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GLOBAL ATMOSPHERIC DISTRIBUTION AND TREND OF METHYLCHLOROFORM (CH_3CCl_3)

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Abstract. Over the last two years atmospheric measurements of methylchloroform (CH_3CCl_3) have been made at six locations using EC/GC techniques. The concentrations are reported, and it is shown that CH_3CCl_3 concentrations increased at rates of 3.8%±2.1% per year at Alaska (∿70°N) between 8/79 and 1/81, 6.6%±3.2% per year at Oregon (∿45°N) between 1/79 and 1/81, 4.3%±4% per year at Hawaii (24°N) between 11/79 and 1/81, 4.1%±4.8% per year at Samoa (14°S) between 2/80 and 1/81, 11.5%±1.5% per year at Tasmania (42°S) between 1/79 and 6/80, and at 8.7%±5.7% per year at the south pole between 1/79 and 1/81. These recent yearly increases are smaller than earlier rates of increase but are consistent with a lifetime of ∿7 years (6 years-10 years) and a decline in the rate of global emissions.

Introduction

Methylchloroform (CH_3CCl_3), manufactured primarily for use as an industrial degreasing solvent, has been released into the earth's atmosphere in steadily increasing amounts since the early 1950's (Neely and Plonka, 1978). In 1974 Molina and Rowland proposed that the inert, man-made fluorocarbons CCl_3F and CCl_2F_2 were being emitted in sufficient quantities that their continued use could release atomic chlorine in the stratosphere which could catalytically destroy enough of the earth's natural ozone layer to cause damage to human health by allowing more ultraviolet radiation, normally absorbed by ozone, to reach the earth's surface. It was also discovered that these man-made gases efficiently absorb infrared radiation so that their accumulation in the troposphere could lead to a global warming, affecting the earth's climatic and agricultural patterns (Ramanathan, 1975; Kellogg, 1980). It soon became clear that large and increasing emissions of other man-made gases such as CH_3CCl_3 and CCl_4 would have similar environmental consequences (Crutzen et al., 1978; McConnell and Schiff, 1978). Unlike CCl_3F and CCl_2F_2, some of the methylchloroform is removed in the troposphere after reacting with atmospheric hydroxyl radicals. Nevertheless, the growing atmospheric burden of CH_3CCl_3 is cause for concern about the earth's future environment (NAS, 1980). Atmospheric measurements of CH_3CCl_3 which can reveal its atmospheric behaviour and ultimate environmental role have been made over the last eight years, first by Lovelock et al. (1973) and systematically since 1975 by Rasmussen et al. (1981), as well as by several other groups (see Rasmussen and Khalil, 1981).

In this paper we discuss the results of global CH_3CCl_3 measurements representing its concentrations at Pt. Barrow and Poker Flats, Alaska (∿70°N), Cape Meares, Oregon (45°N), Cape Kumakahi, Hawaii (24°N), Samoa (14°S), Cape Grim, Tasmania (42°S), and a few from the south pole (90°S).

II. Atmospheric Concentrations and Trends

Once a week three samples were collected in specially designed flasks at the sites in Alaska, Hawaii and Samoa. These were sent by airmail to the Oregon Graduate Center's Atmospheric Trace Gases Laboratory where CH_3CCl_3 concentrations were determined by electron capture-gas chromatographic techniques (EC/GC). Similar measurements were made for flask samples from the south pole, but only during January of every year (Rasmussen et al., 1981). Automated EC/GC measurements made every Friday at the sites in Tasmania and Oregon have been selected for this report. Details of the flask sampling systems and EC/GC analysis sre given by Rasmussen and Khalil (1980).

The results of the observations at the six locations are shown as monthly average concentrations of CH_3CCl_3 in Figure 1. The data from which Figure 1 was derived have been included in the microfilm appendix.

To determine the rates of increase of CH_3CCl_3 we used the model $(1/C)dC/dt = \beta$ and applied classical least squares techniques to estimate the average β (denoted $\bar{\beta}$) which is insensitive to errors in absolute accuracy. The results are reported in Table 1 along with $\delta\bar{\beta}$ where $\bar{\beta}\pm\delta\bar{\beta}$ gives the 90% confidence limits for $\bar{\beta}$ using the t-statistic which is also used to test whether $\bar{\beta}$ is significantly greater than zero at the α level of significance.

A latitudinal profile can be constructed from these data as shown in Figure 2 for two different periods about a year apart (1980 and 1981). The latitudinal profile shows a bump at high northern latitudes where most of the sources are. Taking these features into account, average concentrations over the northern and southern hemispheres were calculated which showed that over the two years from 1/1979 to 1/1981 the global atmospheric concentration rose at 6.7%±2.0% per year. The calculated average concentrations for both hemispheres are also given in the appendix. Rates of increase calculated for the hemispherically and globally averaged data are mean values over two years, whereas the rates of increase calculated for each site span different and generally shorter times.

Independent data (Khalil and Rasmussen, 1981) verify that the atmospheric concentrations of CH_3CCl_3 increased by a smaller percentage during 1980 than during 1979. This is a part of a general decline in the atmospheric rate of increase

[1] Supplement (data, tables) is available with entire article on microfiche. Order from American Geophysical Union, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Document L81-008; $1.00. Payment must accompany order.

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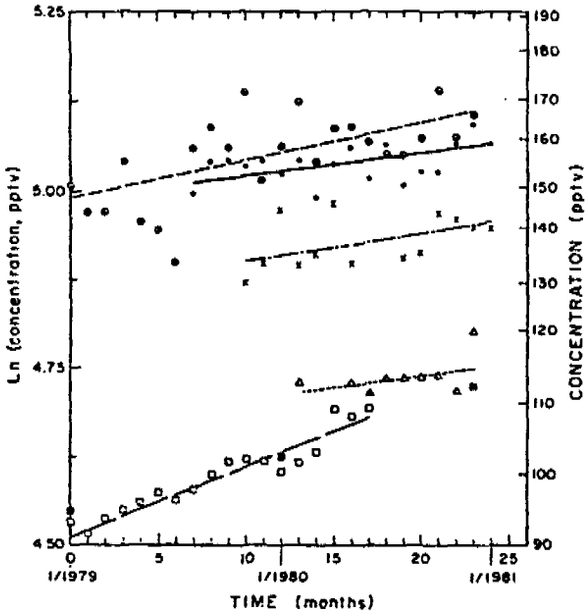

Figure 1. Monthly average concentrations of CH_3CCl_3 at six sites. ——— = Pt. Barrow and Poker Flats, Alaska (~70°N); ⊙- - -⊙ = Cape Meares, Oregon (~45°N); X—— - —— -X = Cape Kumakahi, Hawaii (24°N); Δ - - - Δ = Samoa (14°S); □ —— —— □ = Cape Grim, Tasmania (42°S); ■ = South Pole (90°S).

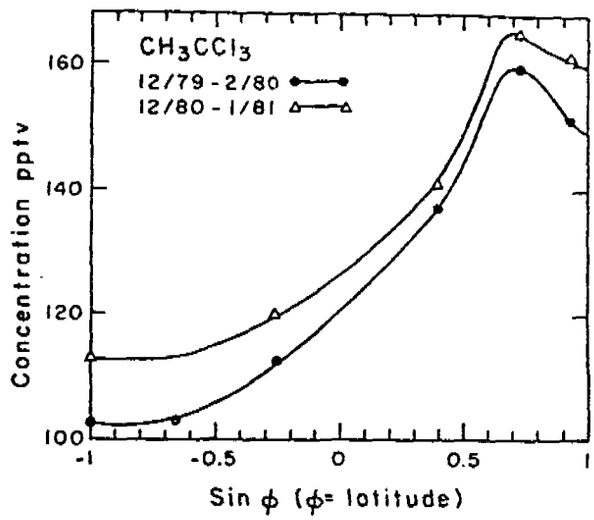

Figure 2. Latitudinal variation in the concentration of CH_3CCl_3 shown at two times about a year apart.

since 1975 which can be explained by the reduction in the rate of increase of emissions. For example, the global emissions of CH_3CCl_3 increased exponentially at about 17% per year between 1956 and 1973, but at only 8% per year on the average between 1974 and 1979 and increased hardly at all over the past three years. Therefore, the average global increase of 6.7% yr^{-1} observed over the last two years is a composite of faster increase during 1979 and a somewhat slower increase during 1980. The calculated rates of increase are consistent within their limits of uncertainties.

Regarding the global emissions as constant since 1979, the average expected rate of increase using a global mass balance can be written as:

$$\bar{\beta} = \frac{1}{T}\left[\ln\left(1 + \frac{S_o}{\eta C_o}\left(e^{\eta T}-1\right)\right) - \eta T\right] \qquad (1)$$

where (0-T) is the time over which the average rate of increase is calculated (here 2 years), C_o is the number of molecules of CH_3CCl_3 in the entire atmosphere at time zero, S_o are the (constant) emissions in molecules per year and $\eta = 1/\tau$ where τ is the global lifetime. Putting $\bar{\beta}$ = 0.067±0.02 per year as calculated from the observations, C_o calculated from a in Table 1, and S_o corresponding to 1.05×10^9 lbs/yr (Neely and Farber, 1980), we obtain a lifetime of 7 years. The ratio S_o/C_o is uncertain enough (±10%) that lifetimes (τ) between 6 years and 10 years are also consistent with eqn. (1) and an increase rate of 6.7±2% per year. Here we want only to demonstrate that the atmospheric trends of CH_3CCl_3 as shown in Figure 1 and Table 1 are in

Table 1. INCREASE OF ATMOSPHERIC CH_3CCl_3 AT SIX LOCATIONS ON THE EARTH'S SURFACE

Location	Duration of Sampling (Number of Months Samples Were Collected)	a (pptv)	$\bar{\beta} \pm \delta\bar{\beta}$ (% per yr)	$\beta > 0$?
Alaska (70°N)	8/79-1/81 (18)	150	3.8±2.1	Yes (α = 0.005)
Cape Meares (45°N)	1/79-1/81 (24)	146	6.6±3.2	Yes (α = 0.005)
Hawaii (24°N)	11/79-1/81 (13)	135	4.3±4.0	Yes (α = 0.05)
Samoa (14°S)	2/80-1/81 (9)	112	4.1±4.8	Undetermined
Tasmania (42°S)	1/79-6/80 (18)	92	11.5±1.5	Yes (α = 0.005)
South Pole (90°S)	1/79-1/81 (3)	94	8.7±5.7	Yes (α = 0.05)
Northern Hemisphere	1/79-12/80	130	6.7±3.0	Yes (α = 0.005)
Southern Hemisphere	1/79-12/80	99	6.7±1.6	Yes (α = 0.005)
Global Average	1/79-12/80	115	6.7±2.0	Yes (α = 0.005)

a is the mixing ratio (pptv = 10^{-12}) of concentrations at beginning of the sampling at each site calculated by least squares techniques. $\bar{\beta}$ is the average increase based on $(1/C)dC/dt = \beta$ and $\bar{\beta} \pm \delta\bar{\beta}$ give the 90% confidence limits of $\bar{\beta}$ based on the t-statistic.

accord with the known sources and lifetime of CH_3CCl_3 (see Jesson, 1980).

In time, as more data are obtained from these sites, an accurate determination of the atmospheric lifetime will become possible. Coupled with information on the sources and specific global sinks of CH_3CCl_3, its potential role in the earth's environment can then be determined.

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