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BIOGEOCHEMICAL ASPECTS OF ATMOSPHERIC METHANE

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Abstract. Methane is the most abundant organic chemical in Earth's atmosphere, and its concentration is increasing with time, as a variety of independent measurements have shown. Photochemical reactions oxidize methane in the atmosphere; through these reactions, methane exerts strong influence over the chemistry of the troposphere and the stratosphere and many species including ozone, hydroxyl radicals, and carbon monoxide. Also, through its infrared absorption spectrum, methane is an important greenhouse gas in the climate system. We describe and enumerate key roles and reactions. Then we focus on two kinds of methane production: microbial and thermogenic. Microbial methanogenesis is described, and key organisms and substrates are identified along with their properties and habitats. Microbial methane oxidation limits the release of methane from certain methanogenic areas. Both aerobic and anaerobic oxidation are described here along with methods to measure rates of methane production and oxidation experimentally. Indicators of the origin of methane, including C and H isotopes, are reviewed. We identify and evaluate several constraints on the budget of atmospheric methane, its sources, sinks and residence time. From these constraints and other data on sources and sinks we construct a list of sources and sinks, identities, and sizes. The quasi-steady state (defined in the text) annual source (or sink) totals about $310(\pm60) \times 10^{12}$ mol $(500(\pm95) \times 10^{12}$ g), but there are many remaining uncertainties in source and sink sizes and several types of data that could lead to stronger constraints and revised esti-

mates in the future. It is particularly difficult to identify enough sources of radiocarbon-free methane.

1. INTRODUCTION

Methane (CH_4) is the most abundant organic gas in Earth's atmosphere. Much of the history of the detection of atmospheric methane and of the earliest systematic measurement data has been reviewed by Ehhalt [1974] and Wofsy [1976] and will not be repeated here. Since the early 1970s a variety of roles of methane in atmospheric chemistry and climate have been identified. For example, methane affects tropospheric ozone, hydroxyl radicals and carbon monoxide concentrations, stratospheric chlorine and ozone chemistry and, through its infrared properties, Earth's energy balance (see section 2).

Recent evidence that atmospheric methane concentrations are increasing globally has made it necessary and more urgent to understand natural processes, both biological and physical, which control methane and to identify the human activities that are involved. This evidence is now overwhelming. Methane increases have been demonstrated at many different locations and with independent measurement techniques, including flame ionization gas chromatography [Rasmussen and Khalil, 1981; Fraser et al., 1984; Blake and Rowland, 1988] and infrared absorption analysis [Rinsland et al., 1985]. Figure 1, from Blake and Rowland [1988] presents globally averaged data gathered between 1978 and late 1987; an annual rate of increase of 0.016 ppm/yr, or about 1% per year, is apparent. Globally averaged methane mole fractions are almost 1.70 ppm. Rinsland et al. [1985], through reanalysis of some solar absorption spectra taken at Jungfraujoch in 1951, deduced an atmospheric methane concentration of 1.14($\pm$0.08) ppm for April 1951. Similar instrumentation and analysis techniques at Kitt Peak in February 1981 yielded 1.58($\pm$0.09) ppm.
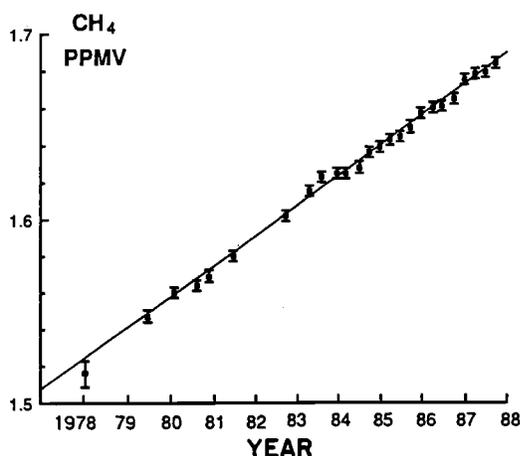
Fig. 1. Globally averaged tropospheric methane mole fractions (parts per million by volume, ppmv) measured between January 1978 and September 1987 and a best fit line through the data [from Blake and Rowland, 1988, reproduced with permission of the American Association for the Advancement of Science].

Whatever the causes of these recent methane increases, they are very rapid in comparison to geological time scales. Also, there is clear evidence from analysis of gases trapped in dated ice cores that atmospheric methane has more than doubled in concentration in the last 200 years [Craig and Chou, 1982; Rasmussen and Khalil, 1984; Pearman et al., 1986] and that its concentration stayed between 0.6 and 0.8 ppm over the last 3,000 years (Figure 2). The data in Figure 2 are from near both poles, Greenland and Antarctica. Similar results have been obtained by Stauffer et al. [1985], who also tested for differences due to gas extraction methods. Stauffer et al. also succeeded in analyzing a very recent ice core (1955 ± 10 years); in that sample the CH_4 concentration was about 1.4 ppm, consistent with other evidence that methane has been increasing in recent decades. While there have been questions about the degree to which ice core air represents the atmosphere [Craig and Chou, 1982], we believe that these questions have been resolved, and that at least for CH_4, we may believe the results. On this point, the ^{13}C isotope data of Craig et al. [1988] are particularly compelling (see also section 4).

The ice core methane record now extends back to nearly 160,000 years ago, as is illustrated in Figure 3. All methane data points from over 100,000 years ago are from the Raynaud et al. [1988] analysis of the Vostok ice core (Antarctica). The solid line in Figure 3 is a smoothed version of the temperature record that Jouzel et al. [1987] constructed from deuterium amounts in the Vostok core. One point (circled in Figure 3), at 27,200 years (650 ppb) is from Craig and Chou [1982]. All remaining points are from Stauffer et al. [1988], who found that during the last glaciation methane concentrations were about 350 ppb as opposed to about 650 ppb afterwards. The Craig and Chou point at 27,200 years is higher than the Stauffer et al. values for the same glacial period. The Vostok core data

from Raynaud et al. show that methane increased from about 320 ppb to 620 ppb between the end of the next to last glaciation and the subsequent interglacial period, about 160,000 to 120,000 years ago. These changes suggest that exposing and warming ice-covered soils produced more methane as glaciers retreated.

In any case, contemporary methane amounts and their rate of increase are unprecedented, at least during the past 160,000 years. Human activities are clearly involved in causes for the increase from 650 ppb to 1700 ppb. Accordingly, there is added motivation to understand the factors and practices that produce methane and release it to the atmosphere, the atmospheric processes that methane affects, and the atmospheric processes that limit the rise of methane concentrations.

In this paper we discuss the roles of methane in atmospheric chemistry and climate (section 2), the microbiology of methane formation and microbial oxidation in soils and waters (section 3), and information from carbon and hydrogen isotopes on the origin of environmental methane (section 4). In section 5 we examine data on atmospheric methane amounts, turnover rates, and isotopes to derive objective constraints on the annual budget (sources and sinks) of atmospheric methane. Methane fluxes are stated in units of 10^{12} g CH_4 or Tg CH_4/yr (1 Tg$=10^{12}$ g).

2. METHANE IN ATMOSPHERIC CHEMISTRY AND CLIMATE

Atmospheric Chemistry

In this section we discuss the important chemical roles of atmospheric methane and then how methane affects the radiative energy balance and hence the climate of Earth.

The chemical reactions that destructively oxidize atmospheric methane affect the chemical state of the atmosphere through the products of the reactions and through consumption of the reactant species. The most important reactant that destroys methane is the gas phase hydroxyl radical, OH, a key radical in atmospheric photochemistry (not to be confused with aqueous OH^-). Methane oxidation produces CO, CO_2, H_2O, H_2, and CH_2O, and it consumes OH. These reaction pathways (see below) affect tropospheric and stratospheric ozone amounts, and they produce important quantities of H_2O in the stratosphere. Also, stratospheric CH_4 reacts with Cl atoms, forming HCl, a reservoir species for Cl atoms. Finally, a portion of the flux of hydrogen carried upward into the stratosphere in CH_4 escapes to space, mostly as H atoms. Escape of H to space represents a source of atmospheric oxygen just like burial of organic carbon in deep sea sediments [Broecker, 1970; Van Valen, 1971].

To be clear as to how these effects arise, consider the key elementary reactions that occur in the atmosphere. First is the production of OH, which stems from ozone, ultraviolet (UV) light, and water vapor:

(R1) $O_3 + h\nu \longrightarrow O(^1D) + O_2$ $\lambda < 315$ nm
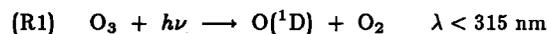
Most of the electronically excited oxygen atoms, $O(^1D)$, that are produced in (R1) are quenched in collisions with N_2 and O_2 as in (R2)
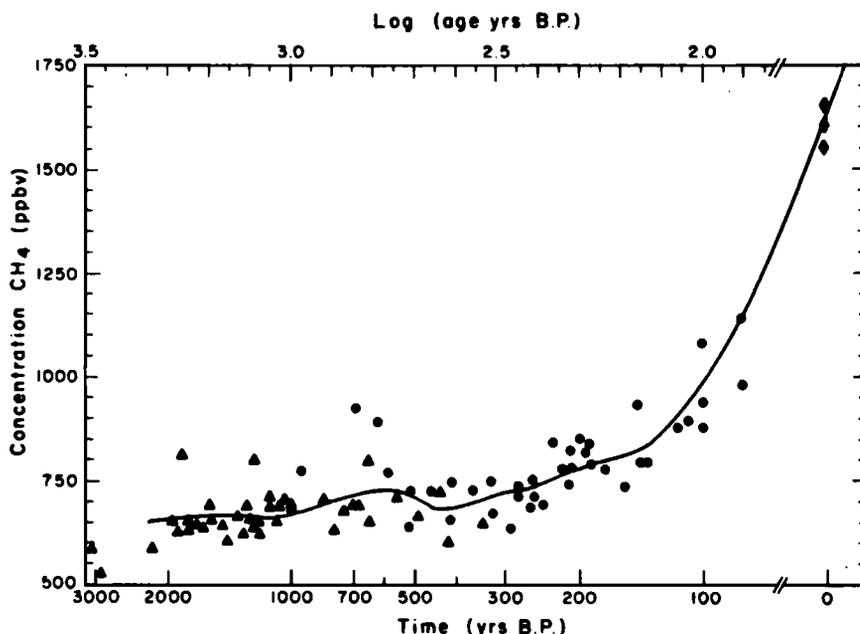
Fig. 2. Concentrations of methane in air extracted from dated ice cores representing 100 to 3000 years before present (B.P.) from Rasmussen and Khalil [1984]. Solid circles are data from Greenland ice, and triangles represent Antarctic ice cores. The solid line is a smoothed fit to the data and near-contemporary air data are represented by diamonds.

(R2) $O(^1D) + N_2 \longrightarrow O + N_2$
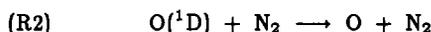
Ozone is reformed in (R3):

(R3) $O + O_2 + M \longrightarrow O_3 + M$

where $M = N_2$, O_2, or any third body with which collisions stabilize the O_3 product. But some of the $O(^1D)$, about 1%, reacts with water vapor to produce hydroxyl radicals:

(R4) $O(^1D) + H_2O \longrightarrow 2OH$
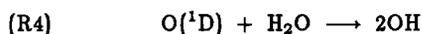
The biggest single sink of atmospheric methane is its reaction with OH in the troposphere.

(R5) $CH_4 + OH \longrightarrow H_2O + CH_3$
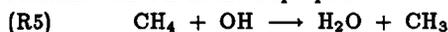
Perhaps 85% of the methane that is emitted into the atmosphere is destroyed by (R5) in the troposphere. In the stratosphere, almost all of the remaining methane is destroyed by OH, by Cl atoms, and by $O(^1D)$ atoms. A small fraction of methane goes through the stratosphere to the mesosphere where an additional sink, very short wavelength UV light (principally Lyman alpha radiation, 121.6 nm) destroys methane photolytically.

Complete oxidation of methane yields CO_2 and H_2O. Schematically, this can be represented by the combustion of methane:

(R6) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
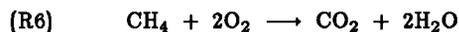
While (R6) seems simple and clear enough, it does not describe the mechanism through which the atmosphere oxidizes methane. In the atmosphere the process is ini-

tiated by OH radicals, not by O_2, and it requires light as discussed below. A pioneering study of this process was that of Levy [1971] (see also Levy [1973]). However, we now know that the mechanism of methane oxidation and the products that are formed are very different in the two cases of high concentrations of nitrogen oxides (NO_x) and low NO_x concentrations (defined below). For example, the methane oxidation chain can either produce or consume ozone. Figure 4 summarizes the principal reactions
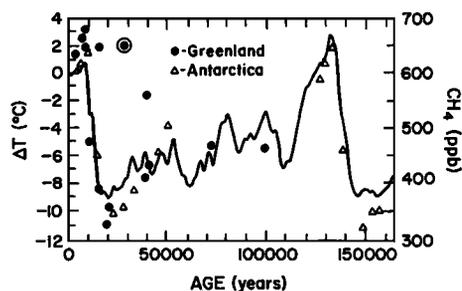
Fig. 3. Methane concentrations (ppb by volume) from dated ice cores plotted as age of air before present. Solid circles are data from Greenland cores, and triangles represent Antarctic cores. Data are from Raynaud et al. [1988] and Stauffer et al. [1988]. The circled point from 27,200 BP is from Craig and Chou [1982]. The solid line is a smoothed version of the temperature record deduced by Jouzel et al. [1987]. Lowest concentrations are from glaciated epochs, and highest values are from interglacial times.
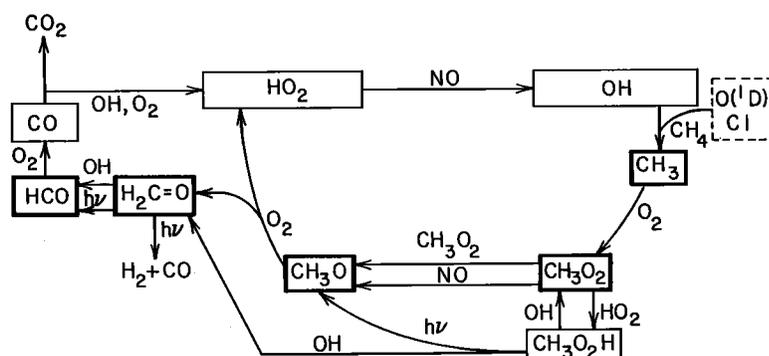
Fig. 4. Principal reactions and species in atmospheric methane oxidation (adapted from Ravishankara [1988]) for the case of adequate to high NO and NO_2 concentrations, defined in text. Dashed box indicates species whose reactions were not included in Levy's early work; otherwise, the scheme is essentially that of Levy [1971, 1973].

and species of methane oxidation for the case of high NO_x concentrations. With low NO_x concentrations there are substantial deviations from the pathways of Figure 4 (see below and Crutzen [1987]). Also, the actual reaction chain can be cut short in the atmosphere when products such as CH_2O are removed, for example, by rainfall before further oxidation.

In high-NO_x air columns, as in polluted or moderately dirty tropospheric air and all of the stratosphere, methane oxidation produces ozone and hydrogen oxides (HO + HO_2). The process begins with (R5) and proceeds first to production of formaldehyde.

(R5) $CH_4 + OH \longrightarrow H_2O + CH_3$

(R7) $CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$

(R8) $CH_3O_2 + NO \longrightarrow CH_3O + NO_2$

(R9) $CH_3O + O_2 \longrightarrow CH_2O + HO_2$

(R10) $HO_2 + NO \longrightarrow NO_2 + OH$

(R11) $2[NO_2 + h\nu \longrightarrow NO + O]$ $\lambda < 400$ nm

(R3') $2[O + O_2 + M \longrightarrow O_3 + M]$

Net reaction

      $CH_4 + 4O_2 + 2h\nu \longrightarrow CH_2O + H_2O + 2O_3$
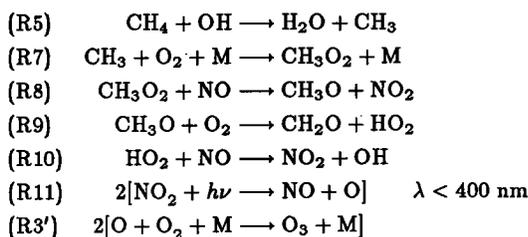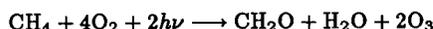
Let us designate this reaction sequence as RS1. In RS1, NO and NO_2 are catalysts. Formaldehyde is oxidized to CO through three reaction pathways.

(R12a) $CH_2O + h\nu \longrightarrow CO + H_2$ $\lambda < 360$ nm

(R12b) $CH_2O + h\nu \longrightarrow H + HCO$ $\lambda < 360$ nm

(R13) $H + O_2 + M \longrightarrow HO_2 + M$

(R14) $HCO + O_2 \longrightarrow CO + HO_2$

(R10') $2[HO_2 + NO \longrightarrow OH + NO_2]$

(R11) $2[NO_2 + h\nu \longrightarrow NO + O]$

(R3') $2[O + O_2 + M \longrightarrow O_3 + M]$

Net reaction

      $CH_2O + 4O_2 + 2h\nu \longrightarrow CO + 2O_3 + 2OH$
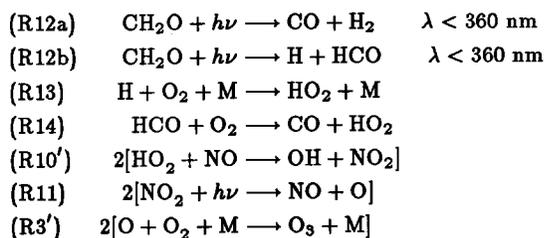
RS2 is defined as the reaction sequence (R12b), (R13), (R14), (R10'), (R11), and (R3'). The sequence RS2 pro-

duces two molecules of ozone and two OH radicals per CH_2O molecule that is consumed. The third pathway from CH_2O to CO is

(R15) $CH_2O + OH \longrightarrow HCO + H_2O$

(R14) $HCO + O_2 \longrightarrow CO + HO_2$

(R10) $HO_2 + NO \longrightarrow OH + NO_2$

(R11') $NO_2 + h\nu \longrightarrow O + NO$

      $O + O_2 + M \longrightarrow O_3 + M$

Net reaction

      $CH_2O + 2O_2 + h\nu \longrightarrow CO + H_2O + O_3$
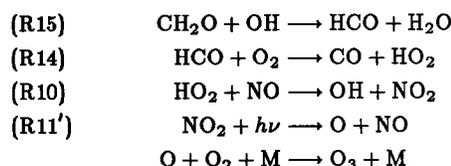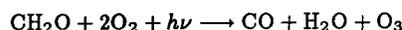
The final step, still assumed to occur in the presence of high NO_x concentrations, is the oxidation of CO to CO_2.

(R16) $CO + OH \longrightarrow CO_2 + H$

(R13) $H + O_2 + M \longrightarrow HO_2 + M$

(R10) $HO_2 + NO \longrightarrow OH + NO_2$

(R11') $NO_2 + h\nu \longrightarrow O + NO$

      $O + O_2 + M \longrightarrow O_3 + M$

Net reaction

      $CO + 2O_2 + h\nu \longrightarrow CO_2 + O_3$
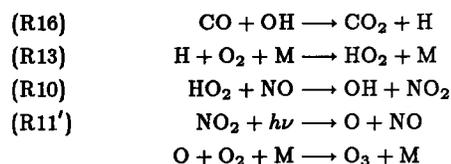
Thus the complete oxidation of CH_4 in the presence of adequate NO_x produces O_3 and depending on the relative fractions of CH_2O oxidized by (R12a), RS2, and RS3, can produce OH radicals. Crutzen [1987] has calculated that the averaged relative fractions of (R12a), RS2, and RS3 are about 50-60%, 20-25%, and 20-30%, respectively, in the troposphere. In this case, methane oxidation to CO_2 and H_2O produces 3.7 O_3 molecules and 0.5 OH radicals per methane molecule destroyed. Note that these numerical relationships are stoichiometric between methane destruction and production of O_3 and OH but are not ratios of number density changes because other processes partially control O_3 and HO_x concentrations, for example, surface deposition and inflows of O_3 from the stratosphere, and there are also photochemical feedbacks in the system. For this pathway (RS1 then (R12a) or RS2 or RS3, then RS4) to proceed there must be enough NO present for HO_2 to
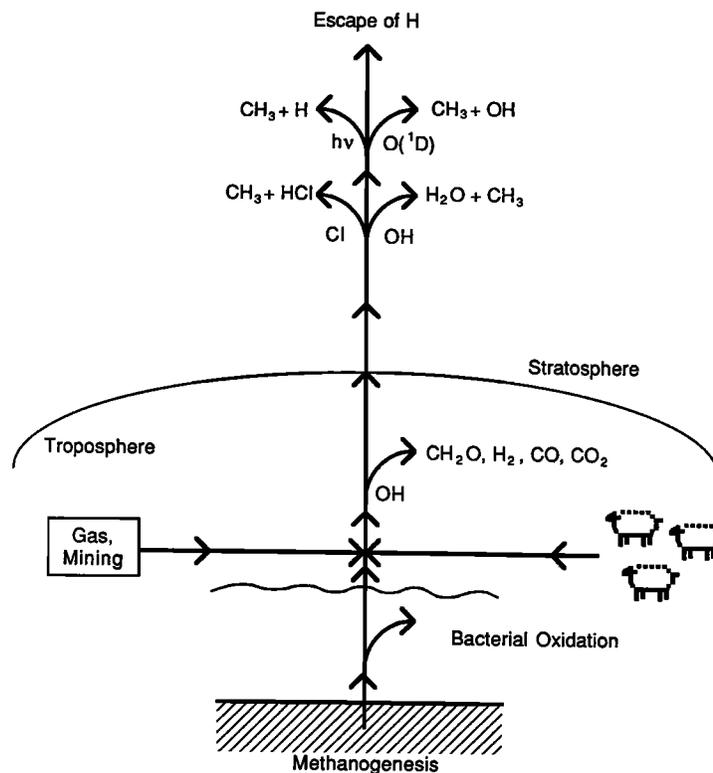
Fig. 5. Schematic illustration of the flow of methane from several representative biological and abiogenic sources through pathways where oxidation occurs in sediments, waters, and the atmosphere. Once in the atmosphere, most methane is destroyed in the troposphere but 10–20% is transported upward to the stratosphere where the remainder is destroyed.

react preferentially with NO rather than with O_3 (see below) and for CH_3O_2 to react preferentially with NO rather than with HO_2; present rate-constant data and model results indicate that NO mole fractions must exceed 5 to 10 ppt for this to occur.

In large fractions of the troposphere, NO mole fractions are probably 10 ppt or less, especially in the altitude range 0 to 6 km [Ridley et al., 1987; Davis et al., 1987]. Under these circumstances, methane oxidation consumes ozone and it consumes HO_x ($OH + HO_2$) species in producing CO_2, H_2O, and H_2. Crutzen [1987] calculated that the oxidation of each CH_4 molecule consumes 3.5 HO_x molecules and 1.7 O_3 molecules. We estimate less HO_x consumption, one to two HO_x molecules, depending on atmospheric OH concentrations, pathways of CH_3OOH reactions, and heterogeneous removal rates for species like CH_3O_2H. Numerical models of tropospheric photochemistry yield more complicated results when CH_4 increases in low-NO_x environments (see references below): OH concentrations decrease, HO_2 and H_2O_2 increase, and O_3 is rather insensitive to methane changes.

A potentially very important consequence of methane oxidation is that of CH_4, CO and OH perturbations. Because OH is the major sink for atmospheric CH_4 and CO, and because these same reactions of OH with CH_4 and CO suppress OH concentrations, there is in principle an instability in the system. Increases in atmospheric CO or CH_4

concentrations can lead to decreases in OH concentrations, thereby further increasing the CO or CH_4 perturbations [Chameides et al., 1977; Sze, 1977]. As the above discussion of methane oxidation reactions and earlier studies show [Hameed et al., 1979; Thompson and Cicerone, 1986; Crutzen, 1987; Isaksen and Hov, 1987], the presence or absence of air instability depends on the background concentration of NO_x. On balance, the contemporary increase of atmospheric CH_4 is probably decreasing OH concentrations [Thompson and Cicerone, 1986; Crutzen, 1987]. In the context of atmospheric methane it is possible that OH decreases with time are causing part of the temporal increase of methane concentrations; these hypothesized OH decreases could be due to the methane increase or to any other factors that suppress OH, such as a CO increase [Cicerone, 1988].

Figure 5 illustrates the flow of methane through the atmosphere and the products of methane oxidation. Methane enters the atmosphere at or near Earth's surface after escape from methanogenic wetland soils and rice paddies, from mining, mineral exploration, natural gas wells, and transmission lines and from other sources such as ruminant animals like cows and sheep (see section 5). About 85% of the total methane input flux (total flux = 540 x 10^{12} g CH_4/yr) is consumed by (R5) with tropospheric OH, producing CO_2, H_2O, CO, H_2 and various intermediate products through the reactions that are listed above, and

consuming oxygen. The remaining methane flux, about 60 $\times 10^{12}$ g/yr, on average, enters the stratosphere. Reaction (R5) with stratospheric OH is the dominant sink, followed by reactions with $O(^1D)$ and with Cl atoms. The reaction

(R17) $CH_4 + Cl \longrightarrow CH_3 + HCl$

is very important in stratospheric chemistry, mostly because it sequesters ozone-destroying Cl atoms into a temporary reservoir, HCl molecules, that are inactive toward ozone [Stolarski and Cicerone, 1974; Brasseur and Hitchman, 1988]. The stratospheric ozone layer is, of course, an important natural shield, absorbing ultraviolet light that would otherwise reach Earth's surface. The analogous reaction between CH_4 and F atoms produces HF in the stratosphere. Chlorine atoms can be released from HCl by reactions between HCl and OH, but the analogous reaction between HF and OH is endothermic and does not liberate F atoms [Cicerone et al., 1974]. The bromine analog to (R5) does not proceed because it is endothermic. Methane oxidation in the stratosphere, where there is NO_x present, produces some ozone through the reactions discussed above and illustrated in Figure 4. In most of the stratosphere the net effect of NO_x reactions is to consume ozone catalytically, but in the lowest parts of the stratosphere their role in methane oxidation leads to (relatively small) ozone production rates [Johnston and Whitten, 1975].

A fraction of the H atoms that are released in methane oxidation and from photochemical decomposition of H_2O in the stratosphere subsequently escape to space (see Liu and Donahue [1974], Hunten and Strobel [1974], and references therein). Because the H atom concentration in the thermosphere and exosphere is furnished in large part by methane oxidation, the temporal increase in atmospheric methane concentrations is also causing an increase in the rate of H escape to space [Ehhalt, 1986].

Methane's Roles in the Climate System

Atmospheric methane exerts influence over Earth's climate in several different ways, both direct and indirect. The more direct roles involve interaction with planetary infrared radiation, warming Earth's surface and near-surface atmosphere and cooling the stratosphere, i.e., the roles of an effective greenhouse gas. The most important infrared spectral feature of methane molecules is their 7.66-μm absorption band; quantitative models of the impact of methane's role in Earth's energy budget focus on this band. Donner and Ramanathan [1980] calculated that the presence of 1.5 ppm of CH_4 in the atmosphere causes the globally averaged surface temperature to be about 1.3 K higher than it would be with zero methane and that larger effects would apply to polar latitudes. Ramanathan et al. [1985] and Dickinson and Cicerone [1986] have computed the global heating due to an increase of CH_4 concentrations from various deduced preindustrial levels to contemporary values and the future heating effects of several methane scenarios. For example, the infrared radiative heating effect of a methane increase from 0.7 ppm (preindustrial revolution) to 1.7 ppm (1988 concentration) is

about half as large as the comparable effect of simultaneously increasing CO_2 from 275 ppm to 345 ppm. Future growth in atmospheric methane concentrations, while not clearly predictable, is likely to contribute more to future climatic change than any other gas except CO_2. It is also interesting to examine the heating effects due to such gases on a decade-by-decade basis (see, for example, Lacis et al. [1981]).

In the paleoatmosphere of 4.25 billion years ago when the Sun was perhaps 30% less luminous, relatively high concentrations of atmospheric gases such as CO_2 and CH_4 could have served to maintain Earth temperatures above freezing (evidence suggests that Earth was not frozen over) [see Kiehl and Dickinson, 1987]. Methane concentrations of about 100 ppm could have decreased the amount of CO_2 required for maintenance of a warm Earth by about a factor of 2 [Kiehl and Dickinson, 1987].

The direct radiative effect of atmospheric methane also extends into the stratosphere; at altitudes above about 20 km, CH_4 molecules act to cool the atmosphere through radiative losses to space [Ramanathan et al., 1985].

There are also several interesting and potentially important indirect ways that methane can affect climate. One that has not received much attention is that the atmospheric oxidation of CH_4 produces CO which is converted further to CO_2. Methane oxidation produces about 8 $\times 10^{14}$ g CO/yr [Logan et al., 1981]. CO molecules survive two to three months on average before conversion to CO_2 by (R16). In this way, about 0.34 $\times 10^{15}$ g C/yr as CO_2 is produced globally. By comparison, total human release of CO_2 due to combustion and cement use is about 5.3 $\times 10^{15}$ g C/yr [Marland and Rotty, 1984]. Thus, we calculate that the atmospheric production of CO_2 from atmospheric CH_4 is about 6% as much as the direct annual release of CO_2 from anthropogenic sources.

Other indirect effects of increasing atmospheric CH_4 are the chemical production of tropospheric O_3 (a greenhouse gas) and increases in tropospheric water vapor. The latter effect is not proven, but it is a common and plausible assumption in climate model sensitivity and a result of some general circulation models that as temperature rises, atmospheric relative humidity will remain rather constant. Accordingly, absolute H_2O amounts would increase. In this way the effect of a greenhouse warming from CH_4 or other causes leads to an amplification of perhaps 50% due to increased H_2O vapor concentrations (see discussion by Ramanathan et al. [1987]). Tropospheric O_3 increases that can result from CH_4 increases in the presence of NO_x (see, for example, Isaksen and Hov [1987]) are also able to affect climate, especially if ozone concentrations should increase in the upper troposphere where O_3 is a particularly effective greenhouse gas.

3. MICROBIOLOGICAL ASPECTS

Methanogenesis

Recent advances in molecular biology have prompted interest in microbial phylogenetic relationships. These advances have shed new light on the patterns of the evolution of microorganisms [Woese, 1987]. One of the initial

findings of this line of work revealed that the methane-generating (methanogenic) bacteria constitute an unusual group of microorganisms which, along with the extremely halophilic and the thermoacidophilic bacteria, form a distinct biological kingdom known as the Archaebacteria. This was deduced from oligonucleotide sequence patterns of the 16s ribosomal RNA of these organisms [Balch et al., 1977]. Together with the kingdoms of Eukaryota and Eubacteria, they comprise all the life forms present on Earth. Methanogens have been the focus of intense scientific interest, and a number of reviews have appeared over the past 10 years concerning aspects of their micro-biology, biochemistry, ecology, and geochemical activities. The reader is referred to these works for greater detail than can be covered in this paper [Mah et al., 1977; Zeikus, 1977; Balch et al., 1979; Rudd and Taylor, 1980; Daniels et al., 1984; Winfrey, 1984; Ward and Winfrey, 1985; Whitman, 1985; Jones et al., 1987; Wolin and Miller, 1987; Oremland, 1988].

Methanogens are strict anaerobes and require highly reducing conditions (Eh = < −300 mV) for growth. Consequently, they proliferate in aquatic sediments, flooded soils, animal gastrointestinal tracts, and sewage. They also occur in extreme environments characterized by high temperatures, such as hot springs or seafloor hot vents [e.g., Ward and Olson, 1980; Stetter et al., 1981; Jones et al., 1983; Anderson et al., 1987]. Other extremes to which certain methanogens are either adapted or which they will tolerate include hypersalinity (reviewed by Oremland and King [1988]), and extremes of pH [Oremland et al., 1982a; Williams and Crawford, 1984]. Thus these organisms can be isolated from and be active in almost any anoxic ecosystem.

Numerous physical, chemical, and biological factors will influence the physiology of methanogenic bacteria and the ecology of anaerobic ecosystems. Hence, the rate of methane production by a given habitat will be reflective of these factors. One of the more obvious of these is temperature. Several studies have found that methane release form ecosystems increases with increasing temperatures, provided that other parameters (e.g., carbon loading) are held constant [Zeikus and Winfrey, 1976; Baker-Blocker et al., 1977; Kelly and Chynoweth, 1981; Oremland, 1981; Svensson, 1984]. Certain metabolic subgroups of the total methanogenic flora, however, may exhibit different optimal temperatures. For example, Svensson [1984] reported that acetate-utilizing methanogens in acidic peat soils had an optimum at 20°C while hydrogen oxidizers had an optimum at 28°C. In general, soils and sediments usually operate well below their optima for methanogenesis for most, if not all of the year. Much research effort has been devoted to the study of thermophilic methanogens because of their possible economic benefit in waste processing and their phylogenetic linkage with thermoacidophilic archaebacteria. However, even though many methanogenic habitats are perpetually cold (for example, deep sea and polar sediments, tundra soils), to our knowledge the occurrence of psychrophilic methanogenic populations or isolations has not been investigated.

Methanogenic bacteria can metabolize only a restricted suite of compounds which provide energy for their growth.

Recognized substrates include hydrogen reduction of carbon dioxide, acetate, formate, methanol, methylated amines, and carbon monoxide. Recently, dimethyl sulfide has been found to serve as a growth substrate [Kiene et al., 1986]. Most methanogens are capable of growth by hydrogen reduction of carbon dioxide, and in addition some can grow on formate as well. Some methanogens, such as *Methanosarcina barkeri*, can grow on almost all of these compounds, while obligately methylotrophic methanogens like *Methanococcoides methylutens* [Sowers and Ferry, 1983] can grow only on methanol and methylated amines. Growth on dimethyl sulfide appears to be restricted to only a few recently isolated, obligately methylotrophic species (R. Oremland et al., Description of an estuarine methylotrophic methanogen which grows on dimethyl-sulfide, submitted to *Appl. Environ. Microbiol.*, 1988). Growth on acetate or other methylated substrates takes place by oxidation of some of the substrate to carbon dioxide, coupled with reduction of the remainder to methane. In the methanogenic metabolism of acetate, methane is derived from the methyl group.

Methanogens are reliant upon other microorganisms for providing them with their required substrates. The breakdown of organic matter in anoxic ecosystems is a complex process generally referred to as an "anaerobic food web" rather than a simpler food chain. A variety of non-methanogenic anaerobic microbes attack complex organics, including biopolymers, ultimately resulting in the formation of these methanogenic substrates (Figure 6). Interactions that methanogenic bacteria form with other microbes are either of a complimentary or a competitive nature. In complimentary interactions, fermentative organisms metabolize a given compound, and the products of this metabolism are consumed by methanogens, with the formation of methane as an end product. The most studied interaction involves "interspecies hydrogen transfer" whereby fermenters channel reducing equivalents away from substrate end products and to hydrogen-consuming bacteria, like methanogens [Wolin, 1982; Mah, 1982; Wolin and Miller, 1987]. This results in the accumulation of soluble end products which are more oxidized than those predicted from culture studies of the fermentative organism grown on its own (for example, acetate instead of ethanol may result from cellulose fermentation). In some complimentary interactions the fermentative bacteria can obtain more energy by transfer of reducing power to hydrogen-consuming methanogens then they could from fermentative growth on their own (for example, see Wolin and Miller [1987]). Some organisms, termed obligately proton-reducing bacteria, cannot grow without methanogens or other types of hydrogen-consuming anaerobes.

Much work has been done on competitive interactions, especially with regard to those of the sulfate-reducing bacteria with methanogens. In these situations, sulfate-reducing bacteria will outcompete methanogens for hydrogen and/or acetate. Because these two substrates are the most important methane precursors in many anaerobic environments [Jeris and McCarty, 1965; Cappenberg and Prins, 1974; Winfrey and Zeikus, 1977; Sansone and Martens, 1981], their removal by sulfate reducers restricts their availability to methanogens [Oremland and Taylor,

ANAEROBIC FOOD WEB: Aquatic Systems
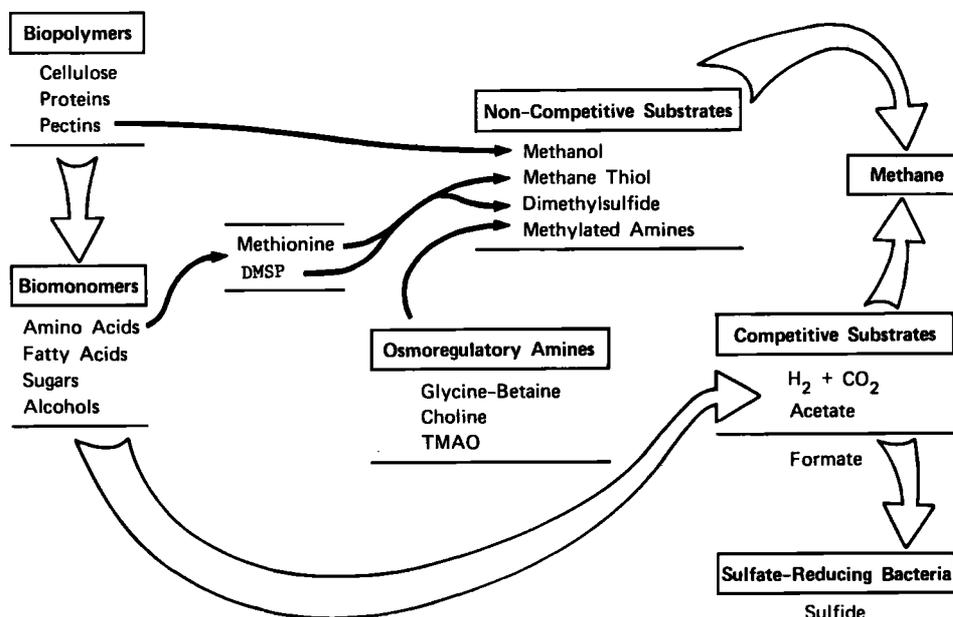
Fig. 6. Anaerobic food web involved in complementary and competitive microbial interactions associated with methanogenesis [from Oremland, 1988] (reproduced with permission of J. Wiley and Sons).

1978; Schonheit et al., 1982; Lovley and Klug, 1983, 1986]. Thus in environments which contain abundant sulfate, such as marine sediments, methanogenesis usually takes place at depths beneath the zone of sulfate depletion [e.g., Martens and Berner, 1974]. However, this is not always the case, and in certain environments methane and sulfate as well as methanogenesis and sulfate reduction can coexist [Oremland et al., 1987]. Several compounds (methylated amines, methanol, dimethyl sulfide) termed "noncompetitive" substrates exist for which sulfate reducers do not have as strong an affinity as they do for hydrogen or acetate [Oremland et al., 1982b; Oremland and Polcin, 1982; King et al., 1983; King, 1984a,b; Kiene et al., 1986; Kiene and Visscher, 1987]. Noncompetitive substrates may be derived from osmoregulatory solutes, such as glycine-betaine or dimethylsulfoniopropionate. Thus they are important methane precursors in saline environments containing abundant plant materials, such as salt marshes [Oremland et al., 1982b]. Methanogens in sediments of this type are adapted to the metabolism of "noncompetitive" substrates like methanol and trimethylamine. Obligately methylotrophic methanogens constitute about half of the total methanogenic population present in salt marsh sediments [Franklin et al., 1988], and methylotrophs can be found in rice paddy soils [Rajagopal et al., 1988] and rumen environments [Patterson and Hespell, 1979]. Methylated amines have been implicated as the substrate precursors for methane found in oceanic surface waters (C. Lee, personal communication, 1986; see section 5). Thus, although the global significance of methylated one carbon

compounds as methane precursors is not known, they may prove to be of more significance than believed currently.

Aside from soils, sediments, and sewage, an important source of methane to the atmosphere is from the flatulence and the eructations of animals. Many herbivorous animals feed upon foods which contain a high proportion of biopolymers, like cellulose. However, most animals do not produce cellulolytic enzymes which can degrade the cellulose to simple monomeric sugars. To overcome this, they have evolved symbiotic relationships with anaerobic microorganisms which inhabit various portions of their gastrointestinal tracts. The microbes have the necessary enzymes to degrade the otherwise indigestible polymers, and as a consequence of this fermentation, methane is evolved. The best studied habitat for this process is the rumen of herbivorous grazers like cows, sheep, buffalo, goats, deer, camels, elk, etc. [Hungate, 1966]. The rumen is a complex foregut in which the grazed grasses are stored for anaerobic fermentation. Gases produced during rumen fermentation are vented to the atmosphere by the animal's belching and typically contain 30–40% CH_4 with the rest composed of CO_2 and traces of N_2, H_2S and H_2 [Hungate, 1966; Bryant, 1979; Phillipson, 1979]. This quantity of CH_4 is more than that formed during in vitro fermentation (15–20% CH_4) because of CO_2 absorption into the animal's blood [Hungate, 1966]. A typical 500-kg domestic cow produces about 200 L CH_4 per day [Wolin, 1979]; however, the quantity and composition of the gas varies with the type of animal, feed type, and time of day. Gas eructation rates for cows can be as high as 20 L/min at 30 min after feeding, but

decline to 5–10 L/min by 4 hours after feeding [Phillipson, 1979]. Most of the methane formed in the rumen is from H_2 reduction of CO_2, because fatty acids are unavailable to the rumen bacteria owing to absorption into the animal's bloodstream. When the animal "chews its cud," it passes the rumen contents (now mainly consisting of digestible microbial cells rather than plant fiber) into its regular stomach (omasum) for digestion. The rumen, however, is not the only evolutionary strategy, as a number of animals (for example, horses, rabbits, etc.) employ their caecums as a site of postgastric microbial degradation. A variety of insects (for example, cockroaches, termites) have hindgut fermentations which achieve postgastric fermentations with formation of methane [Breznack, 1982]. However, only one third of the adult human population has an active flora of methanogens present in the colon [Wolin, 1981].

A variety of methods exist for the estimation of rates of methanogenesis in sediments and the topic has been recently reviewed [Conrad and Schütz, 1988]. Sediment slurries are commonly used to study the nature of methanogenic interactions and the ability of methanogens and associated microbes to attack certain compounds [e.g., Kiene and Visscher, 1987]. However, because these are severely disrupted systems, absolute rates obtained under these conditions probably bear little resemblance to rates in the environment. Incubation of intact sediments in subcores bears a closer resemblance to in situ conditions if they are kept at the proper temperature. Extraction of methane from a series of such cores over a time period can yield an estimate of activity [e.g., Crill and Martens, 1983]; however, initial methane pools may be so large as to obscure small increases, and it is difficult to reduce their size without severe physical disruption [Kiene and Capone, 1985]. Studies of anoxic waters have an advantage over sediments because of the relative ease in removing methane [Iversen et al., 1987]. Specific inhibitors, such as 2-bromoethanesulfonic acid, are useful tools in these investigations, but they are not a panacea and are subject to their own particular difficulties [Oremland and Capone, 1988]. The best method is the use of radio-labeled precursors such as ^{14}C-labeled bicarbonate, acetate, trimethylamine, etc., combined with analysis of the ^{14}C-labeled methane and carbon dioxide produced. However, this approach requires analyses of pool sizes of the substrates in order to obtain rates and can therefore be laborious. In addition, because of the possible diversity of methanogenic substrates, investigations using several precursors may be necessary in order to obtain a summation yielding a rate of methane formation [e.g., Oremland and King, 1988].

Methane-Oxidizing Bacteria

Oxidation of methane by bacteria is relevant to the study of global methane geochemistry for several reasons. First, consumption of methane by these microbes significantly limits the flux of methane to the atmosphere from various ecosystems [e.g., Rudd and Hamilton, 1978; Iversen et al., 1987]. Second, soil bacteria actually remove methane from the atmosphere and therefore constitute a global sink for the gas [Harriss et al., 1982; Seiler

et al., 1984b; W. S. Reeburgh, personal communication, 1987]. Finally, the oxidation of methane can alter its stable isotopic composition, which can complicate assignment of source by stable isotopic methods (for example, Oremland et al., [1987]; see section 4).

Methane can be oxidized by aerobic and anaerobic bacteria. Aerobic oxidation has been well characterized. Several reviews and classic papers have been written on these microorganisms, their microbiology, physiology, and biochemistry [Whittenbury et al., 1970a,b; Davies and Whittenbury, 1970; Ribbons et al., 1970; Quayle, 1972; Anthony, 1975; Quayle and Ferenci, 1978; Colby et al., 1979; Higgins et al., 1981; Haber et al., 1983], and a book was published by Anthony [1982] covering these topics, as was a symposium volume edited by Crawford and Hanson [1984]. Only a few papers have reviewed aspects of their ecology [Hanson, 1980; Rudd and Taylor, 1980]. The microbes and reactions involved in anaerobic oxidation have not as yet been defined. We will now review aspects of both types of oxidation.

Aerobic methane-oxidizing (methanotrophic) bacteria constitute an interesting group of eubacteria which grow only on methane and/or one carbon compounds (i.e., compounds lacking carbon-carbon bonds, like methanol, formate, methylated amines, etc.). Only one species (*Methylobacterium organophilum*) can grow on more complex organics in addition to methane [Patt et al., 1974]. These organisms are divided into two major groups based on the arrangement of their characteristic cell membranes and mode of carbon assimilation. Type 1 methanotrophs have "bundle disc" shaped internal membranes and utilize the ribulose monophosphate pathway for carbon assimilation, while type 2 methanotrophs have peripheral membranes and employ the serine pathway.

All aerobic methanotrophs oxidize methane in a sequential manner, starting with the conversion of methane to methanol by methane mono-oxygenase and followed by subsequent oxidations to formaldehyde, formate, and ultimately carbon dioxide:

$$CH_4 \longrightarrow CH_3OH \longrightarrow HCOOH \longrightarrow CO_2$$
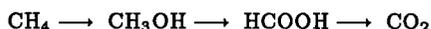
Methane mono-oxygenase is capable of oxidation of higher alkanes like ethane, although it depends upon species whether or not ethane will support growth [Hazeu and de Bruyn, 1980]. This enzyme (as well as whole cells) will oxidize alkanes to corresponding alcohols, epoxidize alkenes, and oxidize a variety of halogenated pollutants [Colby et al., 1977; Hou et al., 1980; Wilson and Wilson, 1985]. Therefore these organisms hold considerable potential for the formation of industrial chemicals as well as the disposal of toxic pollutants.

Methane-oxidizing bacteria need oxygen for growth, however under certain conditions they require low oxygen tensions. All type 2 methanotrophs and some type 1 methanotrophs can fix nitrogen [Davis et al., 1964; de Bont and Mulder, 1974; de Bont, 1976; Murrell and Dalton, 1983]. Under nitrogen-fixing conditions of methanotrophic growth, most species are sensitive to high pO_2 because of their unprotected nitrogenase enzyme [de Bont and Mulder, 1974]. However, in some species capable of ni-

trogen fixation, growth with nitrate as a nitrogen source is more sensitive to oxygen than diazotrophic growth [Toukdarian and Lidstrom, 1984]. These points are significant because they can determine the location and activity of aerobic methanotrophs under natural conditions (see below).

In nature, aerobic methanotrophs will generally be positioned and most active in zones where both methane and oxygen are present [e.g., Harrits and Hanson, 1980; Rudd, 1980]. This is usually at the interface between aerobic and anaerobic environments. Although these organisms are readily isolated from soils, most field work on methane oxidation has been conducted in lakes [Rudd et al., 1974; Rudd and Hamilton, 1975; Harrits and Hanson, 1980], and activity in the marine environment has also been studied [Ward et al., 1987]. Under nitrogen-fixing conditions, methanotrophs require reduced oxygen tensions and therefore are positioned near the oxycline of lakes [Rudd et al., 1976]. Bacterial oxidation affects the dissolved methane content of lake water but has little influence on bubble ebullition or the methane content of rising bubbles. Because sedimentary methane diffusive flux can equal or exceed bubble flux in freshwater lakes [Strayer and Tiedje, 1978], oxidation is an important component of the methane budget. For example, annual methane oxidation was found to recycle ≈65% of the methane formed in a freshwater Canadian Shield Lake (Lake 227) and in addition was the cause of whole lake anoxia during winter ice-over [Rudd and Hamilton, 1978]. Physical mixing can greatly affect the importance of oxidation to the methane budget during periods of stratification. Thus during summer, methane oxidation and evasion to the atmosphere represented 11% and 5%, respectively, of the methane budget of Lake 227 [Rudd and Hamilton, 1978]. By contrast, during summer stratification of the much larger Lake Mendota, oxidation accounted for 45% of the budget, although evasion (≈8%) was comparable. The authors attributed greater wind-derived mixing resulting in a broader zone of methane oxidation with higher unit volume activity as the basis for the difference [Fallon et al., 1980]. Recently, aerobic methanotrophs have been discovered as endosymbionts in the gill tissues of deep sea mussels located around natural gas vents [Childress et al., 1986; Cavanaugh et al., 1987; Fischer et al., 1987]. The importance of this unusual association as a methane sink has not as yet been quantified.

Anaerobic oxidation of methane is an as yet poorly understood process, but nonetheless it appears to be an important methane sink in certain types of anaerobic environments [Alperin and Reeburgh, 1984]. Most of the environments studied are sulfate-containing systems, such as marine sediments or anoxic waters [Reeburgh, 1976, 1980; Reeburgh and Heggie, 1977; Iversen and Blackburn, 1981; Devol, 1983; Lidstrom, 1983; Iversen and Jorgensen, 1985; Devol et al., 1984], although there are reports of such oxidation in freshwater systems [Panganiban et al., 1979]. Early work with pure cultures implied that sulfate-reducing bacteria were involved in this oxidation [Davis and Yarbrough, 1966]. However, inhibition studies with natural systems have failed to confirm this [Alperin and

Reeburgh, 1985; Iversen et al., 1987]. The problem of identifying the microbial agent(s) involved is complicated by the poor energy yield for sulfate-linked anaerobic growth on methane [Wake et al., 1977] which makes it difficult to isolate the organisms. It is possible that methane may be cooxidized as a minor metabolic reaction which does not yield energy for growth [Davis and Yarbrough, 1966]. In addition, an intermediate may be produced, like methanethiol or methanol, which sulfate reducers can oxidize to carbon dioxide. Nonetheless, the process is real and can consume much of the methane formed in certain habitats. Thus in meromictic Big Soda Lake, rates of anaerobic methane in the water column exceeded methanogenesis by several fold (Figure 7). In addition, at least 52% of the methane entering the water column from the bottom sediments was consumed by anaerobic oxidation, while only 0.07% and 5.2% was consumed by aerobic methanotrophs or escaped to the atmosphere, respectively [Iversen et al., 1987]. Similarly, about 43% of the methane entering the water column of meromictic Mono Lake was consumed by anaerobic oxidation [Oremland et al., 1987]. Anaerobic methane oxidation has been estimated to consume 3.0–5.2 × 10^{12} mol CH_4 yr^{-1} in oceanic sediments [Henrichs and Reeburgh, 1987]. The identification of the microorganism(s) involved in this process remains a challenge for future investigations.

Methane oxidation by natural systems can be quantified by straightforward methods. Chambers can be placed over soils, and methane uptake from the atmosphere monitored [Seiler et al., 1984b]. In studies of this type it is important to add an internal standard and to employ a specific inhibitor of methanotrophic bacteria as a control. This is even more crucial if there is a net outward flux of methane from the system. Two effective inhibitors suitable for such studies are methylfluoride and
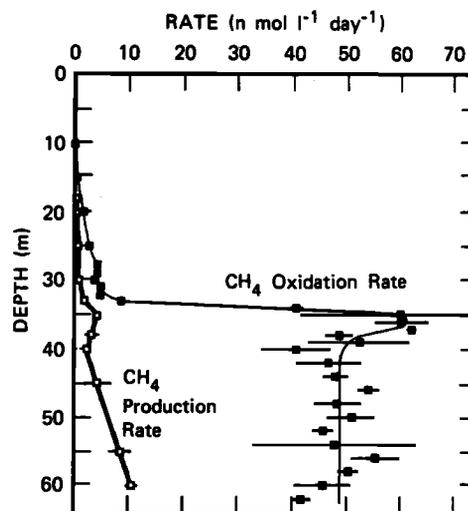
Fig. 7. Rates of methanogenesis and anaerobic methane oxidation in the anaerobic monimolimnion of Big Soda Lake, Nevada [from Iversen et al., 1987] (reproduced with permission of *Limnology and Oceanography*).

TABLE 1. Characteristics of Methane Found in the Earth's Crust

Source	$\frac{C1}{(C2+C3)}$	$\delta^{13}CH_4,$ $^o/_{oo}$	$\delta DCH_4,$ $^o/_{oo}$	$\Delta^{14}CH_4,$ % modern
Microbial (recent)	>>100	< −60	< −150	>>50
Microbial (gas deposit)	>>100	< −60	< −150	<<50
Thermogenic	<100	>> −50	> −275	<<20
Primordial	?	?	?	0

dimethylether [see Oremland and Capone, 1988]. Another common method for quantification of methane oxidation is the addition of $^{14}CH_4$ to natural samples followed by analysis of the $^{14}CO_2$ produced. This method is especially suitable for aquatic systems which have relatively large methane pools. Because the rate of methane oxidation by such systems frequently follows first-order kinetics with respect to methane [e.g., Harrits and Hanson, 1980; Iversen et al., 1987], the ambient methane concentrations must not be allowed to change significantly owing to the manipulation of the system. Furthermore, because impurities (for example, $^{14}CO_2$) are often present in commercially prepared $^{14}CH_4$, it is necessary to cleanse the tracer prior to its use.

4. STABLE ISOTOPES AND RADIOCARBON

Analysis of methane's stable isotopic composition ($^{12}C/$ ^{13}C and H/D), its radiocarbon content (^{14}C), and its abundance in relation to higher alkanes can yield clues as to its origin. These geochemical parameters have revealed that there are at least two different types of methane present in the Earth's crust: methane formed by bacterial gas evolution in anoxic ecosystems ("microbial methane") and methane formed during the thermocatalytic reactions ("thermogenic methane") that take place over geologic time in association with petroleum formation [Tissot and Welte, 1978; Hunt, 1979]. Included in the thermogenic category is methane which is formed by reduction of carbon dioxide by hydrogen occurring within hot basalts and which probably occurs at seafloor spreading centers [Welhan and Craig, 1979]. A hypothesized third source of methane may be derived from the mantle. Because methane is abundant on other planets in the solar system, it has been suggested that "primordial" methane from the original solar nebula may remain in the Earth's mantle and over time outgasses to the crust [Gold, 1979].

In general, microbial gases found in ecosystems are characterized by having methane enriched in ^{12}C, depleted in deuterium,and high in radiocarbon content, and have only traces of ethane and propane present relative to methane (Table 1). About 20% of the natural gas deposits are of microbial origin [Rice and Claypool, 1981]. Therefore bacterially formed natural gas deposits can be distinguished from recently formed bacterial methane only on the basis of their low radiocarbon content. In contrast, methane of thermogenic origin is characterized by ^{12}C depletion, an abundance of higher alkanes relative to methane, and insignificant radiocarbon content (Table 1). A number of papers and reviews have appeared which support and employ this overall scheme [Claypool and Kaplan, 1974; Fuex, 1977; Bernard et al., 1978; Bernard, 1979; Schoell, 1980, 1983; Claypool and Kvenvolden, 1983]. The hypothesized "primordial" methane is as yet only a concept and may not exist. Because a sample of unequivocally primordial methane has never been collected, no classification criteria exist, and therefore it cannot be distinguished from other types of methane [Oremland, 1983].

The basis for stable isotopic discrimination between microbial and thermogenic gases lies in the ability of methanogenic bacteria to enrich for the "lighter" isotope during methanogenesis [e.g., Rosenfeld and Silverman, 1959; Games et al., 1978; Fuchs et al., 1979; Oremland et al., 1982a; Belyaev et al., 1983; Krzycki et al., 1987]. A stable isotopic "scheme" has been proposed whereby methane formed from CO_2 reduction can be discriminated from that formed from methyl groups (for example, acetate, methylamines, etc.), owing to the latter's relative depletion of deuterium [Whiticar et al., 1986]. Plots of hydrocarbon relative abundances versus stable carbon isotopic content (Figure 8) and $^{13}C/^{12}C$ versus D/H ratios (Figure 9) are commonly used to identify sources. In complex situations where several sources of methane are present, use of stable isotopes, hydrocarbon abundances, and radiocarbon dating are all necessary in order to obtain a complete picture [Oremland et al., 1987].

The classification schemes given in Table 1 and Figures 8 and 9, however, should be viewed as generalities, and numerous exceptions can occur in nature. Microorganisms can greatly alter the geochemical "signals" associated with the primary source of hydrocarbon gases. It has been well established that aerobic methane-oxidizing bacteria will fractionate in favor of the light isotope [Silverman and Oyama, 1968; Coleman et al., 1981; Barker and Fritz, 1981], thereby leaving the residual, unoxidized methane enriched in ^{13}C. This also occurs with anaerobic methane oxidation [Alperin et al., 1988]. In some cases, isotopic shifts by oxidation of methane (aerobic and anaerobic) can be extensive enough to alter interpretation of the source (for example, thermogenic instead of microbial). This was found to occur in meromictic lakes (Figure 10); [Oremland and Des Marais, 1983; Oremland et al., 1987], but appears to be associated with more common ecosystems as well [Chanton et al., 1988]. Considerable seasonal variability
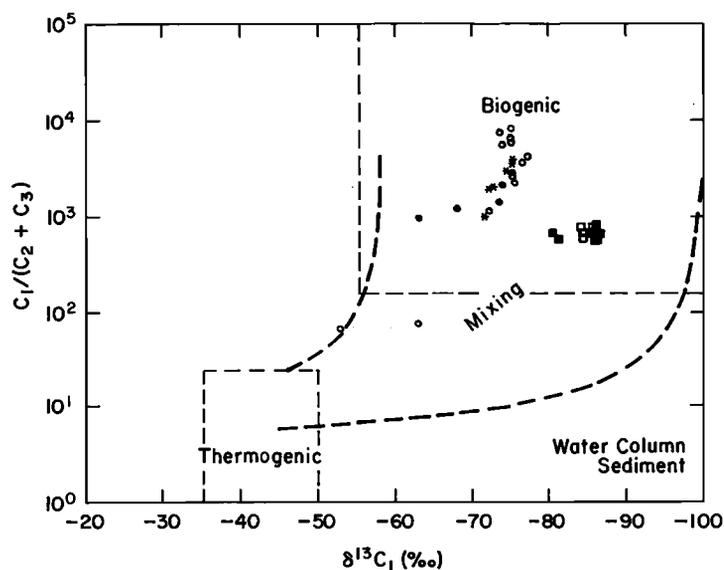
Fig. 8. Methane extracted from the anoxic water volumn and sediments of Mono Lake, California and classified by the criteria of stable carbon isotopic composition $(\delta^{13}CH_4)$ and methane/(ethane + propane) ratios [from Oremland et al., 1987] (reproduced with permission of *Geochimica et Cosmochimica Acta*].

has been observed in the stable carbon and hydrogen isotope ratios for methane bubbles and Cape Lookout Bight sediments [Martens et al., 1986; Burke et al., 1988]. These variations reflect not only the effects of methane oxidation, but changes in the isotopic signature of substrates like acetate as well [Blair et al., 1987].

Another microbial complication of the scheme in Table 1 is the ability of anaerobic bacteria to produce ethane and higher alkanes [Davis and Squires, 1954; Vogel et al., 1982]. In the case of ethane, methanogenic bacteria are the causative agents [Oremland, 1981], and evolve ethane from the metabolism of compounds like diethylsulfide or ethanethiol [Oremland et al., 1988]. In some environments the quantity of microbially produced n-alkanes can approach the transition value for discriminating thermogenic from microbial gas [Vogel et al., 1982; Oremland and Des Marais, 1983; Oremland et al., 1987; Oremland et al., 1988]. Biogenic ethane can exhibit ^{13}C-depleted values of $\delta^{13}C_2H_6$, however the formation of ethane from its immediate precursors involves only a small fractionation effect, implying that fractionation occurs earlier in the pathway of ethanogenesis [Oremland et al., 1988].

When methane enters the atmosphere it carries the isotopic information, if any, of the source. The destruction of atmospheric methane by gas phase hydroxyl radicals is selective for the lighter isotopes of carbon and hydrogen; other possible methane sinks may also fractionate. Thus by measuring an isotopic ratio in atmospheric methane along with the isotopic shift in the atmospheric destruction processes, one can deduce the isotopic ratio of the total source; more generally, if two of these quantities are determined, the third is constrained.

For the stable carbon isotope ^{13}C there are now enough data to allow us to begin to infer constraints on the budget of atmospheric methane (see also section 5). The

δ^{13}C value for atmospheric methane has been measured to be about $-47^o/_{oo}$ (parts per thousand compared to the $^{13}C/^{12}C$ ratio in PDB carbonate) in air samples gathered between 1980 and 1985 [Stevens and Rust, 1982; Tyler, 1986; Stevens and Engelkemeir, 1988]. This value is shown as the dashed vertical line in Figure 11. The carbon kinetic isotope effect in the attack of OH on CH_4 is such that $k_{12}/k_{13} = 1.010$ ($\pm$ 0.007) according to Davidson et al.
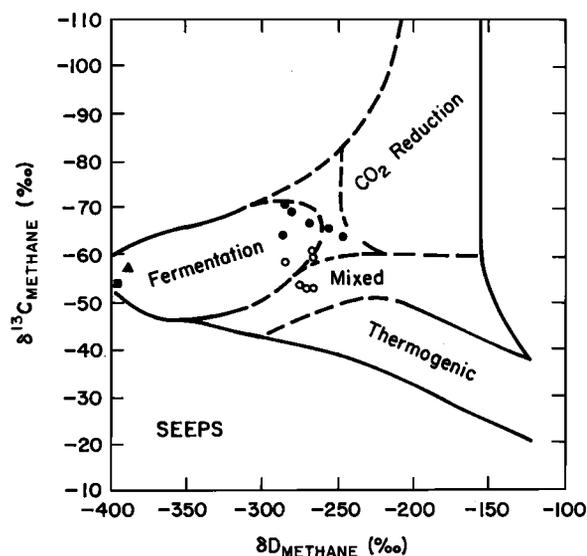
Fig. 9. Classification of natural gases collected in Mono Lake as determined by stable carbon and hydrogen ratios [from Oremland et al., 1987] (reproduced with permission of *Geochimica et Cosmochimica Acta*).
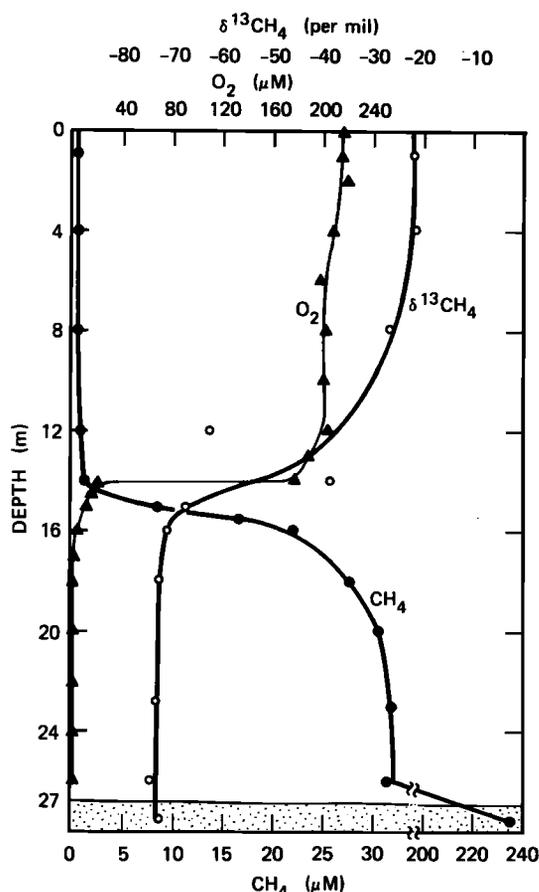
Fig. 10. The enrichment of ^{13}C in the epilimnion $\delta^{13}CH_4$ values in Mono Lake caused by aerobic methane oxidation [from Oremland et al., 1987] (reproduced with permission of *Geochimica et Cosmochimica Acta*).

[1987] where k_{12} is the reaction rate constant for

$$OH + {}^{12}CH_4 \xrightarrow{k_{12}} H_2O + {}^{12}CH_3$$
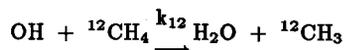
and k_{13} is defined analogously. This implies that the globally averaged total source of methane has a $\delta^{13}C$ of $-57^o/_{oo}$. Several assumptions are involved here: that the spatial pattern of methane sources and sinks is identical and that steady state applies. To estimate the relation between the $\delta^{13}C$ of atmospheric methane and the sources more accurately would require a detailed model of atmospheric transport and chemistry. The $\delta^{13}C$ values for a variety of methane sources are also shown in Figure 11. Generally, the methane released from microbiological processes and the carbon in biogenic methane pools are lighter than atmospheric methane, i.e., $\delta^{13}CH_4$ more negative than $-47^o/_{oo}$, and the methane from abiogenic and high-temperature sources is heavier. Methane from biomass burning has recently been found to have a $\delta^{13}C$ of between $-24^o/_{oo}$ and $-32^o/_{oo}$ [Wahlen et al., 1987; Stevens and Engelkemeir, 1988], not far different from the central value for C stored in plants shown in Figure 11.

(Note: for original references for the data of Figure 11, see Tyler [1988].) Thus there are sources of methane that lie to the left and to the right of the $\delta^{13}C$ value of atmospheric methane, but it is not yet clear that a definitive ^{13}C-weighted source budget can be constructed. For example, there are broad disagreements between the $\delta^{13}C$ for methane from rice paddies; Stevens and Engelkemeir [1988] report $-67^o/_{oo}$; Wahlen et al. [1987], $-63^o/_{oo}$; and Tyler et al. [this issue], -57 to $-63^o/_{oo}$. In reality the ^{13}C content of rice paddy methane may vary with time during the growing season.

New evidence from methane extracted from dated ice cores shows that the $\delta^{13}C$ of atmospheric methane was $-49.6^o/_{oo}$ or about two per mil more negative than in the 1980s [Craig et al., 1988]. The ice in these analyses was 100 to 350 years old but the enclosed air was younger (from 10 to 100 years younger depending on the date of firn closure). If the enclosed air was, say, 50 years younger than the ice, then atmospheric methane is now about two per mil lighter in ^{13}C than it was between 50 and 300 years ago. This change could be due to (1) increased sources of heavy methane (for example, biomass burning and usage of thermogenic natural gas), or (2) decreased sources of biogenic methane or (3) different past fractionation of the sink of atmospheric methane. The first possibility is the most likely, while the third would require that there is another important sink besides atmospheric OH.

There are some indications that $\delta^{13}C$ for contemporary atmospheric methane is changing with time; see discussions by Senum and Gaffney [1985] and Stevens and Engelkemeir [1988]. Although these discussions have been discouraging in that they have deduced temporal trends of $\delta^{13}C$ opposite in sign, it is to be hoped that as data accumulate and they are screened more carefully for comparability, temporal trends or their absence can be determined.

It is conceivable that uptake by soil microbes (see section 5) affects the $\delta^{13}C$ of atmospheric methane, presumably by selectively oxidizing $^{12}CH_4$. In principle, this probably occurs, but its importance depends on the strength of this methane sink globally.

The deuterium content in atmospheric methane has been measured recently by Wahlen et al. [1987]; $\delta D = -80(\pm 8)^o/_{oo}$ relative to standard mean ocean water (SMOW). A few earlier measurements were summarized by Senum and Gaffney [1985]. Pools of methane from sediments, gas deposits, sewage, and other origins have been analyzed for D/H ratios (presumably the CH_3D/CH_4 ratios) by Schoell [1980] and Burke and Sackett [1986]. Biogenic methane exhibits δD values of about $-300(\pm 40)^o/_{oo}$; more positive values in this range (and up to $-180^o/_{oo}$) correlate with environments where surrounding water is heavy and with methane whose origin is CO_2 + hydrogen. Burke and Sackett [1986] and Senum and Gaffney [1985] have noted the need for more data on atmospheric methane before δD can become a very useful constraint on the budget. It is also necessary to improve our knowledge of the reaction rate for OH + CH_3D.

There appear to be no data on natural background amounts of CH_2D_2, CHD_3 or CD_4. Although their concentrations should be very small, their information content would be very high. Microbial sources would be very light
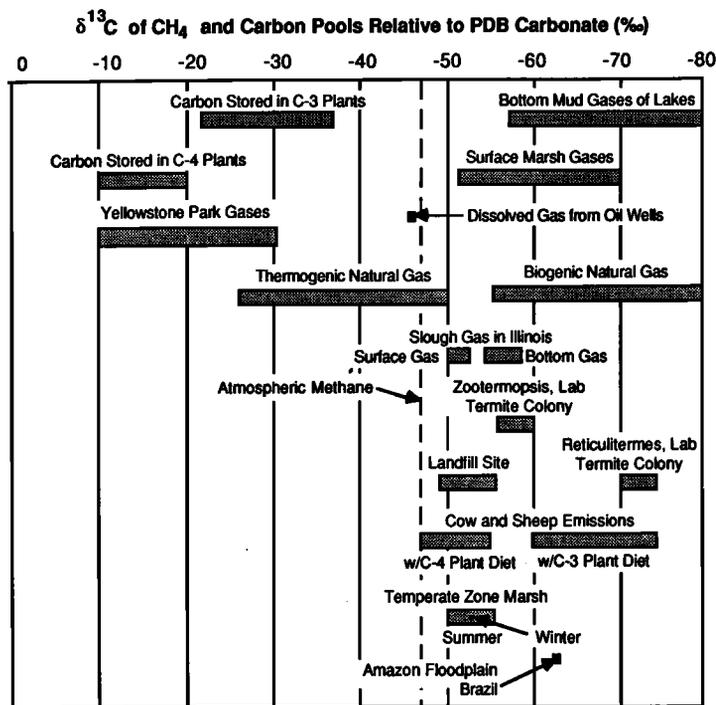
Fig. 11. The δ^{13}C of methane and of carbon from various environmental pools, relative to PDB carbonate ($^o/_{oo}$). Values for sources of methane appear as bars showing range of measured values or single points from individual measurements. Atmospheric methane appears as a vertical dashed line at $-47^o/_{oo}$. Air from dated ice cores exhibits a δ^{13}C of methane of $-49.6^o/_{oo}$ for ice core ages between 100 and 300 years [Craig et al., 1988]. (Adapted from Tyler [1988] where references to original studies appear, with the permission of Springer-Verlag Publishers.)

isotopically, while high-temperature sources should display larger D/H ratios similar to natural isotopic abundances.

As to the radioisotopes ^{14}C and T, ^{14}CH$_4$ data are discussed in section 5. The tritium content of atmospheric methane has been artificially high at least since 1953, owing either to nuclear weapons testing or nuclear industry leaks, or both [see Begemann and Friedman, 1968, and references therein].

5. SOURCES AND SINKS OF ATMOSPHERIC METHANE

There are purely scientific reasons and practical motivations for trying to obtain a quantitative understanding of atmospheric methane amounts and fluxes. Qualitatively, one can argue plausibly that atmospheric methane is increasing simply because certain identified methane sources are growing. But with methane concentrations continuing to increase, it has become more important to learn the relative and absolute sizes of methane sources and sinks, the extent of human influence, and the prospects for human intervention. How accurately can we hope to determine key quantities in the budget of atmospheric methane, for example, annually averaged total sources and sinks, or annual inputs from individual sources? How well do we know such quantities now? In this section we identify the con-

straints and types of data that can be used to place more or less accurate limits on key quantities. From these constraints we derive a candidate budget of methane sources that is as objective as possible.

Data That Constrain Theories

We begin by examining data (Table 2) on atmospheric methane amounts, residence time (often called lifetime or turnover time), and rates of change. Additional data and references appear in Table 3. In quasi-steady state (defined in the appendix) the total atmospheric burden, B, of CH$_4$ is related to the annual source, Q, and the atmospheric residence time, r, for CH$_4$ through

$$B = Qr \qquad (1)$$

For more general equations see the appendix. B is known accurately (probably within 3%) through direct measurements of CH$_4$ at the surface and of its variations with latitude and altitude (from aircraft and balloons) and total column (infrared absorption) data. A 9.6-year residence time and B from Table 2 lead us to a value of Q = 500 × 10^{12} g CH$_4$/yr. A range of r values from 8.1 to 11.8 years implies that

$$Q = 500(\pm 95) \times 10^{12} \text{ g CH}_4/\text{yr} \qquad (2)$$

TABLE 2. Summary of Data for Atmospheric Methane Concentrations, Atmospheric
Residence Time, and Budget Data

Parameter	Value
Tropospheric mole fraction, ppm	
Global average	1.68
Northern hemisphere average	1.72
Southern hemisphere average	1.64
Total atmospheric burden	3×10^{14} mol or
	4.8×10^{15} g
Residence time, years	
Computed value	9.6
Range	8.1 to 11.8
Quasi-steady state source	
(or sink), g/yr	
Computed value	500×10^{12}
Range	$(405 \text{ to } 595) \times 10^{12}$
Rate of increase	14 to 16 ppb/yr, or
	$(40 \text{ to } 46) \times 10^{12}$ g/yr, or
	0.8 to 1.0%/yr
Modern biogenic portion of source	70% to 90%

Global average mole fraction is for September 1987 from Blake and Rowland
[1988]. Residence times are from Prinn et al. [1987]. Rates of increase are from
Blake and Rowland. The quasi-steady state source figure is derived from 1980s
data on methane amounts and residence time (see Table 3).

This quantity Q represents the total annual source needed to maintain the observed atmospheric burden, B, in near-, or quasi-steady state in the 1980s. The annual increase in B of about 43×10^{12} g CH_4 could be due either to a larger than steady state source or to a decreasing annual sink, or both.

This value for Q in (2), based as it is on accurately measured methane amounts and on τ values from independent information, is a strong constraint on the methane budget (see Table 3 and references therein). The value of this constraint is high because of the objective basis for it. Whatever the identities of individual methane sources, they must sum to Q, and in steady state the total of all methane sinks must also equal Q. Briefly, the τ for CH_4 derived by Prinn et al. [1987] and Mayer et al. [1982] is based on independently deduced τ values for the synthetic chemical trichloroethane and the fact that the reaction $C_2H_3Cl_3$ + OH is the dominant sink for $C_2H_3Cl_3$. From the ratios of the reaction rate constants for OH attack on CH_4 and $C_2H_3Cl_3$, the fact that most CH_4 and $C_2H_3Cl_3$ is released in the northern hemisphere, and the known amounts and rates of change of atmospheric $C_2H_3Cl_3$, a reasonably accurate τ can be derived for CH_4 from that for $C_2H_3Cl_3$.

The $^{14}CH_4$ data provide another constraint, but some terminology must be made clear before proceeding. Methane that is radiocarbon free can be either (1) fossil methane of biological origin, or (2) abiogenic methane. When appreciable amounts of ^{14}C are present this could be either (1) recently produced biogenic methane or (2) abiogenic, from pressurized water reactors (see below). For our purposes it is necessary to distinguish between all of these. We will refer to methane from biological sources

whose ^{14}C age is zero to 200 years as "modern biogenic methane." For biogenic methane whose ^{14}C content is less, but still enough to permit dating (ages less than 50,000 years or so) we will refer to "old biogenic methane." "Dead carbon methane" will refer to CH_4 with no radiocarbon content without regard to thermogenic or biogenic origin, for example, natural gas. Until now, only two terms have been used, basically to distinguish between methane from industrial sources (with zero ^{14}C), and from living organisms (with ^{14}C ages near zero).

In earlier studies of the ^{14}C content of atmospheric methane the fraction of the total sources that is biogenic (defined as the carbon having been in recently living organisms) has been deduced. The earliest $^{14}CH_4/^{12}CH_4$ measurements (pre-1960) were simpler to interpret (see Table 3 and Ehhalt [1974]); they imply that about 85 to 90% of the total source was of recent biological origin. Note, however, that about 30 years (three residence times) have elapsed since the measurements. Significant changes in source sizes may have occurred since the late 1950s. More recent $^{14}CH_4/^{12}CH_4$ measurements are difficult to interpret because of the (1) bomb-produced ^{14}C placed in the atmosphere circa 1960 that is still passing through biota and sediments and (2) $^{14}CH_4$ that is released from pressurized-water type nuclear reactors [see Wahlen et al., 1987; Lowe et al., 1988; Levin et al., 1980; Kunz, 1985]. The early radiocarbon methane data led Ehhalt to deduce that 90% of total methane sources were biogenic, while Lowe et al. [1988] estimate that perhaps only 68% of the present source flux is biogenic. Lowe et al. employed recent $^{14}CH_4$ data and $^{13}CH_4$ data and adopted several time constants that are somewhat uncertain. With an expanded

TABLE 3. Summary of Key Rates, Amounts and Fluxes of Atmospheric Methane in Late 1987

Variable	Indicator	Strength of Constraint
Total amount[a] $= 4.8 \times 10^{15}$ g	Direct measurements	H
Spatial distribution[a]	Direct measurements	H
Rate of change[b] $= 0.9\%$/yr	Measured time series from independent workers	H
Residence time[c] $= (10\pm2)$ years	$C_2H_3Cl_3$ data with atmospheric model	H
Residence time[d] $= 14$ years	Atmospheric photochemistry and transport model	M
Total steady state source or (sink)[e] $= (500\pm100) \times 10^{12}$ g/yr	Divide atmospheric burden by 9.6-year residence time	H
Total steady state source or (sink)[d] $= 320 \times 10^{12}$ g/yr	Atmospheric photochemistry and transport model	M
Total steady state source[f] $= (300$ to $1200) \times 10^{12}$ g/yr	Addition of various known sources	L
Total steady state sink[g] $= (300$ to $650) \times 10^{12}$ g/yr	Atmospheric models and soil sink estimates	M
Fraction of source that is modern biogenic[h] 90% 75%	pre-1960 ^{14}C data 1985–1987 ^{14}C data	H
Fossil sources plus biomass burning[i] contribute $<40\%$ of total	$^{13}C/^{12}C$ ratios in air and sources	M
Portion of CH_4 increase due to decreasing OH[j] $= 10$ to 40%	Atmospheric models	L

Indicators or constraints that lead to each estimated quantity are given, along with a measure of the strength of each constraint: H, high value of constraint; M, medium value; L, low value.

[a]Methane amounts and their spatial and temporal variations have been measured by Blake and Rowland [1988], Steele et al. [1987] and others. Variations with altitude are reported by Ehhalt and Heidt [1973], Ehhalt et al. [1975], Fraser et al. [1984], and others [see World Meteorological Organization, 1985, chap. 9].

[b]See Blake and Rowland [1988] and Steele et al. [1987]. Also see Rasmussen and Khalil [1984] and Craig and Chou [1982] for methane contents of dated ice cores and Rinsland et al. [1985] for an analysis of infrared absorption data from 1951 and deduced methane amounts.

[c]Because the principal sink for anthropogenic $C_2H_3Cl_3$ is tropospheric OH, and because its sources are reasonably well known, its measured spatial distribution and temporal trend can be used to deduce the atmospheric residence time for CH_4, at least for the epoch of the data [see Prinn et al., 1987; Mayer et al., 1982; Ehhalt, 1978].

[d]In a global two-dimensional (latitude and altitude) model of atmospheric photochemistry and transport one can calculate losses of CH_4 due to model-predicted OH fields. With a specified CH_4 distribution and calculated OH, the distribution of sources with latitude can be deduced, as can the residence time for CH_4. See Crutzen and Gidel [1983], Chameides and Tan [1981], and note e.

[e]In steady state, in the sense of global and annual averages, source = sink, and total atmospheric amount = source × (residence time). See also appendix.

[f]There are relatively few methane source inventories that employ estimates of individual sources without also constraining the total of all sources [see Ehhalt, 1974; Sheppard et al., 1982].

[g]See notes c and d and soil sink estimates by Seiler and Conrad [1987].

[h]Ehhalt [1974] reviewed pre-bomb test data (1949–1960) on ^{14}C in atmospheric methane and concluded that over 80%, perhaps 90%,of atmospheric methane was of recent biological origin. From new ^{14}C data and ^{13}C data, Lowe et al. [1988] conclude that the corresponding figure for 1986–1987 is only 70%, Wahlen et al. [1987] give 75 to 85% and Manning et al. [1988] give 74%.

[i]The use of $^{13}CH_4/^{12}CH_4$ ratios from atmospheric methane and its sources as a constraint on the size of various methane sources is just beginning (see discussion in the text, sections 4 and 5).

[j]The nonlinearity in the atmospheric chemistry of CH_4, CO, and OH has been modeled by Thompson and Cicerone [1986], Isaksen and Hov [1987], and others earlier. Tropospheric NO_x amounts strongly affect the analysis.

data set, Manning et al. [1989] revised this figure to be 74%. With the 90% figure, and the value of Q from constraints discussed above, the total of all "modern biogenic" sources is 450($\pm$ 80) $\times$ 10^{12} g CH$_4$/yr, or 350($\pm$ 65) $\times$ 10^{12} g CH$_4$/yr if a 70% figure is assumed.

Further, the knowledge that atmospheric methane concentrations are increasing worldwide at a rate of 0.9($\pm$ 0.1)%/year is solid (see Tables 2 and 3 and references). The departure from steady state, i.e., imbalance between sources and sinks, is 43($\pm$ 5) $\times$ 10^{12} g CH$_4$/yr, with relatively high confidence.

In our judgement the constraints on methane budget quantities just discussed, i.e., those that appear in Table 2, are the strongest ones today, for reasons outlined in Table 3 and references therein. There are additional looser or weaker constraints on the same quantities that are listed in Table 3, and there are separate facts that place constraints on other quantities. For example, field experiments have been used to estimate the strength of the soil sink of CH$_4$ and numerical models of atmospheric transport and of atmospheric OH fields have led to estimates of the consumption of CH$_4$ by OH on an annual basis and also by time of year, latitude, and altitude (see Table 3, particularly note g). Guided by these strongest constraints, one can proceed to add information from field experiments on individual identified sources and from models and to construct a candidate methane budget.

A Methane Budget Derived From Constraints

Now we attempt to construct a list of methane sources and sink sizes that is based as far as possible on the available constraints, or at least does not violate constraints.

Table 4 presents a candidate list of methane sources to the atmosphere, as annual release rates, with a likely but not definite range for each source. The total annual source is constrained to be 540 $\times$ 10^{12} g CH$_4$/yr (the quasi-steady state source of 500 $\times$ 10^{12} g CH$_4$/yr plus 40 $\times$ 10^{12} g CH$_4$/yr of annual growth in sources). The likely range is similarly constrained to be (400–640) $\times$ 10^{12} g CH$_4$/yr, even though a simple addition of the possible high figures for each individual source would lead to a much larger number.

Before discussing each entry in this table we note that 80 $\times$ 10^{12} g CH$_4$/yr would have no ^{14}C content. These dead carbon sources would represent 15% of the total, near the low end of the range of Wahlen et al. [1987], but see the extended discussion below in which we suggest a potentially larger role for methane from hydrates and for ^{14}C-depleted methane from wetlands and peatlands. The loose constraint due to present ^{13}C data (see Table 3 section 4) is also obeyed. The fact that the atmospheric ^{13}CH$_4$/^{12}CH$_4$ ratio has increased in the last 50 to 100 years [Craig et al., 1988] probably means that ^{13}C-rich sources have increased with time more rapidly than ^{13}C-poor sources (see Figure 11).

The yearly source from enteric fermentation in ruminant animals, including all cattle, sheep, and wild animals, is taken as 80 $\times$ 10^{12} g CH$_4$/yr from Crutzen et al. [1986], whose best estimate is 78 $\times$ 10^{12} g CH$_4$/yr for 1983. Factors such as variations in methane release from cattle due

to differences in diet type, food amounts, and age of cattle were considered by Crutzen et al., but uncertainties remain. Generally, the higher the quality of the food, the lower the fractional release of methane [Hungate, 1966], but further work is needed to establish more confidence in the methane yields adopted by Crutzen et al. Similarly, animal population data, such as those from the United Nations Food and Agriculture Organization must be verified and improved. Our stated likely range for this methane source is higher on the high side than the Crutzen et al. [1986] range by about 12 Tg CH$_4$/yr. Past values for this source could have been very different because of large populations of North American buffalo (circa 1850 A.D.) and of elephants and smaller populations of domesticated ruminants. Crutzen et al. [1986] have estimated that the methane release from domestic ruminants, principally cattle and sheep, has increased more than a factor of four since 1890. In recent years the rate of increase has been about 1% per year.

The entry of 115 $\times$ 10^{12} g CH$_4$/yr in Table 4 for natural wetlands is essentially that of Matthews and Fung [1987]. Their study of wetland types and areas and of ecological classification schemes led them to employ five major wetland groups: forested and unforested bogs (includes peat bogs), forested and unforested swamps, and alluvial formations. We mention tundra separately in Table 4, although Matthews and Fung included tundra in unforested bogs. Although their estimates of the area of wetlands worldwide was almost double that from earlier estimates, Matthews and Fung deduce a lower value for this global methane source than did previous workers. Their estimate was based on much more field data than earlier estimates, using data that have become available recently such as those from Sebacher et al. [1986], and Harriss et al. [1985] and their ecological classifications are more thorough. Thus we adopt their estimates, after adding 4 $\times$ 10^{12} g CH$_4$/yr to allow more emphasis on tundra. The range in Table 4, (100 to 200) $\times$ 10^{12} g CH$_4$/yr, is our own and it is not well justified objectively.

Methane emissions from all of the natural wetland groups deserve a great deal of attention, and revisions to the figures in Table 4 could be required. For example, a recent experimental study of temporal patterns of methane fluxes from tundra [Whalen and Reeburgh, this issue] uncovered great seasonal and diel variability, as well as great variability between sites. Ecological classification schemes and global area estimates for wetlands require further refinement (see, for example, I. Aselmann and P. J. Crutzen (Freshwater wetlands: Global distribution of natural wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions, submitted to *Journal of Atmospheric Chemistry*, 1988; hereinafter Aselmann and Crutzen (1988)). For example, in the Whalen and Reeburgh study, more emphasis was placed on drier tundra than was given by Matthews and Fung. Natural variability of many kinds influences the methane release rates from wetlands. Soil water levels, temperatures, and possible seasonal variations in methanogenic pathways are already identified as important variables [Svensson, 1984; Sebacher et al., 1986; Harriss et al., 1985; Martens et al., 1986]. Also, as outlined below, the possibility that peat-

TABLE 4. Annual Methane Release Rates for Identified Sources

Identity	Annual Release 10^{12} g CH_4	Range, 10^{12} g CH_4	HEDC, 10^{12} g CH_4
Enteric fermentation (animals)	80	65–100	0
Natural wetlands (forested and nonforested bogs, forested and nonforested swamps, tundra and alluvial formations)	115	100–200	33
Rice paddies	110	60–170	0
Biomass burning	55	50–100	0
Termites	40	10–100	0
Landfills	40	30–70	0
Oceans	10	5–20	1
Freshwaters	5	1–25	0
Methane hydrate destabilization	5?	0–100 (future)	5?
Coal mining	35	25–45	35
Gas drilling, venting, transmission	45	25–50	45
Total	540	400–640	119

This candidate list obeys the constraints derived in the text, but it could be revised as stronger constraints develop. Table entries and references are discussed in the text. "HEDC" represents hypothesized equivalent dead carbon methane.

lands are releasing significant amounts of ^{14}C-depleted methane needs to be investigated.

Rice paddies appear in Table 4 as a major methane source; numerical values are essentially from Holzapfel-Pschorn and Seiler [1986] but are lower by about 10%. The great potential for methane release from rice fields has long been noted [Koyama, 1964; Ehhalt, 1974], but no field measurements were reported before Cicerone and Shetter [1981], who discovered the importance of methane transport through the plants as opposed to diffusion and bubble transport across the water-air interface. Cicerone et al. [1983] reported a strong time-of-season dependence of methane release rates. Both of these effects were confirmed by Seiler et al. [1984a] and Holzapfel-Pschorn and Seiler [1986] in their extensive studies. Many factors control or influence methane production and release rates in rice growing. These include agricultural practices, time of season, irrigation, and soil properties, both physical and chemical. The methane release rates displayed in Table 4 will not be easily improved upon; field studies must recognize numerous possible sources of variation, the possibility of bubble transport, and rapid variations in methane escape rates. Isotope studies could be very useful. It is clear that the effective area of land used for rice growing is increasing with time, partly due to multiple cropping permitted by irrigation and partly due to cultivation of new land areas. Holzapfel-Pschorn and Seiler [1986] have estimated (largely with United Nations Food and Agricultural Organization data) that the effective area used worldwide for rice growing has increased at an annual rate of 1.6% since about 1940. Presumably, the total methane flux from rice paddies has increased proportionately.

Biomass burning has not yet been well quantified as a methane source. The numbers in Table 4 are in the range estimated by Crutzen [1987] and Seiler [1984]; objective evidence is not compelling one way or the other. Esti-mates to date have recognized the large uncertainties and sources of variability: types of burning, moisture content of vegetation, and amounts of biomass that are burned annually. As with many processes, the ratios of CH_4 to CO_2 (and CO) and of CH_4 to total C burned are important to measure. More accurate estimates will require a great deal of experimental work. Biomass burning may yield $^{13}C/^{12}C$ ratios close to those in the living material [Wahlen et al., 1987; Stevens and Engelkemeir, 1988], and it should also be as rich in radiocarbon as the living material was. Although it is believed widely that forest clearing rates (by burning) have increased in recent years, we know of no quantitative trend data.

Termites are listed in Table 4 as a source of 40 × 10^{12} g CH_4/yr with a factor of 10 width in the likely range, from (10 to 100) × 10^{12} g CH_4/yr. The enormous potential of this source was pointed out by Zimmerman et al. [1982], who also performed quantitative laboratory experiments. Significant disagreements have arisen in the extrapolation of these results (see, for example, Seiler et al. [1984b] and Zimmerman et al. [1984]). Difficult ecological evaluations must be performed to better quantify this source: termite populations, amounts of organic material consumed by termites in various biomass, species differences, and activity of methane-oxidizing bacteria.

The possible role of anaerobic decay of organic wastes in landfills and dumps has been growing in recent years [Bingemer and Crutzen, 1987]. We adopt a figure of 40 × 10^{12} g CH_4/yr as the present annual global methane source, toward the low end of the Bingemer and Crutzen range. Several factors require more exploration: amounts of waste material and trends, types of waste material and dependence on landfill practice (for example, shredding and covering), and age and the role of methane oxidizers and methane burning.

Research conducted in the late 1960s and early 1970s

established that the surface waters of the world's ocean represented only a minor source of methane to the atmosphere [see Ehhalt, 1974, and references therein]. Thus the open oceans were slightly supersaturated with methane in relation to its partial pressure in the atmosphere, but because of this region's distance from any sediment influence, the source of this methane was not clear. The common observation of subsurface methane maxima suggested an in situ source in the oxic pelagic waters [Scranton and Brewer, 1977; Traganza et al., 1979; Brooks et al., 1981; Burke et al., 1983]. Oremland [1979] suggested that this methanogenesis occurs within the anaerobic gastrointestinal tracts of marine zooplankton and fish. A proper estimate of the release rate of methane should include not only representative open ocean areas (for example, productive and unproductive), but also coastal regions where the influence of methane from the sediments and drainage (for example, rivers) is stronger. In addition, the quantity of methane oxidized by bacteria in the open ocean surface and intermediate waters is not known, but examination of methane profiles suggests that oxidation in these regions occurs rapidly and results in significant methane undersaturation in the older, deeper waters [Scranton and Brewer, 1978]. To achieve an updated oceanic methane release estimate, extensive sampling of marine surface waters should be undertaken, since very few results have been published beyond those which Ehhalt [1974] drew upon. Methane emissions from oceans in Table 4 are essentially Ehhalt's estimates, based on representative measured supersaturations of seawater of about 30% with respect to air. These data date from circa 1970, when there was probably 15–20% less atmospheric methane. Thus the flux of methane from ocean to atmosphere could have decreased substantially in recent years; it could even reverse sign in the future, as R. Gammon has noted (private communication, 1988). We do not reduce Ehhalt's estimates, however, so as to allow for a possibly larger contribution from more highly supersaturated waters near coasts and elsewhere. Cline et al. [1986] have shown experimentally that nearshore and shelf waters (Bering Sea) could contribute as much methane as open waters and that seasonal variations must be recognized. At present, the discussion is data-poor. In Table 4, freshwaters (rivers, lakes) is a category that has received little attention, these values are from Ehhalt [1974]. Large uncertainties surround these numbers, as the likely range indicates.

Methane hydrates are solid structures, composed of rigid cages of water molecules that surround methane molecules. Large amounts of methane are probably stored in sediments as methane hydrates. The pressure and temperature regime for stability and other factors imply that these hydrates are most prevalent at depth under permafrost and beneath the sea on continental margins [Kvenvolden, 1988]. The possibility that a climatic warming could destabilize methane hydrate deposits and release great quantities of methane has been raised by several reports [e.g., MacDonald, 1982]. How much methane is escaping from these formations now? How much more could escape as a global climatic surface warming penetrates downward, destabilizing nonstable hydrates? Kvenvolden [1988] has reviewed relevant data and theories. Significant questions

include the environmental distribution and origins of hydrates and thus the amounts of gas in the hydrates and the fraction of all the hydrates that are located in layers and in stable thermal environments that are insulated from climate change. Kvenvolden notes that Arctic region hydrates may be vulnerable to a warming and that there is some evidence that hydrates in coastal permafrost are decomposing. He estimates that the expected global warming in the coming century could release 130×10^{12} g CH_4/yr, lesser amounts than had been estimated by others. Kvenvolden did not provide estimates of present annual release rates. Our (questionable) figure of 5×10^{12} g CH_4/yr is not much more than a placeholder; the range of up to 100×10^{12} g CH_4/yr is from Kvenvolden for a warmer Earth. In principle, there is a clear possibility of future atmospheric methane increases due to methane hydrate destabilization, but the size of the effect needs better quantification.

Along with methane hydrate destabilization the other sources that would certainly be radiocarbon-free CH_4 in Table 4 are losses from coal mining and natural gas exploration and distribution. Our knowledge of these sources is poor, and it raises difficulties with the constraint that 15–30% of the total source must be free of ^{14}C. There are very few if any published data on methane releases from coal mining operations; the estimate of Seiler [1984], 30×10^{12} g CH_4/yr for 1975, is traceable to Koyama's [1964] figures, extrapolated to higher coal production rates. In Table 4 our entry of 35×10^{12} g CH_4/yr and the likely range follow from these previous investigations and Ehhalt [1974], and not from new data. For losses due to natural gas exploration and transmission, the state of our knowledge is also unsatisfactory. Previous estimates from Ehhalt [1974], Sheppard et al. [1982], Seiler [1984], and Crutzen [1987] appear to have used figures for annual production of natural gas and assumed loss rates of 2–4% to account for gas escape from transmission networks. Loss figures such as these are usually from industrial representatives who mean them to include all unaccounted for gas, the difference between gas purchased for delivery and gas that is sold. This difference certainly includes losses through leaks, but also metering errors and theft. Unaccounted for gas is typically 2 to 2.5% of total production for the United States, but such figures are poorly documented. Other factors that have not been considered previously are emissions of gas from oil exploration and recovery, and from venting and incomplete flaring at gas wells and losses due to explosive events. Also, natural gas is not all CH_4, but is typically 89 to 93%. Our figure, 45×10^{12} g CH_4/yr in Table 4, obtains from an assumed loss of 2.5% of total production for the early 1980s, plus 14×10^{12} g CH_4/yr to account for unburnt CH_4 in flaring and venting [Marland and Rotty, 1984], underwater venting from offshore production platforms [Sackett and Barber, 1988], and other stray and explosive losses. Methane released from coal mining and natural gas usage has increased in recent years. Seiler [1984] estimates from natural gas usage data that this methane source increased by 600% from 1950 to 1975 while the source due to coal mining increased 50% in the same period.

Our total for the previously identified dead carbon

methane sources in Table 4 is 80×10^{12} g CH_4/yr. These sources are coal mining and gas usage. This value of 80×10^{12} g/yr is only 16% of the quasi-steady source (500×10^{12} g CH_4/yr) for the 1980s, or 15% of the total source in Table 4. There is no clear evidence that methane escaping from coal mining, from the natural gas industry, or from the new entry, hydrate formations, exceeds the quantities in Table 4, but it is possible. Our concern is that the Lowe et al. [1988] and Manning et al. [1989] analyses, based on radiocarbon and ^{13}C amounts, suggest that the dead carbon fraction of contemporary methane sources is about 30%, or twice that of Table 4. Several explanations are possible: (1) the ^{14}C-free sources identified in Table 4 are being underestimated, (2) certain biogenic sources, for example, wetlands and peatlands, are releasing some old biogenic methane (^{14}C ages up to 50,000 years or even more), (3) there are additional dead carbon sources, for example, more venting of natural gas from offshore underwater gas production platforms (5×10^{12} g/yr are assumed in Table 4) and possible methane release from asphalt exposed to sunlight [Sackett and Barber, 1988], and (4) escape of abiogenic primordial methane along fault lines [Gold, 1979]. The $^{14}CH_4$ data do not permit the Gold source to be very large, at least during the last 30 years. The possibility that all of the above candidates are contributing up to 50×10^{12} g CH_4/yr in addition to the amounts shown in Table 4 should be investigated. Another possibility is (5) that the modern biogenic sources in Table 4 (including biomass burning, by definition) and the total of all sources are too large (see total source budget of Crutzen [1987] and Seiler and Conrad [1987], for example).

To highlight the second possibility we hypothesize that some of the methane escaping from peat formations and boreal wetlands is old biogenic methane or even dead carbon methane. In Table 4 we suggest that 33×10^{12} g/yr of effectively dead CH_4 exits natural wetlands predominantly from peatlands and other boreal wetlands rich in old organic matter. The heading "HEDC" in Table 4 represents hypothesized equivalent dead carbon (10^{12} g CH_4/yr). If the 33 Tg/yr of dead carbon methane arise proportionately from all the 115 Tg/yr methane sources of the natural wetland category of Table 4, the average ^{14}C age of this methane would be 2800 years; this is not what we hypothesize. Instead we suggest that there could be significant old biogenic methane fluxes from selected wetland areas and peat bogs. For example, a methane flux of 40 Tg/yr with an average ^{14}C age of 10,000 years would supply 33 Tg/yr of dead carbon methane equivalent. Because most of the world's peats are probably less than 8000 years old (E. Gorham, private communication, 1988), the following parameters are also suggested: 75 Tg of CH_4 emitted annually with an average ^{14}C age of 4800 years, to yield 33 Tg of CH_4 dead carbon equivalent. A methane emission of 75 Tg/yr from peatlands is not unreasonable; Matthews and Fung [1987] estimated that fluxes from peat-rich areas compose 60% of the total global flux from all natural wetlands. There is also evidence that methanogenesis occurs at depth, in the catotelm, of some peat bogs [Clymo, 1984] and that methane concentrations increase with depth. Thus the release of old biogenic methane is possible. In any case, this hypothesis can be tested

by $^{14}CH_4$ measurements; Borneo peats in particular need study. We also suggest in Table 4 that 5 Tg dead carbon CH_4 escape from hydrates annually and 1 Tg/yr from oceans.

With 119 Tg/yr of dead carbon methane or 22% of all sources, the budget of Table 4 approaches the ^{14}C constraint from Lowe et al. [1988], Wahlen et al. [1987] and Manning et al. [1989].

For the fifth possibility to be true, the constraints on the atmospheric residence time and total sources and sinks (see Tables 1–3 and discussion), based largely on $C_2H_3Cl_3$, would be violated. A total quasi-steady state source (and sink) of only 320×10^{12} g CH_4/yr would imply a residence time of 15 years, outside the range discussed in Table 3. If there are other sinks of CH_4 (besides OH radicals) that are significant, for example, if soils consume amounts similar to atmospheric OH, then τ would be less than 8 years (lower limit from Prinn et al., [1987]) and the total sources would be larger than the upper limit of the range of Table 2 and the related discussion. Coincidentally, the list of methane sources derived by Khalil and Rasmussen [1983] totals almost the same as our Table 4 but their dead carbon sources are only half as large as ours.

Sinks of atmospheric methane are interesting in their own right, and quantitative sink estimates can constrain our estimates of sources and residence time. In Table 3 and the related discussion, we described the information available on methane sinks, both from photochemical models of atmospheric OH fields and from empirical deductions based on $C_2H_3Cl_3$ and the present indications that OH is the dominant sink for CH_4 and $C_2H_3Cl_3$. An independent estimate, based on measurements of naturally produced ^{14}CO, of global tropospheric average OH concentrations of about 6.5×10^5 cm^{-3} [Volz et al., 1981], would imply methane residence time near that from Prinn et al., but about 15% longer. The Volz et al. deduced [OH] range actually overlaps that of Prinn et al. so there is little disagreement. Soil oxidation (uptake) of atmospheric methane [Harriss et al., 1982; Seiler and Conrad, 1987] is estimated to consume $32(\pm 16) \times 10^{12}$ g CH_4/yr. It is very important to determine if this sink could be larger. If so, the methane budget constraints from atmospheric $C_2H_3Cl_3$ and ^{14}CO would be weakened.

Atmospheric methane sinks can provide other potentially useful information. First, the attack of OH on methane proceeds about 1% faster on $^{12}CH_4$ than $^{13}CH_4$ [Davidson et al., 1987]. Knowing the difference in reaction rate constants and the average ratio of atmospheric amounts of $^{13}CH_4$ and $^{12}CH_4$ [Stevens and Rust, 1982; Tyler, 1986], one can deduce the isotopic ratio in the total source of atmospheric methane (see section 4). This technique has great potential, although the amounts of data available so far do not yet qualify it as a strong constraint on various source sizes (see Table 3). Also, proper application of this technique could require complex atmospheric models that do not assume steady state conditions and spatially homogeneous distributions of methane sources and of OH. The use of CDH_3 and of mixed carbon and hydrogen isotopes could also be valuable.

Temporal decreases in the atmospheric concentrations of OH and thus the sink of CH_4 may be partly responsible for

the temporal increase of CH_4. Clearly, a decreasing sink is a pseudosource. As noted in section 2, there is in principle a possible feedback between increasing concentrations of CH_4 and CO and decreasing concentrations of OH. In reality the complexities of atmospheric photochemistry and tropospheric NO_x concentrations control the quantitative changes [Thompson and Cicerone, 1986; Crutzen, 1987; Isaksen and Hov, 1987]. Present models indicate that the annual OH sink for CH_4 may be decreasing by as much as 0.1 to 0.5% per year, thus representing a pseudosource of 0.5 to 3 Tg/yr. The CH_4/CO/OH nonlinearity, or any other factor that suppresses OH concentrations, can lead to CH_4 increases larger than CH_4 source increases alone could cause.

Still other constraints can be applied to the quantification of the budget and behavior of atmospheric methane. The net primary productivity (NPP) of ecosystems can provide important guidelines on patterns and rates of methane emissions [Sheppard et al., 1982; Aselmann and Crutzen, 1988]. NPP data and other information can be used to determine the distribution of methane sources with latitude, as has been done for wetlands by Matthews and Fung [1987]. Atmospheric models that simulate global transport and photochemistry can then be employed to derive sources, sinks and atmospheric distributions of CH_4 and to test various hypotheses (see notes to Table 3).

APPENDIX: STEADY STATE AND QUASI-STEADY STATE

In this appendix we derive the relationship between steady state sources, sinks, and atmospheric amounts and we define a useful quasi-steady state.

Consider an atmospheric gas whose mole fraction (volume mixing ratio) is a function $f(x,y,z,t)$ of spatial position (x,y,z) and of time (t). If $N(x,y,z)$ is the number density (cm^{-3}) of all air molecules, the equation of conservation for this gaseous species is

$$\frac{\partial}{\partial t}Nf(x,y,z,t) + \nabla \cdot \Phi(x,y,z,t) = P(x,y,z,t)$$
$$- fNL(x,y,z,t) \tag{A1}$$

where $\nabla \cdot \Phi$ is the divergence of the vector flux $\Phi(x,y,z,t)$, P is the in situ production and fNL the loss rate per unit volume. Now for methane $P = 0$, there is no production in the atmosphere. For an assumed steady state, $\partial/\partial t = 0$ so (A1) becomes

$$\frac{d}{dz}\Phi(z) = -fNL(z) \tag{A2}$$

where for illustrative purposes we consider only vertical (z direction) spatial variations. Integrating from Earth's surface ($z = 0$) to the top of the atmosphere ($z = \infty$),

$$\Phi\bigg]_0^\infty = -\int_0^\infty LfNdz \tag{A3}$$

Equation (A3) states that all of the methane flux that enters the atmosphere is consumed in the atmosphere, L

$= \sum_i L_i$; for example, the loss rate $(cm^{-3} s^{-1})$ due to OH attack on methane is

$$L_{OH} = k(T)[OH]fN$$

where k is the temperature dependent reaction rate constant for reaction (R5) and [OH] is the number density of OH. The right-hand side of (A3) is just the negative of the total atmospheric amount or burden, B, of methane divided by the globally averaged residence time, τ. Also, because no methane escapes the Earth's atmosphere, $\Phi(\infty) = 0$, so

$$\Phi(0) = B/\tau$$

In equation (1) of the text we call the annual average of $\Phi(0)$, the steady state source flux of methane, Q.

Now let us define a quasi-steady state in which atmospheric methane changes are slow enough to permit application of steady state relationships without major errors. Consider a departure from steady state, say a transient response, f_h, to decreased sources. Then

$$f_h = f_o exp(-t/\tau) \tag{A4}$$

would describe the decrease of f. For this transient response $df/dt = f/\tau$, which is about f/10 years at present. The presently observed change in atmospheric methane is

$$\frac{df}{dt} = 0.01f/year$$

so

$$\left.(1/f)\frac{df}{dt}\right]_{observed} \simeq (0.1)(1/f_h)\frac{df_h}{dt} \tag{A5}$$

Because the observed rate of change is only 1/10 as fast as that for responses to natural perturbations, we characterize this as quasi-steady state. The methane amounts and residence time derived from 1980s data (see Tables 2 and 3) define the quasi-steady state source, Q (see text).

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