THE GLOBAL METHANE CYCLE

Martin Wahlen

Scripps Institution of Oceanography, University of California San Diego, La Jolla, California 92093

INTRODUCTION

Methane (CH_4) is the most abundant organic species in the Earth's atmosphere. It is a greenhouse gas, as are water vapor (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), ozone (O_3), and the chlorofluorocarbon compounds. It absorbs long wave radiation emitted from the Earth's surface in the $4-100$ μm atmospheric window and therefore affects atmospheric temperature directly (Lacis et al 1981, Ramanathan 1988, Hansen et al 1988). It is chemically reactive, and influences the abundance of ozone in the troposphere and in the stratosphere (Johnston 1984), and it is a major source of stratospheric water (Ehhalt 1979, Pollock et al 1980). Methane thus affects temperature indirectly through its chemical interactions.

Systematic measurements of the global tropospheric CH_4 mixing ratios since 1978 reveal a steady increase with time by about 1% per year, due to anthropogenic activities (Blake & Rowland 1988, Steele et al 1987). The history of CH_4 atmospheric mixing ratios has been reconstructed from measurements of air occluded in ice cores for glacial and interglacial times, as well as during the more recent 200 years through the industrial era (Chappellaz et al 1990; Pearman et al 1986; Etheridge et al 1988; Stauffer et al 1985; Craig & Chou 1982; Rasmussen & Khalil 1981a, 1981c; Robbins et al 1973). Large natural and anthropogenically influenced variations are observed over different time scales.

In the troposphere CH_4 is oxidized to CO and ultimately to CO_2 and H_2O. This oxidation reaction sequence is initiated by the hyroxyl (OH) radical. This constitutes the major sink for CH_4. The atmospheric lifetime for methane is $8-12$ yr. Methane emitted from inundated anoxic environ-

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ments can be substantially reduced by bacterial methane oxidation in oxic layers above. A small sink can be attributed to bacterial oxidation on relatively dry soils (Born et al 1990), which relies on consumption of atmospheric methane. Some methane is exported to the stratosphere. In the lower stratosphere the same oxidation reaction as in the troposphere occurs, initiated by OH; at higher altitudes reactions with excited oxygen atoms [O(^{1}D)] and with chlorine atoms lead to mixing ratio profiles that decrease with altitude.

Methane is produced by bacteria under anaerobic conditions in wet environments such as wetlands, swamps, bogs, fens, tundra, rice fields, and landfills. It is also produced in the stomachs of ruminants (cattle and other cud-chewing mammals), and possibly by termites. Most of this biogenic methane is generated by two major bacterial pathways, namely by fermentation of acetate and by reduction of CO_2 with H_2 (Whiticar et al 1986, Wolin & Miller 1987, Cicerone & Oremland 1988). Other sources of CH_4 are from leakage of natural gas upon drilling and distribution, and from coal mining. A further source is from biomass burning where CH_4 is a product of incomplete combustion (Crutzen et al 1979). The annual production rates and the magnitude of the different sources and sinks are still somewhat uncertain.

ATMOSPHERIC DISTRIBUTION OF METHANE

The Recent Atmospheric Record

The presence of methane in the Earth's atmosphere was discovered by Migeotte (1948), from infrared absorption features in the solar spectrum. Hutchinson (1954), Koyama (1964), Fink et al (1965), Lamontagne et al (1974), Ehhalt (1974), Ehhalt & Schmidt (1978), and Ehhalt (1979) gave the first accounts on atmospheric methane and attempted to delineate, in principle, its sources and sinks.

Systematic worldwide time series measurements of the tropospheric CH_4 mixing ratio from different latitudes started in 1978. These early measurements established that the global average CH_4 mixing ratio has been increasing approximately linearly by about 1% per year over the past decade and a half (Rasmussen & Khalil 1981b, 1981c, 1984; Steele et al 1987; Blake & Rowland 1988). Figure 1 (from Blake & Rowland 1988) illustrates this trend. Today's average global mixing ratio is about 1750 ppb, corresponding to a global atmospheric inventory of about 4900 Tg of CH_4. This increase is attributed to the anthropogenically-affected methane sources (see separate section) such as those from rice production, ruminants, and biomass burning. In part, such an increase may be due to the decreasing oxidative capacity of the atmosphere, i.e. if the abundances
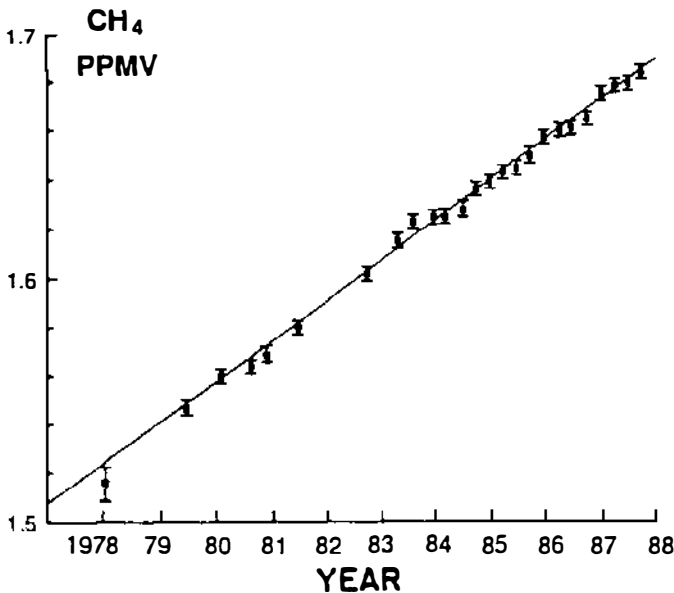
Figure 1   Average worldwide increase of the atmospheric methane mixing ratio after Blake & Rowland (1988). (Reproduced with the permission of *Science*, American Association for the Advancement of Science.)

of CO, CH_4, and nonmethane hydrocarbons increase with time, then the amount of atmospheric OH decreases as it is consumed in oxidation reactions with these trace gases (Thompson 1992; see also Methane Sinks). Other data (Steele et al 1992) indicate a substantial slowing of the global accumulation rate since 1983. The reason for this is not clear.

These studies also show that there is a marked interhemispheric gradient in the tropospheric mixing ratio of methane, with the ratio in the northern hemisphere being about 80–100 ppb or 5% higher than in the southern hemisphere on average. This reflects the larger sources of methane in the northern hemisphere (approximately a factor of three over the southern hemisphere) which, given the 8–12 year atmospheric methane lifetime and an interhemispheric atmospheric air exchange coefficient of $1/1–1/1.3 \, \text{yr}^{-1}$, results in the observed interhemispheric gradient of the atmospheric mixing ratios of methane.

Time series measurements in remote locations at different latitudes also reveal a seasonal cycle in the atmospheric methane mixing ratios (Rasmussen & Khalil 1981b, Khalil & Rasmussen 1983, Steele et al 1987,

Quay et al 1991, Fung et al 1991, Steele et al 1992). The amplitudes of the seasonal CH_4 mixing ratios are strongest in the northern high latitudes (30–40 ppb) and diminish toward the equator. In the southern hemisphere they are smaller (10–20 ppb) and quite constant with latitude. The findings are illustrated in Figure 2 (from Fung et al 1991) which contains the data of Steele et al (1987) and additional data from the NOAA/CMDL network for the years 1984–1987. Atmospheric mixing ratios are lowest during local summer and fall in both hemispheres, and higher during the remainder of the year. This is interpreted to be caused by methane oxidation by OH radicals which are more abundant in summer. Other factors may play a role: Vertical atmospheric mixing is stronger in summer than in winter, as evidenced by seasonal variations in measurements of the chemically inert ^{85}Kr (M. Wahlen et al, unpublished data; P. Povinec, personal communication).

In the stratosphere the chemical destruction of methane by OH, $O(^1D)$, and Cl becomes evident in profiles of decreasing mixing ratios with altitude, as vertical mixing is highly reduced. At about 25 km altitude the CH_4 mixing ratios are reduced by about a factor of two over tropospheric values (Ehhalt & Heidt 1973, Ehhalt & Thonnissen 1980).
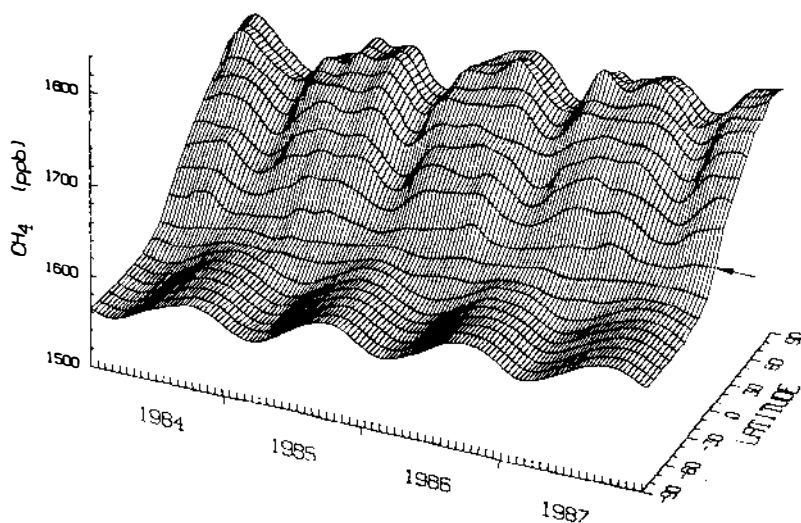

Figure 2 Temporal and latitudinal variation of the tropospheric methane mixing ratio (from Fung et al 1991). (Reproduced with the permission of the American Geophysical Union.)

Reanalyses of solar absorption spectra taken in 1951 at Jungfraujoch (Switzerland) and at Kitt Peak in 1981 bridge the records between ice-core observations and direct atmospheric observations (Rinsland et al 1985). The results were 1.14 ppm (April 1951) and 1.58 ppm (February 1981), respectively.

The Longer Term Record

The atmospheric methane mixing ratios over various periods in the past, up to 160,000 years ago, have been reconstructed from the analyses of air trapped in bubbles of deep ice cores, using wet extraction techniques and flame ionization gas chromatography. These studies reveal substantial variations of the atmospheric mixing ratios through time.

Ice core work compellingly demonstrates that the atmospheric CH_4 mixing ratio has more than doubled from preindustrial times to today (Craig & Chou 1982, Rasmussen & Khalil 1984, Stauffer et al 1985, Pearman et al 1986, Etheridge et al 1988, Pearman & Fraser 1988). This is attributed to anthropogenically influenced sources such as methane from rice production, animals, and from biomass burning. Figure 3 illustrates the increase of atmospheric CH_4 mixing ratios from about 750 ppb to today's value over the last two centuries (Houghton et al 1990).
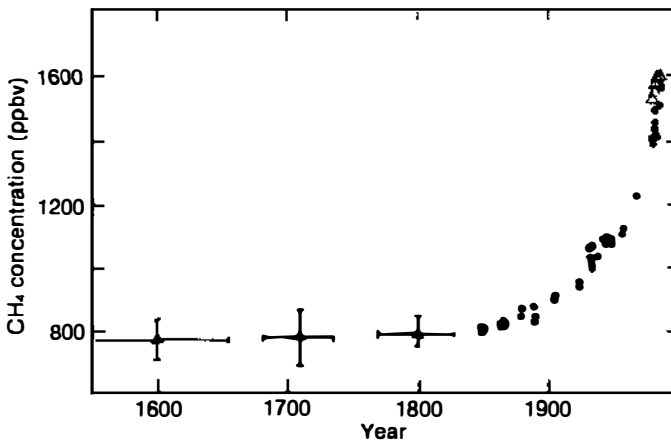
Figure 3   Atmospheric methane mixing ratios for the last several hundred years as deduced from measurements in air occluded in ice cores, and direct atmospheric observations over the last two decades (from Houghton et al 1990). (Reproduced with permission of the University Press, Cambridge.)

Longer term records are from Antarctica and Greenland ice cores (Raynaud et al 1988, Stauffer et al 1988, Barnola et al 1987, Chappellaz et al 1990). They reveal that the atmospheric CH_4 mixing ratios varied by a factor of two between the last glacial maximum (about 350 ppb) and the Holocene (about 650 ppb). The same variations are observed for the penultimate glacial and the previous warm period. There are large oscillations in the methane mixing ratio during the period of the last glacial maximum. These oscillations, ranging from glacial low values to almost Holocene high values, seem to positively correlate with temperature variations, as displayed in Figure 4. Temperature variations are derived from measurements of D/H in the ice, and a change between glacial and interglacial times of 6–8°C is indicated for Antarctica. Thus there seems to be a fundamental link between temperature and atmospheric CH_4, which seems to react to temperature change quickly. This is most likely related to changes in the global methane source strength, and/or to changes in the atmospheric OH mixing ratios. Preindustrial and Holocene methane levels can be reasonably explained by stripping anthropogenically influenced sources, according to population growth. To maintain glacial time CH_4 mixing ratios when the high to mid-northern latitudes were covered with ice would, however, require increased fluxes (over today's) from natural wetlands at low latitudes, which could be accomplished by increased precipitation. This pattern is somewhat supplemented by the observation that precipitation rates were higher at low latitudes in glacial times than in interglacial times—opposite to what is observed in polar regions. Evidence comes from observations in low latitude ice cores (L. Thompson, personal communication) where concentrations of sulphates and nitrates and the abundance of particulates were found to be lower during glacial times. Methane hydrate destabilization upon the decay of the glacial sheets is another possible explanation for increased atmospheric CH_4 during warm times (Kvenvolden 1988), but experimental evidence is lacking.

Spectral analyses of the Vostok CH_4 and temperature records reveal the presence of all major Milankovitch periodicities, namely approximately 100, 41, 23, and 19 kyr. These findings illustrate the important role of methane in the past, present, and future greenhouse effect. Presently, climate forcing by methane is considered to be about 30% of that by CO_2 (Raynaud et al 1988, Chapellaz et al 1990, Lorius et al 1990).

METHANE SINKS

Atmospheric Chemistry

Methane is predominantly destroyed in the troposphere by oxidation reactions initiated by the OH radical:
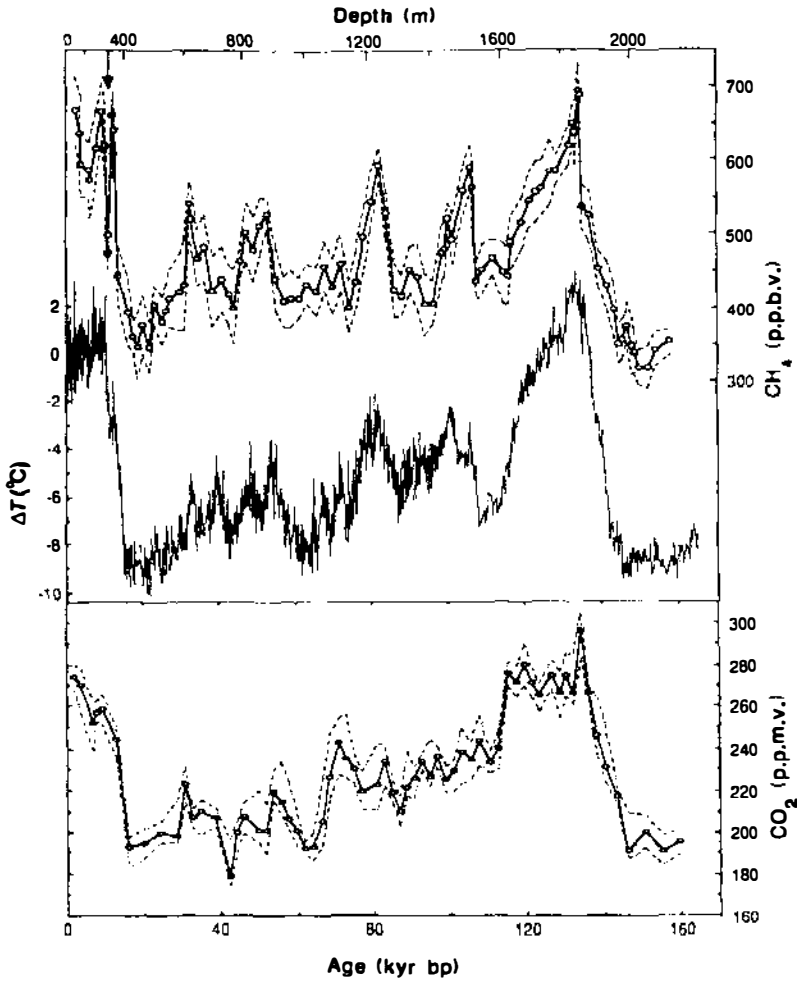
Figure 4 The long term (160,00 years BP) atmospheric CH_4 record as deduced from measurements of the mixing ratio in the air occluded in ice from the Vostok ice core (*top*); CO_2
measurements of D/H in the ice of the core (from Chappellaz et al 1990). (Reproduced with permission from *Science*, American Association for the Advancement of Science.)

$$CH_4 + OH \Rightarrow CH_3 + H_2O.$$

The reaction sequence eventually leads to formaldehyde, then CO, and ultimately to CO_2 and H_2O, consuming additional OH radicals (Ravishankara 1988). The methane chemistry is closely linked with that of CO, as methane oxidation produces as much as 30% of the atmospheric CO. Moreover, atmospheric NO_x abundances influence the CH_4 oxidation chemistry, and the methane oxidation chain can either produce or consume ozone (Thompson & Cicerone 1986). In the presence of adequate NO_x, methane oxidation produces O_3. When NO_x is low, methane oxidation consumes O_3. The oxidation of methane, CO, and nonmethane hydrocarbons in principle controls the tropospheric levels of OH. Thus increasing sources of methane (and possibly CO and nonmethane hydrocarbons) could deplete atmospheric OH, and by feedback, contribute to their atmospheric mixing ratio increase. There is no plausible way to experimentally distinguish between increasing CH_4 sources and decreasing OH, unless the global distribution of OH abundances can be more precisely determined and monitored. Recently two new techniques have been compared to measure the number density of OH in the lower troposphere (Mount & Eisele 1992) with sensitivities accurate enough to test photochemical model predictions. These initial measurements indicate OH number densities below those predicted by photochemical models.

One approach to constructing global OH fields by photochemical models uses compounds for which the source strength and the destruction reaction rate constant is well known. Such a compound is methylchloroform (Mayer et al 1982, Prinn et al 1987) for which the release rates and the oxidation reaction constant with OH are fairly well known. Scaling the methane destruction and atmospheric lifetime results in the values cited above. A recent redetermination of the $CH_4 + OH$ reaction constant by Vaghjiani & Ravishankara (1991) indicates a lower rate constant by about 20%, which would increase the CH_4 atmospheric lifetime or lower the global source strength, respectively. However, more recently a redetermination of the rate constant for the reaction of OH with methylchloroform found a lower value by 15% (Talukdar et al 1992). As this reaction rate constant together with the methylchloroform release rate is used to construct the OH fields, the above two reaction rate constant redeterminations cancel the effect on the global methane source/sink rate and lifetime, and effectively restore the previous values.

Some tropospheric methane (5–15%) is mixed into the stratosphere where it is destroyed by OH, $O(^1D)$, and Cl. Reaction with Cl is important, as it sequesters ozone-destroying Cl into relatively unreactive HCl. Furthermore stratospheric CH_4 oxidation is a substantial source of stratospheric H_2O (Pollock et al 1980).

Bacterial Methane Oxidation

Bacterial oxidation of methane under aerobic conditions, occurring above anaerobic methane production zones in wet environments, influences the net flux of methane emitted to the atmosphere (Harriss et al 1982, Keller et al 1983, King et al 1989, Whalen & Reeburgh 1990a). This is particularly evident in lakes and in the oceans where methane produced in anaerobic sediments cannot escape to the atmosphere due to aerobic methane oxidation in the oxic water column (Oremland et al 1987). Direct uptake and consumption of atmospheric CH_4 on relatively dry soils have been observed by Keller et al (1983, 1990), Whalen & Reeburgh (1990a), Born et al (1990), and Striegl et al (1992). Born et al (1990) estimate that this sink globally amounts to about 1–15% of the chemical sink in the atmosphere.

METHANE SOURCES

Numerous studies have investigated the strengths of various methane sources contributing to the atmospheric inventory. This has been done in a number of ways: by experimental measurements of methane emission rates from various ecosystems and methane producing processes, by investigations of the isotopic composition of methane sources and of atmospheric methane, by biostatistical analyses, and by modeling of the global methane mixing ratio distributions using Global Circulation Models. The results of some of the more recent investigations are summarized in Table 1. These investigations show that there are basically four major CH_4 sources of about equal size contributing to the atmospheric inventory. These are: methane from natural wetlands and tundra, from ruminants, from rice production, and from fossil methane (natural gas and from coal mining). Smaller sources are from biomass burning and from landfills. Termites were once thought to be a major source (Zimmerman et al 1982) but this source is now considered a minor one. Additional minor sources are from freshwater and the oceans. Methane from clathrate destabilization is a potential source which has yet to be quantified (Kvenvolden 1988). Table 1 summarizes some recent methane budgets based on various techniques.

Wetlands, Soils, and Tundra

Extensive efforts have been made to characterize methane fluxes from wet and inundated environments, where methane is produced under anaerobic conditions by bacteria mainly via acetate fermentation and CO_2 reduction (see e.g. Keller et al 1986; Sebacher et al 1986; Crill et al 1988a,

Table 1   Sources and sinks of methane

	Cicerone & Oremland 1988		Wahlen et al 1989	Houghton et al 1990		Fung et al 1991 (scenario 7)
Source						
Natural wetlands (bogs, swamps, tundra, etc)	115	100-200	147 (incl. landfills)	115	100-200	115
Rice paddies	110	60-170	136	110	25-170	100
Enteric fermentation (animals)	80	65-100	119	80	65-100	80
Fossil methane:			123			
Gas drilling, venting, transmission	45	25- 50		45	25- 50	40
Coal mining	35	25- 45		35	19- 50	35
Biomass burning	55	50-100	55	40	20- 80	55
Landfills	40	30- 70		40	20- 70	40
Termites	40	10-100		40	10-100	20
Oceans and fresh waters	15	6- 45		15	6- 45	10
Hydrate destabilization	5?	0-100		5	0-100	5
Total	540	400-640	580	525	290-965	510
Sink						
Reaction with OH in atmosphere	500	405-595		500	400-600	450
Removal by soils				30	15- 45	10
Atmospheric increase		40- 46	55	44	40- 48	

Annual release and range ($Tg\,CH_4^-/yr$)

1988b; Burke et al 1988; Bartlett et al 1988; Quay et al 1988; Whalen & Reeburgh 1988, 1990a, 1990b; Moore et al 1990; Roulet et al 1992a, 1992b). Methane flux measurements for a given ecosystem scatter widely over several orders of magnitude, both in time and space. They exhibit seasonal variations, but there are no other clear correlations with any parameters (such as temperature or precipitation) which could be used to obtain reliable global scale extrapolations. Global extrapolations for the methane flux from these sources therefore remain somewhat uncertain. Matthews & Fung (1987) and Aselmann & Crutzen (1989) have presented global extrapolations for these sources using average flux values and global distribution of these ecosystems, as well as net primary productivity. The resulting annual CH_4 production, approximately $110 \, Tg \, yr^{-1}$ is within the range indicated in Table 1.

Methane production from tundra would be expected to increase with global warming. Warming would lower permafrost levels and make large stores of carbon available for bacterial methane production.

Rice Fields

Rice fields which are flooded for extended periods of the growing season provide, like natural wetlands, anaerobic conditions for bacterial methane production. Methane fluxes from rice fields have been investigated by Cicerone et al 1981; Holzapfel-Pschorn & Seiler 1986; Schuetz et al 1989, 1990; Schuetz & Seiler 1989; and Sass et al 1990. Methane fluxes seem to vary during the growing season, and are affected by environmental factors and agricultural practices. Different fertilization procedures seem to affect the methane production as well. Global extrapolations are difficult, given the limited data base. Experimental data from the major rice growing countries (China and Southeast Asia) are lacking. Matthews et al (1991) compiled a global data base for methane by rice production with an estimated source strength of about $100 \, Tg \, yr^{-1}$. Methane production from rice cultivation is expected to increase with world population growth and therefore will influence the atmospheric CH_4 inventory in the future. Holzapfel-Pschorn & Seiler (1986) estimated that this source has been increasing worldwide by about 1.6% per year since 1940.

Animals

Methane is produced by enteric fermentation in the stomachs of ruminants. Methane production by domestic and wild ruminants is by the CO_2 reduction pathway (Wolin & Miller 1987). Crutzen et al (1986) and Lerner et al (1988) have investigated this source on a global scale. The annual CH_4 production from this source is estimated at about $80 \, Tg \, yr^{-1}$. This CH_4 source is thought to contribute to the atmospheric mixing ratio

increase over the recent past as domestic ruminants likely scale with population growth.

Fossil Methane

Fossil methane is being released to the atmosphere in the drilling and exploration of oil and natural gas. Losses furthermore occur in transmission and distribution of natural gas. Fossil methane is also released from coal mining. There is some discrepancy between fossil methane releases accounted for by statistical analyses and those derived from the analyses of $^{14}CH_4$ which is most suitable to estimate this methane source (see Isotopic Tracing of the Methane Cycle).

Landfills

Anaerobic conditions in soil-covered landfills favor biogenic methane and CO_2 production which is vented to the atmosphere. Biogenic methane production from biodegradable carbon lasts for a long time (about two decades). Bingemer & Crutzen (1987) evaluated the production from waste and its degradable carbon content. They estimated the global methane production rate from this source to be 30–70 Tg yr^{-1}, and found the annual methane emission rate to be somewhat lower due to methane oxidation.

Biomass Burning

Biomass burning produces CH_4 in incomplete combustion. Crutzen et al (1979) realized this to be a substantial source for atmospheric methane. Crutzen & Andreae (1990) estimate that biomass burning in the tropics is contributing 11–53 Tg of methane per year to the atmospheric inventory. Craig et al (1988), Cicerone & Oremland (1988), and Quay et al (1991) estimate the biomass burning contribution to be about 50 Tg yr^{-1}.

ISOTOPIC TRACING OF THE METHANE CYCLE

Rust (1981) and Stevens & Rust (1982) first proposed the isotopic approach to a CH_4 budget using ^{13}C. This approach was carried further to include ^{14}C and deuterium in methane (Burke et al 1988; Wahlen et al 1989, 1990; Quay et al 1991; Manning et al 1990; Levin et al 1992). The isotopic composition is influenced by many steps in the carbon cycle: Atmospheric CO_2 is converted to organic matter, organic matter is broken down into decomposition products, and methane is generated from these products by bacteria in a number of ways. Methane generation also includes aspects

of the hydrologic cycle as hydrogen derived from water is incorporated into the final product methane. All these transformations will introduce isotopic fractionations which are influenced by a number of factors. While most of the details are not known, it appears that the isotopic composition of methane from a particular source is determined by the composition of the substrate material and the isotopic fractionation of the methane generating pathway.

In principle therefore it is possible to derive a global methane budget from the comparison of the isotopic composition of methane from the various sources to that of the atmospheric inventory. This requires the knowledge of the isotopic fractionation in the atmospheric destruction reaction for methane. This fractionation was determined variously in the laboratory for ^{13}C (Rust & Stevens 1980, Davidson et al 1987, Cantrell et al 1990) and was found to be from 3 to 10 permil. Substantially larger fractionation has been observed from measurements in the lower stratosphere by Wahlen et al (1990).

Carbon–14 can be used to assess the contributions by fossil methane to the atmospheric inventory. Fossil CH_4 from natural gas exploration and distribution, from coal mining, and possibly from seepage of natural gas reservoirs on land and near shore is free of ^{14}C, while biogenic methane contains more or less contemporary ^{14}C of about 120 pMC (percent modern carbon). Via ^{14}C analyses, the biogenic contribution has been determined to be $21 \pm 3\%$ of the annual input to the atmosphere by Wahlen et al (1989), 17–25% by Manning et al (1990), and $16 \pm 12\%$ by Quay et al (1991). There is some complication due to a substantial anthropogenic contribution to the atmospheric $^{14}CH_4$ inventory from emissions from pressurized light water reactors (Kunz 1985) which adds to the uncertainty. Figure 5 shows the reconstruction of the atmospheric ^{14}C inventory from dated samples including the turnover of ^{14}C by nuclear atmospheric input from bomb testing, with and without the nuclear reactor contribution. Statistical analyses of fossil methane releases (Cicerone & Oremland 1988, Barns & Edmonds 1990, Fung et al 1991) are lower than those observed by ^{14}C. The discrepancy may be explained by releases of ^{14}C-depleted methane from ecosystems where old carbon is being processed. It is also possible that additional fossil CH_4 is released through seepage from natural gas reservoirs on land and near shore.

The stable isotopic composition of methane sources and of atmospheric methane have been investigated by Schoell (1980), Stevens & Rust (1982), Stevens & Engelkemeir (1988), Tyler (1986), Tyler et al (1988), Chanton et al (1988), Wahlen et al (1989), and Quay et al (1991). The atmospheric ^{13}C concentration is about -47 permil (PDB). Biogenic methane is largely
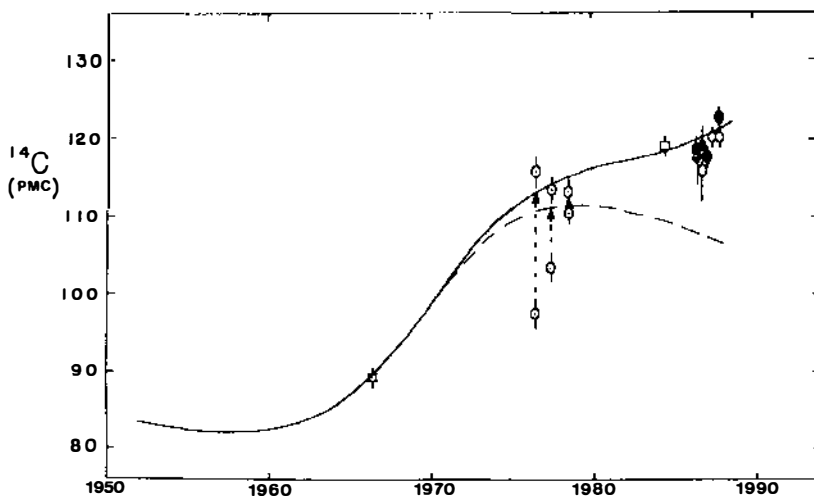
Figure 5   Reconstruction of the turnover of atmospheric bomb-produced ^{14}C into $^{14}CH_4$ in the atmosphere (from Wahlen et al 1989). $^{14}CH_4$ is expressed in pMC, (percent Modern Carbon). Upward corrections are for urban samples which contain excess CH_4 of fossil origin. (Reproduced with permission of *Science*, American Association for the Advancement of Science.)

depleted in ^{13}C due to fractionation. There are seasonal variations in the atmospheric ^{13}C records which are attributed to the OH destruction (Quay et al 1991). Furthermore there is a hemispheric difference in δ^{13}C reflecting a heavy southern hemispheric source from biomass burning (Quay et al 1991).

Figure 6 shows the power of the isotopic approach (from Wahlen 1992, Wahlen et al 1990). The isotopic composition of the various methane sources arc quite distinct. There are more sources than isotopes, thus the system is underdetermined. Nevertheless, strong contraints on the global methane budget can be obtained from the isotopic composition.

CLIMATIC IMPACT OF CH$_4$

The effect of the combined radiatively important trace gases to the terrestrial greenhouse forcing has been estimated to be 45–60% by Lorius et al (1990) from analyses of the gas composition in ice cores. Rodhe (1990) has studied the relative role for the different gases. The findings are summarized in Table 2, which shows the relative importance of CH$_4$. The
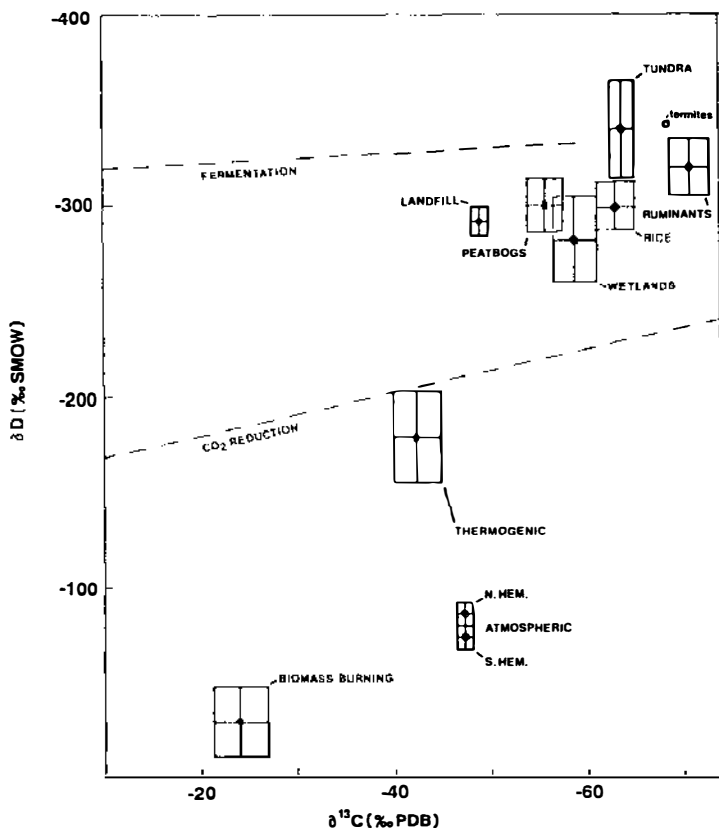
Figure 6 Systematics among the stable isotope composition of methane from various sources and from atmospheric methane (Wahlen et al, unpublished data). Boxes show the mean values for sets of samples for ^{13}C and D in methane.

first and second columns show the abundances and the observed annual increase in the atmospheric mixing ratio of the various gases. Column 3 shows the decay time against additional emission to the atmosphere. These times are essentially exponential, except for CO_2, due to the carbon chemistry in the ocean. Column 4 illustrates the relative importance to the greenhouse effect on a molecular basis. The last column indicates the relative contribution to the terrestrial greenhouse effect by the various trace gases, indicating that methane contributes about 25% of that of CO_2.

Table 2 Trace gas contributions to the greenhouse effect[†]

Species	Mixing ratio (ppb)	Rate of increase (% per year)	Decay time (yr)	Relative contribution (to CO_2) on a per mole basis (Mol^{-1})	Contribution to greenhouse effect (%)
CO_2	353×10^3	0.5	120	1	60
CH_4	1.7×10^3	1	10	25	15
N_2O	310	0.2	150	200	5
O_3 [a]	10–50	0.5	0.1	2000	8
CFC–11 [b]	0.28	4	65	12000	4
CFC–12 [b]	0.48	4	120	15000	8

[†] After Rodhe (1990).
[a] In the troposphere.
[b] Chlorofluorocarbons.

SUMMARY

Methane is a radiatively and chemically important constituent of the Earth's atmosphere, and it substantially contributes to the terrestrial greenhouse effect. Atmospheric mixing ratios of methane are increasing rapidly today, and large natural fluctuations, by a factor of two, have occurred in different climatic periods in the past. Over the recent 200 years, atmospheric methane mixing ratios have increased more than a factor of two over preindustrial values due to anthropogenic influence. While the gross features of the global methane budget are known, the details about individual source strengths are still poorly understood.

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