Tellus (1984), *36B*, 317–332

The atmospheric lifetime of methylchloroform (CH_3CCl_3)

By M. A. K. KHALIL and R. A. RASMUSSEN, *Department of Environmental Science, Oregon Graduate Center, 19600 N. W. Walker Rd., Beaverton, OR. 97006, USA*

(Manuscript received November 29, 1983; in final form June 21, 1984)

ABSTRACT

The lifetime of atmospheric methyl chloroform (CH_3CCl_3) is estimated to be about 6 ($\pm$1.5) years based on extensive measurements taken over the past seven years at remote locations of the world, ranging from inside the Arctic Circle to the South Pole. The average level of tropospheric hydroxyl radicals (OH) deduced from the lifetime of CH_3CCl_3 is about 8×10^5 molecules/cm^3, but this value is uncertain by up to $\pm$75%.

1. Introduction

For many, years methylchloroform (CH_3CCl_3), an industrial degreasing solvent, has been accumulating in the earth's atmosphere, although the rates of increase are now considerably slower than in earlier years (Rasmussen et al., 1980, 1981; Khalil and Rasmussen, 1981a). While present atmospheric levels of CH_3CCl_3 are too low to perceptibly affect the global environment, it has been suggested that the accumulation of CH_3CCl_3 may eventually contribute to a depletion of the stratospheric ozone layer (Crutzen et al., 1978; NAS, 1979). Such global effects are often controlled by the lifetimes of anthropogenic trace gases and in particular by the presence of tropospheric sinks. Since the effects of increasing levels of anthropogenic trace gases, including the depletion of stratospheric ozone, depend on the tropospheric burden of the trace gas, a short lifetime allows for greater emissions before affecting the environment, and provides the opportunity to quickly control undesirable environmental effects should they become significant. Therefore, the controversy on the potential global effects of continuing or increasing emissions of CH_3Cl_3 rests on estimates of its atmospheric lifetime. These estimates have varied over an order of magnitude, ranging from about one year to more than ten years (Yung et al., 1975; Cox et al., 1976; Singh, 1977a, b; Crutzen and Fishman, 1977; McConnell and Schiff, 1978; Rasmussen and Khalil, 1981b; Rasmussen et al., 1980; Makide and Rowland, 1981; Chang and Penner, 1978; Neely and Plonka, 1978; NAS, 1976; Lovelock, 1977; Jesson, 1980; Chameides and Tan, 1981; Logan et al., 1981; Prinn et al., 1983; Chang and Kaufmann, 1977). While many recent calculations tend to cluster around the upper limits, including an average lifetime of around 10 years (range 8–15 years) suggested by Prinn et al. (1983), no consensus has yet emerged. For the case of CH_3CCl_3 in the environment this uncertainty in lifetime is of considerable importance. If the emissions remain at present levels, not enough CH_3CCl_3 will accumulate to significantly affect the future global environment if its lifetime is around 5 years, but the potential effects of CH_3CCl_3 may be cause for concern if its lifetime is ten years or longer.

In addition to the environmental role of CH_3CCl_3, it has also been regarded as an indicator of the average level of tropospheric hydroxyl radicals (OH) (Lovelock, 1977; Singh, 1977a, b; Prinn *et al.*, 1983). OH radicals remove dozens of man-made and natural trace gases from the atmosphere, yet at present no practical means has been found to obtain a direct measure of their global average levels primarily because their concentrations are extremely low and vary enormously in both space and time.

In this paper, we will show that the lifetime of CH_3CCl_3 is about 6 ($\pm$1.5) years based on

world-wide measurements spanning seven years. We will apply our findings to show that average OH levels are probably around 8×10^5 molecules cm^{-3}; however, this estimate is uncertain by up to $\pm 75\%$. We will describe and evaluate the various uncertainties that still exist for determining the lifetime or estimating OH concentrations from the mass balance of CH_3CCl_3.

In Section 2 we will define our mass balance model relating annual emissions, a time series of measured concentrations, and the lifetime so that when any two are measured, the third can be calculated. Both the global burdens and their trend or rate of change are compared with observed values to obtain the best-suited lifetimes. The uncertainties affecting the estimate of the lifetime are evaluated. In Section 3 we discuss the estimate of average OH concentration in the troposphere and show that large uncertainties remain.

2. Lifetime of CH_3CCl_3

2.1. *Lifetime*

The change of the global burden of CH_3CCl_3 with time results from the opposing effects of continuing emissions and losses. Specific mechanisms for the losses need not be known as long as one can assume that they are of first order; namely, proportional to the existing total burden or concentration. For CH_3CCl_3, reaction with OH radicals in the troposphere is assumed to be the principal removal pathway, whereas destruction in the stratosphere and absorption by the oceans remove relatively small amounts. The combined effects of all removal mechanisms constitute the lifetime, τ. The mass balance may therefore be written simply as:

$$dC_B/dt = S_B - \left(\frac{1}{\tau}\right) C_B, \tag{1}$$

where C_B is the global burden (gm), S_B are the global emissions (g yr^{-1}), and τ is the lifetime (years). The global industrial emissions rose unsteadily at an average exponential rate of about 15% per year to about a billion pounds a year around 1978 and have since stayed nearly the same (Neely and Plonka, 1978; Neely and Farber, 1982, personal communication; Khalil and Rasmussen, 1981a, b). Eq. (1) may be solved for C_B so that:

$$C_B(t; \tau) = e^{-\eta t} \int_0^t S_B(v)\, e^{\eta v}\, dv, \tag{2}$$

where $\eta = 1/\tau$ and it is assumed that $t = 0$ when no methylchloroform existed in the atmosphere, here taken to be around 1957 (Neely and Plonka, 1978; Rasmussen and Khalil, 1981b; Crutzen et al., 1978; NAS, 1979). This calculated global burden can be related to the average tropospheric mixing ratio (C) by eq. (3):

$$C(t; \tau) = \frac{N_0}{M(N_T + \alpha N_S)} C_B(t; \tau) \equiv f C_B, \tag{3}$$

where M is the molecular weight of CH_3CCl_3, N_0 Avogadro's number, N_T and N_S the numbers of molecules of air in the troposphere and stratosphere respectively. The average mixing ratio of CH_3CCl_3 in the stratosphere is a fraction (α) of the tropospheric mixing ratio ($\alpha = 0.3$, $N_T = 8.69 \times 10^{43}$, $N_S = 1.95 \times 10^{43}$ (Khalil, 1979)). For each assumed lifetime τ, the expected average tropospheric mixing ratio can be calculated from eqs. (2) and (3) as shown in Fig. 1.

Since early 1975, Rasmussen has taken measurements of CH_3CCl_3 in both hemispheres. All the measurements since January 1976 are referenced to the same primary calibration standard, and have been made with similar gas chromatographs equipped with electron capture detectors. At first, measurements were taken only near the laboratory, in the US Pacific northwest ($\sim 45°$ N), and each January at the South Pole. Since mid-1978, six additional sites have been added one by one. The data obtained are described in Table 1; they are given in complete form in the appendix. Data from six of the sites are obtained by analyzing flask samples collected weekly; data from Tasmania, Oregon, and Samoa are based on nearly continuous measurements taken with automated instruments. It has been demonstrated by periodic analyses of the standards that their concentrations have remained the same over the years since 1976; however, the absolute concentration has been reassigned a value which is 80% of its previous estimate. An interlaboratory calibration study conducted in 1979 (Rasmussen and Khalil, 1981a) had shown that laboratories using Rasmussen's standard tended to report systematically higher concentrations of CH_3CCl_3 than independent

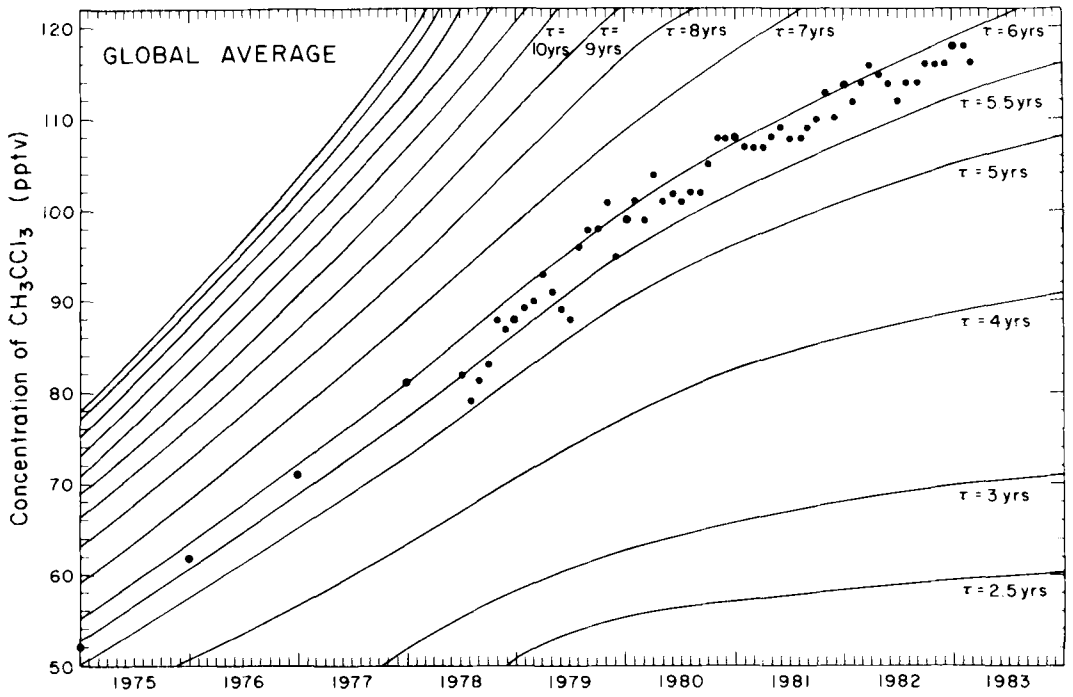

Fig. 1. The average tropospheric concentration of methylchloroform (CH_3CCl_3) from 1975 to 1983. The solid lines are concentrations expected on the basis of estimated global emissions from 1957 to the present. Expected concentrations are shown for various lifetimes between 2.5 years and 15 years. The estimate of global average mixing ratio is shown as solid circles. The best suited lifetime is seen to be between 5 and 6 years.

laboratories, and similar results had been found in earlier interlaboratory calibration exercises. Although the disagreements between the various laboratories were not large, they were sufficient to significantly affect the estimated global lifetime, prompting us to re-evaluate the absolute concentration in the original 1976 calibration standard. The latest calibration standards were prepared from samples of pure methylchloroform injected into 35L internally passivated stainless steel containers. Analyses of these standards showed that the concentration of CH_3CCl_3 in the 1976 standard was only 80% of the originally estimated value. Further details of the procedures and recalibration are discussed elsewhere (Khalil and Rasmussen, 1984).

The data from the eight sites summarized in Table 1 were combined to estimate the average tropospheric mixing ratio so that it could be compared with its expected values obtained from eqs. (2) and (3). The mixing ratio of CH_3CCl_3 changes with latitude, being highest in the northern part of the northern hemisphere, (C_n), where most of the industrial sources are, and declining as one moves southward. In the tropics the concentration of CH_3CCl_3 is found to be lower by about 5 pptv ($\simeq 5\%$) above the planetary boundary layer than at sea level (Rasmussen and Khalil, 1981c, 1982); this effect, though small, has been included in our estimate of the average tropospheric mixing ratio, $C_0(t)$, based on data from the eight sites. The atmosphere was divided into four boxes containing nearly equal amounts of the atmosphere, at latitudes 90° N–30° N, 30° N–0, 0–30° S, 30° S–90° S; these boxes were designated, C_n, C_{nt}, C_{st}, and C_s respectively. $\bar{C} = [C_n + C_{nt} + C_{st} + C_s]/4$, where $\bar{C}$ is the average mixing ratio in eq. (3). Measurements taken simultaneously at Oregon and Alaska were averaged to obtain C_n; measurements taken at Kumukahi (Hawaii) and nearby Mauna Loa (Hawaii) were weighted appropriately to obtain C_{nt}, including the difference of concentrations in and above the boundary layer. Similarly weighted measurements taken at Samoa

Table 1. *Description of the global time series of methylchloroform measurements:*

$$C = A + Bt + Ct^2$$

Location	Latitude	A (pptv)	B (pptv yr^{-1})	C (pptv yr^{-2})	R	N (months)	Span
Barrow, Alaska	70° N	126	9.7	−0.7	0.857	24	Aug. 1980–Nov. 1982
Washington & Cape Meares, Oregon	45° N	64	15.4	−0.8	0.966	76	Jan. 1975–Mar. 1983
Kumukahi, Hawaii	20° N	105	11.3	−1.8	0.855	35	Nov. 1979–Mar. 1983
Mauna Loa, Hawaii	20° N	110	6.2	—	0.707	16	Feb. 1981–Jan. 1982
Samoa	14° S	69	13.0	−1.2	0.987	52	Jan. 1978–Jan. 1983
Cape Point, South Africa	34° S	94	5.0	—	0.621	14	Feb. 1981–Feb. 1983
Cape Grim, Tasmania	42° S	67.6	10.4	−0.6	0.991	54	Jan. 1978–Dec. 1982
South Pole	90° S	46	11.2	−0.5	0.997	7	Jan. 1975–Jan. 1982

R is the coefficient of determination analogous to the correlation coefficient, and N is the number of months during which data were obtained. Data accumulated over long times from the same sites reveal consistent and similar patterns of changing concentrations. At Mauna Loa and Cape Point the data spanned too short a time to expect to see a decline in the rate of accumulation; for these sites a linear model was used.

were used to determine C_{st}. Measurements from South Africa, Tasmania, and the South Pole were averaged to obtain C_s. The resulting monthly averages of mixing ratios (C_0 or $\bar{C}$) are shown in Fig. 1 as circles and given in the appendix.

The observed time series of tropospheric mixing ratio C_0 can be compared to the calculated mixing ratio by defining the sum of the squared deviations V:

$$V = \sum_{k=1}^{N} [C(k; \tau) - C_0(k)]^2. \quad (4)$$

The lifetime τ_* which is most consistent with the observations corresponds to the curve $(C(t, \tau_*))$ for which V in eq. (4) is a minimum so that $\partial V/\partial \tau = 0$ at $\tau = \tau_*$. τ_* by this method turns out to be 5.8 years (±0.4 years) (Table 2 and Parrott, 1961).

The estimated global industrial emissions explain both the present concentration of CH_3CCl_3 and the long-term rate of change or trend in mixing ratio, including the recent slowdown in atmospheric accumulation. If the lifetime of CH_3CCl_3 were much longer, the rate of increase would not have slowed as much as has been observed.

From Fig. 1 it can be seen that not only are the expected mixing ratios different for different lifetimes, but so are the expected rates of increase of CH_3CCl_3. Thus, the observed rate of increase can also be used to estimate the lifetime. Such a model was suggested by Cunnold et al. (1978), which related $\beta = (1/C)\, dC/dt$ to the lifetime. According to eqs. (1)–(3):

$$\beta(t; \tau) = S_B[e^{-\eta t} \int_0^t S_B(v)\, e^{\eta v}\, dv]^{-1} - \eta, \quad (5)$$

$$\beta(t; \tau) \equiv [1/C(t; \tau)]\, dC(t; \tau)/dt. \quad (6)$$

It is argued that since $\beta(t; \tau)$ contains the mixing ratio, C, in both numerator and denominator, it is not sensitive to systematic errors in the absolute accuracy of measurements. Moveover, the systematic errors in estimating emissions also cancel on the right-hand side of eq. (5). Therefore, the best-suited lifetime determined by this method would be similarly insensitive to systematic errors of absolute calibration, atmospheric measurements, and estimated emissions. On the other hand, this method appears to be more sensitive to random

variations than the global mass balance of eqs. (1)–(3) discussed earlier.

We employed this trend method to verify the lifetime estimated earlier by using eqs. (1)–(4). The data spanning the years 1978 to the present are most suitable for this analysis since they are abundant, equally spaced in time, and based on measurements at many latitudes (see Table 1). These data we considered as one group; the older data obtained in January of each year were put into a second group augmented by measurements every January to 1983. The (observed) rate of change $(1/C_0)\ dC_0/dt = \beta_0$ fluctuates enormously over short time spans. We therefore calculated an average $\langle \beta_0(t) \rangle$ over 36-month overlapping intervals of time by a linear least squares technique to smooth the fluctuations. Similarly, we calculated the average expected (smoothed) rate of increase $\langle \beta(t; \tau) \rangle$ based on eqs. (5) and (6) for lifetimes τ, ranging from 2 to 14 years. The results of these calculations are shown in Fig. 2a along with estimates of approximate 90% confidence limits of the observed increase $\langle \beta_0 \rangle$. Similar results were found for the second group of data consisting of observations made every January (Fig. 2b). The sum of the squared deviations defined as

$$V_{(\beta)} = \sum_{k=1}^{N} |\langle \beta(k; \tau) \rangle - \langle \beta_0(k) \rangle|^2$$

is minimum for τ_* (lifetime) of about 7 years for the two groups of data (Table 2).

Inspection of Figs. 2a and 2b shows that the calculated trend (β) is not especially sensitive to the lifetime ($\tau > 4$ years). Therefore, small errors in the observed trend or the random errors in estimated emissions may cause sizeable uncertainty in the lifetime deduced by this method. Although the lifetime of methylchloroform has probably remained the same, the estimated lifetime may vary depending on the period chosen in Fig. 2. For instance, in Fig. 2a during 1978–80 the estimated

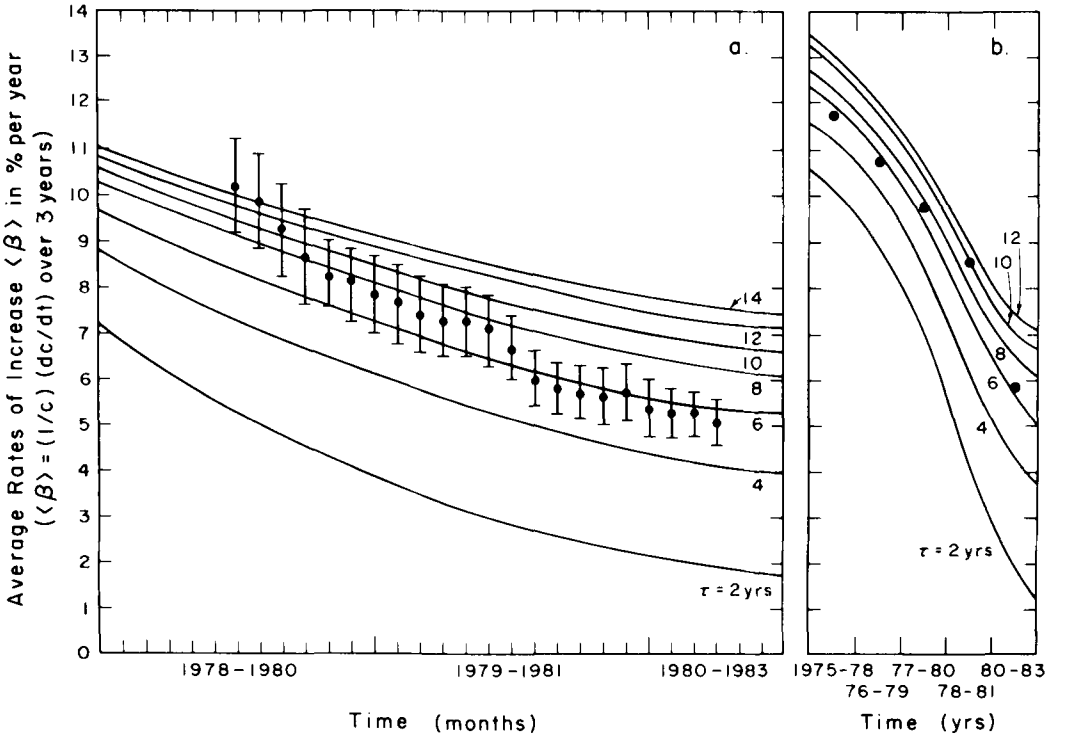

Fig. 2. The rate of accumulation of CH_3CCl_3 in the atmosphere in % per year. Methylchloroform was accumulating faster in previous years than it is now. The calculations and observations shown here are for three year overlapping periods from July 1978 to March 1983 during which period monthly data were obtained all over the world. Fig. 2b is similar to Fig. 2a, except data are taken only for January of each year and spans 1976–1983.

Table 2. *Atmospheric lifetime of methylchloroform (CH_3CCl_3) determined by a global mass balance*

Model	τ (yr)	(τ_L, τ_u) (yr)	Span of data base (years)
Time series of global burden	5.8	(5.4, 6.2)	Jan. 1976–Mar. 1983 (8) All data.
	6	(5.8, 6.2)	Jan. 1976–Jan. 1983 (8) Data only from January of each year.
Average rate of relative increase	7	(wide range)	Jan. 1978–Mar. 1983 (4.5) All data, monthly.
	7	(wide range)	Jan. 1976–Jan. 1983 (8) Data only from January of each year.

τ is the lifetime determined by non-linear least squares techniques; τ_L and τ_u are the approximate 90% confidence limits based only on the observed variability of the data and not on possible errors in global emission estimates or absolute calibration. The systematic errors in calibration and estimated emissions may result in an additional uncertainty of $\Delta\tau = \pm 1$ year.

lifetime may be long (~8–10 years), whereas at later times the lifetime is 6–8 years. On the whole, though, the composite lifetime is 7 years for all the years of the measurements combined. Here we simply demonstrate that all things considered, the results found by the two methods, using average concentrations (Fig. 1) and rate of change (Fig. 2), are in general agreement.

2.2. *Uncertainties*

Estimates of the lifetime are confounded by uncertainties in all aspects of the mass balance. In eq. (1) estimates of the global burden, C_B, and emission, S_B, are subject to both systematic and random errors whose magnitudes cannot be rigorously evaluated. The emissions are uncertain in quantity, year-to-year variation, and seasonality. The monthly burden C_B, although estimated from more experimental stations than ever before, still does not include observational data from all relevant parts of the atmosphere including changes of concentration with height, particularly in the stratosphere. Moreover, samples are collected weekly over short periods of time and may not always represent the month. Concentrations at each site are subject to fluctuations caused by natural variability of air motions including mild, and occasionally more severe, pollution episodes. In addition, experimental errors may be introduced after the samples are collected. A particular sample may be contaminated at the site or while in transit or may be influenced by storage. The laboratory measurement of concentration is based on a prepared calibration standard which at the extremely low concentrations of a few 100's of pptv is subject to systematic errors. The mass balance model itself, although simple, contains assumptions that may lead to inaccuracies. Over the years many of these uncertainties have been considerably reduced or eliminated by new laboratory techniques and experimental design (Rasmussen and Khalil, 1980). Sample collection, storage, and contamination are no longer important problems; the many sites and frequent sample collection reduce the effects of natural variability, and pollution events can be identified and discarded. The random errors in the measurements and natural atmospheric variability are reflected in the observed variability of global concentrations shown in Fig. 1 (C_0). This variability, however, is small, having an estimated standard deviation from the best curve $C(t, \tau_*)$ of only about 2.2 pptv, and it is therefore not a major uncertainty in the estimated lifetime (Table 1), amounting to less than ± 0.5 year for the lifetime. Therefore, since plenty of measurements have been taken over a long time span, the

average lifetime from the mass balance is relatively insensitive to random errors in absolute concentrations or estimated emissions.

Systematic errors may also exist in determining absolute concentrations and global emissions. These potential errors are more important for estimating the accuracy of the calculated lifetime. Calibration errors are likely to be mostly systematic while errors in estimates of emissions are difficult to quantify and may be both random and systematic. The estimates of global emissions are based on industry records of CH_3CCl_3 production in the US and its sales world-wide (Neely and Plonka, 1978; Neely and Farber, 1982, personal communication; Khalil and Rasmussen, 1981a). A recent and detailed account of the global emissions of CH_3CCl_3 is given by Prinn et al. (1983). It is easy to miss losses of CH_3CCl_3 during the production process; moreover, use and emission of CH_3CCl_3 from other industrialized countries such as the USSR, Japan, and China have been extremely difficult to estimate accurately. Thus, emissions are more likely to be under-estimated than over-estimated. The effect of systematic errors in S_B and C_B on the estimated lifetime ($\delta\tau$) may be deduced from eq. (2) and Fig. 1. We chose a simple graphical method to conclude that $\delta\tau \simeq 0.1$ ($\delta C_B - \delta S_B$) when $|\delta C_B - \delta S_B| \leqslant 20\%$, where δC_B and δS_B are percent systematic errors ($\delta x = (x_{true} - x_{est})\ 100/x_{est}$) in absolute calibration and estimated emissions respectively, and $\delta\tau$ is the corresponding uncertainty in the estimated lifetime obtained by the global mass balance method. This equation is obtained from Fig. 1 by estimating the effect of varying the observed C_B systematically by up to $\pm 20\%$. If all the observed concentrations are reduced by say 10%, then in Fig. 1 the new values will fall on the line for the lifetime of 5 years. Therefore, a 10% reduction of absolute concentrations leads to a 1-year reduction of lifetime. Similarly, if the emissions are increased by say 10%, then according to eq. (2) the effect on the lifetime is the same as decreasing the observed concentrations by 10%. The equation discussed above is derived in this matter from Fig. 1. Similar relationships can be derived from Fig. 1 for the case when the sum $|\delta C_B - \delta S_B|$ exceeds 20%. Systematic errors in C_B and S_B may have opposite effects on the calculated lifetime, thus reducing $\delta\tau$. Present laboratory studies suggest that absolute accuracy is about $\pm 5\%$ or $\delta C_B \simeq \pm 5\%$. If the systematic errors in estimated emissions are also $\pm 5\%$ ($S_B = \pm 5\%$), then $\delta\tau \simeq \pm 1$ year. Thus, the likely combined uncertainty in estimated lifetime is about ± 1.5 years due to random variations of the concentration and estimated systematic errors of C_B and S_B. As stated earlier, random errors are reflected in the statistical estimate of variability shown in Table 1. At present possible systematic errors in the estimated global emissions of CH_3CCl_3 cannot be rigorously evaluated and remain an important source of uncertainty for determining the lifetime; however, it is likely that these errors will support a somewhat shorter lifetime rather than a longer one, and the mass balance model is less sensitive to these errors as one goes to shorter lifetimes (see Fig. 1).

3. Global OH concentration

3.1. Estimate of average OH density

If the lifetime of CH_3CCl_3 is estimated by a global mass balance, as in Section 2, then one may estimate the average number of tropospheric hydroxyl radicals required per unit volume of air to explain this independently estimated lifetime (Lovelock, 1977; Singh, 1977a, b). The annual removal rate of CH_3CCl_3 by reactions with OH is $(1/\tau_{OH})\ C_{BT} = K_{eff}[\overline{OH}]\ C_{BT}$; therefore:

$$[\overline{OH}] \simeq (K_{eff}\ \tau_{OH})^{-1}, \qquad (7)$$

where K_{eff} is the effective reaction rate constant and C_{BT} the tropospheric burden of CH_3CCl_3. When these calculations were first carried out, K was believed to be about 1.5 times as fast as the most recent estimates (Kurylo et al., 1979; Jeong and Kaufman, 1979), and the mass balance lifetime of CH_3CCl_3 was thought to be longer than our present estimate. Both these changes suggest that previous estimates of $[\overline{OH}] \simeq 4 \times 10^5$ molecules/cm^3 may have been too low.

As mentioned earlier, the lifetime τ determined by the mass balance eq. (5) reflects the combined effects of all the processes that remove CH_3CCl_3 from the atmosphere. In addition to reactions with OH, photodissociation in the stratosphere is probably the most efficient removal process, whereas removal by oceans, deserts, dust storms, and other tropospheric processes may be less important. Therefore, in eq. (7) $\tau_{OH}^{-1} = \tau^{-1} - \tau_{other}^{-1}$. The rate constant, K, for the reaction of OH and CH_3CCl_3

is strongly dependent on temperature ($K \simeq 5.4 \times 10^{-12}$ cm^3 s molec^{-1} exp(1820/T); see DeMore et al., 1982). The effective rate constant in eq. (7) must therefore account for the temperature variation in the atmosphere.

We estimate that $K_{\text{eff}} \simeq 5.4 \times 10^{-15}$ cm^3 s molec^{-1}., $\tau_{\text{other}} \simeq 30$ years and $\tau \simeq 6$ years (Section 2); thus, according to eq. (7), $[\overline{\text{OH}}] \simeq 8 \times 10^5$ molecules cm^{-3}. The uncertainties, however, are perhaps as large as $\pm 6 \times 10^5$ molec cm^{-3}. Next we will discuss this estimate of $[\overline{\text{OH}}]$ and its associated uncertainties.

The lifetime of CH_3CCl_3 due to reactions with OH is given by eq. (8):

$$\tau_{\text{OH}} = \frac{\int_{\text{trop}} \rho C \, dV_{\text{trop}}}{\int_{\text{trop}} K[\text{OH}]\rho C \, dV_{\text{trop}}}, \tag{8}$$

where C is the mixing ratio of CH_3CCl_3 and ρ is the density of air. The simplest approximate solution of eq. (8) is obtained by realizing that the integrands to not vary appreciably with longitude, and that $\rho \simeq \rho_0 \exp(-z/H)$, where H is the scale height of the atmosphere (~8.4 km). C is constant with height and its latitudinal variation is adequately described as $C = C_N$, a constant, for $30° < \phi \leqslant 90°$, $C = \frac{1}{2}(C_N + C_S) + [(C_N - C_S)/2(\pi/6)]\phi$ for $30° \leqslant \phi \leqslant -30°$, and $C = C_S$, also a constant, for $-30° < \phi \leqslant -90°$. If we ignore the variations of the tropopause height and earth's surface temperature with latitude and the variation of OH concentration with height, eq. 8 can be solved as shown in eq. (9):

$$\tau_{\text{OH}} \simeq \frac{H(1 - e^{-z_T/H})}{\Gamma^{-1}(1 - e^{-\Gamma z_T})} \frac{1}{K(T_0)} [\overline{\text{OH}}], \tag{9}$$

$$K = Ae^{-E/T} = Ae^{-E/(T_0 - lz)} \simeq Ae^{-(E/T_0)(1 + lz/T_0)}, \tag{10}$$

$$\Gamma = El/T_0^2 + 1/H. \tag{11}$$

Therefore,

$$K_{\text{eff}} \simeq K(T_0) \frac{(1 - e^{-\Gamma z_T})}{\Gamma H(1 - e^{-z_T/H})}, \tag{12}$$

where z_T is the average tropopause height (~12 km), T_0 is the average surface temperature (≃285 K), and l is the average temperature lapse rate (~6.5 K/km) (Barry and Chorley, 1978; Walker, 1977).

The average OH density we have calculated is only about 20% less than estimated by Logan et al. (1981) using a photochemical model. Since the concentration of OH is believed to be 2–3 times greater in the tropics than at high latitudes (Logan et al., 1981), our calculations suggest that $[\text{OH}]_h \sim 4 \times 10^5$ mole cm^{-3} at higher latitudes and $[\text{OH}]_t \sim 1.2 \times 10^6$ mole cm^{-3} in the tropics.

Although the use of CH_3CCl_3 as an indicator of average troposphere OH density has been discussed often, the inherent uncertainties have not been fully analyzed (see for example Lovelock, 1977; Singh, 1977a, b; Singh et al., 1983; Jesson, 1980; Logan et al., 1981; Prinn et al., 1983).

3.2. *Uncertainty in K_{eff}*

The largest uncertainty in the estimated $[\overline{\text{OH}}]$ is $\delta_1[\overline{\text{OH}}]$ due to the uncertainty in the laboratory measurement of the reaction rate constant. According to the most recent NASA evaluation at average tropospheric temperatures, the uncertainty factor is about 1.45 so that 1.45 K and 0.69 K represent "...an uper and lower bound (corresponding approximately to one standard deviation) of the rate constant..." (DeMore et al., 1982). According to eq. (7), this uncertainty in K would cause an uncertainty of $\delta_1[\overline{\text{OH}}] = (+3.5, -2.5) \times 10^5$ molec cm^{-3} in estimated $[\overline{\text{OH}}]$. Other uncertainties in K_{eff} may arise from the simplifying assumptions regarding vertical variation of OH and the latitudinal variations of surface temperature and tropopause height. We solved eq. (8) taking these variations into account and used the vertical variation of OH calculated by Logan et al. (1981) in which $[\overline{\text{OH}}]$ levels increase up to 2 km from the surface and then fall off slowly up to the tropopause. The result was only a 10% faster K_{eff} than estimated from eq. (12), making $\delta_2[\overline{\text{OH}}] = -0.8 \times 10^5$ mole cm^{-3}. Therefore, the uncertainties in estimating K_{eff} produce an error $\delta_K[\overline{\text{OH}}] \simeq \delta_1[\overline{\text{OH}}] + \delta_2[\overline{\text{OH}}] \simeq \pm 3.5 \times 10^5$ molec cm^{-3}.

3.3. *Uncertainty in τ_{OH}*

As we have shown in sub-section 3.2, $\tau \simeq 5$–8 years. According to eq. (7), the corresponding uncertainty in $[\overline{\text{OH}}]$ is $\delta_3[\overline{\text{OH}}] \simeq \pm 2 \times 10^5$ molec cm^{-3}. Finally, there is a small uncertainty associated with the effectiveness of the other sinks. For τ_{other} between 20 and 40 years, $\delta_4[\overline{\text{OH}}] \simeq 0.5 \times 10^5$ molec cm^{-3}. Thus, the combined effect is $\delta_t[\overline{\text{OH}}] \simeq 2.5 \times 10^5$ molec cm^{-3}.

It is apparent that the combined uncertainties $\delta_k[\overline{OH}]$ and $\delta_r[\overline{OH}]$ are considerable, perhaps as high as $\delta[\overline{OH}] \simeq \pm 6 \times 10^5$ molec cm^{-3}, although a strict statistical interpretation of the combined $\delta[\overline{OH}]$ is not possible.

4. Conclusions

We estimate the lifetime of methylchloroform to be around 6($\pm$1.5) years. It is unlikely that the lifetime is greater than 8 years or less than 5 years. Possible systematic errors in estimating industrial emissions and global concentrations may alter the estimated lifetime. For the lifetime to be longer than 8 years the combined over-estimate of emissions (δS) and under-estimate of concentration would have to exceed 15%. Neither of these possibilities seems likely since the atmospheric concentration of CH_3CCl_3 has been verified by several independent laboratories, and there is a much greater chance that the industrial emissions are under-estimated rather than over-estimated. The effect on the lifetime of systematically under-estimating industrial emissions is to compensate for any systematic (under-estimation) of absolute concentrations and to keep the lifetime below 8 years. As shown in Fig. 1, for shorter lifetimes, the mass balance model is relatively insensitive to errors in estimated emissions and concentrations. Therefore, a lifetime of less than 5 years is equally unlikely. For instance, lifetimes lower than about 5 years are possible if there are sizeable (constant) natural sources of which we are unaware. The expected atmospheric rate of increase of CH_3CCl_3 would then be much less than observed (Figs. 1 and 2). If both the amount and the rate of increase of industrial emissions have been under-estimated, then a lower lifetime may be compatible with observations. Whether this is a realistic possibility is not apparent at present.

We also estimated the average tropospheric OH concentration to be around 8×10^5 mole cm^{-3} but found upon closer examination that there are large uncertainties in this estimate, perhaps as much as $\pm$75%. The analysis suggests that perhaps the use of CH_3CCl_3 or a similar compound as an indicator of average OH concentration will inevitably result in large uncertainties which cannot be easily reduced or eliminated.

5. Acknowledgements

This work was supported in part by the National Aeronautics and Space Administration, the National Science Foundation, and also by Biospherics Research Corp. and the Andarz Co.

6. Appendix

The measured concentrations of methylchloroform at seven sites all over the world are reported in Table A1. In Table A2 these measurements are combined to obtain average concentrations in four regions of the world ranging in latitude from 90 to 30 ($=C_n$), 30 to 0 ($=C_{nt}$), 0 to -30 ($=C_{st}$), and -30 to -90 ($=C_s$). The concentration of CH_3CCl_3 varies considerably with latitude, and these four areas can account for the variation. The global average is formed from the concentrations in these four regions. Such an average weighs each region equally and is therefore not biased by measurements from any one site. The concentrations in Table A2 are obtained as follows: C_n = 1/2 [C(Barrow) + C(Oregon and Washington)]. If for a given month data are available from only one of these sites, then that alone is used for C_n. This procedure is also followed in the other three regions mentioned above. For C_{nt} ("t" for tropics) = 0.2 C(Kumukahi) + 0.8 C(Mauna Loa). The two Hawaiian sites are a few kilometers from each other; however, Manua Loa is a 3.4 km above sea level. The concentrations of CH_3CCl_3 are slightly lower above the boundary layer than below it. The weighting for C_{nt} and C_{st} takes this effect into account. Such an effect is not apparent at higher latitudes. The proportions used in estimating C_{nt} (and C_{st}) reflect the amount of air above the boundary layer compared to that below the boundary layer. Samoa is the only site in the region C_{st}. The ground levels concentrations are corrected for the reduced concentrations above the boundary layer by C_{st} = 0.95 C(Samoa). The factor 0.95 is an average value obtained from the measurements at Hawaii. This difference of concentration in and above the boundary layer has a small effect on the calculations reported in the paper. C_s = 1/3 [C(Tasmania) + C(South Africa) + C(South Pole)] or the average of the available data from these sites.

The Global Average is obtained as C = 1/4

$[C_n + C_{nt} + C_{st} + C_s]$. Up to 1978 the average is formed from C_n and C_s only, which is an accurate global estimate. Later, when more extensive latitudinal data were available, the average utilized concentrations in all four regions. If there were not sufficient data to directly estimate the concentrations in one of the regions, then these were inferred from the existing data. The following example illustrates how this was done. C_{nt} (for July 1978) is missing. The unbiased average C cannot be obtained from the other concentrations at the other three regions. We obtained the average ratio: $(1/N)\ \Sigma\ C_{nt(j)}/C_{n(j)} = r(nt,n)$ for all the months j when both C_{nt} and C_n can be evaluated directly from measurements. Then we obtain the missing C_{nt} (July 1978) as $= r(nt,n) \times C_n$ (July 1978). In a few cases the method had to be applied to two of the four regions to obtain a value in each region. We have included these interpolated values in Table A2 and marked them with an asterisk.

Table A1. *Global time series of monthly average CH_3CCl_3 concentrations*

	Concentrations (pptv)							
	Northern Hemisphere				Southern Hemisphere			
			Hawaii					
Time	Barrow, Alaska (72° N)	Oregon & Wash. (~45° N)	MLO (20° N)	CK	Samoa (14° S)	Tasmania (42° S)	Cape Town, South Africa (35° S)	South Pole (90° S)
1975								
J		70						34
F								
M								
A								
M								
J								
J								
A		76						
S								
O		74						
N		76						
D								
1976								
J		78						46
F		78						
M		82						
A		82						
M		85						
J		81						
J		81						
A		76						
S		86						
O		84						
N		90						
D		86						
1977								
J		86						56
F		91						
M		94						
A		90						
M		96						

Table A1—*continued*

	Concentrations (pptv)							
	Northern Hemisphere				Southern Hemisphere			
			Hawaii					
Time	Barrow, Alaska (72° N)	Oregon & Wash. (~45° N)	MLO (20° N)	CK	Samoa (14° S)	Tasmania (42° S)	Cape Town, South Africa (35° S)	South Pole (90° S)
J								
J								
A								
S								
O		94						
N								
D								
1978								
J								68
F								
M								
A								
M								
J		94				68		
J		106			71	68		
A					72	66		
S					73	69		
O					74	71		
N		113			74	75		
D		110			75	75		
1979								
J		108			78	73		76
F		115			76	73		
M		115			77	75		
A		124			76	76		
M		114			78	77		
J		110			78	78		
J		106			80	77		
A	118	126			82	78		
S	124	130			82	80		
O	123	127			83	82		
N	122	137		105	85	82		
D	122	121			79	82		
1980								
J	123	126		110	84	80		82
F	118	134		106	86	82		
M	123	124		109	86	82		
A	126	129		119	87	87		
M	121	130		106	88	86		
J	126	127			90	87		
J	120	122			90	88		
A	123	122		108	92	89		
S	122	128		108	92	90		
O	125	136		115	93	90		
N	130	128		114	94	90		

Table A1—*continued*

	Concentrations (pptv)							
	Northern Hemisphere				Southern Hemisphere			
			Hawaii					
Time	Barrow, Alaska (72° N)	Oregon & Wash. (~45° N)	MLO (20° N)	CK	Samoa (14° S)	Tasmania (42° S)	Cape Town, South Africa (35° S)	South Pole (90° S)
D	137	132			96	90		
1981								
J	148	130		113	97	90		90
F	133	133	111	112		90	89	
M	134	129	110	118	98	91		
A	133	129	113	117	96	92	89	
M	134	130	112	119	96	94		
J	132	130	108	118	98	94	106	
J	130	129	113	119	98	94	97	
A	130	125	114	118	99		95	
S	134	128	111	117	100	94		
O	133	130	118	118	98	96	96	
N	152	133			98	96		
D	—	134			99	95		
1982								
J	145	134	119	123	98	95	98	97
F	141	134	116	118	102	95		
M	142	136	118	125	100	96	97	
A	142	139	122	129		98		
M	142	138	120	126		98	102	
J	140	136	119	124	100	100		
J	138	134	112	119	100	102	100	
A	140	130		118	102	102	104	
S	137	132		121	102	102	102	
O	149	134		121	102	104		
N	146	137		123	102	104	100	
D	155	139		119	101	103		
1983								
J	185	139		122	102			
F	164	139		123				
M				126			101	

Table A2. *Time series of average CH_3CCl_3 concentrations in the tropics and at higher latitudes*

Time	C_n (90° to 30°)	C_{nt} (30° to 0°)	C_{st} (0° to −30°)	C_s (−30° to −90°)	Ave
1975					
J	70			34	52
F					
M					
A					

Table A2—*continued*

Time	C_n (90° to 30°)	C_{nt} (30° to 0°)	C_{st} (0° to −30°)	C_s (−30° to −90°)	Ave
M					
J					
J					
A	76				
S					
O	74				
N	76				
D					
1976					
J	78			46	62
F	78				
M	82				
A	82				
M	85				
J	81				
J	81				
A	76				
S	86				
O	84				
N	90				
D	86				
1977					
J	86			56	71
F	91				
M	94				
A	90				
M	96				
J					
J					
A					
S					
O	94				
N					
D					
1978					
J	94			68	81
F					
M					
A					
M					
J				68	
J	106	86*	69	68	82
A	97*	82*	70	66	79
S	100*	85*	71	69	81
O	103*	87*	72	71	83
N	113	92*	72	75	88
D	110	91*	73	75	87
1979					
J	108	92*	76	75	88
F	115	94*	74	73	89

Table A2—*continued*

Time	C_n (90° to 30°)	C_{nt} (30° to 0°)	C_{st} (0° to −30°)	C_s (−30° to −90°)	
M	115	94*	75	75	90
A	124	98*	74	76	93
M	114	95*	76	77	91
J	110	93*	76	78	89
J	106	92*	78	77	88
A	126	101*	80	78	96
S	130	103*	80	80	98
O	127	103*	81	82	98
N	137	102	82	82	101
D	121	99*	77	82	95
1980					
J	126	107	82	81	99
F	134	103	85	82	101
M	124	106	85	82	99
A	129	115	85	87	104
M	130	103	86	86	101
J	127		88	87	102
J	122		88	88	101
A	124	105	89	89	102
S	125	105	89	90	102
O	128	112	90	91	105
N	132	111	89	90	104
D	136		93	90	108
1981					
J	139	110	94	90	108
F	133	111	93	90	107
M	132	112	92	91	107
A	131	114	93	91	107
M	132	113	93	94	108
J	131	110	93	100	109
J	130	114	93	96	108
A	127	115	96	95	108
S	131	112	98	94	109
O	132	118	95	96	110
N	142		96	96	113
D	134		96	95	110
1982					
J	140	120	97	97	114
F	138	116	99	95	112
M	139	119	98	99	114
A	141	123		98	116
M	140	121	97	100	115
J	138	120	97	100	114
J	136	113	98	102	112
A	135	115	103	103	114
S	135	117	102	102	114
O	142	117	99	104	116
N	142	119	102	102	116
D	147	115	97	103	116
1983					
J	162	118	98		119
F	152	119	99	101	118
M		122	98		116

REFERENCES

Barry, R. G. and Chorley, R. J. 1978. *Atmosphere, weather, and climate.* Methuen & Co., London.

Chameides, W. and Tan, A. 1981. A two-dimensional diagnostic model for tropospheric OH: an uncertainty analysis. *J. Geophys. Res. 86*, 5209–5223.

Chang, J. E. and Kaufman, F. 1977. Upper limits of the rate constants for the reactions of $CFCl_3$ (F-11), CF_2Cl_2 (F-12), and N_2O with OH; estimates of corresponding lower limits to their tropospheric lifetimes. *Geophys. Res. Lett. 4*, 192–194.

Chang, J. S. and Penner, J. E. 1978. Analysis of global budgets of halocarbons. *Atmos. Environ. 12*, 1867–1882.

Cox, R., R. Derwent, Eggleton, A. and Lovelock J. E. 1976). Photochemical oxidation of halocarbons in the troposphere. *Atmos. Environ. 10*, 305–308.

Crutzen, P. J. and Fishman, J. 1977. Average concentrations of OH in the troposphere and the budgets of CH_4, CO, H_2, and CH_3CCl_3. *Geophys. Res. Lett. 4*, 321–324.

Crutzen, P. Isaksen, I. and McAfee, J. 1978. The impact of the chlorocarbon industry on the ozone layer. *J. Geophys. Res. 83*, 345–363.

Cunnold, D., Alyea, F. and Prinn, R. 1978. A methodology for determining the atmospheric lifetimes of fluorocarbons. *J. Geophys. Res. 83*, 5493–5500.

DeMore, W. B., Watson, R. T., Golden, D. M., Hampson, R. F., Kurylo, M., Howard, Molina, M. J. and Ravishankara, A. R. 1982. *Chemical kinetics and photochemical data for use in stratospheric modeling: evaluation No. 5.* NASA, JPL, Pasadena, California.

Jeong, K. and Kaufman, F. 1979. Rates of the reactions of 1,1,1-trichloroethane and 1,1,2-trichloroethane with OH. *Geophys. Res. Lett. 6*, 757–759.

Jesson, J. P. 1980. Release of industrial halocarbons and tropospheric budgets. *Proceedings of the NATO Advanced Study Institute on Atmospheric ozone: its variation and human influences.* A. C. Aikin, ed., Department of Transportation, Washington, D.C.

Khalil, M. A. K. 1979. *The Behaviour of Atmospheric trace gases.* Ph.D. Dissertation, Oregon Graduate Center, Beaverton, Oregon.

Khalil, M. A. K. and Rasmussen, R. A. 1981a. Decline in the atmospheric accumulation rates of CCl_3F (F-11), CCl_2F_2 (F-12), and CH_3CCl_3. *J. Air Pollut. Control Assoc. 31*, 1274–1275.

Khalil, M. A. K. and Rasmussen, R. A. 1981b. Methylchloroform: cycles of global emissions. *Environ. Sci. Technol. 15*, 1506–1508.

Khalil, M. A. K. and Rasmussen, R. A. 1984. Methylchloroform: lifetime, tropospheric hydroxyl radicals, and anthropogenic chlorine. *Chemosphere 13*, 789–800.

Kurylo, M. J., Anderson, P. C. and Klais, O. 1979. A flash-photolysis resonance-fluorescence investigation of the reaction $OH + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$. *Geophys. Res. Lett. 6*, 760–762.

Logan, J., Prather, M., Wofsy, S. and McElroy, M. 1981. Tropospheric chemistry: a global perspective. *J. Geophys. Res. 86*, 7210–7254.

Lovelock, J. E. 1977. Methyl chloroform in the troposphere as an indicator of OH radical abundance. *Nature 267*, 32–33.

Makide, Y., and Rowland, F. S. 1981. Tropospheric concentrations of methyl-chloroform, CH_3CCl_3, in January 1978 and estimates of atmospheric residence times for hydrohalocarbons. *Proceedings, National Academy of Sciences (USA), 78*, 5933–5973.

McConnell, J. C. and Schiff, H. I. 1978. Methyl chloroform: impact on stratospheric ozone. *Science 199*, 174–177.

NAS. 1976. National Academy of Science. *Halocarbons: effect on stratospheric ozone* –Washington, D.C.).

NAS. 1979. National Academy of Science. *Stratospheric ozone depletion by halocarbons: 'chemistry and transport* (Washington, D.C.).

Neely, W. B. and Plonka, J. H. 1978. Estimation of time averaged hydroxyl radical concentrations in the troposphere. *Environ. Sci. Technol. 12*, 317–321.

Parrott, L. G. 1961. *Probability and experimental errors in science.* Dover, NY, USA.

Prinn, R. G., Rasmussen, R. A., Simmonds, P. G., Alyea, F. N., Cunnold, D. M., Lane, B. C., Cardelino, C. A. and Crawford, A. J. 1983. The atmospheric lifetime experiment 5: results for CH_3CCl_3 based on three years of data. *J. Geophys. Res. 88*, 8415–8426.

Rasmussen, R. A. and Khalil, M. A. K. 1980. Atmospheric halocarbons: measurements and analyses of selected trace gases. *Proceedings, NATO Advanced Study Institute on Atmospheric ozone: its variation and human influences.* A. C. Aiken, ed., Department of Transportation, Washington, D.C., 209–231.

Rasmussen, R. A. and Khalil, M. A. K. 1981a. Interlaboratory comparison of fluorocarbons 11, 12, methylchloroform, and nitrous oxide measurements. *Atmos. Environ. 15*, 1559–1568.

Rasmussen, R. A. and Khalil, M. A. K. 1981b. Global atmospheric distribution and trend of CH_3CCl_3. *Geophys. Res. Lett. 8*, 1005–1007.

Rasmussen, R. A. and Khalil, M. A. K. 1981c. Differences in the concentrations of atmospheric gases in and above the tropical boundary layer. *PAGEOPH 119*, 990–997.

Rasmussen, R. A. and Khalil, M. A. K. 1982. Latitudinal distributions of trace gases in and above the boundary layer. *Chemosphere 11*, 227–235.

Rasmussen, R. A., Khalil, M. A. K. and Dalluge R. W. 1980. Halocarbons and other trace gases in the antarctic atmosphere. *Antarct. J. of the US. 15(5)*, 177–179.

Rasmussen, R. A., Khalil, M. A. K. and Dalluge, R. W. 1981. Atmospheric trace gases in Antarctica. *Science 211*, 285–287.

Singh, H. B. 1977a. Atmospheric halocarbons: evidence in favor of reduced hydroxyl radical concentrations in the troposphere. *Geophys. Res. Lett. 4*, 101–104.

Singh, H. B. 1977b. Preliminary estimation of average tropospheric HO concentrations in the northern and southern hemispheres. *Geophys. Res. Lett. 4*, 453–456.

Singh, H. B., Salas, L. J. and Stiles, R. E. 1983. Selected man-made halogenated chemicals in the air and oceanic environment. *J. Geophys. Res. 88*, 3675–3683.

Walker, J. C. G. 1977. *Evolution of the Atmosphere*, McMillan Publishers, N.Y.

Yung, Y., McElroy, M. B. and Wofsy, S. A. 1975. Atmospheric halocarbons: a discussion with emphasis on chloroform. *Geophys. Res. Lett. 2*, 397–399.