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GLOBAL INCREASE IN ATMOSPHERIC METHANE CONCENTRATIONS BETWEEN 1978 AND 1980

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Abstract. The concentration of methane has been measured in tropospheric air samples collected in remote locations between 55°N and 53°S during six collection periods between November 1977 and November 1980. The observed concentrations of CH₄ have increased in each of six latitude locations by an average of 0.052±0.005 ppmv between January 1978 and January 1980.

This $(1.4 \pm 0.2) \times 10^{14}$ gram increase in the total atmospheric burden of CH₄ corresponds to 35±12% of the yearly flux of $(4.0 \pm 1.3) \times 10^{14}$ grams needed to maintain the CH₄ concentration in steady-state at its recent level of about 1.6 ppmv. The 1978-1980 excess of about 0.7×10^{14} grams per year of sources over sinks for CH₄ could arise from either an increase in biogenic releases or from a decrease in the average OH radical concentration in the lower troposphere, or from both.

Introduction

The presence of CH₄ in the atmosphere was established more than 30 years ago by infrared spectroscopy {Migeotte, 1948}, and its concentration was measured sporadically over the next 20 years {Junge, 1963; Ehhalt, 1974; Dianov-Klokov *et al.*, 1975}. These measurements prior to 1970 demonstrated that CH₄ concentrations showed some variability with geographic location, but generally had neither frequency nor precision sufficient to permit conclusions concerning the existence of trends with latitude, season or year. The increasing emphasis on CH₄ measurements during the last few years has brought definite proof of a gradient in concentration of approximately 6% between the northern and southern hemispheres {Lamontagne *et al.*, 1974; Ehhalt, 1978; Wilkiss *et al.*, 1979; Mayer *et al.*, 1982}. Evidence has also appeared that the concentrations of CH₄ in particular locations have varied with season and increased with time, and has led to suggestions that the increase is a general worldwide phenomenon {Rasmussen and Khalil, 1981a,b; Fraser *et al.*, 1981; Rowland *et al.*, 1981}. We provide here experimental observations of an increase in CH₄ concentration between 1978 and 1980 at seven latitudes in the western hemisphere from 55°N to 53°S, indicative of a world increase of about 0.052±0.005 ppmv CH₄ over the two year period between January 1978 and January 1980.

Experimental

Tropospheric air has been collected in 2-liter all-stainless steel canisters which were transported to remote locations in an evacuated condition, and opened briefly to atmospheric pressure.

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After return to the laboratory, the CH₄ concentration in aliquots of the contents has been measured by flame ionization gas chromatography {Mayer *et al.*, 1982}. Since the aliquots were drawn while the flasks were kept in an ice bath at -20°C, the vapor pressure of water in the aliquots was negligible and the measurements are effectively the concentrations of CH₄ in dry air.

Several aliquots from each sample were measured alternately with an equal number of aliquots from a secondary standard. The precision of the successive measurements from any particular sample was ±0.005 ppmv, while the absolute reproducibility of the comparison standard is ±0.010 ppmv over a period of more than two years. Repetitive measurements of a series of aliquots from the same sample made over a three-year period have shown no change relative to the comparison standard beyond these limits. The absolute concentration of CH₄ in the secondary standards has been determined by comparison with NBS standards at 4 ppmv and 0.97 ppmv, each of which is stated to be accurate to ±1%.

Our collections in remote locations at ground level began in the western U.S. in November 1977 and were extended early in 1978 to Alaska, the West Indies and Chile. These samples are essentially "oceanic" in terms of the recent air trajectories of the air parcels being sampled. Our data taken at seven different latitudes for six collection periods are given in Tables 1 and 2 and Figure 1. At each of these seven latitudes the CH₄ levels increased from 1978 to 1979 to 1980. No further trend emerged during 1980.

Seasonal Variations and Annual Trends

The determination of a trend over a period of years can be complicated by the possible existence of seasonal variabilities in the concentrations of CH₄. Variations of ±20% have been reported for several locations in the Soviet Union during 1972-1974, with maxima in both the spring and the fall {Dianov-Klokov *et al.*, 1975}. These oscillations in concentration, observed with infrared spectroscopy, are much larger than indicated elsewhere by other techniques. Rasmussen and Khalil {1981a}, have made from 250-2000 gas chromatographic measurements each month during 1979 and 1980 at Cape Meares, Oregon, and have found variations exceeding 0.05 ppmv among the monthly average values in both years. Their CH₄ concentrations showed variations in 1979 and in 1980 of 0.09 ppmv between the 1σ upper limit on the month with highest concentration and the 1σ lower limit on the lowest month, a total range of ±3% around the yearly average. At the same time the monthly averages for 1980 were each higher than for the same calendar month in 1979 by an average difference of 0.029±0.006 ppmv, or an increase of 1.8±0.3% over twelve months.

The release of biogenic CH₄ occurs almost en-

TABLE 1. Methane Concentrations in ppmv in Tropospheric Air, 1978-1980

Latitude, Location	Jan/78	Jun/79	Jan/80	May/80	Aug/80	Nov/80	Increase, '78-'80(Jan)
55°N Ketchikan, Alaska	1.580	1.608 1.619	1.635 1.626	1.654 ^a 1.650 ^a	1.618 1.632	1.635	0.051
18°N St. Croix; Puerto Rico	1.555	1.573	1.599	1.582	1.583	1.592	0.044
13°N St. Lucia; Barbados	1.539	1.564	1.585	1.578	--	1.596	0.046
23°S Antofagasta, Chile	1.458	1.504	1.515	1.528	1.549	1.508	0.057
42°S Puerto Montt, Chile	1.453	1.503	1.505	--	1.519	1.517	0.052
53°S Punta Arenas, Chile	1.467	1.517	1.521	1.519	1.532	1.530	0.054

(a) Søndre Strømfjord, Greenland, 67°N

tirely from land sources and is favored by higher temperatures, with less than 10% of total CH₄ emissions occurring between 15°S-90°S latitudes. Consequently, there is much less opportunity for incomplete atmospheric mixing of recent CH₄ in the south temperate zone, and fluctuations in concentrations can be expected to be dampened at measurement sites in Chile. The standard deviation ($\pm 0.9\%$) among the 11 samples collected during 1980 at three Chilean locations between 23°S-53°S is smaller than that found in single north temperate latitudes such as that of Oregon, and suggests that seasonal variations are not very large in the temperate regions of the southern hemisphere. At each Chilean latitude, the observed concentrations of CH₄ increased by 0.054 ± 0.003 ppmv from January 1978 to January 1980.

Our measurements along the Oregon coast are compared in Table 2 with the daily (22 to 72 measurements each) CH₄ concentrations found at Cape Meares by Rasmussen and Khalil [unpublished data, 1981] on the individual days of our sample collections. Our Oregon data show essentially the same trends found in the much more extensive data set, apart from a systematic difference of 0.014 ± 0.008 ppmv. This 1% difference in absolute CH₄ calibration is not significant since the Cape Meares data are stated to have a precision of $\pm 0.7\%$ but an absolute accuracy of only $\pm 5\%$. Our data are thus fully consistent with both the seasonal and long term trends found by Rasmussen and Khalil. The daily fluctuations of as much as 0.08 ppmv in 1 σ standard deviations (Table 2) suggest the absence of good atmospheric mixing at

TABLE 2. Tropospheric CH₄ Concentrations in ppmv Oregon coast, 1979-1980

Date	This work	Cape Meares ^a
11 1 77	(1.574)	(Idaho)
6 20 79	1.592	1.607 ± 0.016
1 31 80		1.622 ± 0.018
2 2 80	1.607	
2 4 80		1.618 ± 0.018
5 14 80	1.658	1.668 ± 0.024
5 15 80	1.658	1.656 ± 0.031
8 14 80	1.628	1.646 ± 0.040
8 15 80	1.616	1.636 ± 0.037
11 24 80	1.653	1.670 ± 0.008
11 25 80	1.650	1.673 ± 0.008

(a) Rasmussen and Khalil, unpublished.

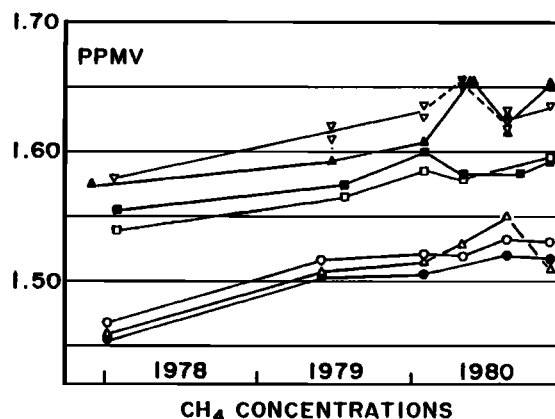
Cape Meares during the summer months, so that the geographic extent of the seasonal variations observed there remains to be established.

Our Alaskan measurements (Table 1) are consistent with the Oregon data, while perhaps indicating less seasonal variation. The West Indies are in latitudes containing major sources of CH₄, although emissions in these islands are only a minor contribution to the world total. The measurements there also showed an increase in CH₄ concentrations between 1978 and 1980.

The observation of a significant increase in CH₄ levels in seven locations well-spread from 55°N to 53°S is clearly not a localized phenomenon, and shows a worldwide increase in CH₄ concentration between 1978-1980. The 24-month increase from January 1978 to January 1980 ranged from 0.044 to 0.057 ppmv in the six locations of Table 1, with an average value of 0.052 ± 0.005 ppmv. The 34-month increase in Table 1 is about the same (0.054 ± 0.010), but the significance is limited by the absence of extensive seasonal data for these locations.

Atmospheric Methane Concentrations before 1978

If the yearly increase in CH₄ observed here for the period from 1978-1980 also occurred prior to 1978 at a similar rate, then the concentration of CH₄ a decade ago would have been 0.2-0.3 ppmv less than now, or about 1.3-1.4 ppmv in 1970. Two series of measurements of CH₄ concentrations were

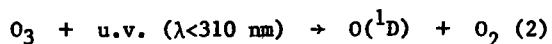
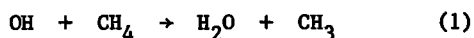
Fig. 1. Methane concentrations during 1977-1980. ∇ 67°N; ∇ 56°N; \blacktriangle 45°N; \blacksquare 18°N; \square 13°N; \triangle 23°S; \bullet 42°S; \circ 53°S.

made in 1972 with samples collected on the same ship on its track from 34°N to 77°S. Both data sets originally gave a worldwide concentration then of about 1.35–1.40 ppmv CH₄. However, a calibration error {Heidt and Ehhalt, 1980} of a factor of 1.2 has led to adjustment of the NCAR data {Ehhalt, 1974, 1978} to a worldwide 1972 average of about 1.6 ppmv, in disagreement with the NRL data {Lamontagne *et al.*, 1974; Wilkniess *et al.*, 1979}, and at least one set must be in error. If the new NCAR values for 1972 are correct the trend in our data during 1978–1980 could represent the "up" leg of a cyclic variation. On the other hand, if the NRL data for 1972 are correct, then our observations would be consistent with a steady increase during the period 1972–1980. Other measurements have been summarized for the 1960–1972 period {Ehhalt, 1974; Dianov-Klovov, 1975} which provide estimates of CH₄ abundances ranging between 1.2–1.7 ppmv. Without resolution of the conflict over the 1972 CH₄ levels we are unable to draw any inferences about CH₄ concentrations or trends with time prior to the period of our measurements.

Sources and Sinks for Methane

The 1979 average worldwide concentration of about 1.56 ppmv CH₄ corresponds to a total of 4.2×10^{15} grams in the entire atmosphere. We have estimated the average atmospheric lifetime of CH₄ as (10.5 ± 1.8) years {Mayer *et al.*, 1982} by analogy with the (6.9 ± 1.2) year lifetime of CH₃CCl₃ inferred from the ratio of its atmospheric concentration to its estimated total atmospheric release {Makide and Rowland, 1981}. Other estimates of the CH₃CCl₃ atmospheric lifetime are in the range from 5–10 years {WMO, 1982}, corresponding to an 8–15 year range for CH₄. The required yearly destruction of CH₄ and replenishment by fresh emissions for a lifetime of 10.5 years and a range from 8–15 years is then in steady-state $(4.0 \pm 1.3) \times 10^{14}$ grams CH₄ per year. An increase of 0.052 ± 0.005 ppmv CH₄ in two years corresponds to $(1.4 \pm 0.2) \times 10^{14}$ grams, or $35 \pm 12\%$ of the estimated yearly steady-state flux.

The observed increase in CH₄ concentration between 1978–1980 requires a yearly excess of 0.7×10^{14} grams for sources over sinks, roughly 17±5% of the yearly total. The only major removal process for CH₄ is through reaction (1) with OH, whose chief atmospheric source is driven by solar photochemistry, as in (2) and (3) {Chameides and Tan, 1981; Logan *et al.*, 1981}. The major removal processes for OH radicals in the lower tropo-



sphere are its reactions with CO and CH₄, while the oxidation of CH₄ is itself one of the several important sources of atmospheric CO {McConnell *et al.*, 1971; Chameides *et al.*, 1977; Chameides and Tan, 1981; Logan *et al.*, 1981}. An increase in CH₄ of 0.05–0.06 ppmv in 24 months could result from a decrease in OH concentrations, which might in turn result from an increase in CO concentrations. No other tropospheric indications of in-

creased CO or decreased OH concentrations seems to have occurred between 1978 and 1980, although measurements with the requisite precision and sufficient global coverage probably do not exist for either CO or OH. The total column abundance of OH has been reported to have increased by $1 \times 10^{13} \text{ cm}^{-2}$ per year over the full years of 1977 and 1978, an increase of about 25% {Burnett and Burnett, 1981}. However, the major reactions of OH with CH₄ and CO occur in the lower troposphere and the column abundance of OH below 6 km represents less than 10% of the atmospheric total.

Most atmospheric CH₄ is biological in origin, and some of the major anthropogenic sources have been increasing steadily in recent years. The land area devoted to rice paddies has increased during the period from 1960–1980, although the absolute emissions from this source have not yet been determined with precision {Cicerone and Shetter, 1981}. Another important source of biological methane is enteric fermentation in mammals, and the number of domesticated mammals has likewise grown steadily during the past 20 years.

Our present data do not provide any conclusive information concerning the origin of the current imbalance between the strengths of the sources and sinks for methane. The magnitude of the OH sink is controlled by CO, CH₄ and other hydrocarbons only if no changes occur in the lower troposphere for the averaged parameters which affect OH production directly: the concentrations of H₂O and O₃ and the ultraviolet fluxes. Adequate data do not now exist to define the limits on possible cyclical or secular changes in these related variables, or in the complex interactions among them which determine the ambient OH concentrations. It is thus possible that the magnitude of the OH sink has been reduced during the last few years by such variations involving reactions (2) and (3). While it seems unlikely that the total release from CH₄ sources could have increased by 15% over the period between 1978 and 1980, changes of a few percent are certainly possible.

If CH₄ concentrations in the atmosphere continue to increase, then other perturbations to the atmosphere become more and more complex and far-reaching in their effects. The absorption of outgoing infrared radiation by CH₄ would increase, contributing to the general rise in tropospheric temperatures now expected from the "greenhouse" effect calculated for CO₂ plus the fluorinated molecules such as CCl₃F and CCl₂F₂ {Wang *et al.*, 1976; Lacis *et al.*, 1981}. Methane is also the most important reactant in the stratosphere for diversion of chlorine from the ozone-depleting ClO_x chain into HCl. The interactions continue to propagate beyond these direct effects, and it is not now possible to estimate all of the long range effects which would accompany continued increases in CH₄ concentrations at 0.02–0.03 ppmv per year.

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