

# Trichloroethylene and tetrachloroethylene in Atlantic waters

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**Abstract.** Measurements of trichloroethylene ( $C_2HCl_3$ ) and tetrachloroethylene ( $C_2Cl_4$ ) in waters of the North Atlantic are reported. They show that at the times of sampling both gases are supersaturated in the surface ocean and that there are therefore fluxes of each into the atmosphere. The water column profiles are unusual in showing increasing concentrations with depth. It is proposed that both gases may be supplied to the ocean from the atmosphere in winter, when their atmospheric mixing ratios are higher due to diminished loss rates resulting from lower concentrations of the hydroxyl radical. This hypothesis is consistent with literature reports of ocean supersaturations of trichloroethylene and tetrachloroethylene but does not require any natural source. In the western Atlantic several profiles of trichloroethylene have, superimposed on the general increase in concentration with depth, maxima lying just beneath the mixed layer which may be indicative of a biological source.

## 1. Introduction

Trichloroethylene ( $C_2HCl_3$ ) and tetrachloroethylene ( $C_2Cl_4$ ) have industrial sources to the atmosphere, where they are destroyed mainly by reaction with the hydroxyl (OH) radical [Itoh *et al.*, 1994]. The average lifetimes in the atmosphere of  $C_2HCl_3$  and  $C_2Cl_4$  are ~7 days and 4-5 months, respectively [Koppmann *et al.*, 1993; Wang *et al.*, 1995]. Atmospheric tetrachloroethylene has been of some particular interest as it can provide information on the relevance of chlorine atom (Cl) initiated oxidation reactions. The reason is that there must be consistency between the observed concentrations of the gas in the atmosphere, its rate of chemical destruction, and its rate of supply. The chemical loss rate would be particularly sensitive to Cl atom concentration because the tetrachloroethylene reacts at a rate ~300 times faster with Cl than with the OH radical [Nico<sup>v</sup>ich *et al.*, 1996]. Any natural sources of tetrachloroethylene (and of trichloroethylene) must also be constrained in size by the need for consistency with observed interhemispheric concentration gradients. McCulloch and Midgley [1996] have pointed out that there is a large discrepancy between the observed atmospheric concentration of trichloroethylene and that calculated from its rate of loss through reaction with OH. This would be consistent with the existence of other sources or with errors in either its rate of reaction with OH or its reported atmospheric concentration. There are several reports that the ocean is supersaturated with tetrachloroethylene and trichloroethylene [Singh *et al.*, 1983; Khalil *et al.*, 1999; Keene *et al.*, 1999] and apparently conflicting reports of whether certain marine algae produce the compounds in laboratory cultures or in the ocean [Abrahamsson *et al.*, 1995a, 1995b; Scarratt and Moore, 1999; Marshall *et al.*, 2000; Abrahamsson and Pedersén, 2000]. In their analysis of the implications of the global budget of tetrachloroethylene on Cl abundance, Singh *et al.* [1996] assumed an oceanic source of 35-70 Gg  $y^{-1}$ , the lower end being consistent with unpublished reports of the level of oceanic supersaturation; they pointed to the need for better

knowledge of the natural sources of  $C_2Cl_4$ . This paper describes the results of two field studies aimed at determining whether there is evidence for fluxes of these compounds from the ocean to the atmosphere or for their production within the oceans.

## 2. Methods

Trichloroethylene and tetrachloroethylene were among a suite of trace gases, including methyl halides, dichloromethane ( $CH_2Cl_2$ ), chloroform ( $CHCl_3$ ) and isoprene, measured in water samples during two cruises in the North Atlantic: a cruise of R/V *Knorr* in July-August 1997 from the Newfoundland shelf to the Suriname shelf, and Leg 2 of the Gas Ex 98 cruise of National Oceanic and Atmospheric Administration (NOAA) vessel *Ronald Brown* from Lisbon to the Azores in May-June 1998 (Figure 1). Vertical profiles of water samples were collected in rosette-mounted Niskin bottles during the ascent of the samplers. The sample spacing was set so as to provide the most dense sampling in the upper 100 m, where biogenic gases are usually produced, and to provide progressively wider spacing deeper in the water column. Water samples were drawn into 100 mL glass syringes which were stored under seawater on deck until they were analyzed, typically within 6 hours. The purge-and-trap and gas chromatography/mass spectrometry (GC-MS) procedure is essentially that described in detail by Moore *et al.* [1996a], differing only in details such as alteration of the GC back flush timing so that compounds that would elute after tetrachloroethylene were vented.

The detection limits for  $C_2HCl_3$  and  $C_2Cl_4$ , here given as the concentration giving a signal equal to twice the instrument noise level, were 0.06 and 0.07 pmol  $L^{-1}$  respectively. Regularly, one sample in each profile would be measured in duplicate, and from these measurements estimates have been derived of overall precisions for the analyses of 0.02 and 0.03 pmol  $L^{-1}$  (1 standard deviation) for  $C_2HCl_3$  and  $C_2Cl_4$ , respectively.

Standard gas was injected into the analytical system in amounts of 25-100  $\mu L$  using Hamilton gastight syringes. A standard of the halogenated compounds ( $CHCl_3$ ,  $CH_2Cl_2$ ,  $C_2HCl_3$ ,  $C_2Cl_4$ , and  $CH_2Br_2$ ) in carbon dioxide was prepared

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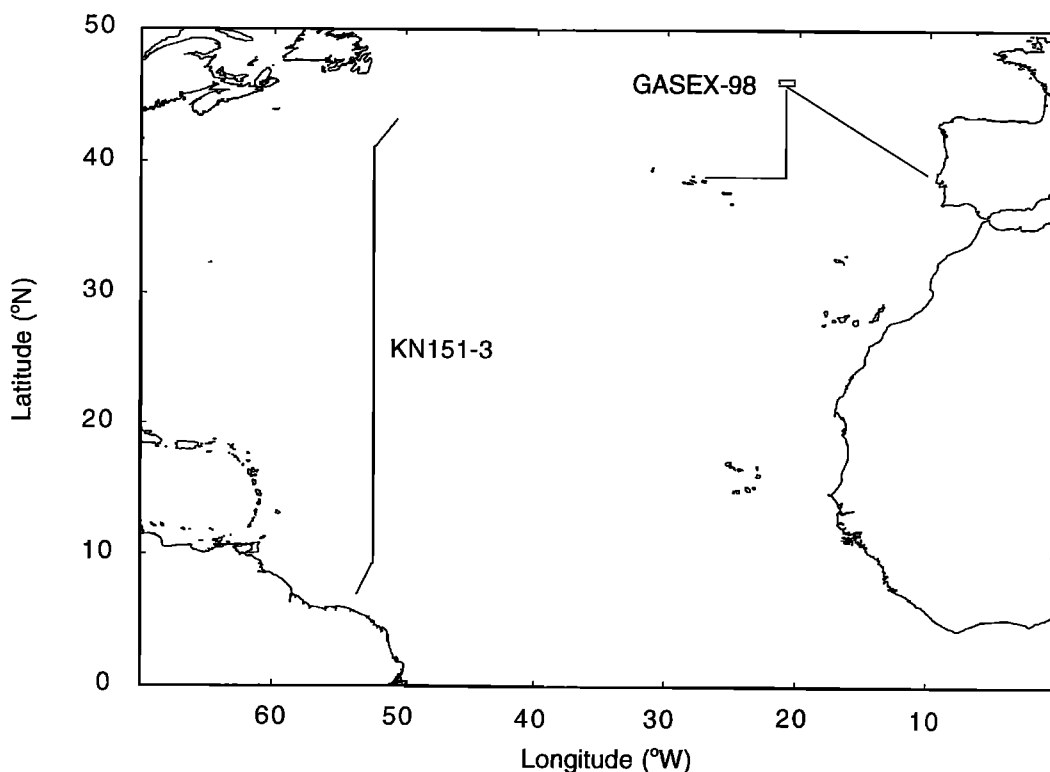


Figure 1. Tracks of R/V *Knorr* (Kn 151) and Gas Ex 98 cruises.

gravimetrically and was diluted in nitrogen into a 33-L stainless steel canister to yield concentrations in the range 30 – 400 nmol mol<sup>-1</sup> (this will be referred to as the Dalhousie University standard). The dilution factor was checked (and corrected by 2.6%) by measuring the CO<sub>2</sub> concentration in the mixture using a pair of CO<sub>2</sub> standards in air for calibration. An intercomparison of this standard and a marine air standard of the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) group indicated good agreement for C<sub>2</sub>HCl<sub>3</sub> but indicated a likely inaccuracy of the C<sub>2</sub>Cl<sub>4</sub> in this gravimetric standard. The error was attributed to incomplete transfer of the weighed C<sub>2</sub>Cl<sub>4</sub> to the primary canister. The corrected C<sub>2</sub>Cl<sub>4</sub> concentration (30.1 nmol mol<sup>-1</sup>) in the Dalhousie University standard was assigned based on the NOAA CMDL standard. The accuracy of the Dalhousie University standard has been estimated as ± 6.5% for each compound on the basis of an intercalibration done on the primary gravimetric CMDL standard together with uncertainties resulting from the dilution of that standard, calibration of the marine air standard (S. Montzka, personal communication, 2001), and its comparison with the Dalhousie University standard.

The accuracy of the measurements depends not only on the accuracy of the standards but also on the elimination of contamination. It was found that contamination of water samples had two main sources: sampling bottles and the shipboard laboratory air. Where sampling bottles were the source, it was manifested as an apparent concentration spike in the water column which could be checked by rotating bottles to different depths. In this way, faulty bottles were removed from use. To avoid contamination of samples from laboratory air, it was found to be effective to store the glass syringes under water outside in the open air. In the earlier of the two cruises, there is evidence that many samples were

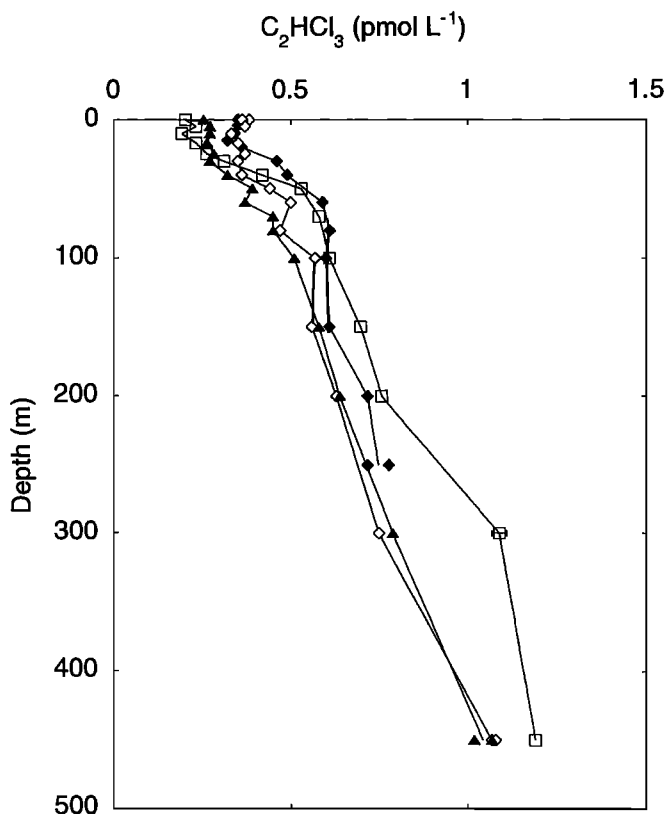
contaminated with C<sub>2</sub>Cl<sub>4</sub>, so in this paper attention will be focused on the Gas Ex 98 data set with comments on only the C<sub>2</sub>HCl<sub>3</sub> measurements in the *Knorr* data set. A limited number of air measurements were also made from samples pumped into stainless steel canisters. In this case the gas was measured into a stainless steel sample loop (206 mL volume).

### 3. Results and Discussion

#### 3.1. Trichloroethylene

Seventeen profiles of C<sub>2</sub>HCl<sub>3</sub>, measured over a period of 3 weeks, consistently showed that concentrations increase downward through the water column, a behavior seldom reported for either biogenic trace gases or for atmospherically derived gases, such as CFC. This is illustrated in Figure 2, which shows four profiles measured at intervals of ~5 days. The consistency of the result argues against substantial contamination because this would tend to occur randomly. The main features of these profiles are lowest concentrations at the surface, relatively rapid increases below the mixed layer, and then gradual increases to 450 m. It should be noted that the precision estimates provided in section 2 are derived from identical samples measured consecutively. Day-to-day variations in the analytical system would yield a larger degree of uncertainty between profiles. Consequently, it is difficult to ascertain how much of the variation between these profiles is attributable to variations in the water masses sampled over the 3-week period.

Trichloroethylene was undetectable (<0.3 pmol mol<sup>-1</sup>) in air samples collected on 2 days. Seawater at equilibrium with an atmosphere having this mixing ratio of C<sub>2</sub>HCl<sub>3</sub> is calculated to have a concentration of <0.04 pmol L<sup>-1</sup>. It is clear that C<sub>2</sub>HCl<sub>3</sub>



**Figure 2.** Trichloroethylene results from Gas Ex 98 cruise. Four profiles of  $C_2HCl_3$  measured at intervals of  $\sim 5$  days are shown (day 151, solid diamonds; day 156, open diamonds; day 162, triangles; and day 167, squares). The error bar ( $\pm 1$  standard deviation) is indicated for a single sample (300 m).

is strongly supersaturated with respect to the local atmosphere (Figure 2). This was also confirmed by two experiments (days 159 and 160) in which a glass syringe of surface seawater was shaken repeatedly with a headspace of ambient air after which the aqueous phase was analyzed;  $C_2HCl_3$  was undetectable in the water.

The question of whether the transport of  $C_2HCl_3$  to the atmosphere from the ocean surface either is compensated by production in the water column or leads to a decrease in its concentration in the water column may be determined by examining the concentration in the mixed layer with time. In Figure 3, mixed layer concentrations are shown, along with the square of the wind speed, which is an index of magnitude of the exchange velocity of dissolved gases. There is evidence that the concentration of  $C_2HCl_3$  decreased with time, but the changes do not show any close relationship with wind speed. While higher wind would increase the rate of exchange with the atmosphere, there is a potentially compensating effect of increasing the upward flux into the mixed layer.

If the observed concentrations of  $C_2HCl_3$  in the water column are the result of prior equilibration of the water with the atmosphere, the concentration that must have existed in the atmosphere may be estimated using the solubility measurements of Moore [1999] and the in situ temperature of the water. In the case of near-surface waters the estimated atmospheric concentration will be a minimum value because the water temperature will have warmed after ventilation occurred in the winter. As an example, an estimation is given

for one of the profiles (day 156) shown in Figure 2. Figure 4 shows the equivalent atmospheric concentration in  $pmol\ mol^{-1}$  with account being taken of the water temperature. This shows that the waters would be at equilibrium with atmospheric partial pressures of between 2.5 (surface) and 5.8  $pmol\ mol^{-1}$  (at 450 m).

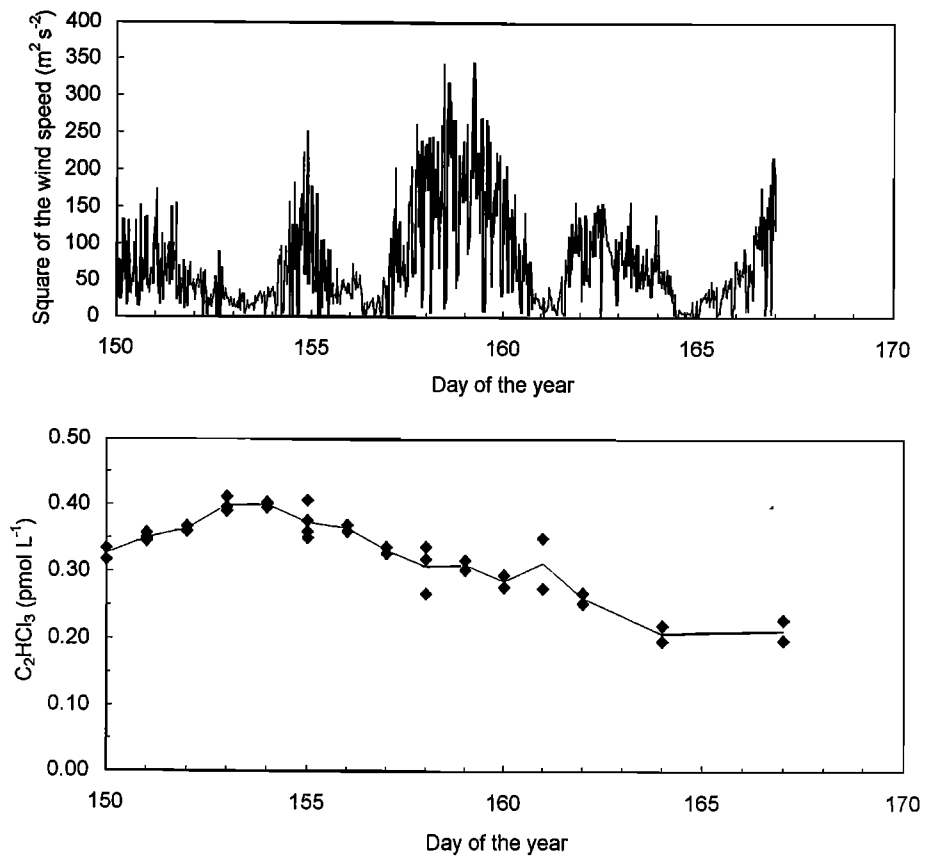
Unfortunately, very few measurements of the concentration of  $C_2HCl_3$  in the marine atmosphere appear to have been made. It is clear that such a compound, having an atmospheric lifetime of  $\sim 7$  days, will show significant seasonal variations driven by the seasonally changing concentration of the OH radical. Koppmann *et al.* [1993] refer to unpublished data showing an average mixing ratio at Alert in 1989-1990 of  $6.7 \pm 0.5\ pmol\ mol^{-1}$  and an amplitude of  $5.2 \pm 0.6\ pmol\ mol^{-1}$  with the maximum occurring in March and the minimum in June/July. At lower latitudes, higher OH radical concentrations would tend to decrease both the concentrations and amplitude. An additional factor that affects the concentration in the atmosphere, and hence the equilibrium concentration in surface ocean waters, is the latitudinal distribution of the anthropogenic source [McCulloch *et al.*, 1999].

### 3.2. Tetrachloroethylene

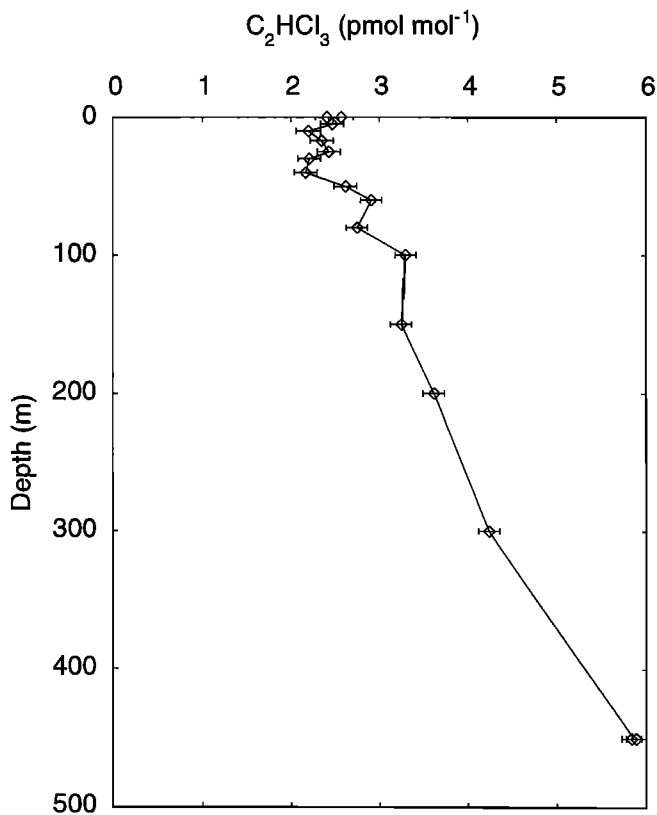
Tetrachloroethylene concentrations increase relatively strongly from within to below the surface mixed layer and then gradually increase with depth to 450 m (Figure 5). The rate of increase in concentration with depth of  $C_2Cl_4$  is less than that for  $C_2HCl_3$ . A more direct comparison may be made between the two compounds by plotting the concentration ratio of  $C_2Cl_4$  and  $C_2HCl_3$  against depth (Figure 6). This shows that the concentration of  $C_2Cl_4$  is  $\sim 3.5$  times higher than  $C_2HCl_3$  in surface waters and decreases to  $\sim 1.4$  times higher at 450 m. An explanation for this in terms of the differing seasonal amplitudes of the atmospheric mixing ratios of the two compounds is proposed below.

There were 2 days on which measurements were made of atmospheric  $C_2Cl_4$ , from these, estimates can be made of the saturation of the gas at the ocean surface (note that such a comparison, as a ratio of concentrations, is independent of the  $C_2Cl_4$  calibration). The average atmospheric concentration was  $6.1\ pmol\ mol^{-1}$  ( $0.1\ pmol\ mol^{-1}$  standard deviation and nine analyses). This would yield an equilibrium concentration in seawater at the average surface temperature of  $15.3^\circ C$  of  $0.46\ pmol\ L^{-1}$ . Surface concentrations were in the range  $0.65 - 0.87\ pmol\ L^{-1}$  (Figure 5), and thus the waters were supersaturated by  $\sim 40-90\%$ . The atmospheric concentrations that would be necessary to support the observed concentrations in the water column are plotted for one profile in Figure 7.

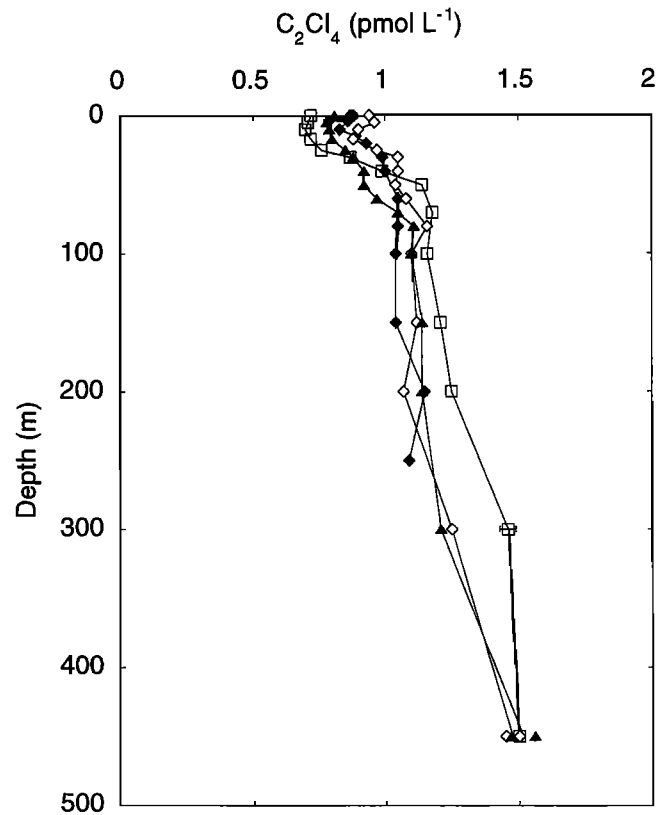
Are the calculated equivalent atmospheric concentrations of such a magnitude that the atmosphere could be a source of the  $C_2Cl_4$  in the water column? The deep water concentrations are 50% higher than the surface values, but when the effect of temperature on solubility is factored out, it is found that the deeper waters are at equilibrium with an atmosphere containing only 20% more  $C_2Cl_4$ . When the calculated equivalent atmospheric concentrations are divided by the measured atmospheric concentration it is found that the ratio at the surface is 1.6, and at 450 m, 2.1. This means that the observed concentrations can be achieved by equilibration of the water column with atmospheres containing up to 2.1 times higher  $C_2Cl_4$  than was observed at the time of the cruise. This estimate, as a ratio of concentrations, would be unaffected by calibration errors.



**Figure 3.** Time series of wind speed squared and surface C<sub>2</sub>HCl<sub>3</sub> concentrations for the Gas Ex 98 cruise.



**Figure 4.** Atmospheric equivalent concentrations of C<sub>2</sub>HCl<sub>3</sub> (in pmol mol<sup>-1</sup>) shown for profile sampled on day 156).



**Figure 5.** Tetrachloroethylene results from Gas Ex 98 cruise. The symbols are as in Figure 2.

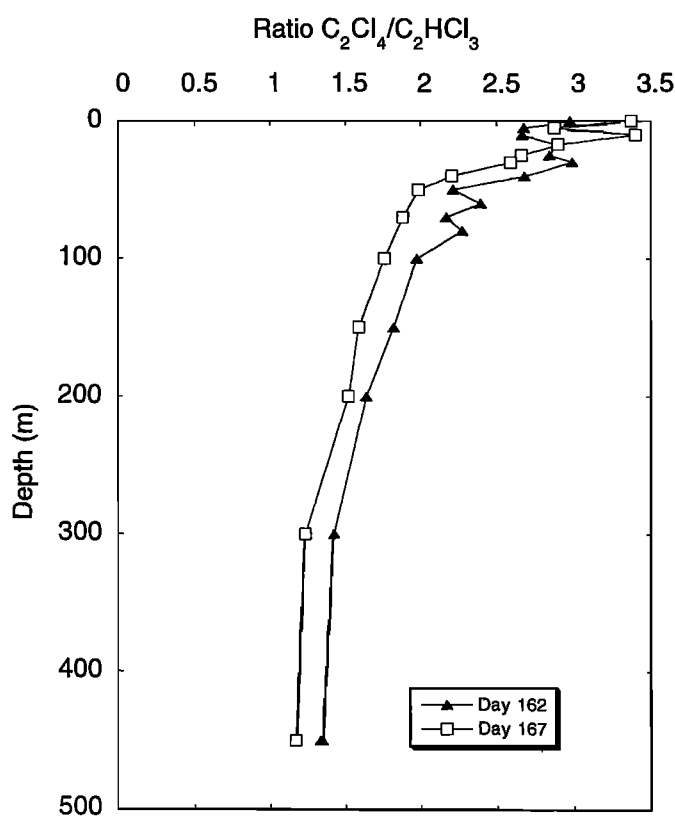


Figure 6. Concentration ratio of  $C_2HCl_3$  and  $C_2Cl_4$  plotted for profiles collected on days 162 (triangles) and 167 (squares).

Measurements of  $C_2Cl_4$  in the marine atmosphere are sparse. A time series from 1994 to 1998 has been reported [Butler *et al.*, 1998; Spivakovsky *et al.*, 2000] which shows a maximum concentration of  $12 \text{ pmol mol}^{-1}$  at a Northern Hemisphere high-latitude site in wintertime 1994 and a clear decreasing trend for those sites. There is a strong seasonal cycle, particularly at the high-latitude sites, as would be expected if its destruction is indirectly linked, through OH radical concentrations, to the seasonal light cycle. The ratio of winter (high) concentration to summer (low) concentration is  $\sim 3$ . Northern Hemisphere mid-latitude concentrations lie in the range  $2\text{--}6 \text{ pmol mol}^{-1}$  [Butler *et al.*, 1998], so the value of  $6.1 \text{ pmol mol}^{-1}$  for the air measurements made during this early summer cruise are higher than would be expected. Deep samples would have been at equilibrium with air containing  $10\text{--}13 \text{ pmol mol}^{-1}$  of  $C_2Cl_4$ . Thus it appears that from the data currently available it is possible neither to demonstrate that the  $C_2Cl_4$  in the deeper samples could have come from the atmosphere nor to discount this possibility.

In the foregoing discussion, attention has been given to whether the observed concentrations of  $C_2HCl_3$  and  $C_2Cl_4$  are quantitatively consistent with equilibration of the waters with the atmosphere. Some attention will now be given to how this equilibration might occur and how it could yield profiles of the pattern observed.

In winter the mixed layer is convectively deepened to varying extent across the North Atlantic, resulting in the formation, in certain areas, of relatively large volumes of Mode Waters having salinity and temperature characteristics of their source regions [McCartney and Talley, 1982]. In general, trace gases may be expected to equilibrate with the atmosphere during the period of Mode Water formation. The

concentrations of  $C_2HCl_3$  and  $C_2Cl_4$  in these waters will depend not only on their temperature (which controls gas solubility) but also on the latitude of the source region. This is because the atmospheric concentrations of short-lived gases like  $C_2HCl_3$  and  $C_2Cl_4$  depend on latitude (as well as season). The study area north of the Azores receives relatively warm ( $>13^\circ\text{C}$ ) Eastern North Atlantic Central Water from the south and deeper subpolar gyre waters formed at  $\sim 47^\circ\text{N}$  and having a temperature of  $\sim 8^\circ\text{C}$ . While additional, deeper water masses will originate at still higher latitudes, and so have higher concentrations of  $C_2HCl_3$  and  $C_2Cl_4$ , it is the two water masses specified that are relevant to the depth range of the Gas Ex 98 samples. The temperature at the bottom of this depth range (450 m) remained above  $11^\circ\text{C}$ . After the end of winter the mixed layer becomes shallower and warmer; at the time and location of this study it had a thickness of 25–30 m. Coincident with these changes in the ocean are changes in the concentration of  $C_2HCl_3$  and  $C_2Cl_4$  in the atmosphere which, having reached their maximum levels in late winter, decline through spring and summer. As the mixed layer becomes shallower it will continue to lose these compounds to the depleted atmosphere. Because the seasonal variation in concentration of a gas with depth is dependent on the amplitude of the concentration cycle in the atmosphere, it will tend to be greater for a gas with a shorter atmospheric lifetime. This is consistent with the steeper change in concentration with depth seen for  $C_2HCl_3$  than for  $C_2Cl_4$  (Figure 6).

#### 4. Alternative Sources of Trichloroethylene and Tetrachloroethylene in the Water Column

An atmospheric source of  $C_2HCl_3$  and  $C_2Cl_4$  at the Gas Ex 98 site has been hypothesized, but other possible sources need

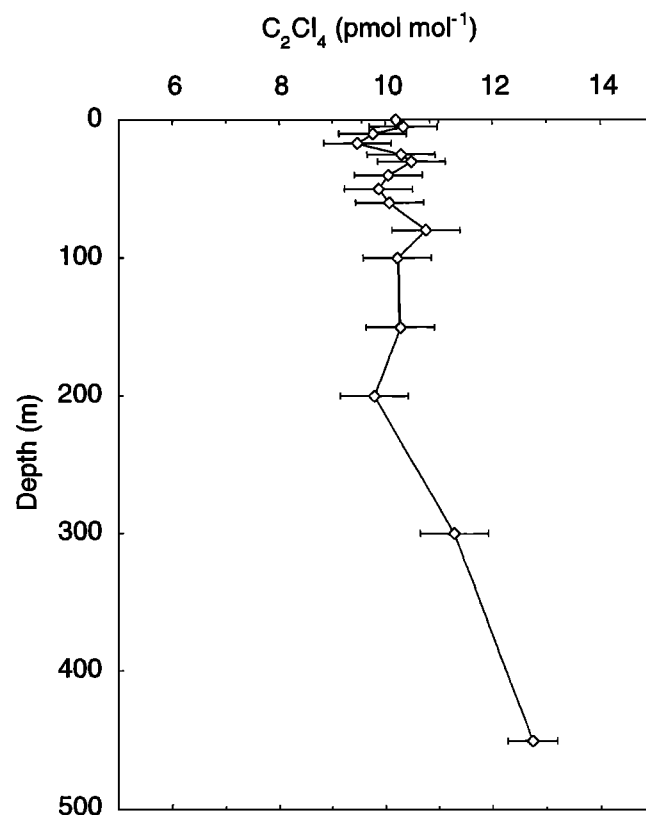
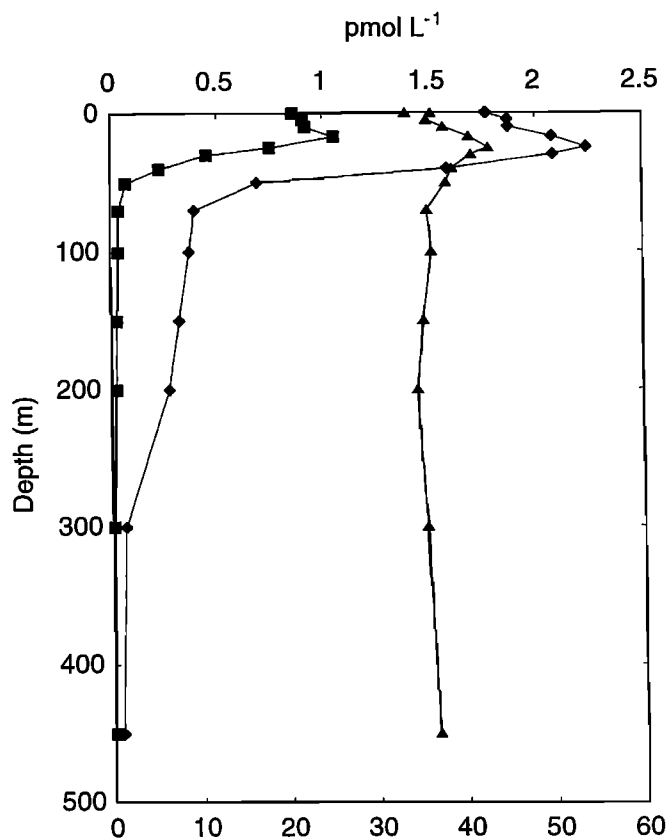


Figure 7. Atmospheric equivalent concentrations of  $C_2Cl_4$  ( $\text{pmol mol}^{-1}$ ) shown for profile sampled on day 156.



**Figure 8.** Vertical profiles of isoprene (diamonds), methyl iodide (squares) and dibromomethane (triangles) for day 167. Top scale applies to dibromomethane, and bottom scale applies to isoprene and methyl iodide.

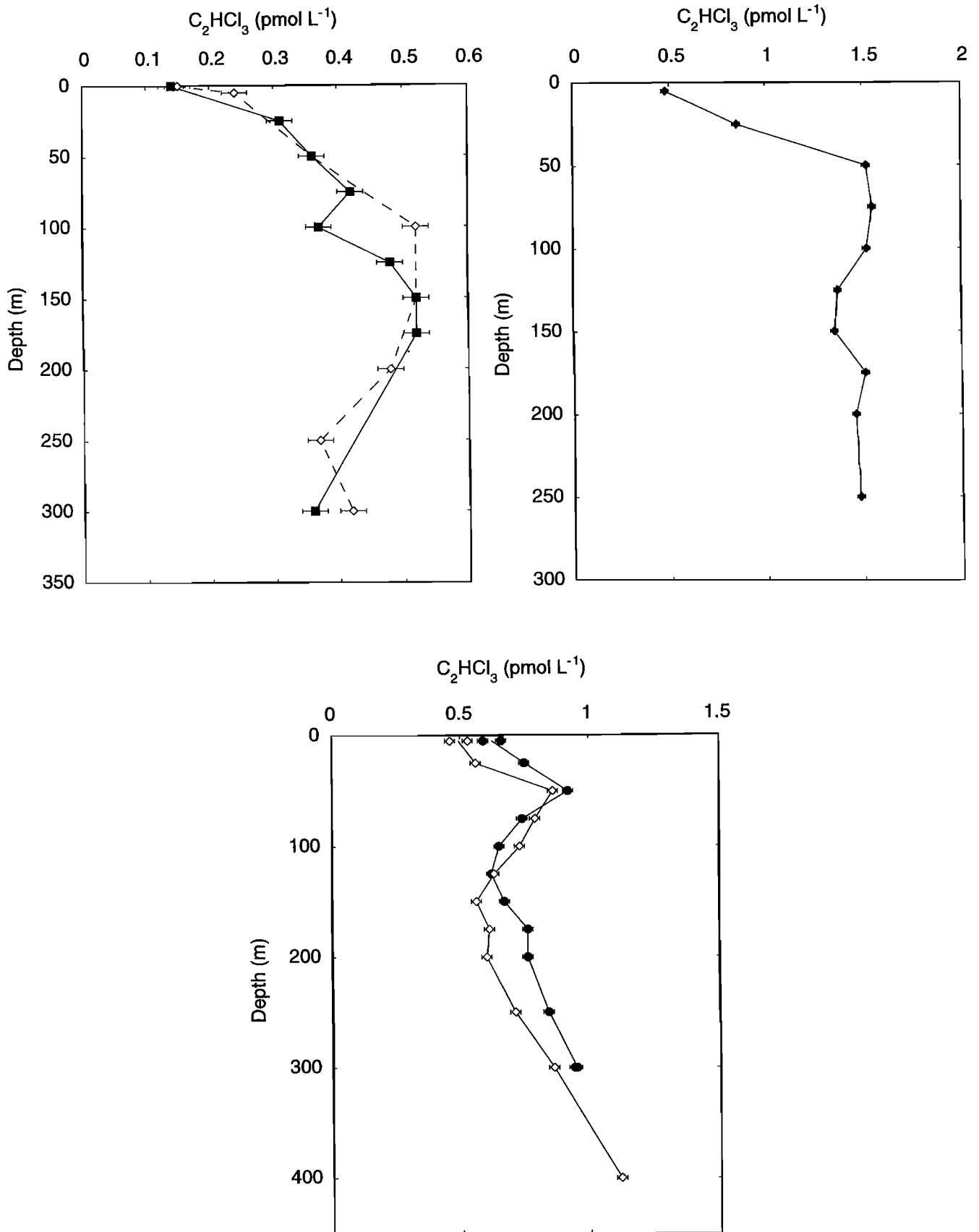
to be considered. In particular, this work seeks to address whether  $C_2HCl_3$  and  $C_2Cl_4$  are produced within the ocean, for example, by biological processes. Some clues are provided by the vertical profiles of the two gases which have in common the unusual feature of increasing concentrations with depth. Many oceanic depth profiles have been measured for different trace gases which are known to have a marine source. Several such gases were measured during the GAS Ex 98 cruise, for example, methyl chloride, methyl bromide, methyl iodide, and isoprene. There is good evidence that all of these are produced in the ocean, and the evidence for an algal source is particularly strong in the case of isoprene since much is known about the release of isoprene from terrestrial plants. Its production by laboratory-cultured marine phytoplankton has also been reported [Moore *et al.*, 1994]. Profiles of isoprene, methyl iodide, and dibromomethane for day 167 are shown in Figure 8. The methyl halides and isoprene have profiles typified by higher concentrations in the upper 60 m of the water column than in deep waters, sometimes with a maximum just beneath the mixed layer (25-30 m thick), probably because loss to the atmosphere is eliminated as an immediate removal mechanism. In general, higher concentrations within the upper 100 m may be attributed to production by phytoplankton which is limited to this illuminated layer. Direct photochemical production also has the potential to cause higher concentrations of some gases within this layer, with production rates tending to decline from the surface downwards as light intensity is attenuated. This occurs in the

case of, for example, carbonyl sulphide [Ferek and Andreae, 1984]. It is clear that these  $C_2HCl_3$  and  $C_2Cl_4$  profiles do not show the features that are commonly observed for marine-produced gases. However, this does not rule out natural production in the ocean. For example, dibromomethane, for which algal sources are well established [Moore *et al.*, 1996b], showed only slight evidence of production in the Gas Ex 98 study area (Figure 8). The production of a particular gas may depend on which species of organism are abundant at a given location, for there is ample evidence that the production rate of many gases varies from organism to organism [e.g., Manley and de la Cuesta, 1997], and only certain species may be producers at all.

In the case of trichloroethylene alone, there are some additional field data that can shed some light on its possible origin in the oceanic water column. The measurements were made in the western Atlantic in 1997, and, although somewhat noisier than the 1998 data, they do appear to be acceptable. In the case of  $C_2Cl_4$ , there is evidence that many samples were contaminated, so all those measurements are set aside. Figure 9a shows  $C_2HCl_3$  measurements made from two separate profiles collected within ~ 7 hours and 11 nautical miles of each other; the generally good agreement suggests that contamination was not occurring (because when contamination has been observed, its magnitude varies widely and randomly between samples). There is evidence that higher concentrations of  $C_2HCl_3$  occurred at the more northerly stations (Figure 9b), which would tend to be consistent with an atmospheric source. Profiles measured at two stations (23°31'N and 20°50'N, both at 52°20'W) (Figure 9c) show, like the Gas Ex 98 data, that concentrations are increasing at depths of 300-400 m. Few deep samples were measured during this cruise, but of them the deepest was from 950 m (25°31'N, 52°20'W) which gave a  $C_2HCl_3$  concentration of 1.1 pmol L<sup>-1</sup>. This would suggest that the compound is likely to have a lifetime of decades in cold seawater, but caution should be exercised in interpreting such sparse data. Dilling *et al.* [1975] measured nonphotochemical decomposition rates of  $C_2HCl_3$  and  $C_2Cl_4$  in water at 25°C and calculated half-lives of 11 and 9 month, respectively. The half-lives will tend to be extended in low-temperature, deep waters, but there could be some compensating effect of possible biological degradation of these chlorocarbons in seawater. However, there is good evidence that  $C_2HCl_3$  has a very much longer lifetime in seawater than in the atmosphere.

A significant difference between the western Atlantic  $C_2HCl_3$  profiles and those from the Gas Ex 98 cruise is that some of the former show a shallow maximum in the water column (Figure 9c), which is coincident with gases for which there is evidence for biological sources: methyl iodide and methyl chloride. These maxima lie, in samples collected at 50 m, immediately beneath the mixed layer, which had a thickness of 35-40 m at the two sites shown in Figure 9c. They are unrelated to the layer of winter-ventilated 18° water lying much deeper at ~250 m. At present, it is not known whether advective processes could be responsible for  $C_2HCl_3$  having higher concentrations at 50 than at ~125 m, so a biological source of  $C_2HCl_3$  must be considered as a possibility.

There is a third possible origin for both  $C_2HCl_3$  and  $C_2Cl_4$  in the ocean. Marshall *et al.* [2000] have pointed out that  $C_2HCl_3$  and  $C_2Cl_4$  could potentially be produced in seawater by dehydrohalogenation of 1,1,2,2-tetrachloroethane and of pentachloroethane, respectively. However, in view of the



**Figure 9.** Vertical profiles of  $C_2HCl_3$  from the western Atlantic (*Knorr 151*). a) Pair of profiles sampled close together at 8°38'N, 52°43'W (squares) and 8°29'N, 52°49'W (diamonds). b) Profile from 42°54'N, 50°54'W. c) Two profiles from 23°31'N, 52°20'W (circles) and 20°50'N, 52°20'W (diamonds).

absence of data on these two precursors in ocean waters, it is not possible to ascertain whether, in fact, a part of the observed  $C_2HCl_3$  and  $C_2Cl_4$  does originate in this way.

## 5. An Estimate of Local Fluxes From Ocean to Atmosphere

The local unit area fluxes driven by the observed supersaturation may be compared with unit area supply needed to support the observed atmospheric concentrations; the result is relevant only locally and only during the sampling period. Using a piston velocity of  $6.3 \text{ m d}^{-1}$ , calculated using Wanninkhof's relationship [Wanninkhof, 1992] for a gas having a Schmidt number of 660, and using an average excess concentration in the surface waters of  $0.32 \text{ pmol L}^{-1}$ , the  $C_2Cl_4$  fluxes would be  $2 \text{ nmol m}^{-2} \text{ d}^{-1}$ , equivalent to a renewal time in the overlying air column of 3 years.

As the renewal time of  $C_2Cl_4$  in the atmosphere calculated on the basis of the loss rate by reaction with OH is  $\sim 4$  months [Wang *et al.*, 1995], these fluxes are small in comparison with the total amount of  $C_2Cl_4$  required to maintain the observed atmospheric concentration. A parallel exercise for  $C_2HCl_3$  is not possible because the local mixing ratio of the gas was unmeasurable, and therefore a local air column burden cannot be assigned. The estimated average flux to the atmosphere, based on an average surface concentration of  $0.33 \text{ pmol l}^{-1}$ , a piston velocity of  $6 \text{ m d}^{-1}$ , and a negligible atmospheric concentration, was  $2 \text{ nmol m}^{-2} \text{ d}^{-1}$ . Because the data set on which this is based is so small, extrapolating this value to a large scale is not justified. But it may nevertheless be compared with the magnitude of anthropogenic emissions to the atmosphere. McCulloch and Midgley [1996] estimated an annual global anthropogenic release to the atmosphere of close to 200,000 t for 1992. On a unit area basis, assuming that the bulk of the release occurs in the Northern Hemisphere, this is equivalent to  $17 \text{ nmol m}^{-2} \text{ d}^{-1}$ . The flux coming from the ocean is therefore not negligible.

Singh *et al.* [1996] estimated that there exists an oceanic source of  $C_2Cl_4$  of  $35\text{-}70 \text{ Gg y}^{-1}$ . If such a flux were spatially and temporally uniform it would equal  $1.6\text{-}3.2 \text{ nmol m}^{-2} \text{ d}^{-1}$ , which is similar to the flux calculated for the Gas Ex area in summer. While it is clear that both compounds were significantly supersaturated, could the resulting fluxes to the atmosphere be supported by wintertime transfers of the gases in the opposite direction? The hypothesis that the supersaturation is a seasonal and reversible effect implies that there is no net flux of  $C_2Cl_4$  to the atmosphere from the ocean. Indeed, since  $C_2Cl_4$  does not have an infinite lifetime in seawater (with respect to hydrolysis and biological consumption), a net loss to the ocean would occur. A further implication would be that the day-to-day fluxes between the oceans of the Southern Hemisphere and the atmosphere are very much smaller than those in the Northern Hemisphere. Because there is relatively little anthropogenic release of  $C_2HCl_3$  and  $C_2Cl_4$  to the atmosphere in the Southern Hemisphere [McCulloch and Midgley, 1996], water column measurements of these gases in Southern Hemisphere waters would be most useful for determining whether they do have some true production within the ocean. For example, any signals of biological production in the upper water column should show up more clearly against a lower background resulting from atmospherically derived material. There is potential value in continued study of marine microalgal

cultures if reproducible evidence can be provided for production of these compounds under laboratory conditions. However, shortcomings of such studies include the fact that the absence of production in these experiments cannot exclude the possibility that biological production occurs in the ocean, and, these laboratory studies are of limited value because they cannot at present be made on phytoplankton species that are typical of the open ocean environment.

## 6. Conclusions

While both  $C_2HCl_3$  and  $C_2Cl_4$  were found to be supersaturated with respect to the atmosphere, vertical profiles of both gases in an area north of the Azores were quite different from those which are found for a number of gases that have algal sources, such as isoprene, methyl chloride, and methyl bromide. The increase in concentration with depth that was observed in these profiles may result from ventilation of the deeper layers in winter, when atmospheric concentrations are near their maximum levels.

It is shown that the supersaturation of the ocean in  $C_2HCl_3$  and  $C_2Cl_4$  is not necessarily indicative of net fluxes to the atmosphere or of production of either gas in the ocean. Data collected in the western Atlantic point to the importance of advective processes in supplying  $C_2HCl_3$  to the intermediate and deep water masses, but a shallow maximum in some profiles is consistent with in situ production. The lifetimes of  $C_2HCl_3$  and  $C_2Cl_4$  in seawater are unknown, but particularly in the case of  $C_2HCl_3$ , the results reported here provide additional evidence that the lifetime of these atmospherically short-lived gases may extend to decades in the ocean.

It is apparent that in the case of atmospherically short-lived compounds, particularly large biases may result if flux calculations are made using measurements that are not made throughout the year, because for these compounds, opposite fluxes are likely to occur in winter and summer. It is commonly the case that there are fewer measurements made in wintertime and in periods of intense ventilation of the water column.

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