oxidation is responsible for loss of headspace CH_4 in other experiments. Sample handling may reduce the rate of CH_4 oxidation, and increasing the CH_4 pool by as much as 10^3-fold by tracer addition and equilibration with the atmosphere could enhance CH_4 oxidation. Clearly, $^{14}CH_4$-derived rates are not directly comparable to *in situ* rates measured using chamber techniques (Table 2).

Summary

These measures provide a range of information about CH_4 oxidation in boreal forest soils. They are not directly comparable in most cases, but give unique insights into the controls on microbial CH_4 oxidation. The short-term unamended chamber measurements, the ^{222}Rn-calibrated flux measurements, and the soil CH_4 distributions show independently that the soils are capable of oxidizing atmospheric CH_4. The jar experiments with free-air headspaces and soil CH_4 profiles give the depth distribution of CH_4 oxidation rates. The jar experiments and chamber measurements with

free-air headspaces show that CH_4 oxidation occurs at low thresholds ($\leqslant 0.9$ ppm). The $^{14}CH_4$-amended jar experiments show that the process is microbially-mediated and give the distribution of end products of CH_4 oxidation. The chamber and jar experiments with amended atmospheres give information on potential CH_4 oxidation rates and CH_4-oxidizing capacity. Methane oxidation in these moist soils consumes atmospheric CH_4 and may serve as a negative feedback on atmospheric CH_4 increases.

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