

## 2.3. METHANE

### 2.3.1. IN SITU METHANE MEASUREMENTS

Quasi-continuous measurements of atmospheric methane continued at Mauna Loa and Barrow observatories at a frequency of four ambient measurements each hour. The relative precision is 0.07%. Details of the measurement techniques and analysis of the in situ data through early 1994 were published in 1995 [Dlugokencky *et al.*, 1995]. Daily averaged methane mole fractions (in  $10^{-9}$  mol mol<sup>-1</sup>, nmol mol<sup>-1</sup>) for 2000-2001 are plotted in Figure 2.10 for BRW and MLO. The data were edited for instrument malfunction using a rule-based expert system [Masarie *et al.*, 1991], and they were selected for meteorological conditions. Briefly, the BRW data are constrained to the clean-air sector, which includes wind directions of 20°-110°, and wind speeds >1 m s<sup>-1</sup>. MLO data are constrained to 0000-0659 local time, which is typically a period with downslope winds. In situ data are available at hourly, daily, and monthly time resolution from the CMDL World Wide Web page ([www.cmdl.noaa.gov](http://www.cmdl.noaa.gov)) or ftp file server's "pub" directory (<ftp://ftp.cmdl.noaa.gov>).

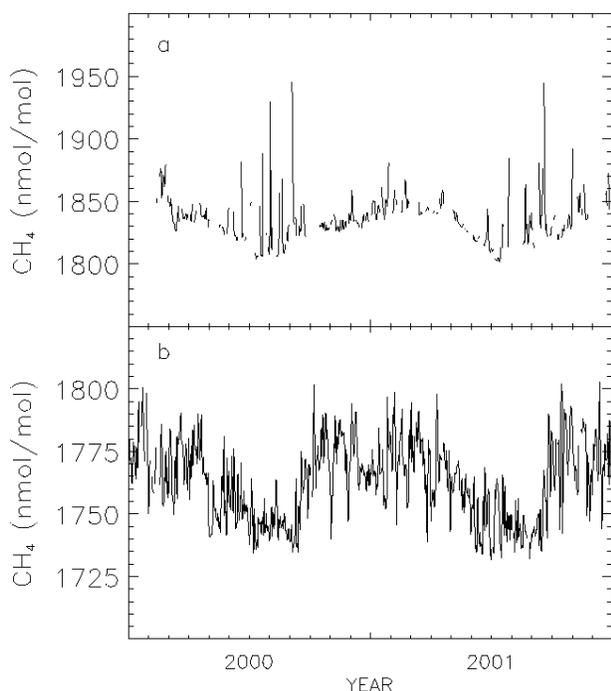


Fig. 2.10. Daily mean CH<sub>4</sub> mole fractions (in nmol mol<sup>-1</sup>) for (a) Barrow and (b) Mauna Loa, for 2000 and 2001. The data are constrained for wind regime (see text), and they have undergone a quality control step to ensure that the analytical instrument was working optimally when they were obtained [Masarie *et al.*, 1991].

### 2.3.2. MEASUREMENTS OF METHANE IN DISCRETE SAMPLES

During 2000-2001 the determination of the global distribution of atmospheric methane continued from 47 sampling

sites of the CCGG Global Cooperative Air Sampling Network. Sampling was started at one new site during this 2-yr period. A new tower measurement and sampling program on the KWKT television transmitter tower in Moody, Texas, began in February 2001. North-south sampling transects of the Pacific Ocean (and in the South China Sea) by ship have been suspended. Because of the importance of these measurements in studies of the global methane cycle, it is hoped that sampling can begin again in the future. Sampling also ended in 1999 at Maldives (KCO) and Malta (GOZ). Provisional annual mean values for 2000 and 2001 are given in Table 2.3. Complete data records and monthly means can be obtained through 2001 for each site from the CMDL World Wide Web page ([www.cmdl.noaa.gov](http://www.cmdl.noaa.gov)) or ftp file server's "pub" directory (<ftp://ftp.cmdl.noaa.gov>).

Globally averaged CH<sub>4</sub> dry-air mole fractions are plotted in Figure 2.11a for the period 1983.5 through 2001 (see Dlugokencky *et al.* [1994a] for details on calculation of global and zonal averages). During this time, CH<sub>4</sub> increased from about 1615 nmol mol<sup>-1</sup> to about 1750 nmol mol<sup>-1</sup>. The instantaneous growth rate for globally averaged

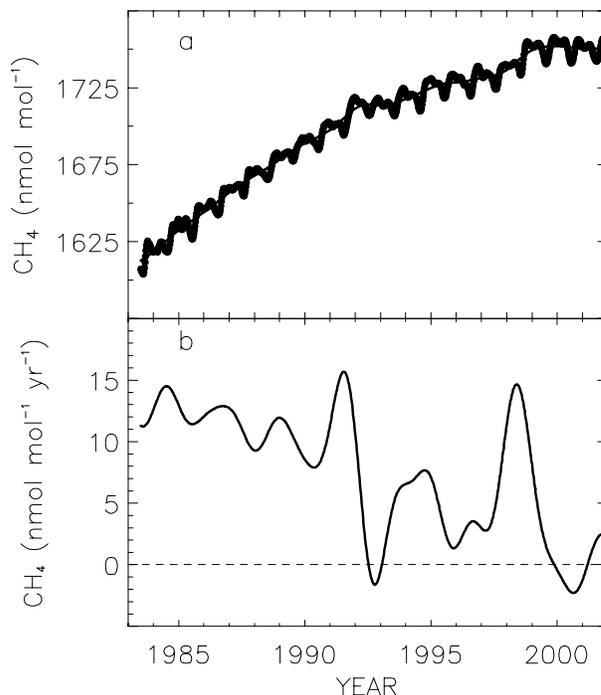


Fig. 2.11. (a) Globally averaged methane mole fractions. The solid line is a deseasonalized trend curve. (b) Instantaneous CH<sub>4</sub> growth rate for the global averages. The growth rate is calculated as the derivative of the solid curve in (a).

CH<sub>4</sub> is plotted in Figure 2.11b; it has decreased from about 14 nmol mol<sup>-1</sup> yr<sup>-1</sup> at the start of the record to approximately zero in 2000 and 2001, with significant interannual variability. An attempt has been made to explain the large variations in growth rate. The increased global growth rate

in 1991 appears to have been driven by CH<sub>4</sub> sink chemistry in the tropics after the eruption of Mt. Pinatubo in July 1991. *Dlugokencky et al.* [1996] showed that SO<sub>2</sub> emitted during the eruption, and subsequent sulfate aerosol produced by oxidation of the SO<sub>2</sub>, affected tropical photochemistry, which temporarily decreased the photochemical CH<sub>4</sub> destruction rate. The decreased global growth rate during 1992 was driven by a decrease of  $0.3 \pm 0.8 \text{ nmol mol}^{-1}$  in the northern hemisphere. *Dlugokencky et al.* [1994b] suggested that the decreased growth rate in 1992 could, only in part, be explained by decreased emissions from natural wetlands. B. Walter (personal communication, 2000) used a process-based model to show that lower-than-normal temperatures and precipitation in high northern wetland regions during 1992 resulted in decreased CH<sub>4</sub> emissions from wetlands. Such a change in wetland emissions would have been temporary; there is now evidence in the measurements that a separate step-like decrease in high northern emissions occurred during 1992 (see later in this section). During 1998, there was a large positive anomaly in global growth rate that corresponded to an increase in the imbalance between sources and sinks of 24 Tg CH<sub>4</sub> (1 Tg = 10<sup>12</sup> g). *Dlugokencky et al.* [2001] attributed this to increased emissions from wetlands in the high-northern and southern-tropical latitudes resulting from warmer and wetter-than-normal conditions. *Walter* [1998] and *Walter and Heimann* [2000] used an adaptation of a process-based model that included soil-temperature and precipitation anomalies to calculate decreased emissions for 1998 of 11.6 Tg CH<sub>4</sub> from wetlands north of 30°N and 13 Tg CH<sub>4</sub> for tropical wetlands compared with the average emissions calculated for 1982-1993. Nearly all (11.5 Tg CH<sub>4</sub>) of the tropical emission anomaly was in the southern tropics (equator to 30°S).

The observed long-term decrease in growth rate is consistent with our previous suggestion that atmospheric CH<sub>4</sub> is approaching steady state [*Dlugokencky et al.*, 1998], if it is assumed that the CH<sub>4</sub> lifetime has been constant over the time period of the measurements. In Figure 2.12a annual global CH<sub>4</sub> emissions are plotted for the period 1984-2000. They were calculated using the measured global CH<sub>4</sub> burden and rate of increase with a constant lifetime of 9 years [*Montzka et al.*, 2000] in a mass-balance equation [*Dlugokencky et al.*, 1998]. Other recent studies, though, suggest that the CH<sub>4</sub> lifetime may not be constant. *Krol et al.* [1998] and *Karlsdóttir and Isaksen* [2000] suggested that global hydroxyl radical (OH) is increasing, with a resulting decrease in CH<sub>4</sub> lifetime of about 0.5% yr<sup>-1</sup> during this measurement period. If confirmed, CH<sub>4</sub> emissions must be increasing, also by 0.5% yr<sup>-1</sup>. Contrary to these studies, *Prinn et al.* [2001] suggest that global OH has decreased by an average rate of  $0.64 \pm 0.60\% \text{ yr}^{-1}$  over the period 1978 to 2000. Further, they state that OH increased by  $15 \pm 22\%$  from 1979 to 1988, and then decreased to levels in 2000 that were  $10 \pm 24\%$  lower than those in 1979. The impact of the *Prinn et al.* [2001] OH changes on CH<sub>4</sub> lifetime is quite large, and the resulting changes in global CH<sub>4</sub> emissions are plotted in Figure 2.12b. CCGG has not yet determined what combination of changes in sources could explain the nearly 100 Tg CH<sub>4</sub> decrease in global emissions between 1991 and 2000.

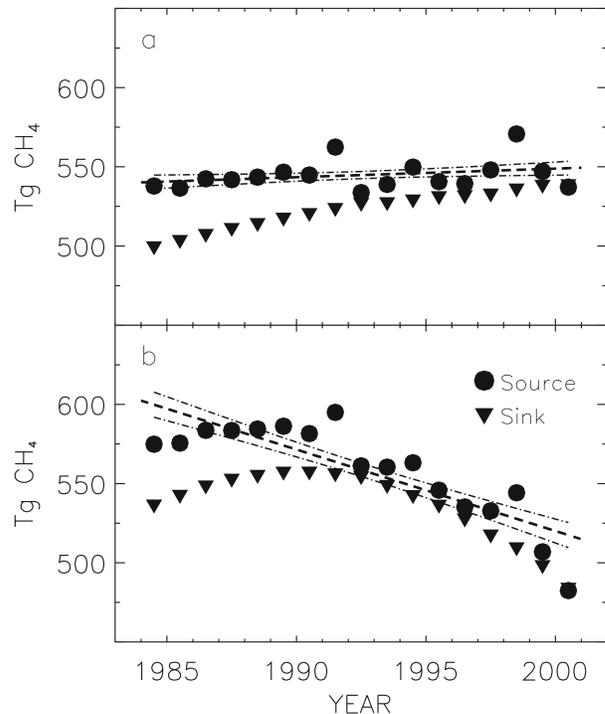


Fig. 2.12. Global annual emissions (circles) and sinks (triangles) for methane calculated using (a) a constant lifetime of 9 years and (b) smoothly varying lifetime determined by *Prinn et al.* [2001]. The dashed lines are linear fits to the emissions with 1 $\sigma$  confidence limits.

Figure 2.12a suggests that a potentially huge change has occurred in the global CH<sub>4</sub> budget; that is, in 2000 it is observed that for the first time in the CCGG record the global sink was larger than global emissions. This indicates a net decrease in the global burden of CH<sub>4</sub>. No one can yet explain, even qualitatively, the changes in CH<sub>4</sub> source-sink imbalance that have occurred over the past decade to cause a net decrease in global CH<sub>4</sub> burden. Without an understanding of the processes causing this change, it is not possible to guess, much less predict, what will happen to the CH<sub>4</sub> growth rate in the future.

One possible change that may have tipped the balance to a net global CH<sub>4</sub> decrease is in emissions of CH<sub>4</sub> from the fossil fuel sector in the former Soviet Union (FSU). In *Schnell et al.* [2001, pp. 33-34], a speculative scenario is described that may have contributed to the observed decreasing burden of atmospheric methane. Evidence for this scenario comes from two recent studies of CH<sub>4</sub> emissions from Russia. *Reshetnikov et al.* [2000] estimated 24-40 Tg CH<sub>4</sub> emissions from the Russian gas industry during the late 1980s and early 1990s. *Dedikov et al.* [1999], using measurements from an extensive program in 1996 and 1997 to determine losses from Russian gas production and transmission facilities, estimated a 3.6 Tg yr<sup>-1</sup> CH<sub>4</sub> emission during that time. The dramatic decrease in emissions suggested by these studies is not supported by CCGG measurements, but an abrupt decrease in emissions

from high northern latitudes is consistent with changes in the observed CH<sub>4</sub> latitudinal gradient. Differences in CH<sub>4</sub> calculated for polar latitudes (53.1°-90°N = PNH; 53.1°-90°S = PSH) are plotted in **Figure 2.13**. From 1984 through 1991, the difference in zonal average increased. In 1992, there was a downward step change in the difference of about 10 nmol mol<sup>-1</sup>, which continued downward after 1992. It is unlikely that this step change is due to a natural source such as wetland emissions or a permanent change in the sink. It is almost certainly an anthropogenic source that can be altered quickly; fossil fuel exploitation is the most likely source. During 2000, the FSU produced 28% of the world's natural gas and about 10% each of coal and oil. Coal, oil, and natural gas production relative to 1990 for the FSU are plotted as a function of time in **Figure 2.14**. Between 1991 and 1997, production of natural gas decreased by 15%, or about 60 Tg CH<sub>4</sub>. Combined with the large decreases in oil and coal production, it is conceivable (but not proved) that these changes are responsible for atmospheric CH<sub>4</sub> sources and sinks coming to steady state.

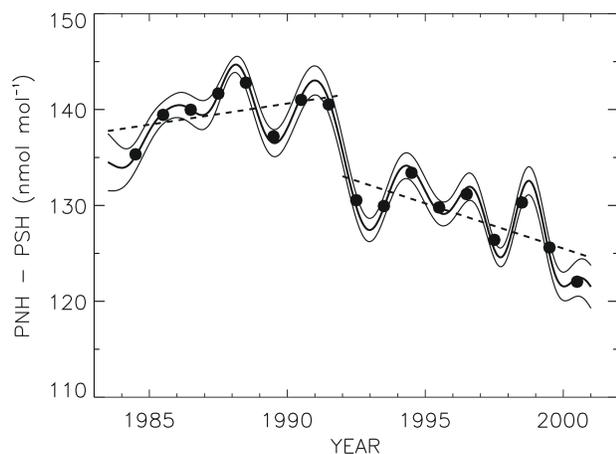


Fig. 2.13. Annual (filled circles) and weekly (solid curve with 1 $\sigma$  confidence limits) differences in zonally averaged CH<sub>4</sub> mole fractions in the latitude zones 53.1°-90°N (PNH) and 53.1°-90°S (PSH). Trends in the differences are plotted for two periods as dashed lines: 1983.5-1991 (0.44  $\pm$  0.36 nmol mol<sup>-1</sup> yr<sup>-1</sup>) and 1992-2000 (-0.94  $\pm$  0.32 nmol mol<sup>-1</sup> yr<sup>-1</sup>). The mean difference for the entire period is 133.9 nmol mol<sup>-1</sup>.

### 2.3.3. ATMOSPHERIC $\delta^{13}\text{C}_4$ SINCE 1998

INSTAAR's SIL has been measuring  $\delta^{13}\text{C}$  in atmospheric CH<sub>4</sub> at 6 sites since 1998, and has recently increased that number to 13 sites. Partitioning atmospheric CH<sub>4</sub> into its sources and sinks is possible through global measurements of its stable carbon isotopic ratio,  $\delta^{13}\text{C}_4$ , in addition to its atmospheric mole fraction. Biological sources, such as wetlands, have a characteristic isotopic composition (typically -60‰) that is more depleted in the heavy isotope, <sup>13</sup>C, than thermal sources like natural gas (-40‰), which in

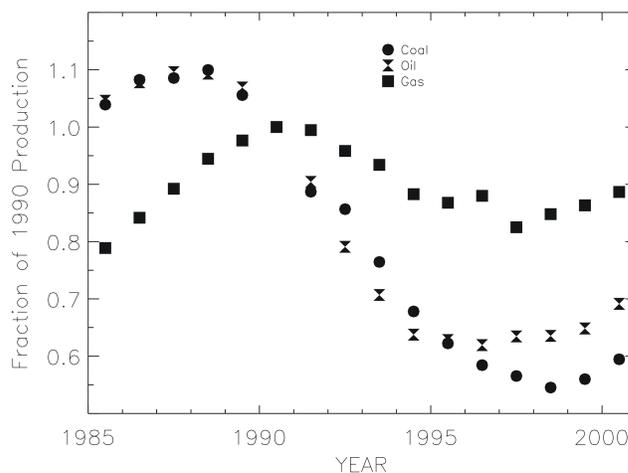


Fig. 2.14. Production of coal, natural gas, and oil in the former Soviet Union relative to 1990. Production in 1990 was 332  $\times$  10<sup>6</sup> tonnes oil equivalent for coal, 684.6  $\times$  10<sup>6</sup> tonnes oil equivalent for natural gas, and 570.5  $\times$  10<sup>6</sup> tonnes oil.

turn, are more depleted than biomass burning sources (-25‰). The measured isotopic ratio of atmospheric CH<sub>4</sub> (-47‰) is a composite of these sources, but it is also influenced by the enrichment in <sup>13</sup>C content (+5‰) that results from the destruction of methane by OH, which is slightly more rapid for <sup>12</sup>CH<sub>4</sub> than for <sup>13</sup>CH<sub>4</sub>.

An automated system was designed for the analysis of <sup>13</sup>C in atmospheric methane [Miller *et al.*, 2002]. Since January 1998, pairs of flasks were analyzed on a weekly basis from six sites (SPO, CGO, SMO, MLO, NWR, and BRW) of the Global Cooperative Air Sampling Network (see Table 2.3 for site acronym definitions). In January 2001, a new automated flask manifold with a capacity of 16 flasks and multiple reference tanks was built and installed. This has allowed an expansion of the number of sites measured from 6 to 13. The new sites are ALT, ASC, AZR, KUM, MHD, TAP, and WLG. The CCGG standard scale is linked to a scale maintained by the University of California, Irvine (UCI). Air tanks calibrated at UCI are used to establish the CCGG suite of working reference tanks. A program whereby both CCGG and the UCI laboratories measure  $\delta^{13}\text{C}$  in small cylinders collected at NWR commenced in summer 2000. Preliminary analysis indicates good agreement between the laboratories.

Figure 2.15 shows the seasonal variations of  $\delta^{13}\text{C}$  and CH<sub>4</sub> at BRW. The seasonal minima for  $\delta^{13}\text{C}$  at BRW occur during September or October and are curiously offset in time from either the seasonal CH<sub>4</sub> maxima or minima. The timing of the seasonal cycle of CH<sub>4</sub> indicates that it is driven, in large part, by seasonal variations in OH, the primary sink for CH<sub>4</sub> in the atmosphere. The seasonal cycle of  $\delta^{13}\text{C}$ , on the other hand, is driven most strongly by emissions from wetlands. The growth rate of  $\delta^{13}\text{C}$  during the summer is negative, which is consistent with the

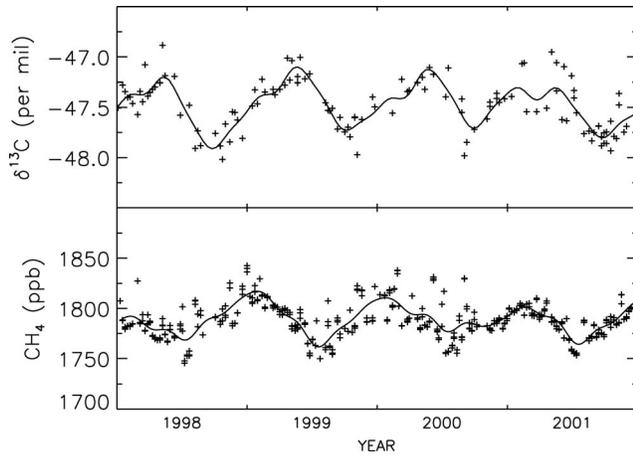


Fig. 2.15.  $\delta^{13}\text{C}$  (top panel) and mole fraction (bottom panel) of atmospheric  $\text{CH}_4$  at Barrow, Alaska (BRW), from 1998 to 2001. Pluses are averages of sample pairs collected sequentially on the same day. The solid curves are smooth fits to the data [Thoning *et al.*, 1989].

addition of isotopically light  $\text{CH}_4$  (more negative  $\delta^{13}\text{C}$ ) that is characteristic of wetlands emissions. This occurs despite the increasing activity of OH during the summer, which, in the absence of other processes, would result in a positive  $\delta^{13}\text{C}$  growth rate. The late summer minima in  $\delta^{13}\text{C}$  are probably the combined result of OH concentrations that are reduced relative to the middle of summer and wetlands emissions that are still significant.

During 1998 at BRW the  $\text{CH}_4$  minimum was less pronounced than in other years, and the minimum in  $\delta^{13}\text{C}$  was more pronounced (see the smooth-curve fits in Figure 2.15). Dlugokencky *et al.* [2001] hypothesized that the growth rate anomaly in  $\text{CH}_4$  associated with the higher-than-normal seasonal minimum was a result of two factors: increased  $\text{CH}_4$  emission from boreal wetlands in Canada and Siberia, and large emissions of  $\text{CH}_4$  from peatland fires in Siberia. With a two-box model of the atmospheric  $\text{CH}_4$ , this hypothesis was tested against the  $\text{CH}_4$  and  $\delta^{13}\text{C}$  observations. It was found that the combination of anomalous wetland emissions and fire emissions fitted the observations better than either emission anomaly on its own.