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Atmospheric chloroform ($CHCl_3$): ocean–air exchange and global mass balance

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ABSTRACT

Based on the observed global concentrations of chloroform ($CHCl_3$) in the air and seawater we demonstrate that the tropical oceans are a source of chloroform to the atmosphere. Even though the total yearly emissions of $CHCl_3$ from the oceans are still uncertain, we estimate the flux to be 0.35 Tg yr^{-1}. Anthropogenic sources we estimate to be 0.25 Tg yr^{-1}. This result suggests that atmospheric $CHCl_3$ may be mostly natural in origin and not entirely man-made as previously thought. The global burden of $CHCl_3$ in the atmosphere is estimated to be about 0.33 Tg and its lifetime is about 6 months. Reaction with tropospheric OH radicals may explain most of the removal of $CHCl_3$ from the atmosphere, but the likelihood of other removal mechanisms is suggested. An average concentration of about 25 ppt was observed at ground level, declining at about 7% km^{-1} with height. The ratio of northern hemisphere to southern hemisphere burden of $CHCl_3$ is found to be about 1.6. A global mass balance model is used to show that these findings are mutually consistent.

1. Introduction

Chloroform ($CHCl_3$) is used in industrial processes such as the production of fluorocarbon 22 ($CHClF_2$), pharmaceutical products, dyes, and pesticides. It is also inadvertently produced in sewage treatment plants, landfills, and paper mills. Chlorination treatment may result in high levels of chloroform in drinking water as found in 80% of the cities sampled in an EPA study reported by the National Research Council (NRC, 1978). The NRC study also reported the risk to human health from long-term exposure to $CHCl_3$ in the air, water, and foods.

The presence of $CHCl_3$ in the environment has often been regarded as man-made, principally because of the many identified primary and secondary anthropogenic sources (Seinfeld, 1981; Graedel, 1978). Over the years evidence has accumulated showing possible natural origins of some or most of the chloroform found in the atmosphere. The most likely natural source is oceanic. The National Research Council report (NRC, 1978) cites studies by Su and Goldberg (1976) and Murray and Riley (1973) showing high concentrations of $CHCl_3$ in seawater from coastal regions and the east Pacific and northeast Atlantic Oceans. The concentrations reported are between 8 and 15 $\times$ 10^{-3} μg l^{-1}. If those levels were representative, the oceans would be a yearly source of several teragrams of $CHCl_3$ to the atmosphere, many times greater than the anthopogenic source. Even though these numbers cannot be easily extrapolated to the global environment, they demonstrate the possibility of the oceanic source for $CHCl_3$. Other indirect evidence for the oceanic source arises from the observations of relatively large concentrations of $CHCl_3$ in the southern hemisphere, even at the south pole. Since the atmospheric lifetime of $CHCl_3$ is thought to be less than a year, if its sources were entirely anthropogenic, then the ratio of the northern hemisphere to southern hemisphere concentrations is expected to be much larger than the observed value of 1.6 (see also Rasmussen and Khalil, 1981).

The main points addressed in this paper are to (1) analyze a few seawater samples, which were carefully handled to virtually eliminate the possibility of contamination. Man-made gases such as CCl_3F (F-11), CCl_2F_2 (F-12), CCl_4, and CH_3CCl_3 are measured in seawater as indicators or tracers of contamination from the ship and sampling or storing procedures. In the open ocean the uncontaminated water contains low concentrations of these gases, nearly in equilibrium with the air concentrations. The water samples studied fulfilled these criteria. Based on these data we demonstrate that the oceans are a source of chloroform amounting to about 0.35 Tg yr^{-1}, although there is still considerable uncertainty surrounding this estimate (Section 4). (2) We then construct a global mass balance model to demonstrate how the oceanic sources, anthropogenic sources, lifetimes, and global atmospheric distributions are mutually compatible (Section 5). (3) The global seawater and atmospheric concentration distributions are also presented based on hundreds of atmospheric measurements made at latitudes ranging from within the arctic circle (72° N), to the south pole (90° S). The seawater concentration data are limited to the northern hemisphere as mentioned earlier (Section 3). Analytical methods are discussed in Section 2.

2. Analytical techniques

2.1. *Measurements in the gas phase*

Analysis of chloroform in air samples is made by first concentrating the sample using a liquid oxygen (−183 °C) freezeout method. Usually 100 ml, and occasionally 200 ml, of air is directed to a 0.635 cm × 15.24 cm (¼ inch diam. × 6 inches long) stainless steel tube with glass beads. This "freezeout-loop" is immersed in liquid oxygen during the filling process. When all the sample has been collected and cooled in the freezeout loop, it is placed in a warm water bath at 85 °C, and the $CHCl_3$ is injected onto the column of a gas chromatograph. This method has been described in detail by Rasmussen et al. (1977) and Hoyt (1982).

The various compounds in the sample are separated by a Perkin Elmer Model 3920B temperature-programmed gas chromatograph equipped with an electron capture detector (EC/GC) which uses a ^{63}Ni source and is operated at a temperature of 360 °C. The peak heights, reflecting the concentrations of trace gases, are measured by a Hewlett-Packard 3388A electronic integrator. The chromatographic column is a 0.635 cm outside diameter × 25.4 cm long (or ¼ inch × 10 inches) stainless steel tube packed with 100% SP2100 on 100/120 mesh Supelcoport. The oven temperature is 10 °C and is programmed to change at 16 °C/min up to a maximum temperature of 80 °C.

A Finnigan 4021 GC/MS/DS mass spectrometer operated at Oregon Graduate Center (OGC) was used to verify the chloroform peak observed on the EC/GC. The detection limit of $CHCl_3$ in 100 ml of sample is 6 pptv (see Rasmussen et al., 1977; Rasmussen and Khalil, 1981; Hoyt, 1982).

2.2. *Vacuum extraction flask and seawater samples*

This technique is a version of a method developed by McAuliffe (1971) for extracting dissolved gases from water.

The vacuum extraction flask is a 1 liter Erlenmeyer flask with a special valve attachment. It is designed to hold pressures of 30 psig and vacuums up to 50 mtorr. These flasks are sent to the field for collection of seawater samples with a 70 mtorr vacuum so that water is aspirated into the flask without using a pump. Pumps sometimes contaminate the sample. The design of the flask includes a Kovar-to-glass seal at the top. A stainless steel NPT pipe of 0.635 cm diameter (¼ inch) is welded to the Kovar to form an air-tight seal. A Nupro B-4H4 brass bellows valve is connected to the coupling with a 0.635 cm NPT pipe. Swagelok® pipe fittings are used at the top of the valve to allow air-tight coupling to a funnel or filter.

The sample is collected either by submerging the evacuated flask under water or putting the water in a stainless steel funnel and drawing it into the flask under vacuum. 650 ml of water is drawn into the bottle without allowing any air to enter. The headspace is then pressurized with 15 psi of zero air. The result is equal volumes of air and water at 25 °C and 1 atm pressure, which simplifies the extraction analyses. The positive pressure in the bottle, after the sample is collected, prevents contamination of the headspace and allows for an easy transfer of headspace air sample to the gas chromatograph.

After collection, the water sample is frozen and

shipped to the laboratory in this state. Biological and chemical activity between the times sampled are collected and analyzed is thus greatly reduced. The ability to bring the sample into the laboratory also facilitates the measurement of not only $CHCl_3$ in seawater, but also a large number of other gases for which specially tuned gas chromatographs are routinely operated in the laboratory. Before these flasks are sent to the field, they are thoroughly cleaned and heated at 120 °C while being pumped with a vacuum pump for 1 h.

To prepare the water samples for analysis, the flasks are taken from the freezer, placed in a water bath and agitated for a half hour until the sample reaches 25 °C. The bottle is connected directly to the gas chromatograph with a Swagelok® fitting. The gases in the headspace can be measured by one or more extractions. If more than one extraction is made, the headspace is flushed with zero air several times, repressurized to 15 psi with zero air, agitated for another 30 min, and re-analyzed.

The first analysis of a gas in the headspace is related to the concentration of the gas in the water sample by Henry's law. Before the sample is frozen, almost all of the trace gas, say $CHCl_3$, is in the water and not in the headspace so that the total amount of gas in the flask is $C_l^{(0)} V_l$ where C_l is the concentration in the water and V_l is the volume of water. Just before analysis, the gas is divided between the headspace (C_g) and water (C_{lf}) as: $C_{lf} V_l + C_g V_g$, where V_g is the volume headspace air would occupy at 1 atm pressure. By Henry's law, $C_{lf} = C_g/H$; thus

$$C_l^{(0)} = C_g (\alpha + 1/H) \tag{1}$$

$$\alpha = V_g/V_l = (V_T - V_l) P/V_l \tag{2}$$

where P is the headspace pressure in atmospheres and V_T is the total volume of the flask (here 1 liter). By this procedure we can determine the initial concentration of a dissolved gas (C_l^0) in seawater. Subsequent extractions can often be used to verify the value of H or obtain concentrations of more gases. This procedure and the experimental uncertainties associated with it are discussed in detail by Hoyt (1982).

3. Oceanic and air concentrations

The concentrations of chloroform in seawater and in air over the open ocean were determined in samples shipped to our laboratory at the Oregon Graduate Center.

The seawater samples were obtained from a NOAA ocean cruise, during the summer of 1981, which went from Adak, Alaska, along 150° W longitude to about 15° N and returned to Seattle, Washington (Hoyt, 1982). Measurements of $CHCl_3$ in seawater at latitudes >30° were obtained from samples collected in the north Atlantic on another cruise, during September 1981, which started at St. John's, Newfoundland, crossed 45° W longitude, went south to 30° N latitude, and returned to the U.S.

Air samples were obtained by two methods. First, flask samples are routinely obtained every week from various remote locations in the world (dark circles, Fig. 1). Second, flask samples obtained on board ocean cruises were also analyzed for $CHCl_3$ and provided the data marked by open triangles in Fig. 1. Whenever several air samples were collected at nearby latitudes, they were combined and averaged. The uncertainties due to the observed variability are expressed in vertical bars (90% confidence limits) in Fig. 1. We believe that the most reliable data are from the fixed sites numbered 1–7 on Fig. 1. Usually a long sequence of weekly measurements were averaged over 1981 to arrive at the concentration and estimated 90% confidence limits shown in Fig. 1 (Snedecor and Cochran, 1973). These data have been tabulated in Table 1, and average concentrations in the four quarters of the world, separated by latitude, are shown in Table 2. The flask sampling system from these sites has been described by Rasmussen and Khalil (1981).

4. Oceanic flux

In order to estimate the global oceanic source of chloroform, we divided the earth's oceans and atmosphere into four regions consisting of latitudes 90° S to 30° S (s), 30° S to 0° (st), 0° to 30° N (nt), and 30° N to 90° N (n). "n" and "s" stand for the northern and southern hemispheres respectively, and "t" designates the tropical and subtropical regions. This model incorporates the established large-scale latitudinal variations of atmospheric and seawater temperatures, atmospheric circulation, and variations of OH (and

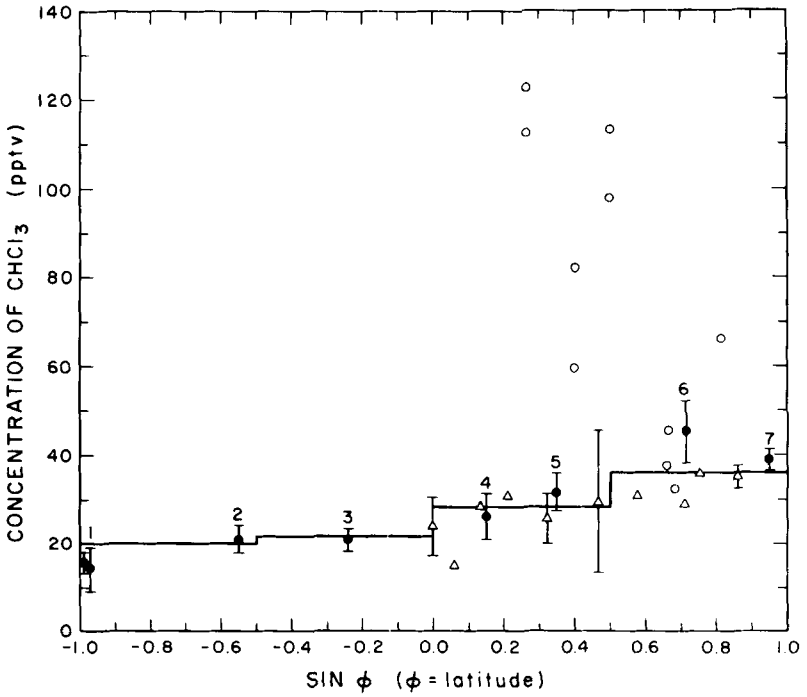

Fig. 1. Atmospheric and seawater concentrations of chloroform ($CHCl_3$). The concentrations found in seawater (C_l) are represented as C_g (equil) = $C_l H(T)$ by open circles (○). $H(T)$ is Henry's constant at temperature T and the product $C_l H$ represents the air concentration needed for the observed seawater concentration (C_l) to be in equilibrium. The triangles (△) and dark circles (●) are the air concentrations (C_g). The flux of $CHCl_3$ from the ocean to the atmosphere is proportional to the difference between C_g (△, ●) and $C_l H$ (○). Triangles represent samples collected on oceanographic cruises, and dark circles are data obtained over a long time from sea level stations. The vertical bars are 90% confidence limits of the average value. (1) = South Pole; (2) = Australia; (3) = Samoa; (4) = Marshall Islands; (5) = Kumukahi, Hawaii; (6) = Cape Meares, Oregon; (7) = Pt. Barrow, Alaska.

solar flux) which remove $CHCl_3$ from the atmosphere. The equations describing the mass balance will be discussed in the next section.

4.1. *The source*

The global sources of $CHCl_3$ may be written as in eqs. (3)–(5).

$$S_J = S_{aJ} + S_{oJ} + \varepsilon_J \tag{3}$$

$$S_{oJ} = \frac{K}{H_J}\left[C_{gJ} - C_{lJ}H_J\right]\zeta_J = \frac{K}{H_J}\zeta_J \Delta C_J \tag{4}$$

$$S_o = \sum_J S_{oJ} \tag{5}$$

In these equations the subscript "J" stands for "n", "nt", "st", or "s". S_{aJ} are the anthropogenic sources (in Tg yr^{-1} = 10^{12} g yr^{-1}), S_{oJ} are the oceanic sources, and ε_J represent other natural sources, here assumed to be zero. In eq. (4) the oceanic flux of $CHCl_3$ is approximated by a two-film model of ocean–air exchange applied to each of the four regions, J (Liss and Slater, 1974; Broecker and Peng, 1974). K, equalling about 11 cm s^{-1} for $CHCl_3$, is the ocean–air exchange velocity, ζ_J is the surface area of the ocean in region J, H_J is the Henry's constant (ml gas/ml water) for $CHCl_3$ in seawater at the ocean temperature of the various regions J, C_{gJ} and C_{lJ} are the concentrations of $CHCl_3$ in the air (gas phase) and seawater (liquid phase) in region J. S_o, as shown in eq (5), is the total oceanic source.

The oceanic flux, S_o, was calculated from the air and ocean concentration data (C_{gJ}, C_{lJ}) discussed in Section 2. The Henry's constant for $CHCl_3$ is

Table 1. *Average concentrations of $CHCl_3$ in air and seawater (pptv)*

Atmosphere

	$\bar{C}$ (pptv)	$(\pm\delta\bar{C})$	n	Time
Barrow, Alaska (72° N)	39	(±2)	35	Feb. 1981–Dec. 1981
Cape Meares, Oregon (45° N)	45	(±5)	56	Apr. 1977–June 1982
Cape Kumukahi, Hawaii (20° N)	32	(±4)	15	Feb. 1981–July 1981
Marshall Islands (10° N)	26	(±6)	9	July 1981–Oct. 1981
Samoa (20° S)	21	(±2)	34	Feb. 1981–Dec. 1981
Near Melbourne, Australia (35° S)	21	(±3)	50	Nov. 1981
South Pole (90° S)	16	(±2)	10	Jan. 1979 and Jan. 1981

Water (pptv)

(ϕ,λ)	C_l	$C_lH(T)$	T(°C)	
(31° N, 135° W)	576	98	21	July 19, 1981
	664	113		
(26° N, 137° W)	326	59	22	July 18, 1981
	457	82		
(15° N, 140° W)	532	112	26	July 15, 1981
	582	122		
(41° N, 68° W)	307	37	14	Oct. 18, 1981
	375	45		
(44° N, 60° W)	225	32	17	
(54° N, 165° W)	732	66	7	Aug. 20, 1982

$\bar{C}$ = average concentration, $\delta\bar{C}$ = 90% confidence limits, n = number of different samples. At Barrow, Cape Kumukahi, and Marshall Islands, the total number of samples collected was $3n$ since three flasks were filled with air at each time. ϕ = latitude, λ = longitude, C_l = concentration in seawater, and $H(T)$ is Henry's constant at temperature T.

Table 2. *Global sources, sinks, and distribution of chloroform ($CHCl_3$)*

	Latitudes				
	90° N–30° N	30° N–0°	0°–30° S	30° S–90° S	Total
Sources (Tg yr^{-1})					
Oceanic	0.02	0.15	0.15	0.04	0.36
Anthropogenic and other	0.20	0.05	0	0	0.25
Total sources	0.22	0.20	0.15	0.04	0.61
Lifetime (years)	1	0.3	0.3	1	0.5
Concentrations (ppt)					
Atmosphere, sea level					
observed	35	26	21	17	25
calculated	36	28	21	19	26
Burden (Tg)	0.11	0.09	0.07	0.06	0.33

taken from Hunter-Smith et al. (1982) and is given by $H = 4.136 \times 10^4\, e^{-3646/T(K)}$. The values obtained agree well with other measurements (McConnell et al., 1975; Dilling, 1977). The flux of $CHCl_3$ from southern hemisphere oceans is estimated by assuming $S_{ost} \simeq (\zeta_{st}/\zeta_{nt})\, S_{ont}$ and $S_{os} \simeq (\zeta_s/\zeta_n)\, S_{on}$.

With these assumptions the total oceanic source turns out to be 0.35 Tg/yr (≥0.2 Tg/yr), most of it being from the tropical oceans. The larger tropical source results from the higher supersaturations of $CHCl_3$ and the warmer waters.

4.2. *Uncertainties*

The uncertainties in our estimate of the oceanic flux are difficult to quantify. Our analysis of uncertainties consists of two parts: the variability of ocean and air concentrations (C_{gJ} and C_{lJ}), which can be estimated from the measurements, and variability or uncertainties in K and H_J, which cannot be estimated directly from the available data.

If we ignore the uncertainties in H_J and K for the moment, we can evaluate the uncertainty in the calculated oceanic flux which arises from the observed variability in air and ocean concentrations of chloroform. At high northern latitudes, because of the few data available and the small observed difference between air concentrations and equilibrium water concentrations, it is not possible to prove that the flux of $CHCl_3$ to the atmosphere is greater than zero ($p = 0.1$). Data from the tropical oceans, however, which we believe produce most of the oceanic $CHCl_3$, show strong evidence for the flux of 0.3 Tg yr^{-1}, with approximate 90% confidence limits ranging from 0.2 Tg yr^{-1} to 0.4 Tg yr^{-1}. These statistical estimates are based on the distribution-free Wilcoxon test (Hollander and Wolfe, 1973).

The uncertainties in K and H_J also affect the accuracy of the calculated flux. When the errors are propagated in the flux equation (2), the resulting estimate of the uncertainty in the calculated flux is

$$\tilde{\sigma}^2_{S_{oJ}} = [\tilde{\sigma}^2_K + \xi_J^{-2}(\tilde{\sigma}^2_{C_{gJ}} + \tilde{\sigma}^2_{H_J}) + (1 + \xi_J^{-1})^2\tilde{\sigma}^2_{C_{lJ}}] \quad (4)$$

$$\tilde{\sigma}_x = \sigma_x/\bar{x};\ \xi_J = (H_J C_{lJ}/C_{gJ}) - 1$$

where uncertainties in the quantity x are expressed as σ_x, and ξ_J is the supersaturation in region J (Meyer, 1975). Ignoring the error in the transport constant (K) for the moment, it can be seen that for tropical regions, since ξ_J (J = nt) is large (≃3), errors in Henry's constant will not contribute much to the error in the estimated flux ($\tilde{\sigma}_{S_{ont}}$). For the high latitudes, since ξ_J (J = n) ≃ 0.3, any error in H_J will add greater uncertainty to the already uncertain flux in this region. The effect of uncertainties in K, the transport coefficient, are expected to be small. More importantly, if the observed values of H_J, C_{gJ}, and C_{lJ} predict that the net flux of $CHCl_3$, or any other gas for that matter, is from the ocean to the atmosphere ($S_{oJ} > 0$), then errors in K will not affect this conclusion, but may affect the estimated magnitude of the flux.

There is one other source of uncertainty for the estimate of the flux, namely ζ_J. ζ_J is the area of the ocean in region J over which the average observed supersaturation is assumed to exist. In our calculation we have assumed that ζ_J is the entire ocean area in region J. There are not enough data at present either to evaluate the validity of this assumption or to propose an alternative. It may be that the Atlantic and Pacific Oceans at high latitudes do not produce the same amount of $CHCl_3$ per unit surface area (see Table 1). The effect of this uncertainty is also to change the calculated magnitude of the flux, but it does not alter the conclusion that the oceans are a source of $CHCl_3$.

In essence the data show that the tropical oceans are a source of $CHCl_3$ to the atmosphere. Because of the natural and experimental variabilities in the concentrations of $CHCl_3$ and uncertainties in our knowledge of the Henry's constant (H_J) and the ocean–air exchange coefficient (K), the estimated magnitude of the flux is uncertain but probably greater than 0.15 Tg yr^{-1}. At higher latitudes, colder water and smaller supersaturations of $CHCl_3$ coupled with the uncertainties in determining the flux make it impossible to prove that regions of the ocean there also release $CHCl_3$ to the atmosphere. More detailed data are needed to evaluate the role of ocean water at latitudes of ≥30° in the global $CHCl_3$ cycle.

5. Global mass balance

The mass balance of chloroform in the earth's atmosphere may be written as eqs. (6) and (7):

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{C} = \mathbf{S} - \mathbf{\Omega C} \quad (6)$$

$$\mathbf{C} = \begin{bmatrix} C_n \\ C_{nt} \\ C_{st} \\ C_s \end{bmatrix}; \quad \mathbf{\Omega} = \begin{bmatrix} (\eta_1 + \eta_{T_0}) & -\eta_{T_0} & 0 & 0 \\ -\eta_{T_0} & (\eta_2 + \eta_{T_0} + \eta_T) & -\eta_T & 0 \\ 0 & -\eta_T & (\eta_2 + \eta_{T_0} + \eta_T) & -\eta_{T_0} \\ 0 & 0 & -\eta_{T_0} & (\eta_1 + \eta_{T_0}) \end{bmatrix} \tag{7}$$

In eq. (6) **C** represents the burdens in Tgs of $CHCl_3$ in each region (J = n, nt, st, or s), **S** are the sources as discussed in Section 3, and $\mathbf{\Omega}$ is a matrix containing the description of transport and removal of chloroform in this model. The η's represent inverse lifetimes or transport times ($\eta = 1/\tau$), where τ_{T_0} and τ_T are the transport times within and across a hemisphere respectively, and τ_1 and τ_2 are the atmospheric lifetimes of $CHCl_3$ at high latitudes and in the tropical regions, respectively. The calculation of the expected concentrations of chloroform based on eq. (6) and (7) requires an analysis of the sources, global burdens, and sinks.

5.1. *Sources*

The observed atmospheric concentration of $CHCl_3$ at high northern latitudes (n) is larger than everywhere else, yet the oceanic source in this region is the smallest. In order to explain the relative concentrations of $CHCl_3$ in the four regions, emissions of about 0.25 Tg yr^{-1} are needed between 30° N and 90° N. Much of this may be from secondary production of $CHCl_3$ due to anthropogenic activities (Yung et al., 1975) since industrial production of $CHCl_3$ is thought to be insignificant compared to 0.25 Tg yr^{-1} (NRC, 1978). The sources are summarized in Table 2.

5.2. *Atmospheric burdens*

The calculation of the atmospheric burden in each region (J) and in the entire atmosphere must take into account the decline of the $CHCl_3$ mixing ratio with height as discussed in Section 2. Thus,

$$\bar{C}(z) = \bar{C}_0 e^{-\lambda z} \tag{8}$$

where $\bar{C}_0$ is the ground level mixing ratio and $\lambda \simeq 0.07$ km^{-1} (Rasmussen et al., 1982; Rasmussen and Khalil, 1982a, 1983; Rasmussen and Khalil, 1981). The burden of $CHCl_3$ in any of the four regions is given by

$$C_J = (\pi R^2 \rho_0 M/N_0)(\lambda + 1/H)^{-1} \times (1 - e^{-(\lambda + 1/H)z_T})\, \bar{C}_{0J} \tag{9}$$

where M is the molecular weight, N_0 Avogadro's number, R the radius of the earth, H the scale height of the atmosphere (~9 km), ρ_0 the surface level density of air in molecules/cm^3, and z_T is the height of the tropopause, here approximated as constant at 12 km. Eq. (9) also provides a relationship between C_J of the mass balance eqn. (6) and $\bar{C}_{0J}$, the ground level mixing ratio. With the atmospheric concentrations shown in Fig. 1, the global atmospheric burden of chloroform turns out to be about 0.33 Tg (see Table 2).

5.3. *Sinks*

Based on the total sources of 0.6 Tg/yr as discussed earlier and a global burden of 0.33 Tg, the average atmospheric lifetime is about 6 months. At least 60% and perhaps all of the yearly removal of $CHCl_3$ from the atmosphere may therefore be attributed to reaction with hydroxyl radicals which are about three times more abundant in the tropics than at higher latitudes ($\geqslant 30°$) (Logan et al., 1982). We assumed $\tau_1 \simeq 1$ yr and $\tau_2 \simeq 1/3$ yr, which is required to balance the sources and the global burden. The measurements of the reaction rate constant between $CHCl_3$ and OH are discussed by DeMore et al. (1982). Assuming η_{T_0} to be 4.8 yr^{-1}, η_T to be 2 yr^{-1}, and the sources and sinks as discussed above, we calculated the concentrations $\bar{C}_{0J}$ according to the mass balance eqs. (6) and (7) and eqs. (8) and (9). The results are shown as solid lines in Fig. 1, and the calculated sea level concentrations are approximately the same as the average measured concentrations.

It is noteworthy that this global mass balance calculation shows that additional sources, either anthropogenic or natural, cannot be added without also finding a new sink, other than reaction with OH radicals. The transport times τ_{T_0} ($= 1/\eta_{T_0}$) and τ_T ($=1/\eta_T$) are approximately those needed to explain the long (8 years) time series of F-11, F-12, and CH_3CCl_3 measurements reported by Rasmussen et al. (1981) and Rasmussen and Khalil (1982b). The values adopted here

are also consistent with those used by other investigators (Chang and Penner, 1978; Newell et al., 1969; Cunnold et al., 1982; Singh et al., 1979; Czeplak and Junge, 1974).

It should be noted that since we are using a four-box model, the transport time τ_T is about half of the usual interhemispheric mixing time used in two-box theories (see also Khalil and Rasmussen, 1983). There are uncertainties in transport times, but they do not significantly affect the conclusions we have drawn in this paper.

6. Discussion

We have discussed the many uncertainties that exist when the few available measurements of $CHCl_3$ in seawater are extrapolated to estimate a global flux. But in spite of these uncertainties, there is strong evidence that at least the tropical oceans are a sizeable global source of chloroform. Our estimate of the oceanic source of about 0.35 Tg yr^{-1}, though uncertain, suggests that chloroform in the atmosphere may be largely natural in origin than entirely anthropogenic as previously thought. No doubt more global measurements of the abundance of $CHCl_3$ in seawater would reduce the uncertainties in our present calculation of the oceanic source.

It has generally been assumed that reaction with OH radicals is the only, or at least the most important mechanism for removing $CHCl_3$ from the atmosphere. Given the sources we have estimated ($\sim$0.6 Tg yr^{-1}) and the global burden of 0.33 Tg, the average lifetime should be about 0.5 yr. This requires average OH levels of about 1.3×10^6 molecules/cm^3 in the region from 30° S to 30° N and about 5.6×10^5 molecules/cm^3 at higher latitudes. These estimates are based on the reaction rates reported by DeMore et al. (1982), and assuming a 15 °C average difference in sea level temperature between the tropics and subtropical zones and high latitudes (>30° N). Although these densities of OH are not excluded by current theories, they are somewhat higher than would be expected on the basis of our atmospheric mass balance of methylchloroform (CH_3CCl_3). If there are other removal mechanisms for $CHCl_3$, then the OH densities required to explain the measured concentrations would be less. In the mass balance equation there are three basic components: the sources, the sinks, and the concentration distributions. One must specify two to obtain the third. Here we have measured concentrations and estimated sources, so we may derive the lifetimes (sinks). As mentioned above, the derived lifetimes require OH densities somewhat higher than expected, but the discrepancy is not large compared to current uncertainties in estimated OH levels or other sinks of $CHCl_3$. The concentration of $CHCl_3$ is also observed to decline with height at a sufficiently rapid rate to suggest a lifetime of perhaps less than 6 months. These observations, though still tentative, raise the possibility that there may be other mechanisms in the atmosphere by which $CHCl_3$ may be removed. Reaction with sunlight is a likely possibility which is currently under investigation. If it turns out that there are other mechanisms that remove chloroform from the atmosphere, then it may be possible to accommodate other additional sources of $CHCl_3$ into the mass balance. At present, though, if reaction with OH is regarded as the only sink, then its reaction rate is slow enough to allow a total global source of no more than about 0.6 Tg yr^{-1} to balance the observed global burden. If 0.3 or 0.4 Tg per year comes from the oceans, the total anthropogenic source can be only about 0.25 Tg yr^{-1}.

We have discussed the sources and sinks of chloroform in the atmosphere and shown that although there are still doubts about the current estimates, a self-consistent mass balance can be constructed as shown in Table 2. The results though speculative do indicate that the oceans release $CHCl_3$ to the atmosphere.

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