

Distribution of Methylchloride, Dichloromethane, Trichloroethene and Tetrachloroethene Over the North and South Atlantic

R. KOPPMANN, F. J. JOHNEN, C. PLASS-DÜLMER, AND J. RUDOLPH

Institut für Atmosphärische Chemie, Forschungszentrum Jülich, Jülich, Germany

During the cruise ANT VIII/1 of the German R/V *Polarstern* in August/September 1989 the latitudinal distributions of the atmospheric concentrations of methylchloride, dichloromethane, trichloroethene, and tetrachloroethene were measured over the Atlantic between 45°N and 30°S by in situ gas chromatography. With the exception of trichloroethene they showed mixing ratios well above the lower limit of detection. The methylchloride distribution was uniform with average mixing ratios of 532 ± 8 and 550 ± 12 ppt in the northern and southern Hemispheres, respectively. Dichloromethane increased linearly between the Intertropical Convergence Zone and 45°N with average mixing ratios of 36 ± 6 ppt and was almost constant in the southern hemisphere with an average of 18 ± 1 ppt. Tetrachloroethene mixing ratios were between less than 1 and 10 ppt in the northern hemisphere and always below 3 ppt in the southern hemisphere. Similar to dichloromethane, tetrachloroethene was nearly constant in the southern hemisphere and increased linearly toward northern latitudes. This is compatible with the predominantly industrial origin of these compounds. Trichloroethene varied between 0.3 ppt and about 15 ppt in the northern hemisphere with an average of 3 ± 1 ppt and was generally lower than 1 ppt in the southern hemisphere with mixing ratios often near or below the detection limit of 0.1 ppt. For CH_3Cl we estimate a global turnover of 3.5×10^{12} g/yr which is compatible with previous results. Using a simple model calculation our measurements imply a global turnover for CH_2Cl_2 and C_2Cl_4 of 0.9×10^{12} g/yr and 0.6×10^{12} g/yr, respectively.

INTRODUCTION

Halogenated hydrocarbons are known to be the source of reactive chlorine in the stratosphere and to act as greenhouse gases in the troposphere. While most investigations focus on chlorofluorocarbons which are photochemically stable in the troposphere, little is known about the shorter-lived chlorinated hydrocarbons such as methylchloride, dichloromethane, and the chloroethenes. Compared to chlorofluorocarbons, these compounds have significant tropospheric removal rates due to the presence of double bonds or abstractable hydrogen atoms. Therefore their mean atmospheric lifetimes are typically less than a few years, sometimes only a few weeks. However, the environmental impact of these compounds is not negligible. Due to its atmospheric lifetime of about 1.6 years, methylchloride is the only natural chlorinated compound which contributes significantly to the chlorine budget of the stratosphere [Fabian, 1986; Schmidt *et al.*, 1985]. The environmental impact of chloroethenes is due to their ability to decompose into highly toxic species. For example, chloroethenes are believed to be a source of phosgene in the atmosphere [Finlayson-Pitts and Pitts, 1986].

The dominant source of methylchloride is believed to be natural production in the surface water of the oceans [Singh *et al.*, 1983]. As a further source, microbial fermentation [Cowan *et al.*, 1973] and smoldering combustion of vegetation are discussed [Crutzen *et al.*, 1979; Rasmussen *et al.*, 1980; Rudolph *et al.*, 1993]. Lobert *et al.* [1991] estimate that biomass-burning emissions contribute up to 40% to the global budget of CH_3Cl . The anthropogenic source of methylchloride seems to be negligible, since methylchloride is almost entirely used as a chemical intermediate in the production of other compounds and does not reach the

atmosphere by direct emission. In contrast to methylchloride dichloromethane, trichloroethene and tetrachloroethene are predominantly man-made. They are primarily used as solvents and degreasing agents [Pearson, 1982]. Thus they can be used as tracers for the source distribution and transport mechanisms of anthropogenic trace gases and supply qualitative and quantitative information about the impact of anthropogenic emissions on the remote atmosphere. Furthermore, chlorinated hydrocarbons such as methylchloroform, CH_3CCl_3 , have been used to study the concentration of atmospheric OH [Fraser and Hyson, 1986; Prinn *et al.*, 1987, 1992]. An investigation of the compounds discussed here can contribute to the knowledge of the variations in the OH distribution. Yet, data sets of the global distribution of halocarbons in the atmosphere are very limited. In this paper we provide measurements of the halocarbons over the Atlantic between 45°N and 30°S.

EXPERIMENT

The halocarbons were measured by gas chromatography aboard the German R/V *Polarstern*. The cruise started on August 5, 1989, at Bremerhaven, Germany, and ended on September 5, 1989, in Puerto Madryn, Argentina. From 30°N to 10°N the cruise track followed the African coast line and between 10°S and 40°S the South American coastline (Figure 1). The measurements were made between August 5, 1989 (53°N) and September 1, 1989 (30°S). Due to technical problems with the electron capture detector halocarbon measurements started on August 9 at 46°N.

The instrument was installed in a container on the navigation deck about 20 m above sea level. Due to a satellite antenna on the portside of the navigation deck, the container had to be set up on the starboard side. Since the general direction of the relative wind during the cruise was from the portside of the ship, the air intake (stainless steel tube, 10 mm ID) was located on that side and had a length of 30 m,

Copyright 1993 by the American Geophysical Union.

Paper number 93JD01864.
0148-0227/93/93JD-01864\$05.00

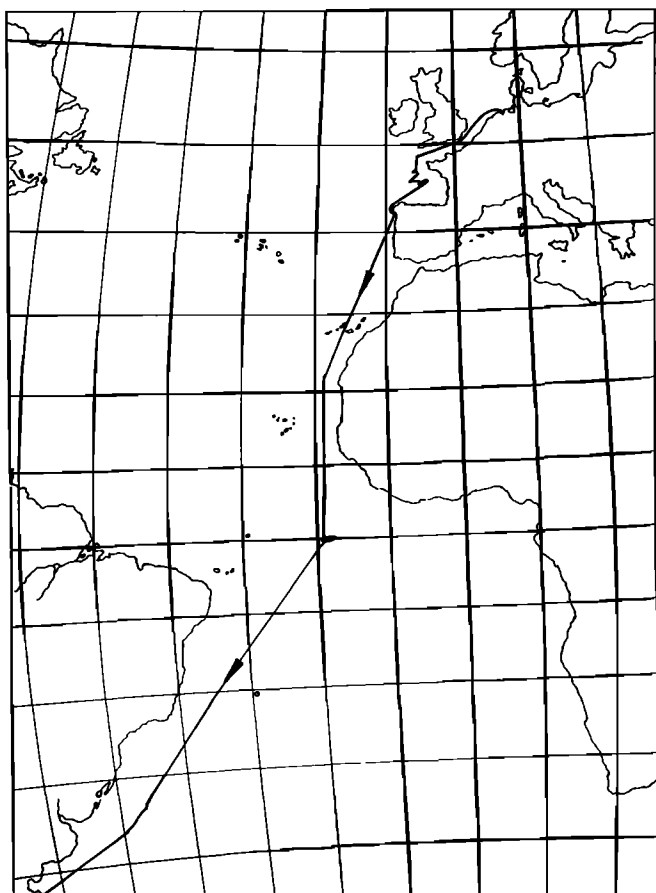


Fig. 1. Cruise track of R/V *Polarstern* in August/September 1989.

including an extension of about 5 m beyond the structure of the ship. The stainless steel inlet line was permanently flushed with outside air at a flow rate of several $\text{dm}^3 \text{min}^{-1}$ to minimize wall losses and memory effects.

The samples were preconcentrated from 1.5 to 4 dm^3 (STP) of air at liquid nitrogen temperature on a preconcentration column packed with porous glass beads and analyzed using a gas chromatograph with a combination of packed and capillary columns [Rudolph *et al.* 1986; Rudolph and Johnen, 1990]. The halocarbons were detected by an electron capture detector (ECD). The instrument and the data acquisition system are described in detail by Koppmann *et al.* [1992].

The atmospheric mixing ratios were calculated by comparing the samples with a reference air of known composition. The reference air was calibrated with individual standards prepared by a three-step static dilution of the pure halocarbons with purified synthetic air. The reference air bottle used during the cruise was compared with our laboratory standard before and after the cruise and during the cruise with an aliquot of the laboratory standard in a 10 dm^3 stainless steel cannister. For CH_3Cl our standard was also compared with a primary standard purchased from the Oregon Graduate Center, Beaverton, Oregon, (R. A. Rasmussen, private communication). The agreement was better than 10%.

During 14 of the measurements the valve between inlet line and preconcentration column was closed. From these measurements without preconcentration of an air sample the

blank values were determined. While no blank peaks were observed for CH_3Cl , C_2HCl_3 , and C_2Cl_4 , a small reproducible blank peak (corresponding to a mixing ratio of about 2 ppt) was observed for CH_2Cl_2 . The peak areas both in the air samples and in the standard measurements were corrected for this blank value. From the standard deviation of the blank determination the 3σ detection limits were calculated to be 2.6 ppt for CH_3Cl and 0.1 ppt for the chloroethenes. For dichloromethane the detection limit was 4.4 ppt. The reproducibility, derived from 12 analyses of the laboratory standard, was better than 10%. Owing to the low mixing ratios of the investigated halocarbons all measurements were within the dynamic range (10^4) of the detector [Rudolph and Jepsen, 1983]. The mixing ratios of the halocarbons in the standard air sample, the calibration error of the laboratory standard, and the 3σ detection limits are given in Table 1.

In all cases where relative wind direction and velocity indicated possible contamination by the ship's exhaust, the measurements were rejected. This was the case for a number of samples in the southern hemisphere and in two areas in the Bay of Biscay (46°N , 4.5°W) and in the mid-Atlantic (0.5°S , 18.5°W). Here, due to geological programs the *Polarstern* sailed on cross profiles for several days.

Four measurements showed unusual low-ethane mixing ratios of less than 200 ppt. Since this indicates problems with the preconcentration procedure, these samples were also rejected. In some chromatograms the water peak was very broad. In these cases methylchloride interfered with the water peak and thus could not be evaluated quantitatively.

RESULTS AND DISCUSSION

Overview

120 measurements of halocarbons were made during this cruise of the R/V *Polarstern*. The latitudinal distributions of methylchloride, dichloromethane, tetrachloroethene, and trichloroethene are shown in Figures 2a–d.

Methylchloride showed a rather uniform distribution with average mixing ratios of 532 ± 8 ppt in the northern hemisphere and 550 ± 12 ppt in the southern hemisphere. This difference is statistically not significant.

Dichloromethane showed constant mixing ratios with an average of 18 ± 4 ppt in the southern hemisphere and an increase between the ITCZ and 45°N of about a factor of 3. The average mixing ratio in the northern hemisphere was 36 ± 6 ppt. The shape of the tetrachloroethene distribution is similar, but the absolute values were about a factor of 8 lower. The mixing ratios were generally below 3 ppt in the southern hemisphere with an average of 2.7 ± 0.1 ppt. After a minimum of 1 ppt in the Intertropical Convergence Zone

TABLE 1. Mixing Ratios in the Reference Air, Calibration Error, and Detection Limit for CH_3Cl , CH_2Cl_2 , C_2HCl_3 , and C_2Cl_4

Compound	Mixing Ratio in Reference Air, pptv	Calibration Error of Laboratory Standard, %	Detection Limit, pptv
CH_3Cl	643 ± 27	<10	2.6
CH_2Cl_2	93 ± 3	<30	4.4
C_2HCl_3	15 ± 1	<10	0.1
C_2Cl_4	4 ± 1	<10	0.1

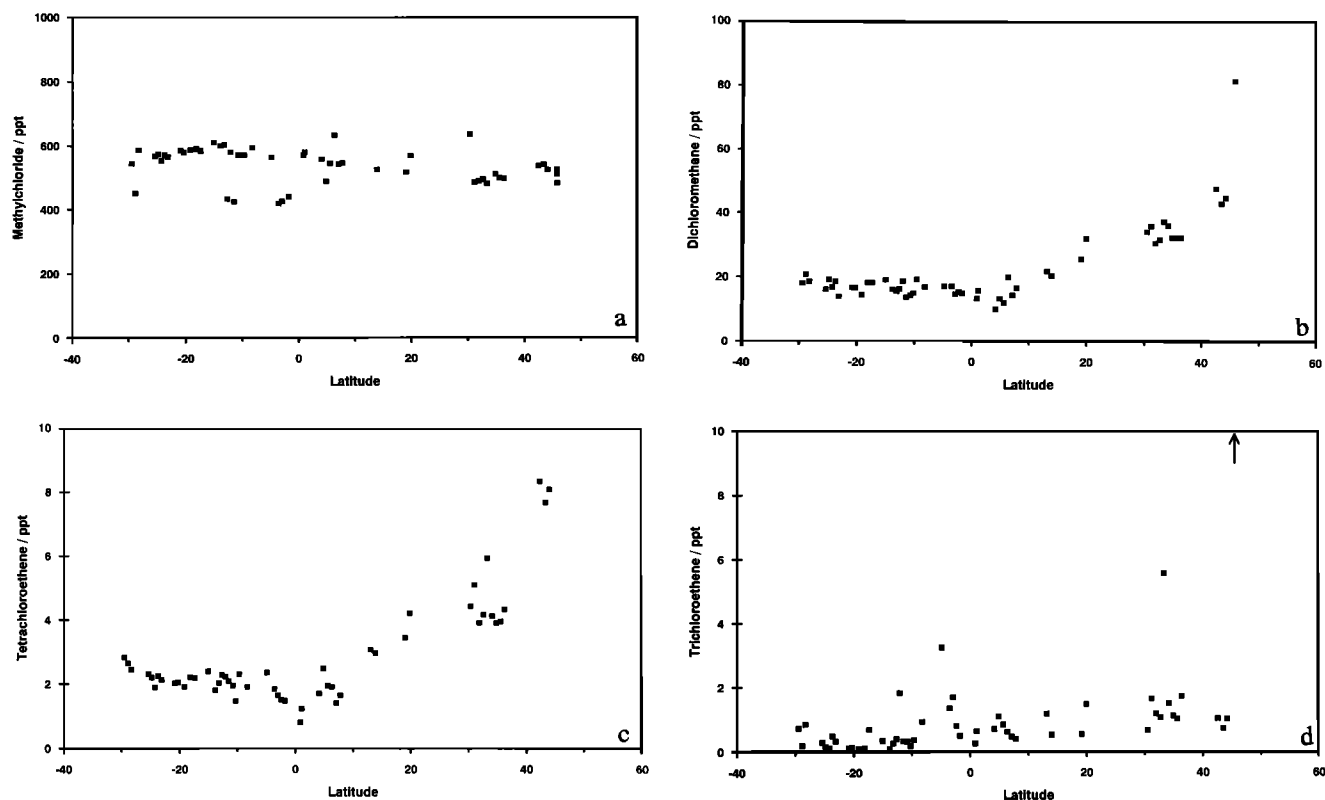


Fig. 2. Plot of halocarbon mixing ratios as function of latitude: (a) methylchloride, (b) dichloromethane, (c) perchloroethene, (d) trichloroethene (the arrow indicates three measurements with mixing ratios between 10 and 15 ppt).

(ITCZ) the mixing ratios increased by a factor of 4 between the ITCZ and 45°N. The average northern hemispheric mixing ratio was 13 ± 6 ppt.

Trichloroethene showed very low mixing ratios of less than 1 ppt in the southern hemisphere, often near the detection limit of 0.1 ppt. The average was 0.6 ± 0.1 ppt. In the northern hemisphere, C_2HCl_3 increased slightly between the ITCZ and 45°N with episodes of elevated mixing ratios up to 15 ppt. In general, northern hemispheric mixing ratios varied between 0.3 ppt and less than 6 ppt with an average of 3 ± 1 ppt.

Although the cruise track followed the northwest African and east South American coastline, an analysis of the backward trajectories (compare Figure 3) and the pattern of the nonmethane hydrocarbons (R. Koppmann, unpublished data) indicated that except for a region around 45°N the conditions during the cruise reflect the remote marine atmosphere. Table 2 summarizes the average hemispheric mixing ratios and the gradients of the halocarbons.

Methylchloride

The most abundant halocarbon in the atmosphere is methylchloride. Figure 4a shows CH_3Cl mixing ratios in the remote atmosphere as reported by different authors. Although our results are at the lower end of the range of mixing ratios reported by other authors they support the results of previous measurement series which indicated that the global distribution of CH_3Cl appears to be very uniform. Some of these data sets were measured at continental background stations [Cox *et al.*, 1976; Khalil and Rasmussen, 1981]. The

other data were measured over the ocean. Over the Pacific Ocean, Singh *et al.* [1979] found mixing ratios of 611 ± 84 ppt and 615 ± 103 ppt for the northern and southern Hemispheres, respectively. Their measurements also showed no latitudinal variation and no difference between both hemispheres. Aircraft measurements by Rasmussen *et al.* [1980] over the Pacific Ocean in 1977 and 1978 revealed mixing ratios of about 620 ppt in the free troposphere with no significant interhemispheric difference. However, for the planetary boundary layer their measurements gave elevated CH_3Cl mixing ratios. They reported a maximum in the planetary boundary layer over the equatorial Pacific of about 780 ppt. Similar results are reported by Khalil and Rasmussen [1981]. During a global aircraft campaign in June 1984 (for details see Rudolph [1988]), two-dimensional distributions of a number of halocarbons were obtained. The average CH_3Cl mixing ratios in the free troposphere were 643 ± 120 ppt for the northern hemisphere and 640 ± 157 ppt for the southern hemisphere (J. Rudolph, unpublished data). Again on the average, no interhemispheric difference was found. However, a maximum near the equator similar to the one reported by Rasmussen *et al.* [1980] and Khalil and Rasmussen [1981] was observed. This equatorial maximum which may be due to enhanced oceanic emissions seems to occur in the northern hemispheric summer and to account for the enhanced average mixing ratios found in the measurement series discussed above. The absence of an equatorial maximum during this cruise is reflected by the relatively low average derived from our measurements.

Using our measured CH_3Cl average of 540 ppt, we can

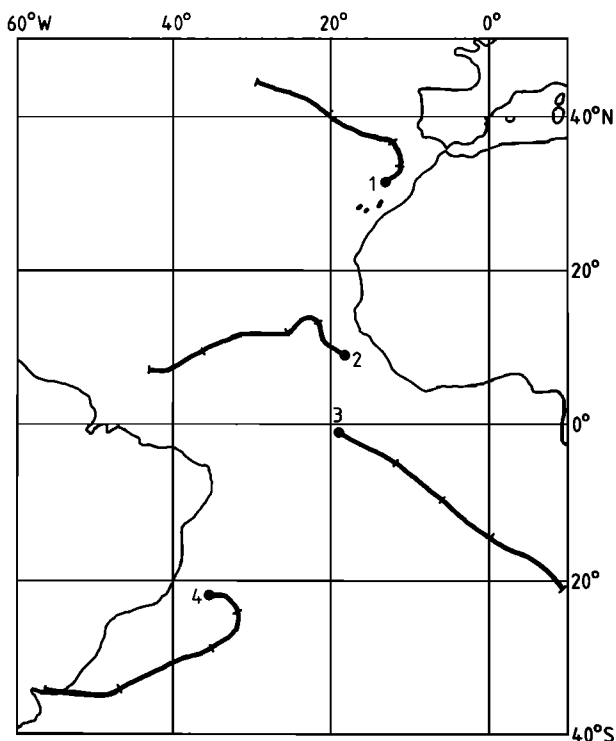


Fig. 3. Four-day backward trajectories on the 850-hPa level. The dots mark the position of the ship on (1) August 16, 1989, (2) August 20, 1989, (3) August 25, 1989, and (4) August 30, 1989.

calculate the global tropospheric burden to be 4×10^{12} g (see Table 2). The corresponding global turnover is 3.5×10^{12} g/yr. This value is consistent with previous estimates of 3×10^{12} g/yr given by Singh *et al.* [1979] and $2.5\text{--}5 \times 10^{12}$ g/yr given by Rasmussen *et al.* [1980].

Dichloromethane and Tetrachloroethene

Dichloromethane and tetrachloroethene showed very similar latitudinal distributions with dichloromethane being on average a factor of 8 more abundant than tetrachloroethene. Dichloromethane increases with a rate of about 7 ppt per 10° of latitude from the equator toward northern latitudes, while C_2Cl_4 shows an increase of only about 1 ppt per 10° of latitude north of the ITCZ. This increase in both halocarbons is compatible with a predominantly industrial origin of these compounds at midnorthern latitudes. In the southern hemisphere both compounds show no significant latitudinal vari-

ation. The uniform distribution of both compounds may be an indication that the sources are located at lower southern latitudes where higher removal rates compensate the enhanced emissions.

Only a few measurements of CH_2Cl_2 in the background troposphere exist (compare Figure 4b). To our knowledge the first measurement of CH_2Cl_2 in the atmosphere was reported by Cox *et al.* [1976]. They found an average mixing ratio of 35 ± 19 ppt in December 1974 and January 1975 in Wiltshire, England. Singh *et al.* [1979] report measurements of dichloromethane over the Pacific Ocean with average mixing ratios of 44 ± 14 ppt in the northern hemisphere and 20 ± 1 ppt in the southern hemisphere.

Figure 5a shows the calculated annual variation of CH_2Cl_2 in the northern hemisphere, assuming the annual variation of the northern hemispheric OH concentration given by Taylor *et al.* [1991] and a constant CH_2Cl_2 source strength for the northern hemisphere. The global production estimates of dichloromethane vary between 0.3×10^{12} g/yr [Finlayson-Pitts and Pitts, 1986] and 0.5×10^{12} g/yr [Pearson, 1982]. From an estimate of the distribution of CO_2 emissions from fossil fuel consumption, Marland *et al.* [1985] show that 90% of the total emissions occur in the northern hemisphere. Assuming that other man-made trace gases are emitted from the same areal distribution, we used 90% of the global production estimates of 0.5×10^{12} g/yr given by Pearson [1982] as CH_2Cl_2 source strength for the northern hemisphere. After a model run of 2 years the annual variation stabilizes with a maximum of 35 ppt at the end of February and a minimum of 27 ppt at the end of August. Compared to our northern hemispheric average of 36 ± 6 ppt for August, this may indicate that compared to the estimate given by Pearson [1982] meanwhile the production rate has increased. The sum of our hemispheric averages would imply a global removal rate of 0.9×10^{12} g/yr (Table 2).

Tetrachloroethene data for the remote troposphere are also very sparse. Rudolph *et al.* [1984] report a latitudinal profile of C_2Cl_4 measured in spring 1983 over the Atlantic. For the southern hemispheric C_2Cl_4 they report quite uniform mixing ratios around 1 ppt and an increase to about 30 ppt between the equator and $50^\circ N$. Compared to our measured distribution in August 1989, their mixing ratios are about a factor of 3 higher in the northern hemisphere and a factor of 2 lower in the southern hemisphere, indicating the existence of a seasonal cycle. J. Rudolph *et al.* (private communication) measured a seasonal cycle for C_2Cl_4 at Alert, Canada. They found an average mixing ratio of 37 ± 2 ppt with an amplitude of 15 ± 3 ppt. Highest mixing ratios

TABLE 2. Mixing Ratios and Gradients of Halocarbons in the Marine Atmosphere

	Northern Hemisphere			Southern Hemisphere			Ratio NH/SH	Mean Atmospheric Lifetime
	Average Mixing Ratio, ppt	Gradient ITCZ– $45^\circ N$, ppt/ $^\circ lat$	Turnover 10^{12} g/yr	Average Mixing Ratio, ppt	Gradient $30^\circ S$ –ITCZ, ppt/ $^\circ lat$	Turnover 10^{12} g/yr		
CH_3Cl	532 ± 8	-1.28 ± 0.54	1.7	550 ± 12	-2.71 ± 1.45	1.8	0.97	1.6 years
C_2HCl_3	3 ± 1	0.08 ± 0.04	2.2	0.6 ± 0.1	0.04 ± 0.01	0.4	5.00	7 days
CH_2Cl_2	36 ± 6	0.87 ± 0.11	0.6	18 ± 1	-0.10 ± 0.04	0.3	2.00	0.5 year
C_2Cl_4	13 ± 6	0.20 ± 0.05	0.5	2.7 ± 0.4	-0.03 ± 0.01	0.08	6.19	0.4 year

Turnover and lifetimes were calculated from reaction rate constants (for an average temperature of 270 K) of the halocarbons with OH radicals [Atkinson *et al.*, 1989] using the average mixing ratios and the OH radical concentrations modeled by Volz *et al.* [1981]. ITCZ, Intertropical Convergence Zone. NH and SH, northern hemisphere and southern hemisphere.

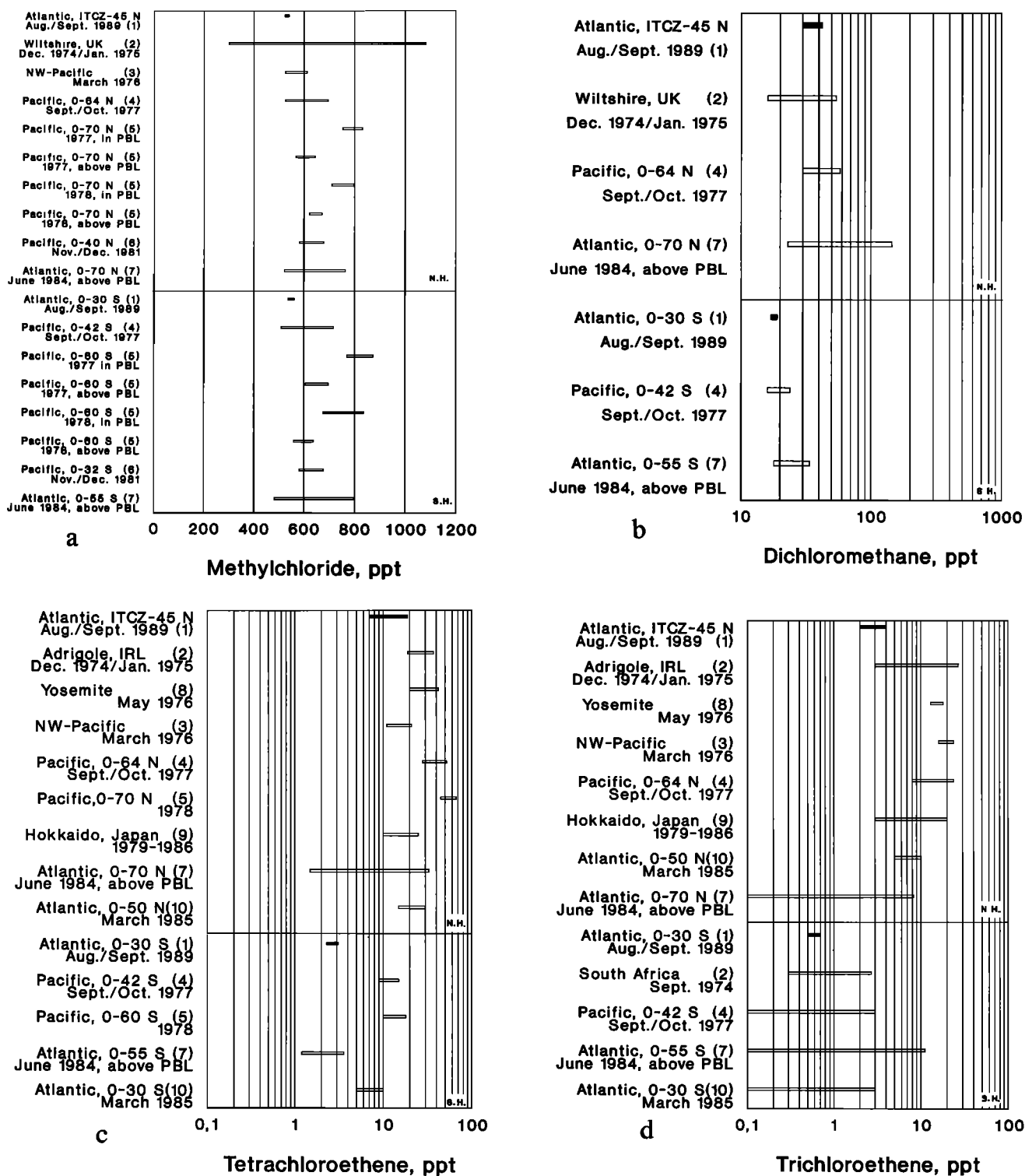


Fig. 4. Mixing ratios of some halocarbons in the marine atmosphere. The references are (1) this work, (2) Cox et al. [1976], (3) Cronn et al. [1977], (4) Singh et al. [1979], (5) Rasmussen et al. [1980], (6) Singh et al. [1983], (7) J. Rudolph, private communication, (8) Singh et al. [1977], (9) Makide et al. [1987], (10) Class and Ballschmiter [1986].

were found in early April and lowest in September. Makide et al. [1987] also found a seasonal cycle for tetrachloroethene with highest mixing ratios in winter and lowest in late summer. However, their mixing ratios varied between less than 10 ppt and about 25 ppt, respectively. Penkett [1982] reports C₂Cl₄ mixing ratios of 34 ± 8 ppt for 35°N. Com-

pared to our results, most of the other measurements [Singh et al., 1977, 1979; Cronn et al., 1977; Cox et al., 1976; Rasmussen and Khalil, 1982] give substantially higher values for the northern hemisphere (see Figure 4c). Also, in Antarctica a seasonal cycle of C₂Cl₄ could be observed (J. Rudolph, unpublished data). The average mixing ratio was

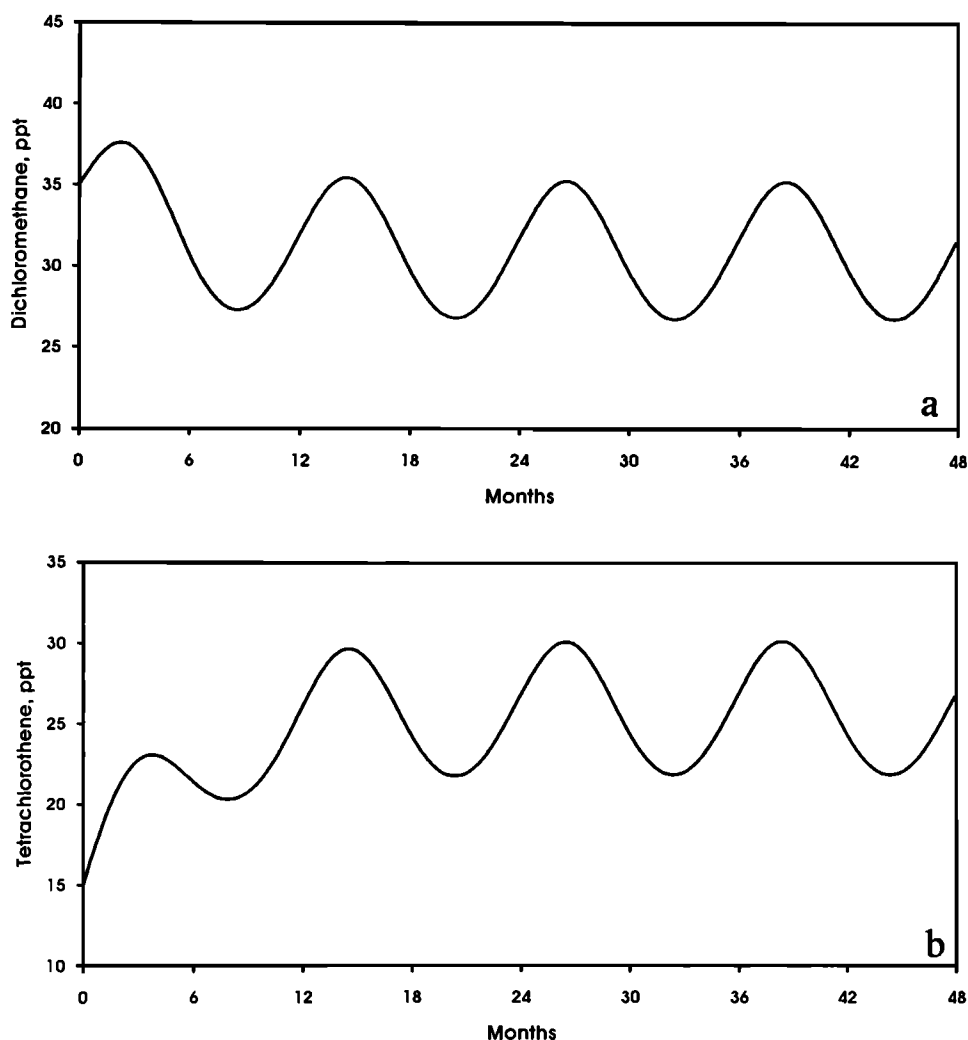


Fig. 5. Calculated annual variation of (a) dichloromethane and (b) tetrachloroethene (for explanations, see text).

2 ± 0.14 ppt with an amplitude of 0.9 ± 0.2 ppt. Here the lowest values were observed in May and the highest in October. From the uniformity of our measurements in the southern hemisphere it seems that our average of 2.7 ± 0.1 ppt is representative for the background troposphere at the season of investigation.

Since also for C_2Cl_4 the reaction with OH is the main sink, we can calculate its seasonal variation for the northern hemisphere as discussed above for CH_2Cl_2 . As source strength of tetrachloroethene in the northern hemisphere, 90% of the global annual production rate of 1.1×10^{12} g/yr estimated by Pearson [1982] was used. We calculate a seasonal variation of C_2Cl_4 with a maximum of 30 ppt in mid-March and a minimum of 22 ppt in mid-September (Figure 5b).

The calculation gives a C_2Cl_4 mixing ratio of about 23 ppt for August. Compared to our measured average mixing ratio of 13 ± 6 ppt, this may be an indication that only part of the annual production is emitted into the atmosphere. An estimate of the global removal rate (Table 2) based on our average mixing ratios gives 0.58×10^{-12} g/yr, which is about one half of the estimated global annual production.

Comparison of the CH_2Cl_2 and C_2Cl_4 Distributions

The similarities in the latitudinal distributions of CH_2Cl_2 and C_2Cl_4 (compare Figure 2) indicate that both compounds have similar source distributions both in the northern and in the southern hemisphere. Since the halocarbons are primarily man-made, it should be possible to describe the source distribution by comparing these compounds with another longer-lived compound like acetylene. Acetylene is known to be emitted primarily by engine exhaust with the dominant sources located at midnorthern latitudes [cf., Ehhalt and Rudolph, 1984]. However, acetylene is also found in biomass burning emissions [Lobert et al., 1991]. The latter is believed to be the dominant source of acetylene in the southern hemisphere, where in September and October, elevated C_2H_2 mixing ratios were found in a latitude band of about 10° south of the ITCZ [Koppmann et al., 1992].

The concentration ratio of a long-lived to a short-lived compound increases with increasing age of an air mass, as discussed in detail by Rudolph and Johnen [1990]. By comparing the ratios of two pairs of atmospheric compounds

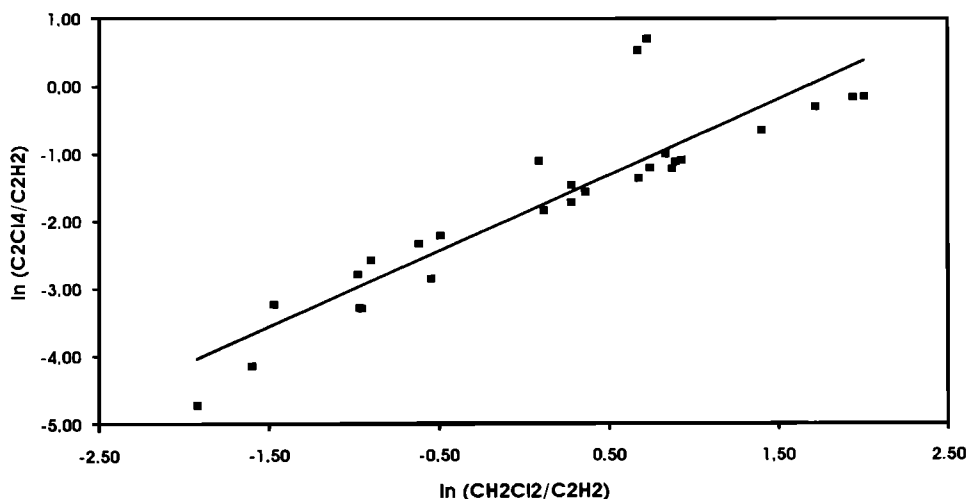


Fig. 6. Plot of the logarithm of the perchloroethene/acetylene concentration ratio versus the dichloromethane/acetylene ratio for the northern hemisphere. The line is a least squares fit to the data points.

assuming that local sources do not contribute to the observed mixing ratios, it is possible to estimate the extent of photochemical aging of the air mass. Figure 6 shows the tetrachloroethene/acetylene versus the dichloromethane/acetylene concentrations in a log-log plot for the northern hemisphere. In the northern hemisphere both compounds have predominantly anthropogenic, continental sources. Plass *et al.* [1992] have shown that oceanic emissions of acetylene which is used here as a reference compound are negligible. A least squares fit for the northern hemisphere gives a slope of 1.12 ± 0.11 , an intercept of -1.88 ± 0.12 , and a regression coefficient of 0.90. The theoretical slope calculated from

$$a = (\text{OH}k_{\text{C}_2\text{H}_2} - \text{OH}k_{\text{C}_2\text{Cl}_4}) / (\text{OH}k_{\text{C}_2\text{H}_2} - \text{OH}k_{\text{CH}_2\text{Cl}_2})$$

with reaction rate constants published by Atkinson *et al.* [1989] is 0.96. Thus the slope of the fit to the experimental data differs by only 14% from the theoretical slope. This indicates that the halocarbons considered above have similar geographic source distributions in the northern hemisphere and the changes in concentration are due to the different removal rates due to the reaction with OH. If a reference compound with a local source contributing significantly to the observed concentrations is used, an estimate, as discussed above, will not give a meaningful result. Indeed, if CH_3Cl is used instead of C_2H_2 , the calculated slope from a fit to the experimental data (not shown here) differs by more than 60% from the theoretical slope. In the southern hemisphere the different types of sources for the various compounds and the different geographical distributions of these sources do not allow a similar interpretation.

Figure 7 shows the concentration ratios of $\text{C}_2\text{H}_2/\text{CH}_2\text{Cl}_2$, $\text{C}_2\text{Cl}_4/\text{CH}_2\text{Cl}_2$, and $\text{C}_2\text{H}_2/\text{C}_2\text{HCl}_3$ as a function of latitude. The latter ratio is found to increase between 45°N and 30°S by 2 orders of magnitude. The atmospheric lifetime of trichloroethene of about 7 days is short compared to the lifetime of acetylene which is in the order of about 1 month. Backward trajectories indicate that during most parts of the cruise the measured air masses had no contact with continents for several days in the northern hemisphere and for more than a week in the southern hemisphere (Figure 3).

Thus the shift of the ratio toward acetylene can be explained by increasing transport times from the sources. The situation is completely different for the ratios of $\text{C}_2\text{H}_2/\text{CH}_2\text{Cl}_2$ and $\text{C}_2\text{H}_2/\text{C}_2\text{Cl}_4$. Dichloromethane and tetrachloroethene have atmospheric lifetimes of about 4 and 6 months, respectively, and show a similar latitudinal distribution (compare Figure 7c). Both concentration ratios decrease with decreasing northern latitudes between 45°N and about 20°N . Four-day backward trajectories indicate that the measured air masses were advected by a high-pressure region over the Atlantic. South of 20°N , the ratios increased and reached a maximum around the equator. In this region the measured air masses originated from the northern parts of South America. The transport times from the continent to the position of the ship was estimated to be in the order of 10 days. Between the equator and 30°S the ratio decreased by about 1 order of magnitude. A comparison of the latitudinal distributions of the individual compounds shows that the pronounced maximum in the concentration ratios found around the equator is due to the increase of acetylene mixing ratios. This indicates that there must be an additional acetylene source, which is not associated with CH_2Cl_2 or C_2Cl_4 emissions, e.g., biomass burning, contributing to the observed acetylene distribution. Compared to September/October 1988 [Koppmann *et al.*, 1992], the center of the bulge in the acetylene mixing ratio was shifted by about 5° to the north. This observation coincides with the observed position of the ITCZ which was found to be at 8°N in 1989 compared to 5°N in 1988. The significant increase in the concentration ratio of $\text{C}_2\text{H}_2/\text{C}_2\text{Cl}_4$ and $\text{C}_2\text{H}_2/\text{CH}_2\text{Cl}_2$ is obviously due to the elevated acetylene mixing ratios, since the halocarbons are fairly constant. Biomass burning is considered to be the dominant source of acetylene in the southern hemisphere. Rudolph *et al.* [1993] have shown that CH_2Cl_2 and to a much lesser extent C_2Cl_4 are also emitted by biomass burning. However, compared to C_2H_2 , the emission rates of the halocarbons is very low. Using the emission ratios given by Rudolph *et al.* [1993] and transport times of a week, an enhancement of CH_2Cl_2 relative to the background concentration is in the order of tenths of a parts per trillion. This is less than the measured variation and therefore cannot be seen in our data set.

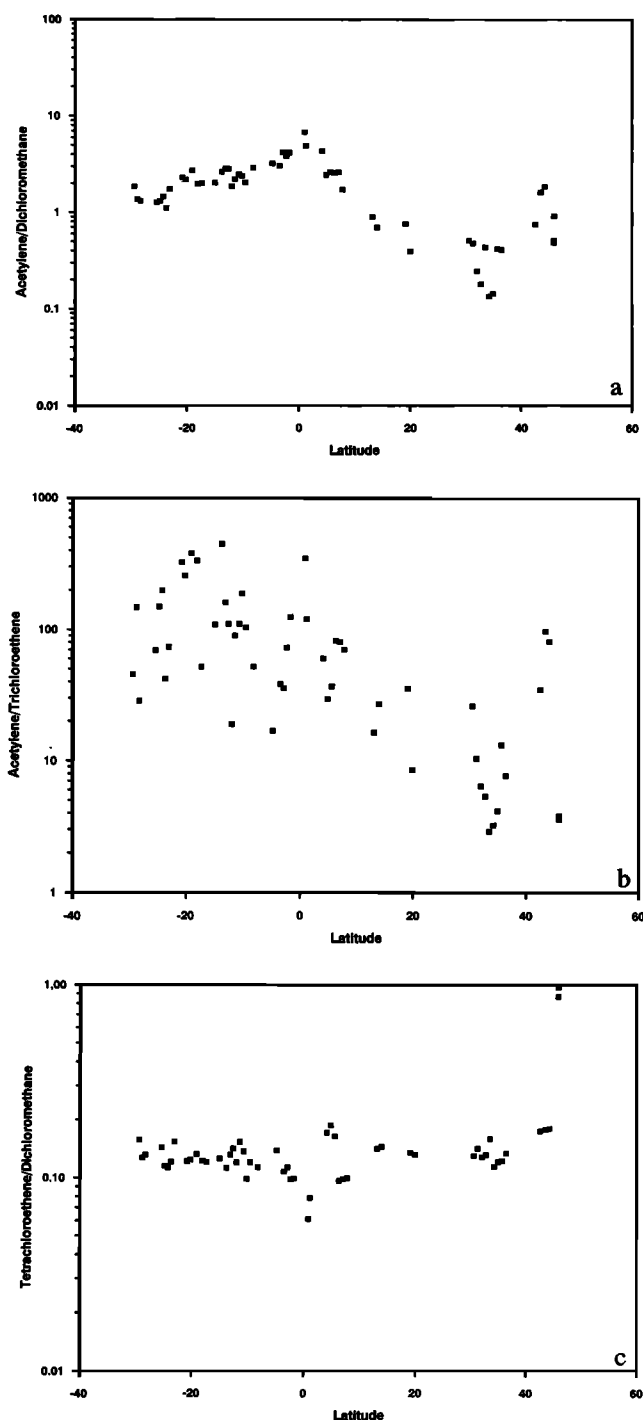


Fig. 7. Plot of (a) acetylene/dichloromethane ratio, (b) acetylene/trichloroethene ratio, and (c) tetrachloroethene/dichloromethane ratio versus latitude.

Trichloroethene

The highest variability was observed for C_2HCl_3 with mixing ratios being generally lower than those of C_2Cl_4 . The short atmospheric lifetime of C_2HCl_3 is reflected in the relatively low averages of 3 ± 1 ppt in the northern hemisphere and 0.6 ± 0.1 ppt in the southern hemisphere and the high variability. Near the French coastline around $45^\circ N$ some measurements gave trichloroethene mixing ratios of

more than 15 ppt. Between the ITCZ and $45^\circ N$, trichloroethene concentrations seem to increase slightly (Figure 2d).

For C_2HCl_3 only few measurements in the remote atmosphere exist. Figure 4d summarizes the measured concentration ranges given by various authors. In general, C_2HCl_3 mixing ratios were found to vary between <0.1 and 25 ppt in the northern hemisphere and between <0.1 and 10 ppt in the southern hemisphere. Cox *et al.* [1976] report mixing ratios measured at Adrigole, Ireland, in December 1974 and January 1975 of 15 ± 12 ppt and southern hemispheric mixing ratios (measured near Cape Town, South Africa, in September 1974) of 1.5 ± 1.2 ppt. Singh *et al.* [1977] report similar northern hemispheric C_2HCl_3 mixing ratios of 15 ± 3 ppt. Class and Ballschmiter [1986] report C_2HCl_3 mixing ratios in March 1983 of 5–10 ppt in the northern hemisphere and below 2 ppt, which was their lower limit of detection, in the southern hemisphere, without giving details about the location. A seasonal cycle for C_2HCl_3 is reported by Makide *et al.* [1987] from measurements between 1979 and 1986 at Hokkaido, Japan. They found highest mixing ratios of about 20 ppt in January and lowest values of about 3 ppt in summer. J. Rudolph *et al.* (private communication) [1992] report measurements from Alert, Canada, covering a period of 2 years (1989–1990). Here also a seasonal cycle for C_2HCl_3 was observed. From a sine fit to the data the average C_2HCl_3 mixing ratio was found to be 6.7 ± 0.5 ppt with an amplitude of 5.2 ± 0.6 ppt. The maximum was in March and the minimum in June/July. In Antarctica (Georg-von-Neumayer Station), average C_2HCl_3 mixing ratios were found to be 0.24 ± 0.02 ppt [Rudolph *et al.*, 1992], but no significant seasonal variation could be observed (J. Rudolph, private communication). Our measured mixing ratios are consistent with these results, indicating that our averages seem to be representative for the background troposphere in August/September in both hemispheres.

CONCLUSION

The latitudinal distributions of methylchloride, dichloromethane, trichloroethene, and tetrachloroethene showed structures which could be assigned to the source distribution, long-range transport, and the photochemical removal in the troposphere. CH_3Cl showed a uniform distribution in both hemispheres with similar mixing ratios, as reported for previous measurement series. This indicates a uniform source distribution and confirms the suggestion that natural production in the surface water of the oceans seems to be the dominant source for CH_3Cl . Elevated mixing ratios over the equatorial oceans, as reported by other authors, could not be observed. Trichloroethene as the shortest-lived compound discussed here showed very low mixing ratios throughout the cruise. C_2HCl_3 mixing ratios decreased by a factor of 10 between $45^\circ N$ and $30^\circ S$. The low atmospheric mixing ratios of C_2HCl_3 are compatible with the short atmospheric lifetime of less than 10 days and emissions from anthropogenic sources, primarily at midnorthern latitudes. Thus C_2HCl_3 plays a negligible role for the chemistry of the remote troposphere, but its low background concentration and good detectability by ECD-GC makes it a useful tracer for the analysis of transport and dilution processes of continental air masses. Two of the other halocarbons discussed here, dichloromethane and tetrachloroethene, can be used as tracers for exchange processes within the northern hemi-

sphere and between the northern and the southern hemisphere. Both compounds showed a linear decrease between 45°N and the equator of 7 and 2 ppt per 10° of latitude, respectively. In the southern hemisphere both compounds showed no significant latitudinal variation. Analysis of the distributions using acetylene as a reference compound showed that photochemical removal during long-range transport from continental sources can explain the observed concentrations. Since the main sources of CH₂Cl₂ and C₂Cl₄ are in the northern hemisphere, their mixing ratios in the southern hemisphere seem to be mainly due to interhemispheric exchange processes. The phases of the annual variations in both hemispheres are shifted by about 180 days and the gradient in the northern hemisphere peaks at the same season as photochemical removal does in the southern hemisphere. Thus one can speculate that due to the annual variation in the northern hemisphere, interhemispheric exchange may to some extent attenuate any annual variation in the southern hemisphere. However, further investigations are necessary to establish the seasonal cycles of the halocarbons and their global distribution. Although the halocarbons discussed here are of minor importance for the global tropospheric chemistry, they can be used as tracers for long-range transport and dilution of continental air masses. Owing to their different atmospheric lifetimes the distribution of these halocarbons can be a measure for the different time scales of these processes. Their global distribution and annual variation may be used as a measure of the distribution and variation of the global OH radical concentration.

Acknowledgments. We thank the Alfred-Wegener-Institut für Polar- und Meeresforschung for the opportunity to participate in the ANT VIII/1 cruise of the R/V *Polarstern*. We further thank the crew of the ship for the valuable cooperation. We are also grateful to H. Franken for his assistance during the installation of the experiments and G. Nohr for technical assistance during the cruise.

REFERENCES

- Atkinson, R. A., D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry, supplement III, *J. Phys. Chem. Ref. Data*, 18(2), 881–1095, 1989.
- Class, T., and K. Ballschmiter, Chemistry of organic tracers in air, IV, Distribution of chlorinated C₁–C₄ hydrocarbons in air over the northern and southern Atlantic Ocean, *Chemosphere*, 15, 413–427, 1986.
- Cowan, M. I., A. T. Glen, S. A. Hutchinson, M. E. Maccartney, J. M. Mackintosh, and A. M. Moss, Production of volatile metabolites by species of fomes, *Trans. Br. Mycol. Soc.*, 60, 347–360, 1973.
- Cox, R. A., R. G. Derwent, and A. E. J. Eggleton, Photochemical oxidation of halocarbons in the troposphere, *Atmos. Environ.*, 10, 305–308, 1976.
- Cronn, D. R., R. A. Rasmussen, E. Robinson, and D. E. Harsch, Halogenated compound identification and measurement in the troposphere and lower stratosphere, *J. Geophys. Res.*, 82, 5935–5944, 1977.
- Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. H. Pollock, and W. Seiler, Biomass burning as a source of atmospheric trace gases CO, H₂, N₂O, NO, CH₃Cl, and COS, *Nature*, 282, 253–256, 1979.
- Ehhalt, D. H., and J. Rudolph, On the importance of light hydrocarbons in multiphase atmospheric systems, *Ber. Kernforsch. Juelich, JUEL-1942*, 1–43, 1984.
- Fabian, P., Halogenated hydrocarbons in the atmosphere, in *The Handbook of Environmental Chemistry*, vol. 4, part A, edited by O. Hutzinger, pp. 23–51, Springer-Verlag, New York, 1986.
- Finlayson-Pitts, B. J., and J. N. Pitts, *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, John Wiley, New York, 1986.
- Fraser, P. J., and P. Hyson, Methane, carbon monoxide, and methylchloroform in the southern hemisphere, *J. Atmos. Chem.*, 4, 3–42, 1986.
- Khalil, M. A. K., and R. A. Rasmussen, Atmospheric methylchloride (CH₃Cl), *Chemosphere*, 10, 1019–1023, 1981.
- Koppmann, R., R. Bauer, F. J. Johnen, C. Plass, and J. Rudolph, The distribution of light nonmethane hydrocarbons over the mid-Atlantic: Results of the *Polarstern* cruise ANT VII/1, *J. Atmos. Chem.*, 15, 215–234, 1992.
- Lobert, J. M., D. H. Scharffe, W. M. Hao, T. A. Kuhlbusch, R. Seuwen, P. Warneck, and P. J. Crutzen, Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning; Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 289–304, MIT Press, Cambridge, Mass., 1991.
- Makide, Y., A. Yokohata, Y. Kubo, and T. Tominaga, Atmospheric concentrations of halocarbons in Japan in 1979–1986, *Bull. Chem. Soc. Jpn.*, 60, 571–574, 1987.
- Marland, G., R. M. Rotty, and N. L. Treat, CO₂ from fossil fuel burning: Global distribution of emissions, *Tellus*, 37B, 243–258, 1985.
- Pearson, C. R., C₁ and C₂ halocarbons, anthropogenic Compounds, in *The Handbook of Environmental Chemistry*, vol. 3, part B, edited by O. Hutzinger, pp. 69–88, Springer-Verlag, New York, 1982.
- Penkett, S. A., Nonmethane organics in the remote troposphere, in *Atmospheric Chemistry, Physical and Chemical Sciences Research Report 4, Report of the Dahlem Workshop on Atmospheric Chemistry, Berlin FRG 1982, May 2–7*, edited by E. D. Goldberg, Springer-Verlag, New York, 1982.
- Plass, C., R. Koppmann, and J. Rudolph, Light hydrocarbons in the surface water of the mid-Atlantic, *J. Atmos. Chem.*, 15, 235–251, 1992.
- Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, Atmospheric trends in methylchloroform and the global average for the hydroxyl radical, *Science*, 238, 945–950, 1987.
- Prinn, R., et al., Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform) data for 1978–1990, *J. Geophys. Res.*, 97, 2445–2461, 1992.
- Rasmussen, R. A., and M. A. K. Khalil, Latitudinal distribution of trace gases in and above the boundary layer, *Chemosphere*, 3, 227–235, 1982.
- Rasmussen, R. A., L. E. Rasmussen, M. A. K. Khalil, and R. W. Dallage, Concentration distribution of methyl chloride in the atmosphere, *J. Geophys. Res.*, 85, 7350–7356, 1980.
- Rudolph, J., Two-dimensional distribution of light hydrocarbons: Results from the STRATOZ III experiment, *J. Geophys. Res.*, 93, 8367–8377, 1988.
- Rudolph, J., and C. Jebsen, The use of photoionization, flameionization and electron capture detectors in series for the determination of low molecular weight trace components in the nonurban atmosphere, *Int. J. Environ. Anal. Chem.*, 13, 129–139, 1983.
- Rudolph, J., and F. J. Johnen, Measurements of light atmospheric hydrocarbons over the Atlantic in regions of low biological activity, *J. Geophys. Res.*, 95, 20,583–20,591, 1990.
- Rudolph, J., C. Jebsen, A. Khedim, and F. J. Johnen, Measurements of the latitudinal distribution of light hydrocarbons and halocarbons over the Atlantic, in *Physicochemical Behaviour of Atmospheric Pollutants, Proceedings of the 3rd European Symposium, Varese, Italy, April 10–12, 1984*, D. Reidel, Norwell, Mass., 1984.
- Rudolph, J., F. J. Johnen, and A. Khedim, Problems connected with the analysis of hydrocarbons and halocarbons in the nonurban atmosphere, *Int. J. Environ. Anal. Chem.*, 27, 91, 1986.
- Rudolph, J., A. Khedim, T. Clarkson, and D. Wagenbach, Long-term measurements of light alkanes and acetylene in the Antarctic troposphere, *Tellus*, 44B, 252–261, 1992.
- Rudolph, J., A. Khedim, R. Koppmann, and B. Bonsang, Field study of the emissions of methyl chloride and other halocarbons from biomass burning in equatorial Africa, *J. Atmos. Chem.*, in press, 1993.
- Schmidt, U., D. Knapska, and S. A. Penkett, A study of the vertical

- distribution of methylchloride (CH_3Cl) in the midlatitude stratosphere, *J. Atmos. Chem.*, **3**, 363–376, 1985.
- Singh, H. B., L. J. Salas, H. Shigeishi, and A. Crawford, Urban–nonurban relationships of halocarbons, SF_6 , N_2O , and other atmospheric trace constituents, *Atmos. Environ.*, **11**, 819–828, 1977.
- Singh, H. B., L. J. Salas, H. Shigeishi, and E. Scribner, Atmospheric halocarbons, hydrocarbons, and sulfur hexafluoride: Global distributions, sources, and sinks, *Science*, **203**, 899–903, 1979.
- Singh, H. B., L. J. Salas, and R. E. Stiles, Methyl halides in and over the eastern Pacific (40°N – 32°S), *J. Geophys. Res.*, **88**, 3684–3690, 1983.
- Taylor, J. A., G. P. Brasseur, P. R. Zimmerman, and R. J. Cicerone, A study of the sources and sinks of methane and methyl chloroform using a global three-dimensional Lagrangian tropospheric tracer transport model, *J. Geophys. Res.*, **96**, 3013–3044, 1991.
- Volz, A., D. H. Ehhalt, and R. G. Derwent, Seasonal and latitudinal variation of ^{14}CO and the tropospheric concentration of OH radicals, *J. Geophys. Res.*, **86**, 5163–5171, 1981.
-
- F. J. Johnen, R. Koppmann, C. Plass-Dülmer, and J. Rudolph, Institut für Atmosphärische Chemie, Forschungszentrum Jülich, P.O. Box 1913, D-52425 Jülich, Germany.

(Received December 23, 1992;
revised June 2, 1993;
accepted July 6, 1993.)