4.03
Global Methane Biogeochemistry

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4.03.1 INTRODUCTION

Methane (CH_4) has been studied as an atmospheric constituent for over 200 years. A 1776 letter from Alessandro Volta to Father Campi described the first experiments on flammable "air" released by shallow sediments in Lake Maggiore (Wolfe, 1996, 2004; King, 1992). The first quantitative measurements of CH_4, both involving combustion and gravimetric determination of trapped oxidation products, were reported in French by Boussingault (1834, 1864) and Gautier (1901), who estimated CH_4 concentrations of 10 and

0.28 ppmv (seashore) and 95 ppmv (Paris), respectively. The first modern measurements of atmospheric CH_4 were the infrared absorption measurements of Migeotte (1948), who estimated an atmospheric concentration of 2.0 ppmv. Development of gas chromatography and the flame ionization detector (GC/FID) in the 1950s led to observations of vertical CH_4 distributions in the troposphere and stratosphere, and to establishment of time-series sampling programs in the late 1970s. Results from these sampling programs led to suggestions that the concentration of CH_4, as that of CO_2, was increasing in the atmosphere. The possible role of CH_4 as a greenhouse gas stimulated further research on CH_4 sources and sinks. Methane has also been of interest to microbiologists, but findings from microbiology have entered the larger context of the global CH_4 budget only recently.

Methane is the most abundant hydrocarbon in the atmosphere. It plays important roles in atmospheric chemistry and the radiative balance of the Earth. Stratospheric oxidation of CH_4 provides a means of introducing water vapor above the tropopause. Methane reacts with atomic chlorine in the stratosphere, forming HCl, a reservoir species for chlorine. Some 90% of the CH_4 entering the atmosphere is oxidized through reactions initiated by the OH radical. These reactions are discussed in more detail by Wofsy (1976) and Cicerone and Oremland (1988), and are important in controlling the oxidation state of the atmosphere. Methane absorbs infrared radiation in the troposphere, as do CO_2 and H_2O, and is an important greenhouse gas (Lacis *et al.*, 1981; Ramanathan *et al.*, 1985).

A number of review articles on atmospheric CH_4 have appeared during the last 15 years. Cicerone and Oremland (1988) reviewed evidence for the temporal atmospheric increase, updated source estimates in the global CH_4 budget, and placed constraints on the global budget, emphasizing that the total is well constrained, but that the constituent sources may be uncertain by a factor of 2 or more. This paper was part of a special section in "Global Biogeochemical Cycles" that resulted from a 1987 American Chemical Society Symposium, "Atmospheric Methane: Formation and Fluxes form the Biosphere and Geosphere." Tyler (1991) and Wahlen (1993) emphasized new information on stable isotopes of CH_4 and $^{14}CH_4$, respectively. Several reviews deal with the microbially mediated CH_4 oxidation. King (1992) reviewed the ecology of microbial CH_4 oxidation, emphasizing the important role of this process in global CH_4 dynamics. Hanson and Hanson (1996) reviewed the physiology and taxonomy of methylotrophic bacteria, their role in the global carbon cycle, and the ecology of methanotrophic bacteria. Conrad (1996) reviewed the role of soils and soil microbial communities as controllers of CH_4 fluxes as well as those of H_2, CO, OCS, N_2O, and NO. Two meetings focusing on CH_4 biogeochemistry were held in 1991: an NATO Advanced Science Workshop held at Mt. Hood, OR, and the 10th International Symposium on Environmental Biogeochemistry (ISEB). A dedicated issue of *Chemosphere* (26(1–4), 1993) contains contributions from the NATO workshop; two additional volumes (Khalil, 1993, 2000) contain a report of the workshop and updates of important topics. Contributions to the ISEB meeting are presented in Oremland (1993). Wuebbles and Hayhoe (2002) reviewed the effects of CH_4 on atmospheric chemistry and examined the direct and indirect impact of CH_4 on climate. The Intergovernmental Panel on Climate Change (IPCC) has published periodic updates (see, e.g., IPCC, 2001).

Substantial advances have resulted from research aimed at understanding the global CH_4 mixing ratio increase. Time-series measurements of atmospheric CH_4 have continued, new CH_4 flux measurements in a range of environments have been reported, and data allowing use of the stable isotope ($^{13}C/^{12}C$, $^{2}H/^{1}H$) composition of CH_4 as an independent budget constraint have increased. The importance of microbial oxidation of CH_4 has been recognized and modeled; the possible role of CH_4 clathrate hydrates in the global budget has been clarified with the introduction of new technology. Studies of CH_4 trapped in ice cores from the Greenland and Antarctic ice caps have continued, resulting in higher-resolution records and new interpretations of past conditions. There have been few recent changes in our understanding of the atmospheric chemistry of CH_4, and since this is covered in Cicerone and Oremland (1988) it will not be covered here. The aim here is not to repeat information contained in the reviews mentioned above, but to present results that have appeared in the literature since their publication, to outline major questions, and to point to promising new approaches.

4.03.2 GLOBAL METHANE BUDGET

The first global CH_4 budgets were compiled by Ehhalt (1974) and Ehhalt and Schmidt (1978), who used available published information to estimate emissions of CH_4 to the atmosphere. They considered paddy fields, freshwater sources (lakes, swamps, and marshes), upland fields and forests, tundra, the ocean, and enteric fermentation by animals as biogenic sources. Anthropogenic sources included industrial natural gas losses and emission from coal mining, and were considered to be ^{14}C free. Observations of $^{14}CH_4$ placed an upper limit on anthropogenic sources. Oxidation by the OH radical, as well as loss to the stratosphere by eddy diffusion and Hadley circulation, were presumed to be methane sinks. In spite of lack of data, this work correctly identified the major atmospheric sources and did a remarkable job of estimating the magnitudes of the source terms in the global CH_4 budget, but it dismissed oxidation by soils as insignificant.

4.03.2.1 Global Methane Increase

The first observations of a possible atmospheric CH_4 increase were reported by Graedel and McRae (1980), who analyzed a 10-year continuous record of total hydrocarbon (THC) data collected at three urban/suburban sites by the New Jersey Department of Environmental Protection. An increasing trend in daily and annual minima was advanced somewhat tentatively because of concerns about calibration techniques, the fraction of the THC signal attributable to CH_4, and the urban locations. Rasmussen and Khalil (1981) used 22 months of automated GC/FID measurements of atmospheric CH_4 at Cape Meares, OR, to show a CH_4 concentration increase of $\sim 2\% \text{ yr}^{-1}$. Rasmussen and Khalil (1981) also compiled independent northern hemisphere GC/FID measurements from 1965 to 1980 to show a similar trend. The Cape Meares station has operated almost continuously since early 1979 and the techniques were used in establishing the National Oceanic and Atmospheric Administration (NOAA) network described below.

Time-series measurements of atmospheric CH_4 have been made at fixed stations as well as at globally distributed stations. Sampling of globally distributed stations started in 1978 and has continued since then by two groups using two different sampling approaches. Although a number of time-series sampling programs were initiated and operated for short periods, only two—the University of California Irvine and the NOAA/Climate Monitoring and Diagnostics Laboratory (CMDL)—have continued from the late 1970s to early 2000s. The University of California Irvine group started measurements in 1978 (Blake, 1984), conducting quarterly quasi-synoptic sampling at a range of locations in the northern and southern hemispheres followed by laboratory analysis. These measurements were averaged areally and temporally to produce an annual global average CH_4 concentration. Figure 1 (Simpson *et al.*, 2002) shows the Irvine CH_4 record from 1978 to 2001. Regular sampling conducted since 1983 at a network of clean air stations maintained by the NOAA Global Monitoring for Climate Change Laboratory (GMCC, now CMDL) in Boulder, CO gives more detailed temporal and areal coverage (Steele *et al.*, 1987) The CMDL CH_4 results through May 1, 2001, are plotted as a "rug" or "flying carpet" diagram in Figure 2. The interhemispheric gradient in CH_4 is evident, and results from larger northern hemisphere CH_4 emissions. Seasonal changes, which are out of phase between hemispheres, are also evident; the CH_4 concentration is highest at the end of winter and decreases due to photochemical oxidation in summer. In addition to the interannual changes cited above, measurements of methane trapped in polar ice sheet cores show that the atmospheric concentration of methane has doubled over the past 250 years (Craig and Chou, 1982; Rasmussen and Khalil, 1984).

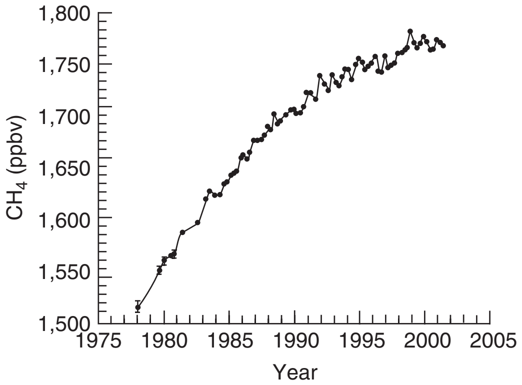

Figure 1 Seasonally averaged global CH_4 mixing ratios (ppbv) from January 1978 to June 2001. The solid line is an interpolated curve fit to the points. Increases and decreases in the global CH_4 mixing ratio are evident after 1992. Reproduced by permission of American Geophysical Union from Simpson *et al.* (2002).

An increasing trend in atmospheric CH_4 was noted by both groups (Blake, 1984; Blake *et al.*, 1982; Blake and Rowland, 1986; Steele *et al.*, 1987). The rate of change has increased (Dlugokencky *et al.*, 1994c, 2001) and decreased (Steele *et al.*, 1992; Dlugokencky *et al.*, 1994a, 1996, 1998). The growth rate increases have been ascribed to changes in natural gas leakage and arctic wildfires, whereas the decreases have been ascribed to volcanic eruptions and decreased northern wetland emission. Khalil and Rasmussen (1985) ascribed the growth rate

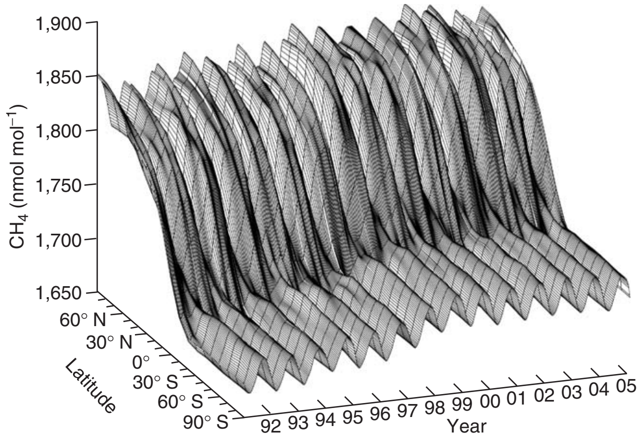

Figure 2 Global distribution of atmospheric CH_4 from 1992 through 2005. Three-dimensional latitudinal distribution of CH_4 in the marine boundary layer is presented. The surface represents data from the NOAA cooperative air sampling network smoothed in time and latitude. Source: National Oceanic and Atmospheric Adminstration (NOAA) Earth System Research Laboratory, Global Monitoring Division, Carbon Cycle Greenhouse Gases. Updated versions are available online at http://www.cmdl.noaa.gov. Supplied by E. J. Dlugokencky.

reductions to decreases in the abundance of OH and increases in sources. Hogan and Harriss (1994) noted the high quality of the time-series data, but emphasized the difficulty in deducing changes in geographically diverse CH_4 sources from the CMDL data. They called for detailed bottom-up analyses to understand changes in source strengths. Dlugokencky *et al.* (1994b) agreed that there are too few data to unequivocally determine causes for variations in the growth rate of CH_4 and indicated that their examples were intended to illustrate the magnitude of source strength changes needed to explain the observations. The causes of the CH_4 increase as well as interannual fluctuations remain a major question.

Several recent studies report progress in understanding the origin and timing of anomalies in the NOAA/CMDL data, especially the effects of biomass burning and drought. These studies have used the NOAA/CMDL data along with satellite observations of fire activity, emission factors, and stable isotope variations in ice cores to estimate the importance of biomass burning on the global CO_2 and CH_4 budgets.

Butler *et al.* (2005) used a simultaneous mass-balance inversion of atmospheric CH_4 and CO to show anomalies in CO that could be related to anomalously high biomass burning, and anomalies in CH_4 that could be related to biomass burning and reduced wetland emissions. This approach has spatial resolution of a semihemisphere and temporal resolution of 1 month. Van der Werf *et al.* (2004) devised a means of isolating the contributions of fire emissions from different continents. This approach combined satellite observations of fire activity to create a burned area time series, which used information on fuel type, fuel density, completeness of burn, biome-dependent emission factors (Andreae and Merlet, 2001), and an Atmospheric Chemistry Transport Model to obtain CO, CH_4, and CO_2 fire emissions. These were related to the CMDL data with an inverse analysis of atmospheric CO anomalies to estimate the timing and extent of contributions of fires and drought during the 1997–1998 El Niño. On a longer (~2,000 years) timescale, Ferretti *et al.* (2005) measured $\delta^{13}C–CH_4$ in Antarctic ice core samples to estimate the time history and contributions of pyrogenic methane. Pyrogenic CH_4 is isotopically heavier (−25‰ for C_3 vegtation; −12‰ for C_4 vegetation) than biogenic (−60‰ for wetlands) or fossil (−40‰) CH_4 emissions (see Section 4.03.2.5).

4.03.2.2 Methane Budget with Constraints

Cicerone and Oremland (1988) reviewed the information on CH_4 sources and sinks that had appeared since Ehhalt's work and emphasized that the atmospheric increase was genuine. They produced a framework of constraints involving CH_4 amounts, turnover rates, and isotopes. The quasi-steady-state annual source was estimated to be $500 \pm 90\ \mathrm{Tg\,yr^{-1}}$ ($1\ \mathrm{Tg} = 10^{12}\ \mathrm{g}$). Table 1, which contains entries from Cicerone and Oremland (1988), gives annual emissions from the major sources as well as estimated ranges. Note that the ranges are high for the large rice and wetland terms.

Table 1 Methane budget source/sink terms (Tg CH_4 yr^{-1}).

Source/sink *Base year*	*Cicerone and Oremland (1988)*		*Fung et al. (1991)*[a]	*Hein et al. (1997)*	*IPCC (2001) TAR*[b] *(1998)*
	Annual release	*Range*	*Annual release (1980s)*	*Annual release*	
Natural sources					
Wetlands	115	100–200	115	237	
Bogs/Tundra			35		
Swamps			80		
Termites	40	10–100	20		
Ocean	10	5–20	10[c]		
Freshwaters	5	1–25			
Hydrates	5?	0–100[d]	5		
Anthropogenic sources					
Energy			75	97	
Mining	35	25–45	35		
Gas drilling, venting	45	25–50	40		
Landfills	40	30–70	40	35	
Ruminants	80	65–100	80	90[e]	
Waste treatment			e		
Rice agriculture	110	60–170	100	88	
Biomass burning	55	50–70	55	40	
Other					
Total source	540		500	587	598
Sinks					
Soils			10		30
Tropospheric OH			450	489	506
Stratospheric loss				46	40
Total sink			460	535	576

[a] Scenario 7. [b] TAR budget based on 1.745 ppb, 2.78 Tg ppb^{-1}, lifetime of 8.4 yr and an imbalance of + 8 ppb yr^{-1}. [c] Oceans and freshwaters combined. [d] Possible future emissions. [e] Waste treatment included under ruminants.

Cicerone and Oremland (1988) made estimates of confidence in terms that comprise the global CH_4 budget (see their table 3). Confidence in the total amount of CH_4, the rate of change, and the residence time is high, resulting in high confidence in the total steady-state source (or sink). Confidence in the fraction of modern biogenic CH_4 derived form $^{14}CH_4$ measurements is also high, while confidence in the total steady-state source derived by addition of known sources is low. Summarizing, we know the total budget with high confidence, but how to apportion the individual sources is less well known. Cicerone and Oremland remarked that it was difficult to identify enough sources of radiocarbon-free CH_4. Because so little was known at the time about the impact of CH_4 hydrates on the budget, they were added to the budget as a "placeholder" term. A budget with constraints like those outlined by Cicerone and Oremland (1988) provides a useful framework for thinking about the magnitudes of terms, and by constraining the magnitude of the total, it served to limit proliferation of source estimates. However, it did not consider uptake by soils, and is much like a snapshot. The budget has no predictive power and provides no information on the causes of the CH_4 increase or the interannual variations.

Although we have confidence in the net global CH_4 budget, surprises are still possible. Keppler *et al.* (2006) reported CH_4 emissions from intact plants and detached leaves that scaled up to CH_4 emissions of 62–236 Tg yr^{-1} for living plants and 1–7 Tg yr^{-1} for plant litter. This source appears to be abiotic, and is consistent with satellite observations (Frankenberg *et al.*, 2005). Uncertainties in the net global CH_4 budget are large enough that a source in the lower part of the range reported might "fit." However, any new source must be accompanied by a decrease in an existing source. Lowe (2006) discussed implications of this report, emphasizing the size of the term and the observation that it occurs under oxic conditions. Lowe also discussed the implications of the Keppler *et al.* (2006) observations on reforestation as a means of sequestering atmospheric CO_2, raising the possibility of new forests leading to an increase in greenhouse warming through CH_4 emissions rather than a decrease by sequestering CO_2. Kirschbaum *et al.* (2006) considered the Keppler *et. al.* (2006) experimental work as probably sound, but showed that their global scaling up based on net primary production (NPP) was conceptually and dimensionally incorrect. Both above- and below-ground production are considered by NPP, while the CH_4 release considered by Keppler *et al.* (2006) applies only to above-ground production. Multiplication of methane emission (CH_4 dry mass^{-1} time^{-1}) and NPP (C area^{-1} time^{-1}) results in units of CH_4 time^{-2}, rather than the mass time^{-1} (Tg CH_4 yr^{-1}) units used in the global methane budget. Kirchbaum *et al.* (2006) presented two methods for scaling up, one using estimates of leaf mass and the other based on photosynthesis. Aerobic plant methane emissions were estimated to be 10–60 Tg CH_4 yr^{-1} with these two approaches, and are more readily reconciled within the uncertainties accepted for the global methane budget. Kirchbaum *et al.* (2006) estimated that aerobic emissions of CH_4 by plants would reduce the benefit of planting trees by only 0–4%.

Geological sources of CH_4, including seeps, mud volcanoes, and gas hydrates, and geothermal sources were summarized by Kvenvonden and Rogers (2005), who estimated that the net CH_4 contribution from geological sources could total 45 Tg yr^{-1}. They proposed addition of a geological source term to the budget.

The Keppler *et al.* (2006) result, as well as the Kvenvonden and Rogers (2005) estimate, will require extensive replication and must satisfy isotope constraints to permit consideration as a major budget term.

4.03.2.3 Gross Methane Budget

All of the above budgets and syntheses consider CH_4 actually entering the atmosphere. Field studies have clearly demonstrated that substantial microbially mediated CH_4 oxidation occurs within soils and aquatic environments, where it is able to limit and even reverse CH_4 fluxes to the atmosphere. Thus, all of the above budgets and syntheses consider net CH_4 emissions. What role does microbially mediated CH_4 oxidation play in these budgets? What is its magnitude in the various source terms? Considering the locations where CH_4 oxidation occurs, the only sources where CH_4 is introduced directly to the atmosphere with no possibility of microbial oxidation are enteric fermentation, biomass burning, natural gas leaks from production, distribution and flaring, and coal mining. The remaining sources are susceptible to modification by microbial oxidation. Söhngen (1906) recognized that CH_4 oxidation occurs in close proximity to CH_4 sources. The so-called Söhngen cycle, emission = production − consumption, can be used as a framework to estimate the importance of microbially mediated CH_4 oxidation.

Reeburgh *et al.* (1993) estimated the role of microbially mediated CH_4 oxidation using limited data on oxidation rates in environments representing the main CH_4 budget source terms. Reeburgh (1996) considered studies since 1993 and highlighted progress in studies of methane oxidation in wetland, rice, and landfills. Table 2 uses the net CH_4 budget of Fung *et al.* (1991) (scenario 7), adds oxidation estimated from oxidation rate measurements and mass balances, and produces an estimate of gross CH_4 production. Although Reeburgh *et al.* (1993) were conservative in their oxidation estimates, neither the oxidation estimates nor the gross production estimates can be constrained by any of the criteria and techniques outlined by Cicerone and Oremland (1988), Fung *et al.* (1991), and Hein *et al.* (1997). Several striking features are evident in Table 2. First, total microbial oxidation is slightly larger than net global emission. More than half of the estimated CH_4 production is oxidized by microbes before emission to the atmosphere. Thus, microbial CH_4 oxidation is most effective before emission, and has remained largely invisible because of our focus on net emissions. The consumption term representing uptake of atmospheric methane is a refinement to the overall budget with a magnitude similar to the annual increment causing the atmospheric increase. Microbial oxidation occurring before emission is clearly more important. This is illustrated by the role of the ocean in the global methane budget. While the ocean and the placeholder hydrate decomposition term have the potential to produce enormous quantities of CH_4, a series of very effective microbially mediated oxidation processes, anaerobic oxidation in anoxic sediments and anoxic water columns, followed by aerobic oxidation in the oxic water column, result in the ocean being one of the net global CH_4 budget's smallest terms. A similar situation holds for wetlands and rice production. It is clear from Table 2 that future attention must focus not only on net CH_4 emission, but also on microbial oxidation.

4.03.2.4 Atmospheric Models

Fung *et al.* (1991) attempted to derive a justified global budget for CH_4 in the 1980s. Geographic and seasonal distributions of major CH_4 sources and sinks were compiled, and oxidation by the OH radical was calculated. A global three-dimensional tracer transport model was used to simulate the atmospheric response to geographic and seasonal

Table 2 Global Net CH_4 emission, consumption, and gross production (Tg CH_4 yr^{-1}).

Source/sink term	E	+	C	=	P
	Net emission[a]		*Consumption*[b]		*Gross production*
Animals	80		0		80
Wetlands	115		27		142
Bogs/tundra (boreal)	35		15		50
Swamps/alluvial	80		12		92
Rice production	100		477		577
Biomass burning	55		0		55
Termites	20		24		44
Landfills	40		22		62
Oceans, freshwaters	10		75.3		85.3
Hydrates	5?		5		10
Coal production	35		0		35
Gas production	40		18		58
Venting, flaring	10		0		10
Distribution leaks[c]	30		18		48
Total sources	500[d]				
Chemical destruction	–450				
Soil consumption	–10		40		
Total sinks	–460[d]		688.3		40[e]
Total production					1,188.3

Adapted from Reeburgh *et al.* (1993).
[a] Scenario 7, Fung *et al.* (1991). [b] From Reeburgh *et al.* (1993), table 1. [c] Should be considered *P*. [d] 500–460 = 40 Tg CH_4 yr^{-1} annual atmospheric (0.9% yr^{-1}) increment. [e] Soil consumption of atmospheric CH_4 added to the gross budget as an equivalent production term.

changes in CH_4 sources and sinks. A number of CH_4 budget scenarios were run and tested for their ability to reproduce the meridional gradient as well as the seasonal variations in CH_4 concentration observed at GMCC stations. The preferred CH_4 emission budget (scenario 7) is included in Table 1. Magnitudes of CH_4 emissions from fossil sources, domestic animals, and wetlands and tundra north of 50° N are reasonably constrained geographically. Individual contributions of the landfill, tropical swamp, rice paddy, biomass burning, and termite source terms could not be determined uniquely because of the lack of direct flux and atmospheric variation measurements in the regions where these sources are concentrated.

Hein *et al.* (1997) also used a three-dimensional atmospheric transport model to calculate the global distribution of OH radicals, the main sink for atmospheric CH_4. They used an inverse modeling method that allowed selection of the source/sink configuration that gave the best agreement between observed and calculated CH_4 concentrations. This allowed objective treatment of the uncertainties in source and sink magnitudes, and reduced the uncertainty of source magnitudes by at least one-third. The Hein *et al.* (1997) results are tabulated for comparison in Table 1. The conclusions of Hein *et al.* (1997) agreed quite well with those of Fung *et al.* (1991) and confirmed that it is not uniquely possible to select only one source–sink combination. The decrease in the atmospheric CH_4 growth rate in the early 1990s could not be uniquely associated with changes in particular sources. For comparison, the CH_4 budget from the IPCC Third Assessment Report (IPCC/TAR) (IPCC, 2001) also appears as a column in Table 1.

4.03.2.5 Stable Isotopes

Stable isotope ratios of carbon ($^{13}C/^{12}C$) and hydrogen ($^{2}H/^{1}H$) in CH_4 were recognized as providing additional constraints for the global CH_4 budget (Stevens and Rust, 1982). Limited data suggested that it might be possible to distinguish or discriminate between CH_4 sources and that a carbon or hydrogen isotope budget for CH_4, parallel to the concentration budget, could be assembled. These measured values are expressed in delta notation (Craig, 1957), which for carbon isotopes is

$$\delta^{13}C = [R_{\text{sample}}/R_{\text{standard}} - 1] \times 1,000$$

where R is the ratio $^{13}C/^{12}C$, sample and standard refer to the carbon isotope ratios in the sample and standard, and the results are expressed as parts per thousand or per mil (‰). Negative values in this notation indicate samples with lower ^{13}C content than the standard. Stevens and Rust (1982) proposed that the mass-weighted isotopic composition of all sources should equal the mean isotope composition of the atmosphere ($\delta^{13}C = -47‰$) when corrected for isotope fractionation effects associated with CH_4 consumption reactions. Kinetic isotope effects (KIEs) result from the light isotope (^{12}C) reacting faster than the heavy isotope (^{13}C) and offer a constraint associated with reactions.

Tyler (1991) summarized the $\delta^{13}C$ of CH_4 ($\delta^{13}CH_4$) from a number of sources. The $\delta^{13}CH_4$ from a given type of environment covers a fairly large range due to variations in methanogenic substrates and mechanisms, and also to fractionation associated with oxidation, so that many sources of CH_4 have overlapping $\delta^{13}C$ ranges. In general, CH_4 from biogenic sources is isotopically lighter (−40‰ to −80‰) than CH_4 from geological or thermogenic sources (−30‰ to −50‰). Plants utilizing the C-3 photosynthetic pathway have carbon isotope composition (−21‰ to −35‰) that differs from plants utilizing the C-4 pathway (−10‰ to −20‰), so that CH_4 produced by decomposition of each type of plant may have a distinctive isotopic composition.

Carefully intercalibrated atmospheric time-series measurements of $\delta^{13}CH_4$ have been made by Quay *et al.* (1991, 1999) and Tyler *et al.* (1994, 1999) in the northern hemisphere and by Lowe *et al.* (1991, 1994, 1997) in the southern hemisphere. Additional atmospheric $\delta^{13}CH_4$ measurements are reported in the modeling study of Gupta *et al.* (1996). This model included KIEs of CH_4 sinks, namely, reaction with OH, reaction with Cl, and oxidation by soils, all of which enrich atmospheric CH_4 in ^{13}C. These models employ a very limited data set and are based on the Oslo two-dimensional (height versus latitude) global tropospheric photochemical model (Gupta *et al.*, 1998). The success of these model treatments of $\delta^{13}CH_4$ depends critically on the values of KIEs. Tables 3 and 4 summarize recent KIE determinations for atmospheric and microbially mediated soil and sediment reactions. It should be noted that studies on soil KIEs have only recently reached a point of agreement with a combination of static chamber, soil profile, and landfill emission studies. Chanton (2005) reviewed the effect of mechanisms of gas transport (diffusion, ebullition, and transport thought emergent plants) on the isotope signature of emitted CH_4.

Tans (1997) derived relationships showing that the timescale for equilibration of atmospheric

Table 3 Microbial methane oxidation kinetic isotope fractionation factors.

Study/(comment)	αC	αH
Aerobic		
Silverman and Oyama (1968) (calculated by Whiticar and Faber, 1986)	1.011	
Coleman *et al.* (1981) (enrichment culture, closed system)	1.013–1.015	1.103–1.325
Barker and Fritz (1981) (enrichment culture, closed system)	1.005–1.103	
Whiticar and Faber (1986) (model calculations, field data)	1.002–1.014	
Zyakun *et al.* (1988) (*Methylomonas methanica*, flow-through system)	1.011–1.039	
Happell *et al.* (1994) (FL swamp floodwater)	1.003–1.021	1.050–1.129
King *et al.* (1989) (tundra, AK)	1.016 (4 °C), 1.027 (14 °C)	
Tyler *et al.* (1994) (forest soil, NH)	1.022 ± 0.004	
Bergamaschi and Harris (1995) (landfill cover soil)	1.008 ± 0.003	1.044 ± 0.020
Reeburgh *et al.* (1997) (forest soil, AK)	1.022 and 1.025	
Bergamaschi *et al.* (1998b) (landfill cover soil)	1.008 ± 0.004	1.039 ± 0.026
Liptay *et al.* (1998) (NE US landfill cover soils)	1.022 ± 0.008	1.046 ± 0.016
Snover and Quay (2000)		
(grassland, WA)	1.0173 ± 0.0010	1.009 ± 0.030
(temperate forest, WA)	1.0183 ± 0.0004	1.066 ± 0.007
Sansone and Graham (2004) Low O_2 W. Mexican Margin waters	1.100–1.0035	
Anaerobic		
Alperin *et al.* (1988) (Skan Bay, AK, 4 °C) maximum AMO rate: 3–4 mM yr^{-1}	1.0088 ± 0.0013	1.157 ± 0.023
Martens *et al.* (1999) (Ekernförde Bay, FRG, 8 °C) maximum AMO rate: 14–16 mM yr^{-1}	1.012 ± 0.001	1.120 ± 0.020

Table 4 KIEs for reactions involving atmospheric CH_4.

Study	*Type*	*αC*	*αH*
CH_4 with Cl			
Wallington and Hurley (1992)	Experimental		1.47±0.09
Saueressig *et al.* (1995)	Experimental	1.066±0.002	1.508±0.041
Tanaka *et al.* (1996)	Theoretical	1.026	
Tanaka *et al.* (1997)	Experimental	1.013–1.020	
Gupta *et al.* (1997)	Theoretical	1.034	
Roberto-Neto *et al.* (1998)	Theroretical	1.06	1.45
Crowley *et al.* (1999)	Experimental	1.066±0.002	
Tyler *et al.* (2000)	Experimental	1.0621±0.0004	1.474±0.026
CH_4 with OH			
Davidson *et al.* (1987)	Experimental	1.010±1.007	
Cantrell *et al.* (1990)	Experimental	1.0054±0.0009	
Gupta *et al.* (1997)	Theoretical	1.010	
Saueressig *et al.* (2001)	Experimental	1.0039±0.0004	1.294±0.018 (D)

$\delta^{13}CH_4$ following changes is considerably longer than the timescale for changes in total CH_4. Changes in the $\delta^{13}CH_4$ result not only from changes in magnitudes of isotopically different sources, but also from isotope dilution by a changing reservoir of total atmospheric CH_4. Tans (1997) noted that the dearth of isotope data for atmospheric $\delta^{13}CH_4$ is a larger problem than possible misinterpretation of trends. Lassey *et al.* (2000) analyzed archived southern hemisphere samples covering time intervals of 10 and 17 years, and used models to show that they are compatible with stabilized CH_4 sources. An analysis of the sensitivity of the atmospheric secular response in both concentration and $\delta^{13}CH_4$ to sustained changes in source and sink showed that $\delta^{13}CH_4$ is a potentially powerful indicator of source and sink changes.

The amount of atmospheric $\delta^{13}CH_4$ and δD–CH_4 data available for modeling promises to increase rapidly in the future through application of new techniques. The development of continuous-flow gas chromatography–combustion isotope ratio monitoring mass spectrometry (GC/C/IRMS) (Merritt *et al.*, 1995; Popp *et al.*, 1995) allows measurements of $\delta^{13}CH_4$. Measurements of δD–CH_4 (Rice *et al.*, 2001) are possible with the more recently developed gas chromatography–pyrolysis isotope ratio monitoring mass spectrometry (GC/P/IRMS) technique. Both techniques permit analyses on small (∼10 cc) atmospheric samples with precision comparable to the classical combustion line techniques using much larger samples. While these techniques promise a large increase in the numbers of samples that can be analyzed, they require great attention to experimental detail and calibration, so careful intercalibrations similar to those conducted by laboratories making the first measurements of atmospheric $\delta^{13}CH_4$ should be carried out before reporting data.

4.03.3 TERRESTRIAL STUDIES

Systematic measurements of CH_4 fluxes as well as some time series from wetlands, rice agriculture, landfills, and ruminants were in progress but unpublished at the time of the previous reviews. Reviews by Aselmann and Crutzen (1989), Bartlett and Harriss (1993), Harriss *et al.* (1993), and Matthews (2000) integrate and summarize a large number of wetland, tundra, and rice studies and have helped refine our understanding of the source strength from these systems. Whalen (2005) reviewed recent observations of methane exchange between natural wetlands and the atmosphere. This section will focus on studies that emphasize controls on CH_4 fluxes and thus provide a basis for development of realistic models.

4.03.3.1 Flux Time Series

Many of the available CH_4 flux measurements have resulted from short-term campaigns that span only a portion of the growing season; these have been summarized by Bartlett and Harriss (1993) and Harriss *et al.* (1993). Flux time-series measurements that provide information on seasonal changes and interannual changes are much less common. Whalen and Reeburgh (1992) reported results of a 4-year time series of weekly measurements conducted at triplicate sites in the University of Alaska Arboretum in Fairbanks, AK. The sites were chosen to represent vegetation and cover types common in tundra systems. Although these sites were not true arctic sites, their growing seasons were only slightly longer than at sites at the Toolik Lake Long-Term Ecological Research (LTER) site, so they were taken as representative. Dise (1993) reported a 2-year CH_4 flux time series from Minnesota peatland sites, and Shannon and White (1994) reported a 3-year CH_4 flux time series from a Michigan bog. The longest CH_4 flux record (17 years) is from Sallie's Fen in southeastern New Hampshire (Crill, unpublished results), where the initial measurements reported in Frolking and Crill (1994) have continued with automated chamber measurements (Goulden and Crill, 1997).

Small, positive CH_4 fluxes from moss sites were observed from the Alaska sites during winter (Whalen and Reeburgh, 1988). These winter emissions amounted to 41% of the annual emission from the moss sites, which were open and aerated, and had lower summer emissions than other sites studied. Dise (1992) reported winter CH_4 fluxes from hummock sites in Minnesota peatlands amounting to 21% of the annual emission, and Melloh and Crill (1996) studied CH_4 concentrations at the freezing front and beneath surface ice in Sallie's Fen and estimated that winter emissions ranged between 2% and 9.2% of the annual emission, averaging 4.3%.

4.03.3.2 Flux Transects

Flux transects, which provide information on spatial variability and are usually conducted over a month-scale time interval, have been reported by Whalen and Reeburgh (1990a), who made CH_4 flux measurements at 10 km intervals along the trans-Alaska pipeline haul road. Christensen *et al.* (1995), using ship and helicopter support, made CH_4 flux measurements on a series of short inland transects along the Arctic Ocean coast of Siberia. Crutzen *et al.* (1998), Bergamaschi *et al.* (1998a), and Oberlander *et al.* (2002) reported atmospheric concentration and isotope measurements of atmospheric CH_4 on a transect across Siberia on the trans-Siberian Railway, which allowed discriminating between wetland, gas production, and biomass burning sources of CH_4. Sugawara *et al.* (1996) reported CH_4 concentration and isotope measurements on samples collected during aircraft transects in Siberia.

4.03.3.3 Process-Level Studies

4.03.3.3.1 Vegetation removal experiments

Vegetation removal experiments were conducted by Torn and Chapin (1993) and Schimel (1995) to understand the role of vascular plants in methane emission and oxidation. King *et al.* (1998) studied sites in the Toolik Lake LTER, where the vegetation was modified (sedge- and moss-removal plots) to determine the role of these vegetation types in wetland CH_4 emission and to study the gas transport mechanism. The study showed an inverse relationship between root density and pore water CH_4 concentration (Figure 3). Parallel experiments involving insertion of gas-permeable silicone rubber tubes show that the tubes are reasonable analogs for the physical process of diffusion through plants.

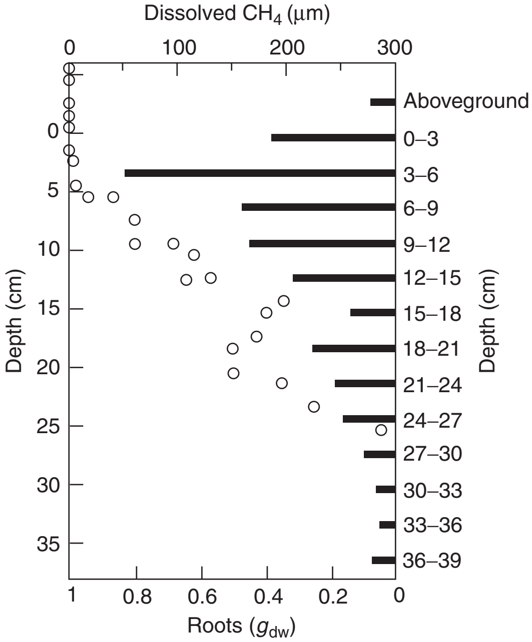

Figure 3 Comparison of pore water CH_4 concentrations (circles) with root density depth distribution (dry weight mass of roots per 3 cm depth interval of a 6.5 cm diameter core) (bars) in a wet meadow site at the Toolik Lake LTER site, 1995. Reproduced by permission of American Geophysical Union from King *et al.* (1998). Copyright 1998.

4.03.3.3.2 Methane flux: net ecosystem exchange relationship

Much of the above work has been directed toward obtaining reliable data-based estimates of wetland emissions for the global CH_4 budget. It has been very difficult to find a single or simple controlling relationship between CH_4 flux and environmental or system variables (Whalen and Reeburgh, 1992). Relationships between the CH_4 flux and subsurface properties (watertable depth, thaw depth, soil temperature, and CH_4 concentration) are site specific and of little value as predictors. Parameters that integrate conditions influencing flux (thaw depth and centimeter degrees, the product of thaw depth and mean soil temperature to permafrost) appear to be the best predictors of CH_4 flux.

A relationship between CH_4 flux and net ecosystem exchange (NEE) (NEE = system CO_2 uptake − system CO_2 release) presented by Whiting and Chanton (1993) showed promise as a basis for estimating CH_4 flux using methods other than the reliable but tedious static chamber measurements. Remotely sensed wetland net primary production (NPP) was suggested as a proxy for NEE, raising the possibility of estimating global wetland CH_4 flux over large areas with synoptic measurements. The Whiting–Chanton relationship used CH_4 flux data from the seasonal maximum in a wide range of wetland types, and implied fairly direct coupling between photosynthesis and CH_4 formation and emission. The fraction of modern $^{14}CH_4$ of emitted CH_4 is ~0.95 (Aravena *et al.*, 1993; Chanton *et al.*, 1995) and supports the notion of direct coupling by indicating that long-term stored carbon was not the major CH_4 source. Subsequent studies show that the Whiting–Chanton relationship applies best to wet systems populated with vascular plants. The relationship between CH_4 flux and NEE is less clear in wetland systems, where oxidation is more important and no transport system exists, namely those with fluctuating water levels and moss cover.

4.03.3.4 Scaling Up

Scaling up site-based CH_4 fluxes to estimate global fluxes is a major problem because of spatial and temporal variability in flux measurements, as well as variability in site types (Matson *et al.*, 1989). The estimate of wetland and tundra emissions by Matthews and Fung (1987) did a very good job of summarizing global areas of likely CH_4 sources, but was limited by a very small amount of CH_4 flux data. Whalen and Reeburgh (1992) used data from 4-year CH_4 flux time series and areally weighted fluxes from sites representative of arctic tundra to estimate a high-latitude global CH_4 flux that agreed reasonably well (42 ± 27 Tg CH_4 yr^{-1}) with the Fung *et al.* (1991) estimate (35 Tg CH_4 yr^{-1}) for high-latitude emissions from tundra. Another study (Reeburgh *et al.*, 1998) attempted to scale up from the site to region level by areally weighting 3-year integrated annual CH_4 fluxes from sites in the Kuparuk River watershed on Alaska's North Slope. These sites represented specific tundra vegetation and land cover types. The sites were chosen and their integrated fluxes were weighted using a Geographic Information System-based vegetation map (Auerbach *et al.*, 1997). Extending this regional estimate to the circumpolar arctic accounted for only 15% of the Fung *et al.* (1991) high-latitude flux estimate. The Reeburgh *et al.* (1998) work shows that arctic CH_4 fluxes are dominated by inundated wetlands, as indicated previously by Matthews and Fung (1987). The poor agreement with the Fung *et al.* (1991) high-latitude CH_4 flux estimate obtained by extrapolating this watershed flux estimate suggests that the Hudson's Bay Lowlands (Roulet *et al.*, 1994) and the West Siberian Lowlands, which have received very little study (Harriss *et al.*, 1993), may be the major global contributors. Clearly, better estimates of inundated wetland areas as well as field flux measurements are needed.

Methane flux measurements can be made at scales larger than chambers with aircraft boundary layer measurements (100 km) or micrometeorological measurements using towers (100 m). Chamber, tower, and aircraft measurements were compared in two field campaigns: the Arctic Boundary Layer Experiment (ABLE 3A) (summarized in the *J. Geophys. Res.* **97**(D15), 1992) and the Northern Wetlands Study (NOWES/ABLE 3B) (summarized in the *J. Geophys. Res.* **99**(D1), 1992). During the latter study, CH_4 fluxes often agreed to within a factor of 1.2 (Roulet *et al.*, 1994). There is, however, a critical need for a field-portable, rapid-response CH_4 detector for a use in aircraft and tower measurements.

4.03.3.5 Wetland Soil Models

A variety of process-based models of methane emission from wetlands have been published, ranging from very complex models requiring a large number of measured input parameters to straightforward special-purpose models involving correlations between measured parameters. These models have been developed to understand controls on CH_4 fluxes from a range of environments, as well as to scale fluxes and soil consumption to global scales.

A biologically based approach to the simulation of CH_4 transformations was undertaken as part of the Canadian "ecosys" model project. The CH_4 studies simulated the interrelated activities of anaerobic fermenters and H_2-producing acetogens, acetotrophic and hydrogenic stoichiometries, and energetics of transformations in a series of papers dealing with methanogenesis (Grant, 1998), methanotrophy (Grant, 1999), and finally, CH_4 efflux (Grant and Roulet, 2002). The emission model predicted efflux events associated with thawing and warming of soil and pond sediments that would likely be missed by observation programs. However, the "ecosys" model required a knowledge of and assignment of almost 30 parameters, so a great deal of fundamental information about microbial populations, rates, and kinetics must be known.

Segers and Kengen (1998) described a model based on the dynamics of alternative electron acceptors, acetate, and methanogenic biomass that relates CH_4 production to anaerobic carbon mineralization. Models incorporating kinetic processes such as CH_4 production, CH_4 oxidation, electron acceptor reduction, electron acceptor reoxidation, and aerobic respiration were employed in a series of subsequent papers describing stepwise scaling up from the single-root scale (Segers and Leffelaar, 2001a), to the soil-layer scale (Segers *et al.*, 2001), and finally to the plot scale (Segers and Leffelaar, 2001b) to estimate methane fluxes.

Frolking and Crill (1994) developed a peat soil climate model driven by daily weather and used correlations of CH_4 flux with environmental parameters to investigate how climate and weather control the observed temporal variability in CH_4 flux at Sallie's Fen. The model agreed well with field data. Further, the simulated fluxes exhibited three modes of temporal variability that were evident in the field data: seasonal, interannual, and event scale (flux suppression by summer rainstorms).

Cao *et al.* (1996) developed a process-based model to estimate seasonal and spatial variations in wetland CH_4 emissions at the global scale. The model calculated methanogenesis from primary production and estimated emission by oxidizing a fraction of the CH_4 produced as it passed through the oxic zone. The process of oxidation becomes more complicated when the wetland soil is not inundated. Global application of the model yielded total emission of 92 Tg CH_4 yr^{-1}. Sensitivity analysis showed that the model response of CH_4 emission to climate change depended upon the combined effects of carbon storage, rate of decomposition, soil moisture, and methanogen activity.

Walter and Heimann (2000) report application of a one-dimensional process-based climate-sensitive model simulating processes leading to CH_4 emission from natural wetlands. The model treats three CH_4 transport mechanisms—diffusion, plant transport, and ebullition explicitly—and is forced with daily values of temperature, watertable, net primary productivity, and thaw depth at permafrost sites. Their objective was to provide a model that could be applied to simulating CH_4 emissions in various regions as a function of the prevailing climate that could also be used on a global scale. The model was tested with time-series data from five different wetland sites. Soil temperature and watertable position explained seasonal variations, but the authors emphasized that the absence of a simple relationship between controlling factors and CH_4 emission requires the process-based approach.

Granberg *et al.* (2001) modeled CH_4 emission from an oligotrophic lawn community in a boreal mire. Their representation of winter conditions (frost and snow) is the main difference between their model and that of Walter and Heimann (2000). The model was forced with daily mean air temperatures and daily accumulated precipitation. Methane was simulated with a model that separated CH_4 emission by ebullition, diffusion, and plant transport. Oxidation was estimated by oxidation potential, which was centered at the watertable. This model indicated that the mean level of the watertable was the most important predictor of simulated CH_4 emission, and that the presence of vascular plants is the most important factor in determining CH_4 emission. These authors point out that their model contains tuning parameters that cannot be replaced by measurable parameters in the field. They called for focusing on mechanisms like gas diffusion through plants and ebullition to produce a robust model that works over a broad range of plant communities and climatic conditions.

Ridgwell *et al.* (1999) developed a process-based model for estimating the consumption of atmospheric CH_4 by soils, and estimated a global soil sink strength of 20–51 Tg CH_4 yr^{-1}, with a preferred value of 38 Tg CH_4 yr^{-1}. Microbial activity, instead of diffusion, limits uptake in tropical ecosystems, which account for almost a third of the total. Del Grosso *et al.* (2000) also modeled methane oxidation as a function of soil water content, temperature, porosity, and field capacity, but emphasized native and cropped grasslands. Using a kinetic model, Cai and Yan (1999) simulated paddy soil methane oxidation activity (assumed to be the product of the number of methanotrophic bacteria and their specific activity) and found it to be dependent on the CH_4 concentration.

4.03.3.6 Animals and Landfills

Ruminant methane emissions, which account for 95% of animal CH_4 emissions, have been reviewed by Johnson *et al.* (2000), who estimated that 81 Tg CH_4 yr^{-1} resulted from enteric microbial activity and another 14 Tg CH_4 yr^{-1} from manure decomposition. Enteric CH_4 production represents a substantial (up to 12%) dietary energy loss, so inhibitors directed at minimizing methanogenesis have been developed and are under study. A common problem has been apparent microbial adaptation, resulting in a return to baseline levels of methane production. Sulfur hexafluoride (SF_6) has been used as a conservative internal tracer in individual animals (Johnson *et al.*, 1994) as well as an external tracer in experiments involving groups of animals in barns (Marik and Levin, 1996) or pens (Johnson *et al.*, 1994). In general, diets that are finely ground and pelleted with high grain content result in lower methane emission.

The review of landfill methane emission by Bogner and Matthews (2003) used four scenarios to obtain estimates ranging from 15 to 81 Tg CH_4 yr^{-1}, which is similar to previous estimates. Landfill sites have been a particularly active area for studies of methane oxidation (Whalen *et al.*, 1990; Jones and Nedwell, 1993) and for studies of isotope fractionation of methane during oxidation (Bergamaschi and Harris, 1995; Bergamaschi *et al.*, 1998b; Liptay *et al.*, 1998). A laboratory study (Kightley *et al.*, 1995) employing soil microcosms successfully reproduced the "methane: oxygen crossover" zone observed in landfill cover soils and confirmed the high methane-oxidizing capacity of this zone as a control on atmospheric CH_4 emissions.

4.03.3.7 Microbial Soil Oxidation

Methane oxidation in soils has received a great deal of attention recently. An example of how rapidly this area has grown is given by two reviews written 8 years apart. The first (Conrad, 1984) used existing kinetic information on cultured organisms to make the case that soil organisms could not utilize, grow on, and control the atmospheric concentrations of CO, CH_4, and H_2. The second (Conrad, 1996) contains some 600 references and clearly shows how soil and atmospheric concentrations of not only CH_4, but also H_2, CO, CH_4, OCS, N_2O, and NO are heavily influenced or controlled by microbial activity.

4.03.3.7.1 Moist soils

The first example of soil consumption of CH_4 was reported by Harriss *et al.* (1982), who observed seasonal concentration decreases (and increases) in flux chamber headspaces. Keller *et al.* (1990) reported similar observations for tropical soils. This work was followed by measurements in tundra environments by Whalen and Reeburgh (1990b), and by more extensive experimental work using chamber measurements, jar experiments, and $^{14}CH_4$ tracer experiments on boreal forest soils by Whalen *et al.* (1992). Koschorreck and Conrad (1993) devised a multiport device for laboratory studies on soil cores.

A number of experimental studies on controls on soil CH_4 oxidation produced relationships that have been incorporated in some of the models discussed earlier. Whalen and Reeburgh (1996) used jar experiments (1 qt; 1 qt $= 9.463 \times 10^{-4}$ m^3 canning jars) to determine CH_4 uptake kinetics of a number of moist boreal soils. Large samples of soil from the CH_4-oxidizing maximum were homogenized and distributed into jars, and first-order CH_4 oxidation kinetics were measured over a range at temperature and moisture conditions. Figure 4 shows typical results. The CH_4 supply to methane-oxidizing organisms is diffusion controlled and decreased under higher moisture conditions, and oxidation rates are lower.

4.03.3.7.2 Waterlogged soils

Similar rate studies in waterlogged boreal bogs required modified techniques (Whalen and Reeburgh, 2000a). Oxygen microelectrode studies showed that waters become anoxic only millimeters below the level of the watertable (Whalen *et al.*, 1995). The watertable is a sharp interface ($\sim$0.5 cm) between oxic and anoxic conditions and is perhaps the most important location for control of CH_4 fluxes by oxidation (Moosavi *et al.*, 1996). The Whalen and Reeburgh (2000a) work focused on concentration and rate distributions adjacent to the watertable. Figure 5 gives results from an experiment that attempted to mimic a rapid change in the level of a watertable, and shows that the microbial communities can respond within a day to changes from anoxic to oxic conditions. This experiment also shows that methanogens are more sensitive than methanotrophs to adverse oxygen conditions. Methane oxidation is a very effective process in limiting CH_4 emission from wetlands inundated with a shallow layer of oxic water (Happell *et al.*, 1994).

4.03.3.7.3 Nitrogen fertilization and disturbance

Several early studies on CH_4 uptake by soils also noted that CH_4 oxidation activity was reduced or inhibited by disturbance or nitrogen additions (Mosier *et al.*, 1991; Steudler *et al.*, 1989; Reay *et al.*, 2001). Enzymes associated with NH_4^+ oxidation are similar to those associated with CH_4 oxidation, so there was concern that increased nitrogen loading of soils by

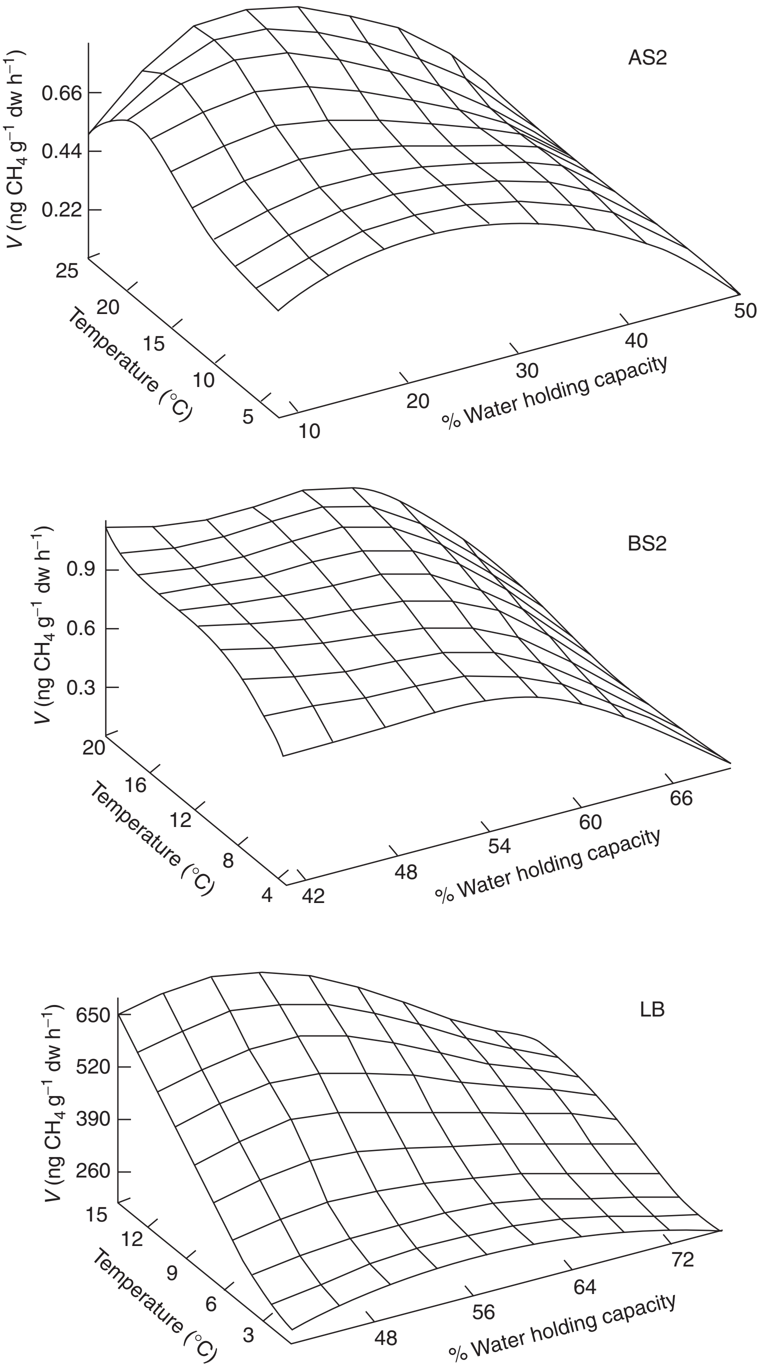

Figure 4 Methane oxidation rates as a function of moisture–temperature interactions for boreal soils. Methane oxidation rates for AS2 and BS2 soils were calculated for 1.5 μl CH_4 l^{-1} from first-order rate constants for each moisture–temperature combination. Methane oxidation rates for LB soil were directly measured in time-course experiments for each moisture–temperature combination. Reproduced by permission of Elsevier from Whalen and Reeburgh (1996).

atmospheric deposition could decrease the soil CH_4 sink strength. Nitrogen inhibition of CH_4 oxidation is known (Bedard and Knowles, 1989). King (1992) reviewed the responses of soils and concluded that increases in ammonium deposition and water stress should inhibit soil CH_4 oxidation. Klüber and Conrad (1998) observed that addition of nitrate to anoxic rice soil slurries caused complete, but reversible inhibition of methanogenesis. No effects on CH_4 oxidation were observed in field fertilization experiments on boreal forest soils. These were

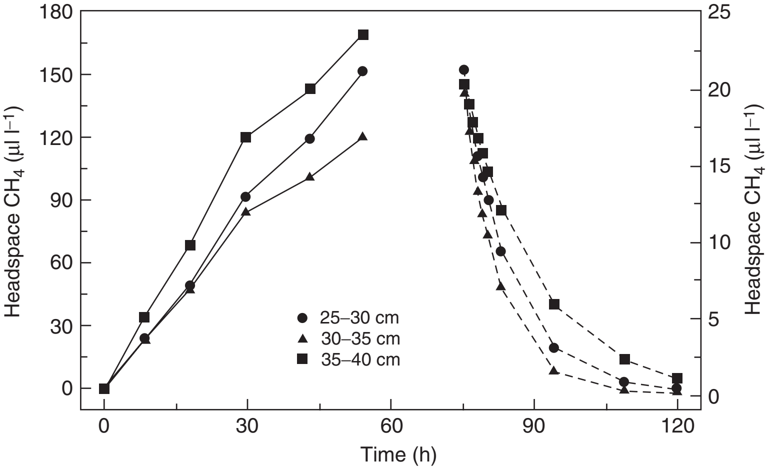

Figure 5 Time courses for CH_4 production (left) and CH_4 oxidation (right) in selected 5 cm core sections (site LB2 in Lemeta Bog) that were alternately made anoxic and oxic in an attempt to mimic response to changing watertable levels. Methane production by anoxic core sections was measured for 54 h. Core sections were drained for 20 h in an oxic environment and then amended with ~20 µl l^{-1} CH_4, after which the time course for CH_4 oxidation (right) was determined. No CH_4 was produced over 48 h by core sections rewetted and made anoxic at 120 h. Reproduced by permission of Taylor & Francis Group, LLC from Whalen and Reeburgh (2000a), http://www.taylorandfranis.com. Copyright 2000.

attributed either to distinct CH_4 oxidizer populations (Gulledge *et al.*, 1997) or to the position of the CH_4-oxidizing community in the soil column (Whalen and Reeburgh, 2000b).

4.03.3.7.4 *Effects of drying on paddy soils*

Water management has a profound effect on methane emission from rice fields (Sass *et al.*, 1992). Mid-season draining, dressing, and fertilizing Japanese rice fields result in greatly reduced overall CH_4 emission (Yagi *et al.*, 1996). Laboratory studies by Ratering and Conrad (1998) and Klüber and Conrad (1998) demonstrated that short-term drying allows air oxidation of reduced nitrogen, sulfur, and iron species in paddy soils. This oxidized reservoir must be reduced before methanogenesis can resume, resulting in a lag before methane emission is evident.

4.03.3.8 New Techniques

Dörr and Munnich (1990) described a technique for estimating gas fluxes from soils using parallel measurements of CO_2 and ^{222}Rn profiles in soils. This technique does not require chambers and has the advantage of using naturally produced ^{222}Rn, which is conservative and is affected only by diffusion and radioactive decay. The technique was extended to measurements of CH_4 consumption (Born *et al.*, 1990). Dörr *et al.* (1993) used soil-texture parameterization to extend local measurements to the global scale, and arrived at an estimate of 28.7 Tg CH_4 yr^{-1}. Whalen *et al.* (1992) used the ^{222}Rn technique in a boreal forest study comparing seven approaches to measuring soil CH_4 oxidation.

The above studies are only able to detect net CH_4 production or net CH_4 consumption, that is, either production or consumption must exceed the competing process to produce an observable positive or negative concentration change in a flux chamber. To separate the effects of oxidation and production, the effect of CH_4 oxidation has been measured by using CH_3F, a specific inhibitor of CH_4 oxidation (Oremland and Culbertson, 1992; Epp and Chanton, 1993; Moosavi and Crill, 1998) or with tracer techniques using $^{14}CH_4$ (Whalen and Reeburgh, 2000a; Whalen *et al.*, 1992). Two additional isotope techniques have been proposed to determine simultaneous CH_4 production and oxidation in soils. Andersen *et al.* (1998) described laboratory work involving additions of $^{14}CH_4$ to soil columns. They observed that $^{14}CH_4$ was consumed faster than atmospheric CH_4, and took this as evidence that although the soil was a net consumer of CH_4, there may be another CH_4 source. Von Fischer and Hedin (2002) describe a field technique utilizing stable isotope dilution of naturally occurring pools to estimate simultaneous production and consumption. This technique was applied to moist soils; its application to waterlogged soils, especially adjacent to the level of watertable, appears to be a natural and needed extension.

One of the questions essential to understanding CH_4 biogeochemistry in wetland and rice systems is the source of emitted CH_4 and the timescale between photosynthetic production of biomass and methanogenesis. This question has been addressed using pulse-labeling experiments, which involve labeling plants by photosynthetic uptake of $^{14}CO_2$ and quantifying the time course of $^{14}CH_4$ release. Pulse labeling with $^{13}CO_2$ has been used in laboratory experiments on rice plants (Minoda and Kimura, 1994; Minoda *et al.*, 1996), where the product $^{13}CH_4$ was quantified mass spectrometrically. Dannenberg and Conrad (1999) conducted similar laboratory experiments on rice using $^{14}CO_2$. Megonigal *et al.* (1999) performed a pot-scale $^{14}CO_2$ pulse-labeling experiment on a single *Orontium aquaticam* plant, and King and Reeburgh (2002) performed a field $^{14}CO_2$ pulse-labeling experiment under near *in situ* conditions using arctic plant mesocosms containing communities dominated by *Eriophorum–Carex*. Results from laboratory *Eriophorum–Carex* mesocosm pulse-labeling experiments were reported by King *et al.* (2002) and Loya *et al.* (2002). All of these pulse-labeling experiments reported rapid emission of $^{14}CH_4$ (within 24 h). Less than 1% of the $^{14}CO_2$ taken up during photosynthesis was emitted over a 2-week period in the nonrice studies. These measurements of net CH_4 emission provide little information on pathways and processes involved in methanogenesis as well as CH_4 oxidation, but they show clearly that recently fixed photosynthates play a major role in CH_4 emission. These findings are consistent with observations of 0.95% modern methane emissions (Aravena *et al.*, 1993; Chanton *et al.*, 1995). Pulse-labeling experiments are labor intensive, so the work above has reported small numbers of samples. King and Reeburgh (2002) point out that the contribution of plant photosynthates to CH_4 emission may be dependent on plant phenology, so pulse-labeling studies at intervals over a growing season are needed in the future.

4.03.4 MARINE STUDIES

4.03.4.1 Ocean Methane Source

The ocean as a CH_4 source in the global CH_4 budget was re-evaluated by Ehhalt (1978) using a much larger database than his 1974 estimate, but the difference was small and the Ehhalt (1974) estimate was not altered in the Cicerone and Oremland (1988) budget. Two recent reviews re-evaluated open ocean (Lambert and Schmidt, 1993) and coastal and estuarine (Bange *et al.*, 1994) CH_4 emissions. Lambert and Schmidt (1993) concluded that the ocean emitted 3.5 Tg CH_4 yr^{-1}. Bange *et al.* (1994) summarized all ocean CH_4 measurements, including those from shelf and estuarine areas, and applied two air–sea transfer models regionally to estimate that the ocean source lies in the range 11–18 Tg CH_4 yr^{-1}. Shelf and estuarine areas contribute ~75% of this total. Bange *et al.* (1994) used a coupled three-layer model to conclude that, even with increasing tropospheric CH_4 concentrations, the ocean will maintain close to the present source strength. These estimates lie within the range of values suggested by Cicerone and Oremland (1988).

4.03.4.2 Aerobic Methane Oxidation

The ocean has received far less attention than wetlands and soils as a source and sink of CH_4. Studies of CH_4 distributions in the Eastern Tropical North Pacific showed two CH_4 maxima (Burke *et al.*, 1983): a surface maximum presumably associated with methanogensesis in fecal fellets (Karl and Tilbrook, 1994) and a deeper maximum. The mass spectrometric GC/C/IRMS technique discussed earlier allows measurement of $\delta^{13}CH_4$ in small samples of seawater (Holmes *et al.*, 2000). This technique was applied in the Eastern Tropical North Pacific (Sansone *et al.*, 2001) to study methanogenesis and methane oxidation. The Sansone *et al.* (2001) results show a distinct difference in the $\delta^{13}CH_4$ from the two CH_4 maxima, leading to the suggestion that the deeper maximum may result from long-distance offshore transport of CH_4 with a shelf or seep source similar to that shown in Cynar and Yayanos (1993, figure 3).

Most direct CH_4 oxidation rate measurements have focused on anoxic sediments and waters, so there have been very few direct oxidation rate measurements in oxic environments. The study of Valentine *et al.* (2001), which was conducted near seeps and vents in the Eel River Basin, provided insights and some credence to the notion of long-distance offshore CH_4 transport. The Valentine *et al.* (2001) study involved tracer measurements of methane oxidation rate using $^3H–CH_4$ and showed high oxidation rates adjacent to the vents (where CH_4 concentrations are high) and much lower rates in the remainder of the lower CH_4 concentration part of the water column. Figure 6 (Valentine *et al.*, 2001) relates CH_4 concentration to turnover time, which for low CH_4 concentrations, was over 40 years. This is consistent with CH_4 oxidation rates estimated by Scranton and Brewer (1978), who calculated

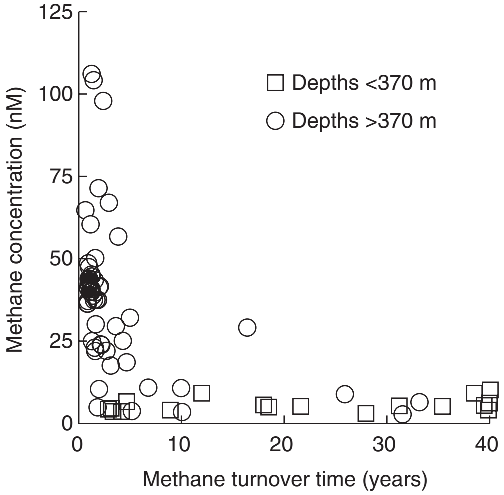

Figure 6 Plot of methane concentration versus turnover time for samples collected in the Eel River Basin seep area. Turnover time is the CH_4 concentration divided by the oxidation rate determined with C_3H_4 tracer experiments. The maximum turnover time of 40 years is the lower detection limit for these studies, but it is consistent with similar estimates by Scranton and Brewer (1978) and Rehder *et al.* (1999). Reproduced by permission of Elsevier from Valentine *et al.* (2001).

rates using methane analyses and water mass ages determined with $^3H/^3He$ and ^{14}C ages to determine "apparent methane utilization" rates. Scranton and Brewer (1978) estimated that the CH_4 consumption rate in 150-year-old water masses is 2.2×10^{-4} nM yr^{-1}. Rehder *et al.* (1999) used CFC-11 distributions and the input function of CFC-11 to deduce a timescale for oxidation of CH_4 in North Atlantic Deep Water of ~50 years. All of these studies indicate that CH_4 present at low concentrations in the ocean interior is oxidized at very low rates. These studies suggest a threshold CH_4 concentration below which CH_4 in the ocean cannot be oxidized. It is important to understand what controls this threshold: availability of suitable organisms, the CH_4 concentration, or the frequency of oxidizer–CH_4 encounters?

4.03.4.3 Anaerobic Methane Oxidation

Based on CH_4 distributions in anoxic marine sediments, anaerobic methane oxidation (AMO) was suggested by Barnes and Goldberg (1976), Reeburgh (1976), and Martens and Berner (1977). The importance of AMO as a CH_4 sink was established by measurements of concentration profiles, diagenetic modeling, oxidation rate measurements using radioactive tracers, inhibition experiments, and measurement of stable isotope budget (reviewed by Hoehler *et al.*, 1994; Valentine, 2002). Anaerobic CH_4 oxidation occurs in a zone near the point of sulfate depletion in anoxic marine sediments (the sulfate/methane transition zone) and is a near-quantitative sink for upward fluxes of CH_4. Although the process has been shown to be an effective and globally important CH_4 sink, it has been controversial because the organisms and mechanism responsible for AMO remain unknown.

Hoehler *et al.* (1994) suggested that AMO might be energetically possible through "reverse methanogenesis." According to the "reverse methanogenesis hypothesis," it is energetically possible for existing methanogens to operate in reverse to anaerobically oxidize CH_4 when the concentration of H_2 is held to concentrations ≤ 0.29 nM. The reverse methanogenesis hypothesis was particularly attractive because it was consistent with all previous field observations, it offered an energetically feasible means for anaerobic CH_4 oxidation, it involved no new organism, and it further explained the close association of the anaerobic CH_4 oxidation zone with sulfate reducers. Valentine *et al.* (2000a) devised an apparatus for testing the reverse methanogenesis hypothesis that involved exposing actively growing methanogen cultures to CH_4, controlled and low H_2 partial pressures, and monitoring the effluent of the reactor for the product H_2. Four pure cultures of methanogens were tested for their ability to mediate reverse methanogenesis, but none demonstrated sustained H_2 production, so the reverse methanogenesis hypothesis was falsified for these cultures (Valentine *et al.*, 2000b). Results from a genomics study on marine methane-oxidizing Archaea (Hallam *et al.*, 2004) showed that nearly all genes typically associated with methane production are present in one specific group of archaeal methanotrophs, offering support for the reverse methanogenesis hypothesis. The main question is whether the genes are expressed.

Studies reporting anaerobic CH_4 oxidation rate and the rate depth distribution studies in anoxic marine sediments subsequent to those of Reeburgh (1980) are summarized by Hoehler *et al.* (1994). Rates of anaerobic CH_4 oxidation have been measured directly in the anoxic water columns of the Cariaco Basin (Ward *et al.*, 1987) and the Black Sea (Reeburgh *et al.*, 1991). Two radioactive tracers were used in these studies: $^{14}C–CH_4$ for the Cariaco Basin and both $^{14}C–CH_4$ and $^3H–CH_4$ for the Black Sea. The parallel rate determinations using $^{14}C–CH_4$ and $^3H–CH_4$ in the Black Sea agreed within a remarkable factor of 2 (Reeburgh *et al.*, 1991). The $^3H–CH_4$ has higher specific activity and is most suitable for water-column measurements since it can be added in tracer quantities and does not affect the low-concentration ambient CH_4 pool size. Samples are incubated in head-space-free vessels, the added tracer is removed by stripping, and the product $^3H–H_2O$ is counted. Radiocarbon-labeled CH_4 has a lower specific activity and is most suitable for sediments, where CH_4 concentrations are higher than water columns and where overwhelming the ambient pool size is of less concern. These measurements involve injecting tracer into core segments of intact sediment and incubating. Following incubation, a sediment slurry is formed and stripped under basic conditions to remove the unreacted $^{14}C–CH_4$ tracer; the slurry is subsequently stripped under acidic conditions and the oxidation product $^{14}CO_2$ is trapped and counted.

Curiously, the most striking and extensive examples of anaerobic CH_4 oxidation, which has been controversial as a contemporary process, are provided by Deep Sea Drilling Project (DSDP) studies. The depletion of sulfate in DSDP cores (Borowski *et al.*, 1996; Dickens, 2000, 2001b) was ascribed to anaerobic CH_4 oxidation. D'Hondt *et al.* (2002) produced global maps based on DSDP cores delineating two provinces of subsurface metabolic activity: a sulfate-rich open ocean province where CH_4 is not abundant, and an ocean margin province where sulfate is restricted to shallow depth intervals because of higher sulfate reducing activity, and where CH_4 is more abundant. AMO was invoked to explain the observed sulfate and methane distributions and differences in the two provinces. The D'Hondt *et al.*(2002) study provides a global map of the sulfate/methane transition zone.

Anaerobic CH_4 oxidation, now referred to as anaerobic oxidation of methane (AOM), has received renewed attention with introduction of new organic geochemical and molecular techniques. Hinrichs *et al.* (1999) applied compound-specific isotope analyses of lipid biomarker molecules associated with specific archaea and culture-independent techniques involving 16S rRNA identification studies to samples collected from an Eel River Basin seep. This work showed that the biomarker compounds were strongly depleted in ^{13}C, suggesting that CH_4 must be the source rather than the metabolic product for the organisms that produced them. Boetius *et al.* (2000) used culture-independent identification techniques (fluorescent *in situ* hybridization (FISH)) to visualize dense aggregates of ~100 archaeal cells surrounded by sulfate reducers. Orphan *et al.* (2001) combined the FISH technique with secondary ion mass spectrometry (SIMS) to measure the stable carbon isotope composition of individual cell aggregates. This work supported the hypothesis that CH_4 was the source of cell carbon. These studies have identified two phylogenetically different communities the ANME-I and the ANME-II, capable of mediating anaerobic oxidation of methane consisting of archaea of the *Methanosarcinales* closely associated with sulfate-reducing bacteria of the *Desulfosarcina/Desulfococcus* group.

The reviews by Hinrichs and Boetius (2002), Valentine and Reeburgh (2000), and Valentine (2002) pointed out the uncertainties regarding the nature of the syntrophic association, the biochemical pathway for oxidation of CH_4, as well as the interaction of the process with the local chemical and physical environment. Based on observations of higher oxidation rates and larger spatial extent, Hinrichs and Boetius (2002) increased the Reeburgh *et al.* (1993) estimate of the extent of anaerobic CH_4 oxidation from 70 to 300 Tg CH_4 yr^{-1}. Valentine (2002) pointed out that anaerobic CH_4 oxidation could involve different organisms depending on the supply rate of CH_4 and that seeps and vents may differ from diffusive environments. Michaelis *et al.* (2002) described massive microbial mats covering up to 4 m high carbonate buildups at methane seeps in the anoxic waters of the Black Sea shelf. Incubation of the mat material showed anaerobic oxidation of methane coupled to sulfate reduction. Hinrichs and Boetius (2002) indicated that AOM may have influenced the carbon isotope record of the Archean and is thus an important link in the biological cycling of carbon in an anoxic biosphere. Michaelis *et al.* (2002) suggested that these reefs may represent the appearance of large parts of the ancient anoxic ocean. Nauhaus *et al.* (2002) demonstrated coupling of methane oxidation and sulfate reduction *in vitro*. Nauhaus *et al.* (2005) demonstrated environmental regulation of ANME-I and ANME-II communities and Girguis *et al* (2005) used a continuous-flow bioreactor to study responses of ANME-I and ANME-II archaeal communities at different pore water flow rates. Anaerobic oxidation has been shown to be a widespread major sink for methane. Although several hurdles remain, we appear to be close to an answer to the question posed over 25 years ago: How does anaerobic CH_4 oxidation occur?

4.03.4.4 Methane Clathrate Hydrates

Methane clathrate hydrates are nonstoichiometric solid structures composed of cages of water molecules surrounding methane molecules. Estimates of the size of the methane reservoir sequestered as hydrates are enormous. Because these CH_4 hydrates are frequently close to the sediment–water interface and because they represent such a large reservoir, hydrate stability has been a major concern. There is extensive evidence of slides and craters on ocean shelves, presumably caused by destabilization and release of gas-phase CH_4 (Hovland and Judd, 1988), but we have little information on the magnitudes of CH_4 release needed to form these features. The global methane budget of Cicerone and Oremland (1988) emphasized how little is known about the role of methane hydrates in the global budget by entering methane hydrates in their budget as a 5 Tg yr^{-1} "placeholder" term.

The physical and thermodynamic properties and stability fields of clathrates, including methane, are presented in Sloan's (1998) text. Methane hydrates have a latent heat of fusion quite similar to that of water (Sloan, 1998), so decomposition of hydrates is a matter of heat flux, not a rise in temperature. Hydrate stability is not a matter of P–T conditions alone, as CH_4 concentrations substantially higher than saturation values are required for hydrate formation and stability (Sloan, 1998). Laboratory data on CH_4 clathrate stability fields in seawater were presented by Dickens and Quinby-Hunt (1994, 1997).

4.03.4.4.1 Methane hydrate reservoir

Reviews by Kvenvolden (1988, 1993) and Kvenvolden and Lorenson (2001) have updated information on the occurrence, stable isotope composition, estimates of total amount, and stability of CH_4 clathrate hydrates. Articles in Paull and Dillon (2001) summarize recent work on CH_4 hydrates, emphasizing geochemical studies in the Gulf of Mexico and at Hydrate Ridge, Cascadia Margin, and geophysical studies at Blake Ridge and the Peru/Middle American trenches. Gornitz and Fung (1994) calculated the potential size of the ocean CH_4 hydrate reservoir using two models for CH_4 hydrate formation: *in situ* bacterial production and a fluid expulsion model. Their models resulted in methane hydrate reservoirs of 14 and 75 Tt (1 Tt = 10^{18} g), respectively, with the most likely value near the lower end of this range. A consensus value of 10 Tt for the amount of CH_4 hydrate was suggested by Kvenvolden and Lorenson (2001). Again, this is an enormous number, 2,000-fold larger than the atmospheric CH_4 inventory and ~30% of the ocean dissolved inorganic carbon reservoir. A recent modeling study (Buffett and Archer, 2004) provides insights into the effect of changes in temperature, deep ocean oxygen content, carbon rain rate, and pressure on the global clathrate reservoir.

4.03.4.4.2 Methane hydrate decomposition rates

Dickens (2003) highlighted the common misconception that present-day CH_4 hydrate systems are stable. Hydrates may be in steady state, but they cannot be stable because of differences in the chemical potential of CH_4 in the hydrate phase and the adjacent dissolved interstitial methane. Thus, CH_4 hydrates must be viewed as dynamic, with large and unknown fluxes to and from the ocean. An understanding of the rate of contemporary hydrate-derived CH_4 additions to the ocean is essential to evaluating the role of hydrates in the global CH_4 budget, but, as of the early 2000s, no measurements permitting this estimate have been made. There are several good reasons for this state of affairs. First, we have no means of discriminating between hydrate CH_4 and diagenetically produced CH_4. Second, CH_4 released by dissociating hydrates is effectively oxidized by microbially mediated processes in anoxic sediments (Reeburgh, 1980; Alperin and Reeburgh, 1984), as well as in the adjacent oxic water column (Valentine *et al.*, 2001), so elevated CH_4 concentrations or "hot spots" are rarely observed. Third, we have been technology poor in this area; hydrates collected by coring or dredging decompose rapidly, and laboratory studies are difficult if not impossible to conduct at sea.

4.03.4.4.3 How can we estimate the rate of CH_4 clathrate decomposition?

Methane clathrate decomposition has been implicated in the Latest Paleocene Thermal Maximum (~55 Ma) by an extraordinary injection of isotopically light carbon into the carbon cycle (Dickens, 2000, 2001a) and in Quaternary interstadials as indicated by observations of isotopically light foraminifera in Santa Barbara Basin sediments (Kennett *et al.*, 2000). Dickens (2001a) compares the functioning of the CH_4 hydrate to a bacterially mediated capacitor.

Research on CH_4 clathrates has been advanced by using remotely operated vehicles (ROVs), which can be equipped not only to synthesize hydrates *in situ* under appropriate P–T conditions (Brewer *et al.*, 1997, 1998), but to locate seeps for sampling and to place acoustic beacons for longer-term stability experiments as well. Rehder *et al.* (2004) made direct measurements of the decomposition rates of pure CH_4 and CO_2 hydrates in a seafloor setting nominally within the gas hydrate P–T stability zone. Their rates represent end members because of the flow field and undersaturation. The water-column CH_4 oxidation rate measurements of Valentine *et al.* (2001) were conducted adjacent to seeps in the Eel River Basin that were previously located with an ROV. These oxidation rate measurements were conducted with tracer additions of ^3H–CH_4, and showed the highest rates near the bottom. These instantaneous rate measurements are difficult to interpret in a dynamic advecting coastal environment, but the fractional turnover rates can be used to infer a CH_4 turnover time of ~1.5 years in the deep waters. The depth-integrated rates (5.2 mmol CH_4 $m^{-2}\,yr^{-1}$) can be used to estimate total oxidation for the 25 km^2 vent field. The amount of CH_4 emitted is unknown, so it is not possible to estimate the oxidized fraction, but results from a closed system oxidation model applied to $\delta^{13}CH_4$ measurements suggested that ~45% of the added CH_4 was oxidized. Grant and Whiticar (2002) concluded from observations of isotopically heavy $\delta^{13}CH_4$ at Hydrate Ridge that substantial aerobic methane oxidation occurred there. These isotopic enrichment measurements indicate cumulative CH_4 oxidation, but provide no rate information. Clearly, many more direct methane oxidation rate measurements similar to those of Valentine *et al.* (2001) are needed.

Recent work indicates that it may be possible to discriminate between hydrate methane and diagenetic methane with measurements of $^{14}CH_4$. If hydrates are formed by fluid expulsion, they will probably involve CH_4 from deep sources and will probably contain no radiocarbon; if they are formed by *in situ* bacterial production, the radiocarbon age will depend on the age of the substrate carbon. There have been a few unpublished measurements of the radiocarbon content of hydrate methane (M. Kastner, personal communication). Winckler *et al.* (2002) reported radiocarbon measurements on CH_4 from massive methane hydrates collected at Hydrate Ridge, Cascadia margin, and showed that they, as well as the unpublished results, are devoid of radiocarbon, indicating that there are no recent (^{14}C-active) contributions to the hydrate reservoir. Measurements of noble gases in hydrates (Winckler *et al.*, 2002) showed that light noble gases are not incorporated into the hydrate structure, but that significant quantities of the heavier noble gases—argon, krypton, and xenon—are present. The heavy noble gases are potential secondary tracers of hydrate decomposition.

4.03.4.4.4 Natural ^{14}C–CH_4 measurements

Measurements of natural ^{14}C–CH_4 were undertaken to test the possibility of discriminating between hydrate methane and diagenetic methane sources in large anoxic basins. These measurements required careful determination of blank and background levels (Kessler and Reeburgh, 2005) as Winckler *et al.* (2002) showed that hydrates contained no ^{14}C–CH_4. The measurements were performed using accelerator mass spectrometry (AMS), which measures ^{14}C atoms individually rather than observing decay events. AMS has high sensitivity and accuracy (0.3% of modern). The Black Sea was chosen because a sink-based methane budget existed (Reeburgh *et al.*, 1991), there were reports of extensive vents (Michaelis *et al.*, 2002), and ^{14}C–CH_4 distributions offered a means of partitioning the methane budget and quantifying the vent source. Temperatures in the Cariaco Basin are too high for hydrates to exist, so it was studied as a hydrate-free control environment.

These measurements of natural ^{14}C–CH_4 distributions in the Cariaco Basin (Kessler *et al.*, 2005) and the Black Sea (Kessler *et al.*, 2006a) have dramatically altered our understanding of methane geochemistry in both environments by highlighting the importance of seeps. Previous work considered the water-column methane source to be diagenetically formed CH_4 from sediments. The ^{14}C–CH_4 results from both basins indicate that the CH_4 has a fossil source and that anaerobic oxidation of CH_4 is the major sink. We reco gnize now that seep and hydrate methane cannot be distinguished with measurements of ^{14}C–CH_4.

Figure 7 shows ^{14}C–CH_4 distributions in the Cariaco Basin water column and sediments. (expressed as percent modern carbon, pMC). The input distribution was estimated using a time-dependent box model (Scranton, 1988) that considered mixing and previous measurements of methane oxidation rate (Ward *et al.*, 1987). The modeled ^{14}C–CH_4 input function agrees within 1% of the observations. These results show clearly that water column and sediment methane distributions are controlled by different processes. Seeps containing fossil methane control the water-column methane, while the sediment CH_4 results from diagenesis of sedimented modern particulate matter. The CH_4 concentration of the Cariaco Basin has been increasing for the past 25 years. The two input maxima coincide with the locations of major faults and the beginning of the increase appears to be coincided with a major earthquake.

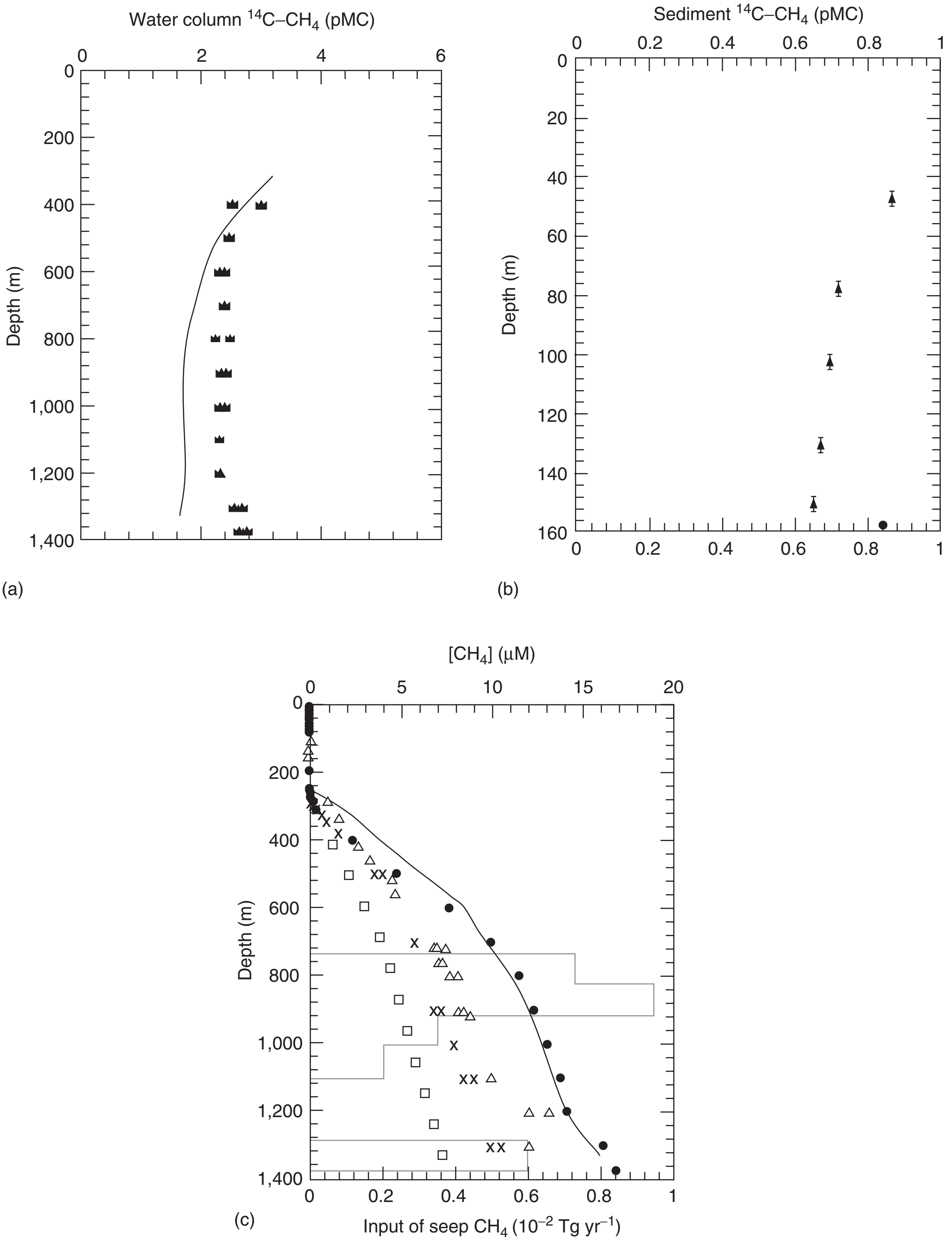

Figure 7 Natural $^{14}C–CH_4$ distributions in Cariaco Basin waters and sediments. (a) Natural $^{14}C–CH_4$ distributions in Cariaco Basin waters expressed in percent modern carbon, pMC. The line is the $^{14}C–CH_4$ distribution based on the seep input model. (b) Natural $^{14}C–CH_4$ distributions in Cariaco Basin sediments. Note that the depth and pMC scales differ from (a). (c) Methane distributions and modeled seep input function. The open squares are 1974 observations, the solid circles are 2004 observations. The gray line shows the model-predicted inputs of CH_4 to the water column not considering the effects of intrusions of oxygenated water. The black line shows the model-predicted CH_4 profile based on the inputs from seeps. Reproduced by permission of American Geophysical Union from Kessler *et al.* (2005a). Copyright 2005.

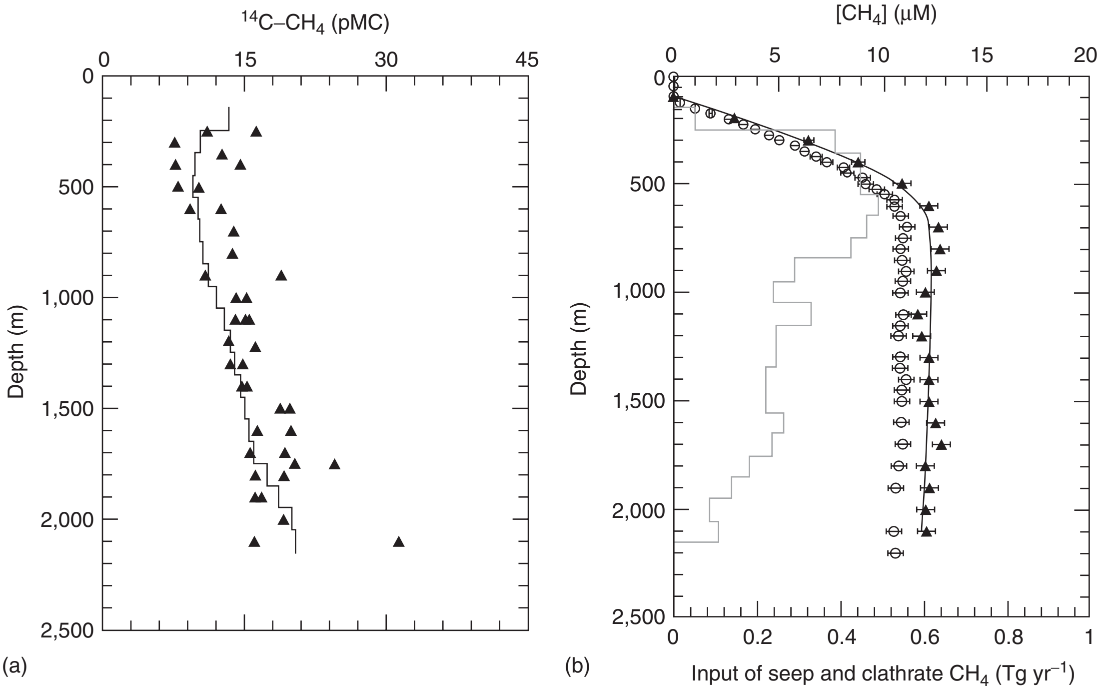

Figure 8 Natural $^{14}C–CH_4$ and CH_4 distributions in Black Sea waters. (a) Natural $^{14}C–CH_4$ expressed as percent modern carbon, pMC. The triangles are 2002 observations. The line shows model-predicted $^{14}C–CH_4$ using the seep input function shown in (b). (b) Methane distributions and modeled seep input function. The filled triangles are 1988 observations; the open circles are 2001 observations. The gray line is the model-predicted input of CH_4 to the water column. The black line shows the model-predicted CH_4 profile based on the input from seeps. Reproduced by permission of Elsevier from Kessler *et al.* (2006a).

The Black Sea water-column distribution of $^{14}C–CH_4$ is shown in Figure 8. The input distribution was estimated using a time-dependent box model similar to that used for the Cariaco Basin with the CH_4 oxidation rate measurements of Reeburgh *et al.* (1991).

Stable isotope measurements ($\delta^2H–CH_4$ and $\delta^{13}C–CH_4$) were performed on subsamples of the samples used for the $^{14}C–CH_4$ measurements (Kessler *et al.*, 2006b). There are differences between the Black Sea and Cariaco Basin CH_4 depth distributions profiles as well as the stable isotope distributions (9‰ in $\delta^{13}C–CH_4$). The stable isotope distributions and between-basin CH_4 differences were successfully interpreted with a model that considered the depth distribution of seep inputs and isotope fractionation due to anaerobic oxidation of methane under open-system steady-state and open-system nonsteady-state conditions. The open-system isotope fractionation relationships are reported in appendix B of Kessler (2005).

4.03.4.5 Other Ocean Methane Sources

Rock–water interactions are also responsible for additions of methane. Methane-rich plumes (22 nM anomalies) have been observed along segments of the Mid-Atlantic Ridge (Charlou *et al.*, 1998). These plumes are believed to result from serpentinization resulting from reaction of water with uplifted ultramafic mantle (peridotite) rocks. The serpentinization reaction produces H_2, which in turn can react with CO_2 at temperatures of 300 °C and pressures of 500 bar to abiogenically form methane and higher hydrocarbons. Kelley *et al.* (2002) have reviewed fluid composition and life at mid-ocean ridge spreading centers.

A recent discovery in the area of hydrothermal vents is the Lost City Vent Field (Kelley *et al.*, 2001). Located about 15 km off the Mid-Atlantic Ridge axis, this vent field has fluids that are relatively cool (40–75 °C), alkaline (pH 9.0–9.8), and spectacular carbonate chimneys that are as tall as 60 m. The fluids contain methane at millimolar concentrations. There is little information on fluid flow, so it is difficult to estimate the methane contribution of these systems to the deep ocean. This area was revisited (Kelley *et al.*, 2005) for closer study of the microbial and macrofaunal communities. Boetius (2005) provides perspective on the system. The chimneys are populated with anaerobic methane-oxidizing communities. Methane oxidation is so effective in the ocean that these hydrothermal vent systems are likely to have only local effects.

Cold vent systems occur in geologically active and passive margins, where fluids enriched in methane are forced upward by pressure gradients (see review by Levin, 2005). Methanotrophic and thiotrophic communities become established at these vents, and reflect fluid-flow conditions. For example, *Beggiatoa* mats are found at higher methane fluxes than *Calyptogena* beds (Orphan *et al.*, 2001). Since anaerobic oxidation of methane results in an increase in alkalinity, isotopically light carbonates are associated with these vents (Michaelis *et al.*, 2002; Jørgensen, 1989).

4.03.5 ICE CORES

Measurements of CH_4 trapped in polar ice cores from Greenland and Antarctica have been reviewed by Raynaud (1993), Raynaud and Chappellaz (1993), Chappellaz *et al.* (2000), and Cuffey and Brook (2000). These studies provide records of atmospheric composition extending to over 4×10^5 years ago, covering important climate periods such as the glacial–interglacial cycles, the Holocene, and the Younger Dryas. The Greenland and Antarctic ice cores agree over 1.1×10^5 years (Blunier and Brook, 2001; Brook *et al.*, 1996), indicating that the cores are recording global-scale phenomena. The length of the ice core gas record, including CH_4, was recently extended to 650,000 years (Siegenthaler *et al.*, 2005; Spahni *et al.*, 2005). Brook (2005) provides useful perspective on the present and past gas observations.

The resolution of these records depends on the snow-accumulation rate. Since the snow-accumulation rate is higher in Greenland than in central Antarctica, the Antarctic cores cover longer time intervals with lower resolution. Previously deposited snow is compacted and sintered under the weight of newly accumulated snow. At the bottom of the porous firn layer, ice forms, and the air is trapped as bubbles. The bubbles disappear with deeper burial. The gases in the firn layer can exchange with the atmosphere until bubble close off, so the age of the trapped gas is younger than the adjacent ice. The air trapping process in ice sheets, which ranges from 30 years at high ($>100\,\mathrm{cm\,yr^{-1}}$) accumulation rates to 2,000 years at low ($<2\,\mathrm{cm\,yr^{-1}}$) accumulation rates, can be modeled (Schwander *et al.*, 1997) to estimate the difference between the ice age and the gas age. The close-off process is a progressive phenomenon, resulting in a distribution of gas ages (see Brook *et al.*, 2000, figure 4). This difference between the ice age and the gas age limits our ability to resolve short-term catastrophic events, such as large clathrate-derived CH_4 releases, as the gas-trapping process best records sustained global-scale changes. For example, CH_4 records in ice core for preanthropogenic times have been interpreted as records of changes in wetland CH_4 emissions.

Abrupt changes in temperature result in thermal fractionation of gases in the firn layer, which are recorded as anomalies in the stable isotopes of N_2 and Ar (Severinghaus *et al.*, 1998). This approach circumvents the problem of differences between the ice age and the gas age by comparing gases with gases in the same sample. This approach was used to show that the CH_4 increase lagged the temperature increase at the end of the Younger Dryas by 0–30 years.

A scenario involving instantaneous release of 4,000 Tg of CH_4 was presented by Thorpe *et al.* (1996). Brook *et al.* (2000) analyzed the ice core response to such an event and concluded that the high-resolution ice core record is inconsistent with the large and rapid release of methane. Shifts in $\delta^{13}C$ in foraminifera preserved in marine sediments suggest large releases of CH_4 that could be important in initiating climate change (Kennett *et al.*, 2000, 2003). There is no question that decomposing methane hydrates contributed to increasing atmospheric methane, but the lag between warming and methane increases (Severinghaus *et al.*, 1998) is difficult to reconcile with the "Clathrate Gun Hypothesis." Recent measurements of δ^2H–CH_4 in Greenland ice cores (Sowers, 2006) covering the late Quaternary show that δ^2H–CH_4 values were stable or constant as well as isotopically lighter than expected for a clathrate methane source. These results suggest that marine clathrates were stable during abrupt warming episodes. Relating events recorded in marine sediments with those in ice cores promises to be an area of continuing debate.

4.03.6 FUTURE WORK

Using the Cicerone and Oremland (1988) review as modern benchmark, this chapter has attempted to summarize our current knowledge of the global methane budget, our understanding of physical and microbiological controls on CH_4 sources and sinks, and how well models are representing these processes. In spite of the remarkable accomplishments since the mid-1980s, we have not been able to ascribe atmospheric CH_4 increases and decreases to specific processes. As of early 2000s, we have no predictive capability.

Atmospheric time-series measurements of both CH_4 concentration and isotopes should continue as a high priority. Efforts should be made to replicate and understand recent measurements suggesting a large abiogenic atmospheric CH_4 source. As increased CH_4 isotope analysis capacity becomes available, we should attempt to produce (with extensive intercalibration) a global CH_4 isotope ($\delta^{13}CH_4$ and δD–CH_4) time series parallel to the concentration measurements of NOAA/GMCC network.

Wetland and tundra flux time series should also continue and possibly be expanded at carefully selected high-latitude wetland sites, preferably sites in the Hudson's Bay Lowlands and Siberian Lowlands. Sites in areas of discontinuous permafrost as well as other areas susceptible to permafrost melting should be part of the network. Static chamber flux measurements are legendary as labor intensive, and they should be replaced where possible with automated chambers and supplemented with continuous eddy flux measurements (Hargreaves *et al.*, 2001). Development of a field-portable, rapid-response CH_4 sensor suitable for continuous eddy covariance measurements should be a high priority.

More direct measurements of methane oxidation rates, particularly in wetlands and ocean waters, are needed. The use of stable isotope estimates of methane oxidation, which give an indication of total oxidation, should continue, but direct rate measurements using both ^{14}C–CH_4 and ^{3}H–CH_4 should be a priority. Pulse-labeling experiments conducted through a growing season are needed to resolve the effect of plant phenology on methane emission. The methane oxidation threshold suggested by a number of open ocean rate measurements should be studied in open ocean samples from areas near and well removed from shelf vent sources.

The role of decomposing methane clathrates in the global methane budget remains a major unsolved problem. Additional seafloor measurements of hydrate decomposition under realistic flowfield and saturation conditions are needed. Models predicting the natural CH_4 hydrate decomposition rate as well as the CH_4 hydrate response to temperature increases are needed so that we can constrain the contributions of CH_4 resulting from hydrate decomposition.

The recent accelerator mass spectrometer-based measurements of natural ^{14}C–CH_4 cannot discriminate between hydrate- and seep-derived CH_4, but have been of great value in identifying and quantifying fossil seeps. These measurements of ^{14}C–CH_4 should be extended from micromolar CH_4 concentrations observed in anoxic basins to the nanomolar levels encountered in the open and coastal ocean. Even with the high sensitivity of AMS, obtaining enough CH_4 for an AMS analysis of ^{14}C–CH_4 will require extracting CH_4 from 1,000 to 2,000 L samples. Insuring low backgrounds and blanks will be a challenge. Observations of extensive benthic methane-consuming communities suggest that fossil methane seeps are much larger than previously believed. Measurements of ^{14}C–CH_4 in coastal and open ocean waters column will provide some idea of the importance of seeps containing fossil methane to the open ocean methane budget.

It is also possible to adapt AMS to measurements of methane oxidation rates in oxic and anoxic systems. This can be accomplished using highly diluted ^{14}C–CH_4 tracer and measuring the increase in ^{14}C–CO_2 following incubation. Calculations suggest that it is possible to dilute the ^{14}C–CH_4 tracer to levels that do not require handling as radioisotopes. Use of such low levels of ^{14}C–CH_4 in future measurements promises to simplify shipping and regulation, permitting many more determinations of methane oxidation rates in unstudied environments.

The rapidly developing area of environmental genomics and culture-independent identification of methanogens and methanotrophs provides a badly needed basis for understanding the microbial ecology of CH_4 production as well as consumption processes. This area promises to continue identifying Archaea capable of anaerobically oxidizing CH_4 under a range of CH_4 supply rates. Identifying the elusive mechanism and responsible organisms remains a major problem.

The overall result of the measurements and studies suggested above should be an improved understanding of controlling processes and alistic models that represent complex systems and allow predictions of future conditions.

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