GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 14, NO. 4, PAGES 999-1019, DECEMBER 2000

General CH_4 oxidation model and comparisons of CH_4 oxidation in natural and managed systems

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Abstract. Fluxes of methane from field observations of native and cropped grassland soils in Colorado and Nebraska were used to model CH_4 oxidation as a function of soil water content, temperature, porosity, and field capacity (FC). A beta function is used to characterize the effect of soil water on the physical limitation of gas diffusivity when water is high and biological limitation when water is low. Optimum soil volumetric water content (W_{opt}) increases with FC. The site specific maximum CH_4 oxidation rate (CH_{4max}) varies directly with soil gas diffusivity (D_{opt}) as a function of soil bulk density and FC. Although soil water content and physical properties are the primary controls on CH_4 uptake, the potential for soil temperature to affect CH_4 uptake rates increases as soils become less limited by gas diffusivity. Daily CH_4 oxidation rate is calculated as the product of CH_{4max}, the normalized (0-100%) beta function to account for water effects, a temperature multiplier, and an adjustment factor to account for the effects of agriculture on methane flux. The model developed with grassland soils also worked well in coniferous and tropical forest soils. However, soil gas diffusivity as a function of field capacity, and bulk density did not reliably predict maximum CH_4 oxidation rates in deciduous forest soils, so a submodel for these systems was developed assuming that CH_{4max} is a function of mineral soil bulk density. The overall model performed well with the data used for model development ($r^2 = 0.76$) and with independent data from grasslands, cultivated lands, and coniferous, deciduous, and tropical forests ($r^2 = 0.73$, mean error < 6%).

1. Introduction

The atmospheric concentration of methane (CH_4) has more than doubled since the early 1800s to ~1.75 ppm in 1998 (www.cmdl.noaa.gov/ccg/figures/ch4trend_global.gif). This is likely a result of both increased CH_4 emissions from anthropogenic sources and decreased CH_4 consumption in soils as a result of land use changes [*Ojima et al.*, 1993]. This radiatively active trace gas is produced biologically during fermentation in anaerobic environments and consumed by reaction with OH^- in the atmosphere and by microbial oxidation in soils. Although oxidation in soils accounts for ~10% of the global CH_4 sink of 350-480 TgC yr^{-1}, the CH_4 consumed annually in soils approximately equals or exceeds the net yearly increase of CH_4 in the atmosphere [*Prather et al.*, 1995]. A major goal of this research is to improve estimates of the contributions of natural and managed ecosystems to the terrestrial CH_4 sink.

Methane is produced in water-logged soils as an end product of organic matter decomposition. In aerated soils, CH_4 may be oxidized by methanotrophs and other CH_4 oxidizing microbes [*Davidson and Schimel*, 1995]. CH_4 produced in saturated soil layers may be oxidized to CO_2 in drier surface layers before diffusing out of the soil [*Conrad*, 1989]. Atmospheric CH_4 may also diffuse into soil and be oxidized. On an annual basis, rice paddies and natural wetlands are net producers of CH_4, while grasslands and forests are net consumers. Our model is designed to simulate CH_4 oxidation in soils that are usually net sinks of atmospheric CH_4. Controls of atmospheric CH_4 uptake include soil water [*Adamsen and King*, 1993], temperature [*Whalen and Reeburgh*, 1996], texture [*Boeckx et al.*, 1997], microbial population [*Willison et al.*, 1997] and mineral N concentration [*Crill et al.*, 1994].

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Paper number 1999GB001226.
0886-6236/00/1999GB001226$12.00

Complex methane oxidation models simulate microbial dynamics [*Grant*, 1999] and CH_4 concentration gradients in soils [*Dörr et al.*, 1993]. Our simpler model is based on the global CH_4 oxidation model developed by *Potter et al.* [1996]. Potter's model assumes that soil gas diffusivity is the major control and that CH_4 oxidation is negligible when soil temperatures are below the freezing point of water. As soils dry, gas diffusivity increases, so Potter's model predicts maximum CH_4 oxidation rates at low soil moisture levels. However, data show that CH_4 oxidation rates peak at 7-20% volumetric water content and that significant rates of CH_4 oxidation can occur at sub zero temperatures [*Mosier et al.*, 1996, 1997; *Sommerfeld et al.*, 1993].

Our general model consists of a submodel for grasslands, coniferous, and tropical forests and a submodel for deciduous forests. Both submodels use soil physical properties to estimate potential CH_4 oxidation rates and, in addition, account for the biochemical effects of water and temperature on methane oxidation. We assume that soil physical properties determine maximum CH_4 oxidation rates for a particular soil and that temporal variations in CH_4 oxidation are correlated with soil water content and temperature. Methane oxidation is assumed to be primarily limited by soil gas diffusivity when water potential is too high and by water stress on biological activity when water potential is too low. These are similar to the assumptions of *Ridgwell et al.* [1999] that methane uptake is controlled by gas diffusivity at high rates of microbial activity and by microbial activity at high diffusivities. However, the CH_4 oxidation model described by *Ridgwell et al.* [1999] is process based, whereas our model is empirically based and has been validated more extensively. The soil gas diffusivity equations developed by *Potter et al.* [1996] are used to infer site specific potential CH_4 oxidation rates in grassland, coniferous, and tropical forest soils. In deciduous systems, potential CH_4 oxidation rates are assumed to increase linearly with mineral soil porosity. Field data from grassland and deciduous forest soils were used to model CH_4 oxidation as a function of soil water content, temperature, and soil physical properties. The U.S. Trace Gas Network (TRAGNET) was accessed to validate the general model with data from various biomes and to compare CH_4 uptake rates in systems under different land use practices. The model is designed to be linked with larger-scale ecosystem models (e.g., CENTURY) [*Parton et al.*, 1994, 1998] so that estimates of CH_4 flux through various systems can be improved.

This paper is a product of the U.S. Trace Gas Network (TRAGNET) and a Trace Gas Fluxes Working Group sponsored by the U.S. Center for Ecological Analysis and Synthesis (NCEAS). TRAGNET was established in 1992 with the goals of documenting contemporary fluxes of CO_2, CH_4, and N_2O, determining the major controls of trace gas flows, and improving our ability to predict future fluxes in response to ecosystem and climate change. The objectives of the NCEAS Working Group responsible for this series of papers were to analyze the TRAGNET database and enhance our understanding of the controls and magnitudes of CH_4 and N_2O fluxes in various natural and managed ecosystems by using models and by comparing fluxes at various scales. This paper contributes to these goals by quantifying some primary controls of CH_4 oxidation and explaining how maximum flux rates and the controlling factors change with biome type and environmental conditions. TRAGNET maintains a long-term data archive to facilitate data comparisons and model building (www.nrel.colostate.edu/programs/atmosphere/tragnet/tragnet.html).

2. Data Sets

Data from grassland soils in the Central Plains Experimental Range (CPER), Colorado [*Mosier et al.*, 1996, 1997], and the High Plains Experimental Research Laboratory at Sidney, Nebraska [*Kessavalou et al.*, 1998] were used to develop the Grassland-Coniferous-Tropical submodel (Table 1a). Gas flux data from Harvard Forest [*Peterjohn et al.*, 1994], Scotland [*Dobbie and Smith*, 1996] and New Hampshire (P.M. Crill, unpublished data, 1990-1996) were used to develop the Deciduous Forest submodel (Table 1a). The data sets used for model building included measurements of soil bulk density, methane gas flux, soil or air temperature, and soil water content. Similar data sets from various soils were used to test the general model and to compare CH_4 oxidation rates in different biomes (Table 1b). Data from soils used for agriculture or subjected to fertilization treatments were used to quantify the effects of these land use practices on CH_4 oxidation rates.

3. Data Analysis and Model Description

To develop the Grassland-Tropical-Coniferous submodel, soil gravimetric water content and bulk density were used to calculate volumetric water content (W) in $cm^3H_2O\ cm^{-3}$soil for each nondeciduous soil in Table 1a. Soil water content at field capacity (FC) is usually not measured for field soils so FC was estimated based on time series of soil water content data. Generally, FC was assumed to be the water content exceeded by 10% of the observed water content measurements. In all figures and discussion, positive CH_4 fluxes represent CH_4 uptake by soil.

To minimize temperature limitation and isolate the response of CH_4 oxidation to soil water content, the data were stratified for soil temperature > 15°C, and CH_4 oxidation rate versus W was plotted for each soil. A beta function was used to model the effect of W because it accounts for biological limitation when water is low and gas diffusivity limitation when water is high. All of the grassland soils used for model building showed significant responses to water (Table 2), but the maximum CH_4 oxidation rate and the water level at which it occurred varied with soil properties related to texture (Figure 1). The parameter controlling curve shape was fixed, but the parameters controlling the maximum CH_4 oxidation rate (CH_{4max}), the optimum water content (W_{opt}), the minimum water content (W_{min}), and the maximum water content (W_{max}) were allowed to vary. Equations were optimized for each soil by minimizing the sum square error [*Statistical Analysis Institute, Inc. (SAS)*, 1990] for simulated versus observed CH_4 oxidation.

Best fitting values for W_{opt}, W_{min}, W_{max}, and CH_{4max} were related to soil physical properties. W_{opt}, W_{min}, and W_{max} were found to increase linearly with field capacity. Plowing

Table 1a. Characteristics of Soils Used for Model Building and Model Testing: Soils used for Model Building

Soil	Location	Vegetation/Land Use	Sand, %	Clay, %	FC_3, cm^3	BD_3, gcm^3	Source
Pasture native	Colorado	Native grassland	74	13	0.21	1.41	*Mosier et al.* [1996]
Midslope native	Colorado	Native grassland	76	13	0.20	1.40	*Mosier et al.* [1996]
Swale native	Colorado	Native grassland	58	24	0.32	1.34	*Mosier et al.* [1996]
Swale clay	Colorado	Native grassland	47	27	0.34	1.32	*Mosier et al.* [1996]
Midslope clay	Colorado	Native grassland	70	13	0.24	1.33	*Mosier et al.* [1996]
Top clay	Colorado	Native grassland	50	24	0.30	1.32	*Mosier et al.* [1996]
5 enclosed	Colorado	Native grassland	39	14	0.28	0.85	A.R. Mosier (unpublished data, 1995-1996)
5 grazed	Colorado	Native grassland	42	14	0.32	1.15	A.R. Mosier (unpublished data, 1995-1996)
7 enclosed	Colorado	Native grassland	68	16	0.19	1.36	A.R. Mosier (unpublished data, 1995-1996)
7 grazed	Colorado	Native grassland	69	10	0.38	1.41	A.R. Mosier (unpublished data, 1995-1996)
19 enclosed	Colorado	Native grassland	35	25	0.40	0.99	A.R. Mosier (unpublished data, 1995-1996)
19 grazed	Colorado	Native grassland	21	39	0.38	0.91	A.R. Mosier (unpublished data, 1995-1996)
Field native	Colorado	Native grassland	70	12	0.21	1.40	*Mosier et al.* [1997]
Field plowed	Colorado	Native grassland	70	12	0.1	1.40	*Mosier et al.* [1997]
Swale fertilized	Colorado	Fert grassland	58	24	0.32	1.34	*Mosier et al.* [1996]
Midslope fertilized	Colorado	Fert grassland	76	13	0.20	1.42	*Mosier et al.* [1996]
Pasture fertilized	Colorado	Fert grassland	74	15	0.21	1.30	*Mosier et al.* [1996]
Plowed pasture	Colorado	Plowed pasture	74	13	0.21	1.30	*Mosier et al.* [1997]
Wheat field east	Colorado	Wheat/fallow	67	13	0.18	1.30	*Mosier et al.* [1997]
Wheat field west	Colorado	Wheat/fallow	66	15	0.18	1.20	*Mosier et al.* [1997]
CRP*	Colorado	Wheat/fallow	64	16	0.22	1.20	*Mosier et al.* [1997]
Sod	Nebraska	Native grassland	35	23	0.40	1.05	*Kessavalou et al.* [1998]
Plow	Nebraska	Wheat/fallow	41	26	0.36	1.27	*Kessavalou et al.* [1998]
Sub till	Nebraska	Wheat/fallow	38	28	0.34	1.20	*Kessavalou et al.* [1998]
No till	Nebraska	Wheat/fallow	33	29	0.40	1.23	*Kessavalou et al.* [1998]
Harvard Forest	Massachusetts	Deciduous forest	-	-	-	0.64	*Peterjohn et al.* [1994]
Durham	New Hampshire	Deciduous woodland	-	-	-	0.86	P.M. Crill (unpublished data, 1990-1996)
Gullane	Scotland	Deciduous woodland	-	-	-	1.08	*Dobbie and Smith* [1996]

*CRP = Conservation Reserve Program

and fertilization treatments did not effect W_{opt}, so data from the grassland, wheat/fallow, plowed, and fertilized soils in Table 1a were used to quantify the effect of field capacity on the water curve (Figure 2a). Functions for W_{min} and W_{max} were similarly based on field capacity. The parameter controlling the maximum CH_4 oxidation rate was correlated with a soil gas diffusivity coefficient (D_{opt}). D_{opt} is a relative index of gas diffusivity through soil assuming a water content of W_{opt} and was calculated as a function of soil porosity and field capacity according to the method of *Potter et al.* [1996]. Plowing and fertilization tended to depress CH_4 oxidation rates so only the native grassland soils in Table 1a were used to regress CH_{4max} with D_{opt}. Soils with high gas diffusivity at optimum water content for CH_4 oxidation exhibited higher CH_4 oxidation rates than soils with low D_{opt} (Figure 2b).

The soils were analyzed individually to derive equations for soil temperature (T_{soil}) because sensitivity of CH_4 oxidation to T_{soil} varied significantly among soils. To isolate

Table 1b. Characteristics of Soils Used for Model Building and Testing: Soils Used for Model Testing

Site/Soil	Location	Vegetation/ Land Use	Code	BD, gcm^3	Source
Oxisol	Puerto Rico	Grassland	GPR	1.36	*Mosier and Delgado* [1997]
Ultisol	Puerto Rico	Grassland	GPR	0.95	*Mosier and Delgado* [1997]
Vertisol	Puerto Rico	Grassland	GPR	1.2	*Mosier and Delgado* [1997]
Höeglwald	Germany	Coniferous forest	CFHG	1.06	K. Butterbach-Bahl (unpublished data, 1995)
Solling	Germany	Coniferous forest	CFSG	1.13	*Borken* [1996]
Alpine	Wyoming	Coniferous forest	CFWY	1.0	*Mosier et al.* [1993]
La Selva	Costa Rica	Tropical forest	TFCR	0.67	*Keller et al.* [1993]
Rondonia	Brazil	Tropical forest	TFB	1.25	*Steudler et al.* [1996]
Darmstadt	Germany	Deciduous forest	DFDG	1.3	*Dong et al.* [1998]
Höeglwald	Germany	Deciduous forest	DFDG	0.94	K. Butterbach-Bahl (unpublished data, 1995)
Transect	New York	Deciduous forest	DFNY	0.23-1.33	*Goldman et al.* [1995]
FAM A	Germany	Agricultural	AGG	1.45	*Flessa et al* [1995]
FAM B	Germany	Agricultural	AGG	1.18	*Flessa et al* [1995]
FAM C	Germany	Agricultural	AGG	1.33	*Flessa et al* [1995]
FAM D	Germany	Agricultural	AGG	1.27	*Flessa et al* [1995]
Set Aside	Scotland	Former agricultural	AGS	1.36	*Dobbie and Smith* [1996]
Wheat	Scotland	Agricultural	AGS	1.27	*Dobbie and Smith* [1996]
Barley	Colorado	Agricultural	AGC	1.26	*Delgado and Mosier* [1996]
Oxisol	Puerto Rico	Fertilized grassland	GPR	1.36	*Mosier and Delgado* [1997]
Ultisol	Puerto Rico	Fertilized grassland	GPR	0.95	*Mosier and Delgado* [1997]
Vertisol	Puerto Rico	Fertilized grassland	GPR	1.20	*Mosier and Delgado* [1997]

FAM = Forschungsverbund Agrarökosysteme München; GPR = Grassland, Puerto Rico; CFHG = Coniferous Forest, Höeglwald, Germany; CFSG = Coniferous Forest, Solling, Germany; TFCR = Tropical Forest, Costa Rica; TFB = Tropical Forest, Brazil; DFDG = Deciduous Forest, Darmstadt, Germany; DFHG = Deciduous Forest, Höeglwald, Germany; DFNY = Deciduous Forest, New York; AGG = Agricultural, Germany; AGS = Agricultural, Scotland; AGC = Agricultural, Colorado.

the temperature effect, the data were stratified to minimize the effects of water limitation. Data points having a water content less than the mean of W_{min} and W_{opt} or greater than the mean of W_{max} and W_{opt} for each soil were eliminated. The data showed little evidence for an optimum temperature, so a linear regression was fit to each soil. Eight of 15 native soils and 6 of 10 agricultural soils showed a significant correlation between CH_4 oxidation and temperature when water was not strongly limiting (Table 2). The response of CH_4 oxidation to T_{soil} tended to be stronger in soils not highly limited by gas diffusivity (Figures 3a and 3b). The magnitude of the temperature response, as indicated by the slope of the linear regression, increased with D_{opt} (Figure 3c). To account for this the interaction between temperature and D_{opt}, rather than the primary effect of temperature, was included in the model.

The grassland soils that were recently or historically fertilized, plowed, or used for agriculture showed average CH_4 oxidation rates ranging from 25 to 100% that of similar native soils. For the CPER and Nebraska soils the decrease in CH_4 oxidation rates associated with agricultural practices was strongly correlated with D_{opt}. For example, a fertilized sandy loam pasture with high D_{opt} had significantly lower CH_4 oxidation rates than a similar native pasture, whereas a fertilized swale clay soil with low D_{opt} showed CH_4 oxidation rates similar to the native swale clay (Figures 4a-4d). For each fertilized, cropped, or plowed soil in Table 1a, an adjustment factor was calculated to compensate for the tendency of the model to overestimate CH_4 oxidation rates in these soils. The adjustment factor derived for each agricultural soil, $F(Ag, D_{opt})$, represents the fractional multiplier of simulated CH_4 oxidation required to obtain nonbiased model predictions. That is,

$$F(Ag, D_{opt})\Sigma(CH_{4model}) - \Sigma(CH_{4observed}) = 0. \quad (1)$$

Table 2. Optimum Water Content for CH_4 Oxidation (W_{opt}) Soil Gas Diffusivity at W_{opt} (D_{opt}) and Correlation Coefficients and Significance Levels Between the Independent Variables and CH_4 Oxidation for the Soils Used to Build the Grassland-Tropical-Coniferous Submodel

Soil	Number of observations	W_{opt}	D_{opt}	r^2 (H_2O)	p-val(H_2O)	$r^2(T_{soil})$	p-val(T_{soil})
Pasture native	261	8	0.2	0.31	0.0001	0.22	0.0001
Midslope native	207	7	0.21	0.38	0.0001	0.35	0.0001
Swale native	246	14	0.14	0.30	0.0001	0.05	NS
Swale Clay	119	12	0.14	0.21	0.001	0.01	NS
Midslope clay	120	9	0.2	0.16	0.001	0.25	0.0001
Top clay	122	13	0.16	0.12	0.001	0.06	0.06
5 enclosed	66	13	0.31	0.33	0.0001	0.25	0.0001
5 grazed	66	17	0.19	0.46	0.0001	0.08	0.09
7 enclosed	66	8	0.23	0.49	0.0001	0.26	0.001
7 grazed	66	9	0.21	0.53	0.0001	0.15	0.01
19 enclosed	60	26	0.16	0.34	0.0001	0.00	NS
19 grazed	62	25	0.2	0.41	0.0001	0.01	NS
Field native	51	6	0.21	0.68	0.0001	0.45	0.0001
Field plowed	51	6	0.21	0.4	0.0001	0.12	0.04
Swale fertilized	226	13	0.14	0.07	0.001	0.01	NS
Midslope fertilized	204	8	0.2	0.27	0.0001	0.20	0.0001
Pasture fertilized	268	8	0.23	0.25	0.0001	0.14	0.0001
Plowed pasture	160	8	0.24	0.05	0.02	0.21	0.0001
Wheat field east	91	6	0.28	0.39	0.001	0.06	NS
Wheat field west	118	7	0.25	0.16	0.001	0.23	0.002
CRP	123	5	0.27	0.37	0.0001	0.25	0.0001
Sod	97	16	0.17	0.40	0.0001	0.00	NS
Plow	97	15	0.13	0.25	0.0001	0.03	NS
No Till	97	18	0.1	0.56	0.0001	0.16	0.01
Sub till	97	15	0.16	0.38	0.0001	0.03	NS

NS = not significant at the 0.10 level.

The required adjustment was stronger in soils less limited by gas diffusivity (Figure 4e).

The Grassland-Tropical-Coniferous submodel uses soil gas diffusivity and land use to estimate maximum CH_4 oxidation rate for a particular site and soil water and temperature measurements to predict daily CH_4 oxidation rates in g C ha^{-1} d^{-1}. The equation for CH_4 consumption in grassland, coniferous, tropical, and agricultural soils that are usually net consumers of methane is

$$CH_4 = CH_{4max} F(W,FC) F(T_{soil}, D_{opt}) F(Ag, D_{opt}). \quad (2)$$

The model first infers optimal water content for CH_4 oxidation (W_{opt}) as a function of field capacity (Figure 2a). Soil gas diffusivity (D_{opt}) is calculated as a function of W_{opt}, field capacity (FC), and bulk density (BD) according to the method for aggregated media described by *Potter et al.* [1996]. D_{opt} is then used to infer CH_{4max} (Figure 2b). CH_{4max} is attenuated by $F(W,FC)$ to account for water limitation. The parameters controlling the minimum, optimum, and maximum values of the water curve are functions of FC (Figure 5a).

$F(T_{soil}, D_{opt})$ is a dimensionless multiplier representing the effect of the interaction between soil temperature and gas diffusivity on CH_4 oxidation (Figure 5b). $F(Ag,D_{opt})$ is a multiplier equal to 1 for native soils and a function of D_{opt} for agricultural soils (Figure 5c).

Data from deciduous soils in the United States and Scotland were used to develop the deciduous forest submodel (Table 1a). CH_4 oxidation rates in deciduous forests tend to vary directly with soil porosity [*Smith et al.*, 2000] and

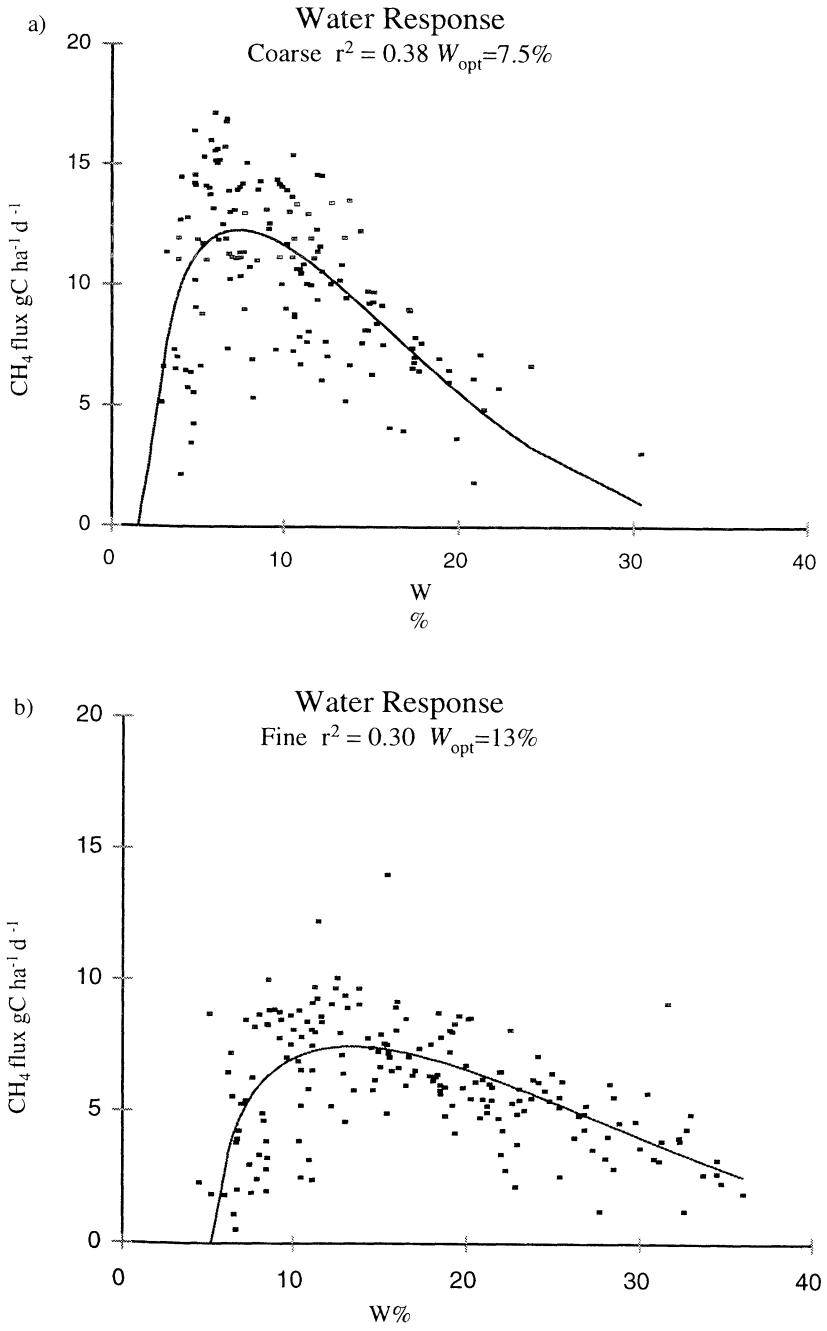

Figure 1. Response of CH_4 oxidation to soil volumetric water and best fitting beta functions for typical (a) coarse and (b) fine textured soils.

temperature [*Dong et al.*, 1998] and inversely with soil water content [*Castro et al.*, 1994]. Soil water was a stronger predictor than temperature for CH_4 oxidation at Gullane Woodland and Harvard Forest but not at Durham (Table 3). The data from the three deciduous forest soils were pooled to quantify the effects of soil water content and temperature on CH_4 oxidation rates. The response of CH_4 oxidation to soil water-filled pore space (WFPS = % relative saturation) tended to be linear, but a beta function was used to model the effect of WFPS because it is unreasonable to assume that maximum CH_4 oxidation rates occur when soils are 100% dry (Figure 6a). A linear regression was used for temperature (Figure 6b). The model was constructed by assuming that mineral soil bulk density sets the potential CH_4 oxidation rate for a particular site and daily water and temperature variations correlate with variations in CH_4 oxidation rate. The equations (Figure 7) were optimized by minimizing the mean square error (MSE) for simulated versus observed CH_4 oxidation rates using the three-way interaction among WFPS, bulk density, and T_{soil} to simulate methane oxidation rates. The

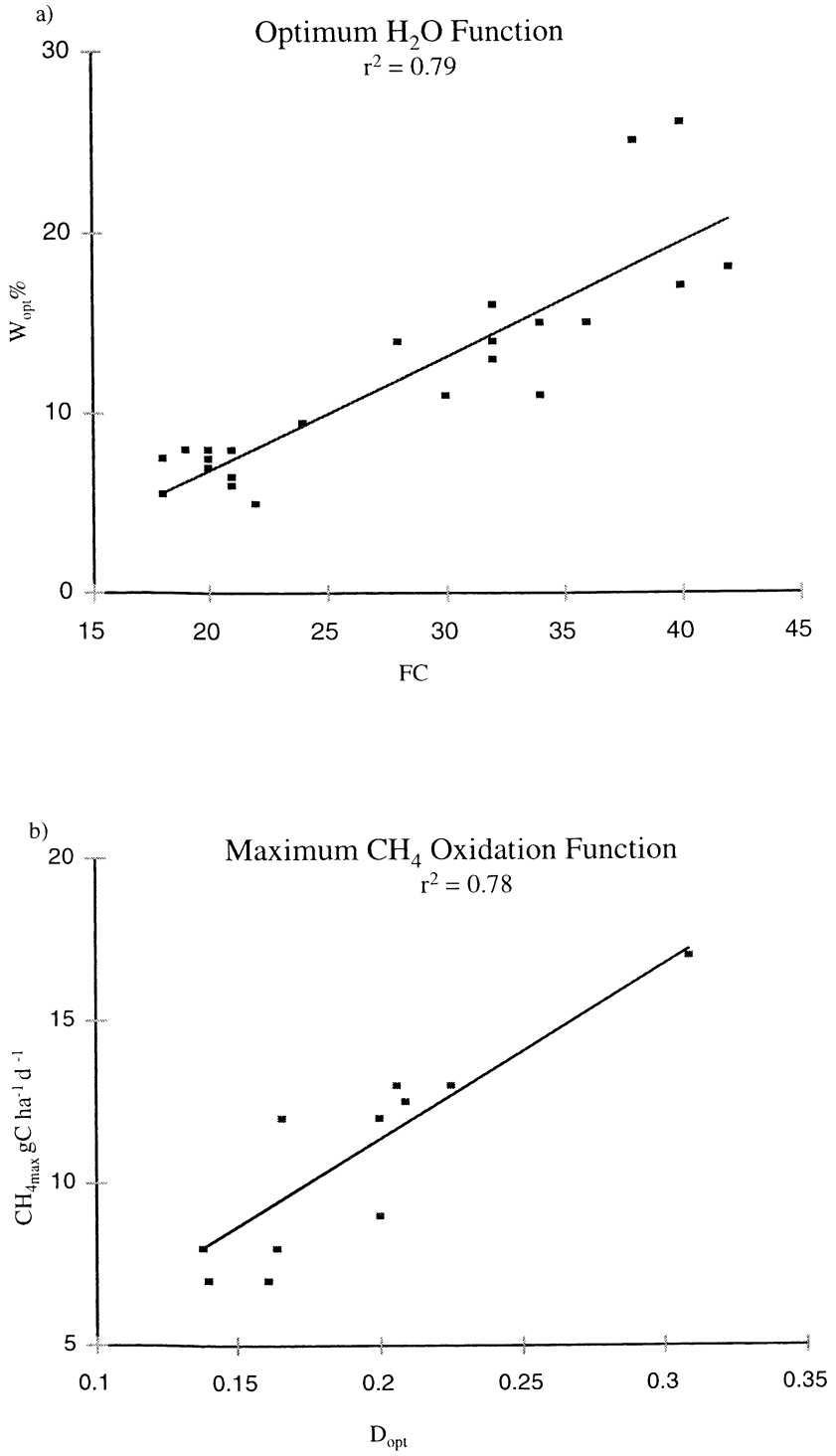

Figure 2. Model parameters related to soil properties: (a) optimum water content for CH_4 oxidation as a function of field capacity (W_{opt}) and (b) maximum CH_4 oxidation rate as a function of soil gas diffusivity calculated at optimum water (D_{opt}).

equation for CH_4 oxidation in deciduous forest soils is

$$CH_4 = CH_{4max} F(\text{WFPS}) F(T_{soil}). \quad (3)$$

CH_{4max} is the estimated potential CH_4 oxidation rate for a particular site based on soil bulk density (Figure 7a). F(WFPS) and $F(T_{soil})$ are functions to account for the effects of soil water content and temperature on CH_4 oxidation (Figures 7b,7c).

4. Model Testing and Ecosystem Comparisons

First the results of tests with the general model on all the soils used for model building and validation are presented;

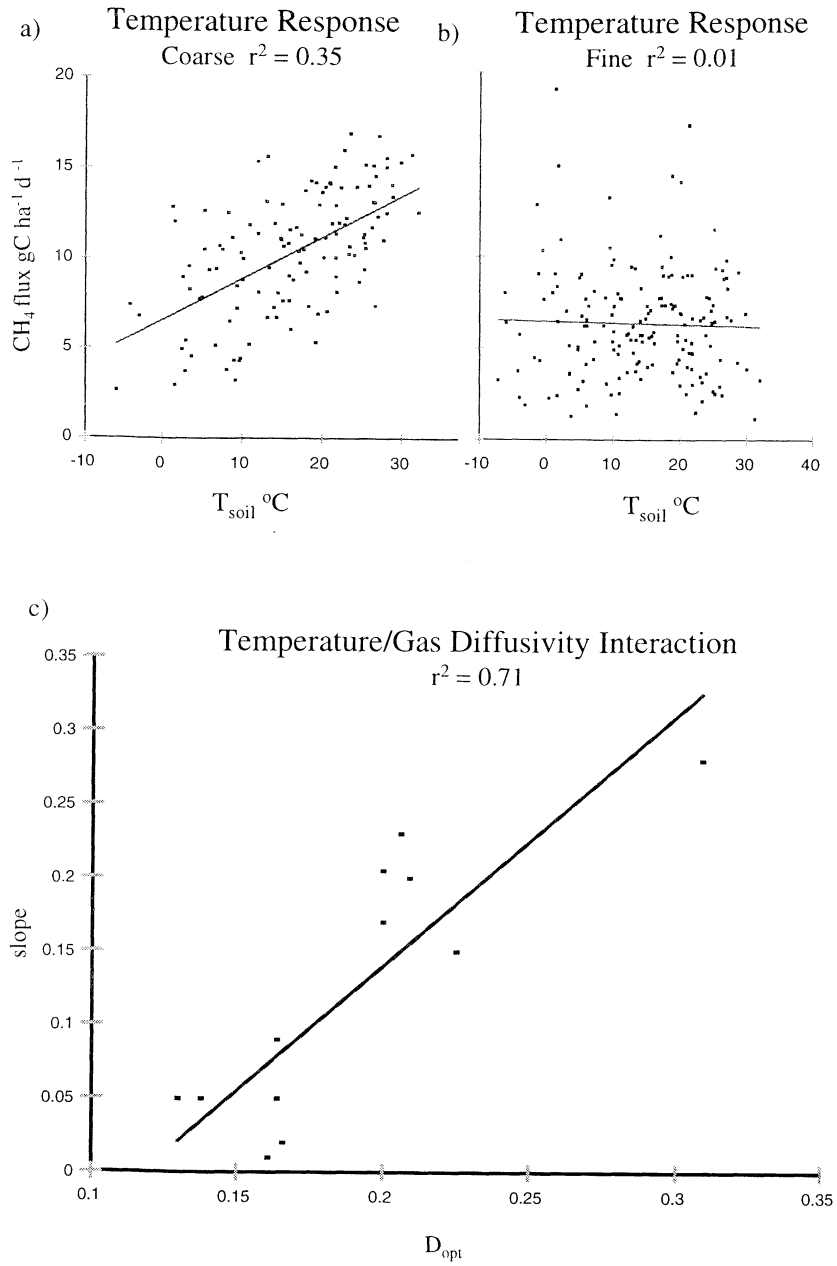

Figure 3. Response of CH_4 oxidation rate to temperature when water was not limiting and linear regressions for (a) typical coarse textured soil, $p<0.0001$, (b) typical fine textured soil, $p=0.68$, and (c) slope of linear regressions of CH_4 oxidation rate with soil temperature versus soil gas diffusivity (D_{opt}) for the native grassland soils used to build the model.

then how the model performed with the individual soils is considered. The soil gas diffusivity model [*Potter et al.*, 1996], upon which the Grassland-Tropical-Coniferous submodel is based, performed well (r^2=0.57) when comparing simulated versus observed CH_4 consumption rates in the soils used to build the general model (Figure 8a). However, our model that includes the biological as well as the physical effects of soil water and temperature on methane oxidation achieved an r^2 of 0.76 with these soils (Figure 8b). Independent data from grasslands, cultivated land, and tropical, coniferous, and deciduous forests (Table 1b) were used for model validation (Figure 8c). Figure 8d shows observed and simulated average annual methane uptake for the sites used for model validation. In 10 of 12 of these sites the simulated average annual flux differed from the observed by < 30%. The success of the overall model (r^2=0.73, mean error < 6% for the validation data set) supports the assumptions that soil gas diffusivity and biological effects of water and temperature are the primary controls on CH_4 oxidation rates in many soils.

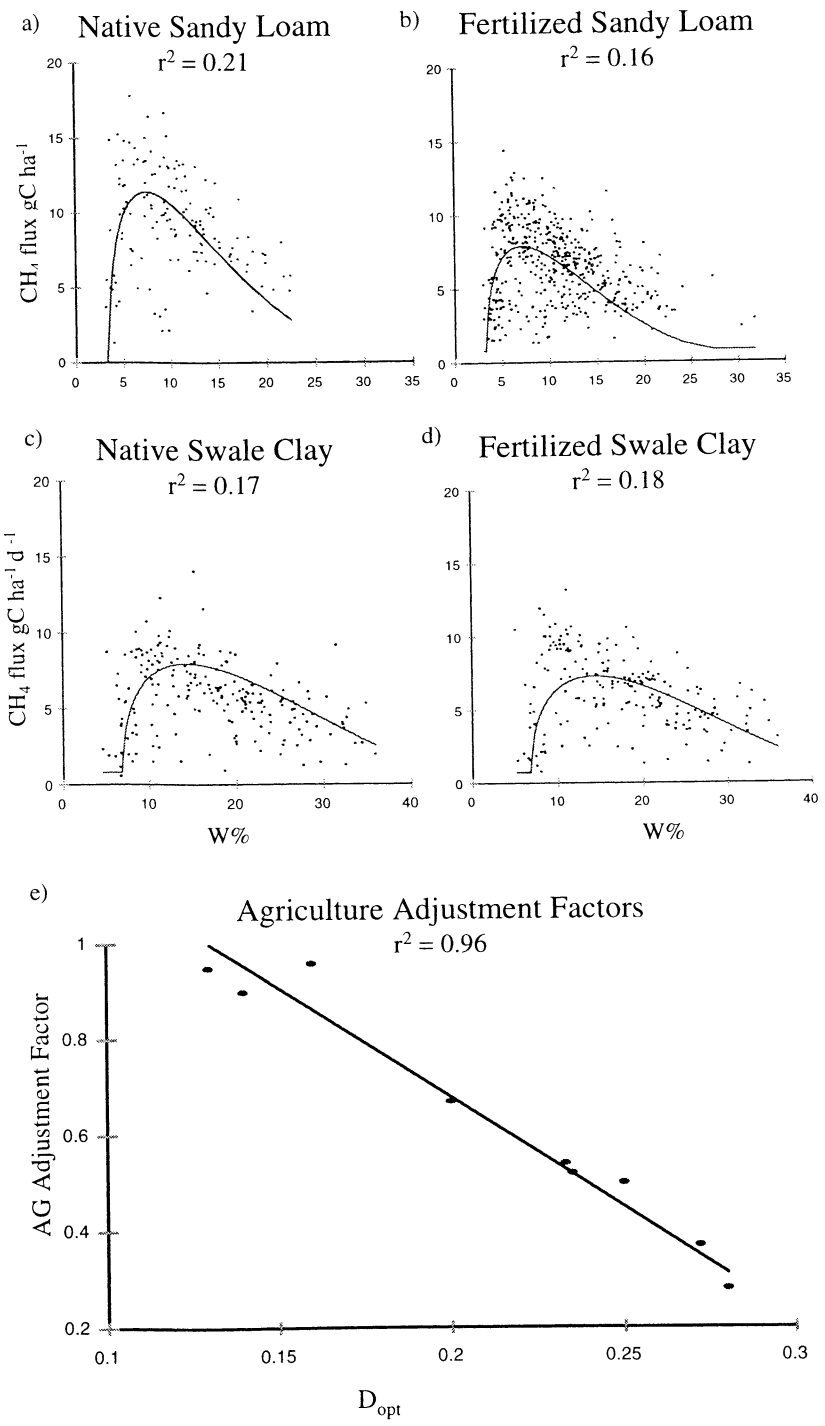

Figure 4. Comparisons of response of CH_4 oxidation rates to soil water content in native and adjacent fertilized pastures for (a, b) coarse textured soil and (c, d) fine textured soil. (e) Effect of fertilization and cropping on CH_4 oxidation rates as a function of soil gas diffusivity after accounting for effects of bulk density (BD), water content, and temperature.

The soils used for model testing showed a clear division in CH_4 uptake rates among biomes. Grassland and agricultural soils had the lowest annual CH_4 uptake (<1.5 kg C ha^{-1} yr^{-1}), coniferous and tropical forests showed intermediate CH_4 consumption (1.2-3.5 kg C ha^{-1} yr^{-1}), and deciduous forest soils had the highest CH_4 oxidation rates (4.5-10 kg C ha^{-1} yr^{-1}). To compare CH_4 oxidation rates among soils we used annual average temperature values for simulations because if the temperature effect is constant, model predictions form a smooth curve and in most cases the temperature effect is minor. The Grassland-Tropical-Coniferous model was tested in Puerto Rican grasslands that were last cultivated 25 years

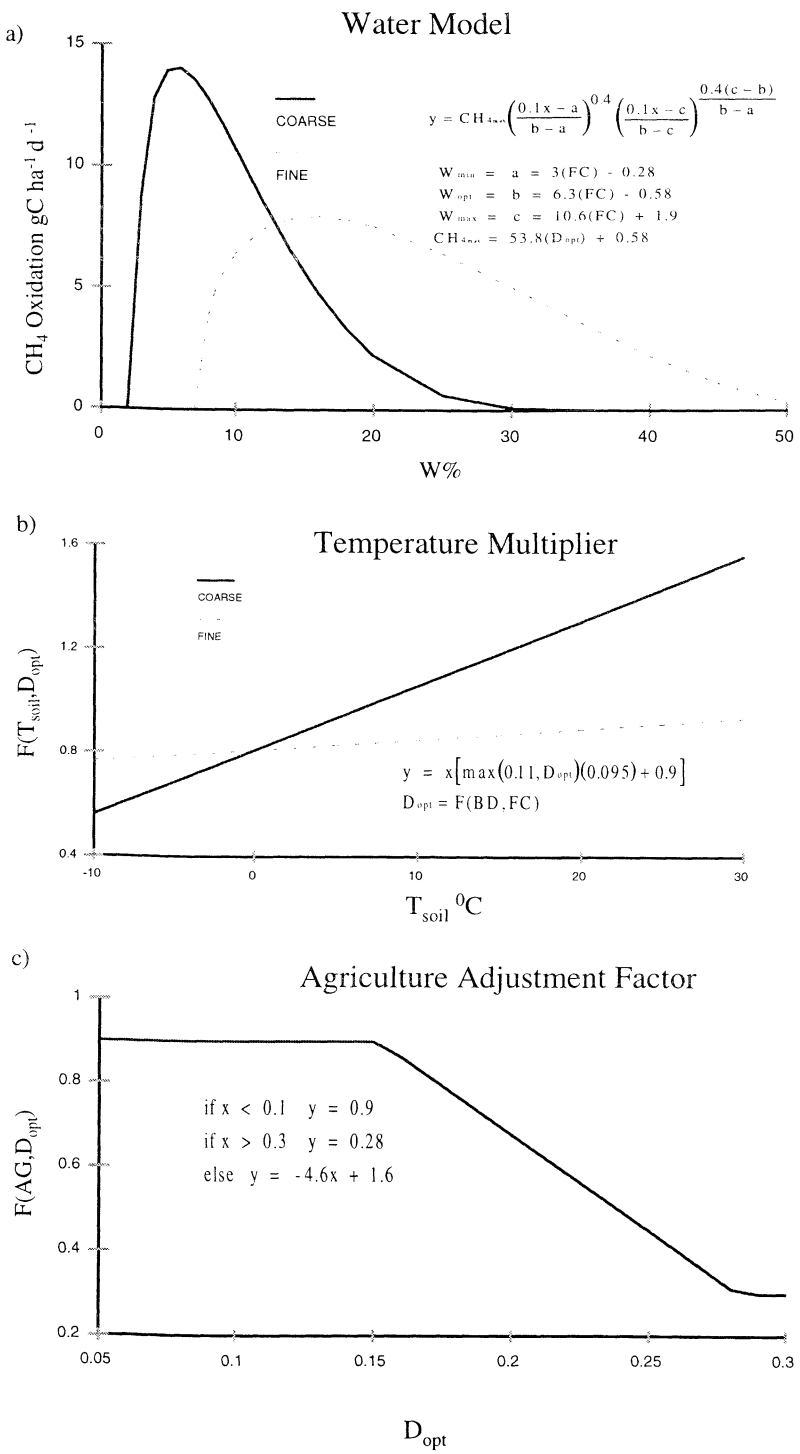

Figure 5. Grassland-Tropical-Coniferous forest submodel (a) CH_4 oxidation rate as a function of soil volumetric water (W), field capacity (FC), and gas diffusivity (D_{opt}). (b) Multiplier accounting for the interaction between soil gas diffusivity and temperature. (c) Effect of cultivation on CH_4 oxidation rates.

before gas flux was sampled [*Mosier and Delgado*, 1997]. These soils showed lower CH_4 oxidation rates than temperate grassland soils, and the model tended to overestimate CH_4 oxidation. Methane consumption rates in the Oxisol and Ultisol soils showed a significant response to water level, but potential CH_4 uptake rates were overestimated by a factor of 2 in the Ultisol (Figure 9). The Ultisol is highly porous (BD=0.95), but CH_4 consumption is low, suggesting a factor other than gas diffusivity limits CH_4 uptake in this soil.

The model predicts that CH_4 uptake rates are more vulnerable to the effects of agricultural practices in soils that are not strongly limited by gas diffusivity than in soils that are

Table 3. Correlation Coefficients and Significance Levels Between the Independent Variables and CH_4 Oxidation Rates for the Soils Used to Build the Deciduous Forest Submodel

Site	$r^2(H_2O)$	p-val(H_2O)	$r^2(T_{soil})$	p-val(T_{soil})
Harvard Forest	0.31	0.0001	0.22	0.0001
Durham	0.07	0.001	0.13	0.0001
Gullane	0.30	0.0001	0.24	0.0001

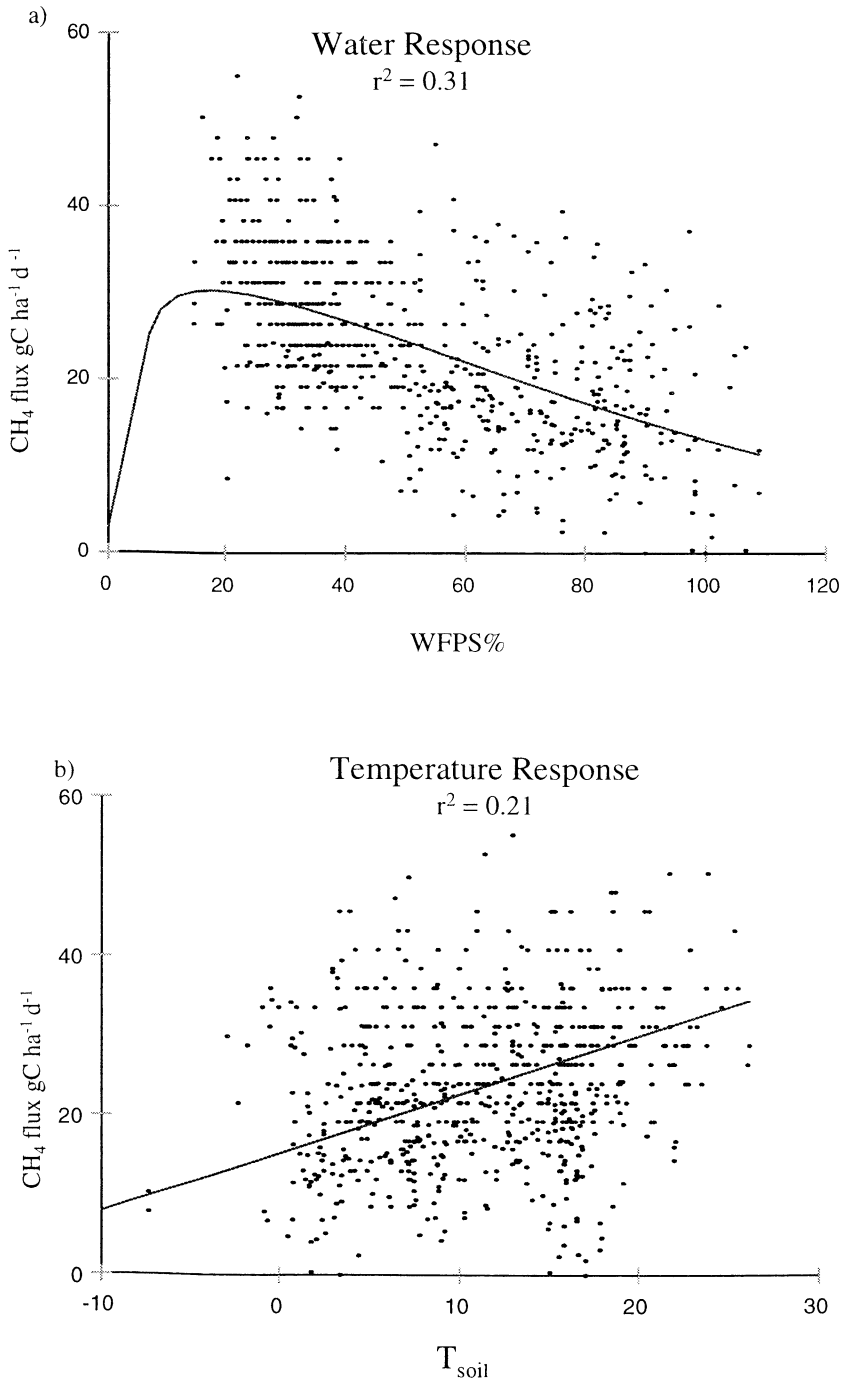

Figure 6. Response of CH_4 oxidation by deciduous forest soils to (a) soil water-filled pore space and (b) soil temperature.

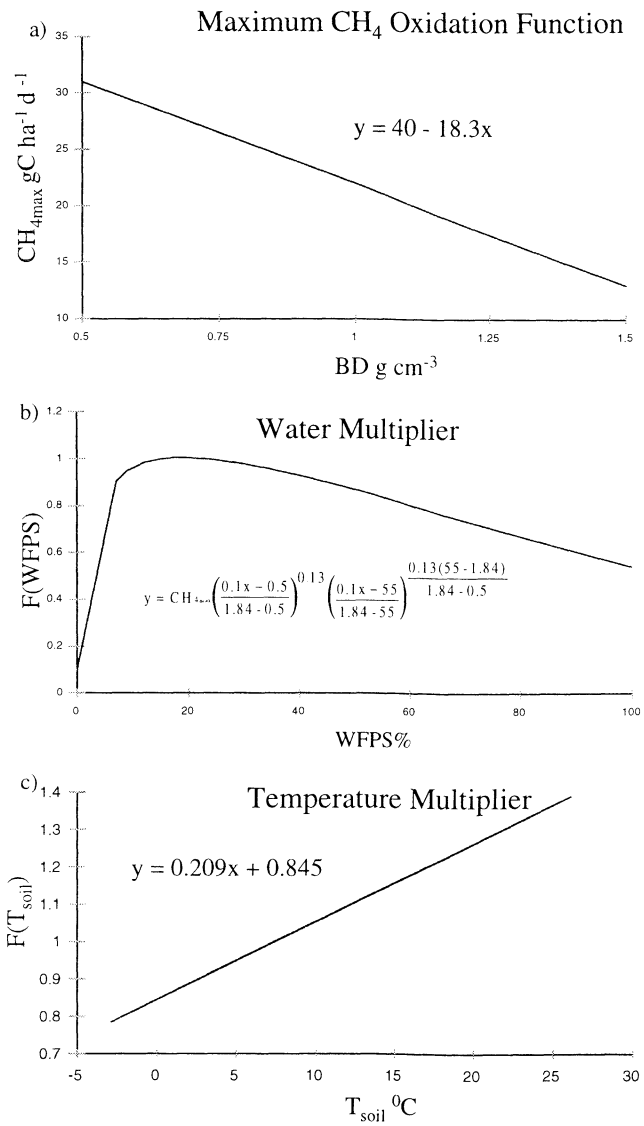

Figure 7. Deciduous Forest submodel. (a) Maximum CH_4 oxidation rate as a function of mineral soil bulk density. Response of CH_4 oxidation rate to (b) soil water-filled pore space (WFPS), and (c) soil temperature.

diffusion limited. This trend held with some of the agricultural soils used for model testing but not universally. The model overestimated CH_4 oxidation in a formerly cropped soil with fairly low D_{opt} (Figure 10a) but was not biased in a currently cropped system with somewhat higher D_{opt} (Figure 10b). The model accurately predicted CH_4 oxidation in a cropped German soil that was strongly diffusion limited but greatly overestimated CH_4 oxidation in a cropped Colorado soil with similar gas diffusivity (Figures 10c and 10d). In addition to being lower, CH_4 oxidation rates in agricultural soils tended to be more variable in response to soil water content than native soils.

All three coniferous forest soils used for model testing [*Mosier et al.*, 1993; *Borken*, 1996; and K. Butterbach-Bahl, unpublished data, 1995], showed a strong response to water and consumed methane at rates similar to the temperate grassland soils used for model development. The model did rather well with these soils, although potential oxidation rates were slightly underestimated (Figure 11). The model also performed well with both of the tropical forest soils used for model testing [*Keller et al.*, 1993; *Steudler et al.*, 1996]. However, tropical forests converted to pastures showed a more variable response to soil water and high CH_4 emission rates at relatively low water contents (Figure 12). None of the coniferous, tropical, or deciduous forest soils used for model testing exhibited water contents low enough to induce limitation of CH_4 oxidation due to moisture stress.

CH_4 oxidation rates in the deciduous forest soils showed a more variable response to soil water content, and CH_4 oxidation rates were generally higher than those observed in the other soils used for model building and testing (Figures 13a and 13b). Soil gas diffusivity as a function of bulk density and field capacity did not reliably predict potential CH_4 oxidation rates in these systems, so a Deciduous Forest submodel that predicts potential CH_4 oxidation rate based on soil bulk density was developed. In general, the model accurately predicted average CH_4 oxidation rates in deciduous forests but often failed to capture the daily variability observed in these soils. This may be due to variations in microbial communities [*Grant*, 1999], thickness of litter acting as a diffusion barrier [*Dong et al.*, 1998], shape of litter, and indirect effects of acidity on soil burrowing activity and litter decomposition rates [*Brumme and Borken*, 1999] or other factors not accounted for by our simple model.

5. Sensitivity Analysis

Sensitivity analyses were performed for soil bulk density and field capacity for the Grassland-Tropical-Coniferous submodel because these parameters must often be estimated for field soils. Response of CH_4 oxidation to BD is illustrated with the wheat/fallow field under no till treatment [*Kessavalou et al.*, 1998]. Field capacity was estimated at 40% volumetric water content for this soil, and the measured average BD was 1.23. These inputs yield a low soil gas diffusivity at optimum water content for CH_4 oxidation, and hence CH_{4max} is low. Consequently, the Grassland-Tropical-Coniferous submodel underestimates CH_4 flux (Figure 14a). However, if a lower BD is used, the model is less biased and the root mean square error is lower, but the correlation coefficient is also lower (Figure 14b). The higher D_{opt} associated with lower BD implies a higher estimate for CH_{4max} so the average error improves, but higher D_{opt} also implies that temperature has a stronger effect on simulated CH_4 uptake rates, which in this case decreases the goodness of model fit.

Field capacity affects the optimum water content, the maximum CH_4 consumption estimate, and the magnitude of the temperature effect. FC can be reliably estimated in coarse textured soils that drain quickly but can be somewhat ambiguous in slow draining or fine-textured soils. Using a high FC estimate (42%) results in the model over predicting low CH_4 oxidation rates and under predicting the high values in a spruce forest (Figure 14c). However, using a value of

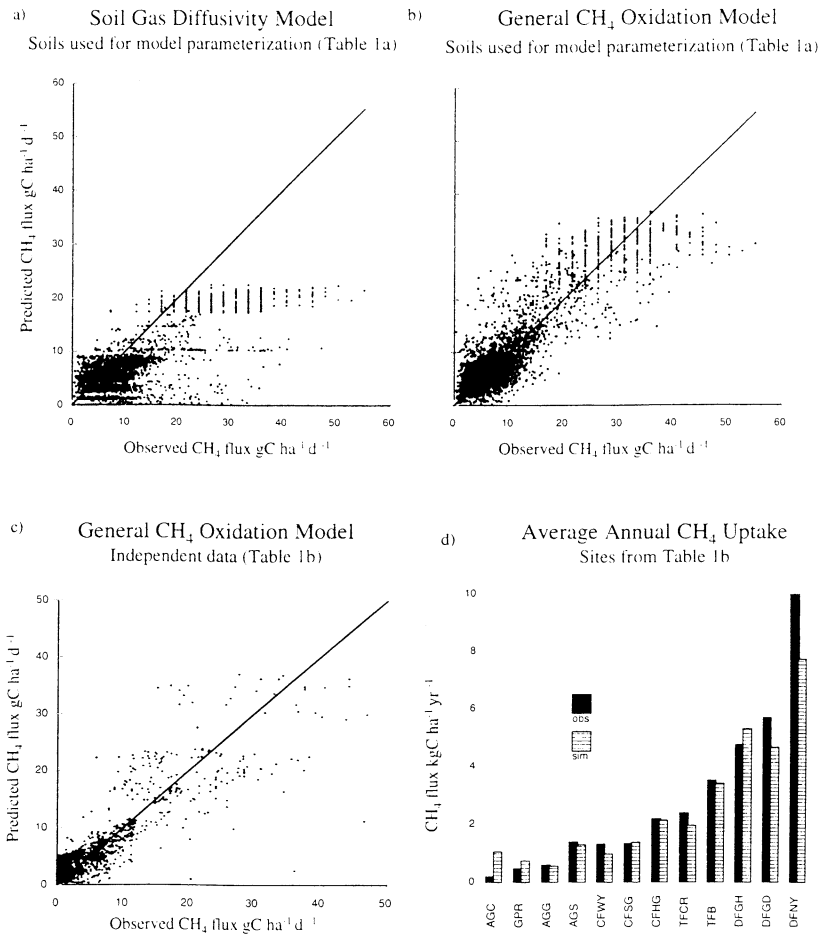

Figure 8. Comparisons of predicted versus observed CH_4 flux rates and 1-1 lines in the soils used for model development and testing; (a) soil gas diffusivity model [*Potter et al.*, 1996], r^2=0.57, (b) our general model, r^2=0.76, (c) results of tests with the general model on independent data from grasslands, agricultural soils, and deciduous, coniferous, and tropical forests (Table 1b), r^2=0.73, and (d) annual observed and simulated CH_4 uptake rates for the soils in Table 1b.

35% shows that FC may be adjusted to improve model fit with the data (Figure 14d). In this case, the more dynamic temperature multiplier associated with a higher D_{opt} improves model fit.

6. Discussion

The general CH_4 oxidation model consists of a Grassland-Tropical-Coniferous submodel and a Deciduous Forest submodel. Both submodels assume that soil physical properties determine the potential CH_4 oxidation rate for a particular site and that variations in soil water content and temperature explain within site variations in CH_4 oxidation rates. Our model assumes that soil gas diffusivity is a primary control of CH_4 oxidation rates and that diffusivity is driven by soil water content and soil physical properties. However, it is actually the concentration of CH_4 in microsites that drives CH_4 oxidation, and soil gas diffusivity is driven by the concentration gradient between CH_4 in the atmosphere and in the soil. Implicit in our model is the assumption that the concentration gradient driving CH_4 diffusion is constant.

The threshold of CH_4 concentration in soil atmosphere below which CH_4 oxidation does not occur has been observed to be < 0.1-0.4 ppm, and observed half saturation constants range from 20 to 45 ppm. [*Dubey et al.*, 1996]. Given that atmospheric CH_4 concentration is ~1.8 ppm, our assumption that diffusion of CH_4 through soil drives CH_4 oxidation rates seems reasonable. However, this assumption may be less valid in soils that overlie strong sources of CH_4. Populations of methane oxidizing microbes in areas where CH_4 in the soil atmosphere is elevated develop a lower affinity for CH_4 than microbes exposed to normal atmospheric methane concentrations [*Dubey et al.*, 1996].

Although our model makes no attempt to account for CH_4 production in soils that are primarily CH_4 sinks, most of these soils probably contain anoxic microsites that facilitate CH_4 production. Our model assumes that oxidation of any CH_4 created in soils that are strong net sinks does not affect the ability of the soil to consume atmospheric methane. This assumption may not hold for soils that are seasonally strong sources of CH_4 or for soils subjected to disturbance that alters the porosity and aggregation such that net CH_4 emission is

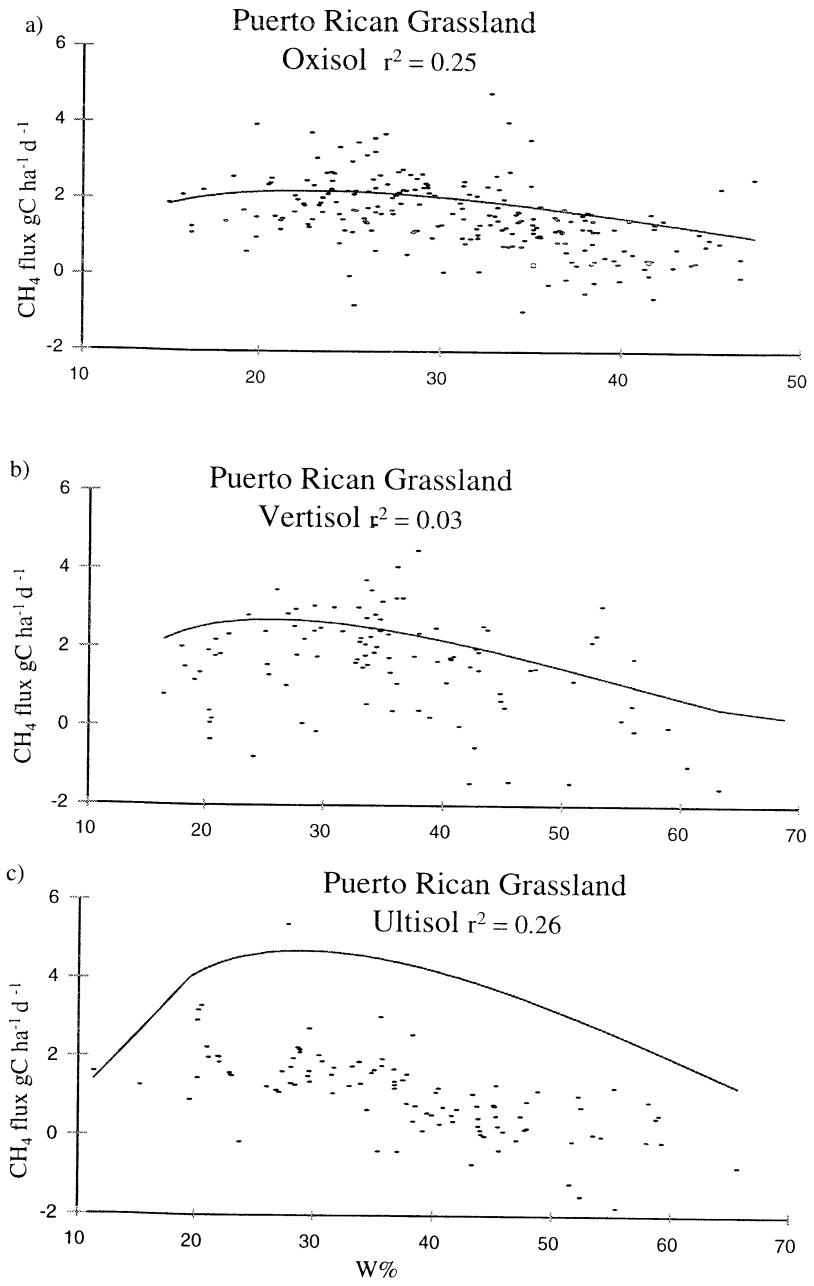

Figure 9. CH_4 oxidation rates and predictions from the Grassland-Tropical-Coniferous water model (Figure 5a) in Puerto Rican grasslands formerly used for sugar cultivation [*Mosier and Delgado*, 1997].

observed under soil water conditions that are normally considered to be aerobic. The tropical forest that was converted to pasture (Figure 12) may be an example of a case where both CH_4 production and oxidation must be accounted to simulate net CH_4 flux correctly.

Given the caveats of our assumptions, we would not expect our model to apply in soils that experience a CH_4 gradient different than typical well-drained soils. For example, methane uptake in a dry soil adjacent to a subalpine wetland that is a strong CH_4 source showed much higher uptake rates than similar soils under similar water and temperature conditions [*Wickland et al.*, 1999]. Similarly, we would not expect our model to apply for soils that are seasonally net CH_4 sources because differences in microbial populations would imply different uptake kinetics than our model assumes. Also, the CH_4 concentration gradient in typical well-drained soils is not constant through time and increased gradients driven by higher atmospheric CH_4 mixing ratios may be responsible for increased CH_4 uptake in these soils [*Ojima et al.*, 1993].

The Grassland-Tropical-Coniferous submodel is based on the soil gas diffusivity model presented by *Potter et al.* [1996]. Potter's model assumes that CH_4 oxidation rates vary

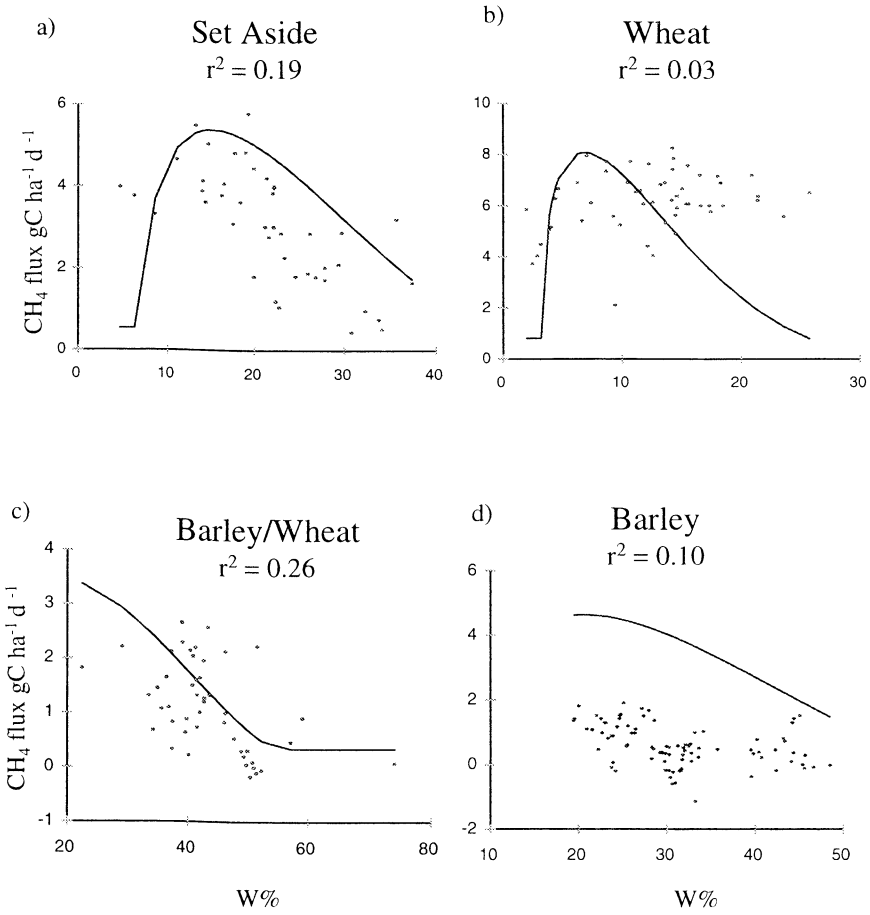

Figure 10. CH_4 flux rates and predictions based on the Grassland-Tropical-Coniferous water model and agriculture reduction factor for (a, b) former and current cropped systems in Scotland [*Dobbie and Smith*, 1996], and cropped systems in (c) Germany [*Flessa et al.*, 1995], and (d) Colorado [*Delgado and Mosier*, 1996].

directly with soil gas diffusivity, which is a function of total pore space, gas-filled pore space, and pore size distribution. As BD or water content increases, gas diffusivity decreases because soil volume favorable for gas transport decreases. Gas diffusivity varies inversely with FC because high FC is associated with a low proportion of pore space consisting of macropores. Less macropores means that the effective path length for gas diffusion is longer, hence decreasing gas diffusivity. Thus Potter's model predicts high-CH_4 consumption rates in dry soils that have a large proportion of macropores. The major difference between the Grassland-Tropical-Coniferous submodel model and Potter's model is that the latter does not account for reduced CH_4 oxidation rates at low moisture levels. Implicit in the Grassland-Tropical-Coniferous submodel model is the suggestion of *Dobbie and Smith* [1996] that CH_4 oxidation may be controlled by gas diffusivity or by biological activity. The model assumes that when soil water content is greater than the optimum, gas diffusivity limits CH_4 oxidation, but when soil water content is below the optimum, water stress limits biological activity, including methanotrophy. Most of the grassland soils used for model building and testing exhibited strong evidence for an optimal water content for CH_4 oxidation. However, none of the forest soils used for model building or testing dried sufficiently to observe reduced CH_4 consumption due to water stress. Nonetheless, our model that assumes an optimum water content for CH_4 oxidation applies to these soils because the observed water contents are always higher than the predicted optimum water content.

Sensitivity of CH_4 oxidation to soil moisture is well established and optimum water content (W_{opt}) for CH_4 oxidation has been observed in field observations [*Boeckx and Van Cleemput*, 1996] and in laboratory experiments [*Saari et al.*, 1998]. The Grassland-Tropical-Coniferous submodel shows that soil FC can reliably predict optimum water content for CH_4 oxidation (W_{opt}) in many soils. The model predicts high W_{opt} in fine-textured soils with high field capacity because water is held more tightly and is less available for biological activity in these soils. In contrast, the model predicts that sandy soils with low FC require lower water contents to induce water stress on biological activity because water is not held as tightly in these soils.

The gas diffusivity model described by *Potter et al.*, (1996) is used to quantify the effect of soil properties related to texture on CH_4 oxidation rather than texture alone because the gas diffusivity model is sensitive to soil porosity and

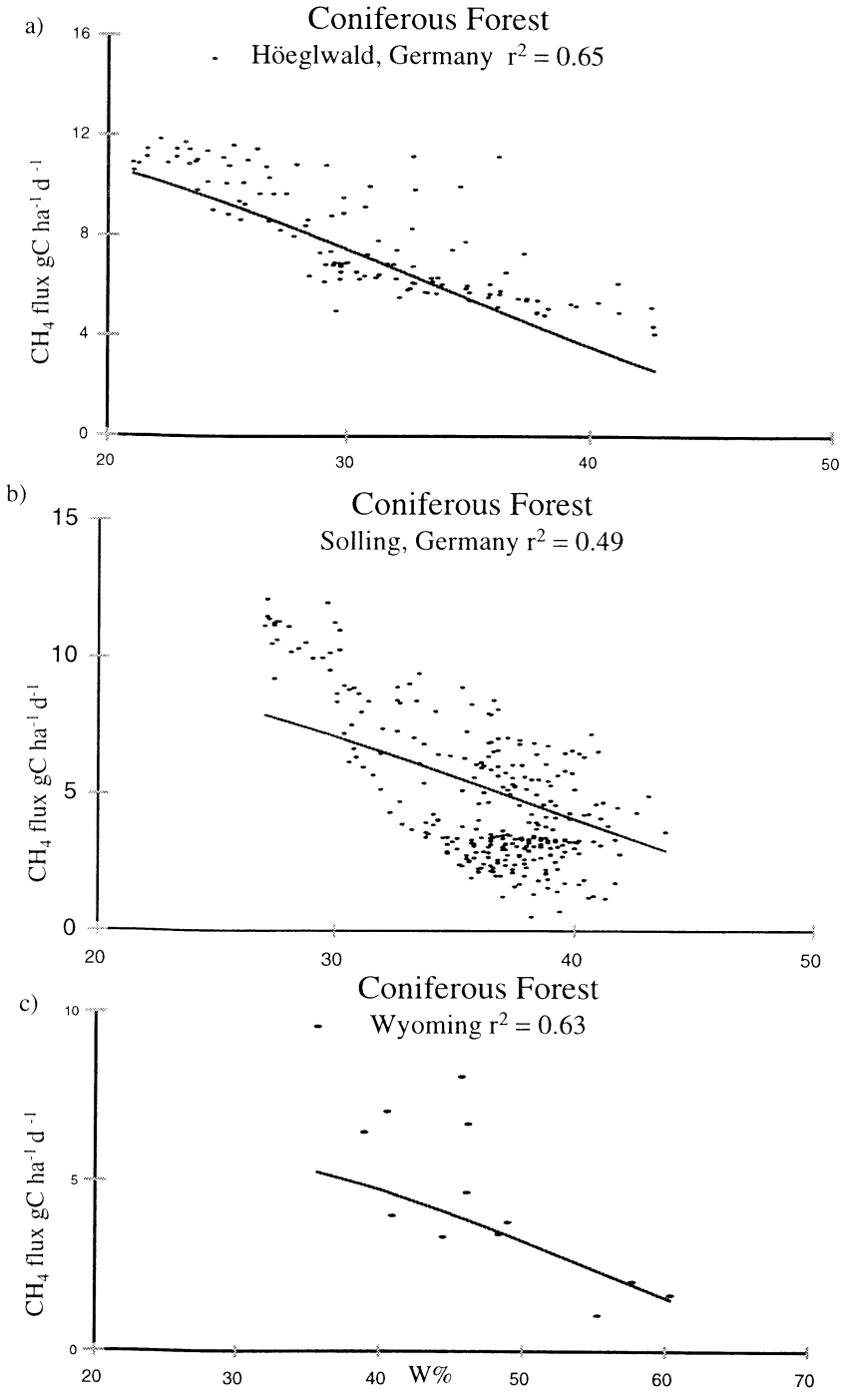

Figure 11. CH_4 oxidation rates and predictions based on the Grassland-Tropical-Coniferous water model for Spruce forests in Germany (a) K. Butterbach-Bahl, unpublished data, 1995, (b) *Borken*, [1996], and (c) Wyoming [*Mosier et al.*, 1993].

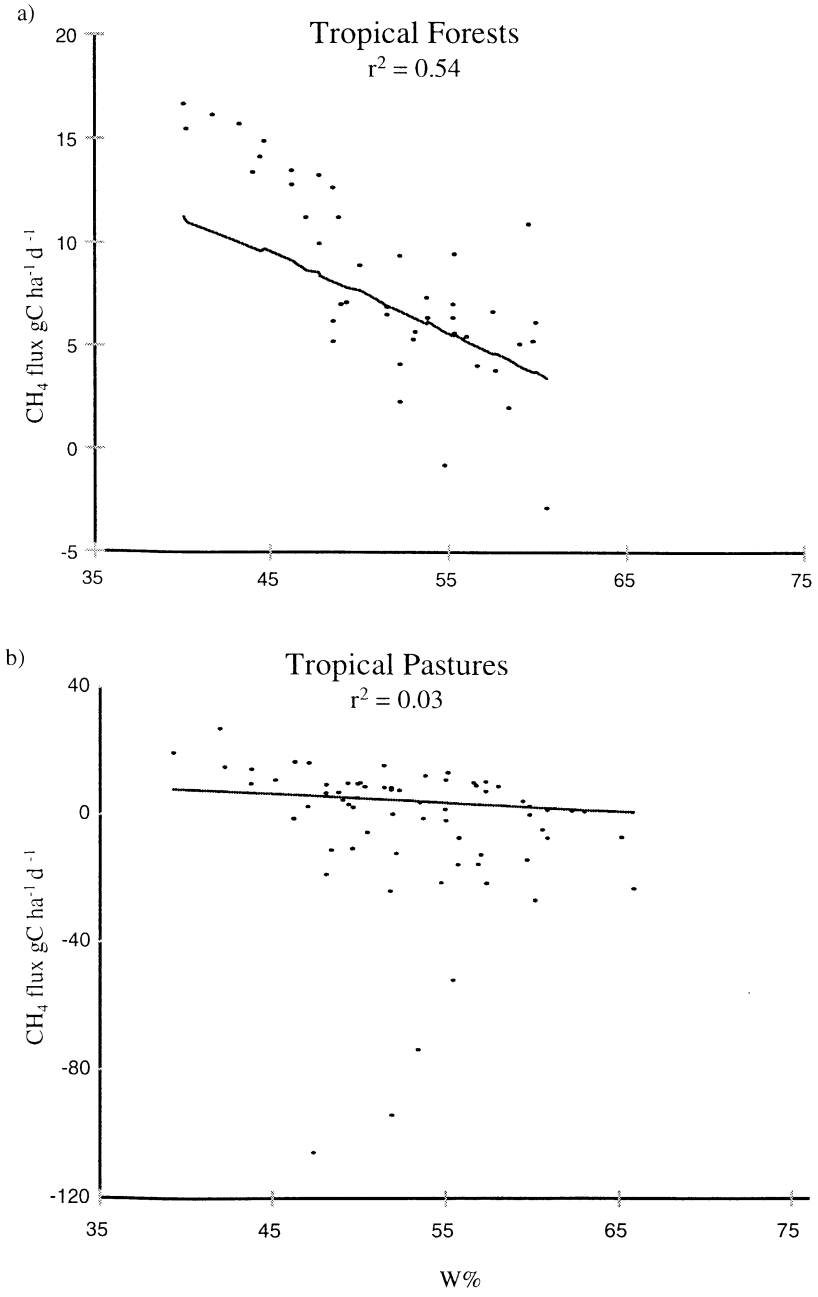

Figure 12. CH_4 flux rates and predictions based on the Grassland-Tropical-Coniferous water model for (a) native forests and (b) forests cleared for pastures in Costa Rica [*Keller et al.*, 1993].

aggregate structure as well as particle size distribution. When calculating the maximum CH_4 oxidation rate for a particular soil, water content is normalized to W_{opt} so that the effects of FC and BD are isolated. Fine-textured soils generally have lower gas diffusivity than sandy soils at an equivalent water potential. However, well-structured clay soils may have lower BD and hence higher gas diffusion and CH_4 oxidation rates than typical clays. Coarse soils generally have high-potential methane oxidation rates because biological activity can continue at low water contents, when CH_4 diffuses readily. However, methane oxidation rates in soils with a small proportion of fine-sized particles may be limited by microbial biomass.

In the original gas diffusivity model [*Potter et al.*, 1996], temperature is included only to the extent that it affects soil gas diffusivity so its effect on CH_4 oxidation is minor. However, temperature tends to increase in reliability as a predictor of CH_4 consumption as other factors become less

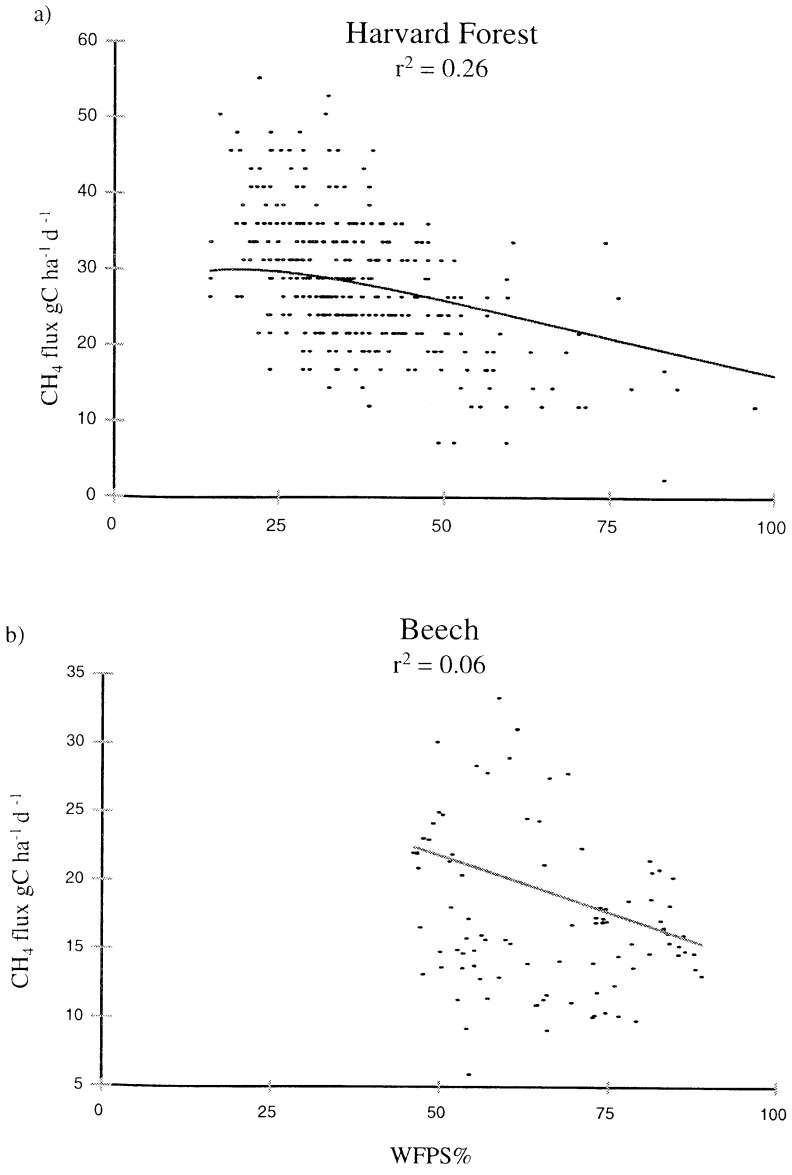

Figure 13. CH_4 oxidation rates and predictions based on the Deciduous Forest water model for (a) mixed deciduous forest in Massachusetts [*Peterjohn et al.*, 1997] and (b) a beech forest in Solling, Germany (K. Butterbach-Bahl, unpublished data, 1995).

limiting. Grassland soils that were not greatly limited by gas diffusivity showed a strong response to temperature when water was not limiting (Figure 4a). Soils that are highly limited by gas diffusivity show little response to temperature (Figures 4b and 4c). To account for this the parameter controlling the sensitivity of CH_4 oxidation to temperature is a function of D_{opt} (Figure 6b). Including $F(T_{soil}, D_{opt})$ in the model resulted in an increase from 0.39 to 0.45 in the r^2 for predicted versus observed CH_4 oxidation rates in the native grassland soils, while including temperature in the deciduous forest submodel resulted in an increase from 0.34 to 0.42 in the r^2 for predicted versus observed CH_4 oxidation rates in the deciduous forest soils used for model building. Other researchers have also reported small effects of temperature on CH_4 oxidation in field [*King and Adamsen*, 1992] and laboratory soils [*Crill et al.*, 1994]. However, soil temperature may have a stronger effect on CH_4 oxidation rates than soil water content, as observed in 24 of 28 soil used for model building (Tables 2 and 3) and the oak/beech forest used for model testing [*Dong et al.*, 1998].

Soils under cultivation or subjected to N fertilization tend to consume methane at lower rates than similar native soils [*Hütsch et al.*, 1993; *Bronson and Mosier*, 1994]. However, the amount of reduction due to land use practices is highly variable among soils. The agricultural soils used for model development suggest that the adjustment of predicted CH_4 uptake rates required to account for the effects of agriculture on CH_4 oxidation is correlated with soil gas diffusivity (Figure 5c). This suggests that either CH_4 oxidation rates are not affected by agricultural practices in soils that are highly

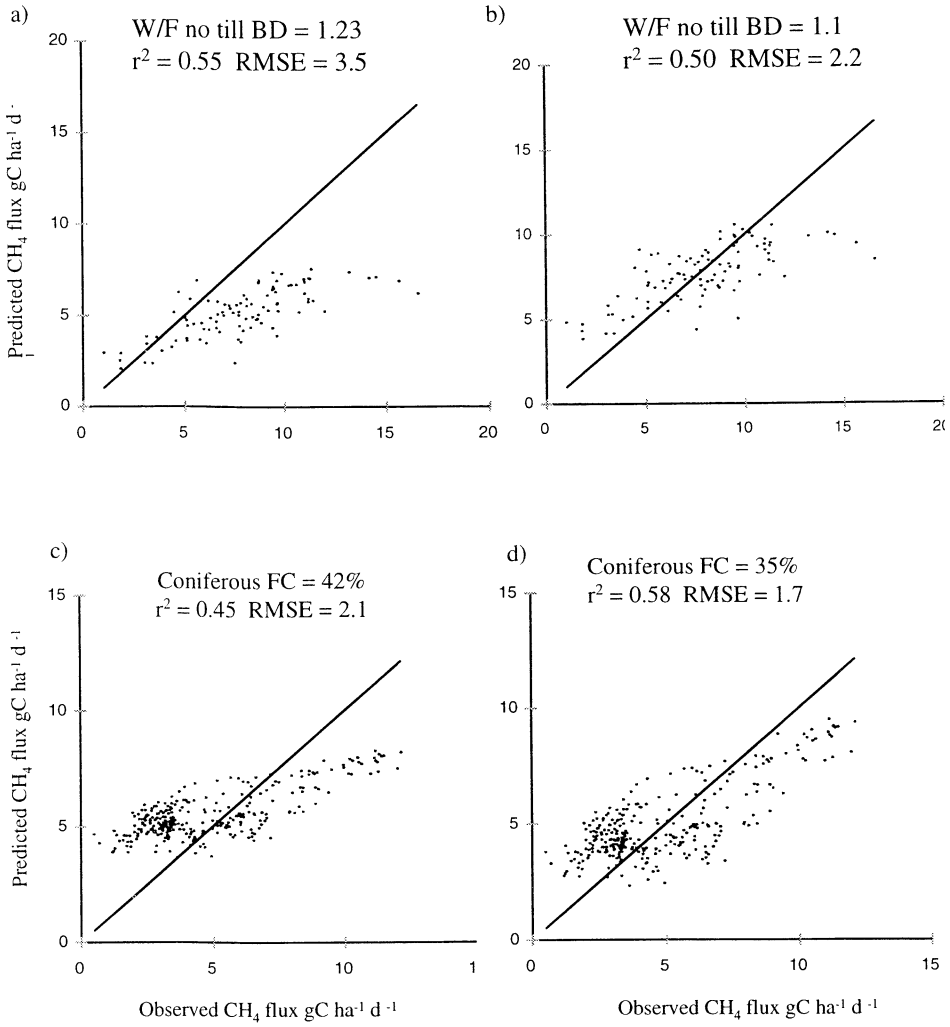

Figure 14. Sensitivity of the Grassland-Tropical-Coniferous forest submodel to (a, b) bulk density in a clay loam soil used for wheat/fallow no till treatments [*Kessavalou et al.*, 1998] and (c, d) field capacity in a spruce forest soil [*Borken*, 1996].

limited by gas diffusivity or, more likely, that the changes in soil porosity, water content, and temperature induced by agriculture explain the observed CH_4 oxidation rates observed in diffusion limited arable soils, and these factors are adequately accounted for by the model. The latter probably also explains why the average reduction required by the model (46%) is not as extreme as the average agriculture reduction (71%) reported by *Smith et al.* [2000]. The model provided unbiased (mean error < 30%) estimates of CH_4 oxidation rates in 6 of 10 agricultural soils used for model testing. The model accounts for some of the changes in soil properties brought about by agricultural practices that affect CH_4 oxidation rates, but changes in nutrient cycling and microbial communities associated with cropping that affect CH_4 oxidation rates in at least some soils are not accounted for by the model.

7. Conclusions

The success of the model in grasslands, cropped land, and coniferous, tropical and deciduous forests shows that potential CH_4 oxidation rates in these biomes can be reliably predicted from soil physical properties and that daily variations in water and temperature explain a large proportion of the variability in CH_4 oxidation rates observed in these systems. Native grasslands, agricultural soils, and tropical and coniferous forest soils rarely show maximum CH_4 oxidation rates >20 g C ha^{-1} d^{-1}, and a single submodel worked adequately in most of the soils from these biomes that were tested. However, five of six deciduous forest soils used for model building and testing showed maximum CH_4 oxidation rates greater than 30 g C ha^{-1} d^{-1}, and a submodel was developed for these systems. However, some deciduous forest soils consume CH_4 at much lower rates than those used for model building and testing [*Brumme and Borken*, 1999].

The general model did a good job at estimating average CH_4 oxidation rates for particular sites and explained a large proportion of the daily variability in CH_4 oxidation rates in most of the native systems used for model testing. Some of the deciduous forest soils and soils used for agriculture showed weak correlations between CH_4 oxidation rates and soil water content. Consequently, the model did poorly at

simulating daily CH_4 oxidation rates in these soils, although estimates of annual site averages were usually within 30% of the observed values (Figure 8d).

None of the forest soils used for model building or testing exhibited water contents low enough to induce biological limitation of CH_4 oxidation rates due to moisture stress. In contrast, most of the grassland systems used for model building and testing showed ranges of water contents sufficiently wide to exhibit limitation of CH_4 oxidation rates due to both gas diffusivity at high water content and biological activity at low water content. However, the majority of the data points observed in the grasslands showed limitation due to high rather than low water content. In all of the soils in which the response of methane uptake to temperature was significant the correlation was positive. These observations suggest that CH_4 oxidation rates in soils will increase if higher concentrations of greenhouse gases lead to rising temperatures and drier soils, thus providing some negative feedback on the accumulation of methane in the atmosphere.

Acknowledgments. This paper is the product of a TRAGNET (Trace Gas Network) collaboration under the IGAC BATREX (Biosphere-Atmosphere Trace Gas Exchange) Activity. TRAGNET was begun with financial assistance from NSF Long-Term Studies Program (Grant DEB 94-16813) and USADA/ARS. Data archives, constructed by Brian Newkirk and Steven Knox, are housed at the Natural Resource Ecology Laboratory, Colorado State University. Analysis and synthesis of the trace gas data was supported by the National Center for Ecological Analysis and Synthesis, a Center funded by NSF (Grant DEB-94-21535), the University of California at Santa Barbara and the State of California. The authors gratefully acknowledge helpful discussions at TRAGNET workshops held at NCEAS in December 1997 and April 1999. The research for this paper was supported by the National Aeronautics and Space Administration, the National Science Foundation, the Department of Energy and the Environmental Protection Agency through the following grants: NASA-EOS NAGW 2662, NSF-LTER BSR9011659, DOE NIGEC LWT62-123-06516, and EPA Regional Assessment R824993-01-0. Partial support for S. J. Del Grosso was obtained from the Environmental Protection Agency (Grant EPA-R824993-01-4).

References

Adamsen, A. P., and G. M. King, Methane consumption in temperate and subarctic forest soils rates, vertical zonation and response to water and nitrogen, *Appl. Environ. Microbiol., 59*, 485-490, 1993.

Boeckx, P., and O. Van Cleemput, Methane oxidation in a neutral landfill cover soil: Influence of moisture content, temperature, and nitrogen turnover, *J. Environ. Qual., 25*, 178-183, 1996.

Boeckx, P., O. Van Cleemput, and I. Villaralvo, Methane oxidation in soils with different textures and land use, *Nutr. Cycling. Agroecosys., 49*, 91-95, 1997.

Borken, W., *Methan-Aufnahme und Kohlendioxid-Freisetzung von Waldboeden*, Ph.D. Dissertation, Univ. of Göttingen, Göttingen, Germany, 1996.

Bronson, K. F., and A. R. Mosier, Suppression of methane oxidation in aerobic soil by nitrogen fertilizers, nitrification inhibitors, and urease inhibitors, *Biol. Fertil. Soils, 17*, 263-268, 1994.

Brumme, R., and W. Borken, Site variation in methane oxidation as affected by atmospheric deposition and type of forest ecosystem, *Global Biogeochem. Cycles, 13*, 493-501, 1999.

Castro, M. S., J. M. Melillo, P. A. Streudler, and J. W. Chapman, Soil moisture as a predictor of methane uptake by temperate forest soils, *Can. J. For. Res., 24*, 1805-1810, 1994.

Conrad, R., Control of methane production in terrestrial ecosystems, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 39-58, John Wiley, New York, 1989.

Crill, P. M., P. J. Martikainen, H. Nykanen, and J. Silvola, Temperature and N fertilization effects on methane oxidation in a drained peatland soil, *Soil Biol. Biochem., 26*, 1331-1339, 1994.

Davidson, E. A., and J. P. Schimel, Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P. A. Matson and R. C. Harriss, pp. 327-357, Blackwell Sci., Malden, Mass., 1995.

Delgado, J. A., and A. R. Mosier, Mitigation alternatives to decrease nitrous oxide emissions and urea nitrogen loss and their effect on methane flux, *J. Environ. Qual., 25*, 1105-1111, 1996.

Dobbie, K. E., and K. A. Smith, Comparison of CH_4 oxidation rates in woodland, arable and set aside soils, *Soil Biol. Biochem., 28*, 1357-1365, 1996.

Dong, Y., D. Scharffe, J. M. Lobert, P. J. Crutzen, and E. Sanhueza, Fluxes of CO_2, CH_4 and N_2O from a temperate forest soil: The effects of leaves and humus layers, *Tellus, Ser. B, 50B*, 243-252, 1998.

Dörr, H., L. Katruff, and I. Levin, Soil texture parametrization of the methane uptake in aerated soils, *Chemosphere, 26*, 697-713, 1993.

Dubey, S. K., A. K. Kashyap, and J. S. Singh, Methanotrophic bacteria, methanotrophy and methane oxidation in soil and rhizosphere, *Tropical Ecology, 37*, 167-182, 1996.

Flessa, H., P. Dörsch, and F. Beese, Seasonal variation of N_2O and CH_4 fluxes in differently managed arable soils in southern Germany, *J. Geophys. Res., 100*, 23,115-23,124, 1995.

Goldman, M. B., P. M. Groffman, R. V. Pouyat, M. J. McDonnell, and S. T. Pickett, CH_4 uptake and N availability in forest soils along an urban to rural gradient, *Soil Biol. Biochem.*, 27, 281-286, 1995.

Grant, R. F., Simulation of methanotrophy in the mathematical model *ecosys*, *Soil Biol. Biochem., 31*, 287-297, 1999.

Hütsch, B. W., C. P. Webster, and D. P. Powlson, Long term effects of nitrogen fertilization on methane oxidation in the soil of the Broadbalk wheat experiment, *Soil Biol. Biochem., 25*, 1307-1315, 1993.

Keller, M., E. Veldkamp, A. M. Weltz, and W. A. Reiners, Effect of pasture age on soil trace gas emissions from a deforested area of Costa Rica, *Nature, 365*, 244-246, 1993.

Kessavalou, A., A. R. Mosier, J. W. Doran, R. A. Drijber, D. L. Lyon, and O. Heinemeyer, Fluxes of carbon dioxide, nitrous oxide, and methane in grass sod and winter wheat-fallow tillage management, *J. Environ. Qual., 27*, 1094-1104, 1998.

King, G. M., and A. P. Adamsen, Effects of temperature on methane consumption in a forest soil and in pure cultures of the methanotroph Methylomonas-rubra, *Appl. Environ. Microbiol., 58*, 2758-2763, 1992.

Mosier, A. R., and J. A. Delgado, Methane and nitrous oxide fluxes in western Puerto Rica, *Chemosphere, 9*, 2059-2082, 1997.

Mosier, A. R., L. K. Klemedttson, R. A. Sommerfeld, and R. C. Musselman, Methane and nitrous oxide flux in a Wyoming subalpine meadow, *Global Biogeochem. Cycles, 7*, 771-784, 1993.

Mosier, A. R., W. J. Parton, D. W. Valentine, D. S. Ojima, D. S. Schimel, and J. A. Delgado, CH_4 and N_2O fluxes in the Colorado shortgrass steppe, 1, Impact of landscape and nitrogen addition, *Global Biogeochem. Cycles, 10*, 387-399, 1996.

Mosier, A. R., W. J. Parton, D. W. Valentine, D. S. Ojima, D. S. Schimel, and O. Hienemeyer, CH_4 and N_2O fluxes in the Colorado shortgrass steppe: 2. Long-term impact of land use change, *Global Biogeochem. Cycles, 11*, 29-42, 1997.

Ojima, D. S., D. Valentine, A. R. Mosier, W. J. Parton, and D. S. Schimel, Effect of land use change on methane oxidation in temperate forest and grassland soils, *Chemosphere, 26*, 675-685, 1993.

Parton, W. J., D. S. Ojima, C. V. Cole and D. S. Schimel, A general model for soil organic matter dynamics: Sensitivity to litter chemistry, texture and management, in *Quantitative Modeling of Soil Forming Processes, SSSA Spec. Pub. 39,* pp. 147-167, *Soil Sci. Soc. of Am.,* Madison, Wisc., 1994.

Parton, W. J., M. Hartman, D. S. Ojima, and D. S. Schimel, DAYCENT: Its land surface submodel: Description and testing, *Global Planet. Change, 19*, 35-48, 1998.

Peterjohn, W. T., J. M. Melillo, P. A. Steudler, K. M. Newkirk, F. P. Bowles, and J. D. Aber, Responses of trace gas fluxes and N availability to experimentally elevated soil temperatures, *Ecol. Appl., 4*, 617-725, 1994.

Potter, C. S., E. A. Davidson, and L. V. Verchot, Estimation of global biogeochemical controls and seasonality in soil methane consumption, *Chemosphere, 32*, 2219-2245, 1996.

Prather, M. J., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou, Other trace gases and atmospheric chemistry, in *Climate Change 1994*, edited by J. T. Houghton, et al., pp. 73-126, Cambridge Univ. Press, New York, 1995.

Ridgwell, A. J., S. J. Marshall, and K. Gregson, Consumption of atmospheric methane by soils: A process based model, *Global Biogeochem. Cycles, 13*, 59-70, 1999.

Saari, A., J. Heiskanen, and P. J. Martikainen, Effect of the organic horizon on methane oxidation and uptake in soil of boreal Scots pine, *FEMS Microbiol. Ecol., 26*, 245-255, 1998.

Statistical Analysis Institute, Inc., *SAS/STAT User's Guide,* version 6, 4th ed., Cary, N.C., 1990.

Smith K. A, K. E. Dobbie, B. C. Ball, L. R. Bakken, B. K. Sitaula, S. Hansen, R. Brumme, W. Borken, S. Christensen, A. Priemé, D. Fowler, J. A. MacDonald, U. Skiba, L. Klemedtsson, Å. Kasimir-Klemedtsson, A. Degórska, and P. Orlanski, Oxidation of atmospheric methane in Northern European soils, comparison with other ecosystems, and uncertainties in the global terrestrial sink, *Global Change Biol.*, in press, 2000.

Sommerfeld, R. A., A. R. Mosier, and R. C. Musselman, Carbon dioxide, methane and nitrous oxide flux through a Wyoming snowpack and implications for global budgets, *Nature, 361*, 140-142, 1993.

Steudler, P. A., J. M. Mellilo, B. J. Feigl, C. Neill, M. C. Piccolo, and C. C. Cerri, Consequence of forest to pasture conversion on CH_4 fluxes in the Amazon basin, *J. Geophys. Res., 101*, 18,547-18,554, 1996.

Whalen, S. C., and W. S. Reeburgh, Moisture and temperature sensitivity of CH_4 oxidation in boreal soils, *Soil Biol. Biochem., 28*, 1271-1281, 1996.

Wickland, K. P., R. G. Striegl, S. K. Schmidt, and M. A. Mast, Methane flux in subalpine wetland and unsaturated soils in the southern Rocky Mountains, *Global Biogeochem. Cycles, 13*, 101-113, 1999.

Willison, T. W., M. S. O'Flaherty, P. Tlustoc, K. W. Goulding, and D. S. Powlson, Variations in microbial populations in soils with different methane uptake rates, *Nutr. Cycling Agroecosys., 49*, 85-90, 1997.

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(Received September 17, 1999; revised February 7, 2000;
accepted March 8, 2000.)