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Carbon tetrachloride and chlorofluorocarbons in the South Atlantic Ocean, 19°S

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Abstract. Exploratory measurements of a suite of anthropogenic halocarbon compounds (CCl_4, CCl_2FCClF_2 (CFC-113), CH_3CCl_3, CCl_3F (CFC-11)) were made using a new analytical technique on RV Meteor cruise 15 along 19°S (World Ocean Circulation Experiment (WOCE) Line A9)) in the Atlantic Ocean during February-March 1991. A separate analytical system was used to determine CCl_2F_2 (CFC-12) and CCl_3F (CFC-11). A limited number of CFC-113 profiles indicated that it was undetectable below 400-500 m. The CCl_4 data indicate that the entire Brazil Basin contains readily measurable levels of CCl_4 (>0.05 pmol kg^{-1}), whereas the deep Angola Basin contains very low levels (≤0.02 pmol kg^{-1}). Slightly higher levels were found close to the bottom in the deep Angola Basin: possibly an anthropogenic signature. In contrast, most of the deep Brazil Basin and all of the deep Angola Basin (>1000 m) had undetectable levels of CFC-11, CFC-12, and CFC-113. Preindustrial levels of CCl_4 in the atmosphere were therefore negligible (atmospheric mixing ratio <0.1 pptv). CCl_4/CFC-11 ratios are used to estimate apparent ages and dilution factors for the North Atlantic Deep Water and Antarctic Bottom Water. Whereas CCl_4/CFC-11/CFC-12 levels are internally consistent in deep waters, suggesting near-conservative behavior, there is evidence for very rapid removal of CCl_4 in the thermocline. Removal rates suggest that in addition to neutral hydrolysis, some other loss pathway must be involved.

Introduction

Attention has recently focussed on using CCl_4 [*Krysell and Wallace*, 1988; *Wallace et al.*, 1992; *Krysell*, 1992] and CFC-113 (CCl_2FCClF_2 [*Wisegarver and Gammon*, 1988]) as deep ocean tracers in addition to the currently utilized CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2). CCl_4 has an input function that is unique among transient tracers: it was introduced to the ocean at the beginning of the twentieth Century as opposed to all other transient tracers, which were added largely during the period since the end of the Second World War (CFC-11, CFC-12, tritium, bomb-radiocarbon). Its input function therefore more closely resembles the fossil-fuel CO_2 input function, implying utility as a tracer of fossil-fuel CO_2 and transient heat-anomaly uptake by the oceans. CFC-113, by contrast, has been introduced to the environment very recently (since the mid-1960s) and gives unique information for recently ventilated water masses. The estimated atmospheric time histories of all these compounds for the southern hemisphere are given in Figure 1.

Analytical problems affecting the accuracy and precision of the measurement have limited the use of these "new" tracers to date. For CCl_4, *Wallace et al.* [1992] pointed out problems with the liquid-liquid extraction technique used for the early oceanic CCl_4 measurements (corroborated by *Krysell*, [1992]). For CFC-113, problems with high blanks alluded to by *Wisegarver and Gammon* [1988], who used a packed-column gas chromatograph, might also have resulted from co-elution of CFC-113 with variable levels of CH_3Br and other naturally occurring compounds on the column they employed (D.W.R. Wallace, unpublished data, 1990).

We have developed a new technique, employing high-resolution gas chromatography and purge-and-trap extraction, which is capable of measurements of an anthropogenic halocarbon tracer suite including CFC-12, CFC-11, CFC-113, CH_3CCl_3, and CCl_4. The new technique gives greatly improved precision, detection limits, and accuracy over the liquid-liquid extraction technique previously employed for CCl_4, and allows four separate tracers to be determined in a single, ~20 min analysis.

The new system was used for the first time during WOCE section A9 aboard the FS *Meteor* (*Meteor* cruise 15/3) along 19°S in the South Atlantic Ocean from February 11 to March 20, 1991 (Figure 2). We selected this cruise for testing the new system, as there was another, packed column, system aboard (operated by the University of Bremen) measuring CFC-11 and CFC-12, which would give an indication of the new system's accuracy. In addition, the cruise track passed through oceanographic basins in which a variety of scientific questions relating to CCl_4 distribution in the ocean could be addressed.

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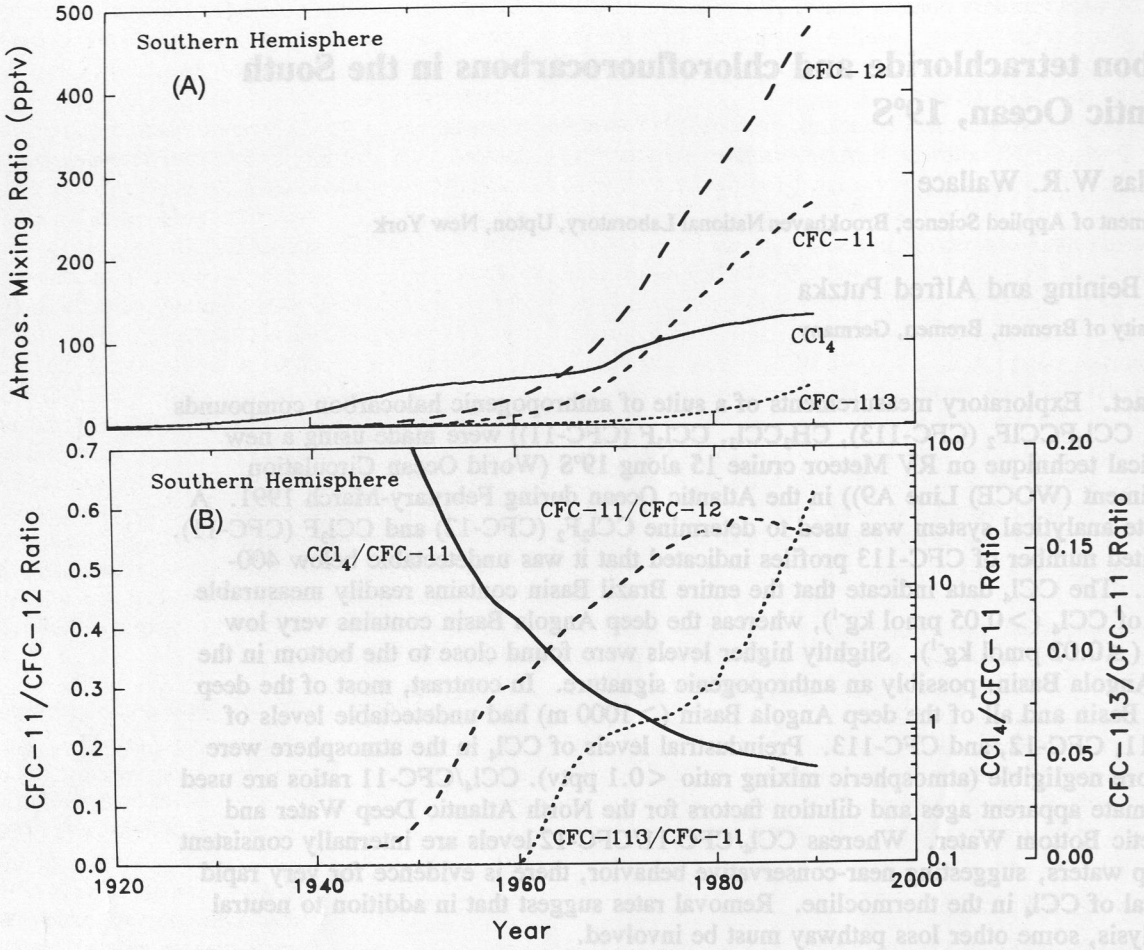

Figure 1. (a) Time-series of atmospheric mixing ratios of the halocarbon tracer compounds in pptv (10^{-12}) for the southern hemisphere. CFC-12 and CFC-11 are presented on the SIO 1986 calibration scale, whereas CCl_4 and CFC-113 are presented relative to the current ALE-GAGE calibration scale (see text). (b) Time-series of three halocarbon ratios in the atmosphere (southern hemisphere). Note that the CCl_4/CFC-11 ratio is plotted on a semilog scale.

Methods and Techniques

The new method was jointly developed by Brookhaven National Laboratory (BNL), Bedford Institute of Oceanography (Canada) and Chalmers University of Technology (Sweden) (R.M. Gershey et al., manuscript in preparation, 1994). Briefly, it employs a purge-and-trap extraction technique similar to that used in previous CFC-analysis systems [e.g., *Gammon et al.*, 1982; *Wallace and Moore*, 1985; *Bullister and Weiss*, 1988]. The most significant differences were as follows.

1. The chromatographic column used was a wide-bore

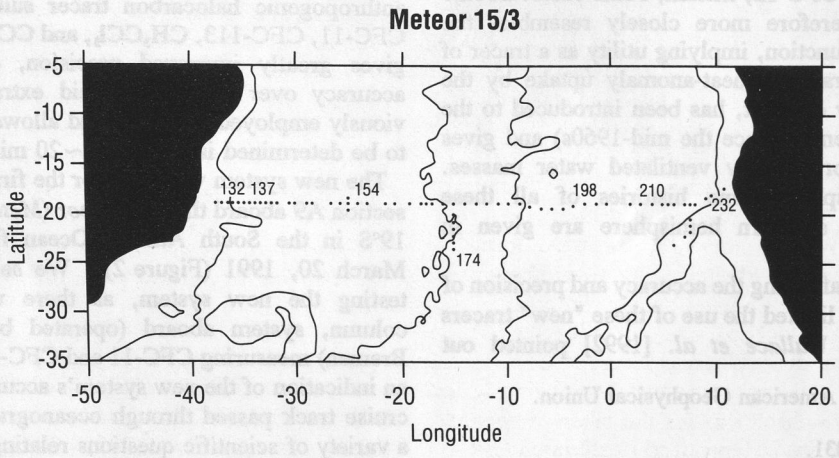

Figure 2. Station map for the *Meteor* 15/3 (WOCE A9) cruise during February-March 1991. Stations referred to specifically in the text are marked.

DB-624 glass capillary column (J&W; 70 m x 0.53 mm OD; 3 μm film) which gives baseline resolution between the tracer compounds of interest and a variety of natural and anthropogenic halocarbons.

2. The purged volatile compounds were trapped onto a short Porapak N column kept at ambient temperature (~20°C). This eliminated the need for taking cryogenic systems to sea. Because CFC-11 and CFC-12 were measured separately, we optimized our system for measuring low levels of CCl_4, CH_3CCl_3, and CFC-113 by using a 20 mL water sample and increasing the purge-gas flow to 5 min at 60 mL/min. Extraction efficiency was >99% for all compounds except CH_3CCl_3 (~85%). These conditions caused CFC-12 to approach breakthrough on the trap, decreasing precision and accuracy for this compound. Hence, all CFC-12 (and most CFC-11) data in this paper are based on measurements using the separate packed column system, which employed low-temperature trapping. Typical air, surface water, and deep water chromatograms from this new system obtained during the cruise are shown in Figure 3.

Two unexpected problems were encountered: a partial chromatographic interference for CFC-113 due to extremely high levels of CH_3I in tropical near-surface waters and a second, more serious problem, arising from a buildup of water on the column, which caused large negative peaks and an interfering baseline shift in the vicinity of the CFC-113 peak. Both of these problems have now been corrected; however, they greatly reduced the number of samples we could run.

Accuracy and Precision

Calibration of the BNL system for CFC-113, CCl_4, and CH_3CCl_3 was achieved through injections of known volumes of marine air collected at the bow of the ship while under way. This approach was required, as we had no compressed gas standard available containing these compounds. For CFC-12 and CFC-11 we used a compressed gas standard which had been previously analyzed by Weiss at the Scripps Institution of Oceanography (SIO). Hence all CFC-12 and CFC-11 data are reported on the SIO 1986 calibration scale. Calibrations for CFC-113, CH_3CCl_3, and CCl_4 are referenced to the current Atmospheric Lifetime Experiment Global Atmospheric Gases Experiment (ALE-GAGE) calibration scales (i.e., with current correction (Φ) factors applied) based on southern hemisphere atmospheric data for the time of the cruise (R. Weiss, personal communication, 1992). Specifically, we assumed clean marine air mixing ratios for this region in early 1991 of the following: 48 pptv (CFC-113), 140 pptv (CH_3CCl_3), and 132 pptv (CCl_4). These levels have had ALE-GAGE so-called "Φ" factors applied (1.00 (CFC-113), 0.80 (CH_3CCl_3), and 0.81 (CCl_4); R.F. Weiss, personal communication, 1992; see *Rasmussen and Lovelock* [1983] for a discussion of Φ factors).

In using marine air as a standard, we were forced to assume that the halocarbon mixing ratios given above were appropriate for all the air sampled during the cruise. The detector response we calculated was, therefore, strictly an apparent detector response. Whereas levels of CFC-11 and CFC-12 were found to be quite constant, we obviously had no definitive means to check this for the other compounds. Detector response for the independently calibrated CFC-11 and CFC-12 was found to be very constant throughout the cruise; it is still possible that any variation in the apparent detector response for the other compounds might have been due to variations in the atmospheric levels in the air samples used for calibration rather than variability in the true detector response.

On the basis of the variability in the apparent response factors, we therefore estimate the uncertainty in the calibrations (relative to the assumed values for clean marine air given above) to be of the order of 5% for CCl_4 and 10-12% for CH_3CCl_3 and CFC-113.

Analytical precision for seawater measurements based on duplicate analyses was the greater of 0.8% or 0.005 pmol kg^{-1} (Bremen CFC-12 and CFC-11), 1% or 0.015 pmol/kg (BNL CFC-11), 0.8% or 0.018 pmol kg^{-1} (CCl_4), and approx. 4% or 0.05 pmol kg^{-1} for CH_3CCl_3. There were insufficient duplicate analyses of CFC-113 to establish the measurement precision for this compound: it is estimated to be of the order of 10%. The poorer precision for CFC-113 is attributable to its low concentration and peak integration problems in the presence of very high levels of CH_3I.

Blanks for the BNL analytical system were as follows: 0.00-0.04, average 0.02 (CFC-11); 0.00-0.018, average 0.008 (CFC-113); 0.00-0.011, average 0.003 (CH_3CCl_3); 0.00-0.06, average 0.023 (CCl_4).

The cruise provided an opportunity to intercompare CFC-11 data collected using the University of Bremen packed column system and the experimental BNL system. The systems were calibrated separately using two independent gas standards, both of which had been analyzed by R.F. Weiss of SIO. A linear fit ($r^2 = 0.998$) of the BNL CFC-11 values against the Bremen values gave a slope of 1.030 and intercept of -0.009 with a fit standard error of 0.045 pmol kg^{-1}. Alternatively, for each sample which was jointly analyzed, a mean ($n=2$) was calculated together with a deviation of the BNL analysis from that mean. Figure 4 shows that these deviations were positively correlated with the mean sample concentration, indicating again that the BNL values were systematically higher than the Bremen values. WOCE data quality criteria [World Hydrographic Program Office (WHPO), 1991] specify 1-2% accuracy, 1% precision and blanks of the order of 0.005 pmol kg^{-1} or less. This implies that the deviations between two independently calibrated data sets should be <4% (or ±2% of the mean). For the *Meteor* 15/3 data set, we found that 68% of the deviations from the mean were less than (the greater of) 2% of the mean or 0.005 pmol kg^{-1}, whereas 53% of the observed deviations were less than (the greater of) 1% of the mean or 0.005 pmol kg^{-1}. For samples with concentrations greater than 1 pmol kg^{-1}, the mean absolute range between the two sets of values was ~3.5%. For comparison, the closest level of agreement (in terms of absolute range) achieved between two groups averaged over a single station during the World Ocean Circulation Experiment (WOCE) CFC intercomparison cruise [*Wallace*, 1992] was 1%. Hence the data agreement from the *Meteor* 15/3 cruise, while inferior to the best agreement achieved during the WOCE intercomparison cruise, approached WOCE accuracy guidelines.

Solubility Data

In earlier work we have used the CCl_4 and CH_3CCl_3 solubility data of *Hunter-Smith et al.* [1983]; however, *Warner and Weiss* [1985] showed that their CFC-11 solubility data deviated significantly from those measured during the former study. We therefore evaluated the CCl_4

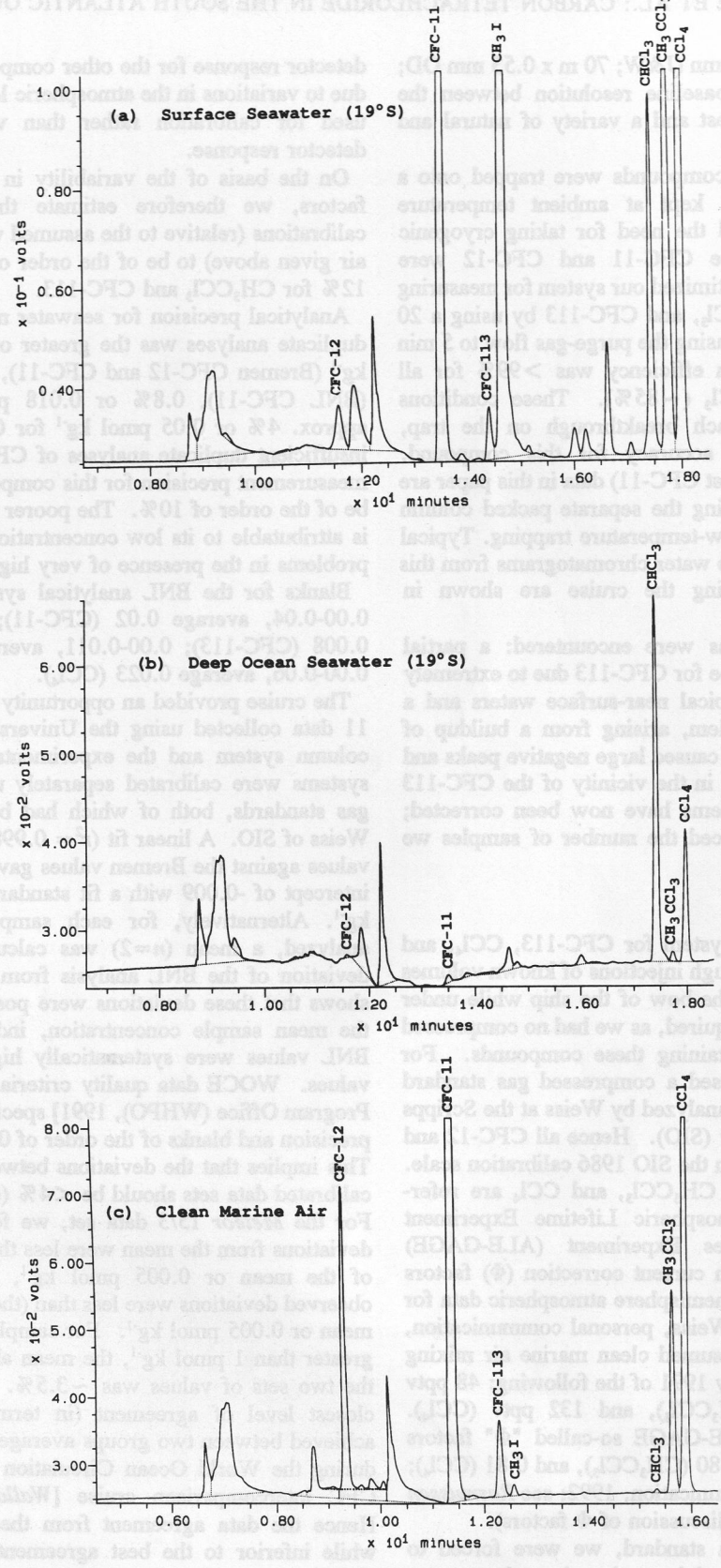

Figure 3. Typical chromatograms collected with the experimental Brookhaven wide-bore capillary column system during the *Meteor* 15/3 cruise. (a) water sample from immediately below the mixed layer: note the high levels of CH_3I immediately after the CFC-113 peak, as well as several other significant but unidentified peaks (likely to be volatile halocarbons of natural origin) following CH_3I. Measured concentrations in pmol kg^{-1} are 1.09 (CFC-12), 2.18 (CFC-11), 0.32 (CFC-113), 6.05 (CH_3CCl_3), and 2.39 (CCl_4). (b) A deep water sample (1200 m). Measured concentrations (not blank-corrected) in pmol kg^{-1} are 0.01 (CFC-12), 0.03 (CFC-11), undetectable (CFC-113), 0.04 (CH_3CCl_3), and 0.19 (CCl_4). (c) An air sample: note the absence of natural halocarbon peaks.

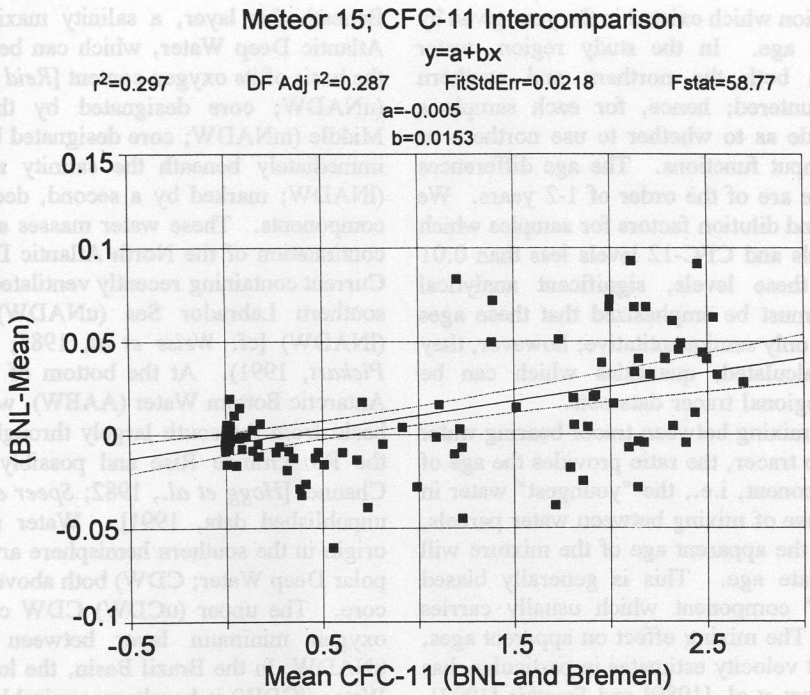

Figure 4. Results of an intercomparison of CFC-11 from seawater samples analyzed separately on the University of Bremen and Brookhaven National Laboratory analytical systems. Plot of the deviations of the BNL analyses from the average of the BNL and Bremen analyses versus that average. Positive deviations indicate that the Brookhaven analysis gave a higher result.

and CH_3CCl_3 solubility data of *Gossett* [1987]. When converted to partial pressure equilibrium constants, K'(mol l^{-1} atm^{-1} [*Warner and Weiss*, 1985]), the *Hunter-Smith et al.* [1983] CCl_4 solubility data for distilled water vary from being 14% lower than the *Gossett* [1987] relation at 0°C, to being 33% higher at 30°C. For CH_3CCl_3 data calculated for the ionic strength of seawater, the solubility data of both studies agrees to within <2% from 0-30°C; however, for distilled water the *Hunter-Smith et al.* [1983] data are 35% higher at 30°C. Whereas the *Gossett* [1987] study determined salting-out coefficients over a range of ionic strengths from 0-1 *M* (KCl) for CH_3CCl_3, such determinations were unfortunately not made for CCl_4. We therefore have continued to use the *Hunter-Smith et al.* [1983] solubility data for both CCl_4 and CH_3CCl_3, while emphasizing an urgent need for accurate CCl_4 solubility data in seawater.

For CFC-113 there have been little or no reliable solubility data available to date. However, X. Bu and M.J. Warner (manuscript in preparation, 1994) recently made measurements of the CFC-113 solubility using a technique similar to that described in Warner and Weiss [1985].

Input Histories

Input functions for the various compounds (Figure 1) have been reconstructed as follows: A compilation of atmospheric measurements from the ALE-GAGE monitoring site in Tasmania was used for the period 1982-1990 (R.F. Weiss, personal communication, 1992). Prior to that, we have reconstructed the atmospheric concentrations based on estimates of production and release to the atmosphere. For CFC-11 and CFC-12 we used the estimates of the *Chemical Manufacturers Association* [1983], which included estimates of production and release from Eastern Europe, India and Argentina. For CFC-113, we used the release estimates compiled by the *Alternative Fluorocarbons Environmental Acceptability Study* [1991], adding 10% for releases due to nonreporting chemical companies. For CCl_4, we used the release data compilation by *Simmonds et al.* [1983] for the period 1908-1958, and that of *Simmonds et al.* [1988] for 1958-1982. We assumed that 95% of the release took place in the northern hemisphere, that the interhemispheric exchange time was 1.25 years, and that atmospheric lifetimes were 111 (CFC-12), 74 (CFC-11), 165 (CFC-113), and 40 (CCl_4) years. Based on these assumptions, we calculated the atmospheric inventories of the four compounds in the southern hemisphere as a function of time. Atmospheric mixing ratios as a function of time were calculated by normalizing these inventories to the ALE-GAGE measured mixing ratios for December 1981. All CFC-11 and CFC-12 atmospheric mixing ratios were subsequently converted to the SIO 1986 scale using intercalibration factors (R.F. Weiss, personal communication, 1992) [see also *Bullister*, 1984].

Apparent Ages and Dilution Factors

Based on the time-varying ratios of one halocarbon compound to another in the atmosphere, apparent age and apparent dilution factors have been calculated. Measured concentrations of CFC-11 and CCl_4 (or CFC-11 and CFC-12) from a seawater analysis were converted to "equivalent atmospheric ratios" based on the potential temperature and salinity dependent solubilities of the two compounds. These ratios were then matched against the atmospheric input functions (see above): the apparent age of the water sample is the time difference between the year in which the atmosphere exhibited this ratio and the time of sample collection. Dilution factors were calculated as the observed concentration divided by the concentration in equilibrium with the

atmospheric concentration which existed in the year given by the sample's apparent age. In the study region, water masses originating in both the northern and southern hemispheres are encountered; hence, for each sample a decision had to be made as to whether to use northern or southern hemisphere input functions. The age differences arising from this choice are of the order of 1-2 years. We did not calculate ages and dilution factors for samples which contained CFC-11 levels and CFC-12 levels less than 0.01 pmol kg^{-1}, since at these levels, significant analytical uncertainty exists. It must be emphasized that these ages and dilution factors are only semiquantitative; however, they are useful, readily calculated, quantities which can be compared with other regional tracer data sets.

In the special case of mixing between tracer-bearing water and water containing no tracer, the ratio provides the age of the tracer-bearing component, i.e., the "youngest" water in the mixture. For the case of mixing between water parcels, both containing tracer, the apparent age of the mixture will reflect some intermediate age. This is generally biased towards the "younger" component which usually carries higher concentrations. The mixing effect on apparent ages, and its effect on current velocity estimates in particular, has been discussed by *Pickart et al.* [1989] and *Smethie* [1993]. There are corresponding implications for the estimation of dilution factors.

The effects of analytical errors and errors in the gas solubility data on the apparent ages have been discussed in detail by *Wallace et al.* [1992]. In brief, CCl_4/CFC-11 age errors arising from these sources would be of the order of 2 years or less for water parcels with apparent ages which indicate ventilation prior to the mid-1970s. The rate of change of the CCl_4/CFC-11 ratio in the atmosphere has decreased considerably since that time implying potentially larger age errors (e.g., <5 years) for more recently ventilated water parcels given current uncertainties in the gas solubility data (see above).

Hypotheses and Hydrographic Background

Based on the hydrographic background of the region and previous tracer studies, we chose the WOCE A9 section for exploratory CCl_4 and CFC-113 measurements in order to address the following questions.

1. Is the CCl_4 distribution in the ocean consistent with its assumed input history and known hydrolysis rates? Could there be additional, unrecognized sources/sinks of CCl_4 in the ocean? We anticipated low or negligible quantities of anthropogenic CCl_4 would be present in the deep Angola Basin: hence measurements there would be a test of the assumption of negligible preindustrial CCl_4. In addition, we expected to find deep water regions where detectable anthropogenic CCl_4 would be present in the absence of detectable CFCs. This would confirm the utility of CCl_4 as a deep water transient tracer over longer timescales.
2. With respect to CFC-113, we wished to test whether the compound could be reliably sampled for, without major contamination problems, and to determine whether the vertical profiles were consistent with its input function.

Brazil Basin Deep Waters

Within the Brazil Basin, along 19°S, the thermocline waters overlie the salinity minimum of the Antarctic Intermediate Water (AAIW; approximately 600-1000 m). Beneath this layer, a salinity maximum marks the North Atlantic Deep Water, which can be further subdivided, on the basis of its oxygen content [*Reid et al.*, 1977] into Upper (uNADW; core designated by the salinity maximum), Middle (mNADW; core designated by an oxygen maximum immediately beneath the salinity maximum); and Lower (lNADW; marked by a second, deeper oxygen maximum) components. These water masses are fed by a southwards continuation of the North Atlantic Deep Western Boundary Current containing recently ventilated water masses from the southern Labrador Sea (uNADW) and Denmark Strait (lNADW) [cf. *Weiss et al*, 1985; *Molinari et al.*, 1992; *Pickart*, 1991). At the bottom of the Brazil Basin is the Antarctic Bottom Water (AABW), which has spilled into the basin from the south largely through the Vema Channel in the Rio Grande Rise and possibly also over the Hunter Channel [*Hogg et al.*, 1982; *Speer et al.*, 1992; A. Putzka, unpublished data, 1991]. Water masses of circumpolar origin in the southern hemisphere are also present (Circumpolar Deep Water; CDW) both above and below the NADW core. The upper (uCDW) CDW core is identified by an oxygen minimum layer between the AAIW and the uNADW. In the Brazil Basin, the lower Circumpolar Deep Water (lCDW) is barely recognizable, so following *Hogg et al.* [1982], we will usually include the lCDW with the AABW.

Earlier transient tracer data (e.g., South Atlantic Ventilation Experiment data from 1989 [*Weiss et al.*, 1989; R.F. Weiss, personal communication, 1993]) indicated detectable CFC-11 and CFC-12 were present at ~20°S in the deep Brazil Basin in the AABW and within the uNADW along the western boundary. In both of these water masses, levels were quite close to the detection limit (e.g., <0.02 pmol kg^{-1}) and were undetectable in most of the deep Basin.

Angola Basin Deep Waters

Much of the Angola Basin is deeper than 5000 m and the midocean ridge appears to restrict entry of water from the Brazil Basin to depths <3500 m. In addition, the deep Angola Basin is cut off to the south by the Walvis Ridge with a maximum sill depth of 4000-4250 m. Hence, the deepest waters of the Angola Basin are derived largely from the north from the equatorial region (i.e., the Guinea Basin where water from the western Atlantic is added [*Schlitzer*, 1987]). At shallower depths (4000 m) there is evidence for deep water entering the Angola Basin from the south across the Walvis Ridge and small amounts of AABW have been detected close to this ridge [*Shannon and Chapman*, 1991]. The circulation of the deep water in the Angola Basin has been extensively reviewed by *Warren and Speer* [1991]. The North Atlantic Deep Water component to the Angola Basin appears fed both from the south (along the midocean ridge) and from the north. The former component has been strongly mixed with lower salinity water masses during eastwards transit across the southern Brazil Basin. There is also some evidence for southwards flow of NADW from the equatorial region along the eastern boundary [*Warren and Speer*, 1991; *Gordon and Bosley*, 1991].

The distribution of natural C-14 [*Broecker et al.*, 1991] suggests the deep waters of the Angola Basin are significantly older (surface isolation time ~240-280 years) than those of the Brazil Basin (isolation time ~100-200 years). Data from the deep Angola Basin collected during previous

expeditions showed no detectable CFC-11 or CFC-12 below 1000 m at ~20°S [*Warner*, 1988].

Circulation of the Upper Waters

The WOCE A9 section along 19°S cuts across a cyclonic gyre which is centered in the eastern tropical South Atlantic. The western edge of this gyre is a broad sweep of northwestward flowing water which stretches across the South Atlantic Ocean [cf. *Peterson and Stramma*, 1991; *Gordon and Bosley*, 1991]. On the eastern side is the southward flowing Angola Current, which carries equatorial waters southward, and which meets the northward flowing Benguela Current at the Angola-Benguela Front. The residence time of thermocline water within the cyclonic gyre has been estimated to be approximately 4-10 years [*Gordon and Bosley*, 1991], and these waters are marked by very low dissolved oxygen content due to the oxidation of organic material produced in the upwelling regions on the eastern margin. Surface water temperatures along the section decreased from west to east, from >26°C in the west to 20-21°C in the east.

Warner and Weiss [1992] have discussed the distribution of CFC-11 and CFC-12 in the AAIW in this region. Within the cyclonic gyre (the southern edge of which the 19°S section cuts across), CFC levels were very low or undetectable within this water mass, which was attributed to restricted lateral exchange or the effects of upwelling.

Results

Full-depth sections of the CCl_4 and CFC-11 data collected during the *Meteor* 15/3 cruise are presented in Figures 5a and 5b. The CCl_4 data are relatively sparse due to the instrumental problems referred to above: in addition, collection of several detailed vertical profiles for CFC-113 in the upper water column restricted deep water sampling.

Deep Water

The most obvious feature is that the penetration of carbon tetrachloride into the deep ocean is much more extensive than that of CFC-11. Throughout most of the Brazil and Angola basins, CFC-11 is undetectable (<0.015 pmol kg^{-1}) below a depth of 1000 m, whereas CCl_4 is present in significant quantities (>0.05 pmol kg^{-1}) throughout the Brazil Basin

Also obvious are strong maxima at depths of 1500-2000 m close to the western boundary, and at the bottom of the Brazil Basin. The upper maximum represents the core of the most recently ventilated uNADW, whereas the bottom maximum corresponds to the AABW. Between these water masses there is additional structure in the tracer profiles which is discussed below.

In the deep Angola Basin, CCl_4 levels are significantly lower, with most of the deep water samples exhibiting levels less than 0.02 pmol kg^{-1}. The lowest (system-blank corrected) levels measured (~0.003 pmol kg^{-1}) might represent a true "background" level in these deep waters, of either natural or anthropogenic origin or, simply, slight contamination during sampling. The deepest waters of the Angola Basin exhibited levels as high as 0.06 pmol kg^{-1} on the eastern side of the Mid-Atlantic Ridge. In general the bottommost water had concentrations greater than 0.02 pmol kg^{-1}. This presumably anthropogenic signal could be derived from the Romanche Fracture Zone or from the overflow through or over the Walvis Ridge. A larger CCl_4 data set might prove to be a useful diagnostic of the deep circulation in the Angola Basin, which is still uncertain due to the relative uniformity of traditional tracer signals such as temperature and salinity [*Warren and Speer*, 1991].

Our data suggest that there is active ventilation of the Angola Basin by waters carrying anthropogenic CCl_4, and it is therefore possible that the very low "background" level referred to above is also of anthropogenic origin. Whatever its origin, this level provides an upper bound to the preindustrial level of CCl_4, which is 30 times lower than the previous lowest levels measured in the ocean of 0.15 pmol kg^{-1} [*Krysell*, 1992]. This confirms that preindustrial levels of CCl_4 in the atmosphere must have been very low indeed (atmospheric mixing ratios at equilibrium with this concentration would be ~0.06 pptv compared to modern atmospheric mixing ratios of ~130-140 pptv).

Antarctic Intermediate Water

At ~600 m there is a strong maximum in CCl_4 (with levels >1 pmol kg^{-1}) found at most stations except those at the far eastern end of the section. The maximum is most pronounced in the west, and lies slightly above the depth of the salinity minimum which is normally perceived as the core of the Antarctic Intermediate Water. The CCl_4 maximum apparently results from a combination of lateral ventilation and the effects of degradation processes operating within the overlying thermocline (see below).

Thermocline

The upper water sections of CCl_4 and CFC-11 are displayed in more detail in Figures 6a and 6b. Within the thermocline in the Brazil Basin and the western Angola Basin, we find a minimum in CCl_4 at a depth of approximately 200-300 m which is not present for any of the other tracer compounds (CFC-12, CFC-11, CFC-113). A section of the "equivalent atmospheric ratio" of CCl_4/CFC-11, calculated using the temperature- and salinity-dependent solubilities of the two compounds, in the upper 1000 m is presented in Figure 6c. The equivalent atmospheric ratios of CCl_4/CFC-11 found in the thermocline are lower than any which have existed in the past, based on the historical input functions (Figure 1b). The section shows that the minimum ratio is found at a depth of about 200-300 m. Ratios below the thermocline return to expected values (i.e., values consistent with the input history of these compounds).

The low ratios in the thermocline represent a deficit of CCl_4 relative to the other tracers, which must be a signal of in situ consumption. A rough calculation is sufficient to indicate that the deficit cannot be explained by hydrolysis alone if published rates [e.g., *Jeffers and Wolfe*, 1990] are correct. The equivalent atmospheric CFC-11/CFC-12 ratios in the midthermocline, where the apparent CCl_4 depletion is strongest, range from 0.53 to 0.55, implying an age of 2-15 years for the transient tracer compounds in this layer.

Given this age range, we would have expected an equivalent atmospheric ratio for CCl_4/CFC-11 of 0.54-0.80 if CCl_4 were conservative. The observed ratios are as low as 0.10-0.15 in the eastern basin, which implies that only ~15%-25% of the original CCl_4 content remains. This in turn implies a half-life of the order of 1-5 years. Freshwater

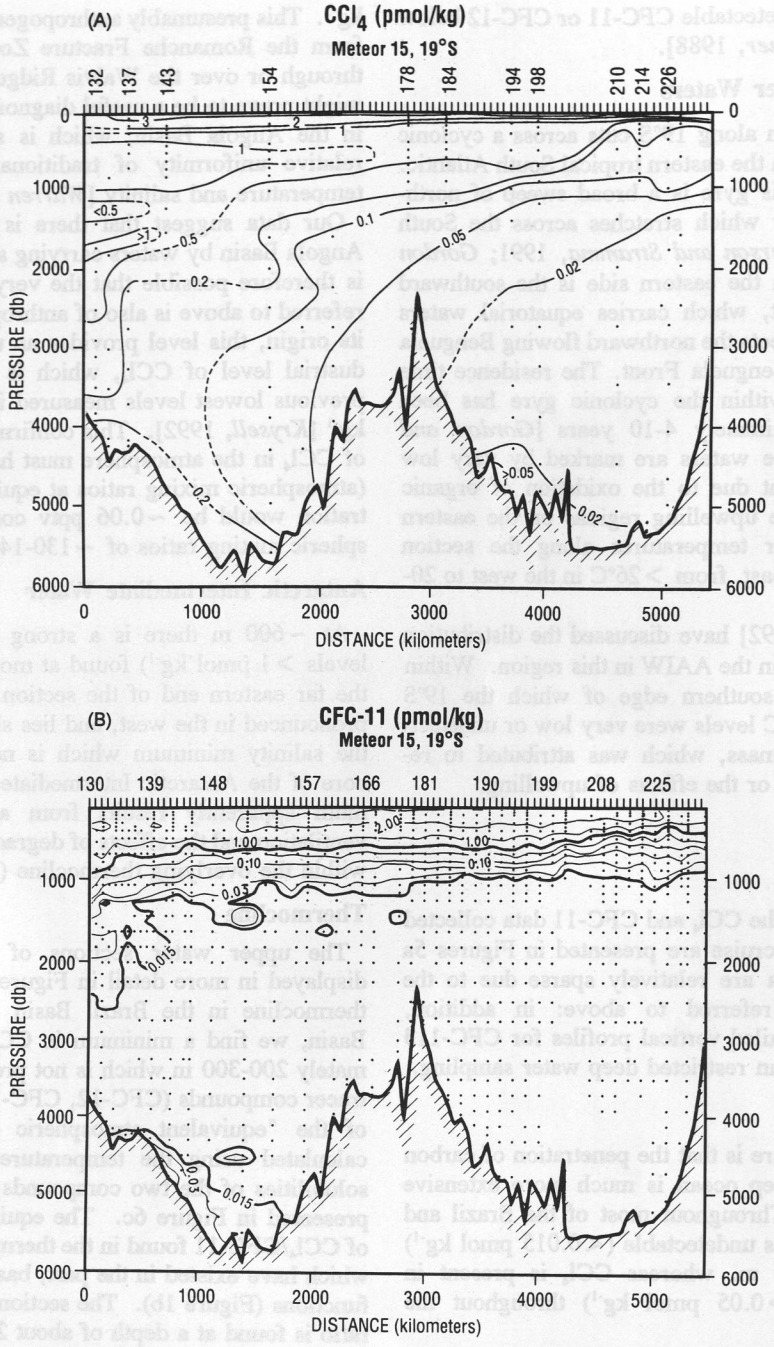

Figure 5. Deep water sections of (a) CCl_4 and (b) CFC-11 along the 19°S section. The CCl_4 section has been hand contoured; the CFC-11 contours have been drawn using a computer algorithm. Note the nonuniform contour intervals on both plots. For CFC-11, contours are drawn at 0.015, 0.03, 0.05, 0.1, 0.25, 0.5, 1.0, 2.0, and 3.0 pmol kg^{-1}.

hydrolysis lifetimes at temperatures appropriate for this layer (12°-16°C) are between 170 and 320 years [*Jeffers and Wolfe*, 1990]. The observed degradation of CCl_4 therefore cannot be explained by the published rates of hydrolysis. A possibility is that these rates, determined for distilled water, might not be appropriate for seawater, although the discrepancy seems too large to be explained in this way (for example, for CH_3CCl_3, hydrolysis rates are ~10% higher in seawater [*Gerkens and Franklin*, 1989]). Alternatively, another, unexpected sink for CCl_4 might be operating.

Examination of the CCl_4 section (Figure 6a) indicates that the 0.5 and 0.25 pmol kg^{-1} isolines shoal by ~500 m between stations 198 and 210, i.e., at the Angola-Benguela Front which is clearly seen in the oxygen section (Figure 6d). The geographical distribution of the equivalent atmospheric CCl_4/CFC-11 ratio minimum in the thermocline shows that the strongest deficit is associated with the very low oxygen waters east of the front; however, there is a deficit throughout the thermocline. More detailed mapping and modelling of CCl_4 in other regions, and laboratory

studies, will be required before any firm conclusions can be drawn about the mechanisms responsible. At this stage it is worth putting forward several hypotheses.

1. The deficit is caused by a strongly temperature-dependent, abiotic reaction with rates orders of magnitude faster than the hydrolysis rates given above. In this case, the magnitude of the CCl_4 deficit would be a function of both the temperature and the ventilation rate of the water mass. This hypothesis is consistent with the distribution, given that the core of the deficit tracks the 15°C isotherm (not shown). The larger deficit in the east is associated with lower CFC-11 levels, and hence with restricted ventilation.

2. The CCl_4 might be removed by bacterial metabolism. Literature data suggest, however, that CCl_4 is only metabolized under anaerobic conditions (see review by *Vogel et al.* [1987]). This could conceivably occur either in low-oxygen seawater (e.g., in microzones within aggregates) or, perhaps, at the sediment-water interface underlying productive regions. There is now evidence from soil and groundwater studies [*Lovley and Woodward*, 1992; *Semprini et al.*, 1992] to suggest that CFC-11 and CFC-12 might also be degradable by active microbial metabolism under such conditions, albeit at a considerably slower rate than for CCl_4. The geographical distribution of the deficit does not clearly

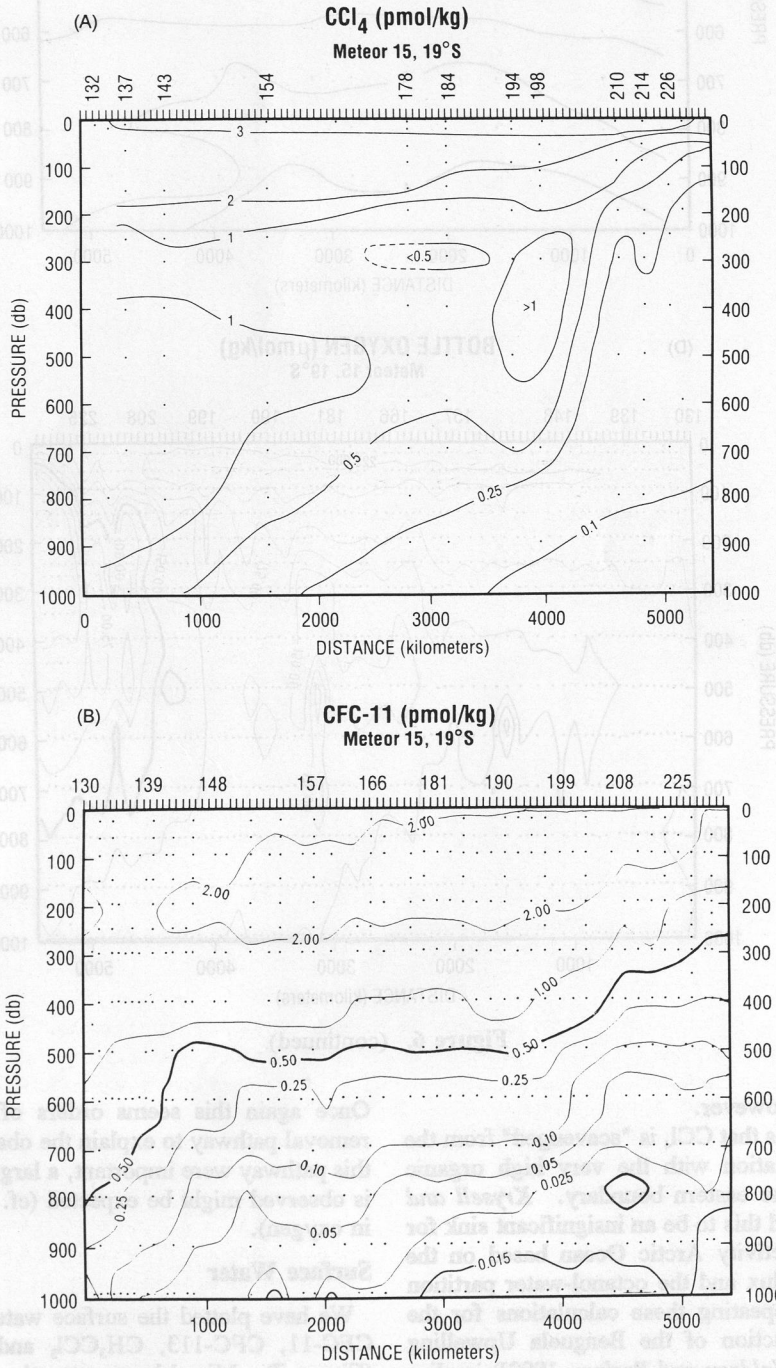

Figure 6. Sections from the upper water column (< 1000 m) along 19°S, of (a) CCl_4, (b) CFC-11, (c) the equivalent atmospheric ratio of CCl_4/CFC-11 (see text for details), (d) dissolved oxygen from bottle samples.

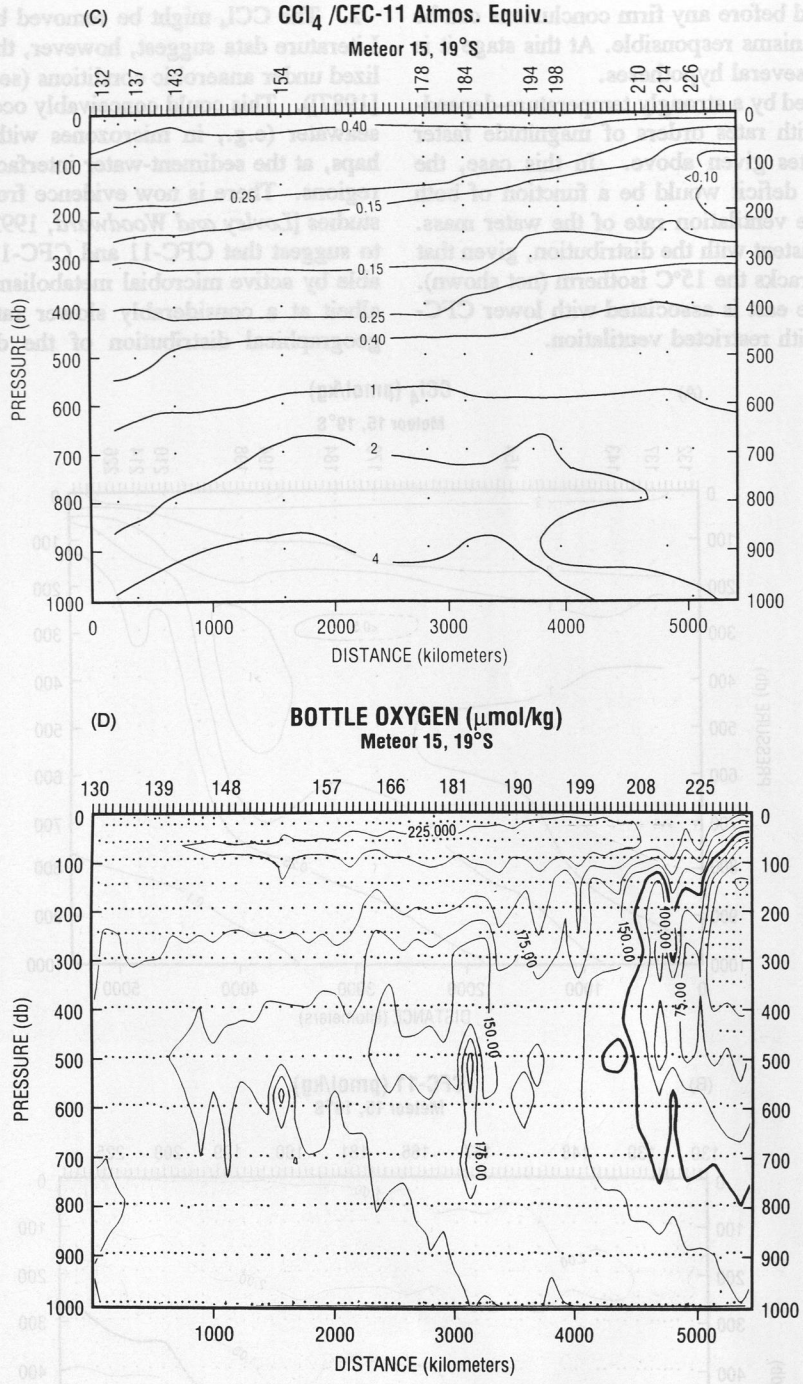

Figure 6. (continued).

correlate with oxygen, however.

3. Another possibility is that CCl_4 is "scavenged" from the water column by association with the very high organic matter sinking flux at the eastern boundary. *Krysell and Wallace* [1988] calculated this to be an insignificant sink for CCl_4 in the low- productivity Arctic Ocean based on the organic carbon sinking flux and the octanol-water partition coefficient for CCl_4. Repeating these calculations for the much higher new production of the Benguela Upwelling (order 240 gC m^{-2} yr^{-1} [*Waldron and Probyn*, 1992]) implies a CCl_4 removal of the order of 260 pmol (CCl_4) m^{-2} yr^{-1} from the upper ocean. If this were removed from a 100 m-thick layer over a period of, say, 5 years, the CCl_4 concentration would decrease in this layer by only 0.01 pmol kg^{-1}. Once again this seems orders of magnitude too small a removal pathway to explain the observed deficit of CCl_4. If this pathway were important, a larger east-west contrast than is observed might be expected (cf. the very strong gradient in oxygen).

Surface Water

We have plotted the surface water saturation of CFC-12, CFC-11, CFC-113, CH_3CCl_3 and CCl_4 versus longitude (Figure 7). Mixed-layer saturations for CFC-11 and CFC-12 averaged 103% (±6%) and 100% (± 4%) across the entire section relative to atmospheric mixing ratios of 260.5 pptv and 483.2 pptv, respectively. Surface saturations decreased from ~100% at the western boundary to 83% in

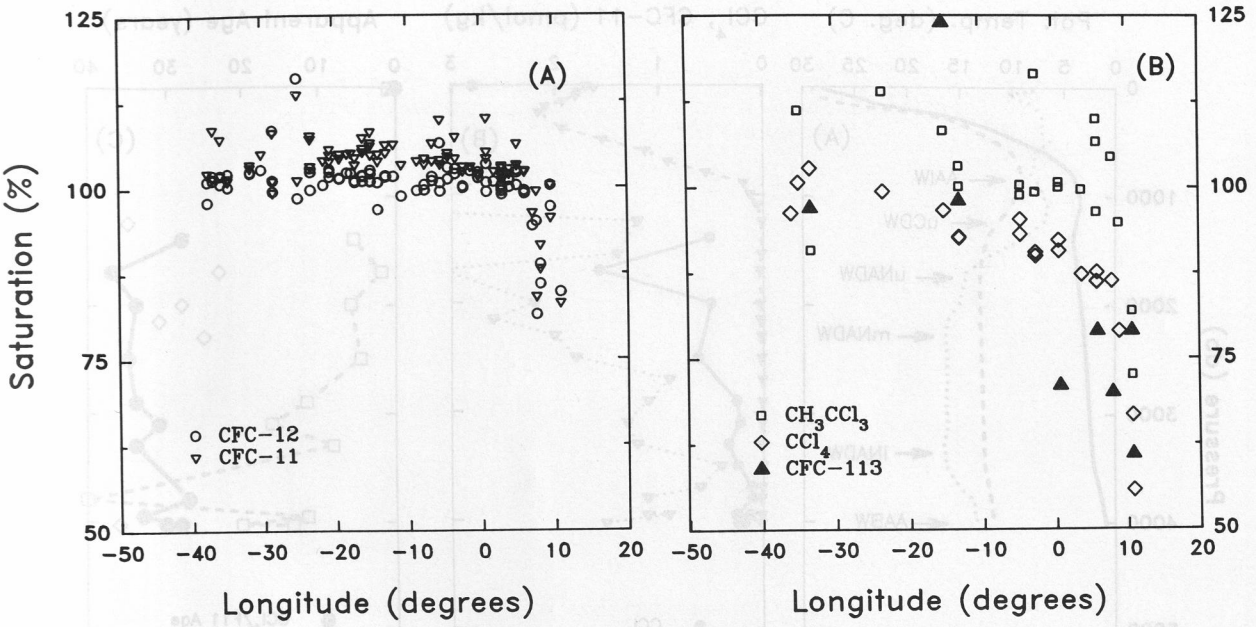

Figure 7. Surface water saturations (in percent) of (a) CFC-12 and CFC-11 and (b) CH_3CCl_3, CCl_4 and CFC-113 versus longitude. Solubility data from *Warner and Weiss* [1985] were used for CFC-12 and CFC-11; from X. Bu and M.J. Warner (personal communication, 1993) for CFC-113; and from *Hunter-Smith et al.* [1983] for CH_3CCl_3 and CCl_4.

the upwelling zone at the eastern boundary. For CCl_4, the average saturation was 90% (±13%) with a clear decreasing trend in surface saturation from the western boundary (~100%) to the eastern boundary (67%). CH_3CCl_3 saturation also decreased from west to east with the mean saturation being 100% (±11%). The lowest saturation (82%) was observed at station 232 at the eastern end of the transect. Our CH_3CCl_3 gas saturations are therefore considerably higher on average than the 90.8% average (minimum of 75%) previously observed in Pacific equatorial and tropical waters [*Butler et al.*, 1991], although caution should be exercised, as our data appear noisy (see Figure 6), are undersampled in space, and are based on solubility calculations, whereas *Butler et al.* [1991] measured the air-sea partial pressure difference directly.

Based on recent CFC-113 solubility data (X. Bu and M.J. Warner, manuscript in preparation, 1994), our data indicate that surface water saturation for CFC-113 along 19°S averaged 88% (±20%). Once again, the lowest saturations were in the east.

The low saturations in the east reflect the effects of upwelling at the eastern boundary of older waters with lower levels of anthropogenic halocarbons; upwelling should also propagate the effects of the subsurface degradation discussed above into the surface layer, which should lead to more significant undersaturation for the more reactive species.

Surface water saturations of anthropogenic halocarbons are likely to be strongly influenced by upwelling and vertical mixing, together with the effects of changes in gas solubility due to changes in mixed-layer temperature. In situ temperature changes will affect the various compounds to roughly similar extents (as their temperature dependence of solubility does not vary greatly). On the other hand, the undersaturation developed as a result of upwelling or vertical mixing processes will depend critically on the relative shapes of the vertical profiles of the different compounds through the thermocline. These profiles in turn will reflect the effects of in situ degradation processes as well as the differing historical input functions. Therefore, the use of mixed-layer CFC-11 saturations to estimate the contribution of physical processes (e.g., upwelling, vertical mixing, air injection) to mixed-layer saturation anomalies of other gases in order to estimate in situ degradation rates in the mixed layer [cf. *Butler et al.*, 1991] should be viewed with caution, at least in upwelling regions.

Vertical Profiles in the Brazil Basin

Selected vertical profiles from the Brazil Basin are presented in Figures 8, 9, and 10. The station locations are marked on Figure 2. Expanded concentration scales are used for the deep water profiles of CFC-11. The profiles are grouped as hydrographic data (potential temperature, salinity and dissolved oxygen concentration), measured concentrations of CFC-11 and CCl_4, and parameters calculated from the tracer and temperature-salinity data (notably the "apparent age" and the "apparent dilution factor", [cf. *Weiss et al.*, 1985]). Two apparent ages are plotted, one based on the ratio of CCl_4/CFC-11 and the other based on the CFC-11/CFC-12 ratio. The CFC-11/CFC-12 age has only been calculated for older waters, as since the mid-1970s the ratio has been relatively time invariant or at least nonunique. The dilution factor is based on the CCl_4/CFC-11 age. As noted earlier, it is important to recognize the limitations and interpretative difficulties of these derived parameters. The thermocline contains waters for which no apparent age can be calculated based on the CCl_4/CFC-11 ratio due to the effects of CCl_4 degradation. Such effects might contribute to errors in the calculation of ages for the Antarctic Intermediate Water. We believe such effects are much less significant for the colder, deeper waters (see below).

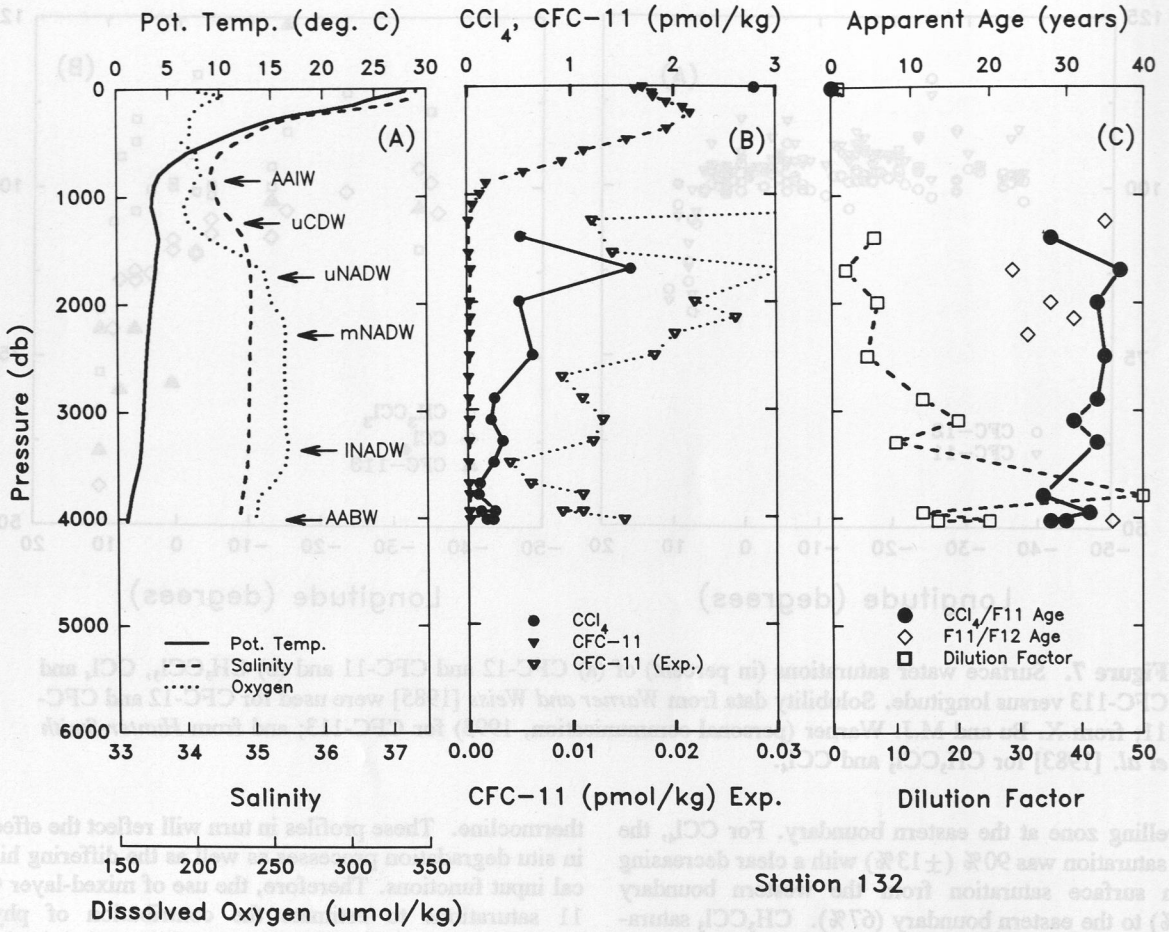

Figure 8. Vertical profiles of various properties from station 132 in the Brazil Basin. Plots are included of (a) basic hydrographic properties (potential temperature, salinity, and dissolved oxygen); (b) tracer profiles (CFC-11 and CCl_4), including CFC-11 on an expanded scale for deeper samples; and (c) parameters derived from the hydrographic and tracer data (apparent ages and dilution factors based on the CCl_4/CFC-11 ratios as well as CFC-11/CFC-12 ratios where they were unique, i.e., pre-1973. In Figure 8a the core layers of several water masses referred to in the text are identified (AAIW, Antarctic Intermediate Water; uCDW, Upper Circumpolar Deep Water; uNADW, mNADW, and lNADW are upper, middle, and lower North Atlantic Deep Water, respectively; AABW, Antarctic Bottom Water). Note that ages (and therefore dilution factors) could not be calculated for all samples (for example, when concentrations were close to the detection limit). Where an age could not be calculated for these reasons, the lines connecting the points in the age and dilution factor profiles have been interrupted.

Based on the discussion of South Atlantic hydrography by *Reid et al.* [1977], we have identified the core layers of the principal intermediate and deep water masses on each of the profiles.

Station 132 (Figure 8)

This was the first station sampled for CCl_4, and sampling was restricted to deep waters. A very strong maximum of CCl_4 (>1.5 pmol kg^{-1}) was encountered at the core of the uNADW: at the same depth the CFC-11 concentration (~0.035 pmol kg^{-1}) was only a factor of ~3-4 above the detection limit, but was also evident as a maximum. Maxima in CCl_4 and, perhaps, CFC-11 (for which levels are almost at the detection limit) are also evident, associated with the cores of the mNADW and lNADW as well as the AABW.

The uNADW has a CCl_4/CFC-11 apparent age of the order of 35-40 years, whereas the AABW is significantly younger (~30 years). The pattern of apparent dilution factors indicates that the uNADW (dilution factors of 2-7) is less dilute than the AABW (dilution factors of ~15-25). Just above the AABW and beneath the lNADW, a sample with an anomalously large dilution factor (50) was observed. The CFC-11/CFC-12 apparent ages are scattered, probably due to the very low concentrations of both compounds encountered in the deep waters and hence the difficulty in accurately determining the ratio; however, the average CFC-11/CFC-12 age below 1000 m (30 years) agrees closely with the average CCl_4/CFC-11 age (32 years).

Station 137 (Figure 9)

Station 137 exhibits lower concentrations of the halocarbons in general than those found at station 132. Note the very strong maximum in CCl_4 found just above the salinity minimum, usually taken to be the core of the AAIW. No such feature is evident for CFC-11, suggesting that the

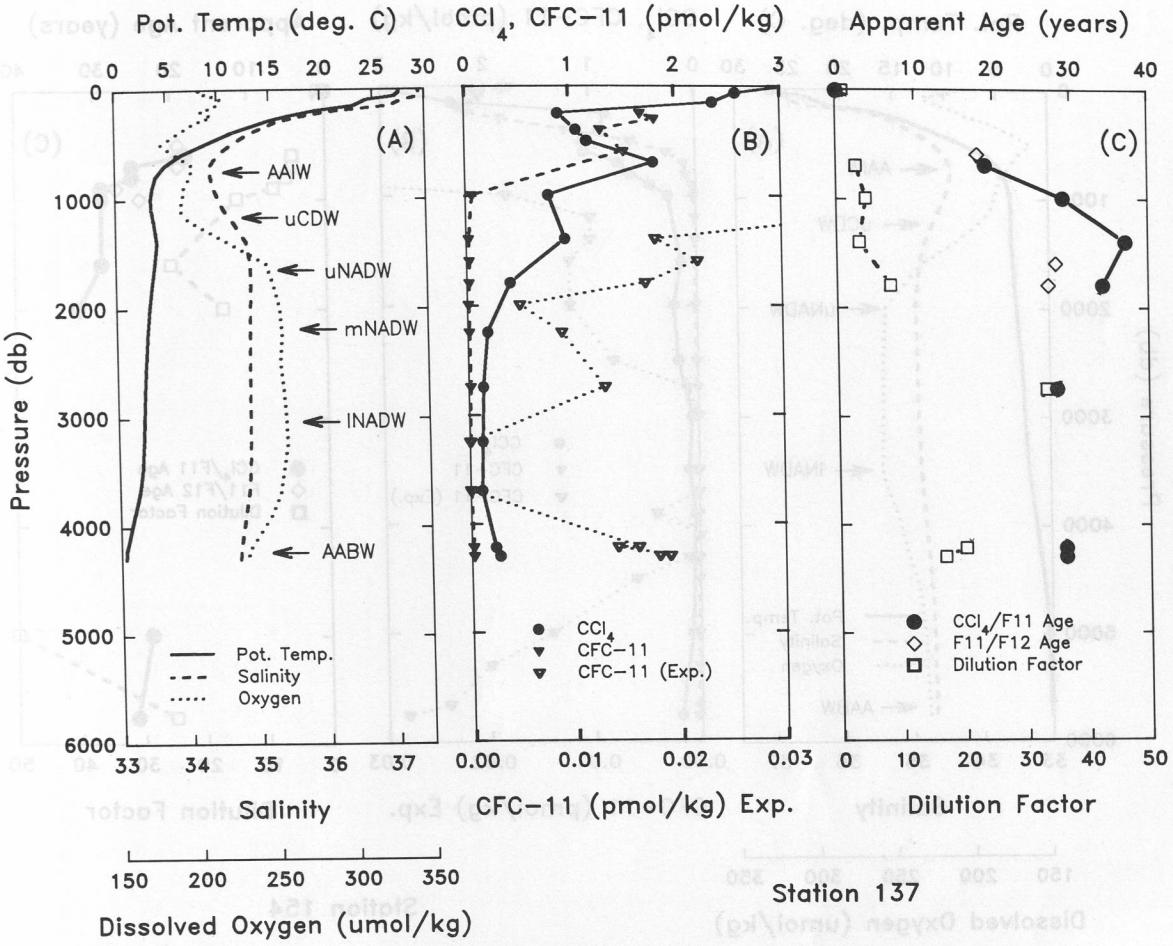

Figure 9. Same as Figure 8, but for station 137 in the Brazil Basin.

maximum is created by CCl_4 degradation in the overlying thermocline together with lateral ventilation of the AAIW [cf. *Warner and Weiss*, 1992]. A CCl_4 minimum is found close to the core of the upper Circumpolar Deep Water (i.e., coincident with an oxygen minimum) and is underlain by a CCl_4 maximum within the uNADW. While our sampling missed the core of the uNADW (i.e., the salinity maximum), CCl_4 levels in the uNADW were still of the order of 1 pmol kg^{-1}. There were no obvious maxima evident at the cores of the mNADW and lNADW, and CFC-11 levels between 3000 m and 4000 m were undetectable. Levels of CCl_4 and CFC-11 increased again in the AABW.

The vertical profiles of CCl_4/CFC-11 ages and dilution factors were similar to those found at station 132. AAIW age and dilution factors (not measured at station 132) were ~20 years and 3-4, respectively. Once again the uNADW was characterized by an age maximum (~35-37 years) and by relatively low dilution factors (~3-6). Ages and dilution factors could not be calculated for the depth range 3000 m to 4000 m due to the very low CFC-11 concentrations; however, the AABW had an apparent age of ~28 years and a dilution factor of ~15-20, similar to that found at station 132. The CFC-11/CFC-12 ages in the uNADW, where they could be calculated, tended to be ~25% younger than the CCl_4/CFC-11 ages; however, this difference is probably not significant given the measurement uncertainty of the former ratio.

Station 154 (Figure 10)

Station 154 continues the trend to lower tracer levels with increasing distance from the western boundary. The AAIW is marked by a CCl_4 maximum, again without any clear signal in the CFC-11 content. The uCDW is characterized by CCl_4 and CFC-11 minima. CCl_4 levels in the uNADW are ~0.2 pmol kg^{-1}, and a slight elevation of CCl_4 appears again at the core of the lNADW, whereas neither the mNADW nor the lNADW have detectable CFC-11 at this station. Once again, the AABW is characterized by very clear maxima in CFC-11 and CCl_4.

The AAIW CCl_4/CFC-11 ages appear similar to those at station 137 (~18 years). The uNADW age remains as an age maximum at ~32 years, but with significantly higher dilution factors (~15-25) than those found further to the west. Beneath the uNADW, CFC-11 levels are too low for an age to be calculated, except for the AABW, which exhibits an age of ~30 years. CFC-11/CFC-12 ages could only be calculated for the AAIW and uCDW, and agreed very closely with the CCl_4/CFC-11 ages.

Profile Summary

The uNADW appears "older" and less dilute than the AABW at all stations. The AABW might be more strongly affected by mixing during its transit northwards along the continental margin, despite its shorter transit time, than the North Atlantic Deep Water during its southward transit.

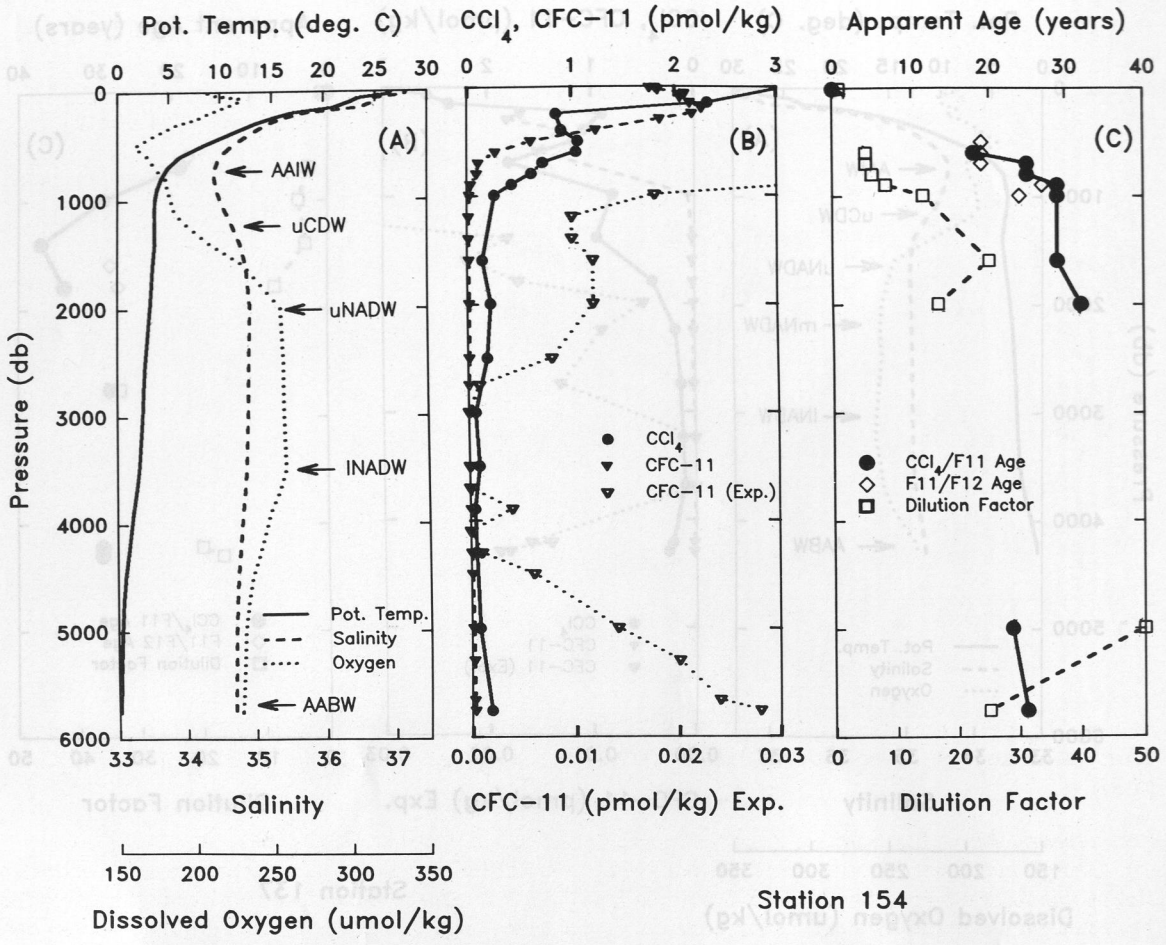

Figure 10. Same as Figure 8, but for station 154 in the Brazil Basin.

The apparent dilution of AABW might reflect the effects of intense mixing in the Circumpolar Current and the Vema Channel prior to entry into the Brazil Basin. In addition, the uNADW, being less dense than the AABW, is likely to have mixed with better-ventilated waters containing higher CFC and CCl_4 levels during transit.

The ages of the uNADW calculated from the CCl_4/CFC-11 ratios compare reasonably well with apparent ages calculated previously for western boundary stations in the equatorial zone using CFC-11/CFC-12 ratios [*Weiss et al.*, 1985]. These authors calculated that the uNADW had an apparent age of ~23 years at the equator, and an apparent dilution factor of 5. Our section at 19°S is located a distance of 4800 km or ~30% further "downstream" of the presumed southern Labrador Sea source of uNADW [*Pickart*, 1991; *Smethie*, 1993]. This is consistent with the apparent ages at 19°S being ~30-35 years, i.e., 30-50% older than ages observed at the equator. Any hint of a decreased apparent current velocity between the equator and 19°S might be due to recirculation between the two sections [cf. *Smethie*, 1993]; however, more detailed sampling will be required to delineate this. Dilution factors within the uNADW at Stations 132 and 137 (2-7) are comparable, on average, to those found by *Weiss et al.* [1985] at the equator.

In addition, where direct comparison of CFC-11/CFC-12 ages with CCl_4/CFC-11 ages could be made, reasonably good agreement was found. If anything, the CCl_4/CFC-11 ratios gave slightly older ages, which implies that the equivalent atmospheric ratio of CCl_4/CFC-11 might have been overestimated either due to measurement error or inaccuracies in the low-temperature gas solubility data for CCl_4. Alternatively, this might be a consequence of the mixing effects on tracer ages discussed earlier. For example, mixing with CFC-free but CCl_4-tagged water during transit along the western boundary would increase the CCl_4/CFC-11 ratio but not the CFC-11/CFC-12 ratio of a water parcel. In this way, the CCl_4/CFC-11 apparent age would become older than the CFC-11/CFC-12 apparent age. In situ degradation of CCl_4 would create the opposite effect, i.e., younger apparent CCl_4/CFC-11 ages.

The general agreement of the two independent tracer ages argues against any significant nonconservative behavior of CCl_4 in the colder waters of the subthermocline ocean, at least over the 30-40 year timescales appropriate to this region.

Vertical Profiles of CFC-113

Only a few vertical CFC-113 profiles of limited quality were obtained due to analytical problems mentioned above. A profile in the western end of the section (station 137; Figure 11a) mimics the behavior of the other tracers. Stations further east (e.g., profile at station 174; Figure 11b), however, exhibited a strong maximum immediately below the mixed layer with ratios of CFC-113/CFC-11 which are implausible in terms of gas solubilities and the

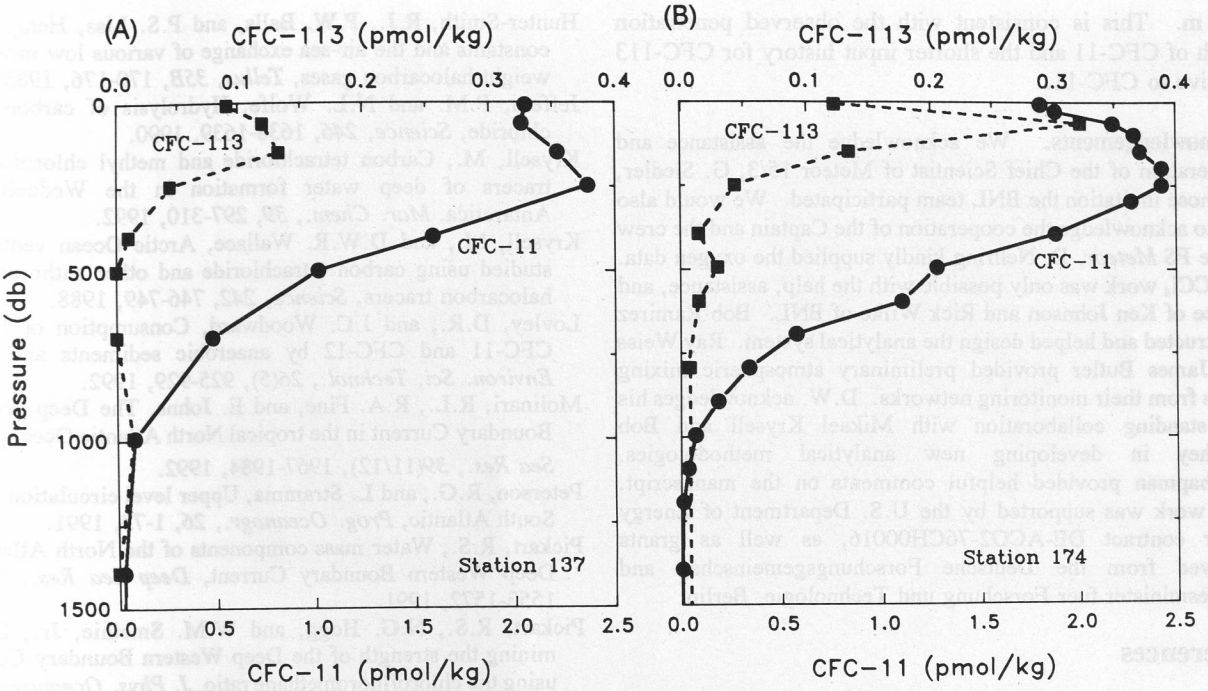

Figure 11. Vertical profiles of CFC-113 and CFC-11 from two stations (see Figure 2): (a) 137 in the Brazil Basin and (b) 174 located over the Mid-Atlantic Ridge, just south of the 19°S section (23°40'S, 15°W).

historical atmospheric source functions for these compounds (Figure 1b). Sample contamination was almost certainly not responsible, as this feature was observed at other stations in samples collected with several different Niskin bottles and we did not observe any serious contamination for this compound at greater depths. We are forced to consider whether these samples might have been affected by a chromatographic interference (i.e., a co-eluting peak); however, further studies with improved technique will be required to confirm or reject this possibility.

A firm conclusion which can be drawn is that CFC-113 was undetectable (i.e., <0.015 pmol kg^{-1}) below a depth of ~400-500 m. The penetration depth [cf. *Gammon et al.*, 1982; *Broecker et al.*, 1979] of CFC-113 is ~350 m, whereas for CFC-11 it is ~600-700 m. After subtracting a mixed-layer thickness of ~50 m for both tracers, the scale depth of tracer penetration, H [*Gammon et al.*, 1982], for CFC-11 is roughly twice that of CFC-113. It is reasonable that the tracer profiles should scale in this way given that CFC-11, at the time of sampling, had been present in the environment in significant quantities for ~50 years, whereas CFC-113 had only been present for ~25 years.

Conclusions

Based on the exploratory study conducted along WOCE A9 (*Meteor* 15/3) at 19°S, we have been able to answer several unresolved questions arising from previous studies in the Arctic and Antarctic and raise some others. Specifically, these are as follows.

1. The preindustrial background of CCl_4 in the oceans was of the order of 0.01 pmol kg^{-1} or less, which corresponds to an atmospheric mixing ratio of <0.1 pptv. Hence the possibility of a significant natural background of CCl_4 in the environment can be firmly ruled out.

2. There is evidence for much more rapid degradation of CCl_4 in the thermocline than would be predicted on the basis of freshwater hydrolysis kinetics. The observed deficit of CCl_4 appears restricted to the thermocline, and is most pronounced to the east of the Angola-Benguela front. The degradation mechanism is presently unknown but may have important implications for the global budget of this man-made gas.

3. The Brazil Basin has significant levels of CCl_4 throughout, including regions where CFC-11 and CFC-12 are undetectable. This indicates the potential of CCl_4 for extending the use of transient tracers into deep waters ventilated in the first half of the twentieth century. The potential of CCl_4 as a tracer is seriously limited by uncertainties in its gas solubility.

4. The uNADW close to Brazil's continental margin has an apparent age signature of 30-35 years, together with a dilution factor of the order of 3-7. Internal consistency with CFC-11/CFC-12 ages (where they could be determined) and with an earlier study by *Weiss et al.* [1985] at the equator, suggest that CCl_4 is conservative in the subthermocline ocean at least over multidecade timescales.

5. The AABW is "younger" (age 25-30 years) but more dilute than the uNADW, perhaps reflecting the effects of mixing in the Circumpolar Current and the Vema Channel prior to entering the Brazil Basin.

6. The deep Angola Basin has undetectable CFC-11 and CFC-12 levels and generally very low CCl_4. Traces of CCl_4 were found near the bottom at a few stations on the eastern side of the Mid-Atlantic Ridge, however. The origins of this presumably anthropogenic signal could include the Romanche Fracture Zone and flow across the Walvis Ridge.

7. At the few stations where clear CFC-113 profiles were determined, it was undetectable below approximately 400 m-

500 m. This is consistent with the observed penetration depth of CFC-11 and the shorter input history for CFC-113 relative to CFC-11.

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