

Influence of atmospheric CO₂ enrichment on methane consumption in a temperate forest soil

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Abstract

Rates of atmospheric CH₄ consumption of soils in temperate forest were compared in plots continuously enriched with CO₂ at 200 μL L⁻¹ above ambient and in control plots exposed to the ambient atmosphere of 360 μL CO₂ L⁻¹. The purpose was to determine if ecosystem atmospheric CO₂ enrichment would alter soil microbial CH₄ consumption at the forest floor and if the effect of CO₂ would change with time or with environmental conditions. Reduced CH₄ consumption was observed in CO₂-enriched plots relative to control plots on 46 out of 48 sampling dates, such that CO₂-enriched plots showed annual reductions in CH₄ consumption of 16% in 1998 and 30% in 1999. No significant differences were observed in soil moisture, temperature, pH, inorganic-N or rates of N-mineralization between CO₂-enriched and control plots, indicating that differences in CH₄ consumption between treatments were likely the result of changes in the composition or size of the CH₄-oxidizing microbial community. A repeated measures analysis of variance that included soil moisture, soil temperature (from 0 to 30 cm), and time as covariates indicated that the reduction of CH₄ consumption under elevated CO₂ was enhanced at higher soil temperatures. Additionally, the effect of elevated CO₂ on CH₄ consumption increased with time during the two-year study. Overall, these data suggest that rising atmospheric CO₂ will reduce atmospheric CH₄ consumption in temperate forests and that the effect will be greater in warmer climates. A 30% reduction in atmospheric CH₄ consumption by temperate forest soils in response to rising atmospheric CO₂ will result in a 10% reduction in the sink strength of temperate forest soils in the atmospheric CH₄ budget and a positive feedback to the greenhouse effect.

Keywords: CH₄ flux, elevated CO₂, forest soil, methane oxidation

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Introduction

Methane and CO₂ are radiatively active trace gases that are currently increasing in atmospheric concentration at rates of 0.8 and 0.4% year⁻¹, respectively (Houghton *et al.* 1995). Methane currently contributes 20% to global warming (Bouwman 1990), but its potential contribution to global warming is 62 times that of CO₂ when normalized to mass on a 20-y time horizon (Houghton *et al.* 1995). Microbial CH₄ oxidation (methanotrophy) in

well-drained soils is the only identified biological sink for atmospheric CH₄ and is similar in magnitude to the current atmospheric increase of 37 Tg y⁻¹ (Houghton *et al.* 1995). Accordingly, any change in soil sink strength is expected to alter the rate of change in the atmospheric CH₄ concentration (Prather *et al.* 1995). In the absence of this sink, atmospheric CH₄ concentration would increase to at least 1.5 times the current rate (Duxbury 1994).

Influences on rates of atmospheric CH₄ oxidation by forest soils include soil temperature, moisture and N status (Mancinelli 1995; King 1997). Ammonium

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(NH_4^+) is often a competitive inhibitor of CH_4 oxidation (Schnell & King 1995), while increasing soil moisture reduces the rate of diffusion of atmospheric CH_4 into the soil (Castro *et al.* 1994a; Castro *et al.* 1995), and increasing temperature enhances microbial activity. Elevated CO_2 has been reported to stimulate plant water-use efficiency (van Veen *et al.* 1991; Jackson *et al.* 1994) and to alter ecosystem carbon and nitrogen cycling (Zak *et al.* 1993; Hungate *et al.* 1997). The effect of increasing atmospheric CO_2 on belowground processes could potentially alter CH_4 cycling dynamics. It is hypothesized that increased soil moisture and reduced substrate availability under CO_2 enrichment would influence CH_4 fluxes at the soil-atmosphere interface, thereby lowering the soil sink strength for temperate forests.

The effects of elevated CO_2 on microbial processes, including trace gas exchange, are poorly understood. Dacey *et al.* (1994) and Megonigal & Schlesinger (1997) demonstrated enhanced CH_4 emission from CO_2 -fertilized wetlands, but long-term observations of the influence of elevated CO_2 on consumption of atmospheric CH_4 by temperate forests are lacking. Forests occupy one-third of the Earth's terrestrial surface, and temperate forests alone annually consume 15 Tg y^{-1} of atmospheric CH_4 (Born *et al.* 1990). Accurate prediction of future trends in soil CH_4 oxidation requires an improved understanding of increasing atmospheric CO_2 to determine if elevated CO_2 will alter the CH_4 soil sink globally.

Atmospheric CO_2 is predicted to exceed $500 \mu\text{L L}^{-1}$ during the present century (Houghton *et al.* 1995). The predicted response of temperate forests to projected future atmospheric CO_2 concentrations rests largely on laboratory experiments and small-scale plots that cannot entirely mimic field conditions (Körner & Arnone 1992). Critical questions concerning feedbacks and interactions between the atmosphere and plant-soil systems can only be addressed on intact forests with plot sizes sufficient to minimize disturbance, which will ensure accurate assessment of energy and material fluxes (Mooney *et al.* 1991). Consequently, a free-air CO_2 enrichment (FACE) experiment was initiated in August 1996 in a 17-y-old loblolly pine (*Pinus taeda*) forest in central North Carolina, USA. Experimental 30-m diameter plots were continuously enriched with CO_2 at $200 \mu\text{L L}^{-1}$ above the ambient level of $\sim 360 \mu\text{L L}^{-1}$, and an interdisciplinary study was initiated to assess the impact on ecosystem function, including soil biogeochemistry. The present two-year investigation was a component of this study and was aimed at determining the effect of atmospheric CO_2 enrichment on the soil-atmosphere exchange of CH_4 and environmental factors influencing rates of gas exchange.

Methods

Field site

The study site is located in Orange County, NC ($35^\circ 58' \text{N}$, $79^\circ 05' \text{W}$), where a 90-ha parcel of even-aged loblolly pine (*Pinus taeda* L.) was planted on a clay loam soil in 1983. Topography is flat, and soils are Ultic Alfisols of the Enon Series, which are relatively low-fertility Hapludalfs typical of uplands in southeastern USA (D. D. Richter, unpubl. results). Average seasonal air temperature ranges from 1°C in January to 36°C in July. Precipitation averages 1150 mm and is distributed evenly throughout the year (State Climate Office 1999).

Six circular, 30-m diameter rings were established within the forest. Each ring was partitioned into 4 quadrants, for a total of 24 individual sectors. Triplicate rings served as controls to which ambient air was added, while the remaining three rings were enriched to maintain atmospheric levels at $200 \mu\text{L CO}_2 \text{ L}^{-1}$ above the approximate ambient concentration of $360 \mu\text{L CO}_2 \text{ L}^{-1}$, for a mean concentration of $\sim 560 \mu\text{L CO}_2 \text{ L}^{-1}$. Liquid CO_2 was vaporized and delivered with ambient air into a circular plenum and then dispersed from ports on vent pipes distributed around the ring. Treatment began on 27 August 1996 and has continued daily without interruption. Sensors within rings continuously tracked CO_2 concentration at 12–16 points at four heights (1, 3, 6, and 9 m). The Duke Forest FACE CO_2 fumigation system was described previously by Ellsworth *et al.* (1995). Actual CO_2 enrichments ranged from 199 to $203 \mu\text{L L}^{-1}$, with concentrations inside the CO_2 -treated rings varying from 550 to $570 \mu\text{L L}^{-1}$ (Hendrey *et al.* 1999).

Field sampling

Methane flux measurements within each sector were determined using the static chamber method (Whalen & Reeburgh 1992). Polyvinyl chloride collars (20 cm diameter \times 11 cm height) were permanently deployed 4 cm into the soil in randomly selected locations within each sector at the beginning of the experiment. Collars were deployed 5 days prior to initial measurements and root disturbance was minimal. Polyvinyl chloride covers fitted with butyl o-rings were placed onto the soil collars during each CH_4 flux determination. Covers were fitted with a capillary bleed to equalize pressure and a Swagelok o-seal equipped with a septum for syringe sampling of headspace gas. Air samples were withdrawn from each chamber at 0.5-h intervals for 2 h using 10-mL SESI nylon syringes equipped with pistons modified to accept a larger diameter sealing o-ring.

Methane was measured using a Shimadzu model GC-8 A flame ionization detection gas chromatograph with a 1-m molecular sieve 5 A (60/80 mesh) column and an

ultrapure N₂ carrier gas (33 mL min⁻¹). Samples were analysed after injecting into a 0.5-mL loop. Column and injector temperatures were 90° and 140 °C, respectively. The precision of analysis expressed as the coefficient of variation for 10 replicate injections of a 1.01- μ L CH₄ L⁻¹ standard was < 3%. Methane fluxes were calculated from chamber geometry and the linear change in CH₄ concentration with time (Whalen & Reeburgh 1992). The annual mean CH₄ flux was estimated by integration of daily CH₄ flux for each chamber. Here, a negative (-) flux was defined as (+) consumption of atmospheric CH₄ by the soil microbial community.

Methane flux was measured at each chamber bi-monthly from February 1998 to December 1999. Volumetric soil moisture was measured at 0.5-h intervals with time domain reflectometry (TDR) probes permanently installed within each sector, integrated for the depth from 0 to 30 cm (K. Schäfer, pers. comm.). Soil temperature was measured at 3-cm intervals from 1 to 16 cm with a multithermistor temperature probe during each site visit. Evidence was found for CH₄ oxidization activity in the 1–16 cm soil depth zone during previous laboratory analyses (data not shown), so average soil temperature was utilized in the data analysis.

Soil cores (5.5 cm diameter \times 15 cm length) were collected three times during the growing season (June to October) during each sample year. One core was collected at random within each sector from each ring for a total of 24 cores on each sampling date. Cores were separated into 0–7.5 cm and 7.5–15 cm depth intervals. Samples were homogenized by ring for each depth interval. Soil organic content was determined by loss on ignition at 550 °C for 4 h for three oven-dry (24 h at 105 °C) subsamples per ring at each depth. Soil particle density was measured pycnometrically, and bulk density was computed as the quotient of oven-dried mass divided by field volume. Soil pH was measured potentiometrically on 1 : 2 soil-deionized water slurries equilibrated for 24 h. Methodologies follow Carter (1993).

Statistical analyses

Methane flux data were analysed using a mixed linear model with repeated measures (Littell *et al.* 1996). Carbon dioxide treatment was the main effect, with moisture, temperature and time (continuous) as covariates. A nested hierarchical model was used with ring nested inside treatment and sector nested inside ring and treatment. Data collection intervals over time were unequal, so a time-series covariance structure was used, where correlations decline as a function of time. All interactions were tested; only significant interactions remained in the model. Calculated annual time-integrated fluxes for each chamber within each treatment group were

compared using a *t*-test. A two-way analysis of variance was used to test for the effect of CO₂ enrichment on soil organic matter at each depth zone. A significance level of $\alpha = 0.05$ was used for all statistical analyses.

Results

Soil properties

Soil temperatures ranged from 4 to 26 °C, with an overall mean for dates sampled of 16 °C (Fig. 1). The lowest soil temperature was found in February 1999 and the highest in August 1998. Average volumetric soil moisture, integrated from 0 to 30 cm, ranged from 5% to 60%, with an overall mean for all sectors and sample dates of 30%. Sites were shaded by the canopy, so chamber temperature during the 2 h incubation period did not exceed 1 °C above ambient. Soil particle density and pH were 2.5 g cm⁻³ and 6.0 units, respectively. Bulk density was 1.05 g cm⁻³ in the 0–7.5 cm zone and 1.3 g cm⁻³ in the 7.5–15 cm zone. Soil organic matter content was 6.4–9.0% in the 0–7.5 cm soil zone and 3.6–6.3% in the 7.5–15 cm soil zone. None of the physicochemical properties measured varied with treatment except for soil organic matter, which was roughly 20% higher for enriched CO₂ plots during June and August 1999 (Phillips *et al.* 2001).

Field CH₄ consumption

Net CH₄ consumption was consistently observed in both 1998 and 1999 (Fig. 2). The average daily CH₄ consumption rate, including both treatments and all sample dates, was lowest in March 1998 (0.05 mg m⁻² d⁻¹) and highest in August 1999 (0.88 mg m⁻² d⁻¹). These extremes coincided with very wet and very dry conditions, respectively (Fig. 1). On two sampling dates in 1999, the atmospheric CH₄ concentrations were 30% greater than the regional average (1.9 μ L L⁻¹ CH₄), and sharp increases in the rates of CH₄ consumption were observed.

In 1998, the average daily CH₄ consumption rate in enriched plots (0.47 \pm 0.02 mg m⁻² d⁻¹) was 16% lower than in control plots (0.56 \pm 0.02 mg m⁻² d⁻¹); while 1999 average daily CH₄ consumption rate in CO₂-enriched plots (0.41 \pm 0.02 mg m⁻² d⁻¹) was 31% lower than in control plots (0.60 \pm 0.02 mg m⁻² d⁻¹). The mean daily rate of CH₄ consumption was lower in CO₂-enriched plots than in control plots on all but two of the 48 sampling dates (Fig. 2). Compiling data for both years, the overall average (\pm 1 SEM) daily rate of CH₄ consumption (0.44 \pm 0.01 mg m⁻² d⁻¹, *n* = 563) for the CO₂ enriched plots was lower than average daily rate of CH₄ consumption for the control plots (0.58 \pm 0.02 mg m⁻² d⁻¹, *n* = 570). The effect of CO₂ enrichment on CH₄ flux was much greater during the summer and fall than in the

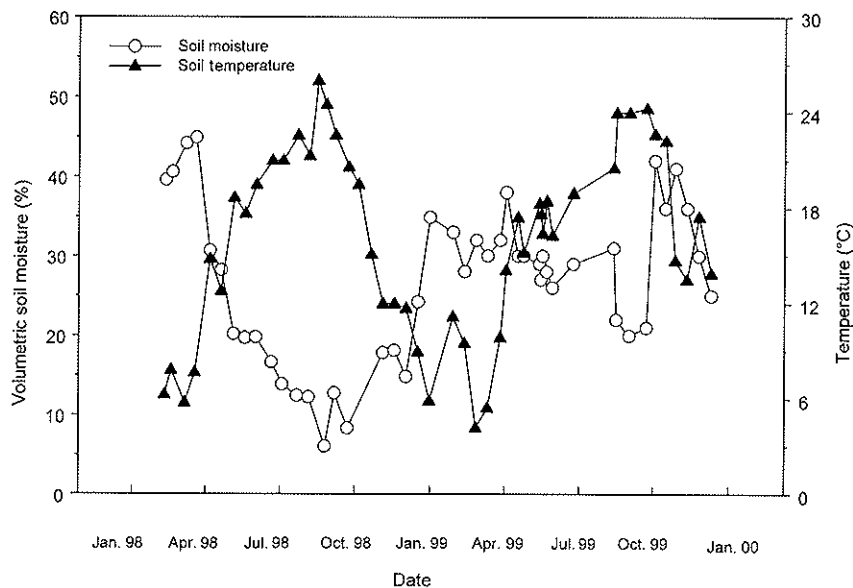


Fig. 1 Soil moisture (integrated from 0 to 30 cm) and temperature (average from 1 to 16 cm) for each sampling date. Each datum is the average for all observations made in both CO₂-enriched and control plots on that date.

winter and spring in both years (Fig. 2). Maximum differences in the daily rate of CH₄ consumption between CO₂-enriched and control plots occurred when soil moisture was < 30% by volume and soil temperatures were > 15 °C. Results of the statistical analysis, using moisture, temperature and time as covariates, showed that elevated CO₂ significantly interacted with time ($F = 4.61$, $P < 0.05$) (Fig. 3) and with temperature ($F = 14.06$, $P < 0.001$) (Fig. 4). Soils under elevated CO₂ consumed less CH₄ than soils in control plots, and the difference between CO₂ treatments increased with increasing temperature or time during this 2- y study.

A time-integrated rate of CH₄ consumption was calculated for each chamber in 1998 and 1999. The average annual CH₄ consumption rate during both years for CO₂-enriched plots (146 mg CH₄ m⁻² y⁻¹) was significantly lower ($t = 3.45$, $P < 0.01$) than the average CH₄ consumption rate for control plots (187 mg CH₄ m⁻² y⁻¹). The mean annual CH₄ consumption rate for CO₂-enriched plots differed by 13% between 1998 (156 mg CH₄ m⁻² y⁻¹) and 1999 (136 mg CH₄ m⁻² y⁻¹). The mean annual CH₄ consumption rate for the control plots differed by 4% between 1998 (183 mg CH₄ m⁻² y⁻¹) and 1999 (191 mg CH₄ m⁻² y⁻¹). Differences between years within a treatment, however, were not statistically significant. Time-integrated rates of atmospheric CH₄ consumption were 22% lower for CO₂-enriched plots than for control plots during both years, and the effect of CO₂ in 1999 was greater than in 1998.

Discussion

Atmospheric CH₄ uptake occurs in a wide range of soils, from tundra to deserts (Keller *et al.* 1983; Whalen &

Reeburgh 1990; Striegl *et al.* 1992), and average rates of consumption typically vary between 0.5 and 2 mg CH₄ m⁻² d⁻¹ (reviewed by King 1997). Rates exceeding 3 mg CH₄ m⁻² d⁻¹ have recently been reported for a deciduous forest (Ishizuka *et al.* 2000). The mean daily rate of CH₄ consumption of 0.6 mg CH₄ m⁻² d⁻¹ found here falls toward the low end of these previous observations but is comparable to rates reported by Koschorreck & Conrad (1993) for temperate forest soils in Germany (0.5 mg CH₄ m⁻² d⁻¹). The annual CH₄ consumption rate of 183–191 mg m⁻² found here for control plots is somewhat higher than the 110 mg m⁻² given by van den Pol-van Dasselaaar *et al.* (1998) for a temperate grassland, but is considerably lower than the 600 mg m⁻² reported by Crill (1991) for a northern temperate forest. The present data show a distinct seasonality, with highest rates of CH₄ consumption occurring during summer months (Fig. 2). Seasonal patterns, showing highest rates of CH₄ consumption during the summer months, have also been reported by Castro *et al.* (1995) and Crill (1991) for northern temperate forests.

Reductions in atmospheric CH₄ consumption of 22–24% in CO₂-enriched plots have been reported for aspen stands (Ambus & Robertson 1999) and grassland soils (Ineson *et al.* 1998) that also normally function as CH₄ sinks. These experiments were similar to herein in that sites were enriched with atmospheric CO₂ at concentrations $\geq 550 \mu\text{L L}^{-1}$; however, CH₄ flux was measured in the summer only for a period of 1–3 months. The reduction in CH₄ consumption under elevated CO₂ reported by Ambus & Robertson (1999) was attributed to an 11% increase in percent water-filled pore space. Ineson *et al.* (1998), however, did not report soil moisture values. Furthermore, liquid N fertilizer, an inhibitor of

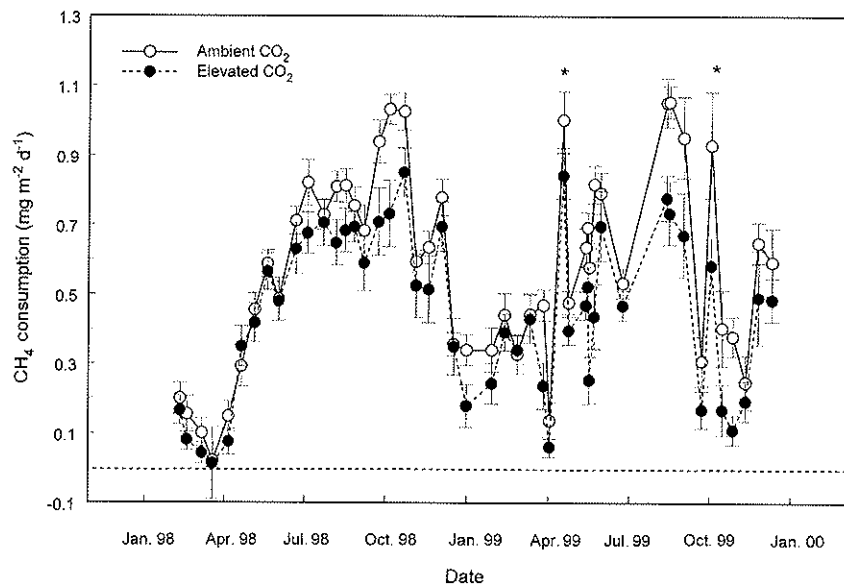


Fig. 2 Net rates of CH₄ consumption measured at the forest floor for 2 years. Shown is the mean of 12 observations for each treatment on each sampling date. Error bars represent 1 SEM. Asterisks indicate sampling dates when the atmospheric CH₄ concentration was 30% higher than the long-term average of 1.9 µL L⁻¹.

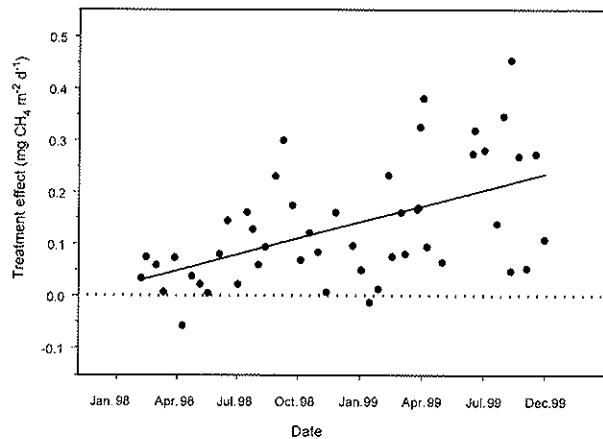


Fig. 3 Effect of CO₂ enrichment on rates of CH₄ consumption during the 2-y observation period. The treatment effect on each sampling date is calculated as the difference between the mean rate of CH₄ consumption in control plots minus the mean rate in CO₂-enriched plots. Line shown is a linear regression of these data to illustrate that the effect of CO₂ on CH₄ flux increased over time ($r^2 = 0.209$).

methanotrophy (Stuedler *et al.* 1996), was also applied to experimental plots. Soil moisture strongly controls CH₄ consumption (Czepiel *et al.* 1995; van den Pol-van Dasselaar *et al.* 1998). Without statistically controlling for soil moisture, it is difficult to evaluate the indirect effects of elevated CO₂ on the soil CH₄-oxidizing community function when soil moisture is also affected by CO₂ enrichment. These studies point to the importance of controlling for environmental factors known to influence CH₄ oxidation to better determine the direct effects of CO₂ enrichment.

The present statistical analysis showed the effect of CO₂ enrichment on soil CH₄ consumption independent of soil moisture and temperature differences over time by statistically controlling for these variables. The significant treatment-temperature interaction indicated that some of the variability (15%) associated with CO₂ treatment was a consequence of soil temperature (Fig. 4). Differences in rates of CH₄ consumption between elevated CO₂ and control plots were greatest during the summer months, when rates of CH₄ consumption were high (Fig. 2) and soils were dry (Fig. 1). Rates of CH₄ consumption tend to increase as soil moisture declines, temperature rises, and CH₄ diffusivity through the soil profile increases (van den Pol-van Dasselaar *et al.* 1998). The present study corroborates these data with enhanced rates of consumption at higher soil temperatures (Fig. 1), but CH₄ consumption rates in CO₂-enriched soil were not as high under these conditions as CH₄ consumption rates in control soil (Fig. 2). Greater differences in rates of CH₄ consumption between treatments at low soil moisture and high soil temperature suggest that the negative effect of CO₂ enrichment on soil CH₄ consumption is most likely to occur during drier, warmer seasons.

Additionally, the present analysis included time as a covariate to discern how the effect of CO₂ enrichment on CH₄ flux might change during the 2-y observation period. The significant treatment-time interaction indicated that some of the variability (20%) associated with CO₂ treatment was related to the time since fumigation was initiated (Fig. 3). Elevated CO₂ influenced CH₄ consumption most dramatically during the summer months, and the treatment effect during the summer of 1999 was greater than in 1998. Differences in soil

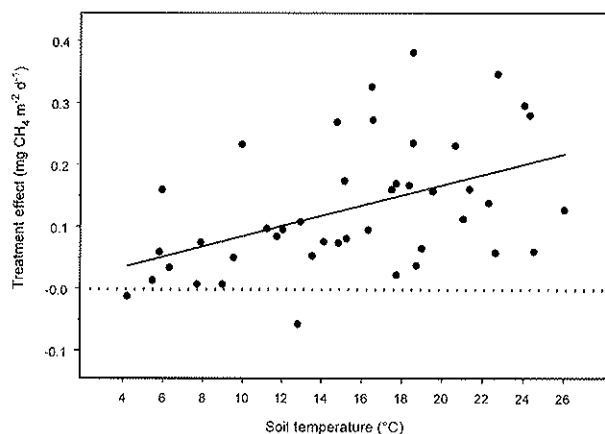


Fig. 4 Effect of CO₂ enrichment on rates of CH₄ consumption as a function of temperature. The treatment effect on each sampling date is calculated as the difference between the mean rate of CH₄ consumption in control plots minus the mean rate in CO₂-enriched plots. Line shown is a linear regression of these data to illustrate that greater soil temperature increased the effect of CO₂ on CH₄ flux ($r^2 = 0.147$).

moisture between 1998 and 1999 could have influenced the effect of treatment over time, but the three-way interaction (treatment \times moisture \times time) was not significant. Differences in soil moisture between years, then, did not account for the increasing effect of CO₂ enrichment on CH₄ consumption rates over time.

The response of this ecosystem over time suggests that at least three years of CO₂ enrichment were necessary to observe the effect of elevated CO₂ on soil CH₄ consumption. Additionally, the increasing effect of CO₂ enrichment over time suggests that potential pre-treatment differences between control and experimental plots do not explain reduced CH₄ consumption rates. The present data suggest that the soil microbial community oxidizes less atmospheric CH₄ following three years of CO₂ enrichment. A gradual shift in the activity of the CH₄-oxidizing community may have occurred in CO₂-enriched soils, but microbial community data are needed to confirm this. It was found that the effect of CO₂ enrichment on CH₄ consumption increased from 1998 to 1999, suggesting that FACE influenced rates of microbial CH₄-oxidizing activity by altering the soil microenvironment.

Factors influencing CH₄ flux at the forest floor, aside from methanotrophy, include methanogenesis, moisture, temperature, nitrogen concentration, rate of N-mineralization, and pH (Mosier *et al.* 1991; King & Adamsen 1992; Ojima *et al.* 1993; Castro *et al.* 1994b; Castro *et al.* 1995). It was demonstrated previously by the present authors that methanogenesis was not significant in soils from both CO₂-enriched and control plots (Phillips *et al.* 2001). Consequently, differences in rates of CH₄ production between treatments do not account for the observed

differences in CH₄ flux. Factors that typically affect CH₄ oxidation (nitrogen concentration, temperature, rate of N-mineralization, pH, and land-use) were not significantly different between control and experimental plots at this site (Allen *et al.* 2000). Furthermore, soil moisture for these 50 sample dates (Fig. 1) was not significantly different between CO₂-enriched and control plots ($F = 2.68$; $P = 0.18$).

Because the factors that commonly influence CH₄ consumption were similar between treatments, CO₂-enrichment likely influenced the size or activity of the CH₄-oxidizing community. Reduced activity is expected when substrate is less available, or when the CH₄-oxidizing organisms are inhibited. If soil moisture was not a suitable proxy for diffusivity at this site, and if CH₄ diffusivity into the soil profile was inhibited under FACE, then diffusivity differences alone might explain lower rates of consumption. Alternatively, FACE may have altered the soil microbial community by increasing soil carbon (Zak *et al.* 1993) and competition for O₂, which may have resulted in repression of the CH₄-oxidizing population or activity levels. Greater soil respiration under elevated CO₂ (Allen *et al.* 2000) may have lowered O₂ availability, thereby inhibiting the oxidation of CH₄ by methanotrophs.

A 16–30% reduction in CH₄ consumption under FACE is demonstrated following 2–3 years of CO₂ treatment, and the trend over time indicates that the CH₄-oxidizing community did not equilibrate to an atmosphere enriched with 560 $\mu\text{L L}^{-1}$ CO₂ during the observation period. However, the persistence of this effect has not been determined. Differences in rates of CH₄ consumption may continue to diverge or may equilibrate at lower levels in response to elevated CO₂. Further work is needed with soil microbial dynamics to determine whether or not FACE results in a permanent shift in this ecosystem function, and whether or not this may be attributed to changes in the size, species composition or activity of the CH₄-oxidizing community. Continued observation is needed to determine the temporal extent of CO₂ enrichment on microbial CH₄ consumption in this ecosystem. Furthermore, research at other FACE sites is necessary to determine if this effect is consistent across temperate forest ecosystems. A 30% reduction in the temperate forest CH₄ sink, as indicated by these data, would result in a 10% reduction in biological soil CH₄ consumption worldwide and a positive feedback to the greenhouse effect.

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