Reports

Continuing Worldwide Increase in Tropospheric Methane, 1978 to 1987

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The average worldwide tropospheric mixing ratio of methane has increased by 11% from 1.52 parts per million by volume (ppmv) in January 1978 to 1.684 ppmv in September 1987, for an increment of 0.016 ± 0.001 ppmv per year. Within the limits of our measurements, the global tropospheric mixing ratio for methane over the past decade is consistent either with a linear growth rate of 0.016 ± 0.001 ppmv per year or with a slight lessening of the rate of growth over the past 5 years. No indications were found of an effect of the El Niño–Southern Oscillation–El Chichon events of 1982–83 on total global methane, although severe reductions were reported in the Pacific Northwest during that time period. The growth in tropospheric methane may have increased the water concentration in the stratosphere by as much as 28% since the 1940s and 45% over the past two centuries and thus could have increased the mass of precipitable water available for formation of polar stratospheric clouds.

THE AVERAGE WORLDWIDE TROPOSPHERIC mixing ratio of methane (CH_4) continued in late 1987 to increase at a steady rate of 0.016 ± 0.001 parts per million by volumes (ppmv) per year, as it has done in our measurements for almost 10 years (*1–4*). The worldwide average mixing ratio in September 1987 was 1.684 ppmv, an increase of 11% over our measured value of 1.52 ppmv in January 1978. Tropospheric measurements of CH_4 concentrations showed indications 8 years ago of a worldwide increase during the late 1970s (*1, 5, 6*), and attention was focused on the time dependence, the probable causes, and the potential consequences of such variations. Subsequent data have confirmed that the increases in concentration have continued into the mid-1980s (*1–12*), whereas data from air bubbles in ice cores from Greenland and Antarctica show that CH_4 concentrations 200 to 3000 years ago were less than half those now observed (*8, 13–15*). Retrospective evaluation of atmospheric infrared spectra has confirmed CH_4 increases of about 1% per year between 1951 and 1981 (*16*), and air sample data from the 1960s have been shown to be consistent with these rates of increase (*5, 17*).

Our own continuing measurements began with a set of air samples collected between November 1977 and February 1978, providing coverage over the latitude range from Ketchikan, Alaska (55°N), to Punta Arenas, Chile (53°S) (*18*). Much larger numbers of samples have been collected periodically over selected narrow time intervals since 1978, and have been assayed for CH_4 and several other trace gases (*1–4, 19, 20*). Additional collections of air samples and measurements of tropospheric CH_4 mixing ratios are currently made every 3 months for latitudes from 71°N (Barrow, Alaska) to 47°S (New Zealand). The air samples for 1982–1987 were collected in remote ground-level locations on land areas adjacent to the Pacific Ocean, including Alaska, U.S. West Coast, Mexico, Hawaii, New Zealand, and smaller Central and South Pacific islands. We have completed our CH_4 assays of 68 remote location samples collected between 6 September and 1 October 1987 and have continued to observe a monotonic increase in its average worldwide concentration. The individual data points from September 1987 (Fig. 1) qualitatively exhibit the gradient of decreasing concentrations toward the south that has always been found for CH_4. The gradient exists because a larger fraction (estimated as ≥70%) of CH_4 is released in the Northern Hemisphere, most of it from rice paddies, swamps, the rumen of cattle, and other anaerobic biological processes (*21–23*). Data from April 1983, and from our secondary standard taken in the California desert in November 1977, illustrate the rapid increase in tropospheric CH_4 mixing ratios (Fig. 1).

The average worldwide mixing ratios of tropospheric CH_4 for 25 separate collection periods for almost 10 years are graphed in Fig. 2. For averaging purposes, we have divided the surface of the earth into 16 equal-area latitudinal bands and obtained an average value for each band for each collection period. The world average is then simply the arithmetic average of the values for all 16 latitudinal bands (*3, 4*). In the last 16 sampling periods, all of these bands except the two southernmost (48.6°S to 90°S) have contained several samples each, and the two unrepresented bands have been assumed to have concentrations equal to the average of those between 22.0°S and 48.6°S. Measurements by our research group at latitudes down to 53°S in Chile (*1–4*) and by others in Antarctica (*8, 12, 24*) have shown negligible gradients in CH_4 mixing ratios south of 40°S. The mixing ratios of four winter 1987 samples from Antarctica were indistinguishable from those collected between 25°S and 47°S and confirm that no serious error is introduced into the global average by our usual averaging procedure south of 48.6°S.

The data of Fig. 2 show a continuous increase in CH_4 concentration that is well described by a straight line. The illustrated line has a slope of 0.0165 ppmv per year. When the collection periods are limited to those in which the Southern Hemispheric samples were obtained from Pacific islands rather than the South American coast (that is, the last 19 collection periods, beginning in September 1982), the best linear fit shows an increase of 0.0159 ± 0.0005 ppmv per year. When we include all of the data points (except the first, which had many fewer samples), the linear increase is 0.0165 ± 0.0003 ppmv per year. We conclude that the best current description of the growth in CH_4 concentrations over our entire measurement period is 0.016 ± 0.001 ppmv per year. The best linear fit for our data reported through 1983 had a slope of 0.018 ppmv per year (*4*). With data from four additional years, the gradient is slightly less than initially reported and can represent either a better estimate of the long-term linear trend or a slow decrease in the gradient in mixing ratios with time. Our present data set cannot distinguish between

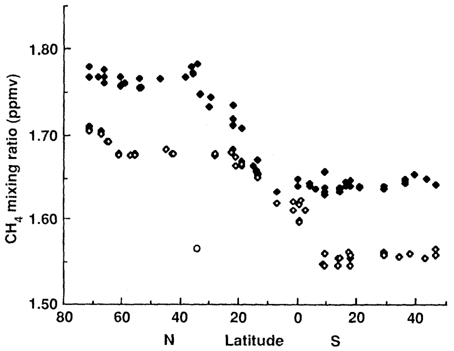

Fig. 1. Tropospheric mixing ratios of CH_4 in September 1987 (closed diamonds) in comparison with April 1983 (open diamonds) and a secondary standard of California air from November 1977 (open circle).

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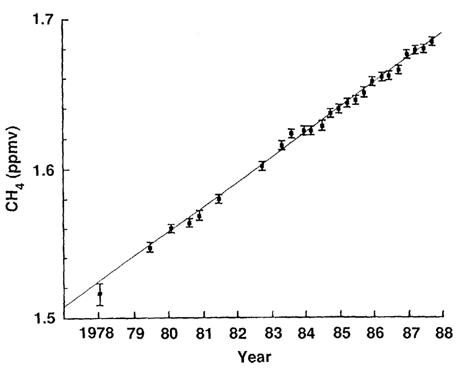

Fig. 2. Worldwide average tropospheric CH_4 mixing ratios versus time from January 1978 through September 1987 (*25*). Least-squares fitting of all the points except the first gives the illustrated slope of 0.0165 ppmv per year (see text).

these two possibilities. Experimental measurements of CH_4 concentrations on a daily or weekly basis in fixed locations have shown seasonal variations of the monthly average as large as 3% in the north temperate zone (*7–12*) and almost as large in the Southern Hemisphere (*7–12, 24*). Our detailed observations also exhibit substantial seasonal variations in CH_4 mixing ratios at individual latitudes. Almost all of this variability is eliminated in the worldwide averages, as shown by the good agreement in Fig. 2 with a simple linear increase with time.

A marked change in the interannual variability with substantial reductions in CH_4 concentrations was reported for data recorded during 1982 at Cape Meares, Oregon, and has been suggested as likely to be of global extent and attributed to the El Niño–Southern Oscillation (ENSO) geophysical events of that period (*10, 22*). In contrast, our data indicate an increase of 0.035 ± 0.004 ppmv between June 1981 and April 1983, corresponding to a yearly growth rate of 0.019 ± 0.004 ppmv per year during this period within the 95% confidence level (*26*). This growth rate is consistent with our decade-long rate and shows no indication of a global reduction in CH_4 mixing ratios during this ENSO–El Chichon period of 1982–83; a possible local ENSO effect on the transport of air to the Pacific Northwest is not excluded by our data.

Steele *et al.* (*12*) have measured the growth rate in CH_4 mixing ratio from May 1983 to April 1985 as 0.0128 ppmv per year and from limited additional data have suggested that the rate of growth in CH_4 concentration has slowed in the last several years. Our data for the periods from April 1983 or August 1983 through June 1985 show increases of 0.030 and 0.022 ppmv, respectively, and correspond to 95% confidence level growth rates of 0.014 ± 0.004 and 0.012 ± 0.004 ppmv per year, consistent with that reported for that period by Steele *et al.* (*12*). Our data (Fig. 2) could contain some structure around the overall linear growth, but any such variation appears to be no larger than our estimated confidence interval for the global assay, and thus not statistically significant in our data set. Continued measurements will be necessary to determine whether significant disagreement remains between our global data set and that of Steele *et al.*

Seasonal fluctuations in total worldwide CH_4 (*12*) are plausible because of the temperature dependences both of some biological releases and of the major CH_4 sink [removal by reaction with hydroxyl (HO) radicals] during the summer months in the temperate zones. However, the graph in Fig. 3 of the deviations in Fig. 2 between the observations and the linear increase versus the time of the year shows no clear seasonal variation in the total global atmospheric CH_4 burden. Changes as large as ±0.005 ppmv could well be hidden in the data, but fluctuations of ±0.01 ppmv away from the overall linear increase in the worldwide average should probably have been detected.

The measurements in different seasons in Fig. 1 display somewhat different structures in the latitudinal concentration gradient, especially in the equatorial region. A striking example of this change in gradient occurred in 1983 when the observed Southern Hemispheric mixing ratios from 10°S to 47°S increased from about 1.56 ppmv in April 1983 (Fig. 1) to 1.59 ppmv in August 1983, a nearly uniform Southern Hemispheric increase of 0.03 ppmv in only 4 months. These changes in the gradient structure represent a combination both of the strong seasonal nature of HO attack on CH_4 in the temperate zone and an increased southerly interhemispheric transport of trace gases during the northern summer. Similar export to the south of an accumulated Northern Hemispheric excess has also been found for CH_3CCl_3 and other halocarbons during the June-August period (*2, 19*).

The two important sources of stratospheric H_2O are its direct vertical transport through the tropical tropopause in mixing ratios of ~3 ppmv, and the subsequent oxidation of hydrogen atoms carried upward in the chemical form of CH_4. The complete oxidation of 1.5 ppmv of CH_4 would produce an additional 3 ppmv of H_2O and raise the stratospheric total in some regions of well-oxidized air to ~6 ppmv (*27*). As the level of tropospheric CH_4 increases, the level of total stratospheric water vapor will also increase after a time delay for the oxidation of CH_4 (*28*). An increase in average tropospheric CH_4 from 1.0 ppmv sometime in the 1940s to 1.684 in 1987 has presumably caused an increase in total stratospheric water vapor over this 40-year period from a maximum of about 5 ppmv to 6.4 ppmv, an increase of 28% (*28*). The corresponding increase from a CH_4 mixing ratio 200 years ago of 0.7 ppmv and a maximum stratospheric mixing ratio of 4.4 ppmv of H_2O is about 45%. An increase in total stratospheric water vapor over the past four decades provides a much larger amount of precipitable water vapor for the formation of polar stratospheric clouds in the 180 to 190 K temperatures of the Antarctic winter. Further enhancement of these clouds has the possibility of adding a positive feedback to the ozone depletion observed there since the late 1970s (*29*).

The steady growth in CH_4 concentrations makes an important direct contribution to the atmospheric greenhouse effect (*22, 30*) because each incremental molecule of CH_4 is about 20 times more effective than each additional molecule of CO_2, partially compensating for the 100-fold larger yearly increase in numbers of atmospheric molecules of CO_2 than for CH_4. This greater effect per molecule of CH_4 is the consequence of its infrared absorptions falling into wavelength regions that are not strongly absorbed by the existing atmospheric concentrations of the predominant O_3, H_2O, and CO_2, in contrast to the effects of any additional molecules of CO_2, for which the absorption

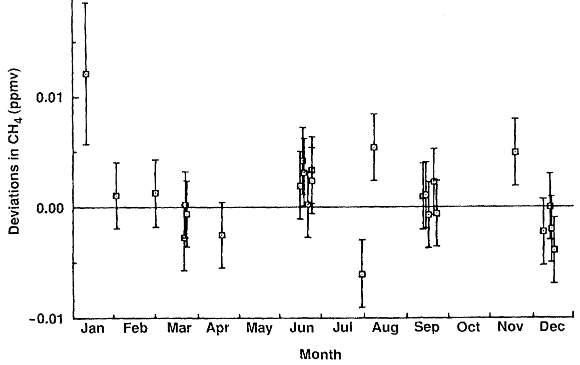

Fig. 3. Deviations in parts per million by volumes of CH_4 versus time of year from linear increase of worldwide average CH_4 mixing ratio (linear fit from Fig. 2 minus observed global averages).

frequencies must be identical to those strongly absorbed by the 345 ppmv of CO_2 presently in the atmosphere (*30*). An increase in H_2O in the stratosphere also contributes to an enhanced greenhouse trapping of infrared radiation as an indirect consequence of the CH_4 increase. Finally, the mutually self-limiting nature of the reactions of CH_4 and CO with HO radical make it plausible that the increase in CH_4 mixing ratio is at least partially the result of a progressively lower steady state HO concentration over recent decades (*16, 31*). Predictions of future trends in CH_4 mixing ratios will remain difficult without greatly improved understanding of both its sources and sinks.

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25. The calculated standard deviation of the points from the straight line in Fig. 2 is 0.0025 ppmv, which includes both our errors in routine measurement and the atmospheric sampling error caused by the limited number of samples for each time period. The indicated error bars are graphed as ±0.003 ppmv because of this observed consistency.
26. The increase is estimated from the measured mixing ratios for the two time periods, each ±0.0025 from (*25*).
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28. The implicit assumption in such an estimate is that no change has taken place in the average temperature of the tropical tropopause. Some calculations suggest that increasing trace gas concentrations can cause an increase in the tropical tropopause temperature, and this alone could cause stratospheric increases in water vapor mixing ratios. The increasing CH_4 concentrations furnish an avenue for increased H_2O even if the temperature of the tropical tropopause has not been changed.
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Synchrotron X-ray Diffraction Measurements of Single-Crystal Hydrogen to 26.5 Gigapascals

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The crystal structure and equation of state of solid hydrogen have been determined directly to 26.5 gigapascals at room temperature by new synchrotron x-ray diffraction techniques. Solid hydrogen remains in the hexagonal close-packed structure under these pressure-temperature conditions and exhibits increasing structural anisotropy with pressure. The pressure-volume curve determined from the x-ray data represents the most accurate experimental measurement of the equation of state to date in this pressure range. The results remove the discrepancy between earlier indirect determinations and provide a new experimental constraint on the molecular-to-atomic transition predicted at higher pressures.

THE BEHAVIOR OF SOLID HYDROGEN at high pressures remains a fundamental problem in modern physics. The theoretically predicted high-pressure metallic phase of hydrogen is potentially the simplest metal (*1*) and may display exotic dynamical properties including high-temperature superconductivity (*2*). The properties of hydrogen under extreme pressures also play a central role in modeling the interiors of the giant planets and the early evolution of the solar system (*3*). With the recent steady progress in the maximum pressure attainable in the diamond-anvil cell (*4*), the insulator-to-metal transition in solid hydrogen may well be within range of static compression experiments. Considerable advances have been made in the experimental study of solid hydrogen at high pressure during the last decade (*5–12*). Most recently, vibrational spectroscopic studies indicate that hydrogen remains an insulating molecular solid to ~150 GPa, but the molecular vibron undergoes a pronounced softening above 30 to 50 GPa, which can be interpreted as precursory to the transition to the metallic state (*7*). Direct information on the structure of solid hydrogen at high pressure has been more difficult to obtain than vibrational measurements, and indirect measure-

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