Biogeochemistry **43:** 253–272, 1998.

Hysteresis in the temperature response of carbon dioxide and methane production in peat soils

KAREN UPDEGRAFF[1,*], SCOTT D. BRIDGHAM[2], JOHN PASTOR[1] & PETER WEISHAMPEL[2]
[1]*University of Minnesota, Natural Resources Research Institute, Duluth, MN 55811, USA;*
[2]*University of Notre Dame, Notre Dame, IN 46556, USA (*Corresponding author: Natural Resources Research Institute 5013 Miller Trunk HWY, Duluth, MN 55811, USA; Phone: 218/720-4338; E-mail: kupdegra@sage.nrri.umn.edu)*

Received April 7, 1997; accepted March 3, 1998)

Key words: carbon dioxide, hysteresis, methane, peat, temperature, wetlands

Abstract. The ability to predict the effects of climate change on trace gas fluxes requires a knowledge of microbial temperature responses. However, the response of a microbial community to temperature in a given substrate may be complicated by its thermal history. To examine the effect of sequentially changing temperature on methane and carbon dioxide production in different peat types, we incubated anaerobic peat samples from 3 types of northern peatlands, a bog, a sedge fen and a cedar swamp, in both rising and falling temperature regimes. Graphic and statistical comparisons of the different temperature regimes suggest hysteresis in microbial response to temperature, although the absolute rates at any given temperature often did not differ. Where regressions for temperature response (Arrhenius plots) were significant, they generally differed between temperature regimes. The greatest differences among treatments occurred during the first half of the 40-d incubation. Increases in carbon dioxide production were similar across all peat types, but methanogenesis varied widely: methane production was uniformly low in the bog peat but increased sharply with temperature in the other two peat types. The complicating effect of history or chronology on substrate responses to environmental stimuli may restrain our ability to model the responses of complex systems to changing conditions.

Introduction

The increasing concentrations of carbon dioxide (CO_2) and methane (CH_4) in the troposphere are predicted to raise global mean temperatures up to 4.5 °C by 2100 (Kattenberg et al. 1996). Northern wetlands are estimated to store one-third of the world's soil carbon (Gorham 1991), but the possible effect of increased decomposition rates in them on atmospheric trace gas loadings is poorly quantified. If, as predicted, warmer conditions convert peatlands from net carbon sinks to net carbon sources (Armentano and Menges 1986; Khalil and Rasmussen 1989; Bridgham et al. 1995), the resulting increase in net carbon dioxide (CO_2) and methane (CH_4) emissions could comprise a significant positive atmospheric feedback.

Wetland carbon dynamics have received considerable attention in recent years, frequently with emphasis on methanogenesis, although even under anaerobic conditions CO_2 is the dominant gaseous end-product (Wieder et al. 1990; Updegraff et al. 1995; Bridgham et al., in press). Methane has been estimated to have approximately 21 times the atmospheric warming potential of CO_2 over a 100-year time horizon (Schimel et al. 1996).

Atmospheric models generally simulate carbon fluxes as responses to more or less linear sums of source and sink functions (Hammeed and Cess 1983; Post 1990; Fung et al. 1991), where factors such as water table, temperature, soil and/or vegetation characteristics affect source dynamics. The complexity of controls over methanogenesis often result in apparently nonlinear responses to environmental change, and consequently most models that simulate CH_4 fluxes on a regional or global scale do so within very broad limits of error.

Efforts to refine predictions of CH_4 fluxes have focussed on broad-scale environmental controls such as soil temperature. The specific effects of temperature on carbon mineralization in saturated soils have proven difficult to isolate from those of other environmental controls, although within restricted ecological zones temperature alone has been shown to be a dominant factor. Dise et al. (1993) found that soil temperature was the dominant control over CH_4 flux within individual peatland ecosystems in northern Minnesota. Soil temperature explained 67–84% of seasonal variation of in situ soil respiration in North Carolina peatlands, while laboratory incubations of these peats showed a stronger effect of temperature on CH_4 than on CO_2 production (Bridgham and Richardson 1992).

More typically temperature is one of numerous state factors that control carbon mineralization processes. Naiman et al. (1991) found that CH_4 flux in flooded beaver meadows correlated with a combination of soil temperature, water-table depth, redox status and pH. CO_2 flux from flooded *Sphagnum* peat cores did not respond to increased temperature, although CH_4 flux did, during 17-wk incubations at varying temperatures and moisture contents (Hogg et al. 1992). Of particular relevance to the current paper are the findings of Yavitt et al. (1987). They found that West Virginia surface peats collected at different seasons but incubated isothermally exhibited significantly different CH_4 flux rates. They speculated that the inherent differences among the serial samples were due to seasonal variations in methanogen populations or in the activity of the hydrolytic organisms controlling their substrate supply.

These findings suggest that short-term microbial response to temperature change in a given substrate should be modulated not only by the type but by the thermal history of that substrate. That is, history-dependent shifts in substrate availability and microbial populations would result in non-symmetrical responses with respect to trace gas emissions. The objective

Table 1. Mean values for various properties determined on at least five samples from each site. Percent C, N and ash were determined by combustion of oven-dried, ground samples while rubbed fiber was determined on fresh sample. Percent rubbed fiber is in inverse proportion to degree of decomposition.

	Fen	Cedar swamp	Bog
% C	38.6 (1.2)	42.4 (1.8)	42.2 (0.8)
% N	2.5 (0.3)	1.9 (0.2)	1.1 (0.1)
% Ash	22.3 (2.4)	13.3 (3.3)	8.4 (0.8)
% Rubbed fiber	29.2 (8.5)	43.8 (7.8)	73.7 (13.8)
% Moisture	85.4 (0.7)	87.5 (0.3)	90.8 (1.6)
Bulk density	0.100 (0.010)	0.095 (0.007)	0.030 (0.016)
Initial pH	4.9 (0.1)	5.5 (0.4)	4.1 (0.0)

of this study was to assess the effect of thermal history on the temperature response of CO_2 and CH_4 production in peat from three wetland sites representing a wide range of substrate quality.

Sites and methods

In February 1995 we collected peat from 3 northern Minnesota wetlands: a cedar (*Thuja occidentalis*) swamp near Voyageurs National Park, a spruce (*Picea mariana*) – *Sphagnum* bog, and an intermediate sedge (*Carex* spp.) fen. The bog and fen sites were located in the large glacial Lake Upham area of north-central Minnesota, near the townships of Toivola and Alborn. All sites were between 46° and 48° N. The peat from these sites has been extensively described in previous studies (S.D. Bridgham et al., in press); the sites were selected to represent a range of peat types from slightly decomposed, recalcitrant *Sphagnum* peat to the more decomposed, minerogenous sedge fen and forested swamp peats. Selected peat characteristics are listed in Table 1. At each site we cut four 15–25 cm deep surface sections of frozen peat using a chainsaw. The peat sections were sealed in polyethylene bags and kept frozen pending processing at the University of Notre Dame.

After removal of surface vegetation each peat core was homogenized by hand, then 5-mL volumetric samples at field moisture (mean dry-weight equivalents of between 1.1 and 2.5 g) were transferred to pre-weighed 120-mL crimp-top serum bottles. The bottles were sealed and their final weight recorded; then they were flushed with N_2 and stored at 4 °C until the initiation of incubation treatments. The N_2 headspace was maintained throughout the incubation. The homogenized peat was also subsampled for initial mois-

Table 2. Experimental design: initiation of incubations was Day 0. Headspace sampling took place after 3-day incubations at the indicated temperatures.

	Treatment number			
	1	2	3	4
Day	Temperature, °C			
3	6	6	30	30
6	6	10	26	30
9	6	14	22	30
12	6	18	18	30
15	6	22	14	30
18	6	26	10	30
21	6	30	6	30
24	6	26	10	30
27	6	22	14	30
30	6	18	18	30
33	6	14	22	30
36	6	10	26	30
39	6	6	30	30

ture content and pH, which was measured in 1:1 peat:water slurries. Post-incubation pH was determined by adding water sufficient to immerse a pH probe to the samples in the serum bottles (resulting in 1:2 or 1:3 peat:water slurries), allowing 30 min to equilibrate, then measuring the pH of the supernatant.

There were 4 treatment groups: treatments 1 and 4 were held isothermally at 6° and 30 °C, respectively, treatment 2 was raised from 6 to 30°, then returned to 6°, and treatment 3 began at 30°, dropped to 6°, then returned to 30°, all in 4° increments (Table 2). Treatments 1 and 4 test the response of the peat to isothermic regimes at the temperature endpoints, while treatments 2 and 3 test its response to histories of temperature gradients between these endpoints. There were 4 replicates of each peat (1 per core) type for each treatment (3 sites $\times$ 4 treatments $\times$ 4 replicates = 48 samples).

At each incubation step (i.e. following each temperature change) the headspaces were allowed 2 d to equilibrate, purged with approximately 8 volumes of N_2, then incubated one more day prior to sampling for CO_2 and CH_4. No agitation was employed. Headspace samples were injected directly and analyzed isothermally on a Varian gas chromatograph equipped with a Porapak-Q columns. Methane and CO_2 could therefore be analyzed simultaneously using, respectively, flame ionization and thermal conductivity detectors, which were installed in series. Production rate at each point was

taken to be calculated concentration (headspace + dissolved) divided by the length of time since purging. In order to minimize disturbance and drying, the samples were not re-purged prior to being moved to the next temperature, but only in time to determine the next rate. In all, 13 sequential sets of headspace samples were analyzed over a period of 39 d.

Statistical analyses. All analyses were performed using the Systat statistial package (Systat, Inc. 1994a & b). The experiment was designed as a 3×4 factorial study with 4 replicates. Since the source sites were selected for contrasting peat characteristics, differences among sites generally overwhelmed treatment (temperature regime) effects. Consequently we blocked all the ANOVA and regression analyses by source site (peat type), examining only the effect of treatment. The cumulative and periodic gas emissions data were analyzed using separate ANOVA comparisons of instantaneous emissions rates at 6,18 and 30 °C, and of total CH_4 and CO_2 production over the entire incubation.

However, it seemed that a more relevant and interesting comparison would be between the actual temperature response surfaces, rather than individual points. In order to do this we employed Arrhenius plots, and energies of activation, E, as defined in Giese (1973):

$$ln\frac{k_2}{k_1} = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (1)$$

where k_1 and k_2 are velocity constants for the rates of reaction at absolute temperatures T_1 and T_2, respectively, and R is the gas constant. We determined E empirically by plotting the logarithms of gas flux rates against the reciprocals of incubation temperature in °K, then multiplying the slope coefficient by *R*.

In order to compare the relative responses dependent on direction of temperature change, it was necessary to define "Periods" and "Modes" within treatment groups. There were two (time) periods within the experiment: period 1 encompassed days 0–21 and period 2 encompassed days 22–39. Within each period samples could be in one of three temperature modes: rising (mode 0), falling (mode 1), or isothermal (mode 2). Thus for treatment 2 (Table 2) the initial period was defined by a rising mode, while the second period saw a falling mode (or "Up" and "Down" for brevity in Table 3). The reverse was true of treatment 3.

To describe the effect of treatment on temperature response we compared the slopes and y-intercepts from separate Arrhenius functions for modes 0 and 1. This approach could not be used within mode on the isothermal treatments (mode 2), since temperature did not vary. However, we did generate E values

Table 3. Arrhenius energies of activation (E, in kJ mol^{-1}) calculated for different treatment/mode combinations in serum bottle incubations, based on mean CO_2 and CH_4 fluxes measured over temperatures ranging from 6° to 30 °C. Treatment numbers 1 and 4 were held isothermally at 6° and 30 °C, respectively, while treatment 2 was subjected to rising then falling temperatures, and treatment 3 the opposite.

Site	Treatment no.	Mode	E(CH_4)	E(CO_2)
Cedar	1 and 4	Isothermal	96.02	31.12
Cedar	2 and 3	Up and Down	93.86	49.34
Cedar	2	Up and Down	144.23	36.60
Cedar	2	Up	158.19	24.28†
Cedar	2	Down	145.76†	49.47†
Cedar	3	Up and Down	5.44†	64.52
Cedar	3	Up	22.01†	40.59†
Cedar	3	Down	2.97†	83.07
Bog	1 and 4	Isothermal	−11.31†	36.87
Bog	2 and 3	Up and Down	4.37†	59.16
Bog	2	Up and Down	37.43†	44.30
Bog	2	Up	−31.22†	7.17†
Bog	2	Down	182.46†	72.08
Bog	3	Up and Down	−14.29†	82.19
Bog	3	Up	27.78†	29.90†
Bog	3	Down	25.61†	111.44
Fen	1 and 4	Isothermal	134.96	24.31
Fen	2 and 3	Up and Down	93.65	51.02
Fen	2	Up and Down	117.93	32.69†
Fen	2	Up	131.34	15.46†
Fen	2	Down	113.21	40.56†
Fen	3	Up and Down	71.02	72.19
Fen	3	Up	93.58†	54.50
Fen	3	Down	55.39†	86.38

† Slope coefficient not significantly different from zero, using a Bonferroni-corrected probability level of $P = 0.001$.

based on the mean differences in rate between treatments 1 and 4 (Table 3) for comparison. For treatments 2 and 3 we included orthogonal pairs of treatment/mode combinations for each Period (e.g. treatment 2, mode 0 and treatment 3, mode 1) in multiple regression models with mode (rising or falling) as a dummy variable coded 0 or 1 (Draper and Smith 1981). An experimental setup with r levels of a treatment can accommodate the

introduction of ($r - 1$) dummy variables; in our case we were comparing only two levels and therefore only one dummy was necessary. The following regression model results:

$$Y = \beta_0 + \beta_1 X + \alpha_0 Z + \alpha_1 (ZX) + \epsilon, \quad Z = 0, 1 \tag{2}$$

where Y = flux rate, X = temperature, and Z = mode. In this combined model, β_0 and β_1 are coefficients for the overall intercept and the main effect of temperature, respectively. The extra sums of squares generated for α enable us to test for variation due to mode in the slope and intercept of the combined model, as follows:

1. H_0: $\alpha_0 = \alpha_1 = 0$. If H_0 is accepted, the models are the same, i.e. the two lines are identical with respect to both slope and intercept, and there is no effect of mode on the response of gas flux to temperature.
2. If H_0 in (1) is rejected, and $\alpha_0 \neq 0$, then the two lines have different intercepts, implying a significant effect of mode on flux rate.
3. If H_0 in (1) is rejected, and $\alpha_1 \neq 0$, then the two lines have differing slopes, or a significant mode μ temperature interaction with respect to flux rate.

In the regression output table, tests (2) and (3) are equivalent to the *t*-tests for the Mode (*Z*) and the Mode *x* Temperature (*ZX*) interaction terms. Therefore, significant *p*-values for those terms in the ANOVA output would indicate, respectively, significant differences in y-intercept and slope between the two modes. Seriously non-linear temperature response curves are automatically rejected since the overall slope coefficients are rendered non-significant.

Results

Estimated cumulative production of CO_2 and CH_4 from each peat type under the four treatment regimes is presented in Figure 1. While cumulative production was not the focus of this study, these data serve to illustrate the wide variability within treatment and peat type. They also make the point that cumulative emissions data do not always reflect transient responses.

Measured ratios of CO_2 to CH_4 production varied from about 400 to 5, depending on site. These ratios were similar to those seen in previous anaerobic incubations of Minnesota peats (Updegraff et al. 1995; Bridgham et al., in press) and also in slurry incubations of peat by others (Valentine et al. 1992; Moore and Dalva 1993). Over half of methanogenesis in non-ruminant systems is from reduction of acetate, which produces CO_2 and CH_4 in at least equal proportions (Mah et al. 1977). Most fermentative processes also produce CO_2 as the gaseous endproduct.

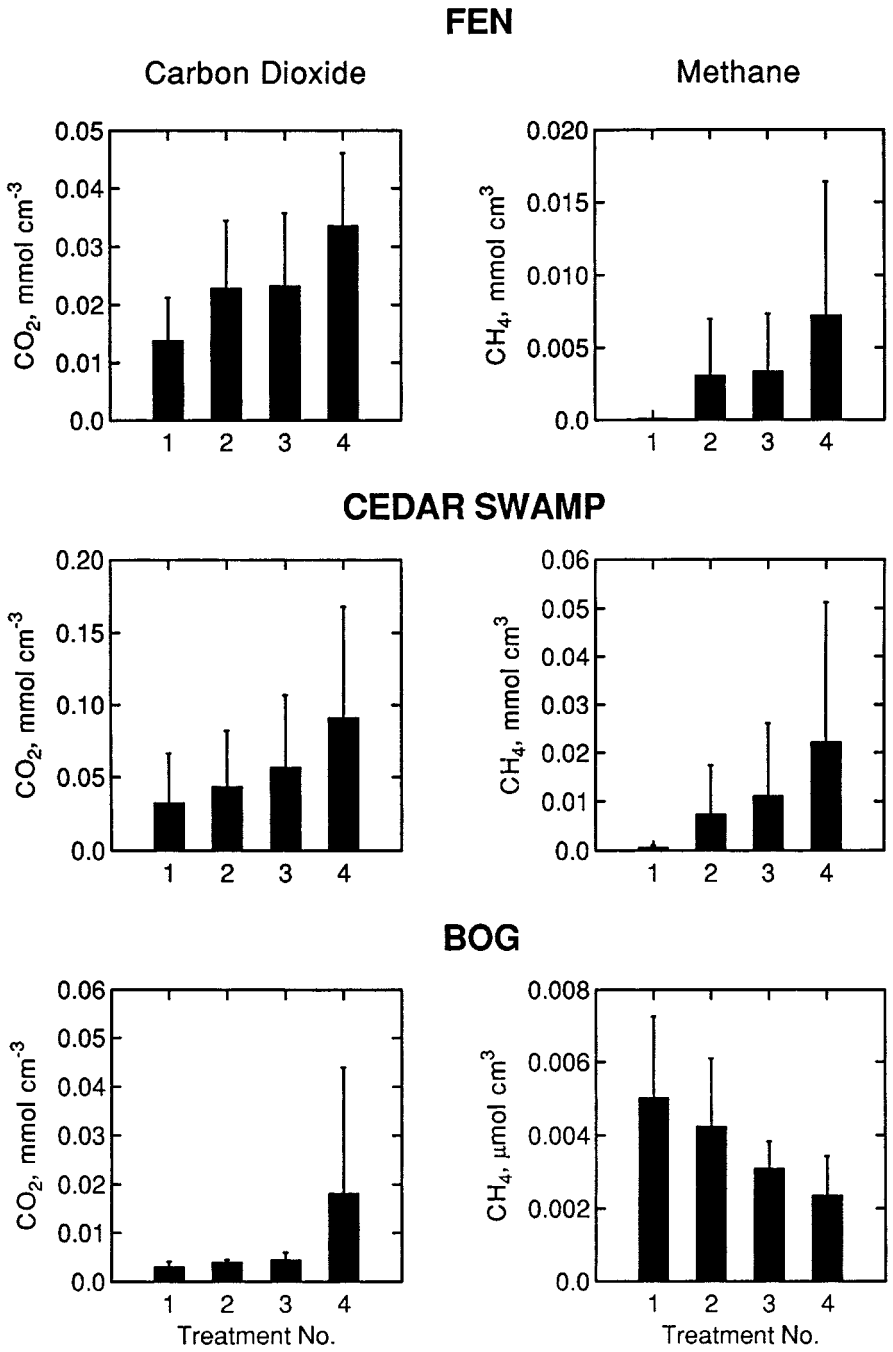

Figure 1. Cumulative (40-d) CO_2 and CH_4 emissions from peat incubations from 3 wetland types, with standard errors, estimated from measurements of instantaneous flux rates at each time step. Differences between treatments are largely non-significant.

We used repeated measures ANOVA analysis to test for time trends in isothermal CO_2 and CH_4 flux rates. There was no significant effect of incubation time on CH_4 flux rate in any of the peats. There was a significant linear decrease ($p = 0.01$) in CO_2 flux rate at 30° in the bog peats (Figure 2b), but no significant linear trends in any of the other peats at either temperature. The mean fluxes for each gas at 6° and 30° are indicated as points in the graphs of Figure 2(a) and (b). Since there were no consistent temporal patterns of increasing or decreasing flux rates in the isothermal incubations, we did not apply those values as corrections to the fluxes resulting from serial temperature changes. We also felt safe in the assumption that measured changes in flux rates in the other treatments were not the result of carryover of dissolved gas from one sample to the next, a particular concern in the case of CO_2, which is highly soluble.

Pairwise comparisons (*T*-tests) of CH_4 and CO_2 flux rates at selected points in time did not differ between rising and falling temperature modes because of wide variance among replicates. In addition, ANOVA comparisons of cumulative CO_2 and CH_4 production showed no significant treatment effect (Figure 1) with the exceptions that isothermal CH_4 production was greater at 30° than at 6° in the fen peat, as was CO_2 production in the bog peat.

Notwithstanding the absence of differences in instantaneous and cumulative CO_2 and CH_4 production, there were significant asymmetries in the relative responses to temperature mode (direction of change). The temperature trend graphs of Figure 2 show that for treatments 2 and 3 there was a clear asymmetry in the response of gas flux rates to temperature change. With respect to CH_4 flux this may have been due in part to initial lags in microbial activity, which occurred whether the starting temperature was 6° or 30°. The sharp increase in slope in rising mode at temperatures in excess of 22°, as well as the rapid maximization of emissions rates at 22° or 26° in falling mode, suggests that labile substrates were rapidly utilized at warmer temperatures, or that new pools of substrate became available for exploitation. Initial lags, especially in CH_4 emissions, are typical in anaerobic incubations of peats (Updegraff et al. 1995; Bridgham et al., in press). These lags were insignificant with respect to CO_2 production, although the initial high respiration rates seen in treatment 3 suggest that mobile substrates were consumed rapidly at high initial temperatures, but more gradually if starting temperatures were low.

Slope coefficients for Arrhenius regressions (the basis for E) including only the isothermal 6° and 30° incubations (treatments 1 and 4) were highly significant in all cases ($p < 0.01$), with the single exception of CH_4 flux in the bog peats, where there was no significant difference between the two temperatures. Where the Arrhenius slope coefficients were significantly different from

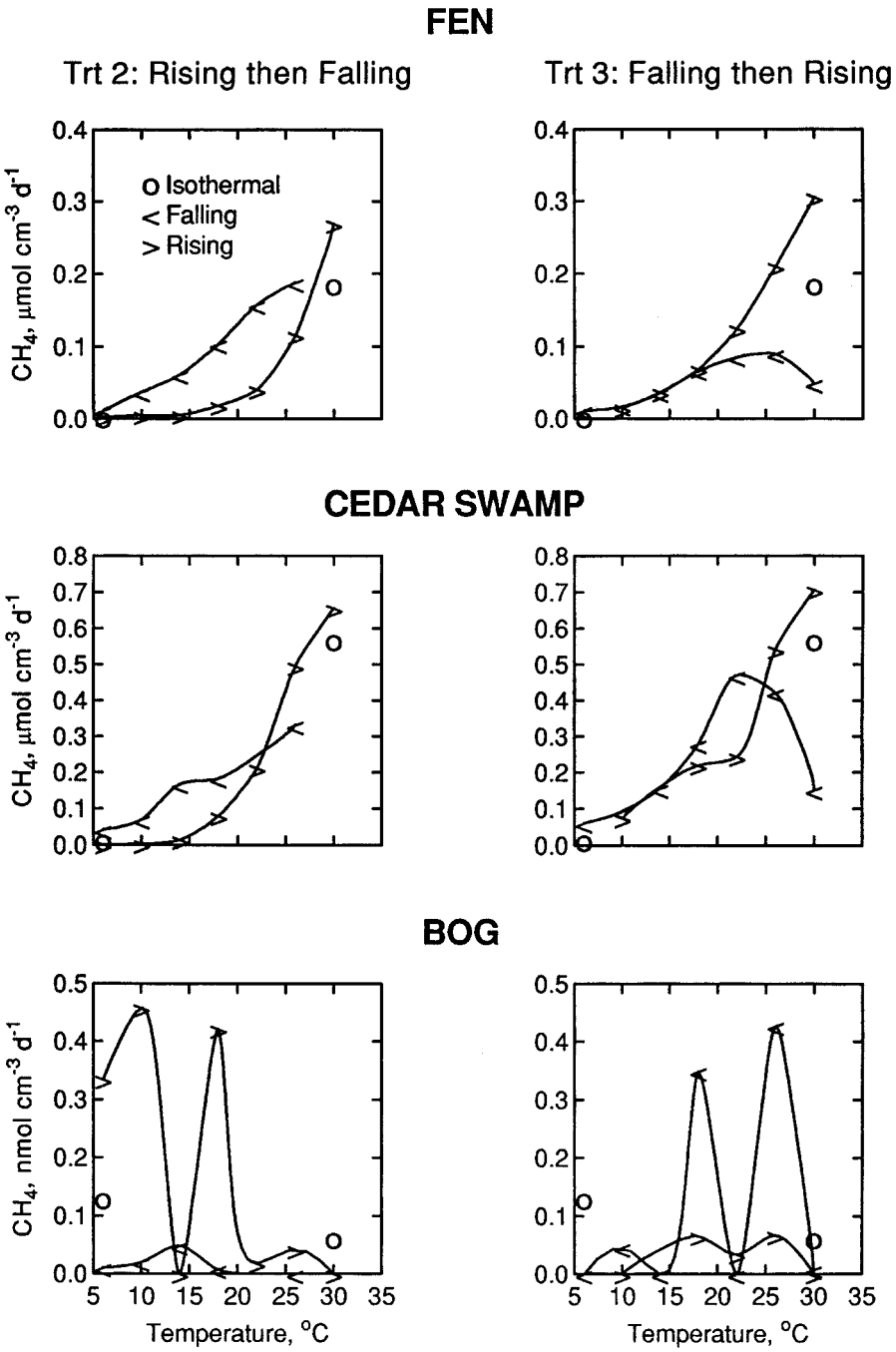

Figure 2. Flux rates of CH_4 (a) and CO_2 (b) with changing temperature during the course of anaerobic incubations of peat from three different sites (Fen, Cedar Swamp and Bog). Circles represent the mean flux rates obtained during isothermal incubations (treatments 1 and 4) at 6° and 30 °C, respectively. Note that in 2(a) the scale for the bog peats is in nmols rather than in μmols. Treatment 2 began with temperatures rising from 6° to 30° then falling back to 6°, while treatment 3 began at 30°, fell to 6° then rose again to 30°, all in 3-day time-steps.

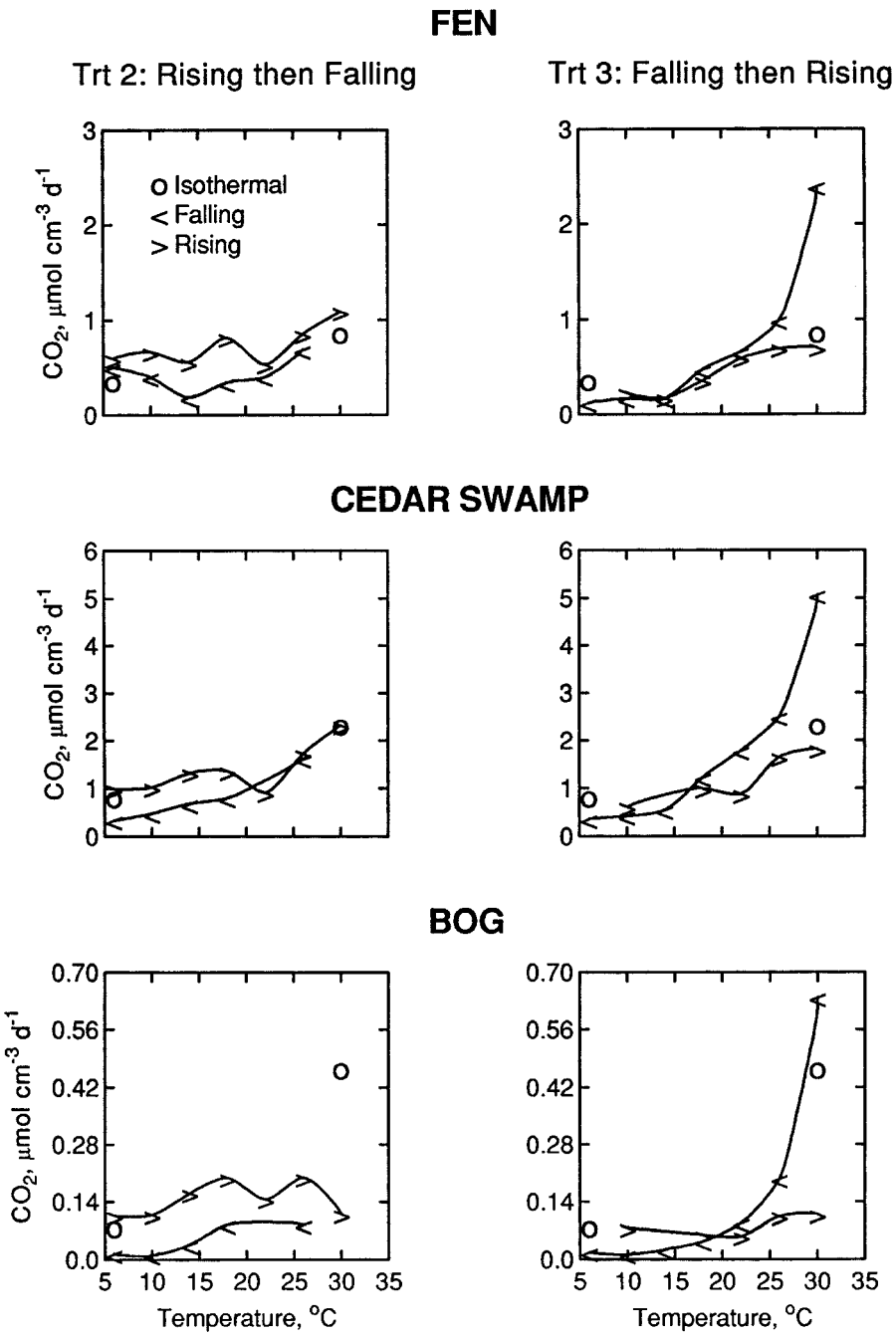

Figure 2. Continued.

zero ($p < 0.001$) E-values ranged from 71 to 158 for CH_4 and from 24 to 111 for CO_2 production. These values fall within the range of literature values for E(CH_4): for example, Westermann and Ahring (1987) reported E values of 92 to 114 kJ mol^{-1} for slurry incubations of alder swamp soils, while Conrad et al. (1987) reported activation energies of about 69 kJ mol^{-1} in paddy soils. Crill et al. (1988) measured *in situ* methane fluxes in various Minnesota peatlands and calculated apparent activation energies ranging from 116 to 177 kJ mol^{-1}.

We have previously found extremely low methanogenesis rates in ombrogenous *Sphagnum* peat, apparently due to lack of labile substrate for anaerobic decomposers (Updegraff et al. 1995; Bridgham et al. in press), although CO_2 emissions from *Sphagnum* peat readily increase in response to warmer temperatures (Table 3). The tendency of CO_2 production to decline over time in all substrates, seen in the isothermal incubations, may partly explain why the values of E were consistently larger for the falling temperature mode, regardless of treatment. By contrast the largest E values for CH_4 production tended to be in the rising mode, possibly because the initial lag effectively exaggerated the effect of increasing temperature.

R^2 values for the Arrhenius regressions (based on treatment means) ranged from 0.00 to 0.98 for CH_4 flux, and from 0.10 to 0.97 for CO_2 flux. However, the distribution of residuals around the Arrhenius regression lines for treatments 2 and 3 displayed a bias depending on mode (i.e. whether temperature was rising or falling). The biased distributions occurred not only between the rising and falling limbs of the same treatment, where timestep was a factor (see Figure 2), but between the falling and rising limbs of the two orthogonal treatments, i.e. in the same time-frame (Period). The paired Arrhenius plots of Figure 3 clearly illustrate the latter effect.

Comparison of the pairs of regressions shown in Figure 3 using dummy variables, as described above, yielded the statistics listed in Table 4. In all cases, the temperature response of CH_4 and CO_2 production was significantly different ($p < 0.01$) depending on mode of temperature change, the exception being CH_4 flux from the bog peat. During Period 1 there were highly significant differences in slope and y-intercept between the rising and falling modes of Arrhenius plots for CH_4 flux and CO_2 flux, especially in the fen and cedar swamp peats. During Period 2, however, the mode effect on CH_4 flux was significant only in the cedar swamp peats. In those samples the overall effect of temperature was not significant, even for the individual modes (see Table 3). The effect of mode on CO_2 flux was significant exclusively during Period 1, encompassing the early stages of decay.

The pattern that emerges is therefore as follows: during the initial phase of the incubation, when a strong temperature response occurred it was invariably

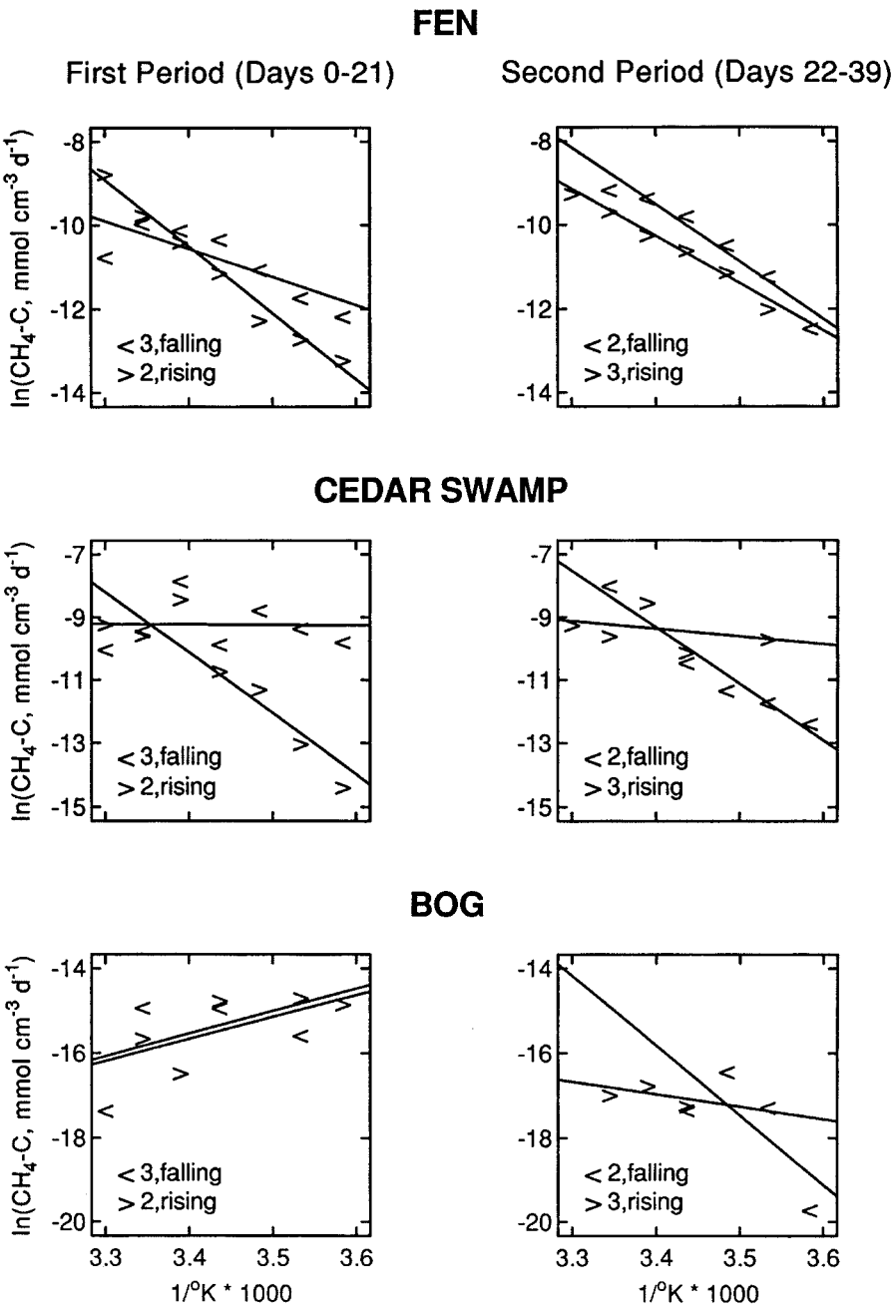

Figure 3. Arrhenius plots of temperature response, comparing orthogonal (treatment,mode) pairs for CH_4 (a) and CO_2 (b) flux rates. The legends indicate both the treatment number (2 or 3) and mode (rising or falling) for each set of symbols. The paired plots represent fluxes measured during the same time frame (Period), in contrast to Figure 2: each graph in Figure 3 incorporates one line (set of points) from each of the pairs of graphs in Figure 2.

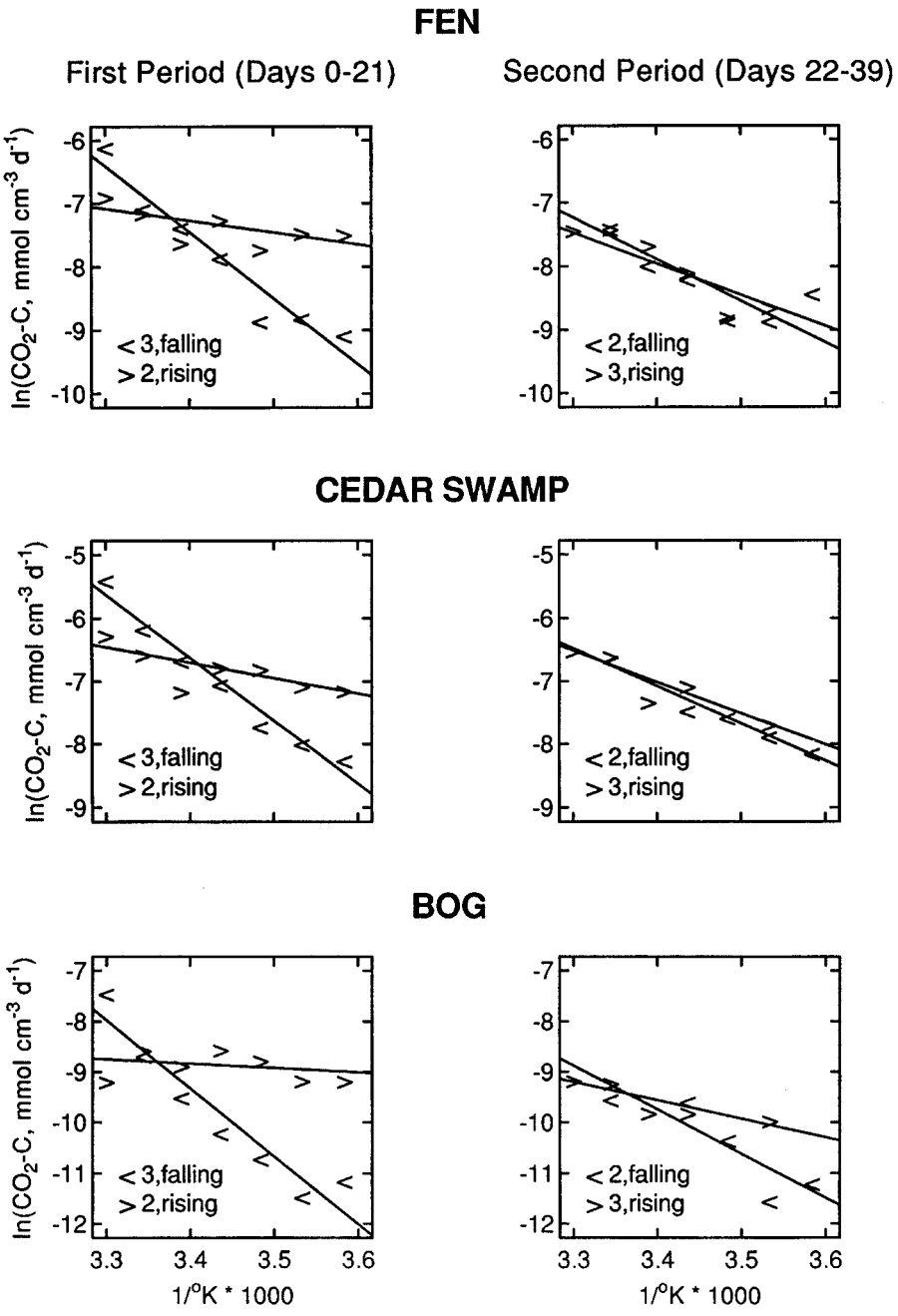

Figure 3. Continued.

Table 4. Differences in Arrhenius function slope coefficients and intercepts (indicated by P-values) between the orthogonal treatment pairs (as illustrated in Figures 2a and 2b). Since the comparison groups fall in the same time-frames (Periods), the effect of length of incubation is controlled for. Reported statistics are the *P*-values from *t*-tests in multiple regressions including a dummy variable for Mode, predicting gas flux in mmol cm^{-3}: $Y = \beta_0 + beta_1 X + \alpha_0 Z + \alpha_1 XZ$, where *X* is temperature and *Z* is mode (see text).

Site	Period	β_0	β_1	Mode effect (α_0)	Temp. × Mode (α_1)
CH_4					
Bog	1	0.091†	0.304	0.985	0.981
	2	0.898†	0.856	0.483	0.490
Cedar	1	0.001	0.000	0.004	0.003
	2	0.937	0.450	0.012	0.012
Fen	1	0.000	0.000	0.002	0.002
	2	0.000	0.000	0.197	0.229
CO_2					
Bog	1	0.304	0.598	0.000	0.000
	2	0.703	0.133	0.144	0.137
Cedar	1	0.601	0.017	0.000	0.000
	2	0.026	0.002	0.522	0.510
Fen	1	0.807	0.121	0.000	0.000
	2	0.029	0.003	0.474	0.475

† Overall *P* for regression was >0.05.

dependent on the direction of temperature change. During the second period of the incubation the overall response to temperature, based on Arrhenius coefficients (Table 3) or the β_o statistic in Table 4, was less clear, and the influence of mode was weak or insignificant.

Discussion

Conventional methods of comparing temperature response (point rates or cumulative values) would not have picked out the mode-dependent differences that we saw in this experiment. Indeed, due to the relatively small number of replicates and the high degree of variability in our measured gas fluxes, a conclusion of no significant temperature response would have been required. However, it is well-established that the Arrhenius function can effectively describe microbial responses to temperature in a variety of circumstances (Abdollai and Nedwell 1979; Westermann and Ahring 1987; Crill et al. 1988; Blet-Charaudeau et al. 1990; Bridgham and Richardson

1992). Therefore we believe that, given our particular focus on response trends with changing temperature, the exclusive comparison of the Arrhenius functions, rather than absolute rates or cumulative production, is the most valid way to proceed. The emissions rates reported in this paper should in no way be interpreted as representing values likely to occur in studies of longer duration or varying incubation conditions, since the very short incubations at each temperature precluded the possibility of microbial acclimation or adaptation to a particular temperature regime. That said, natural systems are rarely in a state of equilibrium, with temperature, at least, cycling on a diurnal or shorter timestep.

The absolute responses of CO_2 and CH_4 flux to temperature and to direction of temperature change varied among peat types, confirming the importance of substrate characteristics in modulating microbial dynamics. However, there were similar patterns of response among all the substrate types. The effect of temperature and of thermal history (mode effect) was most important during the first 21 days of incubation.

That differences between modes of temperature change were greatest during the first period of the incubation suggests that the decomposition of labile material, which is initially more abundant, is more sensitive to thermal history than is that of the more recalcitrant components, which would dominate the later period. Past anaerobic incubation experiments with peat have shown that most mineralization of labile material takes place within the first 4 weeks of incubation (Updegraff et al. 1995), which would correspond to Period 1 of this experiment. As labile material is consumed, decomposition rates decline, and measured flux rates converge toward similar low values. These latter flux rates appear to be controlled by processes that are less sensitive to temperature or thermal history. A similar anaerobic incubation that included the addition of labile substrate after 3–5 weeks would be a good test of this suggestion.

A dependence on history, or hysteresis effect, was also noted by Moore and Dalva (1993) with respect to the response of CH_4 flux to water-table fluctuations in peat columns (see also Moore and Roulet 1993). In that case the higher CH_4 flux response to falling water tables was attributed to the physical release of CH_4 from pore spaces and bubbles. In the case of temperature hysteresis the differences in CH_4 and CO_2 response are likely due to changes in substrate mobilization and consequent changes in the activity of different microbial consortia. Abdollai and Nedwell (1979) suggested that annual variations in the observed Arrhenius constants of microbial populations resulted from variations in factors other than temperature, such as bacterial numbers or concentrations of electron donor or acceptor molecules. This suggestion was reinforced by the findings of Westermann and Ahring (1987), who concluded

that the effects of large annual temperature variations on methanogenesis, denitrification and sulfate reduction were modulated by those other variables. Finally, since these incubations were not slurried, slow substrate diffusion rates may have also contributed to perceived lags in response.

An example of a direct population effect is found in Yavitt and Lang (1990) who observed a lag in the response of methane production to hydrogen amendments in peat slurries, suggesting that a normally small population of hydrogen-utilizing (CO_2-reducing) methanogens multiplied as a result of the amendments. A more common phenomenon is the bottleneck of substrate mobilization, since at least 67% biogenic of CH_4 is derived from acetate produced by fermentation (Mah et al. 1977). We observed lags of up to 10 days subsequent to ethanol amendments to peat slurries, after which there was a sharp increase in measured rates of methane production (Tara Doyle, unpublished data). We, and also Valentine et al. (1992), have stated in the past that the primary role of temperature in methanogenesis is likely that of regulating substrate supply (fermentation) rates (Updegraff et al. 1995). A nonlinear increase in substrate availability would manifest as a nonlinear response to temperature. Substrate availability will lag behind temperature if temperature changes are relatively rapid, as in the present case. That is, substrate availability at any given point in time would reflect the previous as well as the current temperature regime.

The concept that thermal or hydrologic history may be as important as prevailing state factors in controlling short-term microbial response may place limits on our ability to predict these responses. Gas fluxes (for example, CH_4) are frequently predicted as a function of one or multiple factors (H), typically including wetland type, soil temperature, and water table level, over some time period t, with the addition of an error term to correct for unexplained variance (not specifically annual or seasonal variation):

$$\mathrm{CH}_{4(t)} = f(H)_t + \epsilon \tag{3}$$

The differences we found in Arrhenius coefficients among the different temperature regimes suggest that history, in this case thermal history, might be a consideration when deriving the response function f. Moore and Dalva (1993) reached similar conclusions with respect to hydrologic regime. That is, the initial values of state variables in any response model will be dependent on previous history. The Arrhenius model is only one of many models of temperature response; we selected it for its relative simplicity and wide use. The following equation modifies (3) to take into account the effect of history on methanogenic response to environmental controls:

$$\mathrm{CH}_{4(t)} = f(H)_t + \int_{\tau=0}^{t} g(H_\tau) + \epsilon \tag{4}$$

where H represents a state factor(s) that changes as a function (g) of time (τ). The history of changes in these state factors and their effects on flux rates must be integrated over some time frame from $\tau = 0$ to $\tau = t$. In this model the cumulative effect of chronological or seasonal shifts in microbial activity or substrate availability is explicitly accounted for and removed from the error term (ϵ). We are unaware of any current models of C cycling that include this integration term.

The data generated by these incubations are unsuitable for use in longer term or larger-scale process models. Nor do we suggest that Arrhenius-type response functions be incorporated into large-scale models of C flux. However, it seems reasonable to speculate that if the microbially-mediated, micro-scale hysteresis such as that seen in this study drives large-scale variation it would place a fundamental limit on the accuracy of C-flux models, regardless of how carefully the controlling mechanisms are determined, i.e. that in practice model (4) may be impractical to parameterize over extended spatial and temporal scales. As diurnal, seasonal or longer climatic cycles act on wetland ecosystems the effects of past cycles or events could be magnified through time due to the influence of carbon and nutrient mobilization rates on microbial populations, carbon substrate quality, and ultimately on plant community composition and productivity. Models similar to (3), that predict monotonic responses to environmental controls such as temperature and moisture (e.g. Schimel et al. 1990; Fung et al. 1991), may become increasingly biased over the long term. Pastor and Post (1993) reported such a bias in linear models of upland forest response to climate change.

Because of the complex processes that give rise to hysteresis (non-linear responses to dynamic environmental conditions) on a micro-scale, generalized models may have limited capabilities for predicting the effect of climate change on decomposition dynamics and the resulting emissions of "greenhouse" gases from northern wetland ecosystems. Unfortunately, the logistics of experimental design force scientists to treat many aspects of the pedosphere-atmosphere interaction as linear black boxes, ignoring the mechanistic complexity of soil ecosystems. In our extremely simplified ecosystems, in which essentially all environmental variables were controlled, we observed unexpected responses to varying temperature regimes. Even in very detailed models, the lack of information may constrain the accuracy of predictions. Our results suggest that the complex factors controlling microbial community responses at small scales may inherently limit our ability to model regional-scale dynamics of trace gas fluxes in northern wetlands.

Acknowledgements

This research was funded by NSF grants DEB-9496305 and DEB-9707426. The authors would like to thank Ann Lima for statistical support.

References

Abdollai H & Nedwell DB (1979) Seasonal temperature as a factor influencing bacterial sulfate reduction in a saltmarsh sediment. Microb. Ecol. 5: 73–79

Armentano TV & Menges ES (1986) Patterns of change in the carbon balance of organic soil-wetlands of the temperate zone. J. Ecol. 74: 755–774

Blet-Charaudeau C, Muller J & Laudelout H (1990) Kinetics of carbon dioxide evolution in relation to microbial biomass and temperature. Soil Sci. Soc. Am. J. 54: 1324–1328

Bridgham SD, Johnston CA, Pastor J & Updegraff K (1995) Potential feedbacks of northern wetlands on climate change. BioScience 45: 262–274

Bridgham SD, Updegraff K & Pastor J (In Press) Carbon, nitrogen and phosphorous mineralization in northern wetlands. Ecology

Bridgham SD & Richardson CJ (1992) Mechanisms controlling soil respiration (CO_2 and CH_4) in southern peatlands. Soil Biol. Biochem. 24: 1089–1099

Conrad R, Schütz H & Babbel M (1987) Temperature limitation of hydrogen turnover and methanogenesis in anoxic paddy soil. FEMS Microbiol. Ecol. 45: 281–289

Crill PM, Bartlett KB, Harriss RC, Gorham E, Verry ES, Sebacher DI, Madzar L & Sanner W (1988) Methane flux from Minnesota peatlands. Global Geochemical Cycles 2: 371–384

Dise N, Gorham E & Verry ES (1993) Environmental factors controlling methane emissions from peatlands in northern Minnesota. J. Geophys. Res. 98(D6): 10,583–10,594

Draper NR & Smith H (1981) Applied Regression Analysis, 2nd ed. (pp 241–250). John Wiley and Sons, New York, NY

Fung I, John J, Lerner J, Matthews E, Prather M, Steele LP & Fraser PJ (1991) Three-dimensional model synthesis of the global methane cycle. J. Geophys. Res. 96(D7): 13,033–13,065

Giese AC (1973) Cell Physiology, 4th Edition. W.B. Saunders, Philadelphia, PA

Gorham E (1991) Northern peatlands: Role in the carbon cycle and probable responses to climatic warming. Ecol. Appl. 1: 182–195

Hameed S & Cess RD (1983) Impact of a global warming on biospheric sources of methane and its climatic consequences. Tellus 35B: 1–7

Hogg EH, Lieffers VJ & Wein RW (1992) Potential carbon losses from peat profiles: effect of temperature, drought cycles and fire. Ecol. Appl. 2: 298–306

Kattenberg A, Giorgi F, Grassl H, Meehl GA, Mitchell JFB, Stouffer RJ, Tokioka T, Weaver AJ & Wigley TML (1996) Climate models – projections of future climate. In: Houghton JT, Filho LGM Callander BA, Harris N, Kattenberg A and Maskell K (Eds) Climate Change 1995: The Science of Climate Change (pp 285–357). Cambridge University Press, Cambridge, UK

Khalil MAK & Rasmussen RA (1989) Climate-induced feedbacks for the global cycles of methane and nitrous oxide. Tellus 41B: 554–559

Mah RA, Ward DM, Baresi L & Glass TL (1977) Biogenesis of methane. Ann. Rev. Microbiol. 31: 309–341

Moore TR & Dalva M (1993) The influence of temperature and water table position on carbon dioxide and methane emissions from laboratory columns of peatland soils. J. Soil Sci. 44: 651–664

Moore TR & Roulet NT (1993) Methane flux:water table relations in northern wetlands. Geophys. Res. Letters 20(7): 587–590

Naiman RJ, Manning T & Johnston CA (1991) Beaver population fluctuations and tropospheric methane emissions in boreal wetlands. Biogeochemistry 12: 1–15

Pastor J & Post WM (1993) Linear regressions do not predict the transient responses of eastern North American forests to CO_2-induced climate change. Climatic Change 23: 111–119

Post WM (1990) Report of a workshop on climate feedbacks and the role of wetlands, tundra and boreal ecosystems in the global carbon cycle. ORNL/TM-9999 (Envir. Sciences Division)

Schimel D, Alves D, Enting I, Heimann M, Joos F, Raynaud D, Wigley T, Prather M, Derwent R, Ehhalt D, Fraser P, Sanhueza E, Zhou X, Jonas P, Charlson R, Rodhe H, Sadasivan S, Shine KP, Fouquart Y, Ramaswamy V, Solomon S, Srinivasan J, Albritton D, Derwent R, Isaksen I, Lal M, & Wuebbles D (1996) Radiative forcing of climate change. In: Houghton JT, Filho LGM Callander BA, Harris N, Kattenberg A & Maskell K (Eds) Climate Change 1995: The Science of Climate Change (pp 65–131). Cambridge University Press, Cambridge, UK

Schimel DS, Parton WJ, Kittel TGF, Ojima DS & Cole CV (1990) Grassland biogeochemistry: links to atmospheric processes. Climatic Change 17: 13–25

SYSTAT Inc (1994a) SYSTAT for DOS: Advanced Applications, Version 6 Edition. Evanston, IL. 902 pp

SYSTAT, Inc. (1994b) SYSTAT for DOS: Using SYSTAT, Version 6 Edition. Evanston, IL. 871 pp

Updegraff K, Pastor J, Bridgham SD & Johnston CA (1995) Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands. Ecol. Appl. 5: 151–163

Valentine DW, Holland EA & Schimel DS (1992) Ecosystem and physiological controls over methane production in northern wetlands. J. Geophys. Res. 99: 1563–1571

Westermann P & Ahring BK (1987) Dynamics of methane production, sulfate reduction and denitrification in a permanently waterlogged alder swamp. Appl. Environ. Microbiol. 53: 2554–2559

Wieder RK, Yavitt JB & Lang GE (1990) Methane production and sulfate reduction in two Appalachian peatlands. Biogeochemistry 10: 81–104

Yavitt JB & Lang GE (1990) Methane production in contrasting wetland sites: response to organo-chemical components of peat and to sulfate reduction. Geomicrobiol. J. 8: 27–46

Yavitt JB, Lang GE & Wieder RK (1987) Control of carbon mineralization to CH_4 and CO_2 in anaerobic, *Sphagnum*-derived peat from Big Run Bog, West Virginia. Biogeochemistry 4: 141–157