Atmospheric methane and global change

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Abstract

Methane (CH_4) is the most abundant organic trace gas in the atmosphere. In the distant past, variations in natural sources of methane were responsible for trends in atmospheric methane levels recorded in ice cores. Since the 1700s, rapidly growing human activities, particularly in the areas of agriculture, fossil fuel use, and waste disposal, have more than doubled methane emissions. Atmospheric methane concentrations have increased by a factor of 2–3 in response to this increase, and continue to rise. These increasing concentrations have raised concern due to their potential effects on atmospheric chemistry and climate. Methane is important to both tropospheric and stratospheric chemistry, significantly affecting levels of ozone, water vapor, the hydroxyl radical, and numerous other compounds. In addition, methane is currently the second most important greenhouse gas emitted from human activities. On a per molecule basis, it is much more effective a greenhouse gas than additional CO_2. In this review, we examine past trends in the concentration of methane in the atmosphere, the sources and sinks that determine its growth rate, and the factors that will affect its growth rate in the future. We also present current understanding of the effects of methane on atmospheric chemistry, and examine the direct and indirect impacts of atmospheric methane on climate. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Methane (CH_4) is the most abundant organic trace gas in the atmosphere. Concentrations[1] of CH_4 have more than doubled since pre-industrial times, with a current globally-averaged mixing ratio of ~ 1750 ppbv[2] (NOAA CMDL data, Dlugokencky, personal communication). The effects of CH_4 on climate and atmospheric chemistry are the reason for concern over its high growth rate. Following water vapor and carbon dioxide (CO_2), methane is the most abundant greenhouse gas in the troposphere. Both on a molecule and a mass basis, additional methane is actually much more effective as a greenhouse gas than additional CO_2. Methane is also the most abundant reactive trace gas in the troposphere and its reactivity is important to both tropospheric and stratospheric chemistry. The oxidation of CH_4 by hydroxyl (OH) in the troposphere leads to the formation of formaldehyde (CH_2O), carbon monoxide (CO), and ozone (O_3), in the presence of sufficiently high levels of nitrogen oxides (NO_x). Along with CO, methane helps control the amount of OH in the troposphere. Methane also

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[1] Concentration for methane as used here is actually volume mixing ratio (or mole fraction).

[2] ppbv = Parts per billion (10^9) by volume.

affects the concentrations of water vapor and ozone in the stratosphere, and plays a key role in the conversion of reactive chlorine to less reactive HCl in the stratosphere.

The purpose of this paper is to examine the past trends in the concentration of methane, the sources and sinks affecting its growth rate, and the factors that could affect its future growth rate. This study also examines the current understanding of the effects of methane on atmospheric chemistry and on climate.

2. Record and budget of atmospheric CH_4

2.1. Distribution and trend

2.1.1. Atmospheric CH_4 in the distant past

Air bubbles trapped in polar ice provide a continuous record of the atmospheric concentration of methane (e.g., Legrand et al., 1988; Chappellaz et al., 1990; Etheridge et al., 1992, 1998; Jouzel et al., 1993; Nakazawa et al., 1993; Raynaud et al., 1993; Blunier et al., 1995, 1998; Brook et al., 1996). Ice cores from Greenland and Antarctica now extend the record of atmospheric CH_4, CO_2 and temperature back to 420,000 years BP (Petit et al., 1999), covering four glacial–interglacial cycles.

The record shown in Fig. 1 reveals two important characteristics of past CH_4 concentrations with implications for future climate. First, present-day CH_4 levels appear to be unprecedented during any time in the past. Ice core records show glacial–interglacial transitions rising from 320–350 ppbv up to a maximum of 650–780 ppbv (Petit et al., 1999), corresponding to source increases as large as 50–60 $TgCH_4$/year (Brook et al., 1996, based on Chappellaz et al., 1993a). This is less than half of present-day concentrations, which are currently greater than 1700 ppbv. Secondly, CH_4 is closely tied to atmospheric temperature records, decreasing and rising in phase with temperature at the inception and termination of glacial episodes (e.g., Petit et al., 1999; Chappellaz et al., 1993a,b; Raynaud et al., 1988).

The observed synchronicity between temperature and CH_4 concentrations has raised the question of the role of CH_4 in glacial–interglacial climate change. Do increasing CH_4 emissions actually help initiate climate change, or do they respond quickly to rising
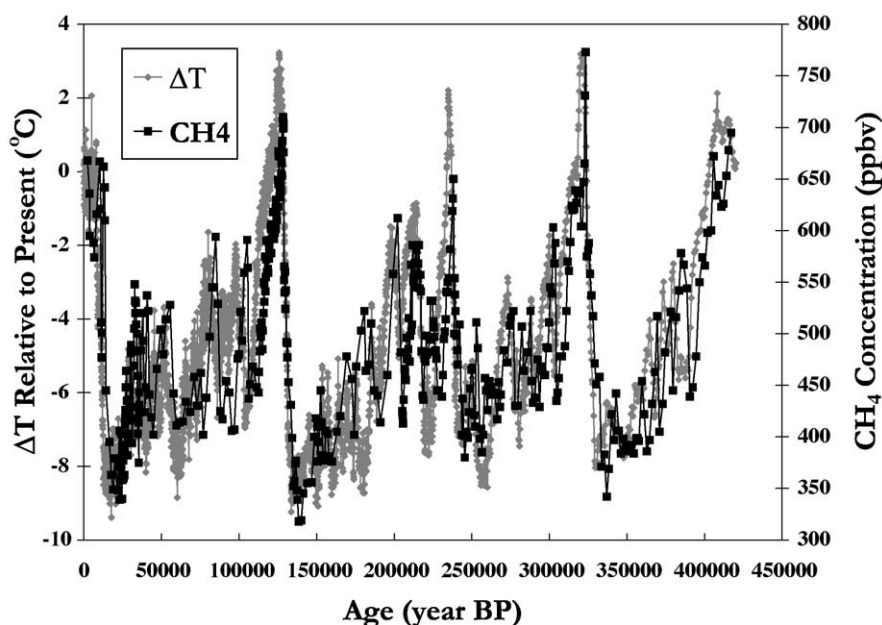

Fig. 1. Vostok ice core records of atmospheric temperature and methane concentration (volume mixing ratio) from 420,000 years BP to present (source: Petit et al., 1999).

atmospheric temperatures? Theories of CH_4 as an instigator of glacial terminations point to the potential destabilization of methane clathrates contained in sediments on continental shelves, as sea level fell due to growing ice sheets. This destabilization could have led to abrupt large-scale releases of CH_4 into the atmosphere, capable of inducing a global temperature increase of up to $1-2\,°C$ over a few decades (Dickens et al., 1997; Thorpe et al., 1996). Such a hypothesis has been shown to be consistent with the geological record of observed perturbations in carbon isotopes (Dickens et al., 1997; Bains et al., 1999), and is not inconsistent with the absence of an observed spike in CH_4 concentrations from ice cores with a 300-year sampling interval[3] (Thorpe et al., 1996). However, results from several ice core studies support the hypothesis that increased emissions from low-latitude, followed by higher latitude, wetlands in response to climate change were responsible for the majority of CH_4 increases (Chappellaz et al., 1993a,b; Thompson et al., 1993; Blunier et al., 1995; Brook et al., 1996). The importance of wetland emissions is emphasized by an observed drop in CH_4 concentrations during the mid-Holocene, when tropical lakes may have dried (Blunier et al., 1995), and interactions between climatic influences and ecosystem dynamics would have reduced wetland emissions (Velichko et al., 1998). A recent modeling study (Dällenbach et al., 2000) also finds large changes in northern latitude sources during warm Dansgaard/Oeschger events during the last glacial period.

An innovative method for extracting temperature data from ice cores has recently shown that CH_4 increases at the end of the Younger Dryas cold period began somewhere between 0 and 30 years following an abrupt temperature increase (Severinghaus et al., 1998). A successive study of four rapid climate transitions over the past 50,000 years reveals that following each transition, temperature increased more rapidly than methane concentrations (Brook et al.,

2000). The fact that the majority of CH_4 increase lagged the warming thus seems to rule out the primarily causal role of CH_4 in glacial–interglacial climate change.

2.1.2. Pre-industrial to present concentrations

Measurements from polar ice cores over the past 1000 years reveal several notable features in global CH_4 concentrations. These include: (1) variations of $10-15$ ppbv about a pre-industrial level of 700 ppb; (2) a pole-to-pole gradient of $30-60$ ppb increasing to around 150 ppb in this century, indicating consistently larger emissions in the Northern Hemisphere, but variable tropical emissions; (3) a continued correlation with temperature during the Little Ice Age around the middle of the millenium; and (4) a significant and monotonic increase beginning between 1750 and 1800 (Etheridge et al., 1998; Chappellaz et al., 1997; Blunier et al., 1993; Nakazawa et al., 1993; Khalil and Rasmussen, 1987; Craig and Chou, 1982). This increase is confirmed by glacial ice cores from the early 1800s (e.g., Dibb et al., 1993), and solar spectra from 1950 (e.g., Rinsland et al., 1985). As seen in Fig. 2, ice core records and observations from ground-based stations show that the global level of methane has more than doubled since pre-industrial times, and continues to increase (Rasmussen and Khalil, 1981; Blake and Rowland, 1988; Steele et al., 1992; Dlugokencky et al., 1994a, 1995, 1998; scientific reviews can be found in IPCC, 1995, 1996).

Numerous modelling studies (e.g., Khalil and Rasmussen, 1985; Thompson, 1992; Crutzen and Bruhl, 1993; Khalil and Rasmussen, 1994b; Osborn and Wigley, 1994; Crutzen, 1995; Brasseur et al., 1998; Lelieveld et al., 1998; Wang et al., 1998) show a decline in the hydroxyl radical sink for CH_4 from pre-industrial times to the present. Modelled OH decreases center around $10-30\%$, depending on the model used, with the range also caused by large uncertainties in past emissions of other trace gases such as CO, NO_x and NMHCs. This range, combined with analyses of past emissions (Khalil and Rasmussen, 1985, 1994a; Lelieveld et al., 1993; Subak, 1994; Stern and Kaufmann, 1996), shows that the majority of the observed increase in methane since pre-industrial times is due to the increase in emissions from anthropogenic sources, as shown in Fig. 3.

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[3] Detailed temporal resolution of changes in temperature and CH_4 concentrations has been complicated by the fact that air trapped in ice and snow continues to be influenced by atmospheric concentrations until sealed into impermeable bubbles. This produces a difference between gas age and ice age that can range from 30 years up to 7000 years, depending on the site's accumulation rate (Bender et al., 1997).
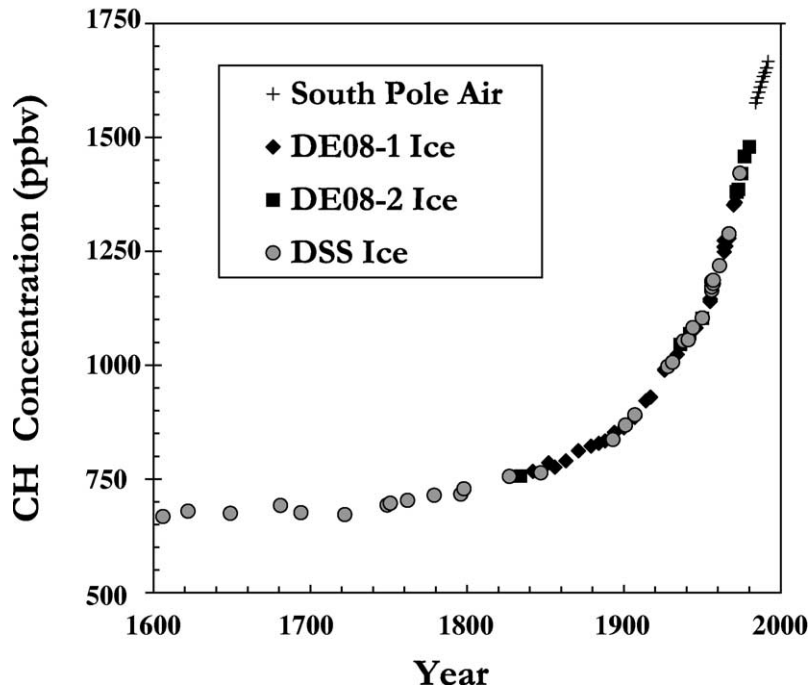
Fig. 2. Ice core and atmospheric records of the increase in atmospheric methane from pre-industrial times to the present (source: Etheridge et al., 1998).

Khalil and Rasmussen (1987, 1994a) find good agreement between increasing population, agricultural emissions, and the observed rise in emissions over the past 200 years, and it is also likely that increasing fossil fuel use has contributed significantly (Etheridge et al., 1992, 1998; Dlugokencky et al., 1994a). However, studies of human populations and activities over the past millenium suggest that discernable anthropo-
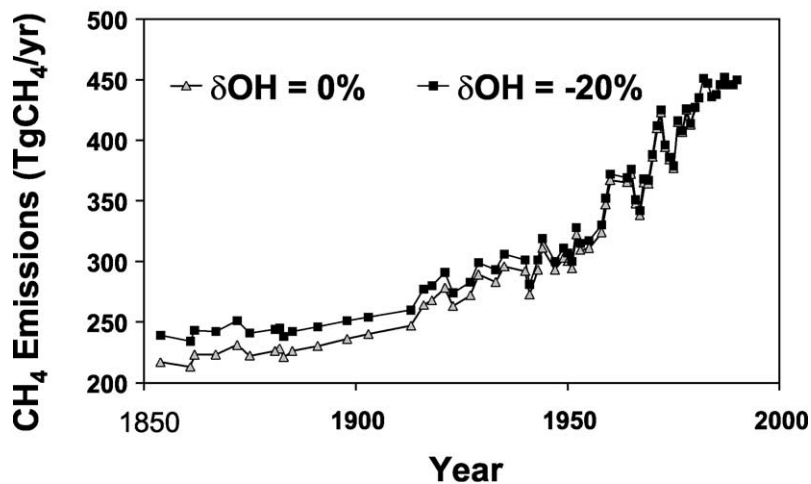

Fig. 3. Increase in methane emissions from pre-industrial times to the present. Based on a top–down analysis by Khalil and Rasmussen (1994a).

genic influence on CH_4 may extend back considerably further than the beginning of the pre-industrial age (Subak, 1994; Blunier et al., 1993).

2.1.3. Decadal changes in methane growth rates

The rate of increase for methane throughout the late 1970s averaged 20 ppbv/year (Blake and Rowland, 1988). However, during the 1980s and 1990s, the rate of methane increase slowed steadily, by an average of −1 ppb/year/year (Fig. 4). Continuous monitoring of methane trends in ambient air from 1979 to 1989 indicated a decreasing trend from 20 to just over 10 ppbv, with an average growth rate of 8.9 ppbv/year from 1984 to 1996 (Dlugokencky et al., 1994a, 1998; Khalil and Rasmussen, 1993, 1994b; Steele et al., 1992). When the data were examined for regional and seasonal effects, it was found that the slowing in the rate of increase is higher between 30 and 90°N (Dlugokencky et al., 1998; Steele et al., 1992), but that the amplitude of the seasonal cycle has exhibited no significant global trends over this time, with typical amplitudes around 30 ppb in the high

Southern latitudes, 60 ppb in the high Northern latitudes, and only a small change in the tropics (Khalil et al., 1993a; Dlugokencky et al., 1994a, 1997).

Following the 1992–1993 anomaly (discussed in the following section), the rate of methane increase continued to fall to a value of 3 ppbv/year in 1996, with a globally-averaged atmospheric concentration of 1730 ppbv and an interhemispherical gradient of 140 ppbv (Dlugokencky et al., 1994a, 1998). If the current decrease in trend had continued, zero growth was expected to occur before 2006, as concentrations slowly stabilized around 1800 ppbv (Etheridge et al., 1998; Dlugokencky et al., 1998).

The long-term slowing in the rate of CH_4 increase over the last few decades must be due to either an increase in methane removal, or declining methane emissions. Observed trends in the seasonal cycle of methane and global OH concentrations inferred from methylchloroform measurements do not support a significant change in OH over the past decades (Dlugokencky et al., 1997; Prinn et al., 1995). Similarly,
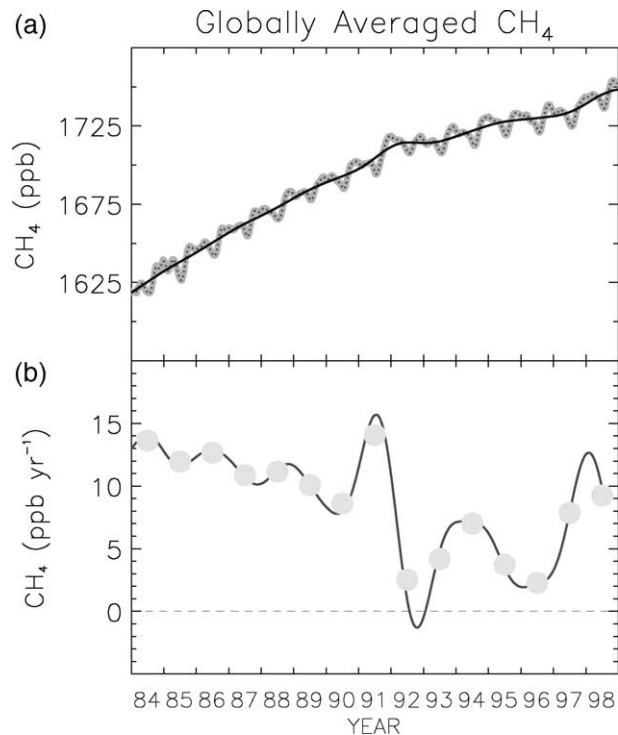

Fig. 4. (a) Observed increase in atmospheric methane concentrations and (b) growth rate (source: Dlugokencky, personal communication).

modelling studies investigating the impact of observed stratospheric ozone depletion and temperature change over the past decade found that, although the resulting increase in OH is compatible with the observed decrease in trend, by themselves these two factors are insufficient to account for the entire decrease in growth rate (Bekki and Law, 1997; Fuglestvedt et al., 1994). Isotopic analysis shows the growth rate of $\delta^{13}C$ over that time to be inconsistent with a substantial increase in the CH_4 sink (Etheridge et al., 1998). It appears, then, that decreasing changes in emissions rather than increasing sink strengths must be responsible for the major part of the observed slowing.

In the absence of any mechanism to explain a long-term decrease in natural sources such as wetlands, the answer appears to lie with anthropogenic emissions. Khalil and Rasmussen (1994a,b) examine the changing relationship between population and agricultural sources, thought to be a major contributor to CH_4 increases from pre-industrial to present times, to show that the growth in agricultural sources may be slowing. Steele et al. (1992) suggest that human sources, particularly those sources which can be reduced quickly, may be the cause of the observed rapid deceleration of the growth rate in the Northern relative to the Southern Hemisphere. Although the exact cause of this long-term decline in the global methane rate is still unresolved, Dlugokencky et al. (1998) suggested that what had been observed was in fact an approach to steady state, as CH_4 net emissions and OH levels were nearly constant over the past decade.

Optimistic projections of stabilizing atmospheric CH_4 levels in the near future have been set back by the latest measurements of CH_4 growth rates that show a jump back up to growth rates of 8–12 ppbv/year in 1997 and 1998 (Fig. 4, Dlugokencky, personal communication). Although net methane sources may have been relatively constant over the past two decades, it is likely that changes in the distribution of methane sources were occurring during that time, with increases in some sources equalling decreases in others (Dlugokencky et al., 1998). What may be occurring now is an increase in emissions from CH_4 source(s) that is larger than can be balanced by concurrent decrease in other source(s). It has been speculated, supported by ^{13}C isotope observations, that the recently observed increase could in fact be the first sign of a biospheric feedback to climate change, as wetland emissions increase in response to the climate warming (Manning, personal communication). Observations of anonymously high temperatures and the lack of an obvious reason for a decrease in the OH sink of methane over this time provide indirect evidence in support of this hypothesis. However, it is equally true that the observed increase in growth rate could also be merely another temporary interannual variation as has been observed before (Dlugokencky, personal communication). Whatever the true cause of this increase, though, it serves at this time to emphasize our limited understanding of the factors that influence methane sources and sinks, and the large uncertainty this introduces in projections of future concentrations.

2.1.4. 1991–1994 drop in growth rates

In 1991, the growth rate of methane increased sharply over a period of 6 months to 1 year following the eruption of Mt. Pinatubo in June. The growth rate then dropped abruptly to very low values and even zero in some locations from 1992 to 1993. Average growth rate in 1992 was only 1.8 ppb/year in the Northern Hemisphere, and 7.7 ppb/year in the Southern Hemisphere (Dlugokencky et al., 1994a,b; 1998), producing a decrease in atmospheric concentrations that has recently been observed in lower stratospheric CH_4 concentrations, which lag 4 years behind the troposphere (Randel et al., 1999). In 1994, global methane growth rates recovered back up to about 8 ppbv/year, before continuing the previously observed long-term decrease (Dlugokencky et al., 1998). A number of theories suggesting reductions in emissions from anthropogenic or natural sources or a slowing in the rate of CH_4 removal have been proposed to explain this short-term anomaly.

Aerosols released by the Pinatubo eruption blocked UV radiation to the troposphere, which may have led to a drop in OH levels and a consequent sharp increase in the methane growth rate. Dlugokencky et al. (1996) show the initial short-lived increased growth rate to be consistent with this theory; however, the causes for the subsequent decrease in the growth rate have not been resolved.

Increases in tropospheric OH have also been proposed as causes for the short-term drop, through mechanisms such as El Niño-induced increases in tropospheric water vapor, an important source of

OH (Khalil and Rasmussen, 1993), or aerosol-induced stratospheric ozone depletion, which would cause an increase in tropospheric UV radiation and a subsequent rise in OH formation (Bekki et al., 1994). Enhanced mixing of stratospheric air, with its lower CH_4 levels, has also been proposed to result from increased stratospheric temperatures following the Pinatubo eruption (Schauffler and Daniel, 1994). Reductions in emissions from tropical biomass burning, Northern Hemisphere fossil fuel sources, or wetlands have also been put forward as possible contributors to the brief but abrupt slowing (Lowe et al., 1994, 1997; Dlugokencky et al., 1994b; Law and Nisbet, 1996; Hogan and Harriss, 1994).

The ability of these theories to match the observed drop have been constrained by a number of observational and modelling studies comparing source strengths, mixing ratios, and isotopic abundances. Comparison of regional mixing ratios with $\delta^{13}C$ isotopic measurements (as discussed in the following section) suggest that changes in atmospheric chemistry or wetland emissions played a minimal role. Instead, observations support a decrease in $\delta^{13}C$-enriched sources such as biomass burning in the Southern Hemisphere or fossil fuel use in the Northern Hemisphere (Lowe et al., 1994, 1997; Gupta et al., 1996). However, using isotopic measurements from six sites, Quay et al. (1999) were unable to distinguish between the possible impacts of changes in biogenic sources, fossil sources, or OH concentration over this time. In addition, it has been shown that a change in the atmospheric CH_4 sink may not be detectable in $\delta^{13}C$ for some time (Tans, 1997; Lassey et al., 1999).

Both modelling studies and recent isotopic analyses therefore conclude that several of these mechanisms may have combined to produce the observed drop in growth rates. Estimated changes in individual sources or sinks, with moderate assumptions of their sensitivity to Pinatubo-induced chemistry and temperature changes and to human activities, are individually insufficient to account for the entire decrease (Bekki and Law, 1997; Lelieveld et al., 1998).

2.2. Sources and sinks

2.2.1. Sources

Methane differs from carbon dioxide in that it is released into the atmosphere by a wide variety of sources, both natural and anthropogenic. Anthropogenic emissions arise from biogenic sources related to agriculture and waste disposal, including enteric fermentation, animal and human wastes, rice paddies, biomass burning, and landfills (Fig. 5). Methane is also emitted by the extraction of fossil fuels such as natural gas, coal, and petroleum. Natural methane emissions arise from wetlands, termites, other wild ruminants, oceans, and hydrates (Fig. 6). Based on recent estimates, current human-related biogenic and fossil fuel-related sources for methane are approximately 275 and 100 $TgCH_4$/year, while total natural sources are around 160 $TgCH_4$/year (IPCC, 1996).

Due to the variety of methane sources, emissions are affected by numerous factors, including energy use, human population distributions, agricultural practices, and climate. As discussed in the previous section, there is strong evidence that methane emis-
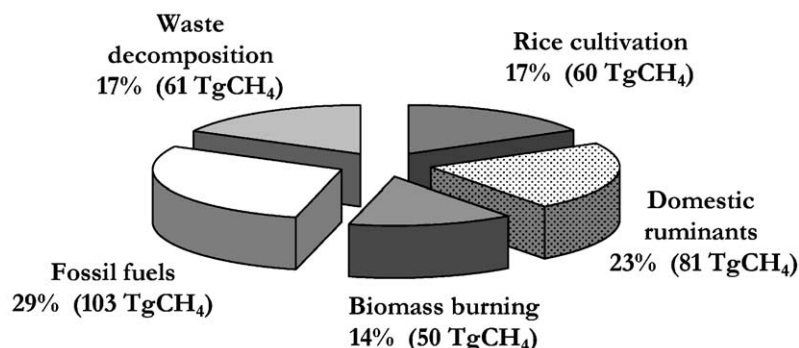

Fig. 5. Contribution of individual sources to total anthropogenic methane emissions (based on Khalil, 2000).
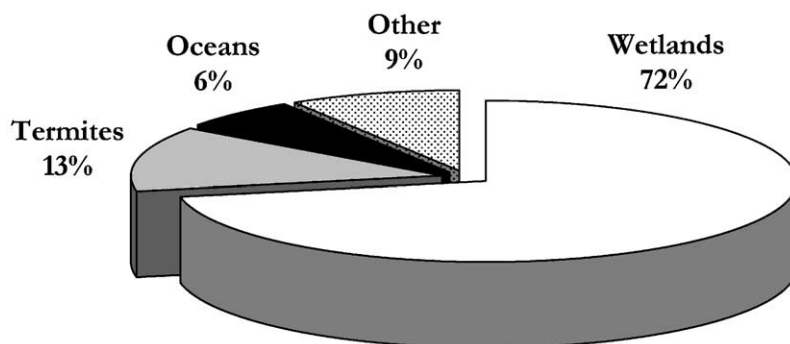
Fig. 6. Contribution of individual sources to total natural methane emissions (based on Khalil, 2000).

sions are changing over time. Here, we briefly describe the main factors influencing the magnitude of emissions from each major source, and how those factors could change under greenhouse gas controls or climate change.

2.2.1.1. Biogenic sources. Methane emissions from biogenic sources result from anaerobic decomposition and reduction of organic material by bacteria — in flooded soils, in landfills or other waste disposal sites, and in the digestive tracts of domestic ruminants such as cattle or sheep, wild ruminants such as buffalo or termites, and even humans. It has been determined that methane production is temperature-dependent, with maximum growth temperature ranging from 37°C to 45°C (Boone, 2000). This temperature dependence is an important factor with implications of future changes for emissions from flooded soils, such as wetlands or rice paddies. It represents an important positive feedback on climate change — as the atmosphere warms, emissions from these sources will increase, raising the concentration of CH_4 in the atmosphere and enhancing the warming.

Emissions from natural wetlands are influenced by a wide range of environmental parameters. These include soil characteristics such as the availability of organic carbon and nutrients (Cao et al., 1996b; Miller et al., 1999; Smith et al., 2000; Yavitt et al., 2000), vegetation type and cover (King et al., 1998; Bellisario et al., 1999; Joabsson et al., 1999; Van der Nat and Middelburg, 2000), and, most importantly, water table depth and soil temperature. A number of studies have demonstrated the high sensitivity of wetland emissions to seasonal and interannual variations in water table and

temperature (e.g., Moosavi and Crill, 1997, 1998; Oberbauer et al., 1998; Van den Pol-Van Dasselaar et al., 1999; Wickland et al., 1999; Nakano et al., 2000; Otter and Scholes, 2000; Worthy et al., 2000; see review in Matthews, 2000). This sensitivity will play a significant role in determining future wetland emissions, as local temperature and precipitation patterns are altered under global climate change. Based on projected temperature increases alone, CH_4 emissions are expected to increase, particularly at high latitudes (Cao et al., 1996b; Matthews, 2000; Worthy et al., 2000). However, the influence of soil moisture and water table level complicates predictions of future wetland emissions. The impact of global climate change on the hydrological cycle at regional levels is highly uncertain; thus, future changes in soil water may result in either increases or decreases in current wetland areas and their emissions (e.g., Wahlen and Reeburgh, 1992; Roulet et al., 1993; Moosavi et al., 1996; Moosavi and Crill, 1997; Van den Pol-Van Dasselaar et al., 1999; Hilbert et al., 2000).

In rice fields, emissions are dependent on the conditions and agricultural practices employed during cultivation, such as climate, soil characteristics, and cultivation practices including water management, fertilizers, other additives, and different varieties of rice plants (e.g., Minami and Neue, 1994; Cao et al., 1995, 1996a; Huang et al., 1997, 1998; Neue et al., 1997; Sass and Fisher, 1997; Khalil et al., 1998; Neue and Roger, 2000). Emissions are also determined by the number of crops per year and the total area under cultivation, which is a function of the demand for rice, and the amount of rice produced per hectare, or 'yield'. Practices such as occasional draining of the

fields, the addition of oxidents or other mineral fertilizers, and selection of low CH_4 cultivars have been found to reduce emissions by approximately 40–55%, 20–70% and up to 60%, respectively (EPA, 1993a,b; Neue et al., 1997; Sigren et al., 1997; Yagi et al., 1997; Butterbachbahl et al., 1997; Cole et al., 1997; Minami, 1997; Sass and Fisher, 1997; Mitra et al., 1999). Alternatively, the addition of organic fertilizers has the potential to increase emissions by over 50% relative to non-organic fertilizers (e.g., Buendia et al., 1997; Denier van der Gon and Neue, 1995; Yagi et al., 1997).

Direct emissions from ruminants, including cattle, sheep, buffalo, goats, and other domestic animals, are affected by diet (Johnson et al., 2000; EPA, 1993a,b; Cole et al., 1997; Harper et al., 1999). Methane emissions are a byproduct of incomplete digestion. In general, higher quality diets will allow animals to digest their food more completely, improving protein uptake while reducing CH_4 emissions. This is particularly true of ruminant diets in developing countries, where improving the relatively poor quality of cattle feed could lead to emission reductions per kg of milk produced of up to 75% (Ward et al., 1993; Crutzen et al., 1986). The addition of production-enhancing supplements to cattle diet has also been suggested as a means to improve digestion and reduce emissions by up to 40% (EPA, 1993a,b; Cole et al., 1997 and references therein). Animal manure is an additional source of methane. If animal waste is allowed to remain in the field, the manure dries quickly and methane emissions are minimal. However, if the waste is pooled and stored, methane emissions can rise by a factor of 10 (Bogner et al., 1995).

Methane is also emitted by the decay of biogenic waste in the anaerobic environments provided by landfills and wastewater pools. Emissions from landfills are affected by numerous environmental and technical variables, including temperature, soil moisture, and CH_4 concentration within the landfill; the amount, organic composition, and age of the waste; and the thickness of the overlying layer. (Bogner and Spokas, 1993; Peer et al., 1993; Czepiel et al., 1996). Emissions from landfills, wastewater, and manure collection lagoons can be reduced by trapping the methane before it is released to the atmosphere, and either flaring it or using it as an energy source. Depending on the capture efficiency, this method can reduce emissions by over 90% (e.g., Bogner et al., 1995; Borjesson and Svensson, 1997).

Biomass burning releases numerous pollutants into the atmosphere. When combustion is complete, most of the emissions consist of carbon dioxide. However, if the fires smolder and combustion is incomplete, large amounts of CH_4 and other higher-order hydrocarbons can be produced. Methane emissions from biomass burning depend on the stage of combustion reached, as well as on the carbon content of the biomass, and the amount of biomass burned (Levine et al., 2000).

2.2.1.2. Non-biogenic sources. The main source of fossil-fuel related methane emissions are the leaks that occur during natural gas processing, transmission, and distribution, since natural gas is over 90% methane (e.g., Beck et al., 1993; EPA, 1993a). The magnitude of this source depends directly on the loss rate, which has been estimated to average between 1% to 2% of natural gas production for developed countries (GRI, 1997; Beck et al., 1993; EPA, 1993b; Barns and Edmonds, 1990). Uncertainty remains substantial, however, as these values are based mainly on the analysis of gas systems in developed countries where transportation is likely to be more tightly controlled than in less developed nations (Kirchgessner, 2000). Regional leakage percentages have been estimated to range from 1% to 15% of total natural gas production, depending on the quality of the pipelines, the extraction process, leakage control, the method used to estimate gas losses, and other factors (e.g., Mitchell, 1993; Matthews, 1994; Bazhin, 1994; Beck et al., 1993).

Methane is also emitted from coal mines, when gas that has been trapped between layers of coal during its formation is released as the coal is mined. Global and even regional estimates of CH_4 emissions from coal and mines depend on many assumptions regarding the type of coal, the depth of the mine, mining practices, the methane content of the coal seam, and whether methane is flared or released (Beck et al., 1993; Kirchgessner, 2000, and references therein).

Lacking viable sources of alternative energy, methane emissions from coal mining and natural gas use may be more easily reduced by altering mining practices and improving gas leakage controls than

by avoiding coal or gas use. If methane emitted from these sources can be trapped, it can be used as an energy source, providing additional benefits.

2.2.2. CH₄ sinks

In contrast to the numerous sources of methane, there are only one major and two minor sinks for tropospheric methane. Reaction with the hydroxyl radical (OH) is responsible for the removal of approximately 500 $TgCH_4$/year (almost 90% of the total sink), making the concentration of OH the most important determinant of the rate at which methane is removed from the atmosphere. The remainder of the CH_4 is removed through dry soil oxidation, 30 $TgCH_4$/year ($\sim$5%), and transport to the stratosphere, estimated at 40 $TgCH_4$/year ($\sim$7%) in IPCC (1996), but recently found to be only 27 $TgCH_4$/year based on data from the Upper Atmosphere Research Satellite (Gettelman et al., 1997).

OH is formed from the photodissociation of tropospheric ozone and water vapor. It is the primary oxidant for most tropospheric pollutants, including carbon monoxide, NO_x species, and organic compounds (e.g, Crutzen, 1995). As the most abundant organic species in the atmosphere, methane plays an influential role in determining the tropospheric oxidizing capacity, initiating an important series of chemical reactions (see discussion in Wuebbles et al., 2000). The oxidation of methane by OH is so effective that almost 90% of methane destruction currently occurs in the troposphere due to these reactions (e.g., IPCC, 1996). The amount of methane removed is constrained by OH levels and the rate constant of the reaction.

With sharp spatial and temporal gradients, and average concentrations of one part per 50 trillion, the actual concentration of OH is difficult to determine, much less its rate of formation or destruction, which depends non-linearly on the other factors mentioned above (e.g., Thompson, 1992; Crutzen, 1995). A few measurements of OH have been made at certain locations using long-path absorption spectroscopy (e.g., Hofzumahaus et al., 1991; Poppe et al., 1995), and confidence in the accuracy of direct measurements is growing (Brune, 1992). However, most estimates of OH concentration have been obtained through measuring the concentration of a tracer molecule such as methylchloroform (CH_3CCl_3) that can be used to infer the OH concentration with a chemical transport model. Using CH_3CCl_3 data from 1978 to 1994 obtained at five ALE/GAGE stations around the globe, modelling studies deduced the average globally integrated concentration of OH to be 9.7×10^5 (Prinn et al., 1995) and 1.07×10^6 molecules/cm³ (Krol et al., 1998). Over the same time period, the studies by Prinn and Krol obtained a change in OH concentration of $0.0 \pm 0.2\%$ /year and $0.46 \pm 0.5\%$ /year, respectively. Based on changes in emissions of CO, NO_x, and NMHCs evaluated with a three-dimensional model of the troposphere, Karlsdottir and Isaksen (2000) estimated that tropospheric OH concentrations have increased by about 7% from 1980 to 1996, or 0.43% /year. According to Karlsdottir and Isaksen (2000), the corresponding decrease in atmospheric lifetime of CH_4 when combined with the observed record would imply overall CH_4 emissions increasing at a rate of 0.67% /year over this period.

OH concentrations are affected not only by direct emissions of methane but by its oxidation products, especially carbon monoxide. Methane has an atmospheric lifetime of 8.9 ± 0.6 years based on CH_3CCl_3 analyses and good knowledge of the loss rate with OH (Prinn et al., 1995). This is lower than the previous estimate of 10 years (WMO, 1991, 1995). Although most trace gases have a turnover time which describes the length of time they are present in the atmosphere, methane is removed by OH on an 'adjustment' time scale that exceeds the atmospheric lifetime by approximately 3 years (e.g., Prather, 1994; IPCC, 1996). The feedback factor that describes this relationship, which is the ratio of the adjustment time of methane to its atmospheric lifetime, varies from 1.2 to 1.7, depending on the model used in the evaluation. Comparisons of 2D and 3D models suggest that the factor does not depend strongly on the background atmospheric OH levels (IPCC, 1996).

This discrepancy between adjustment time and chemical lifetime is due to the fact that the hydroxyl radical is removed not only by interactions with CH_4, but also with its product, CO. CH_4, CO, and OH are involved in a chemical feedback cycle whereby even a small rise in the background level of methane — due to growing emissions — will reduce OH and produce CO. The carbon monoxide produced by CH_4 oxidation will in turn be oxidized by OH,

causing a further drop in OH levels. This extra decrease in OH results in an increase in the lifetime of methane, thereby enhancing the original perturbation. The result is a positive feedback, whereby increasing methane emissions can lead to an overall decrease in the oxidizing capacity of the troposphere, a slowing in the removal of methane, and a consequent build-up of methane concentrations. Thus, an incremental perturbation in CH_4 will return to an equilibrium concentration at a slower rate than expected from the atmospheric lifetime, even though there may be no apparent measurable change in OH.

2.2.3. Isotopic composition

The isotopic composition of atmospheric methane is determined by specific chemical and physical processes that, when understood, can yield valuable information concerning the strength of methane sources and sinks, and their contribution to changes in atmospheric methane. The most commonly measured isotope of atmospheric methane is ^{13}C, which is generally expressed as $\delta^{13}C$, the ratio of ^{13}C to ^{12}C relative to a reference standard. The $\delta^{13}C$ ratios can be used to differentiate between methane from bacterial sources, which are ^{13}C-depleted relative to atmospheric methane, and the ^{13}C-enriched methane emitted from non-bacterial sources such as natural gas and biomass burning, which is generally 20–30‰ greater (Tyler, 1986; Tyler et al., 1987; Cicerone and Oremland, 1988; Quay et al., 1988; Stevens and Engelkemeir, 1988; Conny and Currie, 1996, and references therein).

The global average atmospheric $\delta^{13}C$ ranges from −47.3‰ to −46.2‰ (Stevens and Rust, 1982; Stevens, 1993; Quay et al., 1991, 1999; Tyler et al., 1999). Atmospheric $\delta^{13}C$ is enriched relative to the global composite of methane sources, which is approximately −53‰, based on estimates of source strengths (Quay et al., 1991; Lassey et al., 1999). This $\delta^{13}C$ enrichment is due to the kinetic isotope effect (KIE) during the reaction of CH_4 with OH, which preferentially removes ^{12}C with a fractionation effect at least 1.0054 (Cantrell et al., 1990). Soil oxidation also preferentially removes ^{12}C, as do reactions with Cl in the stratosphere. Fractionation effects for these sinks are thought to be larger than those for OH (King et al., 1989, Tyler et al., 1994, 2000; Brenninkmeijer et al., 1995; Saueressig et

al., 1995; Crowley et al., 1999; Snover and Quay, 2000).

The radioactive isotope ^{14}C also provides valuable information on CH_4 sources. ^{14}C from bomb tests in the 1960s and current ^{14}C emissions from pressurized light-water reactors enables differentiation between modern (enriched) sources of methane and fossil (depleted) sources. Based on ^{14}C measurements, fossil sources are estimated to range from 16 to 25% of total CH_4 emissions (Wahlen et al., 1989; Manning et al., 1990; Quay et al., 1991, 1999). Together with the $\delta^{13}C$ ratio, this information can be used to deduce the contribution of biomass burning — a modern but non-bacterial source — to the current budget. Estimates center around 10–11% (Wahlen et al., 1989; Fung et al., 1991; Quay et al., 1991; Stevens, 1993).

Systematic $\delta^{13}C$ measurements have shown a seasonal cycle that increases with latitude, 180° out of phase with the seasonal change in CH_4 concentrations (Quay et al., 1991, 1999; Lassey et al., 1993; Lowe et al., 1994, 1997; Francey et al., 1999). In the tropical latitudes the cycle may be due to seasonal variations in OH concentrations, whereas at higher latitudes it is thought to be source-driven (Quay et al., 1999). In the Northern Hemisphere, seasonal isotopic variability may be caused by a strong pulse of $\delta^{13}C$-depleted CH_4 emissions together with possible transport from lower latitudes, while seasonal variations in biomass burning are thought to be responsible for the Southern Hemisphere cycle (Quay et al., 1991, 1999; Lassey et al., 1993; Lowe et al., 1994; Tyler, 1999). The role of biomass burning is emphasized in a recent study by Lowe et al. (1999), who find seasonal variations to be divided into three distinct latitude bands, two of whose cycles — tropical and Southern Hemisphere extra-tropical — correlate strongly with seasonal emissions from biomass burning and their transport to higher latitudes.

$\delta^{13}C$ records also indicate long-term trends. Isotopic measurements from ice cores give a pre-industrial atmospheric $\delta^{13}C$ of −49.7‰ (Craig et al., 1988). Together with an estimate of the sink fractionation factor, this implies an increase in the global composite $\delta^{13}C$ of approximately 2‰ since pre-industrial times (Quay et al., 1988; Etheridge et al., 1998). A lower $\delta^{13}C$ suggests that historical emissions were controlled primarily by natural sources. Comparison of present-day atmospheric isotope ratios with

ice core data gives flux estimates for current bacterial emissions around 70% of the total budget (Quay et al., 1991).

Systematic $\delta^{13}C$ measurements taken for over two decades at various sites distributed around the globe indicate that the atmosphere is becoming progres-sively more enriched in ^{13}C, as shown in Fig. 7 (Stevens, 1993; Etheridge et al., 1998; Francey et al., 1999; Quay et al., 1999). Studies suggest that the global increase may be source-driven, caused by increases in $\delta^{13}C$-enriched emissions from biomass burning in the Southern Hemisphere, and a possible
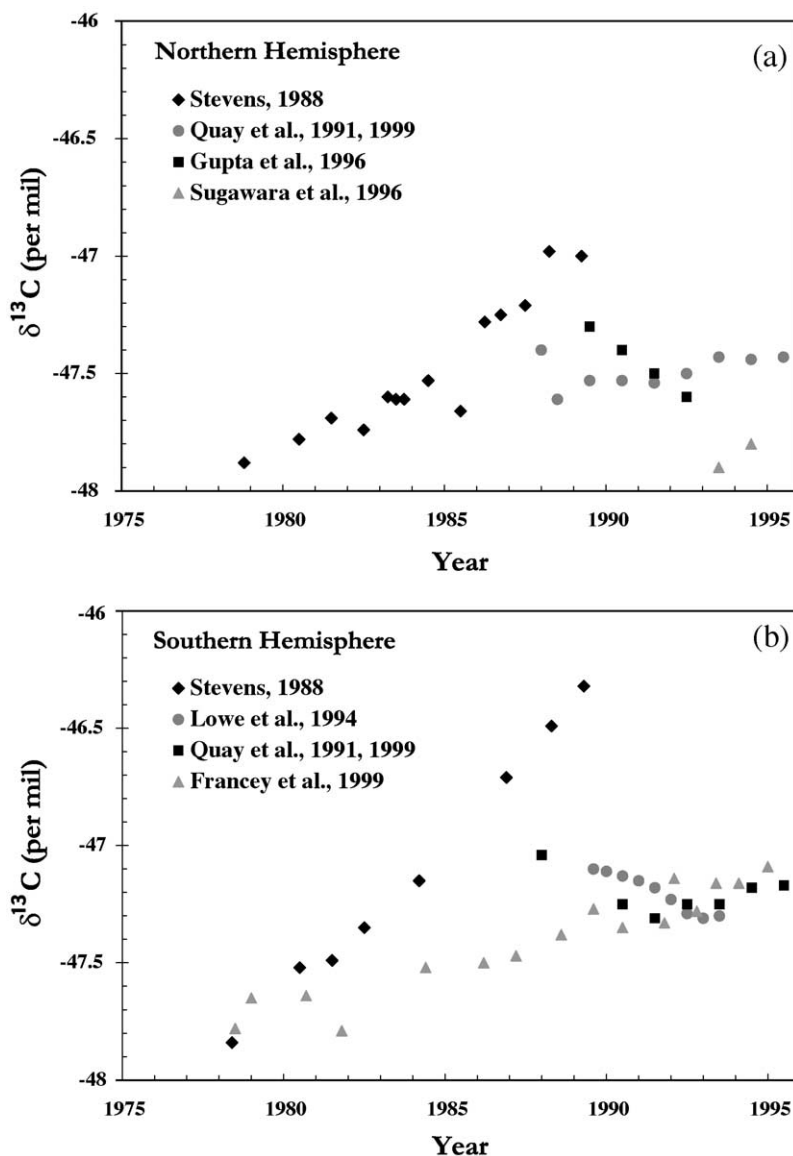

Fig. 7. Measurements of the carbon-13 isotopic composition of atmospheric methane from 1978 to 1995. Hemispherically and annually averaged data was collected at a number of sites in (a) the Northern Hemisphere, and (b) the Southern Hemisphere (Source: Stevens and Wahlen, 2000, and references therein).

decrease in ^{13}C-depleted Northern Hemisphere sources such as wetlands and rice paddies (Stevens, 1993). Recent Southern Hemisphere measurements covering the period from 1978 to 1996 indicate any such redistribution in sources to have been relatively small (Francey et al., 1999). Measurements over the same time period also show steady increases in ^{14}C due to emissions from reactors; however, its growth rate began to slow in 1993 due to a shift away from nuclear power (Quay et al., 1999).

2.2.4. Budget modelling

Uncertainties in sources and sinks of methane are constrained by direct estimates of the individual magnitudes of each source and sink. Source-specific estimates are generally made by multiplying an average emission rate, determined experimentally, by an extrapolant that applies that emission rate over the globe.[4] Although conceptually simple, this bottom–up method contains numerous uncertainties. First, point measurements taken at a limited number of locations and times must be assumed to be representative of global emissions. In the past, this has led to over-estimates of emissions from a number of sources, including rice cultivation (Sass et al., 1999), livestock (Johnson et al., 2000) and possibly wetland emissions (Worthy et al., 2000). It is also primarily responsible for the large ranges in estimates of emissions from other sources such as coal mining (Kirchgessner, 2000), biomass burning (Levine et al., 2000) and waste management (Thorneloe et al., 2000) seen in Table 1. However, as data coverage improves, attention is being re-focused on a second issue, that of resolving temporal and spatial variations in those emissions. Such variations are particularly important for biogenic sources such as wetlands and rice fields whose emissions can vary by several orders of magnitude depending on the location, time of day, season, or year (Matthews, 2000; Shearer and Khalil, 2000). Although these uncertainties continue to produce a range of values in the emission estimates for individual sources (Table 1), the range of estimates for most sources has decreased significantly not only due to the increase in the amount of experimental field data, but

also due to the application of atmospheric CH_4 data and other types of inventory estimates to the methane budget, as described next.

The methane budget is constrained by the spatial and temporal changes in atmospheric CH_4 mixing ratios and isotopes discussed previously in Section 2.2.3. Isotopic composition of atmospheric methane is a particularly valuable source of information, as it reflects the relative strength of bacterial vs. non-bacterial and modern vs. fossil sources of CH_4, as well as differentiating between various formation pathways (Cicerone and Oremland, 1988; Conny and Currie, 1996; Whiticar, 2000).

Mass-balance approaches use spatial and regional variations in isotopic composition as well as hemispheric and global averages as input to box models. Atmospheric observations are then compared with the flux-weighted composition of total emissions plus the fractionation effects of sinks, taking into account the effects of atmospheric transport. In this way, the magnitudes of individual sources as well as entire budgets have been estimated (e.g., Khalil and Rasmussen, 1983; Stevens and Engelkemeir, 1988; Cicerone and Oremland, 1988; Tyler, 1989; Lassey et al., 1993, 1999; Lowe et al., 1994, 1997; Quay et al., 1999).

Two- and three-dimensional chemical transport models are also used to perform calculations that match modelled emissions, concentrations, and carbon isotopes with observed abundances. In this way, uncertainties in sources and sinks can be reduced, and the relationships between methane emissions, atmospheric chemistry, and the climate system better quantified. A number of studies (Fung et al., 1991; Hein et al., 1997; Gupta et al., 1996) have used this approach, while others have developed new inversion methods (Brown, 1995; Kandlikar and McRae, 1995; Kandlikar, 1997; Houweling et al., 1999). These analyses, combined with multi-box and source-specific studies, produce comprehensive budgets of CH_4 sources and sinks such as the composite estimate shown in Table 1 (Khalil, 2000).

2.3. Projections of future concentrations

Atmospheric methane concentrations have doubled since pre-industrial times. Increases in methane emissions from human sources such as rice cultivation, domestic ruminants, and increased fossil fuel use are

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[4] See Khalil and Shearer (2000) for a full discussion of the methods and constraints of bottom–up emissions estimates.

Table 1

(a) Estimated natural and anthropogenic sources of methane (TgCH$_4$/year)

Source	Emissions (TgCH$_4$/year)	Range of estimate	References
Wetlands	100	92–232	Fung et al., 1991; Bartlett and Harriss, 1993; Cao et al., 1996b; Hein et al., 1997; Matthews, 2000
Termites	20	2–22	Sanderson, 1996; Sugimoto et al., 1998
Oceans	4	0.2–2.0	Bates et al., 1996; Holmes et al., 2000
Marine sediments	5	0.4–12.2	Judd, 2000
Geological sources	14	12–36	Judd, 2000, after Lacroix, 1993
Wild fires	2		Levine et al., 2000
Total Natural	145		
Ruminants	81	65–100	Crutzen et al., 1986; Johnson et al., 2000; IPCC, 1995
Rice cultivation	60	25–90	Cao et al., 1996a; Neue and Sass, 1998 and Yagi and Minami, 1998 as cited in Sass et al., 1999; Shearer and Khalil, 2000
Total Agricultural	141		
Natural gas	30	25–50	Cicerone and Oremland, 1988; Fung et al., 1991; Kirchgessner, 2000
Coal mining	46	15–64	Cicerone and Oremland, 1988; Boyer et al., 1990 as cited in Kirchgessner, 2000; Fung et al., 1991; Kirchgessner et al., 1993
Other fossil fuels	30	6–60	Khalil et al., 1993b; Piccot et al., 1996
Biomass burning	50	27–80	Levine et al., 2000; based on estimates by Seiler and Crutzen, 1980; Crutzen and Andreae, 1990; and Hao and Ward, 1993;
Waste disposal	61	40–100	Johnson et al., 2000; Thorneloe et al., 2000
Total Non-Agricultural Anthropogenic	217		
TOTAL	503	410–660	

(b) Estimated sinks of methane in TgCH$_4$/year (based on IPCC, 1995)

Sink	Uptake (TgCH$_4$/year)	Range of estimate
Tropospheric OH	445	360–530
Removal to stratosphere	40	32–48
Soil uptake	30	15–45
TOTAL	515	430–600

'Best guess' estimates are those given by the methane budget in Khalil (2000). Range of estimates is based on the most recent studies as cited here.

thought to be the primary contributors to the rapid rise that has been observed through records preserved in ice cores, solar spectra, and direct atmospheric measurements.

It is likely that future methane concentrations, however, will be strongly affected by changes in both sources and sinks of atmospheric methane. Projections of future methane concentrations therefore require modeling changes in both emission and removal rates of atmospheric methane, as well as considering feedbacks from climate change and emissions of other trace gases that affect both sources and sinks of CH$_4$.

2.3.1. Projections of CH₄ sources

In the past, increasing emissions have correlated well with population (e.g., Khalil and Rasmussen, 1993). However, recent variations in the methane growth rate have challenged our understanding of the many factors that affect the sources of atmospheric methane. This abundance of factors complicates the resolution of past emissions and makes predictions of future CH_4 emissions difficult.

Although methane emissions have climbed rapidly over the past four decades, the relative importance of agricultural sources may be declining, with non-agricultural sources related to fossil fuel use and waste disposal on the increase (Fig. 8). These sources are directly influenced by human activities and energy demand in ways that may not be easily predictable. In addition, they lack a well-resolved history of past emission trends to extrapolate into the future, a fact that greatly complicates methane emission prediction.

The magnitude of methane sources depends on numerous factors including human population, energy demand, crop yield, agricultural practices, land use area, temperature, precipitation, and other possible natural or anthropogenic influences not yet resolved, but that are expected to change significantly in the future. Methane concentrations are projected to continue to rise well into the next century, as shown by the "business as usual" IS92a emission scenario (Fig. 9). The "low emissions" scenario, IS92c, also shows a continued increase in methane concentration for a number of decades. However, several of the new SRES (IPCC Special Report on Emissions Scenarios) emissions scenarios for CH_4 that have been developed for the current ongoing IPCC assessment show reduced increases in emissions compared to the earlier scenarios (Fig. 10).

The majority of a projected increase in CH_4 emissions is expected to be from human sources related to agriculture, waste, or energy. Projections of future emissions are additionally uncertain because of the high level of ignorance concerning potential biospheric feedbacks to climate change. Observations of the response of biogenic sources to seasonal changes in temperature have shown that emissions from wetlands, rice paddies, and other ecosystems may increase in response to increases in global mean temperature, producing a positive feedback to climate warming (e.g., Hameed and Cess, 1983; Lashof, 1989; Roulet et al., 1992; Neue and Roger, 2000; Boone, 2000; Bartlett and Harriss, 1993; Slanina et al., 1994; Panikov, 1999). With high levels of warming, methane stored in methane hydrates and clathrates could
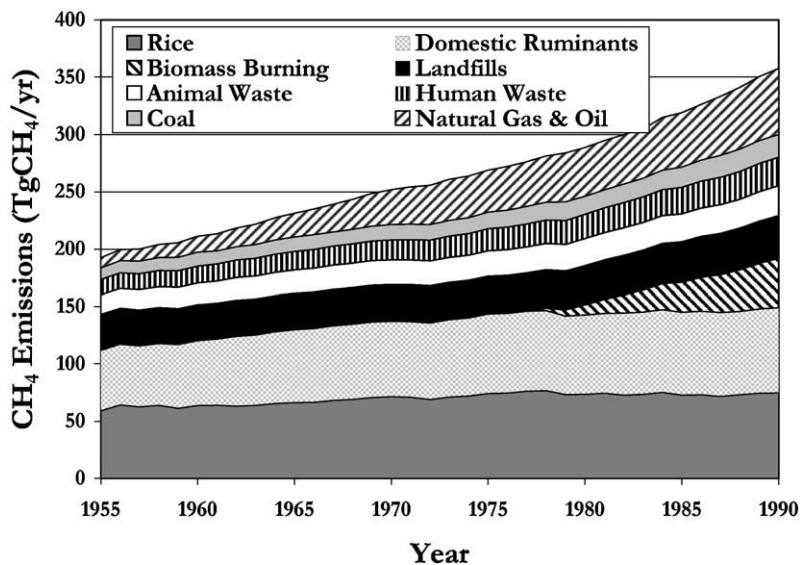

Fig. 8. Evolution of anthropogenic methane emissions, 1955–1990 (source: Hayhoe, 1997).
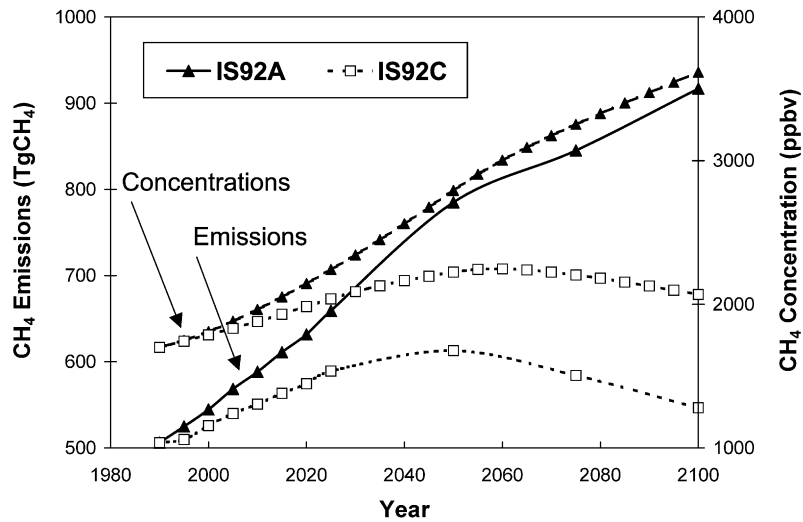
Fig. 9. Projected emissions and concentrations from IS92 scenarios A and C (source: IPCC, 1996; IPCC DDC CD-ROM).

also become destabilized, releasing large amounts of methane into the atmosphere (Nisbet, 1990a,b; Mac-Donald, 1990; Harvey and Huang, 1995), and increasing climate forcing.

Although methane concentrations are projected to continue to increase, it must be noted that recent decreases in the growth rate of methane have occurred without any controls on human emissions. If the declining trends in the growth rate over the past few decades had continued, rather than increasing as they have in the past 2 years, it is almost certain that a CH_4 reduction strategy involving reductions of more than 5% of the anthropogenic source could have stabilized or even lowered atmospheric concentrations of meth-
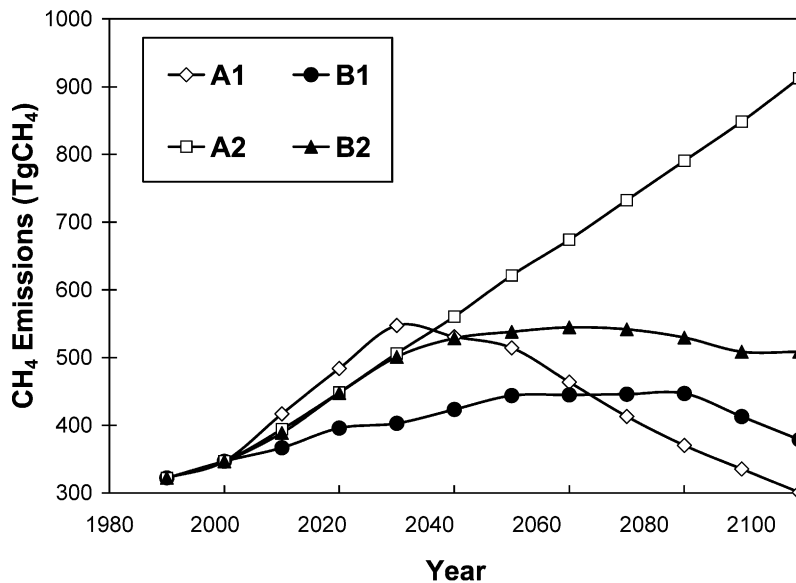

Fig. 10. New SRES emission projections for CH_4 (source: IPCC DDC CD-ROM).

ane (IPCC, 1996; Dlugokencky et al., 1998; Etheridge et al., 1998). However, as shown by Kheshgi et al. (1999), the trend in the concentration of methane is greatly dependent on any changes in the emissions of CO and NO_x.

2.3.2. Projections of CH_4 sinks

Concentrations of OH, the main sink of atmospheric methane, are already closely linked with CH_4 concentrations through the CH_4–CO–OH cycle. Most modelling studies conclude that OH concentrations have decreased by 10–30% since pre-industrial times, mainly due to increasing levels of CH_4 and CO in the atmosphere (e.g., Thompson, 1992; Wang and Jacob, 1998). At the present time, OH concentration appears to be relatively steady or perhaps increasing, with the effects of increasing CH_4 and CO balanced by increases in tropospheric O_3 concentrations and in emissions of NO_x and NMHCs (Prinn et al., 1995; Krol et al., 1998; Karlsdottir and Isaksen, 2000). Although OH has no significant radiative effect, it is the primary oxidizing agent of the troposphere, responsible for the removal of methane, carbon monoxide, and NMHCs as well as numerous other pollutants and long-lived greenhouse gases. Changes in its concentration will therefore impact the abundances of many trace species, affecting local air pollution in addition to global chemistry and radiative properties of the atmosphere.

Projections of OH concentrations are highly uncertain — even more so than past changes. Future changes in atmospheric composition induced by trace gas emissions and climate change are expected to have major impacts on the rate of OH production and destruction. A number of modelling studies predict up to a 25% decrease in OH concentrations by 2050 (e.g., Thompson and Cicerone, 1986; Thompson et al., 1990; Pinto and Khalil, 1991; Lu and Khalil, 1991; Osborn and Wigley, 1994; Brasseur et al., 1998; Lelieveld et al., 1998; Wang and Jacob, 1998). This small range belies the major changes in OH production and destruction that are projected to occur. These changes balance each other out to a certain extent, particularly in the studies that predict little or no change in net OH levels.

OH loss rates are projected to increase in the future due to rising anthropogenic emissions of CH_4, CO, NMHCs, and other gases that are oxidized by OH.

However, there are a number of additional factors that may balance net OH concentrations by increasing OH production.

OH is formed when O_3 is photo-dissociated into $O(^1D)$, which in turn combines with water vapor to form two OH radicals, as shown by the following equations:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{1}$$

$$O(^1D) + H_2O \rightarrow OH + OH \tag{2}$$

Emissions of NO_x, an important component of local air pollution in urban areas, result in O_3 formation that in turn increases OH production (Eq. (1)). Increasing NO_x emissions have been modeled to result in an increase in global OH, and hence in the global methane sink (Fuglestvedt et al., 2000). A reduction in stratospheric ozone, such as that seen in recent decades, increases the flux of ultraviolet radiation reaching the troposphere, also promoting OH formation (Tang et al., 1998). As climate warms, the relationship between temperature and water vapor concentration may cause tropospheric water vapor levels to rise. This will also increase OH production (Eq. (2)). On the other hand, increases in tropospheric water vapor could also increase global mean cloud cover, which would decrease the flux of photons to the troposphere and decrease OH formation rates. Temperature increases also have an additional impact on temperature-dependent reaction coefficients, affecting many atmospheric reaction rates.

Although global average OH levels determine the average lifetime of CH_4, several studies emphasize the importance of tropical OH levels in determining future changes in OH (Thompson et al., 1989; Crutzen and Zimmermann, 1991; Lelieveld et al., 1998). OH levels are highest in the tropics, with abundant water vapor and UV radiation ensuring high production rates. CH_4 emissions from important sources such as rice cultivation, biomass burning, and domestic ruminants are also highest in the tropics. However, the tropics are also the region where the greatest changes in land use and industrialization are expected to occur in the future. What happens in this area will to a large part determine the future of OH concentrations in the atmosphere.

The soil sink for methane, although substantially smaller than the OH sink, is also expected to change in the future. Methane oxidation in soil is sensitive to temperature and soil water content (Mancinelli, 1995; King, 1997), both of which may be altered by climate change. Perhaps more importantly, arable land has a much smaller CH_4 uptake rate than untreated soils, particularly when treated with certain fertilizers (e.g., Boeckx et al., 1997; Mosier et al., 1997b, Powlson et al., 1997). Land use change, as forests and grasslands are converted to agriculture, has already decreased the soil sink, and is likely to continue to do so in the future (King, 1997; Mosier et al., 1997a). Even when converted back to its natural state, previously cultivated land continue to have a lower oxidation rate than untouched areas (e.g., Dobbie and Smith, 1996; Hudgens and Yavitt, 1997; Prieme et al., 1997). This apparent irreversibility of human impacts on CH_4 oxidation rates has important implications for the future of land management strategies, as growing populations continue to exert pressure on natural ecosystems.

3. Impact of CH_4 on tropospheric and stratospheric chemistry

3.1. Methane and tropospheric chemistry

As discussed previously, methane oxidation is one of the major reaction pathways affecting atmospheric concentrations of hydroxyl on a global scale. Depending on nitric oxide levels, methane oxidation can be either a production or destruction process for odd-hydrogen ($OH+HO_2$). Thus, different chemically coherent regions (Thompson et al., 1989) can be distinguished on the basis of concentrations of nitrogen oxides. Polluted (high NO_x) environments where odd hydrogen is produced include the temperate zone of the Northern Hemisphere and planetary boundary layer of the tropics during the dry season. Unpolluted (low NO_x) environments where odd hydrogen is destroyed include marine areas, the free troposphere over the tropics, and most of the Southern Hemisphere (e.g., Fishman et al., 1979; Crutzen, 1988; Cicerone and Oremland, 1988; WMO, 1991, 1995). Under warm, humid conditions, nitrogen oxide levels must be substantially higher to produce odd hydrogen,

conditions that generally apply to the boundary layer. Most current modeling studies suggest that an increase in methane will decrease hydroxyl and increase ozone throughout the remainder of the troposphere.

The methane oxidation cycle is an important source of carbon monoxide, accounting for roughly a quarter of the carbon monoxide in the troposphere. Carbon monoxide concentrations are a great deal more variable than methane, due to its relatively short atmospheric lifetime (approximately 1–3 months) and because of the variety of natural and anthropogenic sources that contribute to its budget. These sources include fossil fuel combustion, biomass burning, and the oxidation of natural hydrocarbons emitted by vegetation (e.g., isoprene). As in the case of methane, the carbon monoxide oxidation cycle also depends on the levels of nitric oxide present in the atmosphere.

Based on the reaction sequences for methane, formaldehyde, and carbon monoxide in polluted as well as unpolluted environments, the effect of the complete oxidation of 1 mol of methane is an increase from 0.4 to 0.5 mol of odd hydrogen in the high NO_x case and a decrease from −3.5 to −3.9 mol of odd hydrogen in the low NO_x case. Correspondingly, the change in ozone for complete oxidation of methane is an increase of +3.6 to 3.8 mol for the high NO_x case and a decrease of −1.7 to −1.8 mol for the low NO_x case. According to our calculations (Wuebbles et al., 2000), the catalytic subcycle involving the reaction of methylperoxyl (CH_3O_2) with hydroperoxyl (HO_2) and the reaction of methyl peroxide (CH_3O_2H) with OH has a sizeable impact on the amount of odd hydrogen loss in the low NO_x case. Crutzen (1988) included this cycle in his results, whereas lower effects determined by Cicerone and Oremland (1988) did not include its effect. Our analyses of the resulting changes in odd-hydrogen and ozone are substantially in agreement with Crutzen (1988) for both cases. The resultant destruction of odd hydrogen depends on the hydroxyl concentration, the methyl peroxide chemical reaction pathways, and the heterogeneous removal rates of important intermediate species.

Formaldehyde is an important intermediate in the removal processes of methane and other hydrocarbons as well as being important in the general chemical reactivity of the troposphere. Regardless of NO_x levels, methane oxidation is responsible for the formation of

much of the formaldehyde in the atmosphere. Based on the estimate of Lowe and Schmidt (1983), the formaldehyde production rate is on the order of 10^{14} g/year. The other major photochemical precursors of formaldehyde consist of nonmethane hydrocarbons and higher aldehydes. The non-methane hydrocarbons are emitted from natural and anthropogenic sources while the higher aldehydes are produced by in situ photochemistry. There are appreciable anthropogenic sources of formaldehyde as well (e.g., automobile exhaust).

In order to analyze the photochemical mechanisms that produce formaldehyde, we must distinguish between different regions on the basis of NO_x levels. In the methane oxidation mechanism under low NO_x conditions, methyl peroxide reacts with OH to produce formaldehyde. Since methyl peroxide has a long lifetime against photolysis, heterogeneous processes (which occur on aerosols) can serve as a loss mechanism for this species in unpolluted environments. This implies that formaldehyde production is controlled by aerosol concentrations in remote regions. However, in polluted environments, formaldehyde formation does not involve methyl peroxide. In this case, it would be regulated by nitric oxide concentrations because methylperoxyl is reduced to methoxyl. Methoxyl then reacts with oxygen to produce formaldehyde.

Once it is generated, formaldehyde is quickly destroyed under direct insolation. During the daytime, photolysis is the dominant loss process for formaldehyde in the remote troposphere, while in polluted atmospheres, reactions with hydroxyl and hydroperoxyl are comparable to photolytic degradation. At night, the only appreciable formaldehyde consumption is by reaction with nitrate radical (NO_3) but this is slow in comparison to the daytime reactions with hydroxyl and hydroperoxyl.

Approximately 10% of the ozone in the atmosphere is located in the troposphere. The downward transport of ozone from the stratosphere traditionally was thought to be the major source of tropospheric ozone (Crutzen, 1988 and references therein). It is now generally accepted that the net tropospheric photochemical production of ozone is of similar magnitude to the downward transport source (e.g., Fishman et al., 1979; Fishman, 1985; WMO, 1985, 1995; Isaksen, 1988; Penkett, 1988; Hough and Derwent, 1990).

Nitrogen dioxide photolysis is by far the primary photochemical mechanism for producing ozone in the troposphere. This implies that the generation rate is roughly proportional to the concentration of nitric oxide. High concentrations of NO_x over the continental boundary layer signify that this region is likely a net source of ozone. Increases in NO_x emissions may lead to further ozone increases, especially in the tropics. However, the magnitude of odd oxygen ($O+O(^1D)+O_3$) production is ultimately limited by the supply of CO, CH_4, and NMHCs. The oxidation of 1 mol of CO can form 1 mol of ozone. In contrast, the complete oxidation of a mole of methane can produce 3–4 mol of ozone. Because there is insufficient NO_x present in the background troposphere, it is estimated that only about 10% of the potential tropospheric ozone production is being realized.

3.2. Methane and stratospheric chemistry

Although ~90% of total emissions of methane are consumed by reaction with tropospheric hydroxyl and about 5% by soil uptake (IPCC, 1995), the remaining 5% of methane flux, on average about 27 $TgCH_4$/year (Gettelman et al., 1997), enters the stratosphere.

In the stratosphere and higher layers of the atmosphere, the reaction with OH continues to be the dominant sink for CH_4, but reactions with chlorine atoms and excited oxygen atoms are also important. Reactions with chlorine atoms account for about 9% of the methane loss in these regions (Brenninkmeijer et al., 1995). Measurements also suggest that the increased oxidation of methane resulting from increasing concentrations of chlorine in the stratosphere has led to enhanced production of stratospheric OH (e.g., Burnett and Burnett, 1995).

In order to put the role of methane in stratospheric chemistry into context, it is useful to first discuss the importance of ozone and the changes occurring in its distribution. Changes in the distribution and amount of ozone in the global troposphere and stratosphere have received much attention over the past few decades. Much of the concern about ozone has centered on the importance of ozone as an absorber of ultraviolet radiation, as its concentrations determine the amount of ultraviolet radiation reaching the Earth's surface. Ozone is also a greenhouse gas and can influence climate.

Approximately 90% of the ozone in the atmosphere is contained in the stratosphere. In the stratosphere, the production of ozone begins with the photodissociation of oxygen (O_2) at ultraviolet wavelengths less than 242 nm. This reaction produces two ground-state oxygen atoms that can react with oxygen to produce ozone. Since an oxygen atom is essentially the same as having an ozone molecule, it is common to refer to the sum of the concentrations of ozone and oxygen atoms (both ground state and excited state) as odd-oxygen. The primary destruction of odd-oxygen in the stratosphere comes from catalytic mechanisms involving various free radical species. Nitrogen oxides, chlorine oxides, and hydrogen oxides participate in catalytic reactions that destroy odd-oxygen.

Chlorine and bromine catalytic mechanisms are particularly efficient in destroying ozone. These mechanisms have been the subject of much study due to their effects on concentrations of stratospheric ozone over recent decades, particularly since levels of reactive chlorine in the stratosphere have been growing rapidly over this time as a result of emissions of trichlorofluoromethane ($CFCl_3$), difluorodichloromethane (CF_2Cl_2), bromine-containing halons, and other halocarbons. The chlorine- and bromine-catalytic cycles can turn over thousands of times before the catalyst is converted to a less reactive form. Because of this cycling, relatively small concentrations of reactive chlorine or bromine can have a significant impact on the amount and distribution of ozone in the stratosphere. The total amount of chlorine in the current stratosphere is ~ 3 ppbv, much of which is in the form of less reactive compounds like hydrochloric acid (HCl).

Methane plays an important role in the chlorine chemistry of the stratosphere, serving both as a source and a sink in key reactions affecting reactive chlorine. The direct reaction of methane with a chlorine atom is the primary source of hydrochloric acid, the main chlorine reservoir species. However, OH produced through the oxidation of methane in the stratosphere can react with the hydrochloric acid to return the chlorine atom, thus reinitiating the chlorine catalytic mechanism. Although the most important effect of increasing methane is the increasing conversion of reactive chlorine to HCl, there is also a smaller increase in the conversion rate of reactive chlorine to HCl. Thus, increasing chlorine tends to slow down the effects of chlorine on ozone. Conversely, controls on methane could exacerbate the effects of chlorine on ozone by slowing down the conversion to HCl. It should be noted that a similar mechanism is not important for bromine because of the slow reactivity of Br with CH_4.

In addition to being involved in the reaction taking reactive chlorine to the less reactive HCl, methane has several other effects on stratospheric ozone. Hydrogen oxides produced from the dissociation of methane can react catalytically with ozone, particularly in the upper stratosphere. In the lower stratosphere, the primary effect of these hydrogen oxides is to react with nitrogen oxides and reactive chlorine, reducing the effectiveness of associated ozone destruction catalytic cycles. The hydrogen oxides at these altitudes can also react catalytically to destroy ozone.

3.3. Model-calculated effects on ozone

Changing atmospheric concentrations of a number of compounds, including methane, are currently affecting the distribution of ozone in the troposphere and stratosphere. A number of research studies have used numerical models to examine the combined effects on ozone from the increases in concentrations of methane and the other gases described in the previous section (e.g., Wuebbles et al., 1983; Stordal and Isaksen, 1987; WMO, 1985, 1989, 1995, 1999). When combined with the effects of other trace gas emissions, it is difficult to evaluate the specific contribution of methane to the observed and projected ozone trends. For this reason, it is useful to examine studies that have only considered the effects of increasing methane on ozone.

Numerical models of atmospheric chemical and physical processes generally find that increasing methane concentrations result in a net ozone production in the troposphere and lower stratosphere and net ozone destruction in the upper stratosphere (Owens et al., 1982, 1985; WMO, 1985, 1991, 1995; Isaksen and Stordal, 1986). The net effect from these calculations has been that methane by itself causes a net increase in ozone. For a doubling of the methane concentration (early papers studied CH_4 increases from 1.6 to 3.2 ppmv, while recent analyses assume a globally-averaged change from 1.7 to 3.4 ppmv), published effects on the calculated change in total ozone range from +0.3% (Prather in WMO, 1985) to +4.3% (Owens et al., 1985). With radiative feedback effects included (allowing temperature changes in the

stratosphere), the published model results tend to be in the upper end of this range (Owens et al., 1985; WMO, 1985; Isaksen and Stordal, 1986).

The effects on tropospheric and stratospheric ozone for a doubling of the methane surface concentrations from the UIUC zonally-averaged model (Wuebbles et al., 1998; Rahmes et al., 1998) are given in Fig. 11 (change in total ozone as a function of latitude and season) and Fig. 12 (change in ozone with altitude and latitude for July). This two-dimensional model analysis, which includes radiative feedbacks, gives a 3.4% increase in globally-averaged total ozone from a doubling of methane surface concentrations.

Calculations of the effect of methane increases on stratospheric ozone give a small percentage increase in the lower stratosphere, a larger increase near 40 km altitude, and a decrease in ozone above 45 km. As mentioned earlier, the hydrogen oxides produced by methane oxidation affect the efficiency of the nitrogen

oxide and chlorine oxide catalytic ozone destruction mechanisms. However, the effect of methane in the lower stratosphere will depend on the efficiency of the nitrogen oxide catalytic cycle; if the amount of reactive odd nitrogen is reduced, then the additional hydrogen oxides from methane could destroy ozone in this region. Additional heterogeneous reactions involving N_2O_5, $BrONO_2$ and $ClONO_2$ reduce the efficiency of the nitrogen oxide catalytic cycle, and increased HO_x from increases in atmospheric methane has a larger effect on the lower stratosphere as compared to previous calculations (Wuebbles et al., 2000). In the upper stratosphere, the additional hydrogen oxides react catalytically with ozone, causing models to find a decrease in ozone at these altitudes.

The version of the model used here includes convective mixing processes in the troposphere and also includes a number of non-methane hydrocarbons. The change in column ozone resulting from a calculation
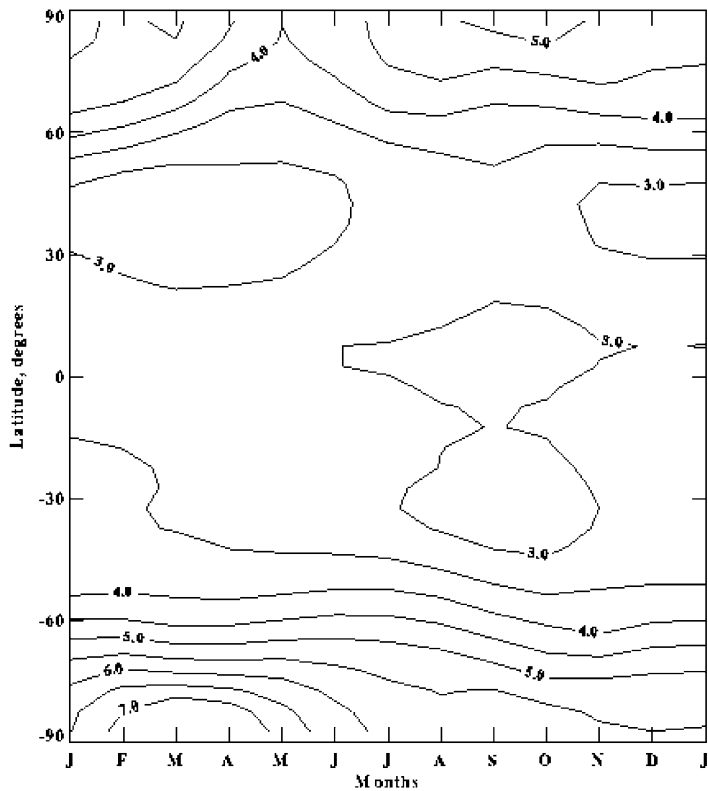

Fig. 11. Calculated percentage change of total ozone for a doubling in the concentration of atmospheric methane from 1.7 to 3.4 ppmv. Based on the UIUC two-dimensional chemical-transport model.
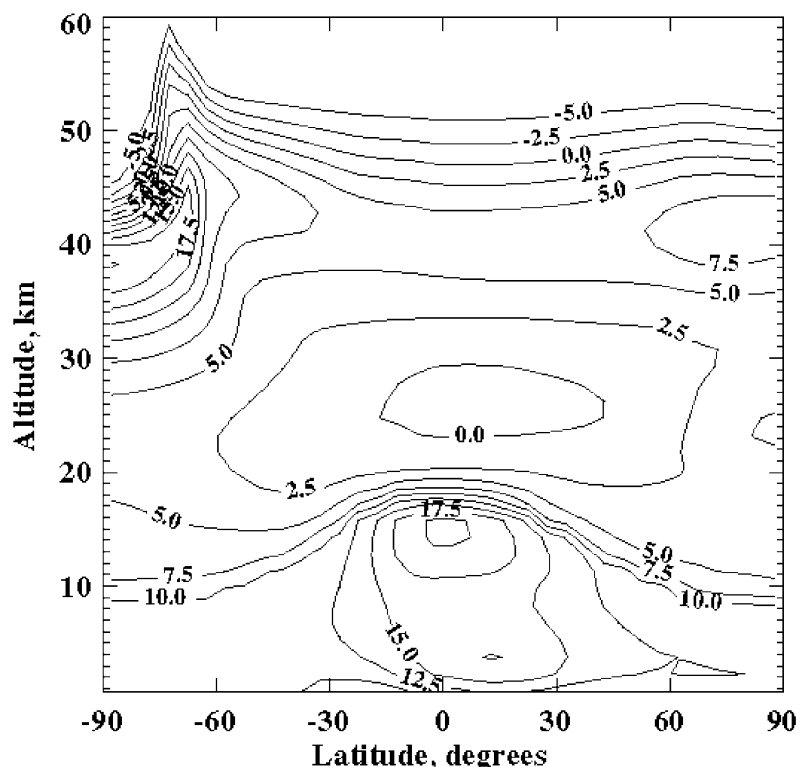
Fig. 12. Calculated percentage change of local ozone in July for a doubling in the concentration of atmospheric methane as in Fig. 10.

for doubling CH_4 without NMHCs compared to a simulation with NMHCs is an increased response ranging from 3% to 8% larger than that when the effect of NMHCs is included. The effect on the Southern Hemisphere is negligible, as there are no significant non-NMHC emissions from this region. Thus, the model response is damped for a doubling of methane surface concentration when non-methane hydrocarbons are included in the model. This damping results from the additional sources of reactive oxides available in the lower troposphere from hydrocarbons sources. The current model gives a feedback factor, defined as the percentage change in OH for a 1% change in CH_4 of 0.32%, which is well within the range of those calculated in WMO (1995).

3.4. Upper atmospheric water vapor

The spatial distribution of water vapor in the troposphere is primarily determined by evaporation, condensation and transport processes. Very little of the tropospheric water vapor penetrates into the stratosphere. The mechanisms limiting the transport of tropospheric water vapor into the stratosphere are still not well understood. Concentrations of water vapor increase with altitude in the stratosphere, from 3 ppmv in the lower stratosphere to about 6 ppmv in the upper stratosphere. This increase in concentration with altitude occurs as a result of the oxidation of methane.

Methane oxidation reactions produce roughly two mol of water vapor for each mole of methane that is destroyed. Stratospheric water vapor concentrations should increase as concentrations of methane increase. Since methane concentrations have increased from about 0.7 ppmv in the pre-industrial atmosphere to the current concentration of 1.7 ppmv, this implies that upper stratospheric water vapor concentrations have increased by roughly 2 ppmv over this time period. In actual fact, the increase in water vapor should be somewhat less than this due to methane reactivity with chlorine and oxygen atoms. Both modeling and data analysis studies (e.g., Le Texier

et al., 1988; Hansen and Robinson, 1989; Randel et al., 1998; Zoger et al., 1999) are in agreement with this conclusion, indicating that the overall stratospheric water vapor yield from methane is slightly less than two. A doubling of methane surface concentration in the UIUC two-dimensional model of the global atmosphere gives an increase in the amount of water vapor at the stratopause, near 50 km, of approximately 40% or about 3 ppmv.

Increasing methane concentrations should also be leading to increasing concentrations of water vapor in the mesosphere. In conjunction with carbon dioxide, increasing methane concentrations should also lead to cooler temperatures in the stratosphere, mesosphere, and thermosphere (WMO, 1985, 1989; Brasseur and Hitchman, 1988; Roble and Dickinson, 1989). With the increase in water vapor and the cooler temperatures, there is the potential for increased occurrences of noctilucent clouds near the mesopause (Thomas et al., 1989). Roble and Dickinson (1989) also point out that other changes in mesospheric and thermospheric composition should occur due to both the cooler temperatures and direct chemical effects from increased concentrations of methane and carbon dioxide. In addition, exospheric hydrogen will increase with increasing methane (Ehhalt, 1986).

4. Impact of methane on climate

4.1. Direct effects

In the past, the concern that human activities may be affecting global climate has largely centered around carbon dioxide because of its importance as a greenhouse gas and also because of the rapid rate at which its atmospheric concentration has been increasing. However, it is clear that other greenhouse gases have also significantly affected climate over the past few centuries. Rising methane concentrations are a major contributor to the increase in radiative forcing since pre-industrial times, second only to carbon dioxide. The combined effect of methane and the other greenhouse gases has been to approximately double the overall increase in the greenhouse radiative forcing on climate relative to that from CO_2. Like other greenhouse gases, methane absorbs infrared radiation (also called longwave or terrestrial radiation)

emitted by the relatively warm planetary surface and emits radiation to space at the colder atmospheric temperatures, leading to a net trapping of infrared radiation in the atmosphere. This is called the greenhouse effect. The balance between the absorbed solar radiation and the emitted infrared radiation determines the net radiative forcing on climate.

Although its atmospheric abundance is less than 0.5% that of carbon dioxide, methane is an important greenhouse gas. Donner and Ramanathan (1980) calculated that the presence of methane at current levels causes the globally-averaged surface temperature to be about 1.3 K higher than it would be without methane. On a molar basis, an additional mole of methane in the current atmosphere is about 24 times more effective at absorbing infrared radiation and affecting climate than an additional mole of carbon dioxide (WMO, 1999). Correspondingly, on a mass basis, an additional kilogram of methane is about 66 times more effective as a greenhouse gas than a kilogram of carbon dioxide. It should be noted that the actual lifetime of carbon dioxide in the atmosphere is much longer than the atmospheric lifetime of methane (IPCC, 1990, 1996). However, it should also be recognized that the dissociation of methane eventually produces carbon dioxide, leading to additional climatic forcing from methane emissions from fossil sources.[5]

The strongest bands for absorption by methane in the infrared are in the short wavelength edge of the 'window region' (~ 7–13 μm, where there is little absorption by H_2O or CO_2). The most important infrared spectral feature of methane is the 7.66 μm (1306 cm^{-1}) absorption band. Due to saturation of the line cores for methane and emissions from the pressure-broadened Lorentz line wings, radiative forcing from methane increases approximately as the square root of its concentration (IPCC, 1990; Wigley, 1987). Overlap with absorption by water vapor and other species (particularly nitrous oxide) also affects the efficiency of methane absorption.

Wang et al. (1991) show that the greenhouse radiative forcing for methane has different spatial effects on climate than carbon dioxide, and that methane needs to be accounted for explicitly when attempting

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[5] The oxidation of methane from biogenic sources also results in CO_2 production, but the forcing of CO_2 from these sources has already been taken into account as part of the carbon cycle.

to predict the climate response to increasing concentrations of greenhouse gases. Calculations with three-dimensional global climate models (GCMs) are beginning to consider the explicit effects of methane on climate. Hansen et al. (1988) and Wang et al. (1991) have explicitly considered the effects of methane in GCM studies, while many other studies have included methane only through accounting for its radiative forcing through use of an increase in carbon dioxide as a proxy.

Increasing concentrations of methane are thought to be a significant fraction of the increase in radiative forcing from greenhouse gases over the last two centuries. IPCC (1996) calculated that the direct radiative effect of the increase in methane since the mid-1700s has produced a radiative forcing increase of 0.47 W m^{-2}.[6] This is about 19% of the total change in radiative forcing due to CO_2 and other greenhouse gases over this time period.[7] Inclusion of indirect effects of methane increases on stratospheric water vapor, ozone, and carbon dioxide (see next section) could increase this percentage by at least 10–35% (e.g., IPCC, 1995; Bruhl, 1993; Lelieveld et al., 1993, 1998; Fuglestvedt et al., 1996).

A recent analysis of the radiative forcing for methane (Jain et al., 2000), accounting for the latitudinal and seasonal variations in methane concentrations, calculates a larger radiative forcing contribution from methane than earlier studies. The globally- and annually-averaged radiative forcing based on the new calculations was 4.67×10^{-4} W m^{-2} for a 1-ppb change in methane, compared to 3.7×10^{-4} W m^{-2} in IPCC (1996). The estimated change in radiative forcing from pre-industrial times to 1992 was 0.55 W m^{-2} compared to 0.47 in IPCC (1996). Minschwaner et al. (1998) also determined a radiative forcing for methane from 1750 to 1992 of 0.55 W m^{-2} based on the observed distribution of methane from the Upper Atmosphere Research Satellite.

Over the last decade, increases in atmospheric methane concentration are calculated to have increased

radiative forcing by about 0.06 W m^{-2}, 11% of the total increase in radiative forcing from greenhouse gases over this time period (WMO, 1999).[8]

Various studies have evaluated the potential effects of a doubling of methane concentrations on radiative forcing and surface temperature using radiative–convective models. For an increase from 1.6 to 3.2 ppmv, resulting increases in surface temperature range 0.2–0.3 K (Owens et al., 1985; Ramanathan et al., 1987; MacKay and Khalil, 1991; IPCC, 1995), with the differences in model results primarily relating to uncertainties in the band strengths for methane infrared absorption. For a doubling from 1.7 to 3.4 ppmv, Owens et al. (1985) calculated a direct 0.34 K increase in surface temperature, along with an additional 0.26 K due to indirect effects from methane-induced effects on carbon dioxide and ozone. For a 25% increase in methane concentrations, Ramanathan et al. (1985) determine a 0.08-K increase in surface temperature when overlap with the radiative absorption with other greenhouse gases is included, and a 0.19-K increase in surface temperature without overlap.

Other modeling studies have included increasing methane concentrations in studies evaluating scenarios for potential future changes in radiative forcing and global temperatures (Wang and Molnar, 1985; Ramanathan et al., 1985, 1987; WMO, 1985; Dickinson and Cicerone, 1986; Wang et al., 1986; Wigley, 1987; Hansen et al., 1988, 1989; IPCC, 1990, 1995, 1996). In Table 2, the change in radiative forcing due to increasing methane is compared to the total change in forcing due to all greenhouse gases for three IPCC emission scenarios (high, medium and low) (IPCC, 1996). These more recent scenarios generally show a somewhat increased role for methane in determining future radiative forcing. However, these studies do not consider the significant indirect effects from chemical interactions as discussed next.

4.2. Indirect effects

In addition to its direct radiative forcing effect on climate, methane can also influence climate indirectly through chemical interactions affecting other radia-

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[6] Climate models indicate that the 4 W m^{-2} forcing associated with a doubling of CO_2 from 300 to 600 ppmv would give approximately a 1.5- to 4.5-K increase in surface temperature.

[7] Other research studies have found similar percentages for the effect of methane over this period: e.g., Rodhe (1990) derived 15%, while Hansen et al. (1989) and MacKay and Khalil (1991) calculated ~22%.

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[8] Note that these estimates ignore the effects on radiative forcing due to changes in global ozone and aerosols over this time period.

Table 2

Change in radiative forcing (W m^{-2}) due to increasing methane, as compared to total change in forcing due to all greenhouse gases. Radiative forcing given by IPCC (1996) for their high (IS92e), medium (IS92a), and low (IS92c) emission scenarios

Time period	Scenarios								
	IS92a			IS92c			IS92e		
	CH$_4$	All	%	CH$_4$	All	%	CH$_4$	All	%
1765–2025	0.66	4.01	16.4	0.59	3.63	16.2	0.69	4.31	16.0
1765–2050	0.83	5.37	15.4	0.65	4.37	14.9	0.89	6.12	14.5
1990–2025	0.19	1.61	11.8	0.12	1.23	9.7	0.22	1.91	11.5
1990–2050	0.36	2.97	12.1	0.18	1.97	9.1	0.42	3.72	11.3

tively important gases. Methane is an important influence on concentrations of hydroxyl, the primary tropospheric oxidizing agent, which in turn determines the rate at which methane is removed from the atmosphere. Methane oxidation is also a significant source of tropospheric and stratospheric ozone, stratospheric water vapor, and its eventual final product, carbon dioxide.

Resolving changes in tropospheric OH due to CH$_4$ emissions is difficult because of uncertainties associated with modeling the non-linear relationships in the CH$_4$–CO–OH cycle. Increases in the response time of methane to a perturbation can result in a much larger apparent lifetime for the perturbed methane than the overall atmospheric lifetime of methane (Prather, 1994; IPCC, 1995, 1996). Tropospheric OH concentrations are expected to change in the future due to increases in CH$_4$ as well as other trace gases such as CO, NO$_x$, O$_3$, NMHCs and water vapor. Depending on the emission scenario examined, trace gas emissions can either lengthen or shorten the lifetime of CH$_4$, resulting in a positive or negative indirect effect (Hayhoe et al., 2000; Bruhl, 1993; Lelieveld et al., 1993, 1998).

Changes in tropospheric ozone associated with increasing methane are the most important indirect effect, capable of adding 19 ± 12% to the direct radiative forcing from methane (IPCC, 1995; based on UIUC and other two-dimensional model studies). The large remaining uncertainty is associated with the overall uncertainties in understanding the processes affecting ozone in the troposphere.

Methane oxidation in the stratosphere is an important source of water vapor. Although the concentration of water vapor in the stratosphere is several orders of

magnitude smaller than tropospheric concentrations, at the low temperatures found in the lower stratosphere, relatively small changes in water vapor levels can significantly impact radiative forcing. Therefore, an increase in stratospheric water vapor concentrations resulting from increasing methane concentrations will enhance the greenhouse effect, and provide a positive indirect effect that will enhance the direct radiative forcing from the added methane. While earlier studies assuming a mixing ratio increase in methane suggested that the increase in water vapor could enhance the radiative forcing by as much as 30% (IPCC, 1990), more recent studies (Lelieveld and Crutzen, 1991, 1992; Bruhl, 1993; Lelieveld et al., 1993; Hauglustaine et al., 1994; IPCC, 1995) using flux boundary condition changes in methane have shown the effect of the water vapor increase to be much smaller, 4–5% of the total direct radiative forcing from methane.

Increasing water vapor could also lead to an increased amount of polar stratospheric clouds. Ramanathan (1988) showed that both water and ice clouds, when formed at cold lower stratospheric temperatures, are extremely efficient in enhancing the atmospheric greenhouse effect. He also noted that there is a distinct possibility that large increases in future methane may lead to a surface warming that increases nonlinearly with the methane concentration.

Finally, methane oxidation eventually ends in the production of carbon dioxide, one of the most important greenhouse gases. However, about 500 Tg/year of methane are destroyed by reaction with hydroxyl and converted to carbon dioxide, accounting for production of only 380 TgC/year as carbon dioxide; in contrast, emissions of carbon dioxide from anthropogenic fossil fuel use and cement manufacturing are ∼6000 TgC/year. In addition, CO$_2$ produced by the oxidation of methane from biogenic sources is already included in the carbon cycle budget; only CO$_2$ from methane emitted by fossil fuel sources contributes to the indirect effect.

4.3. Global warming potentials

Global Warming Potentials (GWPs) have been developed as an analysis tool for policy makers to assist in the evaluation of possible policy actions related to greenhouse gas controls. The Kyoto Protocol uses GWPs to weight emissions of the six green-

house gases that can be included in national emission reduction strategies (UNFCCC, 1997). Based on emission reductions required under the Kyoto Protocol, we recently analyzed greenhouse gas abatement scenarios for the U.S. (Hayhoe et al., 1999). Using a 100-year GWP for methane, as specified in the Protocol, our results indicate that the cost of achieving a reduction of 650 GtC_{eq} by 2010 would be reduced by at least 25% if methane were included in a previously CO_2 only strategy.

The GWP of a greenhouse gas is defined as the time-integrated commitment to climatic forcing from the instantaneous release of a kilogram of the gas relative to the climatic forcing from the release of 1 kg of carbon dioxide, and is generally calculated for constant background concentrations. Published GWPs are derived for integration periods from 20 to 500 years, with the 100-year values generally thought to provide a balanced representation of the various time horizons for climatic response. Under this measure, the latest 100-year GWP for methane, including both direct and indirect effects, is 24 ± 7.5 (WMO, 1999; IPCC, 1995), compared to 1.0 for carbon dioxide. The GWPs from IPCC (1996) for direct plus indirect effects from methane for the 20- and 500-year integrations are 62 ± 20 (64 in WMO, 1999) and 7.5 ± 2.5, respectively. As shown in IPCC (1990, 1995), indirect effects can more than double the direct methane GWP value (see also Fuglestvedt et al., 1996; Lelieveld et al., 1998). Additional uncertainties are introduced by the assumption of constant background concentrations over the length of the integration. Projected changes in atmospheric concentrations of CH_4 and other trace gases such as OH, CO and NO_x affect the removal rate of CH_4 and hence its GWP (Hayhoe et al., 2000). Uncertainties in GWPs of methane and other important greenhouse gases in turn affect their optimal contribution to emission reductions and hence to the prevention of climate change.

5. Summary and conclusions

The atmospheric concentration of methane has increased dramatically over the last century and continues to increase. While budget and isotopic analyses have confirmed the causal role of human activities in this increase, significant uncertainties remain in un-

derstanding the factors that affect emissions from various sources and how these will change over time. Uncertainties in how the sources and sinks of methane will change in the future limit our ability to develop meaningful climate change policies aimed at controlling methane emissions.

The 1998 increase in the growth rate of methane has renewed the debate about future levels of methane. This increase could just be a short-lived anomaly. However, if this increase is the first sign of one of the most important biogenic feedbacks to climate change — the response of wetlands to the increases in global temperatures — this raises urgent questions concerning the magnitude of the response of methane concentrations to the much larger increases in global temperatures projected to occur over the next century.

More research is needed to fully understand the growth rate in methane and its future projection. More complete analyses will require increased coordination between programs measuring atmospheric abundances and isotopic ratios, and modelling efforts that couple biospheric and oceanic biogeochemistry with atmospheric processes.

Acknowledgements

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