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COMMISSION ON ATMOSPHERIC CHEMISTRY*

# ASSESSMENT OF UNCERTAINTIES IN THE PROJECTED CONCENTRATIONS OF METHANE IN THE ATMOSPHERE

**(Technical Report)**

Report based on Proceedings of the International Workshop held in Moscow, Russia, July 20–21, 1992. Organized by the Russian Academy of Science, Siberian Branch and the Netherlands Energy Research Foundation, ECN, Petten, Netherlands. Co-sponsored by the International Institute for Applied System Analysis, IIASA, Laxenburg, Austria

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*Membership of the Commission during the period (1991–1995) in which the report was prepared was as follows:

*Chairman*: 1985–1993 J. Slanina (Netherlands); *Secretary*: 1987–1995 P. Warneck (Germany); *Titular Members*: H. Akimoto (Japan; 1987–1995); L. Barrie (Canada; 1991–1995); N. M. Bazhin (Russia; 1991–1995); R. H. Brown (UK; 1991–1995); X. Tang (China; 1987–1995); *Associate Members*: E. H. Adema (Netherlands; 1991–1995); J. G. Calvert (USA; 1991–1995); K. H. Eickel (Germany; 1989–1993); J. A. Kerr (UK; 1987–1995); L. Klasinc (Croatia; 1991–1995); O. Lindqvist (Sweden; 1989–1993); L. F. Philips (New Zealand; 1991–1995); H. I. Schiff (Canada; 1991–1995); S. E. Schwartz (USA; 1991–1995); Wm. E. Wilson (USA; 1989–1993); *National Representatives*: T. M. Tavares (Brazil; 1992–1993); H.-J. Grosse (Germany; 1986–1993); B. Bonsang (France; 1990–1993); S. Glavas (Greece; 1991–1993); L. Horváth (Hungary; 1990–1993); O. N. Singh (India; 1989–1993); I. Allegrini (Italy; 1991–1993); Ø. Hov (Norway; 1985–1993); Y. Y. Lee (Korea; 1991–1993); U. Özer (Turkey; 1987–1993).

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# Assessment of uncertainties in the projected concentrations of methane in the atmosphere (Technical Report)

Abstract - Sinks and sources of methane have been examined in the papers presented at the IUPAC sponsored Workshop held in Moscow in July 1992. The conclusion reached was that very large uncertainties exist in the assessment of sources. The emissions from wetlands and rice paddies could be much lower than formerly assumed. The emissions from other sources, e.g. from landfills, could be larger. The most important sink, oxidation by OH-radicals in the atmosphere, has an uncertainty of 40% or more and cannot be used to evaluate the quality of the emission data. As a consequence, it is very difficult to predict future atmospheric concentrations, as function of changes in land use and economic activities. The prediction of the radiative balance of the earth is very difficult not only because of the uncertainty in future greenhouse gas concentrations but also because important factors, like the influence of aerosols, are insufficiently characterized.

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## INTRODUCTION

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### 1. General background

Infrared active gases in the atmosphere keep earth's surface temperatures in a range which is comfortable to life. The gases intercept and partly store thermal radiation that otherwise would be lost directly to space. The concentrations of many of these so-called greenhouse gases are currently increasing with the consequence that the global radiative balance is influenced. Methane, the most important greenhouse gas next to carbon dioxide in the atmosphere is projected to contribute about 19% to total greenhouse warming compared to 50% for $CO_2$ (Slanina, 1991). The mixing ratio of methane has been rising at a rate of about 1% per year during the past decade and has now reached 1.7 µmol/mol of air. Other greenhouse gases whose mixing ratios have been found to increase are the chlorofluorocarbons, ozone and nitrous oxide. Human activities are largely held responsible for these effects. Model calculations predict a global temperature rise on the order of 3 K over the next century, and this has led to an intense debate concerning possibilities of climatic changes.

As a sequel to a very successful workshop dealing with uncertainties of future carbon dioxide concentration in the atmosphere (Slanina & Okken, 1991), IUPAC has now sponsored a meeting designed to assess uncertainties in the projected concentrations of methane in the atmosphere. This workshop, which was cosponsored by the International Institute of Applied Systems Analysis, took place in Moscow in July 1992. The programme was organized jointly by the IUPAC Commission on Atmospheric Chemistry (VI.4) of the Applied Chemistry Division, the Netherlands Energy Research Foundation, and the Institute of Chemical Kinetics and Combustion of the Russian Academy of Science, Siberian Branch. The workshop was to review the current knowledge of sources and atmospheric behaviour of methane in order to identify major areas of uncertainty. Leading experts, invited to report on recent developments, included drs. M.A.K. Khalil, E. Matthews and M. Wahlen. In addition, members of the Commission on Atmospheric Chemistry were asked to review specific subjects and, in particular, the situation in Russia and the Asian countries. The full programme is shown in Table 1.

**TABLE 1.** Programme of the workshop on uncertainties in the projected concentrations of methane in the atmosphere.

| | |
|---|---|
| J. Slanina | Climatic consequences from observed and projected increases in greenhouse gases. |
| M.A.K. Khalil | Trends, cycles and relation to sources and sinks of observed mixing ratios of atmospheric methane. |
| J.G. Calvert, | Tropospheric $CH_4$ uncertainties in its chemical loss rate. |
| E. Matthews | Assessment of methane sources and their uncertainties. |
| P. Warneck | Methane emissions from biomass burning. |
| L. Barrie | Methane emissions from northern wetlands source strength and uncertainties in estimates. |
| M. Wahlen | Use of isotopes in defining the budget of methane in the atmosphere. |
| S.E. Schwartz | Climate forcing by aerosols. |
| N.M. Bazhin | Sources of methane in Russia. |
| H. Akimoto | Emissions of methane in Japan. |
| X. Tang | Emissions of methane in China. |
| O.N. Singh | Indian methane budget and its global perspective. |

The important role of methane in climatic forcing has been highlighted in the literature. The emissions of methane could rise very considerably in the future, due to increasing agricultural and industrial production and population growth.But many uncertainties exist in our present estimates of temperature changes, due to the enhanced greenhouse effect.

Measurements of methane in Greenland and Antarctic ice cores indicate pre-industrial $CH_4$ mixing ratios in the atmosphere of about 0.65 µmol/mol. Wetlands have perhaps been the dominant source of methane under these conditions with an estimated global source strength of 180-380 Tg/a. The current total source strength is estimated to be about 500 Tg/a. Table 2 gives the present estimates of the source strength for the most important methane emissions.

**TABLE 2.** Sources of methane in the atmosphere and global strength estimates (Tg/a[1]).

| | |
|---|---|
| Fossil fuel | |
| Coal mining | 35 |
| Natural gas | 40 |
| venting | 10 |
| transmission losses | 30 |
| Biomass burning | 35 |
| Natural wetlands | 115 |
| High latitude (bogs, tundra) | 35 |
| Low latitude (swamps, alluvial) | 80 |
| Rice cultivation | 100 |
| Animals (mainly domestic ruminants) | 80 |
| Termites | 20 |
| Oceans | 10 |
| Landfills | 25 |
| TOTAL | 500 |

**TABLE 3.** Parameters of a simplified calculation of future greenhouse gas emissions. Expressed as % change per year.

| | Northern Hemisphere | Southern Hemisphere |
|---|---|---|
| economic growth | 2 | 4 |
| emission reduction | 1 | 0.5 |
| population growth | -0.1 | 2 |

These data indicate that about 70% of methane arises from human activities. But the uncertainties in these estimates are very large. Recently indications were presented that the estimates for the emissions of wetlands and rice paddies could be much lower that formerly assumed. Sources like landfills and winning and distribution of natural gas could be more important. An assessment of the uncertainties of these sources has been made during this workshop.

In the atmosphere, methane is attacked by OH radicals and is then oxidized toward CO and $CO_2$. Although these processes are well understood, the direct measurement of OH concentrations is difficult, and, consequently, the rate of destruction of methane is quite uncertain.

Continuing economic development, following the existing patterns, and population growth will lead to a very large increase in the concentration of greenhouse gases in the atmosphere. If it is assumed that the current estimates of emissions are correct, that limited economic growth will take place in the future and that the population will increase at the present level, a very sharp increase in the concentrations of greenhouse gases is predicted.

The parameters of a very simple model are given in Table 3. In this simple scenario the emissions of methane increase in the Northern hemisphere with approx. 70% over the period 1990 to 2040, but the increase in the Southern hemisphere is one order of magnitude. The total emissions of greenhouse gases (expressed in $CO_2$ equivalents) as deduced by this simple linear model is given in Fig. 1.

The consequences of such an increase in the emission of greenhouse gases could be enormous. It is very important to establish whether the present estimates of the emissions are correct, whether a linear relation between economic activity, emission controls and population growth can be assumed in order to assess the future situations. These items were discussed in depth during this Workshop.

## 2. Conclusions regarding uncertainties in sources

The overview of Dr. Schwartz (*Climate forcing by aerosols*) provided a general introduction to the radiation balance of the earth and showed that many uncertainties exist in our present estimates of temperature changes, due to the enhanced greenhouse effect. It can be argued that most of the climatic forcing by greenhouse gases during the last century has been compensated by cooling due to increased concentrations of aerosols in the atmosphere.

In the atmosphere, methane is attacked by OH radicals and is then oxidized toward CO and $CO_2$ (J.G. Calvert, *Tropospheric $CH_4$ uncertainties in its chemical loss rate*). Hydroxyl radicals, OH, are generated in a reaction of excited oxygen atoms with water vapour, the oxygen atoms being formed by

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[1] The correct symbol for year is "a" rather then "yr", but because "yr" is widely recognised, this symbol will also be used in this report.

photolysis of ozone in ultraviolet sunlight. The direct measurement of OH concentrations is difficult, and the OH concentration field has to be calculated. Although most of the input data are reasonably well known, it was surprising to learn how much uncertainty still exists in this respect.

An overview of the present estimates of methane emissions (see Table 2) was presented by E. Matthews (*Assessment of methane sources and their uncertainties*). It was emphasized that the uncertainties in a number of sources is very large, even to the point that the uncertainties at present are about in the same magnitude as they were 5 years ago.

Biomass burning is an important source of methane emissions (P. Warneck, *Methane emissions from biomass burning*), but it is very difficult to extrapolate the few data which are available, to global estimates of the strength of this source.

Methods available for estimating the strengths of sources generally combine emission factors determined by field measurements with statistical data on the extent of source areas, animal populations, etc.. The errors involved in deriving such estimates can be appreciable. Therefore one has looked into other data that might conceivably provide further constraints to the methane budget, as is the case for carbon isotope ratios (M. Wahlen, *Use of isotopes in defining the budget of methane in the atmosphere*). For example, fossil methane would be depleted in radiocarbon compared with methane of recent biological origin, since the source of $^{14}C$ is the interaction of cosmic radiation with atmospheric nitrogen, and $^{14}C$ has a half life of 5700 years. A wide variety of data on carbon and hydrogen isotopes in methane from various sources and in the atmosphere is now available. Unfortunately, this additional information still leaves the relative contributions of many biogenic sources undefined.

Measurements of methane in Greenland and Antarctic ice cores indicate pre-industrial $CH_4$ mixing ratios in the atmosphere of about 0.65 µmol/mol (M.A.K. Khalil, *Trends, cycles and relation to sources and sinks of observed mixing ratios of atmospheric methane*). Wetlands must have been the dominant source of methane under these conditions with an estimated global source strength of 180-380 Tg/a. The current total source strength is estimated to be about 500 Tg/a. Table 2 gives a breakdown into individual processes that contribute to the global budget. The data make evident that about 70% of methane arises from human activities. Methane is produced naturally by microbial breakdown of organic material under anaerobic conditions. Whereas methanogenic bacteria are strict anaerobes, a host of other bacteria feed on methane once it reaches aerated strata in water-logged

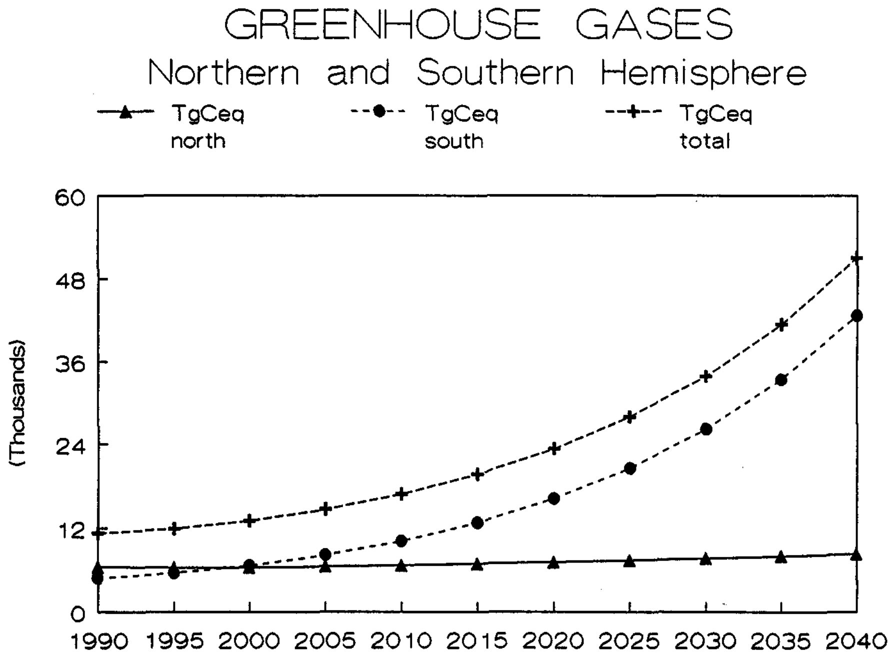

**Fig. 1.** Projected emission of greenhouse gases

soils, thereby reducing the flux of methane escaping to the atmosphere. Thus, shallow ponds, alluvial wetlands, rice paddy fields, etc.. are the most important source areas. In addition methane is microbially produced in the intestines of and exhaled by cattle sheep and other domestic animals. Table 2 shows that more than 60% of human related sources are associated with agricultural practices, only 25% stem from coal mining and other fossil fuel related activities. There can be no doubt that the recent growth in the concentration of methane in the atmosphere is due to an expansion of agricultural activities that were needed to feed a growing human population. Indications exist that no longer a 1 to 1 correlation can be observed between increase of methane concentration in the atmosphere and population growth. This correlation has been observed during a period of several decades.

The latest reports about the emissions of Northern Wetlands, (L. Barrie, *Methane emissions from northern wetlands source strength and uncertainties in estimates*) indicate that these emissions are substantially lower as formerly assumed. The emissions of Northern wetlands are probably in the order of 20 Tg/a instead of 80.

It is of great importance that the main rice growing countries have been alerted to the problem of methane increase in the atmosphere, and more detailed information on the contribution of rice cultivation to atmospheric methane is now being sought on the basis of an improved knowledge of local conditions (O.N. Singh, *Indian methane budget and its global perspective*). An unexpected conclusion of the workshop was that India, one of the main rice growing countries, contributes no more than 7% of global emissions from rice crops, because most Indian paddy crop is taken from irrigated field and only a small portion from water-logged fields.

The losses of natural gas in Russia (N.M. Bazhin, *Sources of methane in Russia*), during exploration and transport, are certainly not as large as assumed in some West-European studies (up to 25%). So leakage of natural gas in Siberia cannot fill, according Russian data, the gap in emission strength, caused by the much lower emissions of wetlands and rice paddies.

On the other hand, the emissions of landfills could be much larger as previously assumed, based on the first results of measurements in China (X. Tang, *Emissions of methane in China*). The first observations in China indicate that the emissions of rice paddies is lower than assumed previously, analog to the Indian observations.

Japan has started environmental programs for abatement of methane emissions (H. Akimoto, *Emissions of methane in Japan*). The emissions in Japan are not as high as expected, based on former estimates, again because of lower emissions of rice paddies.

## 3. Recommendations for research

It is clear that large uncertainties exist regarding the emissions of methane and that the uncertainty in atmospheric oxidation is so large (in the order of 40% according the estimates of Dr. Calvert) that this mechanism cannot be used to check our emission inventories. Better estimates of reaction rates and OH concentration fields are needed.

Measurement of isotope ratios ($^{14}C/^{12}C$ and $^{13}C/^{12}C$) can also provide data to validate emissions, but at present this technique is insufficiently precise to check detailed emission inventories
These measurements should be carried out in background as well in polluted areas to check local emission inventories.

Specific validation measurements, to evaluate emissions on regional and (sub)continental scale are required to check whether the extrapolation of measurements of methane emissions, carried out on very small scale, to global dimensions has been carried out correctly in the past.

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# TRENDS OF ATMOSPHERIC METHANE

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## 1. Introduction

The observed concentrations of atmospheric methane result from two factors - processes that release methane into the atmosphere and processes that remove it. When these processes are out of balance methane concentrations rise or fall or undergo cyclical variations. On the time scale of a year, methane concentrations undergo seasonal variations that are large at high latitudes and smaller at tropical and equatorial latitudes. The entire global burden of methane undergoes seasonal variations. On longer time scales during recent years, the trends of methane are characterized by persistently increasing concentrations. This paper is about the increasing trends and the possible reasons for the increases.

## 2. Past and present trends

There are three types of data currently available to address the trends of methane. Data on concentrations before the early decades of the 20th century come from analyses of bubbles of old and ancient air preserved in polar ice. This record now extends back to some 160,000 years. The detailed record over recent millennia comes from Greenland and Antarctic cores, while the very long term record back the last glacial maximum comes from the core drilled by Soviet scientists at Vostok station in Antarctica (Rasmussen & Khalil, 1984; Stauffer *et al.*, 1988; Raynaud *et al.*, 1988; Chappellaz *et al.*, 1990). For the 1950s to recent times, methane concentrations have been calculated from stored solar spectral plates. During the decades of the 1960s and 1970s direct measurements of methane were taken sporadically by many investigators using reliable gas chromatographic instrumentation. These data show considerable variability because of differences in absolute calibration and the quality of instrumentation (Khalil *et al.*, 1989). From about 1979 onwards there are several independent records of careful, systematic global measurements of atmospheric methane (Rasmussen & Khalil, 1981; Khalil & Rasmussen, 1983, 1987, 1990; Steele *et al.*, 1987; Blake & Rowland, 1988). Figures 1-4 show the records of methane during various periods from about 1000 years B.P. to the detailed records of the last decade (from Khalil & Rasmussen, 1987, 1990; and Khalil *et al.*, 1989).

From these records we can conclude the following:

1. The concentration of methane appears to be only about 350 nmol/mol during glacial times, which is about half of the natural inter-glacial levels.

2. The natural inter-glacial concentrations of methane are 650-700 nmol/mol.

3. Methane started to increase rapidly only during the last 100-200 years. Before that time the concentrations appear to have been stable at the levels characteristic of inter-glacial periods.

4. During the last decade or so, concentrations of methane have been increasing at relatively fast rates of about 1% per year or about 16 nmol/mol.yr. Present globally averaged concentrations are 1685 nmol/mol (in 9/1988) or about two and a half times higher than natural inter-glacial levels.

Several independent data sets have mutually verified these conclusions which are currently taken as fact. There are, however, remaining questions about the ice-core data that leave open the possibility that the true pre-industrial and glacial concentrations may be different from those reported in the scientific literature. In contrast, the global trends over the last decade are incontrovertible since they are based on direct and highly precise atmospheric measurements.

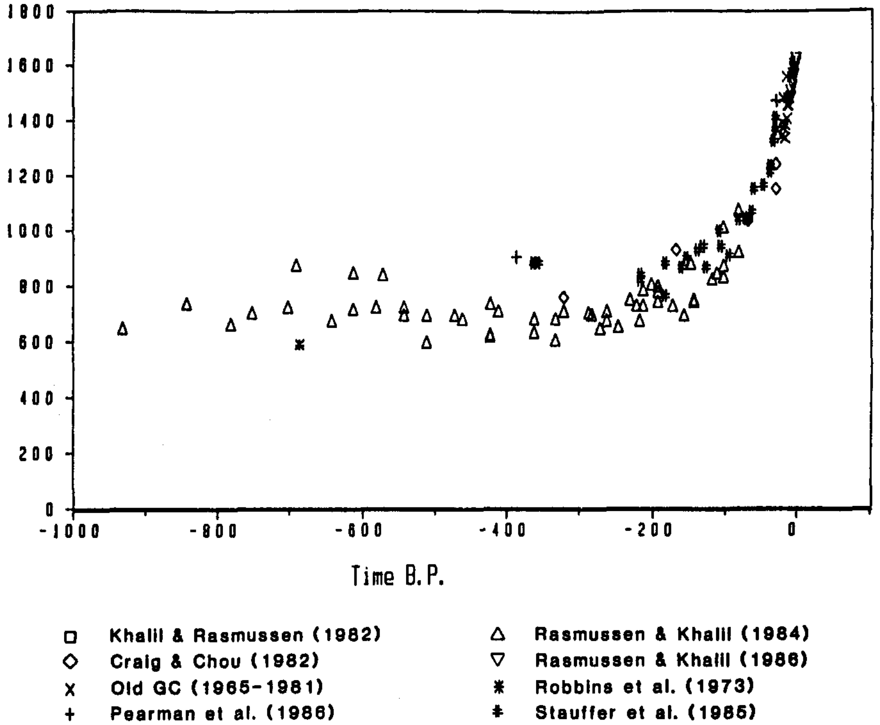

Fig. 1. The concentrations of methane during the last 1000 years.

## 3. Details of present trends

The data during the last decade are so detailed that they record not only the overall decadal average trends but also the changes in the trends. These data show several features; the most significant is that the rate of increase of methane is slowing. The rate of increase has been slowing from the very beginning of the systematic measurements in 1979. The change has been quite dramatic. In the early part of the data, the trend was about 20 nmol/mol.yr, and in recent years it is about 10 nmol/mol.yr or about half as much.

The slowdown of the trends was first reported by Khalil & Rasmussen (1990), including evidence from other published data. Figure 5 shows the slowdown of the global average concentration. In this graph the trends are shown as the linear rates of increase during 3-year overlapping periods (unpublished data). In these calculations the first point is the trend during months 1 to 36, the second point is the trend for months 2 to 37, and so on.

There are yet other features in the detailed data sets that show the changing nature of current trends. The Cape Meares record shows four features:

1. As for data from all sites, the rate of increase is slowing.

2. The rate of increase is higher in winter than in summer. This is equivalent to an increasing amplitude of the seasonal cycle.

3. The rate of increase is higher at middle and higher northern latitudes compared to southern latitudes.

4. The trend is likely to be affected by natural events such as the El Nino. Methane concentrations may decline during El Nino events from a combination of factors. The higher sea surface temperatures may lead to more water vapour in the tropics and hence to a greater production of OH radicals that remove methane, and possibly to a shift of rainfall patterns that may leave more dry soils that remove methane. Thus, the reduced concentration of methane during El Ninos may result from more efficient removal.

All these effects, except the slowdown of the rate of increase, are small and are still under investigation. If these effects exist, they provide new challenges that may sharpen our knowledge of the sources and sinks of atmospheric methane. Global mass balance models would have to include these effects that will put constraints on the estimates of global emission rates.

## 4. Facts and speculations on the causes behind the trends

As stated in the beginning, the causes for these trends must lie with either changes of sources or the removal processes (also called sinks). The main processes that remove methane from the atmosphere are reaction with tropospheric OH radicals and removal at the earth's surface by dry soils. There are some other lesser processes that remove small amounts of methane. The main sources affected by human activities are cattle, rice fields, biomass burning, landfills, and leakages from natural gas use. The main natural source is the wetlands with smaller contributions from the oceans, lakes and tundra. A number of other natural and anthropogenic sources of methane also exist.

There is considerable evidence that the change of methane concentrations from about 700 nmol/mol a hundred or so years ago to the 1650 nmol/mol today is caused mostly by increasing sources and to a much lesser extent by decreasing OH (see Khalil & Rasmussen, 1985; Levine *et al.*, 1985; Thompson & Cicerone, 1986; Pinto & Khalil, 1991; Lu & Khalil, 1991).

The decrease in the trend is of particular importance in deciding whether the global oxidizing capacity is changing (or equivalently that OH is increasing) or whether some of the sources controlled by human activities are no longer increasing as rapidly or perhaps even decreasing. In this paper we can only make qualitative arguments in favour of changing sources rather than changing sinks.

It is noteworthy that it was generally believed that the OH concentrations should be decreasing (this would cause the trend of methane to increase, all other factors being the same). The decrease of OH was expected because CO and $CH_4$ were both increasing and these gases can are the major sinks of

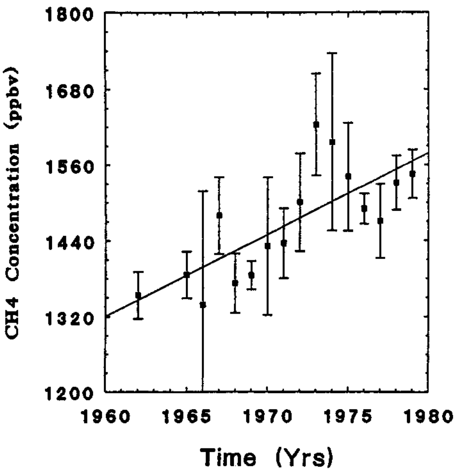

Fig. 2. Trends and concentrations during the 1960s and 1970s.

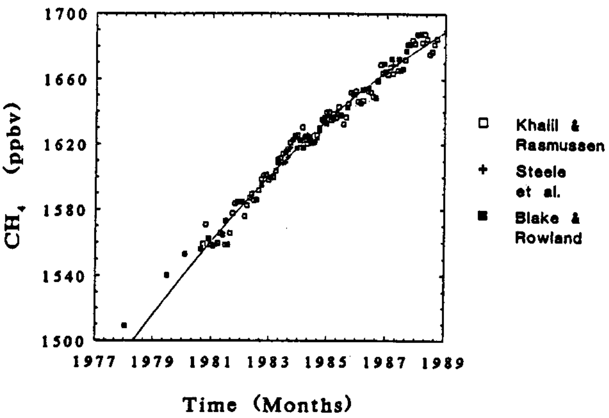

Fig. 3. Global average concentrations of methane during the recent decade, 1979-1989.

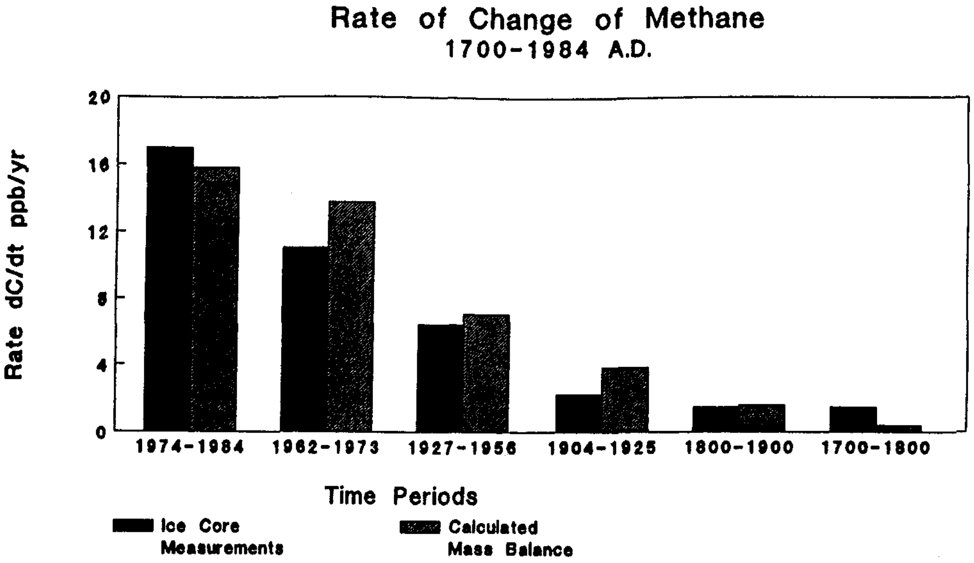

Fig. 4. The past trends of atmospheric methane.

OH. Now it appears that these factors may be compensated by enhanced production of OH, particularly because of increasing tropospheric $O_3$ and also because of other considerations. It appears that the OH concentrations are stabilized against changes (see Pinto & Khalil, 1991; Lu & Khalil, 1991).

If an increase of OH is not the main cause for the slowdown in the methane concentration, then it must be explained by the changes of sources. In fact, it is now evident that the area of rice agriculture is no longer expanding. Higher yields are being achieved by use of hybrid species and artificial fertilizers; neither is likely to increase methane emissions. Thus, a slower increase in the area of rice planted may lead to a lesser increase of methane emissions from this source. Similarly, the world cattle populations are no longer increasing, because of various reasons including lack of suitable range lands. It seems, therefore, that the two major sources affected by human activities, rice agriculture and domestic cattle (and perhaps also other animals), are no longer increasing because of natural limitations on these activities. Cattle and rice agriculture were the major causes of the increase of methane over the last century; these sources increased with increasing population. The lack of increase in these large sources over the last decade may well be the cause of the slowdown in the trends of methane.

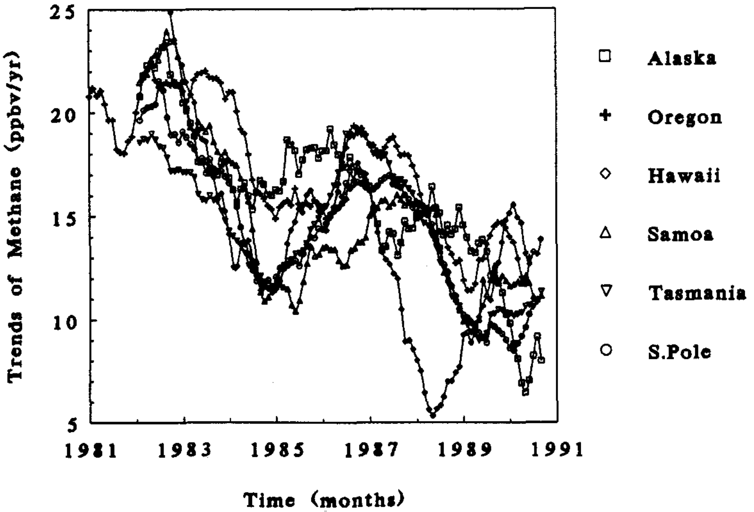

Fig. 5. The slowdown in the trend of methane at various latitudes.

If these ideas are correct, two important conclusions emerge:

1. If the sources that contributed to past increases of methane are not increasing any more, then the past record of methane is becoming uncoupled from the future. Future increases of methane will be caused by other (newer) sources that were not important in the past; thus, the past does not serve as an indicator of the future. Population increase, for instance, is no longer an indicator of future methane emissions. Thus, reliable projections of methane concentrations into the future are virtually impossible at present.

2. The second conclusion is that the global methane trends are slowing without any legislative intervention, most likely from natural limits to growth of the major anthropogenic sources. This aspect is particularly interesting since most control strategies cannot guarantee the reduction of the growth rate by a factor of two within a decade as has already occurred. The notion that any trend of an atmospheric trace gas can continue for decades or centuries has no philosophical or scientific basis but is commonly assumed in many assessments of the future levels of man-made trace gases, including methane.

It is clear that the current data on the global trends of methane are challenging conventional predictions of future methane concentrations and leading to refinements of the current global budget.

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# TROPOSPHERIC $CH_4$: UNCERTAINTIES IN ITS CHEMICAL LOSS RATE

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## 1. Introduction

Methane has been identified as the most important of the trace gas species (excluding $H_2O$ and $CO_2$) in contributing to the greenhouse warming of the Earth (Ramanathan *et al.*, 1985; Mitchell, 1989). There is concern today since its concentration in the troposphere has continued to rise at an average rate of about 1%/yr from 1980 to 1988 (Steele *et al.*, 1987; Khalil & Rasmussen, 1987, 1990; Blake & Rowland, 1988). The reasons for the observed trends in atmospheric methane concentration are not well established. Of course the rate of growth of $CH_4$ in the troposphere is equal to the rate of input from all methane sources minus the rate of its removal by all sinks. Our understanding of the magnitude and location of all sources and sinks of methane has increased greatly in recent years (Cicerone & Oremland, 1988; Taylor, *et al.*, 1991), but a definitive assignment of source strengths and sinks remains an unattained goal of atmospheric scientists. Methane enters the atmosphere by a variety of pathways: emissions from wetlands, rice paddies, fossil fuels, animals, biomass burning, landfills, termites, oceans, and other sources; these are addressed by others in this series of articles. Here we will review our understanding of the atmospheric methane removal processes and the uncertainties in these which remain today. Some loss of atmospheric methane occurs from soil oxidation processes, but this is currently thought to be much less important than the atmospheric chemistry; Keller *et al.*, (1986) estimate that about 3% and Seiler & Conrad (1987) about 6-10% of the total global $CH_4$ emissions are lost through soil oxidation processes. By far the largest of the loss terms for methane results from its atmospheric chemistry.

## 2. The gas-phase chemistry of methane removal in the troposphere

It is the consensus of scientists today that the major loss of methane in the atmosphere (90-97%) comes from its reaction with the HO-radical, and this reaction is thought to occur largely within the lower 6 km of the troposphere. There is general agreement that the elementary reaction (1) describes this process well:

$$CH_4 + HO \rightarrow CH_3 + H_2O \qquad (1)$$

The rate coefficient ($k_1$) for this reaction has been determined by a number of different investigators over the past 25 years. However only a few of these studies relate directly to the conditions of the troposphere. Recently measurements of $k_1$ by Ghyanshyam & Ravishankara (1991) have shown that for the temperatures of the troposphere the rate coefficient is described well by the function, $k_1 = 1.59 \times 10^{-20}\, T^{2.84} \exp(-978/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (precision, $\leq 5\%$, $2\sigma$; accuracy unknown); this gives estimates of $k_1$ at typical tropospheric temperatures (273 K) which are about 15% smaller than the values which have been accepted until recently. This finding is of major importance in that it suggests that 490 Tg yr$^{-1}$ of $CH_4$ removal by reaction (1) occurs rather than the 590 Tg yr$^{-1}$ based upon the earlier $k_1$ estimates. Alternatively, if the previously suggested 590 Tg yr$^{-1}$ tropospheric input of $CH_4$ is correct, then there must be a large missing sink for $CH_4$ in the troposphere.

The isotopic composition of tropospheric methane can be used as a marker to test the consistency of the suggested importance of the various sources and the removal reactions for methane in the troposphere. This is based upon the fact that many of the different sources of methane have a characteristic $^{12}CH_4/^{13}CH_4$ ratio (*e.g.*, see: Stevens & Rust, 1982; Tyler, 1986; Stevens & Engelkemeir, 1988; King *et al.*, 1989) which can be compared with that seen for methane collected in the troposphere in various regions. The observed atmospheric $^{12}CH_4/^{13}CH_4$ ratio depends not only on the distribution and strength of the various sources, but on the extent of discrimination between the two isotopic species which is shown by the HO-radical in its reactions (1a) and (1b) and in soil oxidation as well:

$$HO + {}^{12}CH_4 \rightarrow H_2O + {}^{12}CH_3 \quad (1a)$$

$$HO + {}^{13}CH_4 \rightarrow H_2O + {}^{13}CH_3 \quad (1b)$$

The ratio $k_{1a} / k_{1b}$ has been determined in several studies (Stevens & Rust, 1982; Davidson *et al.*, 1987; Cantrell *et al.*, 1990). In the most recent of these, Cantrell *et al.* (1990) give: $k_{1a} / k_{1b} = 1.0054 \pm 0.0009$, independent of temperature (0-80°C). The kinetic isotope effect for soil oxidation of methane is significantly larger ($k_{12CH4} / k_{13CH4} \approx 1.021$). These kinetic data and source strength and sink inventories have been used to test our estimates of the magnitudes of the various sources and sinks, but the large uncertainties in the estimates available today, do not allow an unambiguous check on their consistency.

The carbon-containing species formed as HO reacts with $CH_4$ are indicated in Fig.1. Each of transformation reactions has been reasonably well characterized in previous studies and evaluated in a recent review by Ravishankara (1988). It can be seen in Fig.1 that the transformation of $CH_4$ into CO and ultimately into $CO_2$ occurs following a series of intermediate reactions. Transient reactive species, including the HO-, $HO_2$- and $CH_3O_2$-radicals, are involved in the transformation, and these radicals lead to molecular products including methyl hydroperoxide ($CH_3O_2H$), methanol ($CH_3OH$), methylperoxynitrate ($CH_3O_2NO_2$), and formaldehyde ($CH_2O$). The interaction of these molecular products and radicals influence the level of ozone in the atmosphere. Not shown in the Fig.1 are the reactions of the transient peroxy radicals with NO in which $NO_2$ and ultimately $O_3$ are formed in the chain reaction sequence (2) through (6); $O_3$ is destroyed in (7) and (8):

$$HO_2 + NO \rightarrow HO + NO_2 \quad (2)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (3)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad (4)$$

$$NO_2 + h\nu \rightarrow O(^3P) + O_2 \quad (5)$$

$$O(^3P) + O_2\ (+O_2/N_2) \rightarrow O_3\ (+O_2/N_2) \quad (6)$$

$$HO + O_3 \rightarrow HO_2 + O_2 \quad (7)$$

$$HO_2 + O_3 \rightarrow HO + 2O_2 \quad (8)$$

Whether ozone is made or destroyed in the troposphere depends largely on the magnitude of $[NO_x]$ ($[NO] + [NO_2]$) which is present (Liu & Trainer, 1988). $[NO_x]$ is highly variable in the troposphere, reflecting variations in the magnitudes of the anthropogenic and natural inputs of $NO_x$. Whether the local $[NO_x]$ results in $O_3$ formation or destruction is a very important question, since the concentration of ozone is critical in determining the rate of the methane loss; see the following discussion.

## 3. Estimation of the methane tropospheric loss rates

It may seem at first sight that the problems of estimating the rate of methane loss should not be great, since there is a single reaction (1) which dominates methane's destruction in the troposphere, and its rate coefficient is known reasonably well today. At any point within the troposphere the rate of methane loss should be given simply by: $R_{CH_4} = k_1[CH_4][HO]$. However accurate estimates of the rate of reaction (1) which occur in the troposphere are nontrivial, since these require not only a knowledge of the rate coefficient, but also concentrations of both reactants in (1), including the transient hydroxyl (HO) radical. The HO-radical concentration is determined by the complex chemical interactions of many trace gases present in the troposphere including the many products of the oxidation of methane itself. Clearly the accurate estimation of tropospheric methane loss rates is fraught with difficulties.

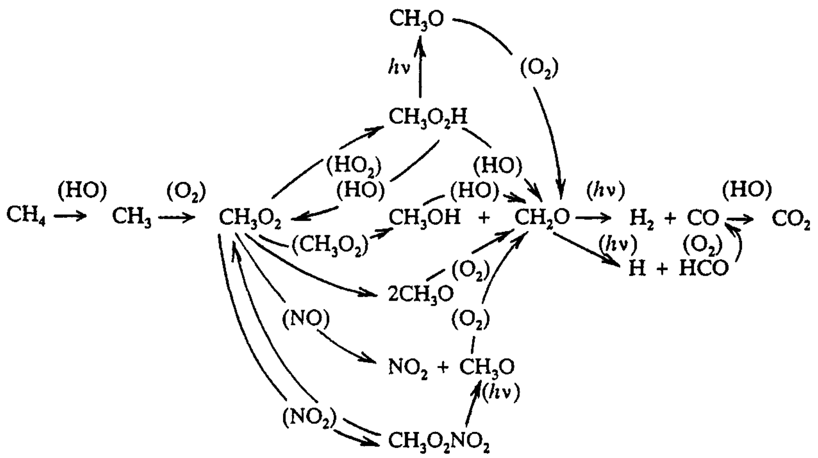

**Fig. 1.** The transformation pathways of the carbon-containing species in the HO-radical initiated oxidation of methane in the troposphere

*A. The theoretical estimation of tropospheric methane loss rates.* Although various methods for the direct detection of HO-radicals in the troposphere have been developed (*e.g.*, Felton *et al.*, 1990; Ehhalt *et al.*, 1991; Eisele & Tanner, 1991; Hofzumahaus *et al.* 1991; Mount & Eisele, 1992), these methods have been employed to date in very restricted use to measure [HO] at isolated ground positions; they are not now suitable to make measurements throughout the troposphere which will be representative of all seasons and locations for the variety of conditions (various latitudes, longitudes, altitudes, cloud cover, aerosol content, solar zenith angle, overhead $O_3$ column, etc.) which are commonly present. Direct measurements will probably be an important input for our use in the near future. For now we must rely on more indirect methods of [HO] estimation. Atmospheric chemists often model the chemistry of the troposphere to derive theoretical [HO] distributions and average hydroxyl radical concentrations which can be used to estimate $CH_4$ removal rates (*e.g.*, see the summary Table 1 of Taylor *et al.*, 1991). The accuracy of such theoretical estimates is unknown, but their uncertainty is very high in view of the many unknown yet important parameters (reactant concentrations, cloud cover, etc.) which must be estimated.

The generation of ozone in the troposphere is key to the rate of methane removal in reaction (1), since the photodecomposition of ozone is the major atmospheric source of the HO-radical through reactions (9) and (10):

$$O_3 + h\nu(\lambda<330\text{ nm}) \rightarrow O(^1D) + O_2(^1\Delta_g \text{ or } ^3\Sigma_g^-) \qquad (9)$$

$$O(^1D) + H_2O \rightarrow 2HO \qquad (10)$$

$$O(^1D) + M(N_2,O_2) \rightarrow O(^3P) + M \qquad (11)$$

The narrow band of wavelengths from about 290-330 nm which penetrates the earth's ozone layer and arrives within the troposphere is responsible for the occurrence of reaction (9). The $O(^1D)$ atom produced is an electronically excited oxygen atom (O-singlet D) which is highly reactive toward gaseous water molecules; each $O(^1D)$ atom forms two HO-radicals in nearly every collision with a water molecule. However quenching of the $O(^1D)$-atom occurs as it collides with the more abundant molecules of oxygen and nitrogen in the atmosphere (reaction 11). The resulting encounter creates a ground state oxygen atom ($O(^3P)$) which quickly associates with an oxygen molecule to reform ozone in (6). For many reasons which we will discuss, it is the estimation of the rate of HO-radical generation which introduces the greatest uncertainty in the estimation of the methane loss rate in the troposphere.

Commonly the rate of $O(^1D)$ formation in the atmosphere, $j_{O_3}$, is calculated from equation (12) and a knowledge of the ozone cross sections, $\sigma(\lambda)$, the quantum yields, $\phi(\lambda)$, of $O(^1D)$ formation from $O_3$ photodecomposition, and the spectral actinic flux, $S(\lambda)$, in the troposphere (*e.g.*, Madronich & Granier, 1992):

$$j_{O_3} = \int \sigma(\lambda)\phi(\lambda)S(\lambda)d\lambda \tag{12}$$

The integral in (12) extends over all wavelengths where the product $\sigma(\lambda)\phi(\lambda)S(\lambda)$ is non-zero. The rate of HO-radical generation from reaction (10) can be determined using the calculated $j_{O_3}$ and equation (13):

$$\text{Rate of HO generation from (10)} = [O_3]2j_{O_3}\{k_{10}[H_2O]/(k_{10}[H_2O] + k_{11}[M])\} \tag{13}$$

Reaction (10) is not the only source of OH-radicals, but there are sereral minor sources as well; e.g., $HO_2 + NO \rightarrow HO + NO_2$. The estimation of the total rate of HO-radical generation requires additional information on these processes (e.g., $[HO_2]$, [NO], rate coefficients, etc.). The total rate of HO-radical generation, $R_{HO(total)}$, is somewhat greater than given by equation (13). The calculation of the concentration of OH at a given location in the troposphere through equation (14) requires a knowledge of HO-radical loss terms as well as $R_{HO(total)}$:

$$[HO] = R_{HO(total)} /(\Sigma k_i[X_i]) \tag{14}$$

Here $k_i$ is the rate constant for the reaction of HO-radical with $X_i$, the *i*th component of the trace gases in the troposphere which is reactive toward HO. $X_i$ represents the many HO-reactive species including methane, carbon monoxide, formaldehyde, methanol, methyl hydroperoxide, hydrogen peroxide, oxides of nitrogen, etc. Obviously if we are to calculate [HO] accurately at many representative locations within the troposphere, then we must know or estimate the local concentration of the major reactants with HO ($[X_i]$) as well as the local $[O_3]$ and $[H_2O]$. This is a very complicated and seemingly impossible task; resort of modellers to the use of approximate modelling efforts is understandable.

If one utilizes equations (13) and (14) to derive the rate of HO generation and the concentration of HO, respectively, then major inaccuracies result from the uncertainties in the experimental estimates of $\sigma$, $\phi$, and $S$. Current recommendations show a combined uncertainty in the product $\sigma\phi$ of 40% (DeMore *et al.*, 1990). Uncertainties in the values of $S$, the actinic flux, are also probably high and variable in magnitude as atmospheric conditions change. Clear sky values of $S$ have been estimated from solar flux measurements by extrapolation from high altitude measurements by attenuating the radiation using the measured $O_3$ columns for the particular location and appropriate molecular and aerosol scattering (*e.g.*, Luther & Gelinas, 1976; Demerjian *et al.*, 1980; Michelangeli *et al.* ,1992). The presence of clouds in the troposphere, a common occurrence, introduces further uncertainties in calculations as a result of the change in albedo in regions above the clouds and changes (increase or decrease) in the intensities of light transmitted and scattered through the clouds in regions below clouds (*e.g.*, Madronich, 1987; Harrison *et al.*, 1990; Hartmann & Doelling, 1991). There are some relatively unexpected complications in estimating the appropriate $S$ values in atmospheres rich in aerosols. For example, Michelangeli *et al.* (1992) estimate theoretically that one consequence of a volcanic eruption similar to that of El Chichon in 1982 is an increase in the midday surface actinic flux at 20°N latitude, summer, by as much as 45% in the $j_{O_3}$-sensitive region at 290 nm.

The decrease in stratospheric ozone and the increase in tropospheric ozone concentrations which have been noted in recent years add further complications to the theoretical estimation of tropospheric $j_{O_3}$ values. Liu & Trainer (1988), Gery (1989), and Thompson (1992) have examined various aspects of the sensitivity of tropospheric chemistry to UV changes resulting from stratospheric ozone depletion and tropospheric ozone increases. Madronich (1992) has estimated from the ozone depletion reflected in the total atmospheric ozone measurements of Herman *et al.* (1991) and Stolarski *et al.* (1991), that the extent of penetration of the short wavelength UV is expected to have increased substantially in recent years, particularly at mid and high latitudes of both hemispheres. Madronich & Granier (1992) have shown in theory that the zonally and annually integrated trends in the tropospheric $j_{O_3}$ values are +3.8 ± 2.9% per decade in the Northern hemisphere and +4.1 ± 2.7% per decade in the Southern hemisphere. They note that this effect alone could account for a large part of the slowing in the rate of increase of methane (about 4.7-11.8% per decade) which has been reported in a recent WMO assessment (1992).

Note in equation (13) that not only the $j_{O_3}$ values are critical to the estimation of HO levels, but also the $[H_2O]$ in the given region of the atmosphere is directly involved as well. Local water concentrations in specific regions of the troposphere have been determined in many previous studies. However $[H_2O]$ estimates for locations throughout the troposphere are usually of uncertain accuracy, since they are derived by extrapolation from the very limited number of rather site specific measurements which may or may not be representative. One must conclude that theoretical estimations of the rate of reaction (1) in the troposphere must be highly uncertain, largely as a result of the great uncertainties in the estimations of $j_{O_3}$.

*B. Estimation of tropospheric methane loss rates through $j_{O_3}$ experimental estimates.* Both the theoretical and experimental determinations of $j_{O_3}$ have inherent problems which lead to significant uncertainties; however the direct measurement of $j_{O_3}$ in the troposphere offers an attractive alternative to its theoretical calculation described above. One can determine $j_{O_3}$ values experimentally at specific points in the atmosphere through the use of specially designed actinometers. Chemical actinometer methods have been employed in some previous determinations. Bahe *et al.* (1979), Dickerson *et al.* (1982), and Blackburn (1984) have exposed dilute mixtures of ozone in $N_2O$ to sunlight; the $O_3$ photolysis and the subsequent rate of product generation from the $O(^1D)$ reactions (15) and (16) with $N_2O$ constitute the scientific basis for the use of the instruments in $j_{O_3}$ measurements:

$$O(^1D) + N_2O \rightarrow 2NO \qquad (15)$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (16)$$

Bahe *et al.* measured $N_2$ formed in (16), while Dickerson *et al.* and Blackburn measured the products of the reaction of $O_3$ with the NO produced in (15). Both methods require a knowledge of the fraction of the $O(^1D)$ which reacts by each of two channels. DeMore *et al.*(1990) estimate that the uncertainty in $k_{15}$ and $k_{16}$ is about 30%; the required ratios, $(k_{15} + k_{16})/k_{15}$ or $(k_{15} + k_{16})/k_{16}$, probably have a somewhat lower uncertainty, since only ratios of reactant and products are required. New estimates of these ratios should be made so that $j_{O_3}$ and [HO] can be made with less uncertainty from actinometric data in the future.

In view of the experimental complications in the measurement of $j_{O_3}$ over wide regions of the earth and for the many atmospheric conditions which are encountered, the use of calibrated radiometers appears to offer an attractive alternative. However a suitable radiometer should have the following characteristics: (1) it should integrate with equal efficiency the light independent of the angle of incidence; *i.e.*, it should have either a $4\pi$ angular response or have combined $2\pi$-upward looking and $2\pi$-downward looking detectors (not a flat-plate receiver); 2) it should be calibrated at regular intervals with a reliable chemical actinometer system; and 3) it should have a wavelength response very similar to the action spectrum of ozone within the troposphere (290-330 nm). A radiometer which appears to satisfy most of these requirements has been employed to derive $j_{O_3}$ estimates in the atmosphere at the surface of the Atlantic Ocean from 50°N to 30°S during September and October, 1988 (Brauers & Hofzumahaus, 1991).

An alternative approach which combined measurements and theory has been used by Hanser & Sellers (1980) to estimate $j_{O_3}$ in the 1977 GAMETAG flights. An ultraviolet spectro-irradiometer was used to measure downward-going solar flux in the 290 to 410 nm spectral region. Broadband pyranometers were used to measure the ratio of upward-going to downward-going flux in the 300 to 400 nm range to derive a ground albedo. These data were combined with atmospheric scattering calculations, and published values of $\sigma$ and $\phi$ to derive local estimates of $j_{O_3}$. They concluded that the accurate determination of $j_{O_3}$ requires measurement of UV fluxes.

## 4. Summary

The estimation of the rate of change of methane in the troposphere from source and sink terms is encumbered by the large uncertainties in the various terms. The largest sink term involves the HO-radical attack on methane for which the rate of reaction at any point in the troposphere is given by $[HO][CH_4]k_1$. Both theoretical and experimental approaches to the estimation of [HO] have inherent uncertainties which we have discussed. In view of the large uncertainties which must accompany a theoretical estimation of the rate of $CH_4$ removal by HO-radical attack, the experimental methods which utilize $j_{O_3}$ measurements to estimate [HO], although themselves subject to considerable uncertainty, appear to offer a more accurate determination of this quantity at this time.

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# ASSESSMENT OF METHANE SOURCES AND THEIR UNCERTAINTIES

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## 1. Introduction

Measurements of methane from Greenland and Antarctic ice cores indicate atmospheric concentrations of ~350 nmol/mol during the Last Glacial Maximum rising to 650 nmol/mol during the preindustrial Holocene (Stauffer *et al.*, 1988; Chappellaz *et al.*, 1990). Pre-industrial source strengths of methane, consistent with historical concentrations and estimates based on isotopes, have been estimated at ~180-380 Tg ($10^{12}$ g) per year (Khalil & Rasmussen, 1987; Stauffer *et al.*, 1985; Chappellaz *et al.*, 1993). Wetlands are understood to have been the dominant source with small contributions from wild fires, animals and oceans. During the last two hundred years, atmospheric methane concentrations have more than doubled to ~1700 nmol/mol (atmospheric burden of ~4800 Tg) and currently are increasing at ~0.7% per year (Rasmussen & Khalil, 1981; Craig & Chou, 1982; Khalil & Rasmussen, 1982, 1983, 1985; Ehhalt *et al.*, 1983; Blake, 1984; Rasmussen & Khalil, 1984; Stauffer *et al.*, 1985; Blake & Rowland, 1986, 1988; Pearman *et al.*, 1986; Steele *et al.*, 1987; Khalil *et al.*, 1989; Lang *et al.*, 1990a,b). Currently, the total annual emission of methane is about twice that estimated for the pre-industrial period, but both the relative and absolute contribution of wetlands is smaller than in the past. The total annual source strength is estimated to be ~450-500 Tg, dominated by natural wetlands, rice cultivation, animals, biomass burning, landfills, and fossil fuel extraction, transmission and distribution, but considerable uncertainties remain with respect to contributions of these individual sources.

Information about the sources and sinks of methane is intrinsic in its atmospheric concentration and its variations. In addition to the globally averaged concentration and the annual rate of increase, additional source/sink information is contained in the north-south gradient, and seasonal and geographic variations. Also, because some sources or source groups have distinctive signatures in $^{13}C$ and $^{14}C$, geographic and temporal variations in the composition of these isotopes provide additional quantitative constraints on the budget of methane.

The suite of data available to analyse the global methane budget has expanded considerably during the last decade. A globally distributed network of stations measuring atmospheric constituents has yielded important information characterizing the seasonal, temporal and geographic variations of atmospheric methane. The total data set of measurements of methane production and efflux, as well as laboratory manipulations investigating controlling factors, has expanded significantly for wetland ecosystems and landfill environments. Measurements of the isotopic composition of methane in the atmosphere and from a variety of sources are increasing. Large-scale interdisciplinary field campaigns, designed to characterize chemistry and dynamics of the regional troposphere, have been conducted in wetland habitats of Alaska, Canada, Central Africa and the Amazon Basin. Compilations of fundamental data on the distribution of source categories, crucial for extrapolating methane emission data, have been completed at country, regional and global scales for most of the major sources such as wetlands, rice, animals, landfills, and energy use. Finally, modelling and synthesis techniques for analysing and evaluating the information have improved.

The following sections provide a brief overview of the major methane sources and estimates of their magnitude as well as a review of uncertainties and possible techniques and/or data to reduce them. The discussion relates to a methane budget (Table 1) adapted from a variety of recent sources (Cicerone & Oremland, 1988; Fung *et al.*, 1991; Khalil, 1993 and others). This should be viewed as a candidate budget that satisfies the general constraints imposed by the mass balance of methane and its carbon isotopes.

## 2. Natural sources and their uncertainties

*2.1 Wetlands.* Natural wetlands occupy ~5.3-5.7 x $10^9$ $m^2$ globally (Matthews & Fung, 1987; Aselmann & Crutzen, 1989). About half the area occurs in high-latitude environments north of 50°N, while about a third are tropical/subtropical swamps and alluvial formations; temperate environments account for the small balance. Wetlands are most likely the largest natural source of methane to the atmosphere. Their methane emissions are estimated to be about 100 Tg annually (Matthews & Fung, 1987; Aselmann & Crutzen, 1989; Bartlett *et al.*, 1990; Fung *et al.*, 1991; Bartlett & Harriss, 1993), with about 30% associated with peat-rich, temperature regulated northern wetlands and the remainder from low latitude systems dominated by precipitation and flood cycles. Methane characteristics of most major wetland environments have been studied; notable exceptions are the wetlands of Russia which occupy about 25% of the global total, and non-riverine tropical grasslands such as the Pantanal in Brazil. Characterization of seasonal and inter-annual flux variability via full-season, full year and multi-year measurements has been accomplished by measurements carried out in South American wetlands along the Amazon River, African wetlands in the Congo, Alaska, the Hudson Bay Lowlands of Canada and northern Minnesota peatlands in the USA (see Bartlett & Harriss, 1993 for a complete review). Quantitative relationships between flux and controlling variables such as temperature and water status have been developed from measurements in various ecosystems but are not constant among all wetlands. Both flux measurements and large-scale modelling studies confirm the dominance of low-latitude wetlands and the smaller role of northern ecosystems in methane emissions for current climate conditions. There is general agreement concerning the global area and distribution of wetlands although uncertainties remain as to seasonal variations of wetland environments and dynamics of methane production periods. Less tractable problems relate to the confirmed importance of highly local controls (topography, water table, organic content) on fluxes as well as to the large role played by episodic efflux events such as ebullition, degassing, hydrostatic pressure changes and wind in total seasonal emissions in some wetland habitats (Bartlett *et al.*, 1988, 1990; Crill *et al.*, 1988; Devol *et al.*, 1988, 1990; Wilson *et al.*, 1989; Keller, 1990; Moore *et al.*, 1990; Wassmann *et al.*, 1992). The relative role of bubbling apparently varies with ecosystem; ebullient fractions of total seasonal fluxes increase from open water to grass mats and flooded forest. Furthermore, bubbling events appear to be more pronounced during periods of falling and low water and in shallow lake waters. In subarctic boreal fens, episodic degassing pulses have been associated with lowered water tables following

**TABLE 1.** Candidate budget that satisfies the constraints imposed by the mass balance of methane and its carbon isotopes. Adapted from Cicerone & Oremland (1988), Fung *et al.* (1991), and others.

| | Methane $10^{12}$ g (Tg) |
|---|---|
| Atmospheric Burden | 4600 - 4800 |
| 1670 nmol/mol in 1988<br>Lifetime: 8 - 12 years | |
| Annual Trend | 40 - 45 |
| 14 - 16 nmol/mol per year<br>(~0.7% per year) | |
| Annual Sources | 500 |
| 1. Fossil fuel: | |
| Coal mining | 35 |
| Natural gas: | 40 |
| Venting | 10 |
| Transmission loss | 30 |
| 2.Biomass burning | 55 |
| 3. Natural wetlands | 115 |
| High latitude (bogs, tundra) | 35 |
| Low latitude (swamps, alluvial) | 80 |
| 4. Rice cultivation | 75 |
| 5. Animals - mainly domestic ruminants | 80 |
| 6. Termites | 20 |
| 7. Oceans | 10 |
| 8. Landfills | 25 |
| 9. Methane hydrate destabilization | 5 (future ?) |
| 10.Wastewater treatment and animal waste | 40 |
| Annual Sinks | 460 |
| 1. OH destruction | 450 |
| 2. Absorption dry soils | 10 |

several weeks of reduced precipitation. The response particularly of high-latitude wetlands under a changing climate is highly uncertain; they may become larger or smaller methane sources or methane sinks (Livingston & Morrissey, 1991; Harriss & Frolking, 1992; Roulet *et al.*, 1992; Whalen & Reeburgh, 1992; Frolking, 1993)

*2.2 Termites.* The source strength of termites has been estimated with a very large range of 0-200 Tg methane per year (Zimmerman *et al.*, 1982, 1984; Zimmerman & Greenberg, 1983; Rasmussen & Khalil, 1983a,b; Seiler *et al.*, 1984; Fraser *et al.*, 1986). Extrapolations from laboratory and field measurements have been made using estimates of termite populations, amounts of organic material consumed by termites, species differences, and activity of methane-oxidizing bacteria. Despite the very wide range in total emission, the habitat distribution of the termite source is similar among several studies; termites are concentrated in tropical grasslands and forests: about 40% of the methane is assumed to emanate from savannas and about 35% from tropical forests. Given the current estimate of ~450-500 Tg methane as the total annual source, the upper range of estimates for this source is difficult to support. Recent estimates suggest emissions of 15-20 Tg/year (Rouland *et al.*, 1993)

*2.3 Oceans* The ocean source is very poorly known but considered minor. Measurements in the open ocean indicate a steady supersaturation coefficient of about 1.3. Coastal ocean regions exhibit higher and more variable concentrations and very high supersaturation values. The emission estimate of 10 Tg, presented several decades ago, is essentially identical to more recent estimates/calculations based on significantly more measurements (Lambert & Schmidt, 1993).

*2.4 Methane hydrates* Methane hydrates, rigid water cages surrounding methane molecules, are known or inferred to be found on the continental shelf at all latitudes (Kvenholden, 1988); it has been hypothesized that those hydrates located in the Arctic, in particular the offshore permafrost, are most subject to destabilization from climate warming (Bell, 1983; Revelle, 1983; Kvenholden, 1988). However, stability of hydrates requires high pressure and cold temperatures, meaning that most occur at depths and in regions insulated from climate change. The dispersed nature of this source makes it especially difficult to evaluate. At present, the methane source from hydrates is considered minor, but the large pool of methane in gas hydrates implies that a small perturbation under a changing climate could produce a considerable source of methane.

## 3. Anthropogenic sources and their uncertainties

*3.1 Rice Cultivation.* Rice cultivation may account for 10-20% (~50-100 Tg) of the total annual methane emission (Khalil & Rasmussen, 1983; Holzapfel-Pschorn & Seiler, 1986; Aselmann & Crutzen, 1989; Schutz *et al.*, 1989, 1990; Neue *et al.*, 1990; Matthews *et al.*, 1991). Since the mid-1970s, rice production has risen by ~30% . This was achieved through the combined effects of increased harvest areas (4%), and higher yields (40%); the latter includes increases from multiple cropping. Globally, about 60% of the area is managed under a triple crop system, ~15% is double cropped, and 25% is harvested from fields planted to rice once a year, suggesting that much of the potential for multiple cropping is already exploited (Matthews *et al.*, 1991). Although the cultivation of rice extends from 50°N to 50°S, half of the ~1500 x $10^9$ $m^2$ harvested area occurs in a narrow subtropical zone from 30°N to 20°N and over 90% is confined to Asia. The climatically regulated concentration of rice cultivation telescopes more than 50% of the methane emission into a few months (July through October). A large number of factors affect the production, transport and efflux of methane in flooded rice fields, among them temperature, water status, fertilizer application, soil properties, and plant phenology. Laboratory and field studies suggest that as much as 90% of methane produced in sediments may oxidize during transport to the water surface. Basic information readily available, by country, for estimating methane emissions from rice cultivation includes: harvested rice area, rice yield and rice production; planting and harvest dates of crops; number and area of crop cycles, and length and timing of crop cycles. Less available is information on local soil temperatures, type and application rate of fertilizers (especially non-commercial organics), seasonal and annual variations in water status, and soil chemistry. Furthermore, even with sufficient data on such factors, considerable uncertainties remain in determining quantitative relationships between methane flux and these factors.

*3.2 Domestic Animals.* Animals contribute about 80 Tg methane per year (Crutzen *et al.*, 1986; Lerner *et al.*, 1988). About half of the global emission comes from India, China, the former USSR, USA, and Brazil. Non-dairy cattle and dairy cows together contribute about 75% of the total methane source from animals; the remainder is from water buffalo, sheep, goats, pigs, camels and horses. Methane production from animals, which results from fermentation of carbohydrates in the rumen, is affected by factors such as quantity and quality of feed, body weight, age and activity level. Therefore, it varies among animal species as well as among individuals of the same species. Because of the economic importance of domestic animals, statistics on their populations are reasonably reliable. Furthermore, since methane emission from animals represents a loss in the conversion of feed to product, and many domestic animals in commercially developed economies are raised under highly managed feeding systems, a large body of information on methane emissions from animals and on feed, age, size and activity profiles of animals is available for the more developed economies. Greater uncertainties exist with respect to such profiles for less developed countries. Nevertheless, emissions from animals may be one of the better known sources in the methane budget.

*3.3 Fossil Fuel.* Methane is the major component of coal gas and natural gas. Fossil sources of methane include coal mining and processing, and natural gas exploration, production, transmission, and distribution. Direct and indirect methods have been employed to evaluate and place constraints on the fossil fuel source. Indirect methods involve inferring the fossil source from carbon-14 measurements of the atmosphere and sources themselves. Carbon-14 based estimates of methane emission associated with fossil fuel sources range from ~16 to 24% of the total source strength (Quay *et al.* , 1991; Wahlen *et al.* , 1989; Manning *et al.* , 1990) equal to about 80-120 Tg. Alternatively, researchers have attempted to estimate methane release directly using country and/or regional statistics of energy production and delivery in conjunction with global inventories of coal and gas production activities and assumptions about fractions of fuel released as methane (e.g., Fung *et al.*, 1991; Beck *et al.*, 1993). Estimates from such direct methods, although subject to large uncertainties and not inclusive of all fossil sources, appear to be consistent with the lower end of the emission range established by isotopic analysis.

Methane released to the atmosphere during mining and processing of coal is associated directly with coal removed from mines as well as with releases from coal left behind, overlying and underlying seams and nearby gas deposits . As with other fossil fuel sources, determining the distribution of the source (i.e., coal mines) is relatively straightforward and statistics on coal production for regions and countries are abundant. Various emission estimates combining statistics on coal production with assumptions about its methane content, and including post-mining releases, range from about 35 to 65 Tg methane per annum. A recent review by Beck *et al.* (1993) indicates that most of the variation among estimates results from inclusion and/or exclusion of processes or particular coal products as well as from large variations in the emission factors used in the studies.

Methane emissions associated with natural gas production and consumption include venting and flaring at oil and gas wells, explosive events at well sites, and losses during processing, transmission and distribution. Estimates of the vented and flared fraction of natural gas production vary with region and with time. For example, in 1984, venting and flaring was 2% of marketed production in Europe, 18% in Central and South America and 61% in the Middle East; vented and flared fractions of global natural gas production were as high as 12% in the early 1970s and were at a minimum of 5% in the early 1980s. Using an estimate of 20% for the uncombusted portion of flared and vented natural gas that is released as methane gives emission values around 15 Tg methane for the 1980s.

In practice, natural gas transmission losses are the difference between gas purchased for delivery and gas sold, differences which may be due to theft and metering errors as well as to actual leaks. Since some fraction of this gas is not leaked, calculations based on 'unaccounted for' gas (UAG) probably overestimate methane emission. In a recent review of emission estimates for the natural gas industry, Beck *et al.* (1993) demonstrate the strong dependence of calculated emissions upon assumed loss rates; these rates have varied from 1-10% of total pipeline throughput in studies published between 1972 and 1991, although typical rates are 1-4%. Transmission/distribution system loss rates appear to vary considerably by country. For instance, losses for Brazil have recently been estimated at 1.2% while those of the United Kingdom may be as high as 3.6% (Beck *et al.*, 1993). Using various methods and assumptions, recent estimates of methane emissions from natural gas transmission are in the range of ~30-50 Tg but the geographically- and sectorially-dispersed nature of this source makes direct estimates difficult . However, constraint on the total contribution of fossil ($^{14}C$-free) sources may be provided by isotopic measurements of atmospheric methane.

*3.4 Biomass burning.* The contribution of biomass burning to the global emission of methane is highly uncertain due to the innate variability of the process itself as well as to severe data limitations (Levine, 1991). The amount of methane released when vegetation is burned is a function of burning technique and temperature, moisture and carbon content of the vegetation, amount and type of vegetation burned etc. A considerable portion of burning takes place in association with poorly documented agricultural activities in the tropics. Recent estimates based on area, biomass density and burning efficiencies of disturbed vegetation, as well as fuelwood use and burning of agricultural wastes, indicate annual methane releases of ~10-50 Tg (Crutzen & Andreae, 1990; Andreae, 1991); $^{13}C/^{12}C$ ratios of atmospheric methane have been used to infer a methane release of ~50 Tg (Craig *et al.*, 1988).

*3.5 Waste Disposal* Decomposition of biodegradable organic material in landfills produces both carbon dioxide and methane. The initial oxidation of carbon, which produces $CO_2$, results in increasingly anaerobic sites within landfills which facilitate the changeover to methane production. Field measurements confirm that some, perhaps a significant fraction, of the methane produced in landfills is consumed during transport through the cover material. One early global estimate of methane emission from landfills gave a range of 30-70 Tg/year (Bingemer & Crutzen, 1987). This is considered to be the upper limit since the study assumes maximum rates of decomposition and methane production under ideal conditions as well as assuming that the total production potential is emitted. More recent estimates suggest that the landfill methane source may be more in the range of ~25 Tg for several reasons (Bogner & Spokas, 1993; Peer *et al.*, 1993). First, methane consumption in landfill soil or clay caps reduces the emitted fraction of total methane production. Second, the early study may have underestimated waste production and landfilled municipal solid waste while overestimating the methane-generating potential of the waste, resulting in an overestimate. Uncertainties remain with respect to the magnitude and composition of waste production and the fraction of waste placed in landfills. Furthermore local factors such as climate, age of refuse, and landfill design, construction, and management affect the amount of methane produced, consumed and emitted in these sites. The very high variability in these factors among disposal sites suggests that the problem is data limited.

A very sparse information base is available for estimating methane emissions from wastewater treatment and from lifestock; preliminary estimates indicate that these poorly known and difficult to quantify sources may be comparable to landfills with respect to methane emission (Thorneloe *et al.*, 1993).

## 4. Summary

The result of research during the past 20-30 years has been a trend toward declining estimated source strengths for the major sources accompanied by an increase in the number of sources identified as potential contributors to the methane cycle. Methane sources under anthropogenic control currently account for approximately 70% of the total annual emission. Several of these (e.g., animals, rice cultivation, energy-related sources) may be prone to future increases due to demands of increasing human populations. The general magnitude of the remaining natural sources, dominated by wetlands, is probably reasonably well known. Currently, boreal wetland emissions contribute about one-third of the world's total wetland emissions while the tropics account for most of the remainder. However, wetland response to climate change predicted for the next century is highly uncertain. Depending on local interactions among temperature, water status, nutrients etc., wetland ecosystems may become larger or smaller methane sources, or methane sinks. A varied collection of additional sources such as volcanoes, oceans, seabed seepage, gas hydrates, and peat mining are highly uncertain but considered minor, probably accounting for a total of ~20 Tg.

Although analysis techniques and the body of data available for direct estimates of methane emissions and for evaluation and constraint of emission scenarios has expanded considerably during the last decade, the methane budget cannot yet be uniquely defined. Understanding wetland emissions is limited less by data than by lack of understanding of the processes of production, transport and release in climatically and ecologically distinct habitats. Improvements in the accuracy and coverage of $^{14}C$ and $^{13}C$ measurements of methane in the atmosphere and from sources are crucial to establishing credible limits on sources such as fossil fuels and biomass burning. Expansion of atmospheric trace-gas measurements to source regions in Southeast Asia, tropical South America and Africa, and boreal habitats will help to characterize source signatures and their variations. Finally, photochemical-transport models that synthesize and evaluate suites of source/sink distributions provide a crucial integrative pathway to narrowing current uncertainties about sources in the global methane budget.

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# GLOBAL METHANE EMISSIONS FROM BIOMASS BURNING AND COMPARISON WITH OTHER SOURCES

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## Abstract

The major applications of biomass burning by humans are in the clearance of forests and brushlands for agricultural use, energy production for cooking and heating, and the removal of agricultural waste, primarily in the tropics. $CH_4/CO_2$ emission factors for these processes, derived from laboratory and field observations, are reviewed and combined with estimates for land use and biomass fuel consumption to obtain a global estimate for the emission of methane from biomass burning. The best estimates derived for individual processes are (in Tg $CH_4$/a): 11.9 from shifting agriculture and permanent deforestation in the tropics, 4.6 from extratropical forest fires, 8.6 from savanna fires, 14.8 from the use of biomass as fuel, and 3.6 from the burning of agricultural wastes, summing to a total of 43, with a range of 22-75 Tg $CH_4$/a. Compared with other methane sources, mainly microbiological and fossil fuel related, biomass burning contributes about 8.5% to a total emission rate of about 500 Tg $CH_4$/a.

## 1. Introduction

Fire has been an important tool in the hands of humans ever since our distant ancestors learned to tame and manipulate fire for various purposes. One of the most widespread applications has been, and still is, the use of fire in agriculture. Especially in the tropics the burning of biomass, which consist of both living and dead plant organic matter, serves to clear land for shifting cultivation, to convert forests to agricultural fields and pastures, and to remove dry vegetation in order to promote new growth and higher yields. In addition, agricultural wastes are burned and fuel wood is used for cooking and heating purposes (Crutzen & Andreae, 1990, Andreae, 1991). In contrast to the massive quantities of fossil fuels which are consumed predominantly in the industrialized world, biomass burning takes place largely in the developing countries. Biomass fires emit much the same pollutants as the combustion of fossil fuels, but as biomass burning usually occurs in the open air no emission controls can usually be applied. As a consequence, open fires often lead to an extensive pollution of the atmosphere. The main gases released are carbon dioxide, carbon monoxide, hydrocarbons and nitrogen oxides. The latter three gases in particular combine to furnish the principal ingredients for the formation of photochemical smog in the atmosphere.

In this article we focus on biomass burning as a source of methane. We shall first discuss the mechanism of biomass burning and the generation of methane during this process, then estimate the global rate of biomass consumption by fire, and finally derive an estimate for the global yield of methane from this source. This will then be compared with the strengths of other sources of atmospheric methane.

## 2. Role of methane in the atmosphere

Methane contributes strongly to the greenhouse effect. In this regard it has 11-35 times the efficiency per mole as $CO_2$ (Houghton *et al.*, 1992). The atmospheric abundance of methane currently is about 1.7 µmol per mole of dry air, and it is rising at a rate of about 1% per year (Blake & Rowland, 1988; WMO 1992). The residence time of methane in the atmosphere is about 10 years (Warneck, 1988), sufficient time for $CH_4$ to enter the stratosphere. The oxidation of methane is initiated mainly by reaction with OH radicals.

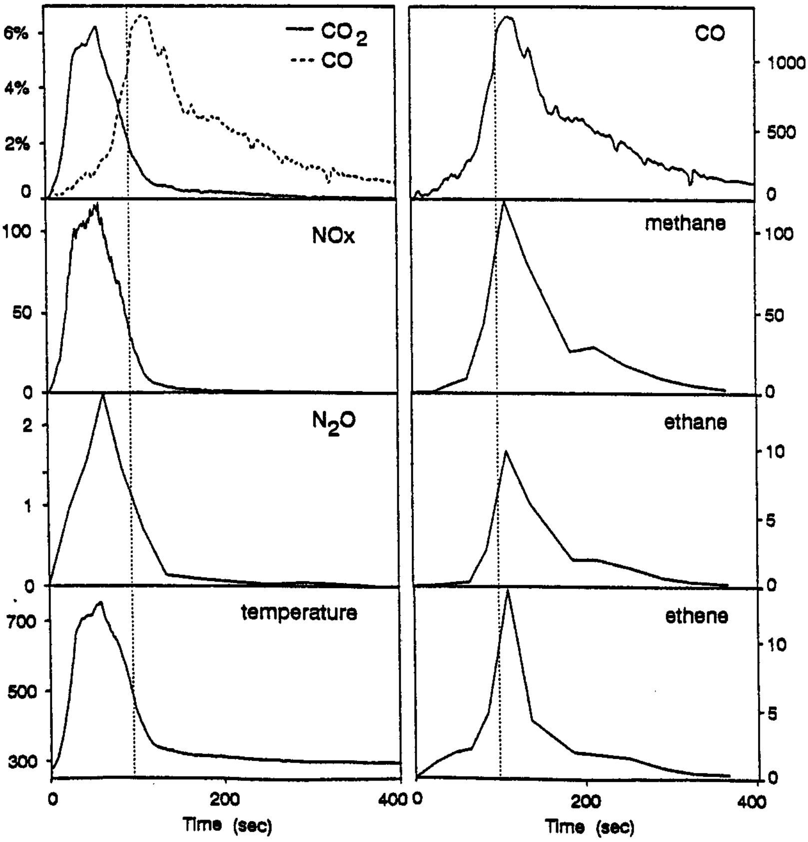

Fig. 1. Evolution of $CO_2$, CO and other trace gases from laboratory scale open air fires. Mixing ratios above background are given in volume percent for $CO_2$ and in µmol/mol for other gases, stack-gas temperature in Kelvin. The vertical dotted lines indicate the transition from flaming to smouldering combustion. (Data from Lobert *et al.*, 1991)

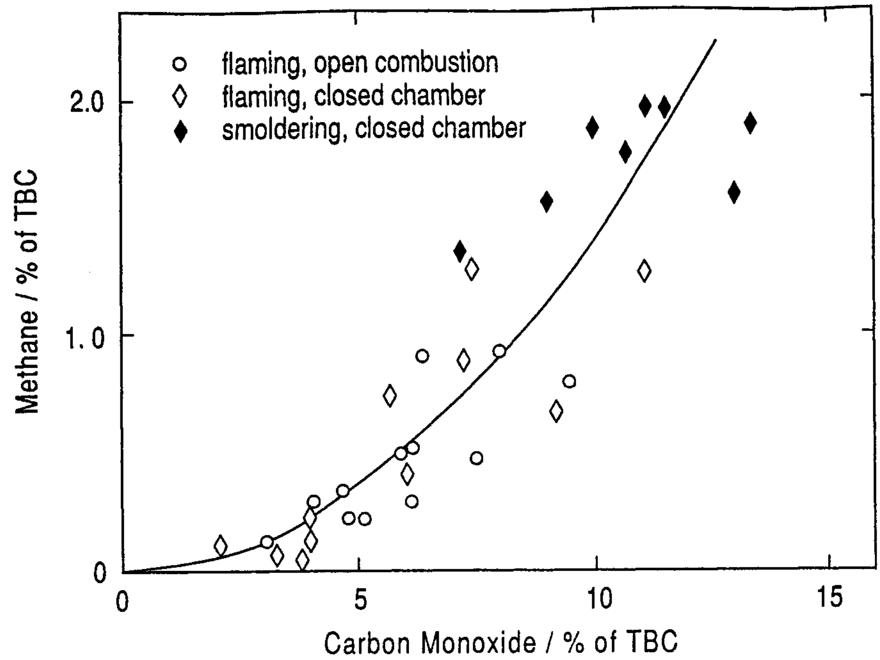

**Fig.2.** Plot of integrated amounts of methane versus those for carbon monoxide observed in various laboratory combustion experiments, in percent of total burned carbon (TBC). Open symbols indicate fires with a definite flaming stage, filled symbols are for smouldering combustion only. The solid line is a quadratic fit to the data. (Experimental data from Lobert, 1989; and Kuhlbusch *et al.*, 1991)

The oxidation ultimately leads to the formation of two moles of $H_2O$ per mole of $CH_4$, and thus the process adds substantially to the water content of the stratosphere. By reacting with Cl atoms methane converts them to hydrochloric acid, thereby interrupting the chain reaction involving Cl and ClO radicals that are responsible for much of the destruction of stratospheric ozone. In the troposphere, as well as in the stratosphere, methane is a precursor of formaldehyde and carbon monoxide, and it is also one of the reagents that control the concentration of OH radicals and consequently the oxidizing potential of the atmosphere.

*Mechanism of biomass burning* The combustion of biomass occurs in three stages that can be differentiated as follows (Lobert *et al.*, 1991): The first stage involves pyrolysis of the fuel and the emission of volatile organic compounds; in the second stage the organic volatiles are burned in a turbulent, high temperature flame; and the last stage consists of smouldering combustion, which sets in when the rate of volatile formation decreases so much that it can no longer sustain a turbulent flame. The combustion zone then retreats to the surface of the residual (highly charred) fuel, and oxygen is transported to the combustion site by molecular diffusion rather than turbulent mixing.

Figure 1 shows in a generalized fashion results from laboratory studies on the evolution of several gaseous combustion products. The apparatus used to obtain such data consists of a burning table placed on a high resolution balance whereby the weight losses due to gaseous emissions are registered. Usually about 500 g of biomass are subjected to combustion. Fuels studied include Australian and Venezuelan savanna grasses, straw, hay, deciduous wood, pine needles, needle litter, green grass and tobacco. Product gases are collected in a hood and then forced to flow through a smoke stack with a fan providing the necessary draft. Flow rate and temperature of the stack gases are continuously monitored. The contents of $CO_2$ and CO were determined by continuous sampling and non-dispersive infrared analysis. $NO_x$ was determined similarly with a chemiluminescence analyzer. Methane, other hydrocarbons and various nitrogen-containing gases are determined discontinuously by taking grab samples followed by gas chromatographic analysis. Analytical and experimental conditions have been described in some detail elsewhere (Lobert *et al.*, 1991).

Figure 1 shows that stack temperature as well as mixing ratios for $CO_2$ and $NO_x$ peak during the first 100 s of biomass burning, that is during flaming combustion, whereas the mixing ratios of CO and a number of other reduced compounds occurring in the stack gases rise more gradually and exhibit a maximum after the flame has died out and smouldering combustion has taken over. It appears that because of the limited supply of oxygen during smouldering combustion a greater fraction of organic volatiles can escape unoxidized into the surrounding air, in contrast to conditions existing during the flaming phase. However, it should also be noted that certain reduced compounds, for example nitrous oxide, $N_2O$, and molecular nitrogen, $N_2$, are formed primarily in the high temperature environment of the flame. These experiments were characterized by an almost complete combustion of the fuel. In a series of 41 experiments the percentage of carbon volatilized was 95.3±4.6 %, with 80.9±10.0 % of volatile carbon appearing as $CO_2$. The percentage of carbon dioxide emitted during the flaming stage was 62.8±14.6, on average (Lobert, 1989).

*The production of methane by biomass burning.* Methane belongs to the group of gases that like CO are formed primarily by smouldering combustion. Figure 2 shows the close relation between methane and carbon monoxide. The figure combines results obtained with the open combustion system described above and data from combustion experiments in a closed chamber in which smaller amounts of fuel (about 5 g) were burned in mixtures of oxygen with either helium or argon (Kuhlbusch *et al.*, 1991). Because of the higher thermal conductivity of helium, its use increased heat losses and resulted in a greater extent of smouldering combustion. In these cases the $CH_4/CO$ emission ratio was particularly high with an average of 0.178±0.041, whereas flaming combustion events resulted in a $CH_4/CO$ emission ratio of 0.078±0.043 in both combustion systems. As Figure 2 shows, the complete data set cannot be fitted to a straight line that meets the origin. The data are better described by a quadratic curve as shown. The reason for this behaviour presumably is the combustion of methane in the flame and the production of carbon monoxide as an intermediate during this process.

*Methane emission ratios.* The production of methane by biomass burning has been observed not only in the laboratory but also in the field. The majority of such studies utilized air samples collected onboard small aircraft operating in the vicinity of fires. Since carbon dioxide is the major gaseous product from biomass burning, the amounts of methane are related to those of carbon dioxide by determining the ratio of both components. The procedure involves measurements of the mixing ratios of methane and carbon dioxide in air samples taken inside and outside the plume generated by the fire. The emission ratio is calculated from the difference against background air. Table 1 summarizes data obtained in this manner.

The major problem of determining realistic methane emission ratios from laboratory experiments is the uncertainty in the extent of flaming versus smouldering combustion occurring in the field. Flaming combustion in laboratory experiments may be more pronounced because the fuel usually is drier and becomes more completely volatilized. These factors would tend to reduce the $CH_4/CO_2$ emission ratio. On the other hand, the emission ratio depends also considerably on the material that is burned.

Savanna grass set on fire at the end of the dry season is expected to behave fairly much like that burned under laboratory conditions, whereas biomass fuel from tropical forests may lead to a greater extent of smouldering combustion even after extensive drying. From such considerations it appears that field determinations of methane emission factors should give results closer to reality. However, as Table 1 makes apparent, the observed emission ratios are quite variable, even within samples of the same fire. They compare nevertheless reasonably well with the average molar $CH_4/CO_2$ ratio obtained in the laboratory, which is (6±4) x $10^{-3}$, derived mainly from straw and savanna grasses. Delmas *et al.* (1991) have recently compared methane emission ratios from ground-based measurements in plumes of various fires in the African savanna and reported the following values (in percent): bushfire 0.28±0.04, forest fire 1.23±0.6, fire wood 1.79±0.81, burning of charcoal 0.14, and emissions from charcoal kilns 12.06±2.86. Five to six samples were taken to derive averages in each case. On the basis of these data we shall use values of 4 x $10^{-3}$ for tropical savanna grasses, 1.2x$10^{-2}$ for forest fires, and 1.4 x $10^{-2}$ for fire wood.

**TABLE 1.** Methane from biomass burning. Relative emission factors derived from aircraft measurements in the plumes of fires.

| authors | $CH_4/CO_2$[a] mol percent | $CH_4/CO$[b] mole ratio | type of fire |
|---|---|---|---|
| Crutzen *et al.* (1979) | 2.1 (1.6-2.5) | 0.17 | forest and agricultural wastes |
| Greenberg *et al.* (1984) | 0.6 (0.2-2.4) | 0.08 | grassland |
| | 1.1 (0.5-2.3) | 0.09 | tropical forest |
| Cofer *et al.* (1988) | 0.36 (±0.6) | 0.07 | chaparral fires, flaming |
| | 0.43 (±0.1) | 0.07 | mixed flaming/smoldering |
| Cofer *et al.*(1989) | 0.76(0.24) | 0.12 | chaparralfires,flaming |
| | 0.87 (0.23) | 0.09 | smoldering |
| | 0.61 (0.07) | 0.11 | mixed |
| Hegg *et al.* (1990) | 0.49 (±0.11) | 0.06 | average for various forest and brush fires |
| Cofer *et al.* (1990a) | 0.64 (±0.20) | 0.1 | boreal forest, flaming |
| | 1.21 (±0.32) | 0.1 | smoldering |
| | 1.12 (±0.31) | 0.1 | mixed |
| Cofer *et al.* (1990b) | 0.26 (0.18-0.37) | 0.55 | wetlands, flaming |
| | 0.36 (0.22-0.49) | 0.63 | wetlands, smoldering |
| Susott *et al.*(1990) | 0.48 (±0.41) | 0.055 | logging slash, flaming |
| | 1.5 (±0.65) | 0.085 | logging slash, smoldering |
| | 0.9 | 0.067 | weighted average |
| Griffith *et al.* (1991) | 1.32 (1.2-1.6) | 0.08 | sagebrush and coniferous forest waste |
| Delmas *et al.* (1991) | 0.39 (0.23-0.73) | - | tropical savanna and bushland |
| Ward *et al.* (1991) | 0.09 | 0.04 | savanna |
| | 0.82 (±0.28) | 1.0 | rainforest clearing |

(a) average and either range or standard deviation. (b) ratio of the average emission factors for $CH_4$ and CO relative to $CO_2$.

*Amounts of biomass burned worldwide.* The major applications of biomass burning by humans are in the clearance of forests and brushlands for agricultural use, energy production for cooking and heating, and the removal of agricultural waste. The associated rates of biomass consumption were first estimated by Seiler & Crutzen (1980). Recently, a renewed effort has been made by Hao *et al.* (1990) and Andreae (1991) to improve these estimates. In all cases, the estimates are based on land use and population statistics. Table 2 gives a summary of the amounts of biomass exposed to fire, actually burned, and carbon released on a global scale. We can here indicate only briefly how these estimates were derived.

In *shifting agriculture* fallow forests are usually cleared and the land is cultivated for about two years. Thereafter the land is abandoned and left to regrow a secondary forest for 10-20 years. This type of agriculture affects an area of about 3 x $10^5$ $km_2$ annually. With biomass densities of 4-12 $kg/m^2$, of which 70-80% are above ground, 1-2 Pg of dry biomass is exposed to fire per year. The corresponding amount of carbon is 400-1100 Tg (the average mass content of carbon in biomass is 45% of dry matter). An estimated 40% of this amount is burned and released promptly, predominantly as $CO_2$, whereas the rest is left to rot and is converted to $CO_2$ more slowly by microbial action. The wide range given in Table 2 for biomass burning by shifting cultivation is due to two disparate estimates of the areas involved.

**TABLE 2.** Global estimates of amounts of biomass burned annually and the resulting release of carbon and methane to the atmosphere[a]

| type of activity | biomass exposed to fire | | | carbon released | carbon released as $CO_2$ | $CH_4/CO_2$ | carbon released as $CH_4$ |
|---|---|---|---|---|---|---|---|
| | tropical | extratropical | total | | | | |
| | Pg dry matter per annum | | | % | Tg C/a | % | Tg $CH_4$/a |
| shifting agriculture[b] | 0.8 - 2.3 | - | 0.8 - 2.3 | 45 | 170 - 470 | 1.2 | 5.2(2.7-7.5) |
| permanent deforestation[c] | 1.0 - 3.2 | - | 1.0 - 3.2 | 45 | 200 - 650 | 1.2 | 6.7(3.2-10) |
| forest fires (extratrop.)[d] | - | 0.6 - 1.8 | 0.6 - 1.8 | 40 | 110 - 320 | 1.2 | 4.6(2.3-6.9) |
| savanna burning[b] | 2.2 - 6.6 | - | 2.2 - 6.6 | 80 | 790 - 2410 | 0.4 | 8.6(4.2-13) |
| biomass fuel[d] | 0.9 - 3.5 | 0.1 - 0.4 | 1.0 - 3.9 | 90 | 400 - 1590 | 1.4 | 14.8(7.4-30) |
| agricultural waste in fields[d] | 0.2 - 0.8 | 0.2 - 0.8 | 0.4 - 1.7 | 90 | 190 - 680 | 0.8 | 3.6(1.8-7.2) |
| totals | 6.9 - 14.1 | 0.9 - 3.1 | 6.0 -17.2 | | 1860 - 6120 | | 43(22-75) |

(a) Biomass dry matter contains about 45% carbon by mass; (b) biomass exposed to fire according to estimates of Hao *et al.* (1990); (c) estimated by Crutzen & Andreae (1990); (d) estimated by Andreae (1991, 1992).

Permanent removal of forests now occurs at an increasing rate due to an expanding population. An area of about 1 x $10^5$ $km^2$ is cleared every year, but the areal extent is again rather uncertain. Most of the activity takes place in tropical America, which contributes as much as Africa and Asia taken together. Total biomass cleared is on the order of 2.4-8 Pg/a, corresponding to 1.1-3.6 Pg C/a (Houghton, 1991). About 60% of this biomass is below ground, including soil organic matter, so that ca. 1.0-3.2 Pg dry matter are exposed to fire annually. About 40-50% of this material is consumed by fire, the rest is decomposed by microorganisms (Crutzen & Andreae, 1990). Tropical savannas and brushlands are estimated to cover an area of about 13 million $km^2$ worldwide.

Savannas are burned every 1-4 years during the dry season with the highest frequency in the humid tropics. The amount of above-ground biomass carbon exposed to fire is estimated to range from 90 to 300 g $C/m^2$, depending on location, which would expose about 0.6-2.0 Pg C/a to fire in savanna regions. If 80% of it were volatilized by combustion, the corresponding release would be 0.47-1.64 Pg C/a for a biannual intermittent burning. Hao *et al.* (1990) estimated total biomass exposed to fire and burned annually in savannas to sum to 4.4 and 3.7 Pg dry matter, respectively, which they consider uncertain to +50%. These figures were used as entries in Table 2.

Fuel wood and agricultural waste is difficult to separate, because much of the waste is consumed domestically. The estimated per capita fuel need in developing countries ranges from 350 to 2500 kg per annum. An appropriate average would be 500 kg/a. The number of people living in the tropics is about 3800 million. The corresponding dry mass of fuel consumed would be 1.9 Pg per year or 0.9 Pg C/a. The entry in Table 2, which is partly based on Food and Agriculture Organization statistics used by Andreae (1991, 1992), is more conservative. Charcoal for domestic and industrial uses finds increasing application but represents still a relatively minor fraction of the total so that it can be ignored for the present purpose, even though its production leads to rather high methane emissions. Agricultural wastes, that is crop residues, have been estimated to amount to 3.4 Pg dry matter per year, with about 1.5 Pg produced in the developed and 1.9 Pg in developing countries. If, as assumed by Andreae (1991), 50 and 80%, respectively, were burned (much of it as domestic fuel), it would amount to a rate of carbon volatilization of about 1 Pg C/a. The lower rate of the range given in Table 2 is due to an independent estimate by Hao *et al.* (1990).

### 3. Global rate of methane emissions from biomass burning

The last column of Table 2 contains the global rates for methane emissions from the various biomass sources considered. We find that the amounts of methane released are rather similar for the various sources. Although with regard to $CO_2$ emissions, savanna fires are most productive, because of the large areas involved, the methane emission factor is rather small in this case, so that savanna fires contribute only about 20% to total methane from biomass burning. Forest clearance, either due to shifting cultivation or permanent deforestation, and wood used as fuel dominate the production of methane. The sum of global emissions is 21.6-74.5 Tg $CH_4$/a. This is only about half the rate estimated by Bolle *et al.* (1986) as 55-110 Tg $CH_4$/a but agrees closely with the most recent Intergovernmental Panel on Climate Change assessment (Houghton *et al.*, 1992). On the basis of the data provided by Hao *et al.* (1990), Crutzen & Andreae (1990) and Andreae (1991, 1992), the best estimates derived from the present study are, in Tg $CH_4$/a, 16.5 from shifting agriculture, permanent deforestation and extratropical forest fires combined, 8.6 from savanna fires, 14.8 from the use of biomass fuel, and 3.6 from the burning of agricultural wastes, summing to a total of 43 Tg $CH_4$/a on a global scale.

Table 2 shows that the uncertainties associated with individual estimates are large, and this is also reflected in the range for the total emission rate. The upper limit value is probably not applicable because it is unlikely that all of the individual emission rates have values near the upper end of the respective ranges of estimates. Although it might be possible to improve statistical data for land use and deforestation by using better methods such as satellite observations, uncertainties are expected to remain large. For example, biomass fuel consumption will be difficult to determine more accurately unless a reasonably complete census can be organized.

### Biomass burning in relation to other sources of methane

Table 3 gives an overview on global sources of methane and selected estimates for individual source strengths. The earliest estimate by Ehhalt (1974) is of historical interest. His major sources were domestic ruminants, rice fields and natural wetlands. Recent estimates for all three sources are greatly

**TABLE 3.** Methane emissions from various sources, global estimates.

| | Ehhalt (1974) | Bolle *et al.* (1986) | Cicerone & Oremland (1988) | Houghton *et al.* (1992) |
|---|---|---|---|---|
| Enteric Fermentation Vertebrates | 101-220 | 70-100 | 80 (65-100 | 80 (65-100) |
| Termites | - | 2-5 | 40 (10-100) | 20 (10-50) |
| Rice Paddy Fields | 280 | 70-170 | 110 (60-170) | 60 (20-150) |
| Natural Wetlands | 130-260 | 25-70 | 115 (100-200) | } 115 (100-200) |
| Tundra | - | 2-15 | 5 | |
| Ocean/Lakes | 6-45 | 1-7 | 15 (2-20) | 5 (1-25) |
| Domestic Sewage | - | - | - | 25 |
| Organic Waste Burial | - | 10 | 40 (30-70) | 30 (20-70) |
| Animal Waste | - | - | - | 25 (20-30) |
| Natural Gas Leakage | - | 30-40 | 45 (25-50) | }100 (70-120) |
| Coal Mining | 15-50 | 35 | 35 (25-45) | |
| Biomass Burning | - | 55-100 | 55 (50-100) | 40 (20-80) |
| Permafrost $CH_4$ Hydrates | - | - | - | 5 (0-5) |
| Total | 533-854 | 300-552 | 540 (370-855) | 500 (426-855) |

reduced but a number of new sources have been identified with smaller contributions. This is exemplified by the distribution of Bolle *et al.* (1986). Cicerone & Oremland ( 1988) have additionally considered the measured isotope ratios in order to provide constraints for the total budget of methane in the atmosphere. The last entry in Table 3 (Houghton *et al.*, 1992) represents the most recent assessment. Surprisingly, the total emission rate of about 500 Tg/a has remained about the same for the last twenty years. About two thirds of total emissions are related to human activities. Biomass burning, which belongs to this category, contributes about 8.5% to the total emission rate.

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# METHANE EMISSIONS FROM NORTHERN WETLANDS: SOURCE STRENGTH AND UNCERTAINTIES IN ESTIMATES

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## Abstract

Northern wetlands are of great interest as a natural source of methane in the atmosphere. Next to carbon dioxide, $CH_4$ is the most important greenhouse gas that is changing rapidly in the atmosphere. In 1990, the Canadian Northern Wetlands Study (NOWES) was undertaken to better understand the contribution of large continuous wetlands such as the Hudson Bay Lowlands and the Western Siberian Lowlands to total northern wetland $CH_4$ emissions. This large international study resulted in the conclusion that emissions from the continuous wetlands were 10 to 15 times lower than was previously estimated and that this translated into a decrease in emissions estimates for all northern wetlands by a factor of 2 to 4 from previously. The current best estimate is 16 Tg $yr^{-1}$ or 3% of the total global emissions from all sources. Uncertainties in emissions estimates are related to spatial and temporal variability within a wetland type and between wetlands as well as to the accuracy of current wetland classifications used to scale-up local emissions observations to larger regions. An accurate estimate of uncertainty is difficult. It is felt that current emissions estimates are no better than a factor of 2.

## 1. Introduction

Atmospheric methane, $CH_4$, has more than doubled in concentration since the industrial revolution, currently increasing at a rate of ≈ 0.8 to 1.0% $yr^{-1}$ (IPCC, 1990). It has no single dominant source, but rather many small ones. Delineation of these sources is required to predict the direct and indirect effects of $CH_4$ in present and future climate scenarios (Wuebbles and Tamaresis, 1991). However, while the sources are generally known, their absolute size is poorly defined. It is reasonably clear that anthropogenic sources account for ≈ 60 to 70% of the annual atmospheric burden of 505 Tg $yr^{-1}$, while natural sources account for the remainder (Crutzen, 1991). The largest natural source of $CH_4$ is wetlands.

The distribution of wetlands is usually divided into two groups: wetlands north of 40°N are referred to as northern wetlands, and all others as southern wetlands (Aselmann & Crutzen, 1989; Bartlett *et al.*, 1990). In this paper, we review past and present estimates of the $CH_4$ flux from northern wetlands and discuss their uncertainties. There are four sources of uncertainties that arise in making regional or global source estimates of biogenic gas fluxes: (**1**) uncertainties in the areal extent and classification of the ecosystems that are important in production and consumption of the gas; (**2**) uncertainties in the average flux attributed to each classified ecosystem in a specific climate region; (**3**) the uncertainties from seasonal and inter-annual variability in fluxes and (**4**) uncertainties due to measurement and analytical problems. Type-4 uncertainties have been discussed elsewhere (Moore & Roulet, 1991; Schütz & Seiler, 1989)

## 2. Past and present estimates of $CH_4$ emissions from northern wetlands

Past and present estimates of total annual flux from northern wetlands are summarized in Table 1. In the first estimate, made by Matthews & Fung (1987), global wetlands contributed over 20% of the total annual atmospheric burden, most of which (16%) was attributed to northern wetlands. This made the northern wetland source equal to that of animals or rice paddies (Cicerone & Oremland, 1987). However, at the time of the Matthews & Fung (1987) estimate, there were very few flux measurements available from northern wetlands (eg. Harriss *et al.*, 1982; Harriss *et al.*, 1985; Sebacher *et al.*, 1986; Svensson & Rosswall, 1984). Subsequent estimates, up to that of Harriss *et al* (1991) in Table 1, benefited from a larger, and more spatially diverse set of observations published between 1987 and 1991 (eg. Crill *et al.*, 1988; Moore & Knowles, 1987; Moore & Knowles, 1990; Moore *et*

**TABLE 1** Estimates of $CH_4$ emissions from northern wetlands

| Area of Northern Wetlands ($km^2$) | Total Annual Flux ($Tg\ CH_4\ yr^{-1}$) | Reference |
|---|---|---|
| $3.021 \times 10^6$ | 73.3 | Matthews & Fung (1987) |
| $2.420 \times 10^6$ | 22.4 | Aselmann & Crutzen (1989) |
| $3.021 \times 10^6$ | 35.0 | Fung *et al.* (1991) |
| $2.607 \times 10^6$ | 30.3 | Harriss *et al.* (1991) |
| $2.420 \times 10^6$ | 16.2 | Roulet *et al.* (1992) |

*al.*, 1990; Whalen & Reeburgh, 1988; Whalen & Reeburgh, 1990). The contribution of the northern wetland source to global emissions decreased considerably from 16% to between 4 and 7% of the annual atmospheric burden. The role of southern wetlands, particularly those between 10°N and 20°S was then much larger than previously estimated (Fung *et al.*, 1991). However in these estimates, there was still poor observational coverage of the major continuous wetland regions of the northern hemisphere, namely, the Hudson Bay Lowlands (HBL) and the Western Siberian Lowlands (WSL) (Fig. 1). The HBL and WSL comprise 34% of all northern wetlands. With the exception of the work of Moore *et al.* (1990), Sebacher *et al.* (1986) and Whalen & Reeburgh (1988), measurements covered only the southern fringe of the North American northern wetland region and even these were on relatively small and isolated wetlands.

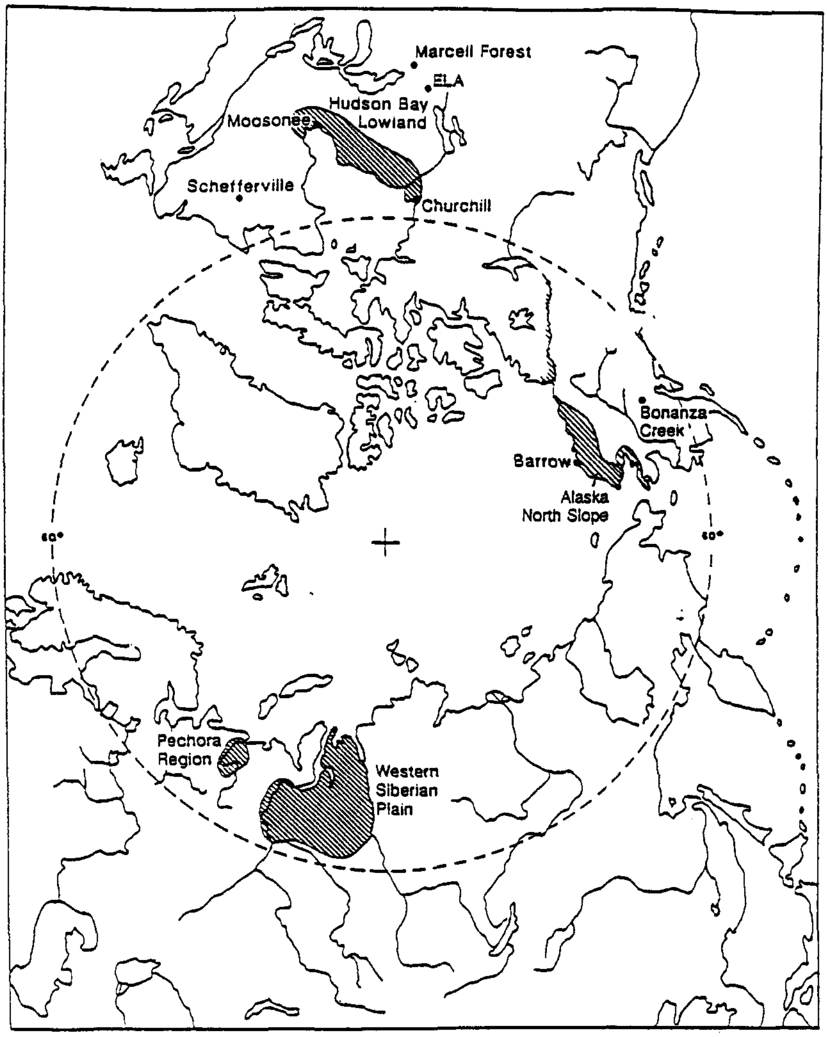


**Fig. 1** Map showing large continuous wetlands in the northern region that make up 34% of all wetlands north of 40°N.

In 1990, a major international field program, the Canadian Northern Wetlands Study (NOWES), was undertaken to determine the $CH_4$ flux from the HBL (Roulet *et al.*, 1992a). Observations showed that $CH_4$ emissions were 10 to 15 times lower than expected for individual wetland types (Moore *et al*, 1992) and that the annual flux for the entire HBL was only 0.5 Tg $yr^{-1}$ (Roulet *et al*, 1992b) compared to 7 Tg $yr^{-1}$ estimated earlier by Matthews and Fung (1987) using measured fluxes from the large wetland regions of Alaska (Morrissey & Livingstone, 1992; Bartlett *et al.*, 1992). Temperature and precipitation regimes in the HBL during the NOWES study were within one standard deviation of long term climatological means(Mortsch, 1992). Assuming that the flux estimates from the HBL are also

**TABLE 2** Definition of wetland types used in the Canadian Wetland Classification System

| Type | Definition |
|---|---|
| Wetland | "land that has the water table at, near, or above the land surface or which is saturated for a long enough period to promote wetland or aquatic processes as indicated by hydric soils, hydrophytic vegetation, and various kinds of biological activity that are that are adapted to the wet environment" |
| Peatland | "a wetland with more than 40 cm of peat" |
| Bog | "a peatland, generally with the water table near the surface. The bog surface, which may be raised or level with the surrounding terrain, is virtually unaffected by nutrient-rich groundwaters from the surrounding mineral soils and is thus generally acid and low in nutrients. The dominant materials are weakly to moderately decomposed *Sphagnum* and woody peat, underlain at times by sedge peat. The soils are mainly Fibrosols, Mesisols, and Organic Cryososls. Bogs may be treed or treeless, and they are usually covered with *Sphagnum spp.* and ericaceous shrubs." |
| Fen | "a peatland with the water table usually at or just above the surface. The waters are mainly nutrient-rich and minerotrophic from mineral soils. The dominant materials are moderately to well decomposed sedge and/or brown moss peat of variable thicKiless. The soils are mainly Mesisols, Humisols, and Organic Cryosols. The vegetation consists predominantly of sedges, grasses, reeds, and brown mosses with some shrubs, and at times, a sparse tree layer." |
| Marsh | "a mineral wetland or peatland that is periodically inundated by standing or slowly moving water. Surface water levels fluctuate seasonally, with declining levels exposing drawdown zones of matted vegetation of mudflats. The waters are rich in nutrients, varying from fresh to highly saline. The substratum usually consists of mineral material, although occasionally well decomposed peat. The soils are predominantly Gleysols with some Humisols and Mesisols. Marshes characteristically show zonal or mosaic surface patterns composed of pools or channels interspersed with clumps, or emergent sedges, grasses, rushes, and reeds, bordering grassy meadows and peripheral bands of shrubs or trees. Submerged and floating aquatic plants flourish where open water area occur." |
| Swamp | a mineral wetland or peatland with standing water or water gently flowing through pools or channels. The water table is usually at or near the surface. There is pronounced internal water movement from the margin or other mineral sources: hence the waters are rich in nutrients. If peat is present, it is mainly well-decomposed wood, underlain at times by sedges peat. The associated soils are Mesisols, Humisols, and Gleysols. The vegetation is characterized by a dense cover of deciduous or coniferous trees or shrubs, herbs, and some mosses. |
| Shallow water | "characteristic if intermittently or permanently flooded or seasonally stable water regimes, featuring open expanses of standing or flowing water which are variously called ponds, pools, shallow lakes, oxbows, reaches, channels, or impoundments. Shallow water is distinguished from deep water by mid-summer water depths of less than 2 m, and from other wetlands by summer open water zones occupying more than 75% of the wetland surface area." |

representative of those in Siberia and using the flux estimates of Aselmann & Crutzen (1989) and Fung *et al.* (1991) for the remaining 66% of northern wetlands, the total northern wetland source drops to ≈ 16 Tg $yr^{-1}$ (Roulet *et al.*, 1992b), or ≈ 3% of the total annual atmospheric burden.

## 3. Sources of uncertainty in northern wetland $CH_4$ emissions

*Areal extent and classification of northern wetlands* The most extensive data set on global wetland distribution is that of Matthews & Fung (1987). It was derived by integrating the UNESCO vegetation data base, the FAO soil data base, and ONC (Operational Navigation Charts) inundation data base at a 1° resolution. Five broad classifications of wetlands were used: forested bog; non-forested bog; forested swamp; non-forested swamp; and alluvial wetlands. Aselmann & Crutzen (1989) put together an alternative wetland distribution based on previously published wetland distribution maps of various regions of the globe. They collapsed 45 different freshwater wetlands into six categories: bogs, fens, swamps; marshes; floodplains; and shallow lakes. This classification is somewhat closer to main wetland types defined in Table 2 by the Canadian Northern Wetland Working Group. The total areal extent of northern wetlands by the two approaches differed by only 25%. Aselmann & Crutzen (1989) estimated fewer northern wetlands and more southern wetlands than Matthews & Fung (1987). There is no independent check on either data base, and given the methods used and the high variability in the quality of the data on which the estimates were based, the difference between these two distributions has to be considered well within the margin of error.

A more difficult problem, but one that can not be resolved at present, is the poor spatial resolution of wetland classification. Many flux studies have found very large differences in $CH_4$ emissions from wetlands that were lumped together in either of the global data sets. For example, Crill *et al.* (1988) observed average summer fluxes from forested bogs, open bogs, and fens in northern Minnesota of 77 ± 21, 294 ± 30, and 142 ± 19 mg $CH_4$ $m^{-2}$ $d^{-1}$, respectively, while Roulet *et al.* (1992c) observed average summer fluxes from the same type of wetlands in central Ontario of 6 ± 17, 21 ± 28, and 3.0 ± 12.3 mg $CH_4$ $m^{-2}$ $d^{-1}$. Both wetlands areas are located in the low boreal ecoclimate region at approximately the same latitude (≈ 48°N) yet the fluxes differ by factors of 12 to 47. This problem is inherent in all regional and global estimates and is a function of incompatibility of the scale at which production and consumption of $CH_4$ takes place in wetlands (< 1.0 $m^2$) and of the scale of resolution that is practical for global extrapolations (> 1° which is ≈ 100 x 100 km at the equator).

*Spatial variability of $CH_4$ emissions from wetlands.* Numerous studies have reported extremely high spatial variability of $CH_4$ emissions within a single wetland type. In Table 3, the mean, standard deviation, and coefficient of variance (CV) (standard error/mean x 100%) of $CH_4$ fluxes from various studies are shown. The variation ranges from a low of 4% to a high of 500%, while the average is ≈ 80%. This variation includes spatial and short-term (day to day) and seasonal temporal variations. If temporal changes are removed as for instance in the studies of Svensson & Rosswall (1984) and Sebacher *et al.* (1986) done over short periods of time, the variance is still about 40%. In another temporally invariant study, Moore & Roulet (1991) examined the spatial variation of $CH_4$ flux from three sites within one wetland over a 24 hour period. They used up to 35 enclosures, located beside each other along two sides of a boardwalk, and found that emissions were normally distributed in space at two sites and log-normally distributed at a third flooded site (Fig. 2). The latter was always covered with 35 cm of water (Moore *et al.*, 1990). The CV of emissions due to spatial variation ranged from 42 to 89%.

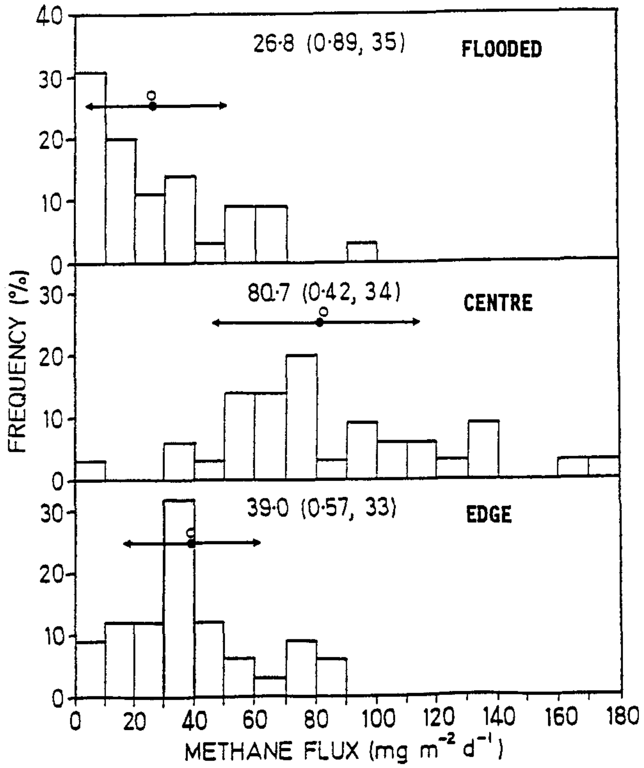
The sample size used to calculate the mean flux has considerable influence on the uncertainty of an emissions estimate. Bartlett *et al.* (1989a) found that the CV dropped from a minium and maximum of <2% and >40% with 2 flux samples to 10 and 14% with >20 samples, respectively. After 20 samples, it did not drop below 10 to 15%. This is mainly type-2 uncertainty caused by natural spatial variability. Moore *et al.* (1992) performed the same analysis on samples from subarctic wetlands and the type-2 CV to be ≈25%. This agrees with estimates made earlier by Schutz & Seiler (1989).

**Table 3** Mean, standard deviation, and coefficient of variance (CV) for $CH_4$ fluxes (mg $m^{-2}$ $d^{-1}$) representative of various types of northern wetlands. A single observation was taken over a period of several hours to a day and over multiple locations in the wetland.

| LOCATION | WETLAND TYPE | PERIOD | PERIOD MEAN | PERIOD STAND. DEV. | CV (%) | REFERENCE |
|---|---|---|---|---|---|---|
| Northern Sweden | ombrotrophic bog/fen | May - Sept | 2.4 | 0.9 | 37.5 | Svensson (1980) |
| Northern Sweden - subarctic | ombrotrophic hummocks | 5 days (summer) | 1.0 | 0.7 | 70.0 | Svensson & Rosswall (1984) |
| | ombrotrophic hollows | 5 days (summer) | 2.6 | 2.0 | 76.9 | |
| | ombrotrophic depressions | 5 days (summer) | 16.5 | 7.7 | 46.7 | |
| | deep ombrotrophic depressions | 5 days (summer) | 25.9 | 6.4 | 24.7 | |
| | mesotrophic fen | 5 days (summer) | 58.2 | 28.0 | 48.1 | |
| | minerotrophic fens | 5 days (summer) | 360.0 | 67.8 | 18.8 | |
| Alaska - low arctic | wet coastal peatlands | August | 119.0 | 27.8 | 23.4 | Sebacher *et al.* (1986) |
| | moist coastal peatlands | August | 4.9 | 2.6 | 53.1 | |
| | wet meadow | August | 39.9 | 20.0 | 50.1 | |
| | alpine fen | August | 289.0 | 14.2 | 4.9 | |
| | boreal marsh | August | 106.0 | 4.6 | 4.3 | |
| Minnesota - low boreal | forested bog | May - August | 77 | 21 | 27.3 | Crill *et al.* (1988) |
| | fen | May - August | 142 | 19 | 13.4 | |
| | open bogs | May - August | 294 | 30 | 10.2 | |
| Northern Quebec - subarctic | transitional fen | June - August | 39.4 | 21.4 | 54.3 | Moore & Knowles (1987) |
| | rich fen | June - August | 18.4 | 14.4 | 78.3 | |
| | transitional fen | June - August | 19.2 | 8.3 | 43.2 | |
| | rich fen | June - August | 46.4 | 22.2 | 47.8 | |
| Northern Quebec - subarctic | forest margins | May - Sept. | 18.4 | 21.5 | 116.8 | Moore *et al.* (1990) |
| | fen margins | May - Sept. | 26.3 | 23.5 | 89.4 | |
| | fen central | May - Sept. | 69.1 | 42.5 | 61.5 | |
| | fen flooded | May - Sept. | 33.3 | 25.7 | 77.2 | |
| | patterned fen - ridges | May - Sept. | 8.3 | 7.1 | 85.5 | |
| | patterned fen - pools | May - Sept. | 32.4 | 13.5 | 41.7 | |
| Ontario - low boreal | beaver ponds | April - Oct. | 55.9 | 61.7 | 110.4 | Roulet *et al.* (1992a) |
| | conifer swamps | | 1.9 | 9.6 | 505.3 | |
| | mixed swamps | | 0.7 | 1.9 | 271.4 | |
| | thicket swamps | | 34.8 | 48.9 | 140.5 | |
| | marshes | | 0.9 | 3.6 | 400.0 | |
| | bogs | | 13.2 | 22.3 | 168.9 | |
| | fens | | 3.0 | 12.3 | 410.0 | |
| Alaska - subarctic | uplands | July - August | 2.2 | 0.4 | 18.2 | Bartlett *et al.* (1992) |
| | wet meadow | July - August | 208.1 | 8.6 | 4.1 | |
| | uplands | July - August | 3.0 | 2.5 | 83.3 | |
| | wet meadow | July - August | 79.2 | 25.0 | 31.6 | |
| Ontario - subarctic | HBL - water | June - Oct. | 12.3 | 7.3 | 59.3 | Roulet *et al.* (1992b) |
| | HBL - marshes | June - Oct. | 30.9 | 37.2 | 120.4 | |
| | HBL - treed fens | June - Oct. | 2.5 | 0.3 | 12.0 | |
| | HBL - open fens | June - Oct. | 7.9 | 0.9 | 11.4 | |
| | HBL - open bogs | June - Oct. | 53.5 | 44.8 | 83.7 | |
| | HBL - shrub bogs | June - Oct. | 47.5 | 72.3 | 152.2 | |
| | HBL - treed bogs | June - Oct. | 1.8 | 0.6 | 33.3 | |
| | HBL - upland forests | June - Oct. | 3.3 | 3.2 | 97.0 | |

Note: the standard deviations reported are the average deviations reported for the study.

Fig. 2 The frequency distribution for the $CH_4$ flux from three sites in a subarctic fen. The value outside the bracket indicates the arithmetic mean and the values inside the brackets are the coefficient of variation (standard deviation/mean) and the sample size. Diagram taken from Moore & Roulet (1991).



*Temporal Variability of $CH_4$ Flux from Northern Wetlands.* There are four periods of time over which the temporal variability of $CH_4$ flux from wetlands has been examined: diurnal, several days, seasonal and inter-annual. There appears to be little diurnal variability in $CH_4$ flux (Moore & Roulet, 1991; Whalen & Reeburgh, 1988) except when vegetation is active in surface air exchange (Morrissey & Livingstone, 1992) and when emissions are from an area dominated by open water (Edwards *et al.*, 1992). Edwards *et al.* (1992) measured emissions from a northern bog in the HBL using eddy correlation micrometeorological techniques with sensors at two elevations: 5 and 18 m. All other variables constant, the area of integration or "footprint" of this technique depends on height of sampling above the surface. At 5 m, the "footprint" contained little water, but at 18 m, it included between 3 and 20% open water. At the lower elevation, the mean half-hourly flux ranged from 6.9 to 24 mg $m^{-2}$ $d^{-1}$ and the mean daily flux was 16 mg $m^{-2}$ $d^{-1}$, while at 18 m the flux ranged from -1.7 to 47 mg $m^{-2}$ $d^{-1}$, but the mean was similar, 15 mg $m^{-2}$ $d^{-1}$. Over a period of five weeks the $CH_4$ flux was normally distributed.

In using observations to make annual estimates, it is common for researchers to use mean flux measurements from a very short period of the year as representative of the mean for the entire emissions season. The net emissions are obtained by multiplying the mean flux by an assumed duration of emissions which is usually based on temperature. In the case of Aselmann & Crutzen, (1989) the duration of emissions ranged from 100 days at high latitudes to 150 days at 45°N .

The bulk of flux measurements are done during July and August, the period of greatest flux (Moore *et al.*, 1990; Whalen & Reeburgh, 1988). The percent of the total warm season emissions that occurred among the months from May to October for three low boreal wetlands is given in Table 4. Also shown is a comparison between the actual integrated flux and warm season emission calculated using the mean summer flux and the mean July and August flux assuming a 150 day emissions period. The total calculated using the means is between 0 and 22% higher than the actual integrated flux.

**Table 4** Seasonal distribution of $CH_4$ emissions expressed as a percentage of the warm season integrated $CH_4$ flux from low boreal wetlands (Roulet *et al.*, 1991c) as well as a comparison of the actual $CH_4$ flux for the warm season with estimates thereof using the product of mean flux for the warm season or for only July and August with a 150 day emissions period. Bracketed numbers are the percentage over-estimate of actual emissions by other parameters. Units for the flux are g m$^{-2}$ yr$^{-1}$.

| Wetland | May | June | July | Aug. | Sept. | Oct. | Actual Flux | Mean * 150 days | Jul-Aug Mean * 150 Days |
|---|---|---|---|---|---|---|---|---|---|
| Beaver pond | 3.8 | 24.2 | 21.9 | 28.0 | 13.6 | 6.5 | 11.6 | 13.6 (+17.2%) | 14.2 (+22.4%) |
| Thicket swamp | 13.4 | 31.5 | 24.2 | 24.6 | 4.7 | 1.6 | 9.3 | 10.4 (+11.8%) | 11.2 (+20.4%) |
| Bog | 13.3 | 32.4 | 13.5 | 27.2 | 7.1 | 6.5 | 1.7 | 3.1 (+82.4%) | 1.7 (0%) |

There are very few flux studies that have been made of cold season methane emissions. Whalen & Reeburgh (1988) found that the flux from subarctic wetlands was insignificant once the soil had frozen. In contrast, Dise (1992) working in more southern peatlands, found between 4 and 21% of the annual flux occurred while the peatlands were snow covered. Thus, the assumption that total warm season fluxes represent annual methane emissions introduces a bias that results in underestimation of emissions by an as yet undetermined amount although wetland researchers feel it is less than 20%.

Year to year variation in $CH_4$ emissions introduces another major source of uncertainty. Whalen & Reeburgh (1992) have made the longest continuous observations of $CH_4$ emissions from a northern wetland. Measurements have been done at the same location by the same technique for four years. In the first three years (1987 - 1989), the inter-annual variability was 20 to 70%, but in 1990 the flux from one of five wetland types, a *Carex spp.* dominated site, was 18 times larger than the average of the three previous years. Yet the large scale climatological situation was not extremely different from year to year. At the same time little variation was observed at the other four sites. Using the data from the *Carex spp.* wetland to calculate a global tundra $CH_4$ emission, the estimates range from 19.3 - 32.8 Tg yr$^{-1}$ for 1987 to 78.4 - 119.1 Tg yr$^{-1}$ for 1990. This of course is a gross overestimate of interannual variability of $CH_4$ emissions from all wetlands since deviations from normal in one location are likely to be counteracted by opposite deviations from normal in other locations.

*Tests of Scaling-Up of Observations.* There have been two experiments that have compared the results obtained by extrapolating point chamber observations using a land classification to obtain estimates of large scale emissions with actual observations of larger scale emissions. Bartlett *et al.* (1989) used SPOT satellite imagery (20 x 20 m) to classify Alaska tundra into wet lowlands, dry uplands, and lakes and then obtained regional fluxes using the chamber measurements of Bartlett *et al.* (1992). The summer average agreed to within a factor of 2 with the average fluxes obtained by eddy correlation measurements made on a tower and aircraft. Roulet *et al.* (1992b) compared the flux for a three week period in July 1990 obtained for the entire HBL using a combination of small chamber enclosures, LANDSAT Thematic Mapper and ecological survey with the spatial average obtained by eddy correlation measurements done on 19 regional aircraft flights over the Lowland. The extrapolated mean flux was 20 mg $CH_4$ m$^{-2}$ d$^{-1}$, while the average observed aircraft flux was 16 mg $CH_4$ m$^{-2}$ d$^{-1}$, a difference of only 25%. This demonstrates that extrapolations from scales of 100 m to $10^4$ m driven by an ecosystem classification supported by small scale flux observations are reasonably accurate.

## 4. Summary

Global methane emissions estimates are subject to multiple errors. Currently, there are no estimates of the absolute error associated with current wetland classifications. However, there is approximately a 25% relative uncertainty associated with two wetland classifications currently in use. The sampling uncertainties due to spatial and within-year temporal variability of $CH_4$ emission within a wetland is over 50%. The inter-annual variability could introduce at least another 50% error in the estimate from any one year, but presumably some wetlands yield less than average and some wetlands more than average $CH_4$ in any one year, so this error may be significantly reduced when averaged over the entire northern region. Finally, uncertainties due to lack of observations for cold season fluxes likely bias observations low by an unknown amount that is thought to be less than 20%.

Taking all these factors into consideration, the $CH_4$ flux estimate from northern wetlands is probably no better than a factor 2. This means that the difference between the Aselmann & Crutzen (1989), Fung *et al.* (1991), and Harriss *et al.* (1992), based on very similar data are insignificant. The estimate of Roulet *et al.* (1992b) which incorporates a significantly larger body of observations than those made previously and is about half that of Fung *et al.* (1991) and Harriss (1992) is probably significantly different.

To improve on $CH_4$ emissions estimates from northern wetlands, several actions are recommended: (1) Improve the accuracy and resolution of global wetland classifications; (2) Make long term, multi-year flux measurements in wetlands in different climate regions; (3) Better delineate the sampling uncertainty due to spatial and temporal variations in emissions from an apparently homogeneous wetland and (4) Make observations that improve estimates of the cold season methane emissions. Some of these recommendations have been made before (Roulet *et al.*, 1992a).

It is important in terms of priority to emphasize that given the relatively low contribution of the northern wetland $CH_4$ source to the total global emissions and the considerable effort that has been expended on this source, it may be a better investment of limited resources to concentrate on improving emissions estimates for other sources (eg. biomass burning, cattle, fossil fuels and landfills) and, for wetlands, to concentrate more on understanding the controls on $CH_4$ emissions under past and future climate scenarios (eg. Harriss *et al.* 1992; Roulet *et al.* 1992b).

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# CLIMATE FORCING BY GASES AND AEROSOLS

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## Abstract

Infrared active gases in the atmosphere exert a warming influence on climate by increasing the intensity of infrared radiation that is exchanged between the earth and the atmosphere. The possible influence of increased concentrations of infrared absorbing gases such as carbon dioxide and methane on the radiative balance of the atmosphere, leading to a warming of global climate, has been appreciated for some time and is the subject of much active research. Aerosol particles exert a radiative influence on climate by scattering and absorbing shortwave radiation and, through their action as cloud condensation nuclei, by modifying cloud radiative properties. Climate forcing by anthropogenic aerosols is estimated to be comparable on global and annual average to that of anthropogenic greenhouse gases but of opposite sign, and is therefore likely to be offsetting a considerable fraction of the warming influence of anthropogenic greenhouse gases. However the spatial and temporal distribution of the aerosol forcing is quite different from that of the greenhouse gases, and therefore this forcing cannot *a priori* be treated as a scalable anti-greenhouse forcing. Assessment of the climate influence of the aerosol forcing requires studies with global climate models, but the accuracy of these analyses will be limited by present uncertainties in key parameters necessary to describe this forcing.

## 1. Introduction

To excellent approximation the earth climate may be viewed as a system in steady state with respect to absorbed incoming radiation from the sun and outgoing emitted infrared radiation. A schematic illustration of this is shown in Figure 1. In the figure all fluxes represent annual and global average values, in units of W $m^{-2}$. The average flux of shortwave solar radiation incident upon the is earth-atmosphere system is $1/4\ F_T \approx 343$ W $m^{-2}$; $F_T$ is the solar flux outside the atmosphere (the solar "constant"), about 1370 W $m^{-2}$. Of this incoming solar radiation, a fraction $R \approx 0.3$ is reflected, where $R$ is the global-mean planetary albedo (Ramanathan, 1987; Ramanathan *et al.*, 1989); this corresponds to about 106 W $m^{-2}$. The principal contribution to the reflected shortwave radiation is from clouds; other contributions come from Rayleigh scattering by air, scattering by atmospheric aerosol particles,

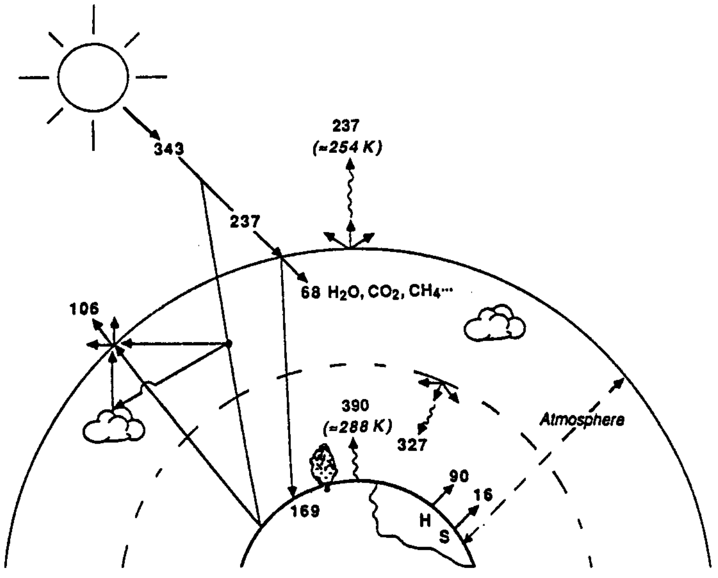

**Fig. 1.** Schematic of major fluxes constituting the radiation balance of the earth-atmosphere system. Numbers represent global, annual average values in W m$^{-2}$. H and S denote latent and sensible heat fluxes from the earth to the atmosphere, respectively. Modified from Ramanathan, 1987.

and surface reflectivity. The complement of the albedo 1- $R$ corresponds to absorbed shortwave radiation and represents an average flux of $1/4\,F_T(1\text{-}R) \approx 237$ W m$^{-2}$. This shortwave absorption is matched, on an annual, global average basis, by long-wave (infrared) emission.

The flux of infrared radiation emitted at the surface of the earth, *ca.* 390 W m$^{-2}$ substantially exceeds the outgoing infrared flux at the top of the atmosphere. Since the constituents of the atmosphere, clouds, water vapour, and other infrared absorbing gases, are not transparent in the infrared, they absorb some of the radiation emitted at the surface, and since these infrared absorbing species are at high altitudes, they are cooler than the surface and therefore emit at a lower radiant intensity. Thus the mean emitted power of the earth-atmosphere system, 237 W m$^{-2}$, corresponds to a lower black-body temperature (254 K) than does the emission flux at the surface, 390 W m$^{-2}$, which corresponds to a much more temperate value of 288 K. This increase of surface temperature relative to the black-body temperature of the earth atmosphere system is known as the "greenhouse effect".

## 2. Enhanced greenhouse effect

It is well established that human activities have substantially altered the chemical composition of the global atmosphere. Concentrations of infrared absorbing gases $CO_2$, $CH_4$, $N_2O$, and chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have increased substantially during the industrial era; Figure 2 shows the time histories of atmospheric $CO_2$ and $CH_4$ concentrations over this

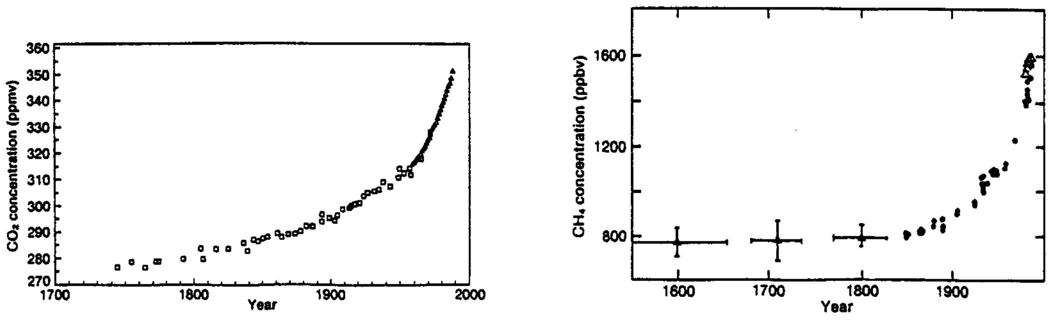

**Fig. 2.** a. Atmospheric $CO_2$ concentrations over the past 250 years, as indicated by measurements of air trapped in ice in dated Antarctic ice cores (squares) and direct measurements at Mauna Loa, Hawaii (triangles). b. Atmospheric $CH_4$ concentrations from dated ice cores. From Watson *et al.*, 1990.

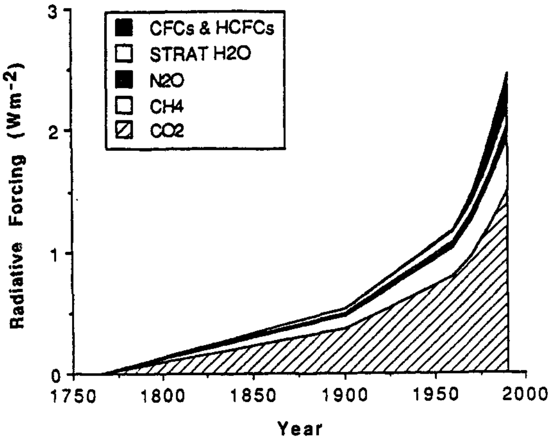

**Fig. 3.** Changes in longwave radiative forcing, relative to 1765, due to increases in greenhouse gas concentrations between 1765 and 1990. From Shine *et al.*, 1990.

period. These increases in concentrations substantially increase the infrared absorption of the atmosphere resulting in an increase in longwave forcing of the troposphere, as shown in Figure 3. That figure also shows a second, indirect influence of increased concentrations of $CH_4$, due to an increase in stratospheric water vapour concentration resulting from oxidation of $CH_4$ in the stratosphere. An increase in radiative forcing over the industrial period such as is indicated in the figure is expected to result in an increase in surface temperature (the so-called "enhanced greenhouse effect") and perhaps other climate changes (Houghton *et al.*, 1990, 1992). However the magnitude of these changes, and in particular the increase in mean surface temperature, are not well established and are the subject of much research.

Research into the response of the earth climate to the enhanced greenhouse effect is proceeding principally along two lines. Modelling studies are attempting to calculate the magnitude of climate changes due to increased radiative forcing by means of so-called general circulation models (GCMs) of the earth's atmosphere. These models are attempts to physically simulate the important processes of the earth weather system and numerically integrate them over decades to centuries to ascertain climate change resulting from a specified change in radiative forcing. However such models embody numerous approximations, parametrizations, and empirical adjustments that give rise to concerns over their accuracy for the purpose of predicting climate change. Moreover the sensitivity of models differs substantially from model to model. In a study comparing 19 GCMs (Cess, *et al.* 1990) it was shown that the equilibrium global temperature sensitivity coefficient varied from model to model by factors of as much as three (range 0.39 to 1.23 K/W $m^{-2}$; mean 0.65; standard deviation 0.26). Such a range is much too large for confident predictions of future climate change. Moreover, it represents the range of the global average sensitivity; variations in regional model properties are much greater. Additionally, of course, since these are model predictions, there is no assurance that the true value even lies within this range.

A second approach to estimating climate change is based upon empirical studies. Studies of the change in the mean surface temperature of the earth over the period of instrumental measurement, from roughly the middle of the past century, indicate an increase in mean global temperature over this period of about 0.5 K (Folland *et al.*, 1990). If one takes the enhanced greenhouse gas forcing over this period as 2.5 W $m^{-2}$ (Figure 3), and assumes that there is no other significant change in forcing over this period, one infers a global sensitivity coefficient of 0.2 K/W $m^{-2}$. This value is substantially lower than that given by model calculations noted above. A possible reason for this may be that the observed quantity does not represent an equilibrium value. However a further reason may be that there are perturbations in forcing over this period other than those due to increased concentrations gases, specifically, an enhancement of planetary albedo due to anthropogenic aerosols.

## 3. Radiative forcing by anthropogenic aerosols

As may be inferred from Figure 1, any increase in planetary albedo will decrease the shortwave radiation absorbed by the earth-atmosphere system and therefore exert a cooling influence on the planet. A major influence on planetary albedo is cloudiness, since clouds are generally much more reflective than underlying land or ocean surfaces. Aerosol particles affect the albedo of cloud-covered regions by influencing cloud radiative properties; they also affect the albedo of cloud-free regions, by directly scattering and absorbing shortwave radiation. Recently it has become appreciated that aerosol particles arising from industrial activity can perturb the earth's radiation balance by altering shortwave reflectivity on regional and global scales and that this change in radiative forcing can have climatic implications. However this effect has received much less attention by the climate research community than has the enhanced greenhouse effect, in part because of the more recent awareness of the phenomenon and in part because this phenomenon is more complex than the greenhouse effect and is not sufficiently well understood to be described with confidence.

In the unperturbed atmosphere, the principal aerosol constituents are sulfate from biogenic gaseous sulfur compounds and organic carbon from partial atmospheric oxidation of gaseous biogenic organic compounds such as terpenes (Jaenicke, 1988). Sea salt and windblown soil dust contribute substantially at some locations but their effect on the global climate is not very important because the particles are large and usually short lived and thus transported only short distances. Other aerosol substances may also be locally important, especially those that are sporadic such as from volcanoes, wildfires, and windblown dust from deserts.

Industrial activity contributes substantially to atmospheric aerosols in industrial regions and throughout much of the Northern Hemisphere (NH). This anthropogenic aerosol influences climate by scattering and absorption of solar radiation and by modifying cloud properties. Both influences are thought to be significant climatically (Charlson *et al.*, 1992).

Anthropogenic light-scattering aerosols are produced in the atmosphere by chemical reactions of sulfur-, nitrogen-, and carbon-containing gases, mainly oxidation of $SO_2$ to sulfate. Anthropogenic sulfate is restricted predominantly to the NH (Schwartz, 1988) because $SO_2$, the principal industrial precursor of this aerosol, is emitted predominantly (>90%) in the NH (Cullis & Hirschler, 1980; Spiro *et al.* 1992) and because the short atmospheric residence times of $SO_2$ and sulfate aerosol preclude interhemisphere transport. This $SO_2$, which is due mainly to combustion effluents, has an emissions history, shown in Figure 4, similar to that of anthropogenic $CO_2$. It is seen from the figure that anthropogenic $SO_2$ emissions exceeded natural emissions in the NH in the early years of this century and globally by about 1940.

Aerosol light absorption is dominated by particles containing elemental carbon produced by incomplete combustion of carbonaceous fuel. Mass ratios of sulfate to elemental carbon near source regions are typically 10 to 20 (Ogren & Charlson, 1984; Heintzenberg & Mészáros, 1985). Because the scattering cross section of sulfate and the absorption cross section of elemental carbon are comparable (~10 $m^2/g$) at representative relative humidities in the planetary boundary layer, these concentration ratios imply single scattering albedo values $\omega$ of 0.9 to 0.95. These values are consistent with measured values in rural U. S. locations (Waggoner *et al.*, 1981; White, 1991). A further contribution to climate forcing by anthropogenic aerosols is from smoke aerosols produced by biomass burning (Penner *et al* 1992). These aerosols also are characterized by rather high single scattering albedo (0.85 to 0.95) (Ferrare *et al.*, 1990; Radke *et al.*, 1988).

The relative contribution of light scattering and absorption was examined in model calculations of the influence of tropospheric aerosol on the earth radiation budget by Coakley *et al* (1983), who concluded that for an aerosol of single scattering albedo $\omega \sim 0.94$, representative of what they considered background NH aerosol, and for surfaces with low albedo (< 0.1) characteristic of most of the earth, the presence of the aerosol leads to an increased albedo. It has subsequently become clear, however, that what at that time had been considered "background" aerosol is substantially influenced by anthropogenic emissions. It follows that the increase in concentrations of aerosol particles over the industrial era may be expected to have exerted a negative radiative forcing (cooling influence) concurrent with the positive forcing (warming influence) of anthropogenic greenhouse gases. This is consistent with enhancement of albedo due to anthropogenic aerosols that is inferred from satellite observations (Durkee *et al.*, 1991; Lyons 1980; Fraser *et al.*, 1984; Rao *et al.*, 1988).

Although aerosol particles also absorb longwave (infrared) radiation, this effect is usually small because the opacity of aerosols decreases at longer wavelengths and because the aerosols are most concentrated in the lower troposphere, where the atmospheric temperature, which governs emission, is practically the same as the surface temperature (Coakley *et al.*, 1983; Grassl, 1988).

In addition to scattering light directly, anthropogenic aerosol particles are thought also to influence planetary albedo, indirectly, by modifying cloud reflectivity. Aerosol particles, especially sulfate particles, are efficient cloud condensation nuclei (CCN) (Radke & Hobbs, 1976; Twomey, 1977). Increased CCN concentrations result in increased concentrations of cloud drops (Twomey, 1977; Leaitch *et al* 1986, 1992; Pueschel *et al.*, 1986; Gillani *et al.*, 1992), enhancing multiple scattering within clouds and thereby enhancing their shortwave reflectivity. The effect is greatest over the oceans, where concentrations of natural CCNs are low, and for clouds of intermediate cloud-top albedo, $0.3 < R_{CT} < 0.7$ , such as marine stratus (Twomey, 1977; Twomey *et al.*, 1984; Charlson *et al.*, 1987). Enhancement of cloud albedo by this mechanism has been observed in specific situations (Durkee, 1988; Radke *et al.*, 1989), although the effect on hemispheric albedo has yet to be convincingly demonstrated (Schwartz, 1988). The influence on the longwave absorption by clouds is considered minimal because of the generally high optical density of clouds in the infrared. An increase in cloud droplet concentration is also thought to inhibit precipitation formation, resulting in increased cloud persistence (Fitzgerald & Spyers-Duran, 1973; Braham, 1974; Albrecht, 1989; Baker & Charlson, 1990), which would contribute further to shortwave radiative forcing as well as to longwave forcing both by the clouds and, upon cloud evaporation, by the resulting water vapour.

## 4. Estimates anthropogenic aerosol forcing

The magnitude of global average clear-air and cloud forcing by anthropogenic aerosols has recently been examined by Charlson *et al.* (1992) using estimates of the anthropogenic perturbation to the mass-budget of sulfate aerosol. Other estimates have been based on a spatial distribution of aerosol derived from a chemical transport model (Charlson *et al.*, 1991). These studies indicate that anthropogenic aerosols exert a climate forcing that is comparable in global-average magnitude to that of anthropogenic greenhouse gases. However the uncertainties in these estimates are substantial. These estimates are briefly reviewed here and key uncertainties identified.

*Direct forcing*. Following Charlson *et al.* (1992) the areal mean shortwave forcing resulting from an increase in sulfate aerosol concentration can be evaluated as:

$$\overline{\Delta F_R} = -1/2\, F_T(1-A_c)T^2(1-R_s)^2\,\overline{\beta}\,\alpha_{SO_4^{2-}}f(\mathrm{RH})Q_{SO_2}Y_{SO_4^{2-}}\tau_{SO_4^{2-}} \Big/ A \qquad (1)$$

Here $F_T$ is the solar radiative flux at the earth's orbit, $A_c$ is the fractional cloud cover in the area of concern, $T$ is the fraction of incident light that is transmitted through the atmosphere above the aerosol layer, $R_s$ is the albedo of the underlying surface, $\beta$ is the fraction of the radiation scattered upward by the aerosol, $\alpha_{SO_4^{2-}}$ is the light-scattering cross section of sulfate at a reference low relative humidity (30%), $f$(RH) is the relative increase in scattering cross-section with increasing humidity, $Q_{SO_2}$ is the source strength of anthropogenic $SO_2$, $Y_{SO_4^{2-}}$ is the fractional yield of emitted $SO_2$ that reacts to produce $SO_4^{2-}$ aerosol, $\tau_{SO_4^{2-}}$ is the sulfate lifetime in the atmosphere, and $A$ is the area of the geographical region to which the material is confined, for example the entire Earth, the NH, or some smaller region.

Equation (1) has the advantage of explicitly delineating the dependence of $\overline{\Delta F}_{\mathrm{R}}$ on all of the variables on which it depends, and allowing identification of key uncertainties. The negative sign denotes that the forcing represents a cooling tendency. The factor $(1-A_c)$ is introduced because the albedo enhancement is applicable only for non-cloud-covered portions of the planet. Estimates of the several variables and their uncertainties are given in Table 1. These estimates place the global mean direct radiative forcing due to sulfate aerosol at about -1 W $m^{-2}$. Propagation of the several uncertainties under assumption that they are uncorrelated leads to an estimated uncertainty in the forcing of a factor of about 2.4. The calculated forcing is comparable in magnitude to that ascribed to the increase in greenhouse gas concentrations above preindustrial values. Major contributors to the uncertainty in the aerosol forcing are seen to be chemical in nature, that is having to do with the fractional yield of emitted $SO_2$ that is converted to sulfate aerosol and the lifetime of sulfate aerosol in the atmosphere.

Since the (1/*e*) time for removal of accumulation-mode particles by dry deposition is tens of days (see, e.g., Slinn, 1983), the removal of the aerosol sulfate is dominated by precipitation processes. There is an abundance of theoretical (e.g., Slinn, 1983), modelling (e.g., Langner & Rodhe, 1991), and empirical evidence in support of a residence time for sulfate aerosol of about one week. Measurements of ratios of atmospheric concentrations of radon daughters, which attach to aerosol particles in proportion to their surface area and are therefore highly appropriate for the accumulation-mode sulfate particles of concern here, yield tropospheric residence times of 5 to 10 days (Junge, 1963; Chamberlain, 1991). The decay of concentrations of aerosol $^{137}$Cs in the weeks following the Chernobyl accident is closely fitted by a mean residence time of 7 to 9 days at locations widely distributed in mid latitudes of the Northern Hemisphere (Cambray *et al.*, 1987). Inferences of $\tau_{SO_4^{2-}}$ based on atmospheric concentrations or concentrations of sulfate in precipitation, although necessarily ambiguous because of continuous and distributed sources and because of sulfate formation by atmospheric oxidation of $SO_2$ (Schwartz, 1989), yield similar results. From the decrease in $SO_4^{2-}$ concentration in precipitation with distance over the North Atlantic Whelpdale *et al.* (1988) inferred a (1/*e*) decay distance of 2400 km. For a mean transport velocity of 300 to 500 km per day (Summers & Young, 1987), the corresponding mean residence time is 5 to 8 days.

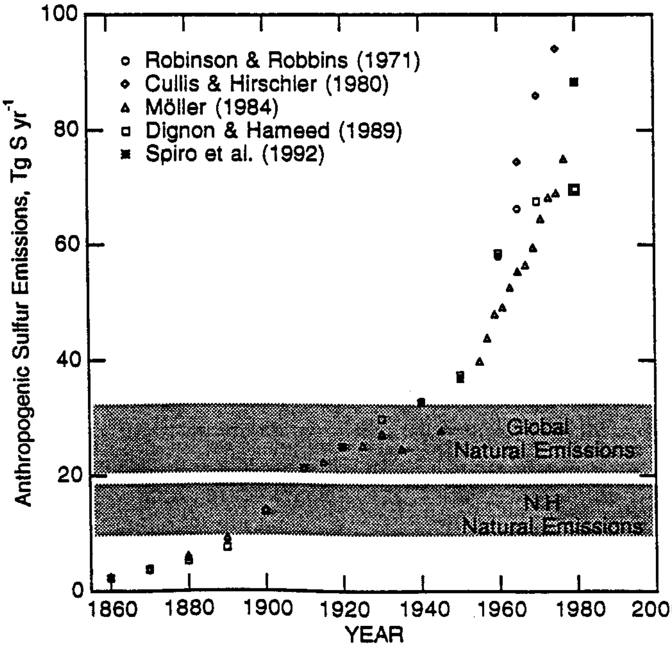

**Fig. 4.** Rate of emissions of anthropogenic $SO_2$ over the industrial era as estimated by Robinson & Robbins (1971) (○); Dignon & Hameed (1989), augmented for non fossil-fuel emissions by values from Robinson & Robbins (1971), Cullis & Hirschler (1980), and Spiro *et al.* (1992) (□); Cullis & Hirschler (1980) (◇); Möller (1984) (△); and Spiro *et al.* (1992) (*). Stippled bands denote estimates of total global and NH natural emissions of gaseous reduced-sulfur compounds and $SO_2$ (Bates *et al.*, 1992).

In addition to the mass concentration of the sulfate aerosol it is necessary to have information about the size distribution of the aerosol particles, since this size distribution affects the radiative properties of the aerosol and also its cloud nucleating properties, which govern the rate of removal from the atmosphere. The evolution of the size distribution of an aerosol (in clear air) is a resultant of new particle formation and coagulation and removal processes. These processes depend in complex and not completely understood ways on the properties of the existing aerosol and the rate of generation of new condensible material. The size distribution is strongly a function of relative humidity, increasing with increasing relative humidity (Charlson *et al.*, 1984; d'Almeida *et al.*, 1991). The size distribution is also greatly influenced by cloud processes (e.g., Hoppel, 1990; Hegg *et al.*, 1990).

*Indirect (cloud) radiative forcing.* Under the assumption that cloud liquid-water content remains constant, the perturbation in hemispheric- or global-mean shortwave forcing due to an increase in cloud droplet number concentration N, can be evaluated as:

$$\overline{\Delta F_{\mathrm{C}}} = - 1/48\ F_{\mathrm{T}} T A_{\mathrm{mst}} \Delta \ln N \qquad (2)$$

where $A_{\mathrm{mst}}$ is the fraction of the surface covered by marine stratus clouds (Charlson *et al.*, 1992). Schwartz (1988) has suggested, based on comparison of measured concentrations of excess (non-seasalt) sulfate at remote marine locations in the Northern and Southern Hemispheres that the NH perturbation in sulfate due to anthropogenic emissions is about 30%, i.e., 15% global average. Under assumption that the increase in cloud droplet concentration scales linearly with sulfate concentration and for $A_{\mathrm{mst}} = 0.25$ (Charlson *et al.*, 1987) the calculated global-mean indirect perturbation in radiative forcing is -0.9 W $m^{-2}$ (Charlson *et al.*, 1992). Substantially greater perturbations, -10 W $m^{-2}$ or more, would be expected in regions directly influenced by industrial emissions, where CCN number concentrations are commonly enhanced by a factor of 5 or more above natural background (Radke & Hobbs, 1976 ; Pueschel *et al.*, 1986).

The above estimate must be considered highly uncertain, resting as it does on a quite limited data base of observations and on a questionable assumption of linearity between excess sulfate and increased cloud droplet concentrations. A key issue is the fractional incorporation of aerosol particles in cloud droplets. Earlier work has yielded a fairly wide spread in this fractional incorporation. More recent work indicates a high fractional incorporation at low concentrations of aerosol particles decreasing as the aerosol particle loading increases (Leaitch *et al.*, 1992; Gillani *et al.*, 1992). Although the atmospheric chemistry of sulfate aerosols is relatively well understood, based on research directed toward understanding acid deposition, much of the microphysics of aerosol particle formation and interaction of aerosols with clouds leading to removal in precipitation is not adequately understood to permit inclusion in climate models with confidence.

The indirect (cloud) forcing is more difficult to address than the direct forcing. Additional key phenomena that must be considered are: (**i**) relations between mass and number concentrations and composition of pre-cloud aerosol concentrations and the number, concentration, and size distribution of cloud droplets formed in air containing the aerosol; and (**ii**) the dependence of the aerosol perturbation to cloud radiative forcing on the nature of the cloud fields. Because the optical and cloud nucleating properties of an aerosol depend on the size and composition of the particles comprising it, the influence of the aerosol cannot be uniquely and unequivocally ascribed to specific chemical substances. Rates of new particle formation and of the time evolution of the size distribution of aerosols are highly dependent on the rate of production of condensible material and the concentration and size distribution of aerosol particles already present. Description of these rates is uncertain to orders of magnitude and is a major unsolved problem of atmospheric physical chemistry.

## 5. Conclusion

The perturbation in longwave radiative forcing by enhanced concentrations of greenhouse gases is relatively well described, although the climate response to this forcing remains uncertain. In contrast, the perturbation in shortwave radiative forcing by anthropogenic aerosols is much more uncertain, both in global average magnitude and in spatial distribution.

**TABLE 1.** Evaluation of global mean direct radiative forcing due to anthropogenic sulfate (after Charlson *et al.*, 1992).

| Quantity | Value | Units | Uncertainty Factor | Reference/Note |
|---|---|---|---|---|
| $F_T$ | 1370 | $W\ m^{-2}$ | | Ramanathan (1987) |
| $1\text{-}A_c$ | 0.4 | | 1.1 | Warren *et al.* (1986, 1988) |
| $T$ | 0.76 | | 1.15 | Charlson *et al.*(1991) |
| $1\text{-}R_s$ | 0.85 | | 1.1 | Robock (1980) |
| $\bar{\beta}$ | 0.29 | | 1.3 | Wiscombe & Grams (1976) |
| $\alpha_{SO_4^{2-}}$ | 5 | $m^2(g\ SO_4^{2-})^{-1}$ | 1.5 | Waggoner *et al.* (1976, 1981); Whitby (1978); White (1986); ten Brink *et al.* (1987) |
| $f(RH)$ | 1.7 | | 1.2 | Charlson *et al.* (1984) |
| $Q_{SO_2}$ | 80 | $Tg\ S\ yr^{-1}$ | 1.15 | Fig. 4 |
| $Y_{SO_4^{2-}}$ | 0.4 | | 1.5 | (1) |
| $\tau_{SO_4^{2-}}$ | 0.02 | yr | 1.5 | (2) |
| $A$ | $5 \times 10^{14}$ | $m^2$ | | |
| $\overline{\Delta F_R}$ | -1.1 | $W\ m^{-2}$ | 2.4 | |

(1) Mean dry deposition velocity of $SO_2$, 0.5 cm $s^{-1}$; height of mixed layer, 2 km; $k_{SO_2\text{-}OH}$, $1 \times 10^{-12}$ $cm^3$ $s^{-1}$; mean OH concentration, $1 \times 10^6$ $cm^{-3}$; in-cloud conversion assumed equal to gas-phase.

(2) $\tau_{SO_4^{2-}}$, 1 week, representing frequency of precipitation removal.

Quantitative estimates of the climate influence of anthropogenic aerosols are necessary in models of past, present, and future climate. Such estimates are essential for (i) evaluating climate sensitivity from observed climate change, (ii) evaluating the performance of climate models, and (iii) predicting reliably potential future climate changes. To date climate models have emphasized forcing by $CO_2$ and other greenhouse gases but have not treated the influence of anthropogenic aerosols. Since this forcing appears to be comparable to that of the greenhouse gases, it is necessary that it be accurately represented in climate models if climate change is to be accurately represented. The representation of greenhouse gas forcing only, that is, neglecting the forcing due to anthropogenic aerosols, in present climate models may account for the greater increase in global mean temperature given by these models than has been experienced over the industrial era.

Aerosol forcing of climate is qualitatively different from greenhouse gas forcing. As a shortwave forcing it is effective only during daytime, and more in summer than in winter, in contrast to greenhouse forcing, which is effective at all hours and seasons. Also the aerosol forcing is quite nonuniformly distributed over the earth in contrast to the greenhouse forcing. These differences require that the aerosol forcing be explicitly treated in climate models.

It is necessary to take into account aerosol concentrations and radiative influence as a function of location and secular time as governed by emissions of sulfur gases. In view of the high spatial variability associated with anthropogenic aerosol a fairly high degree of spatial resolution (1000 km or better) is required to assess regional climate influences. Moreover, because cloud microphysical processes depend of the nonlinearly on the concentration of aerosol particles and because cloud forcing depends nonlinearly on the concentration of cloud droplets even the global mean forcing will be inaccurate unless the spatial distribution of aerosols is accurately treated.

Models should accurately represent the direct light scattering effect and also the influences of these aerosols on cloud optical, radiative, and persistence properties. At present none of these influences can be assessed with confidence. Further, there is only a meager data base of observations with which to bridge the gap and with which to confirm models of atmospheric chemistry, transport, and removal processes that are required to relate aerosol concentrations to emissions. There is similarly only a small data base relating aerosol microphysical properties to cloud microphysical properties, relating aerosol and cloud microphysical properties to their radiative properties, and relating cloud microphysical properties to cloud persistence.

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# SOURCES AND SINKS OF METHANE ON THE TERRITORY OF THE FORMER USSR

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## 1. Introduction

Methane is the most abundant organic compound in the atmosphere. Its concentration is substantially larger than those of other organic compounds. In the last years, the amount of methane in atmosphere has gradually increased at a rate of 1% per year due to the anthropogenic activities.

The aim of the present paper is to describe the sources and sinks of methane on the territory of the former USSR.

## 2. Sources of methane

*Peatlands.* In the former USSR most peatlands are situated in Russia (92.5%)[1]. According to reference [2], the peatlands of Russia cover 1.13 x $10^{12}$ $m^2$ (1.5 x $10^{12}$ $m^2$ in ref [3]) and occupy much of the area north of 60 degree latitude. In these northern peatlands, methane is assumed to be emitted for about 100 days per year with a flux of 0.03-0.2 g/$m^2$ [4]. If these assumptions are correct, the peatlands of Russia can produce 3-25 Tg/year of methane.

*Tundra.* Dry tundra possesses low methane productivity (about 5 mg/$m^2$/day [5]). In Russia, tundra occupies about 7.7% of the area [6] which amounts to $1.7 \cdot 10^{12}$ $m^2$. Since the summer season in tundra regions lasts for 100 days [4], a global flux for tundra of approximately 0.85 Tg/year is obtained.

*Animals.* Animals, particularly ruminants, provide a rather a strong source of methane due to fermentation processes occurring the rumen [7]. As shown in Table 1 the contribution of animals living on the territory of the former USSR, is 6.2±1.5 Tg/year or 8.2% of the total contribution from all animals of the world.

*Landfills.* Landfills can be an appreciable source of methane owing to the abundance of organic substances buried. In the countries of the former USSR, about 10.7 Tg of biologically decomposable carbon have been estimated to be deposited annually in landfills [10]. Assuming conversion to methane with an efficiency of 45% [10], this accounts to a flux of 4.7±1.5 Tg/year.

*Rice paddies.* Rice paddies are a strong source of methane as they are covered with water almost throughout the entire year. This favours the development of anaerobic methanogenic bacteria. On the territory of the former USSR, the following area was covered with rice paddies (see Table 2).
Assuming that the flux of methane is 20 g/$m^2$/year [11], the rice paddies on the territory of the former USSR emit about 0.14 Tg of methane per year.

*Coal mining.* Coal mining is accompanied by the emission of large amounts of gas consisting mainly of methane. The emissions, even from an single mine, are highly time-dependent [12]. On the average, however, for the mines of the former USSR, the release of gas is assumed to be 13 $m^3$ per ton of coal produced [12].

On the territory of the former USSR, coal mining produces about 735 million metric tons per year. (For more details see Table 3). Assuming an emission of gas of 13 $m^3$ methane per ton coal, the mines on the territory of the former USSR, emit about 6.4±1.9 Tg of methane per year.

**TABLE 1.** The amount of methane emitted by animals and people living on the territory of former USSR (as of 1990).

| Species | Number of individual mln, [8] | Methane flux from one ind. kg, [9] | Methane flux from population Tg |
|---|---|---|---|
| Cattle | 115,7 | 45.0 ± 10 | 5.2 ± 1.2 |
| Sheep | 133,3 | 6.5 ± 1.5 | 0.77 ± 0.2 |
| Goats | 7,3 | 5.0 | 0.037 |
| Pigs | 75,6 | 1.25 ± 0.25 | 0.094 ± 0.02 |
| Horses | 5,9 | 18.0 | 0.11 |
| People | 300,0 | 0.05 | 0.015 |
| Sum | | | 6.2 ± 1.5 |

**TABLE 2.** The area covered with rice paddies, mln of ga [8]

| Year | 1980 | 1985 | 1986 | 1987 | 1988 | 1989 | 1990 |
|---|---|---|---|---|---|---|---|
| Area | 0.7 | 0.7 | 0.6 | 0.7 | 0.7 | 0.7 | 0.6 |

**TABLE 3.** Coal mining, million metric tons [8].

| Year | 1980 | 1985 | 1988 | 1989 | 1990 |
|---|---|---|---|---|---|
| Coal mining | 716 | 726 | 772 | 740 | 703 |

**TABLE 4.** Gas production, $10^9$ $m^3$ [8].

| Year | 1980 | 1985 | 1988 | 1989 | 1990 |
|---|---|---|---|---|---|
| Gas production | 435 | 643 | 770 | 796 | 815 |

**TABLE 5.** Oil production, mln of ton [8].

| Year | 1980 | 1985 | 1988 | 1989 | 1990 |
|---|---|---|---|---|---|
| Oil production | 603 | 595 | 624 | 607 | 571 |

*Losses from natural gas production.* In developed countries, gas losses during its production and transportation, accounts no more than 1% [13]. Gas production on the territory of former USSR can be assessed from Table 4. It is assumed that the average annual production amounts to 800 x $10^{11}$ $m^3$. Natural gas contains 90% methane [13]. Gas losses in the USSR are estimated to be 6% [14], 6-9% [15]. This means that 30±6 Tg/year of methane is lost and emitted to the atmosphere every year. But, the uncertainty in this case is high (from 3.7 to 36 Tg/year). This value is, however, far from being reliable. There is no great difference between the produced and consumed amount of gas. Therefore, it is assumed that the losses due to gas leak to the atmosphere are the same as in the developed countries (to within 1%). Thus, the input of methane to the atmosphere will be 3.7 Tg/year.

*Oil production.* Gas losses caused by oil production are usually not considered as a possible source of methane because the strength of this source is low. Data on oil production in the former USSR are listed in Table 5.

As follows from the Table 5, oil production is about 600 millions of metric tons on the average. According to reference [16], gas emission is 112.6 $m^3$ per ton of oil, and 34% methane is present in the gas. The question arises how much of this gas is lost during oil production, storage, and refining.

If it is assumed that the gas losses during oil production are the same as during gas production amounting up to 6% [14], 6-9% [15], then 0.8 Tg of methane will enter the atmosphere every year. The uncertainty of this estimate is large, but its value of 0.8 Tg constitutes the upper limit. The real value is in the range 0-0.8 Tg/year.

*Methanehydrates.* The supply of methane in the Earth's crust in the form of gashydrates is large ($10^{18}$-$10^{21}$ tons [17]). Future climatic warming could cause destabilization of these supplies and cause the release of methane. Emissions due to this cause are observed already at present [17]. The Arctic of Russia is the area, where these emission of methane from gashydrates most likely will occur. No estimates of this effect are available yet.

*Biomass burning.* Biomass burning occurs on a substantially larger scale in the tropics where, according to [18], 11-53 Tg/year of methane are emitted to the atmosphere. In reference [19] a value of 55 Tg/year is given. In the countries of the former USSR, this source of methane is, most likely, unimportant.

*Lakes.* On the territory of the former USSR, there are 2.8 millions of lakes covering an area of 490000 km$^2$ [20]. Nothing definite can be said about lakes as a source of methane.

*Insects (termites).* Some insects emit methane due to the digestive processes, particulary insects that feed on cellular tissue. This species of insects involves, first of all, termites existing mainly in the tropics. On the territory of the former USSR, a few species of termites are found in the regions of Middle Asia, the Southern Ukraine, Moldavia, and the Far East [21]. Unfortunately, their number is unknown as nobody counted them. Presumably their number is small compared to that of the termite population in the tropics.

## 3. The methane flux from the territory of the former USSR

Table 6 lists the magnitudes of methane source strengths on the territory of the former USSR. As follows from the table, the uncertainties in source strengths are very large.

## 4. Sinks of methane

Forests and steppes have been found to consume methane after wetting of the soil by precipitation. If the total global absorption of methane by soil is assumed to be 30±15 Tg/year [15], then the contribution of the countries of the former USSR to the total will be about 5±2.5 Tg/year.

## 5. Conclusion

New extensive and detailed studies are necessary to improve estimates for the strengths of methane sources and sinks on the territory of former USSR.

**TABLE 6.** Methane emission to the atmosphere from the territory of former USSR.

| Source | Amount of methane, Tg/year | Source | Amount of methane, Tg/year |
|---|---|---|---|
| Peatlands | 3 - 25 | Gas leakage | 3.7 (36?) |
| Tundra | 0.85 | Gas losses upon oil production | 0 - 0.8 |
| Animals | 6.2 ± 1.5 | Methanehydrates | 0 - 5 |
| Landfills | 4.7 ± 1.5 | Insects | 0 |
| Rice paddies | 0.14 | Forest | - (5 ± 2.5) |
| Coal mining | 6.4 ± 2 | Steppes | |
| TOTAL | 15.7 - 57.8 (93.8?) | | |

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# EMISSIONS OF METHANE IN JAPAN

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In order to evaluate the relative importance of infrared trapping gases and their sources contributing to the increase of global background concentrations, emissions of methane in Japan have been surveyed by the Environment Agency in 1989 and 1990[1,2]. The present paper is based on the data given in these reports. Anthropogenic emissions are taken as reported for the years 1985-1988.

## 1.Emission sources and strengths of methane in Japan

### *1.1 Anthropogenic sources*

(1) Agriculture and forestry

(a) Rice paddies. Although the area of rice paddies in Japan, 21.5 x 103 km$^2$, is only 1.5 % of the total in the world (1.44 x 106 km$^2$) in 1985, extensive studies on the flux of methane emission from rice paddies have been conducted in Japan due to its relative importance in this country and also in Asia. Emissions of methane from paddy fields differ significantly depending on temperature, soil character, fertilizer, rice species, water management, etc. Considering the flux data for different soils and fertilizers, and the area of each soil type of paddy fields, the annual emission of methane from rice paddies in Japan has been estimated as 150- 300 Gg/yr, which corresponds to an average flux of 7-14 g-$CH_4$/m$^2$/yr.

(b) Livestock. Enteric fermentation of ruminants is known to be important source of methane from livestock. Headcounts of livestock in Japan are reported as cattle, 4.69 x $10^6$; sheep, 26 x $10^3$; goats, 48 x $10^3$; and pigs, 11.35 x $10^6$ and emissions of methane per head are given in the literature as 55, 8, 5 and 1.5 kg/yr for these livestock respectively. Thus, the emissions are 258, 0.2, 0.2 and 17 Gg/yr, for cattle, sheep, goats and pigs, respectively, giving a total of 275 Gt/yr. Due to the large number of pigs raised in Japan, they contribute substantially to the methane flux although they are not ruminants.

(c) Biomass burning. Forest fires have burned annually 43 km$^2$ in average between 1984-88, whereas the total forest area in Japan is 360 x 103 km$^2$, which contains 1.4 Gt dry-matter weight or 0.63 GtC. Assuming that 80 % of burned carbon is emitted as $CO_2$ and the $CH_4/CO_2$ emission ratio is 0.01-0.02, forest fires emit methane at a rate of 0.8-1.6 Gt/yr. Emission of methane due to the burning of rice straw and other agricultural waste has been estimated as negligible taking into account the volume of biomass involved.

(2) Waste disposal

(a) Landfill/reclamation of city refuse.City refuse is subjected to anaerobic fermentation after landfill. The emission of methane reaches nearly a constant level one year later and continues at nearly the same level for about five years according to studies conducted in Japan. After six years, both the gas evolution and the concentration of methane therein decreases rapidly. Based on experimental data and the assumption that methane content in the evolved gas is 50 %, the emission factor of methane for the landfill/reclamation was set to 16-110 l-$CH_4$/kg-dry refuse/5 yr. Multiplying by the annual total amount of city refuse, the emission of methane is estimated to be 68-427 Gg/yr.

(b) Incineration of wastes. Incineration of city refuse, sludge, waste oil and waste plastics emits 20-100, 3-10, 10-20 and 20-50 µmol/mol of methane in exhaust gases, respectively. Based on the data of the amount of gases thus generated, the emission factors of methane have been determined as 102-512, 51-170, 58-116 and 200-500 l-$CH_4$/T-waste, which in turn give the total amount of methane emitted from the incineration as 2.1-10.7, 0.1-0.4, 0.0-0.1 and 0.1-0.2 Gg/yr for city refuse, sludge, waste oil and waste plastics, respectively. Thus, the incineration of waste is a minor contributor as compared to landfill/reclamation.

(c) Digestion of sewage sludge and excrements. Sewage sludge and excrements are in general treated as anaerobic digestion which generates methane during the process. It has been assumed that the involved gases contain up to 65% methane in both cases, and the emission factors used are 360 l-$CH_4$/T-organic matter in sludge and 7600 l-$CH_4$/kl-excrement. The 80 % and 90 % of methane generated at these facilities are used as fuel in Japan, and are not released into the atmosphere. The estimated amounts of emitted methane are 16.0 and 6.7 Gg/yr for the disposal of sewage sludge and excrete, respectively. Although no estimate was made for the disposal of livestock droppings due to lack of data, it may emit substantial amount of methane contributing to the total.

(3) Fossil fuel combustion

(a) Stationary sources. Emissions from the following economic sectors (in an energy balance table) are treated here; energy transformation sector, energy sector own-use, industrial and residential sectors. Emission factors for each sector for each fuel category are taken from literature for particular facilities. Since the methane emission factors depend significantly on boiler types, combustion conditions, installation of flue-gas control facilities, etc., the assumed emission factors may not be representative for each emission source categories. Fuel consumption data for each emission source categories taken from the energy balance table have been multiplied to obtain the emission of methane from stationary sources. The estimated emission of methane thus obtained is 5-10 Gg/yr.

(b) Mobile sources. Literature values of emission factors of methane for automobiles (light-duty gasoline vehicles, LDGV) varies by an order of magnitude, e.g. 6-109, trace-60, 3-25 and 2-20 g-$CH_4$/GJ for uncontrolled, controlled, oxidation catalyst installed- and three-way catalyst installed-cars, respectively. Assuming that the emission factors as 2-109 (average 20) g-CH4/GJ both for LDGV and HDGV (heavy-duty gasoline vehicles), and as 2-8 (average 5) g-$CH_4$/GJ for LDDV and HDDV (diesel vehicles). Total emissions of methane from automobiles are calculated to be 4.4-149 (average 31) Gg/yr using the fuel consumption data. Similarly, emissions from railways, navigation, and aviation are estimated to be 0.14, 5.2 and 0.26 Gg/yr, respectively, giving a total of 5.6 Gg/yr from mobile sources other than automobiles.

**TABLE 1.** Estimated Emissions of Methane in Japan

| Source | Japan | | Global[a] | |
|---|---|---|---|---|
| | Total<br>Gg-$CH_4$/yr | per capita[b]<br>kg-$CH_4$/yr | Total<br>Tg-$CH_4$/yr | per capita[b]<br>kg-$CH_4$/yr |
| Anthropogenic | 1,062 (754-1457) | 8.8 | 360 (270-505) | 73 |
| Agriculture and Forestry | 501 (425-577) | 4.1 | 180 (105-280) | 37 |
| Rice Paddies | 225 (150-300) | 1.8 | 60 (20-100) | 12 |
| Livestock | 275 | 2.3 | 80 (65-100) | 16 |
| Biomass Burning | 1 (0.8-1.6) | 0.0 | 40 (20-80) | 8 |
| Waste Disposal | 278 | 2.3 | 80 (65-125) | 16 |
| Landfill/Reclamation | 248 (68-427) | 2.0 | 30 (20-70) | 6 |
| Incineration | 7 (2-11) | 0.1 | -- | -- |
| Digestion | 23 | 0.2 | 25[c] | 5 |
| Animal Wastes | -- | -- | 25 (20-30) | 5 |
| Fossil Fuel Combustion | 45 (15-165) | 0.4 | -- | -- |
| Stationary Sources | 8 (5-10) | 0.1 | -- | -- |
| Mobile Sources | 37 (10-155) | 0.3 | -- | -- |
| Natural Gas Usage/Coal Mining | 238 | 2.0 | 100 | 20 |
| Natural Gas Usage | [78 ( 61-94)] | 0.6 | -- | -- |
| Coal Mining | [160] | 1.3 | -- | -- |
| Natural | 93 | 0.8 | 150 (116-295) | 30 |
| Freshwater | 5 | 0.0 | 5 (1-25) | 1 |
| Marginal Sea | 75 | 0.6 | 10 (5-20)[d] | 2 |
| Wetlands | 13 (7-20) | 0.1 | 115 (100-200) | 23 |
| Termites | ng | 0.0 | 20 (10-50) | 4 |
| Total | 1,155(832-1557) | 9.6 | 510 | 104 |

a) WMO, UNEP; 1992 IPCC Supplement.
b) Population in 1986 is used.
c) Domestic sewage treatment.
d) Ocean
ng : negligible
-- : not given
[ ]: based on estimation by the US EPA Methane Workshop (1990).

(4) Natural gas usage and coal mining

(a) Natural gas usage. Production of natural gas in Japan is about 2.1 x $10^9$ $m^3$ in 1988 which is only 0.1 % of the global yield. Strict control for leakage of natural gas at mining sites is enforced in this country for the purpose of safety and preserving a limited amount of resources, and the release would not be significant. Japan imports about 40.6 x $10^9$ $m^3$ of natural gas so that leakage during the pipeline distribution and at usage sites may not be negligible. Since no explicit data is available in Japan, an estimated value of 61-94 Gg/yr at the US EPA Workshop (1990) is cited here for the leakage during gas distribution.

(b) Coal mining.Coal production in Japan is 11 x $10^6$ T which is only 0.3 % of the global yield of 3.3 x 109 t in 1988. Methane extracted in coal mining in Japan is estimated as 90 Gg/yr of which 80 % is used for the generation of electricity for own use. Estimate by the US EPA Workshop (1990) for methane emission from coal mining in Japan amounts to 200 Gg/yr. When the amount of effective utilization for electric generation as stated above is subtracted, release of methane from coal mining would be about 160 Gg/yr base on the above estimate.

### *1.2. Natural sources*

(1) Freshwater. Methane emissions flux from lakes and marshes are known to be well correlated with the net production of organic matters therein, reflecting the balance of anaerobic production by methanogenic bacteria and destruction by oxidizing processes in water. The 68 major lakes and marshes in Japan have been classified into three categories of oligotrophic, mesotrophic and eutrophic, for which methane fluxes have been assumed to be 0.6, 2.3 and 3.5 g-$CH_4$/$m^2$/yr, respectively. The total emission of methane has been estimated by multiplying the area of each type of lakes and marshes (total 2.1 x $10^3$ $km^2$) yielding the value of 5 Gg/yr.

(2) Coastal areas. Similar treatment was made for estimating flux of methane from coastal areas. Thus, these areas have been categorized into continental shelves, and oligotrophic, mesotrophic and eutrophic bays and estuaries. A methane flux of 0.026 g/$m^2$/yr was assumed for continental shelves and the same fluxes were postulated for bays and estuaries as lakes and marshes with the same trophic states. Total area of continental shelves, and bays and estuaries are 278 x $10^3$ and 31 x $10^3$ km2, which may be compared with the total terrestrial area of Japan, 378 x $10^3$ km2. The total methane emission from coastal areas thus is estimated as 75 Gg/yr.

(3) Wetlands. Bogs and fens are the major wetlands in Japan although their area is only 0.03 % of the global total. Taking into consideration the literature values of methane flexes for bogs and fens at different latitudes, annual emission of methane from wetlands are estimated as 7-20 Gt/yr assuming that methane are emitted only during a limited time-period when the temperature is over 0°C.

(4) Termites. Although some species of termites inhabit in Japan, their number is limited and the contribution to methane emissions from this sources would be negligible compared to other sources.

## 2. Summary of methane emission

Table 1 summarizes the emission of methane in Japan comparing with the global sources estimated by IPCC. For comparison, emissions per capita are also given. As shown in Table 1, emission in Japan is about 1.2 Tg/yr which is about 0.2 % of the global total. Anthropogenic sources stands more than 90 % of the emission, and rice paddies, livestock, and landfill/reclamation are three contributor in Japan. The accuracy of the values for natural gas usage / coal mining is uncertain at this stage of investigation. In terms of per capita, emission in Japan is about one-tenth of the global average reflecting the area ratio of ca. 0.28 % and population ratio of ca. 2.5 %.

## Action Plan to Reduce Methane Emissions

The following plans have been proposed for reducing the emissions of methane in Japan.

(1) Waste Disposal

(a) Reduction of the amount of city refuse by promoting its use as resources.

(b) Reduction of flammables to be disposed as landfill/ reclamation by promoting incineration with effective use of waste heat.

(c) Re-use of industrial wastes as resources.

(d) Promotion of semi-aerobic landfill/ reclamation, and collection and utilization of evolved methane as fuel.

(2) Agriculture

(a) Improvement of drainage and water management of rice paddies and appropriate management of organic matters therein.

(b) Promotion of aerobic fermentation processing of livestock excrete.

(3) Energy Production and Use

(a) Improvement of collection and utilization of gases from coal mining which is extracted for the purpose of safety.

(b) Increase of control of leakage in the gas-supplying business.

(c) Improvement of energy efficiency in a transportation sector, and examination of technological feasibility of the installation of methane emission control devices.

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# METHANE EMISSION IN CHINA

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Methane is an important greenhouse gas, which accounts for about 20% of the current contribution to the increase in global warming. The main anthropogenic sources of the methane emission are rice field and ruminant emission, also natural gas use, biomass burning, coal mining, landfills, etc.. China is one of the largest rice producing country in the world with an area of rice paddies 3.25 x $10^5$ $km^2$ (FAO, 1989), amounting to 22.4% of the total rice fields in the world. An estimate of methane emission from Chinese rice fields is necessary to obtain a whole global emission estimate. In order to evaluate the total emission and emission inventory of methane in China, China has started programmes to determine the methane flux from Chinese rice fields as of 1985. These studies are partly sponsored or by executing collaboration with foreign research institutions and agencies. Since 1990, a National Key Project on Greenhouse Gases Studies (1991-1995) has been organized by the State Commission of Science and Technology. The emission inventory study regarding methane is one part of the project. In addition to studying the emission from rice paddies, other studies related to on methane emission from livestocks, biomass burning, coal mining and landfills are being carried on.

## I. The measurement of emission flux from rice paddies

China has a 5000 years history in growing rice. The rice fields in China are distributed over a very wide range, about 35 degree of latitude. Thus farming procedures, weather, soil conditions which effect the methane emissions vary from place to place. In order to obtain the emission data more accurately certainties, a large number of experiments in different areas of China is needed. Several batches of measurements have been performed in the past several years.

A) From 1995 to 1987, experiments to determine methane fluxes from rice fields were conducted around Chengdu city in Sichuan province. Measurements during a full rice growing season at Tuzu in Sichuan province (29°40'N, 103°50'E) were accomplished during 1988-1990. It was found that the methane flux increased rapidly with increasing soil temperature, and the flux varied with the type of rice seed. The emission flux of a single harvested rice in Sichuan province was around 60 $mg/m^2.hr$ and 216 $g/m^2.yr$, which might be the highest flux observed in the world.

**TABLE 1.**

| | Paddy area ($10^{12}$ $m^2$) | Vegetation period (days) | Flux $g/m^2.day$ | Emission $10^{12}g/yr$ |
|---|---|---|---|---|
| Early rice | 9.58 | 90-100 | 0.19 | 1.6-1.8 |
| Late rice | 20.30 | 100-120 | 0.69 | 14.0-16.8 |
| Single-Harvest | 2.32 | 120-150 | 1.60 | 4.5-5.6 |
| Total | 32.20 | | | 20.1-24.2 |

**B)** A series of $CH_4$ emission measurements was conducted in a rice paddy field at Hangzhou, Zhejiang province (30°19'N, 120°12'E) for early rice in 1988, 1889 and late rice in 1987 to 1989 during entire growing seasons. It was found that $CH_4$ emission rates showed strong diurnal variations. Bi-moded patterns with maxima in the afternoon and at midnight were found for early rice, and a single peak pattern with the maximum in midnight for the late rice. This behaviour can be explained by the diurnal variations of the soil temperature and the activity of rice plants. Strong seasonal variation with a single peak in the tillering stage and a double peak in the flowering stage of rice plants were also observed. These maxima apparently resulted from the activities of rice plants, availability of organic substrates in the soil and the activity of soil bacteria. $CH_4$ emission rates of 7.8 $mg/m^2.hr$ for the early rice and 28.6 $mg/m^2.hr$ for the late rice (or 16.2 $g/m^2.yr$ and 75.9 $g/m^2.yr$ respectively) were obtained.

$CH_4$ emission from rice fields and the effects of different field managements to $CH_4$ were studied in Beijing area (40°N, 120°E) during 1990-1992. Experiments showed that the $CH_4$ emission was strongly affected by irrigation, temperature, the mode of fertilizing and agriculture management. Investigation in this area has been focused mainly on the influence of irrigation and fertilization in order to decrease of $CH_4$ emission with the increase of rice production.

Results indicated that the proper use of chemical fertilizer led to a suppression of anaerobic production of $CH_4$ to a certain extent and that a scientific irrigation to flood the fields alternatively, might be an effective way to improve rice production and to reduce $CH_4$ emission. $CH_4$ emission rates in the range of 8-18 $mg/m^2.hr$ were found in the Beijing area.

**TABLE 2.** Estimated anthropogenic emissions of methane in China (Tg $CH_4$/Yr)

| Source | A | B |
|---|---|---|
| Rice paddies | 22±2 | 25 |
| Live stock | 5.5 | 5.5 |
| Coal mine | 6.1 | 4.0 |
| Animal waste | 9.7 | |
| Digestion | | 0.5 |
| Natural gas leakage | | 0.37 |
| Biogas pits | <0.1 | |
| Biomass burning | | 2.5 |
| Fossil | | 7.3 |
| Urban area | 0.6 | |
| Total | ≥44.0 | ≥45.17 |

## 2. The estimation of $CH_4$ emission flux from rice paddies

Recently some results were reported for the estimation of $CH_4$ emission from rice paddies in China based on the different classifications of rice paddies. A preliminary estimate of $CH_4$ emission based on the classification of rice harvests is presented (Table 1).

A total of (22±2) x $10^{12}$ g/yr has been derived for the average $CH_4$ emission from rice fields in China.

## 3. Preliminary estimation of methane emissions in China

Two series of data are reported for anthropogenic $CH_4$ emissions in China. Set A was obtained by calculations based on field experiments. Set B was obtained by calculations based on the emission factors recommended in foreign reports. Results for these two methods are shown in Table 2.

# INDIAN METHANE BUDGET AND ITS GLOBAL PERSPECTIVE

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## 1.Introduction

Methane, a chemically and radiatively active trace gas, is produced from a wide variety of anaerobic processes. Its global cycle is driven by emissions about 525-550 tg/yr from both natural sources and those related to anthropogenic activities. The main sources affected by human activities are rice fields and ruminants, mostly cattle. Other anthropogenic sources also include biomass burning, coal mining, oil and gas use, landfills, automobiles and a variety of even smaller sources. The major natural source is from the wetlands, with smaller contributions from other sources, such as tundra, lakes and rivers, the oceans and the activities of termites. It is estimated that 60% of the total emissions are from manmade sources. Once methane gets into the atmosphere it has a life time of 8-12 years. It is removed primarily by reacting with OH radicals (~500 tg/yr) but smaller amounts (~30 tg/yr) are also removed by soils, and still smaller amounts are removed by other chemical processes in the troposphere and stratosphere. The present imbalance between sources and sinks is about 45 tg/yr, which is observed as an increasing atmospheric trend of 0.9% per year and has led to the current atmospheric methane concentrations, at about 1.8 μmol/mol, which is more than double the preindustrial value of 0.8 μmol/mol.

The emissions of methane from rice fields and domestic ruminants have increased steadily over the past 100 years and have presumably reached a value of 190-200 tg/yr. There is enough uncertainty in the methane production levels due to these two major anthropogenic sources. According to the IPCC (Intergovernmental Panel on Climate Change) Document (1990) "One difficulty in obtaining an accurate estimate is that almost 90% of the world's harvested area of rice paddies is in Asia and of these about 60% are in China and India from which no detailed data is available". Since total Indian paddy cultivation area is about 35% of the global paddy fields, and its domestic animal population is about 500 million, it becomes essential to obtain an accurate estimate of methane emission in India from these two major anthropogenic sources.

## 2. Current status

Monitoring of methane in India is recent. During the last few years a source intensive study has been taken up for the estimation of methane emissions from Indian rice fields. Gaschromatographs with flame ionization detectors (GC-FID) have been used for the measurements. In-situ measurements with portable gaschromatographs and also laboratory investigation by collecting air samples in teflon bags have been carried out. Methane standards for comparison were prepared in the laboratory. These investigations confirmed that methane emissions from rice fields critically depend on water-logging, pH values, temperature, texture and moisture of the soil, crop duration, the variety of the paddy, the mode of cultivation and the phase of the growing season. The methane emission has been found to decrease by two orders of magnitude as one goes from waterlogged to nonwaterlogged areas. Maximum emission is observed from waterlogged paddy fields. The total annual paddy cultivation area of over 42 mha in India, 41 mha under Kharif (July -October), and about 2 mha under Rabi (November - March) season, has been broadly divided into irrigated waterlogged and upland categories (Table 1). Taking these into consideration, a methane emission study from rice paddies was carried out by National Physical Laboratory New-Delhi, in collaboration with some other Institutes in four typical locations at New-Delhi (28°48 N, 77°12 E; 22-28 June 1989 and 25-28 September 1989),Dehradun (30°19 N, 78°04 E; 6-7 October, 1989) Karnal (29°42 N, 77°02 E; 13-16 October 1989) and Hyderabad (17°6 N, 78°0 E; 20-24 March 1990). The methane efflux measurements obtained from these locations have been used to calculate the methane emission from the various categories. The methane budget has been estimated by taking the highest emission rates as well as the average emission rate. These considerations, coupled with mapping from satellite remote sensing

**TABLE 1.** Paddy cultivation area distribution in mha (Mitra, 1992; Parashar *et al.*, 1992)

| Region/State | Total Area | Irrigated Area | Waterlogged area | | Upland area |
|---|---|---|---|---|---|
| | | | Rainfed | Deep water | |
| **Eastern Region** | | | | | |
| West Bengal | 5.610 | 1.593 | 2.457 | 0.677 | 0.883 |
| Bihar | 5.330 | 1.892 | 2.235 | 0.672 | 0.531 |
| Orissa | 4.390 | 1.440 | 2.109 | 0.150 | 0.691 |
| Assam | 2.430 | 0.525 | 1.590 | 0.100 | 0.215 |
| N.E states | 0.823 | 0.244 | 0.219 | 0.040 | 0.320 |
| TOTAL AREA | 18.583 | 5.694 | 8.610 | 1.639 | 2.640 |
| **Southern Region** | | | | | |
| Andhra Pradesh | 4.190 | 2.705 | 1.245 | 0.240 | - |
| Tamil Nadu | 2.010 | 1.417 | 0.593 | - | - |
| Karnataka | 1.180 | 0.710 | - | - | 0.470 |
| Kerala | 0.570 | 0.238 | 0.017 | - | 0.315 |
| Pondicharry | 0.025 | - | 0.025 | - | - |
| Andamans | 0.012 | - | 0.012 | - | - |
| TOTAL AREA | 7.987 | 5.070 | 1.892 | 0.240 | 0.785 |
| **Northern Region** | | | | | |
| Uttar Pradesh | 5.360 | 1.458 | 3.174 | 0.233 | 0.495 |
| Punjab | 1.910 | 1.910 | - | - | - |
| Haryana | 0.620 | 0.620 | - | - | - |
| J & K | 0.276 | - | - | - | - |
| Himachal Pradesh | 0.093 | - | - | - | 0.384 |
| Sikkim | 0.015 | - | - | - | - |
| Delhi | 0.003 | 0.003 | - | - | - |
| TOTAL AREA | 8.277 | 3.991 | 3.174 | 0.233 | 0.879 |
| **Western Region** | | | | | |
| Madhya Pradesh | 5.040 | 0.912 | - | - | - |
| Maharashtra | 1.520 | 0.280 | 3.377 | 0.322 | 1.669 |
| Gujrat | 0.600 | 0.390 | 0.210 | - | - |
| Dadra N H | 0.011 | - | 0.011 | | |
| Rajasthan | 0.160 | 0.160 | - | - | - |
| Goa, Daman & Diu | 0.054 | - | 0.054 | | |
| TOTAL AREA | 7.385 | 1.742 | 3.652 | 0.322 | 1.669 |
| **GRAND TOTAL** | 42.232 | 16.497 | 17.328 | 2.134 | 5.973 |

systems, lead to the methane budget estimate from Indian rice paddy to be 3-9 tg/yr. This preliminary estimate based on the data generated, estimated the Indian contribution to be only 3-8% of the global methane budget of 110 tg/yr and not 30% of the global methane budget due to rice paddy fields, as reported in some calculations.

To confirm the preliminary study made during 1989-1990 and to arrive at a more accurate estimate, 18 sites spread over all types of paddy growing areas have been selected in 1990-1991. The monitoring of methane under the leadership of NPL along with a dozen other groups, has been carried out on all these stations right from the sowing till the harvesting of the Kharif paddy crop. The chamber technique with a aluminium channel base has been employed for collection and GC-FID with a molecular sieve 5A was used for analysing all the air samples at various centers. Huge amount of data has been generated and the integrated methane fluxes (IF) are reported in Table 2.

TABLE 2. Methane Budget Estimates from Indian Paddy Fields (Mitra 1992. Parashar *et al.* 1992)

| Areas/Regions/States | Cultivation area (mha) | Integrated seasonal methane flux ($g/m^2$) | | | Reference stations | Total methane emission (tg/yr) | | |
|---|---|---|---|---|---|---|---|---|
| | | Max. | Mean | Min. | | Max | Mean | Min. |
| A. RAINFED WATERLOGGED AREAS | | | | | | | | |
| *I .Eastern Region* | | | | | | | | |
| a) West Bengal | 2.457 | 22±10 | 17 | 12±6 | Garia, Purulia, Kalyani, Brkpor | 0.54±0.25 | 0.42 | 0.30±0.15 |
| b) Bihar | 2.235 | 26±2 | 22 | 19±4 | Dehri | 0.58±0.05 | 0.49 | 0.43±0.09 |
| c) Orissa | 2.109 | 14±5 | 12 | 10±3 | RRB, CRRIC | 0 30±0.11 | 0.25 | 0.21±0.06 |
| d) Assam | 1.590 | 60±2 | 46 | 35±3 | RRLJ | 0.95±0.03 | 0.73 | 0.56±0.05 |
| e) N.E. States | 0.219 | 60±2 | 46 | 35±3 | RRLJ | 0.13±0.004 | 0.10 | 0.08±0.007 |
| *II.Southern Region* | | | | | | | | |
| a) Andhra Pradesh | 1.245 | | | | | | | |
| b) Tamil Nadu | 0.593 | 13±2 | 11 | 9±2 | CLRIM | 0.26±0.04 | 0.21 | 0.17±0.04 |
| c) Pondicherry | 0.025 | | | | | | | |
| d) Kerala | 0.017 | 13±1 | 9 | 5±1 | RRLT | 0.002+0.0002 | 0.002 | 0.001+0.0002 |
| e) Andaman and Nicobar Islands | 0.012 | 22±10 | 17 | 12±6 | W.B. Stations | 0.002±0.001 | 0.002 | 0.0014±0.0007 |
| *III.Northern Region* | | | | | | | | |
| Uttarpradesh | 3.174 | 26±2 | 22 | 19±4 | Faizabad | 0.83±0.06 | 0.70 | 0.60±0.13 |
| *IV.Western Region* | | | | | | | | |
| a) Madhya Pradesh | | | | | | | | |
| b) Maharasthtra | 3.377 | 16±8 | 14 | 11±4 | Orissa, Bihar and Tamil Nadu | 0.54±0.27 | 0.47 | 0.37±0.14 |
| c) Gujarat | | | | | | | | |
| d) Goa, Daman and Diu | 0.275 | 13±1 | 9 | 5±1 | RRLT | 0.0361±0.003 | 0.03 | 0.014±0.003 |
| e) Dadar N.H. | | | | | | | | |
| TOTAL | 17.328 | | | | | 4.17±0.82 | 3.40 | 2.74±0.67 |
| B. DEEP WATER AREAS | 2.434 | 24±2 | 19 | 14±1 | CRIJAF, Koirapur | 0.58±0.046 | 0.46 | 0.342±0.025 |
| C. IRRIGATED AREAS | 16.497 | | | | Delhi, Allhabd., Barakpore, Devoke | 0.335±0.078 | 0.164 | 0.061±0.007 |
| D. UPLAND AREAS | 5.973 | | Negligible | | (ref: IPCC Report) | Negligible | | |
| GRAND TOTAL | 42.232 | | | | | 5.1±0.9 | 4.0 | 3.1±0.7 |

It may be emphasized that 94% of the total methane emission from the Indian paddy cultivation comes from the waterlogged fields comprising only 41% of the total paddy harvested area; and the contribution from the large irrigated and upland areas is found to be low. From the current study the Indian paddy methane budget is estimated between 4 to 5 tg/yr, which is very different from 37.8 tg/yr projected in the US EPA report.

Hardly any comprehensive analysis and data are available with regard to the methane flux from the Indian domestic animals and wetlands. Considering that only ~30% of the 500 million Indian animals are cattle and the rest are sheep and goat; and that the average weight, size and energy intake of the cattle in India are much smaller than that in the developed countries, the methane contribution from the Indian domestic ruminants is estimated approximately around 5 tg/yr against the global average of 80 tg/yr. The estimate of the methane emission from the Indian wetlands is still uncertain, but is guessed to be less than either of the above mentioned two sources. Swamps and marshy lands cover relatively smaller area in India, and which furthermore is possibly decreasing. As such no methane increasing trends from the Indian wetlands is expected.

## 3.Concluding remarks

The Indian scientific community and the government subscribe the view that the actual methane emission both due to Indian paddy cultivation and its livestock is much smaller than what is being projected. The main reasons for this discrepancy are: (**i**) major part of the Indian paddy crop is taken from the irrigated fields, (**ii**) the energy intake of Indian domestic animals and their weight and size are much smaller than their counterparts in the developed countries. The current estimates suggest that the total methane emission in the Indian atmosphere is not more than 4-7% of the total global emission. Thus it is felt necessary to look for the missing source of methane or the over estimate of its some sink. It may be mentioned that the recently determined rate constants for the reaction at temperatures more typical of the troposphere, suggest a reduction of around 20% in the sink strength of the same OH field. Nevertheless, the national policy is to make more thoroughly the source intensive study of methane emission particularly from the paddy fields, domestic remnants and wetlands; and to arrive at an accurate estimate.

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