5. Nitrous Oxide and Halocarbons Division

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5.1. CONTINUING PROGRAMS

5.1.1. FLASK SAMPLES

Air sample pairs were collected and analyzed for CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and nitrous oxide (N_2O) on the original HP 5710A GC. Both CFCs, particularly CFC-11, show a decrease in growth rate during the past few years that is apparent at all flask locations. In 1992 the growth rates of CFC-11 and CFC-12 were about 3 ppt yr^{-1} (Figure 5.1) and 11 ppt yr^{-1} (Figure 5.2). For a complete discussion of the slowdown of the growth rates, refer to *Elkins et al.*, [1993]. The global slowdowns of the growth rates observed after 1989 are also supported by estimates of reduced emissions [*AFEAS*, 1993; *McFarland and Kaye*, 1992] made by the CFC producers and are directly attributed to the international efforts of the Montreal Protocol [*UNEP*, 1987] and voluntary reductions from producers and users to reduce stratospheric ozone depletion. If the observed slowdowns in the growth rates continue at 1990-1992 levels, global atmospheric CFC-11 and -12 mixing ratios would reach a maximum well before the turn of the century, and thereafter begin to decline [*Elkins et al.*, 1993].

The growth rate of N_2O in the northern hemisphere has dropped significantly in 1992 and the decline may have started as soon as June 1991 (Figure 5.3). From 1977 to 1985, the growth rate was about 0.5-0.6 ppb yr^{-1}. From 1986 through mid-1991, the growth rate reached near 1 ppb yr^{-1}, with the peak value in 1989. In 1992, the growth rate dropped to about 0.5 ppb yr^{-1}. Whether this drop is a long-term feature remains to be seen. The cause of this slowdown is unknown because the relative magnitudes of the sources of atmospheric N_2O are still uncertain. The gap in the N_2O and CFC-12 data are the result of a GC problem that did not affect CFC-11.

5.1.2. RITS CONTINUOUS GAS CHROMATOGRAPH SYSTEMS AT CMDL STATIONS AND NIWOT RIDGE

In situ measurements of tropospheric air were made at the CMDL baseline stations, BRW, MLO, SMO, SPO, and at a cooperative site on Niwot Ridge (NWR). CMDL GCs made 24 measurements per day at each site. Each in situ GC system has three channels to measure different species of halocarbons; (1) N_2O, (2) CFC-12, and (3) CFC-11, CFC-113, CH_3CCl_3, and CCl_4. Each channel is equipped with a chromatographic column and an electron capture detector (ECD).

During a scheduled maintenance trip to SPO, a new sampling inlet system was installed. This system draws air from the meteorological tower in the clean air sector of the South Pole station via two sections of 0.9 cm o.d. Dekabon

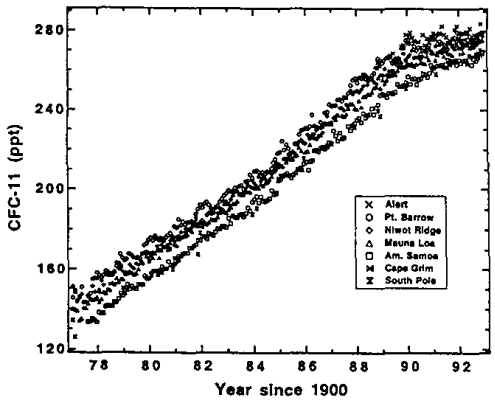

Fig. 5.1. Long-term trend of CFC-11 (dry, ppt by mole fraction) at the seven flask sites. A color plot of the figure is available from the NOAH division. Each tick mark on the x-axis is January 1st of every year.

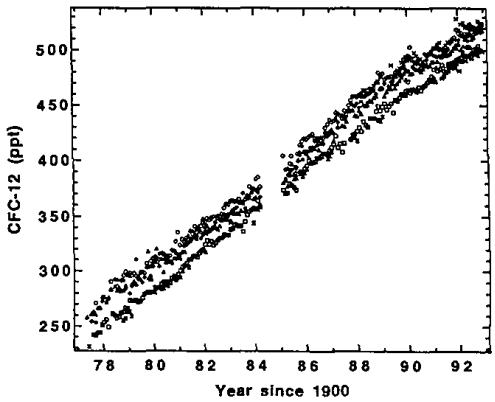

Fig. 5.2. Long-term trend of CFC-12 (dry, ppt by mole fraction) at the seven flask sites. A color plot of the figure is available from the NOAH division. Each tick mark on the x-axis is January 1st of every year.

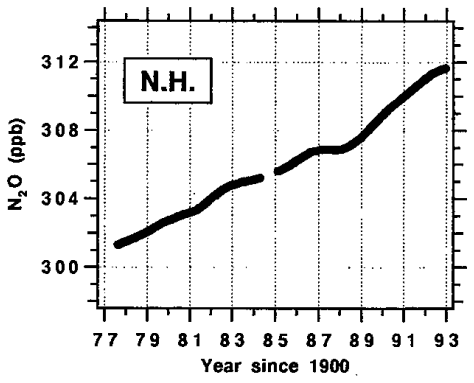

Fig. 5.3. Northern hemispheric mean mixing ratios of N_2O (dry, ppb by mole fraction) from 1977 through 1992. A loess fit (f ~ 24 months) was applied to the data.

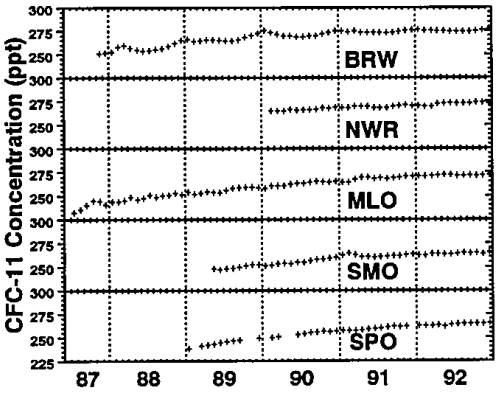

Fig. 5.5. Daily average CFC-11 mixing ratios in ppt from the in situ GCs.

tubing to a continuously operating pump mounted near the GC system. A stream select valve allows air to be sampled either from one of the two lines or from calibration cylinders. The installation of this air sampling system at SPO completes the upgrade for the RITS network. At this time, all of the RITS systems use this air sampling method.

During 1992, we found the mixing ratios of CFC-11 and CFC-12 indicate a change in trend from increasing or stable growth toward decreasing growth in data from SPO [*Swanson et. al.*, 1992]. The daily means for N_2O, CFC-12, CFC-11, and CCl_4 from the in situ systems are shown in Figures 5.4-5.7, respectively. The long-term trend of increasing mixing ratios of the CFC's is apparent in the graph of the data. Observations seem to indicate that the growth rate of CFC's has decreased since 1989. To illustrate the change in growth rates of the CFC's, an estimate of the growth rates for CFC-11 and CFC-12 was calculated by differentiating the mixing ratio data sets. Prior to 1989 the growth rate of the CFC's in the troposphere at SPO was approximately 11 ppt yr^{-1} for CFC 11 and 19 ppt yr^{-1} for CFC 12. After 1989 the growth rate of CFC's is calculated to be approximately 4 ppt yr^{-1} for CFC 11 and 14 ppt yr^{-1} for CFC 12.

These decreased overall growth rates are encouraging. Our laboratory plans to continue to monitor CFC molecules to further document their decline and to extend our

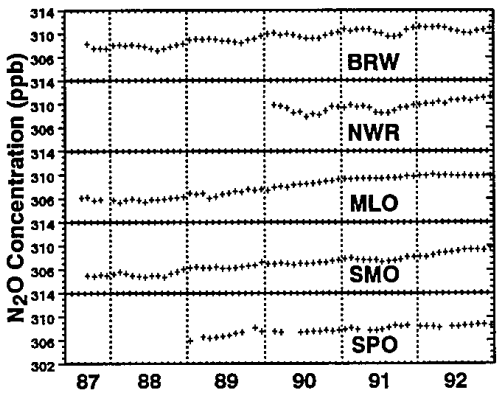

Fig. 5.4. Daily average N_2O mixing ratios in ppb from the in situ GCs.

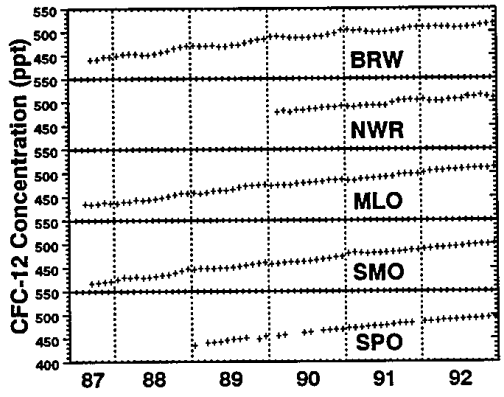

Fig. 5.6. Daily average CFC-12 mixing ratios in ppt from the in situ GCs.

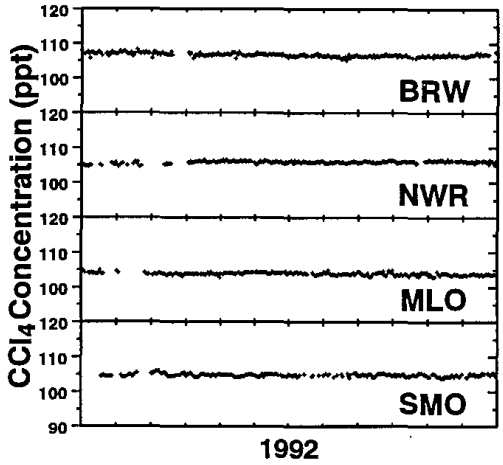

Fig. 5.7. Daily average CCl_4 mixing ratios in ppt from the in situ GCs.

understanding of the transport of these compounds to the atmosphere over Antarctica.

5.1.3. Low Electron Attachment Potential Species (LEAPS)

The LEAPS program was marked by two significant developments in 1992. The old GC system was replaced with a new system that yields higher precision and better accuracy. Also, year-round samples from SPO were collected and analyzed for the first time.

Near the end of the year, the old LEAPS analysis system, consisting of a Shimadzu GC-9A and Chrompack cryotrap, was replaced with an HP5890 Series II GC and a modified Tekmar dual cryo-trapping unit (Figure 5.8). The new analysis system yields precisions (1 s.d.) of ±0.02 ppt for a single measurement of halon H-1301 and ±0.04 ppt for H-1211, which are almost an order of magnitude better than with the old system. On the new system, gases of interest are first trapped onto a porous adsorbent (Porapak Q) at -60°C, separating them from O_2 and N_2. Sample volume is determined accurately by monitoring the temperature and pressure of an evacuated bulb downstream of the trap. (On the old system, sample volume was determined indirectly by ratio to CFC-12.) Trapped gases are then focused onto a megabore (0.53 mm i.d.), Al_2O_3/KCl-lined, capillary trap (Chrompack) at -60°C at the head of the column. Gases are injected at 100°C onto a wide-bore (30 m × 0.32 mm i.d.) DB-1 column (J and W) at 30°C. After 3 minutes, the column is heated at 8°C min^{-1} to 100°C, during which most gases are eluted to the ECD's. The column is then purged for 5 minutes at 150°C.

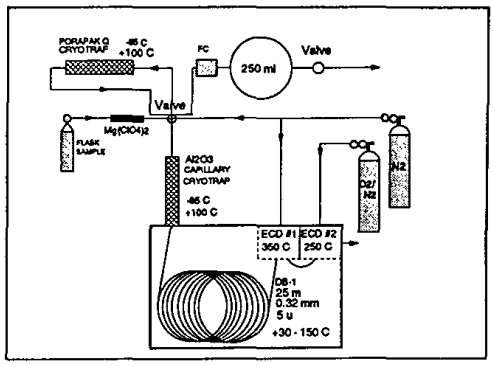

Fig. 5.8. New GC system for analysis of LEAPS gases.

Most flasks collected during 1992 were analyzed with the old system, but those from SPO, which were returned to Boulder at the end of the year, were all analyzed with the new GC and dual cryotrap. In previous years flask samples from SPO have been collected only during summer months. In November of 1991, however, flasks were shipped to SPO for sampling throughout the year. Most of these flasks were 0.85-L electropolished flasks suitable for analysis of low-concentration or poorly responding gases. Flasks were filled monthly throughout the year and shipped to Boulder in November 1992 after SPO opened for the next summer season.

These large flasks were analyzed for H-1301 and H-1211 on the newly configured LEAPS GC. There was no apparent serious degradation or enhancement of either of these compounds during storage, as the numerical values were similar to those for other sampling sites in the southern hemisphere. The growth rate of H-1301 during this sampling period was 7.3% yr^{-1}. H-1211 appeared to increase at 3.9% yr^{-1}, although the growth rate was not significantly different from 0 because of larger variability in the data (Figures 5.9 and 5.10). These trends are consistent with those reported for the other CMDL sampling sites during 1992 [*Butler et al.*, 1992].

The absolute values for H-1211 reported here differ from those in previous annual reports and from those in *Butler et al.*, [1992] because of a calculation error in the calibration scale of H-1211. The revised scale will be published in the next annual report, as additional re-calibrations are also necessary on the new instrument.

5.1.4. Alternative Halocarbon Measurements

In response to warnings of stratospheric ozone depletion and global warming, the production of many industrial chlorine-containing compounds will be banned within the next few years [*UNEP*, 1987]. Although the ultimate goal of this legislation is to replace chlorinated compounds with

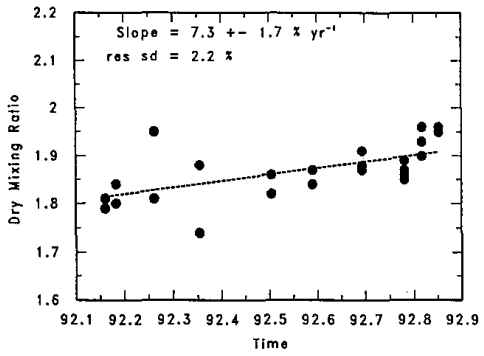

Fig. 5.9. 1992 H-1301 results from SPO.

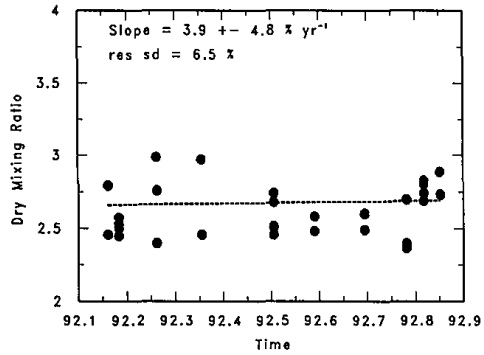

Fig. 5.10. 1992 H-1211 results from SPO.

non-chlorinated substitutes, such as hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) are currently being used until suitable non-chlorinated materials are developed. HCFCs are viewed as suitable temporary replacements for CFCs because current technology for their production and use in air-conditioners and refrigeration devices is already in place, and because model calculations suggest that the adverse effects of HCFCs on the atmosphere will be substantially less than those of CFCs. Accurate and precise measurements of these compounds in the atmosphere are essential in order to validate these predictions. These measurements also allow for accurate predictions of atmospheric impacts of other proposed substitute compounds, such as HFCs, because both HFCs and HCFCs are destroyed mostly in the troposphere by reaction with hydroxyl radical (OH). This is in contrast to CFCs, which are decomposed primarily by photolysis in the stratosphere. Presently, estimates of global OH are based on the atmospheric budget of a single industrial compound, 1,1,1-trichloroethane. Because there is considerable error in such a limited estimate there is a need for other trace species to test model-generated distributions of OH [*Prather and Spivakovsky*, 1990].

It is within this framework that a program for measuring alternative halocarbons was begun at CMDL. Measurements of chlorodifluoromethane (HCFC-22) from flasks collected in the NOAH flask network were initiated in 1991 and continued in 1992. In addition, 1-chloro-1,1-difluoroethane (HCFC-142b) and 1,1-dichloro-1-fluoroethane (HCFC-141b) were detected and first measured in ambient air samples during 1992.

The measurements were conducted as described by *Montzka et al.* [1992, 1993*a*,*b*] from paired air samples that were collected on a monthly basis (on average) at BRW, MLO, SMO, SPO, and at the three cooperative flask sampling locations of ALT, NWR, and CGO.

Chlorodifluoromethane (HCFC-22)

Chlorodifluoromethane is the major HCFC in use today and represents a second trace species available for testing models that estimate the global tropospheric abundance of OH [*Midgley and Fisher*, 1993; *Fraser et al.*, 1991]. Unfortunately, significant discrepancies among measurements of HCFC-22 by different techniques have been reported in the past. Mixing ratios determined from ground-based chromatographic measurements of northern hemispheric air [*Khalil and Rasmussen*, 1988, 1990, 1991] are 10-30% higher than those determined from long-path absorption measurements within the troposphere and lower stratosphere [*Rinsland et al.*, 1989, 1990; *Zander et al.*, 1992], and a small set of grab samples obtained in the lower troposphere [*Pollock et al.*, 1992]. Furthermore, the lifetime of HCFC-22 suggested by a comparison of emission estimates and ambient measurements varies from 13 to 40 years [*Midgley and Fisher*, 1993]. Lifetime estimates that are based on 3-D models and the reaction rate constant between HCFC-22 and hydroxyl radical, suggest a lifetime for HCFC-22 of 14-16 years [*Prather and Spivakovsky*, 1990; *Golombek and Prinn*, 1989].

Our analysis of air collected in flasks during 1992 at the four CMDL stations and three cooperative flask sampling sites indicates that the latitudinally-weighted, global mean mixing ratio of HCFC-22 in 1992 was 102 ppt (Tables 5.1 and 5.2). These results are plotted as bi-monthly averages together with measurements of air from archived samples [*Montzka et al.*, 1992, 1993*a*] and data from previous

TABLE 5.1. Mean Mixing ratios of HCFC-22 in 1992 (ppt)*

	Mixing Ratio
Global mean	101.9
Northern hemisphere	108.4
Southern hemisphere	95.4

*All values were weighted by cosine of latitude. Numbers believed accurate within ±2.5%.

TABLE 5.2. Atmospheric Measurements of HCFC-22 From Flasks in 1992

Station	Date	ppt	Station	Date	ppt
ALT	1992.052	110.0	MLO	1992.893	108.4
ALT	1992.128	109.5	MLO	1992.913	105.0
ALT	1992.328	110.5	MLO	1992.970	111.6
ALT	1992.385	113.4	MLO	1992.989	111.0
ALT	1992.620	111.5			
ALT	1992.713	112.1	SMO	1992.046	93.6
ALT	1992.907	115.0	SMO	1992.112	90.4
			SMO	1992.262	95.2
BRW	1992.022	112.2	SMO	1992.301	95.7
BRW	1992.120	109.1	SMO	1992.456	95.5
BRW	1992.268	110.7	SMO	1992.530	95.0
BRW	1992.372	111.2	SMO	1992.607	96.3
BRW	1992.459	110.0	SMO	1992.686	98.2
BRW	1992.538	110.4	SMO	1992.784	98.3
BRW	1992.618	111.4	SMO	1992.921	97.5
BRW	1992.866	114.5			
BRW	1992.940	116.3	CGO	1992.036	90.3
BRW	1992.959	115.7	CGO	1992.115	92.4
			CGO	1992.153	92.4
NWR	1992.131	107.3	CGO	1992.306	94.2
NWR	1992.265	108.4	CGO	1992.363	95.1
NWR	1992.322	112.7	CGO	1992.402	94.8
NWR	1992.552	111.5	CGO	1992.555	94.5
NWR	1992.571	109.7	CGO	1992.587	96.2
NWR	1992.609	111.7	CGO	1992.669	96.3
NWR	1992.727	111.8	CGO	1992.705	96.6
NWR	1992.877	108.7	CGO	1992.746	96.2
NWR	1992.954	115.1	CGO	1992.798	96.0
			CGO	1992.951	97.6
MLO	1992.033	104.4	CGO	1992.970	98.6
MLO	1992.109	101.8			
MLO	1992.262	103.7	SPO	1992.063	92.1
MLO	1992.281	103.6	SPO	1992.079	90.3
MLO	1992.473	105.7	SPO	1992.434	93.8
MLO	1992.530	106.1	SPO	1992.506	96.9
MLO	1992.596	108.5	SPO	1992.590	96.2
MLO	1992.607	104.3	SPO	1992.694	96.4
MLO	1992.691	103.0	SPO	1992.781	96.8
MLO	1992.740	109.1	SPO	1992.817	96.2
MLO	1992.779	106.3	SPO	1992.853	97.1

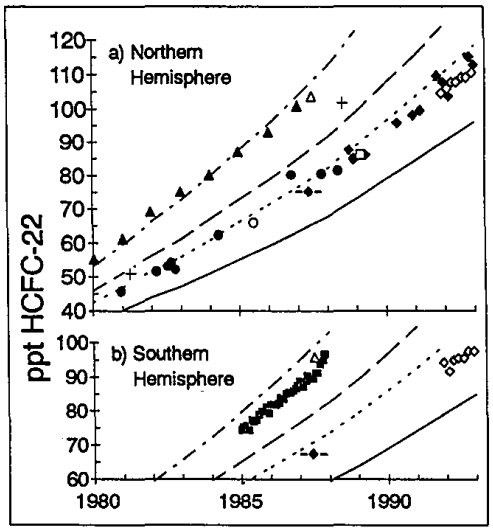

Fig. 5.11. Measurements of HCFC-22 and results of a 2-box model as described in the text for the northern (a) and southern (b) hemisphere. Results from flasks collected at the four CMDL stations and three cooperative flask sampling sites are bimonthly, latitudinally-weighted hemispheric means (◊, *Montzka et al.*, [1993]). Flasks collected during the SAGA II Cruise (-♦-, *Montzka et al.*, [1992]; Δ, *Khalil and Rasmussen* [1988]) are presented as latitudinally-weighted hemispheric means. Archived samples were collected at Niwot Ridge (♦, *Montzka et al.* [1992]). Other measurements from flasks are from northern mid-latitudes in the upper troposphere (□, *Pollock et al.*, [1992]), Mauna Loa, USA (▲, *Khalil and Rasmussen* [1991], and C. Grim, Australia (■, *Fraser et al.*, [1988, 1989]). Long path absorption measurements were made at 12.5 km (○, *Zander et al.*, [1992]), throughout the troposphere (•, *Rinsland et al.*, [1989]), and below 15 km (+, *Rinsland et al.*, [1990]). Measurements of *Rinsland et al.* [1989] were increased by a factor of 1.28 to account for an updated cross-section estimate [*Rinsland et al.*, 1990]. Model calculations were performed for different lifetimes of HCFC-22, 10 years (——), 15 years (- - -), 20 years (— — —), and 50 years (— · — · —). Abscissa tic marks correspond to the beginning of the year indicated.

investigators over a broad time-scale in Figure 5.11. In the northern hemisphere, measurements based on the CMDL calibration standards agree with long-path absorption measurements of HCFC-22 in the troposphere near 30°N [*Rinsland et al.*, 1989]. They also agree with the results obtained at 30°N and above 12.5 km with the Atmospheric Trace Molecule Spectroscopy (ATMOS)-Fourier transform spectrometer on board Spacelab 3 [*Zander et al.*, 1992]. Although it is difficult to accurately compare ground-based measurements directly with measurements at altitudes above 12.5 km, a limited number of studies suggest that the mixing ratio of HCFC-22 within the troposphere is fairly constant, making these comparisons valid [*Leifer et al.*, 1981; *Rasmussen et al.*, 1982].

The results of *Pollock et al.* [1992] were obtained from a small set of samples collected in the upper troposphere in the northern mid-latitudes and are also in close agreement with the results based on the CMDL standards. Their results were obtained from GC-MS analysis of air collected in flasks. The similarity between the results of *Pollock et al.* [1992] and those reported by *Montzka et al.* [1992, 1993*a*] suggest that these two independent calibration scales agree to within 5%.

The measurements of *Khalil and Rasmussen* [1988, 1990, 1991] and *Fraser et al.* [1989] are ~28% higher than measurements based on the CMDL calibration standards (Figure 5.11). Their measurements were based on a calibration scale that was developed in the late 1970s and believed accurate to within ±10% on the basis of comparisons with another laboratory at that time [*Rasmussen et al.*, 1980]. The differences between these results and those based on the CMDL standards are likely the result of different calibration scales for HCFC-22. Given that measurements by different techniques are converging towards a lower atmospheric burden of HCFC-22 than suggested by *Khalil and Rasmussen* [1988, 1990, 1991] and *Fraser et al.* [1989], it is possible that calibration standards used for their measurements were inaccurate. Overestimation of HCFC-22 by these investigators could explain the large discrepancies reported in the past between measured atmospheric mixing ratios and emission estimates [*Khalil and Rasmussen*, 1981] and between surface-based flask samples and long-path absorption measurements [*Rinsland et al.*, 1990].

Using the emission estimates of *Midgley and Fisher* [1993], atmospheric mixing ratios of HCFC-22 were calculated with a 2-box, finite increment model [*Elkins et al.*, 1993]. The factor "f" [*Butler et al.*, 1992] was used to account for the vertical distribution of HCFC-22 throughout the atmosphere, and was estimated at 1.07 (±0.2) [*Zander et al.*, 1992; *Leifer et al.*, 1981; *Fabian et al.*, 1985]. The model was initialized with 10 ppt of HCFC-22 in 1970 to account for emissions in years before 1970. Emissions after the end of 1991 were estimated by a linear extrapolation of emissions from 1985 to 1991.

When compared to mixing ratios calculated with the model and data in *Midgley and Fisher* [1993], measurements based on CMDL standards, suggest an atmospheric lifetime for HCFC-22 of 13.6 (+1.9, -1.5) years (Figure 5.11). A similar lifetime can be estimated from the results of *Zander et al.* [1992], *Rinsland et al.* [1989], and *Pollock et al.* [1992]. Recent estimates of the atmospheric lifetime of HCFC-22 from global 3-D models yield values of 14.2-15.5 years, and are based on an atmospheric lifetime for CH_3CCl_3 of 5.7 or 6.3 years [*Prather and Spivakovsky*, 1990, *Golombek and Prinn*, 1989]. However, revised estimates of the reaction rate constant between OH and CH_3CCl_3 suggest that HCFC lifetimes should be shortened by 15% [*Talukdar et al.*, 1992]. Given a lifetime for CH_3CCl_3 of 5.7 yr^{-1} [*Prinn et al.*, 1992], and rate constant for CH_3CCl_3 loss to the oceans of between 1/59 and 1/129 yr^{-1} [*Butler et al.*, 1991], the lifetime of HCFC-22 is estimated at 12-14 years. Although error estimates for the lifetime of CH_3CCl_3 and emission of HCFC-22 are ±10% and ±12%, respectively, it is clear that our measurements agree well with this revised lifetime estimate.

Until measurements of HCFC-22 are extensive enough to allow for calculation of lifetime directly (as done by *Prinn et al.*, [1992] for CH_3CCl_3), estimates of HCFC-22 lifetime, and most other HCFCs and HFCs, are dependent on the accuracy of rate constants and calibration of CH_3CCl_3 and are subject to change as these latter parameters are refined.

Measurements of archived air and air obtained from flasks allow for an estimate of the growth rate of HCFC-22 from 1987 to the present. From the data based on CMDL calibration standards shown in Figure 5.11, a linear growth rate of 6.3 (±0.3) ppt yr^{-1} or compounding growth of 7.3 (±0.3)% yr^{-1} (in which the mixing ratio (X) since an initial time is defined as $X = X_o*(1 + GR)^{\Delta t}$, and X_o is the initial mixing ratio, GR is the fractional increase per year, and Δt is the time elapsed since time t_o) is obtained for HCFC-22 between 1987 and December 1992.

The global distribution of HCFC-22 as defined by flasks collected in 1992 (Figure 5.12) can also be used to estimate an instantaneous growth rate in the southern hemisphere (SH) during this year [*Butler et al.* 1992]. Given an interhemispheric difference of 13 (±1) ppt, an interhemispheric exchange time of 1.1 (±0.1) yr^{-1}, and a 1992 mean SH mixing ratio of 95.4 (±2) ppt, we estimate a 1992 SH growth rate for HCFC-22 of 5.0 (±1.6) ppt yr^{-1} or 5.2 (±1.7)% yr^{-1}.

These estimates of growth for HCFC-22 between 1987 and 1992 agree with predictions from our model calculation and that reported by *Midgley and Fisher* [1993]. Previous estimates of HCFC-22 growth from ambient air measurements suggest that between 1984 and 1989 HCFC-22 was increasing at 6 to 8% yr^{-1} [*Fraser et al.*, 1991]. Our measurements, when combined with these earlier estimates, suggest that the relative growth rate of HCFC-22 has remained fairly constant (±2%) since 1984 through 1992.

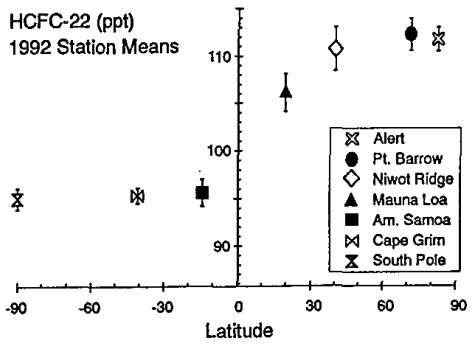

Fig. 5.12. Mean mixing ratios of HCFC-22 in 1992 as determined from air samples collected in flasks at the seven sampling stations. Vertical bars represent ±1 standard deviation of residuals from a linear fit to the data obtained at each station.

1,1-Dichloro-1-Fluoroethane (HCFC-142b)

HCFC-142b was recently incorporated in air conditioners and refrigeration devices where mixtures of CFC-11 and CFC-12 were formerly used. This compound was identified in ambient air collected at all seven stations around the globe in 1992. The only other reported measurement of this compound from air samples in the remote atmosphere was by *Pollock et al.* [1992]. These investigators reported an ambient mixing ratio for HCFC-142b of 1.1 ppt in air collected in 1989 from the upper troposphere in the northern hemisphere. These investigators reported that the mixing ratio of HCFC-142b was increasing over time at a rate of approximately 7% yr^{-1}.

Measurements of HCFC-142b from air collected as part of the NOAH flask sampling network are summarized in Figure 5.13. The mean global growth rate of this compound was estimated using linear regression at approximately 1 ppt yr^{-1} in 1992. Using the methods of *Butler et al.* [1992] the growth rate in the southern hemisphere is estimated at 0.9 ppt yr^{-1} over this period. This corresponds to an atmospheric growth of ~30% yr^{-1} for HCFC-142b in 1992. These numbers are preliminary and will be finalized in 1993 after standards are made at CMDL. While the scale reported in Figure 5.13 is preliminary at this time, the relative rate of growth of HCFC-142b indicated by the results in this figure are independent of calibration and are robust, assuming that no drifts have occurred in reference gases. A growth of 30% yr^{-1} for HCFC-142b is large compared to atmospheric growth rates of other CFCs and HCFCs currently being used by industry. However, the yearly increase in the atmospheric chlorine burden due to HCFC-142b is small at this point in time as the mixing ratio of this compound is less than 10 ppt.

1-dichloro-1,1-difluoroethane (HCFC-141b)

HCFC-141b is a compound currently in use as a substitute for CFCs and is also present as an impurity in samples of HCFC-142b. This compound was identified in air samples in the northern hemisphere during 1992. Levels in the southern hemisphere were at or below the detection limit of the instrument so as to preclude precise quantitation. Work in 1993 will focus on developing calibration standards and increasing the sensitivity of the GC-MS instrument.

5.1.5. GRAVIMETRIC STANDARDS

Chlorodifluoromethane (HCFC-22)

The focus of the standards laboratory was on completing the work started in 1991 for developing a primary calibration scale for HCFC-22 (chlorodifluoromethane). Research was conducted into the stability of the gas contained in specially treated aluminum cylinders both as single-component and multi-component mixtures ranging from 50 parts per trillion to 1 part per thousand using gas chromatography/mass spectrometry (GC/MS) techniques [*Montzka et al.*, 1993*b*] and by GC using an oxygen-doped electron capture detector. The comparison of standards prepared in May 1989 to standards prepared recently, indicate that stability in Aculife-treated aluminum cylinders is maintained. The response curve for gravimetric standards containing HCFC-22 by GC using an oxygen-doped ECD is shown in Figure 5.14.

To investigate the containers and techniques used to generate calibration standards for HCFC-22, standards from levels as low as 50 ppt to as high as 1 part per thousand (Figure 5.15) were analyzed with GC/MS techniques [*Montzka et al.* 1992, 1993*a,b*]. Standards at levels below 15 ppb were analyzed in the same manner as flask air

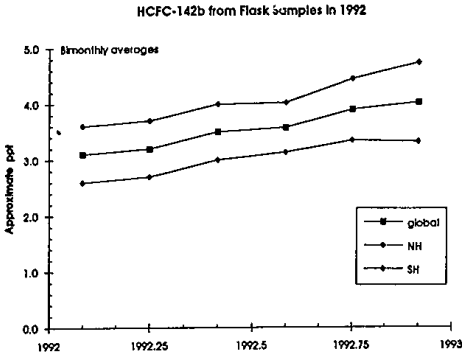

Fig. 5.13. Bimonthly mean mixing ratios of HCFC-142b for both hemispheres and the globe in 1992. Stated mixing ratios are preliminary and based on a NOAA scale (see text).

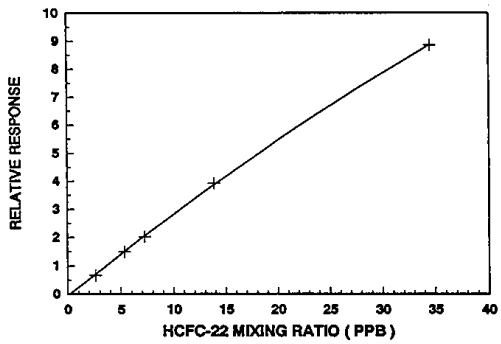

Fig. 5.14. Response curve of HCFC-22 gravimetric standards with an oxygen-doped electron capture detector.

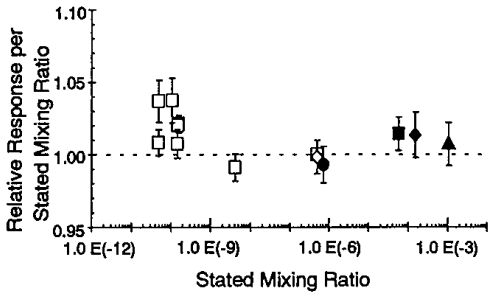

Fig. 5.15. The response per stated mixing ratio of HCFC-22 in different gravimetric standards from 50 parts per trillion to 1 part per thousand. Vertical bars correspond to one standard deviation of the results. All standards are plotted relative to the standard at 489.9 ppb, to which a response per ppt of 1.00 was assigned. Standards made from "pure" HCFC-22 are indicated with shaded symbols. The parent cylinder of lower level standards is indicated by the symbol shape. Standards below 10 ppb were multi-component mixtures containing carbon dioxide, methane, nitrous oxide, and numerous chlorofluorocarbons.

samples, but without the presence of a drying agent. For standards above 10 ppb, sample loops of 81.8 and 13.1 μL were filled to atmospheric pressure and injected directly onto the column. Loop volumes were determined gravimetrically to within 1% with multiple injections of deionized distilled water onto a desiccant. The volume of the evacuated chamber (used for cryo-collection of low level samples) was determined barometrically by reference to a known volume. When two standards of widely varying mixing ratios were compared, different loop sizes and cryo-collection volumes were used to minimize the difference in the amount of HCFC-22 reaching the detector, thereby minimizing non-linearity effects. For standards below 1 ppm this difference was always less than a factor of 6 and was typically a factor of 2. For standards above 1 ppm, the amount of HCFC-22 in standards being compared never differed by more than a factor of 20. Linearity has been confirmed (within 1%) over a range of 6.5x for HCFC-22 by injections of different loop volumes of the same standard directly onto the column. For standards containing CFC-12 and CFC-11, we have found that the detector responds linearly (within 2%) over a range of greater than 100x in the region of interest. With the exception of two standards above 100 ppm (Figure 5.15), the HCFC-22 standards were referenced to loop injections of the standard at 489.9 ppb. The two standards above 100 ppm were directly compared only to the standard at 56 ppm shown in Figure 5.15.

The response per ppt of our standards is consistent within ±2% (±1 s.d.) and these data suggest that the integrity of HCFC-22 is maintained in Aculife-treated aluminum cylinders even at the 50 ppt level (Figure 5.15). In addition, the data demonstrate that ambient levels of CO_2, N_2O, CH_4, or other halocarbons in a sample do not affect our analysis for HCFC-22. We feel that the different conditions under which these standards were made and the lack of impurities found in our starting reagents (none above 1 part per thousand) allow us to estimate the accuracy of our HCFC-22 scale by the variance among these standards. At the 95% confidence level, we believe our standards accurate to within ±2.5%.

Blended Multi-Component Standards

Research started this year into preparing synthetically blended multi-component standards for use as calibration standards for our GCs located at our observatory stations and in the standards laboratory. Our division was also contracted by the Aeronomy Laboratory to provide a suite of round-robin standards for worldwide inter-laboratory analysis comparisons. Nine single-component gravimetric mixtures were prepared from pure reagents in specially treated aluminum cylinders using various dilution techniques. These parent mixtures were then used to prepare single-component gravimetric standards at lower concentrations. The standards were then blended together into three nine-component mixtures containing CFC-11, CFC-12, CFC-113, methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), HCFC-22, N_2O, CH_4, and CO_2 in blended air. These were then used to prepare two cylinders each of gases containing concentrations matching real air. Each of the three cylinders contained the gases at various mixing ratios found in atmospheric air ranging from the mid-latitude to the arctic stratosphere. The gases contained in all of the cylinders were analyzed over time to insure stability. Unfortunately, the six cylinders used for preparing the low concentration standards were found to readily absorb CH_3CCl_3 and CCl_4 from the gas mixtures. Losses ranging from approximately 10 to 100% were observed for CH_3CCl_3 and from approximately 5 to 90% for CCl_4 within 1 week after preparing the standards. The cylinders were returned to the vendor and were retreated using their proprietary treatment process. The same cylinders were then used to remake the standards. The new suite of standards were analyzed and were found to be acceptable except for one that exhibited CFC-113 contamination due to a dirty cylinder valve. A standard similar to one of the six has been placed online at the NWR station for calibrating the GCs.

Two gravimetric standards containing approximately 100 ppm of CO in air and two containing ambient concentrations of CH_4 in air were prepared for NCAR. The standards were used to calibrate a tunable diode laser system.

Three CO in air gravimetric standards were prepared for use as supplemental primary standards to the CO reference scale maintained by the Carbon Cycle Division. The three standards were prepared at nominal concentrations of 50, 100, and 150 ppb. The intercomparision of these standards to the current scale showed no significant bias.

Several cylinders containing dilute mixtures of N_2O in N_2 and N_2O in air were analyzed for the NASA Ames Research Center. The analyses of these cylinders required the preparation of six gravimetric standards. Four of the primary calibration standards were prepared containing N_2O in blended air and two were prepared containing N_2O in N_2. The mixing ratios of the primary standards were targeted in order to closely bracket the mixtures to be analyzed. This analysis proved interesting in that it allowed us to intercompare NOAA N_2O in N_2 standards to N_2O in air standards to determine if mixtures containing different diluents (e.g., N_2, air) had any effect on ECDs and/or presented a problem involving chromatographic peak integration. The results of this experiment indicated there was a small bias between analyzing N_2O-in-N_2 mixtures using N_2O-in-air and N_2O-in-N_2 standards. The calculated value for a N_2O in air mixture using N_2O in N_2 standards was approximately 0.8% higher than what was calculated using N_2O in air standards (Figure 5.16).

Instrumentation

Two GCs with ECDs were added to the standards laboratory this year. The two were combined with a third on hand to create an automated analytical system similar to the systems used by the RITS program at the observatory stations. Previously, analysis of standards was conducted on the flask analysis system. More time can now be devoted to both flask analysis and standards analysis with the use of two separate systems. The system for standards analysis is capable of measuring CFC-11, CFC-12, CFC-113, CH_3CCl_3, CCl_4, and N_2O. It is also capable of measuring HCFC-22 concentrations as low as 1 ppb without injecting cryogenically collected samples. This is made possible with the use of a Carbopack B column operated at ~70°C which gives good separation of the HCFC-22 and CFC-12 peaks from the air peak and by doping the electron capture detector with a 5% mixture of oxygen in N_2.

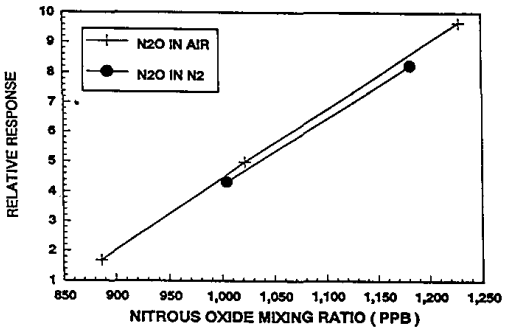

Fig. 5.16. Response curve of N_2O in air and N_2O in N_2 with an electron capture detector and 5% CH_4 in Ar carrier gas.

Standards with concentrations lower than 1 ppb are measured on the GC/MS by cryogenic collection.

There were 56 gravimetric standards prepared in the standards laboratory for the year of 1992 (Table 5.3). In addition, there were seven calibration standards replaced at our various observatory stations for the RITS program. To reduce vibrations, our gas standard laboratory was relocated from the third floor of building RL-3 to the ground floor of building RL-6.

5.2. Special Projects

5.2.1. Aircraft Measurements of the CFCs

The Airborne Chromatograph for Atmospheric Trace Species (ACATS) instrument has had considerable success over the past 2 years in measuring CFC-11 and CFC-113 in the troposphere and lower stratosphere. ACATS was built inside the reactive nitrogen instrument [*Fahey et al.*, 1989] and was described in last year's Summary Report [*Montzka et al.*, 1992]. Since its construction in 1991, ACATS has participated in two major projects, NASA's stratospheric ozone program and High Speed Research Program (HSRP). These projects use CFC measurements as anthropogenic tracers to indicate stratospheric ozone loss. Using an airborne platform, in this case the ER-2 (a civilian version of the U-2), allows ACATS to measure vertical profiles extending into the lower stratosphere. Vertical profiles of trace species, including CFCs, have become an integral component of the NOAH division's research and is NOAA's

TABLE 5.3. Summary of Gravimetric Standards

Compounds	Quantity	Concentration Range	Prepared For
HCFC-22	12	ppt, ppm	NOAH/AL
CFC-11, CFC-12, CFC-113, CCl_4, CH_3CCl_3, N_2O, HCFC-22	3	ppt, ppb	ACATS/NOAH
CFC-11	1	ppb	NOAH/AL
CFC-12	2	ppm	NOAH/AL
CFC-113	1	ppb	NOAH/AL
CH_3CCl_3	1	ppb	NOAH/AL
CCl_4	1	ppb	NOAH/AL
CH_4	5	ppm, percent	NOAH/AL/ CC/NCAR
CO	5	ppb, ppm	CC/NCAR
N_2O	8	ppb, ppm	NOAH/U. of N.H./CANMET
CFC-11, CFC-12, CFC-113, CCl_4, CH_3CCl3, N_2O, HCFC-22, CO, CH_4	17	ppt, ppm	NOAH/AL

key responsibility to the Global Climate Change Program [*GCRP*, 1993]. The Airborne Arctic Stratospheric Expedition II (AASE II) and the forthcoming Stratospheric Photochemistry, Aerosols, and Dynamics Expedition in 1993 (SPADE, a component of HSRP) missions have used and will continue to utilize ACATS CFC measurements. In November test flights for SPADE were conducted at NASA Ames, Moffitt Field, California. Although the primary goal of the November flights was to integrate new and modified instruments into the ER-2 payload, ACATS made measurements on two 2-hour flights. For the future 1993 SPADE project, ACATS will have an additional N_2O-doped ECD channel to measure CH_4 and CO in collaboration with Carbon Cycle Division [*Goldan, et al.*, 1982].

AASE-II mission

The AASE-II mission was designed to primarily focus on photochemistry of the lower stratosphere and ozone destruction or production due to chemical perturbations. Addition of these two CFC molecules to the complement of species already measured on the ER-2 platform offers new science opportunities. Atmospheric CFC-11 and -113 are important ozone depleting chemicals, which together represent about 30% of the total organic chlorine in the atmosphere. The use of high resolution CFC measurements along with correlations between different tracers generated by dynamic models [*Solomon et al.*, 1992] permits calculation of the total organic chlorine over the complete flight. Since 1989, the growth rates of both chemicals, particularly CFC-11 [*Elkins et al.*, 1993], have been slowing down in the troposphere. Monitoring the slowdown of the growth rates in the troposphere and stratosphere, together with accurate tracking of emissions, will further aid in the refinement of chemical lifetimes of the these species and may provide for a more complete understanding of the transport properties of the atmosphere.

These CFC molecules are excellent tracers of stratospheric dynamics. High levels of chlorine monoxide (ClO) indicate that O_3 has been destroyed. The decrease in CFC mixing ratios that were observed on the ER-2 aircraft flight of January 16, 1992, in a region where ClO mixing ratios increased delineates the extent of the polar vortex (Figure 5.17). The slow, steady photochemical destruction of the CFCs is the source of the chlorine atom for the more

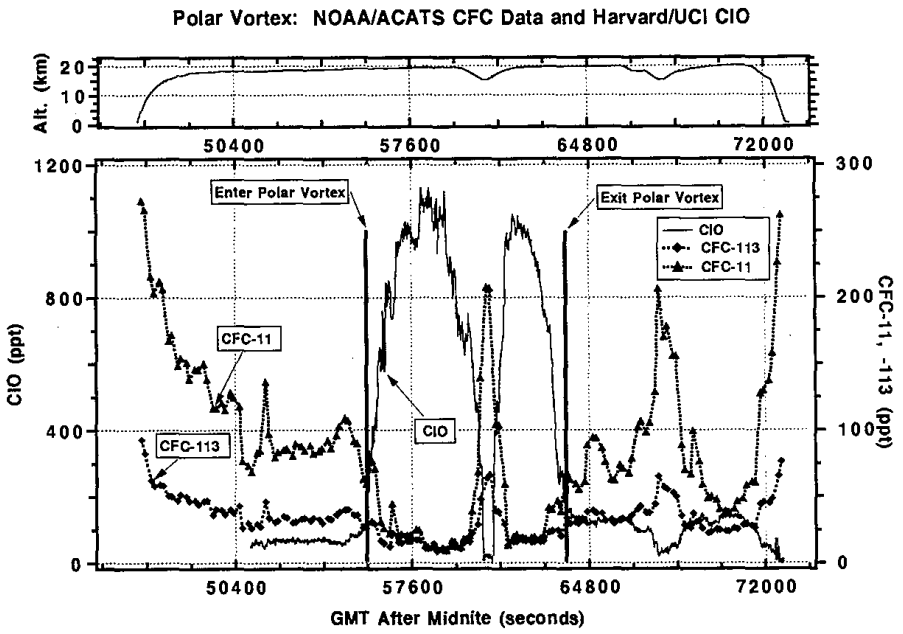

Fig. 5.17. Altitude in km (top) and mixing ratios of CFC-11 (▲) and CFC-113 (♦) from ACATS and of ClO (—) in parts-per-trillion (ppt) on the ER-2 flight (bottom) of January 16, 1992. The boundaries of the polar vortex are clearly defined by the increase in mixing ratios of ClO and by the decrease in CFC levels. Mixing ratios of ClO were measured by methods described by *Brune et al.*, [1989] and preliminary values from AASE-2 were made available by *Toohey et al.* [1993].

reactive and destructive ClO molecule. It was this flight and one on January 20 showing high levels of ClO over the United States that convinced President Bush to move up the timetable for the complete phaseout of the CFCs from the year 2000 to 1996, 4 years ahead of the schedule mandated by the Montreal Protocol. All signatory nations agreed to this new schedule in the Copenhagen Amendment of 1992 for the Montreal Protocol. The concern over the timetable was the long atmospheric lifetimes of the CFC molecules. The lifetime for CFC-11 is about 55 years [*Elkins et al.*, 1993] and for CFC-113 is 110 years [*WMO*, 1992], whereas the chemical lifetimes of ClO plus its dimer are about 1 month [*Salawitch et al.*, 1993]. This diversity in the lifetimes of tracers will allow modelers to check theories on transport inside the stratosphere. Linear correlations are found for molecules with similar lifetimes or at altitudes where the local lifetimes are greater than the time scales of vertical transport [*Plumb and Ko*, 1992]. Correlation of mixing ratios of CFC-113 versus CFC-11 (Figure 5.18) shows a strictly linear relationship for mixing ratios of ~50 ppt for CFC-11 and considerable curvature at lower values where CFC-11 is more rapidly destroyed than CFC-113. During previous missions, ozone depletion at a particular altitude was calculated relative to the long-lived tracer, N_2O. Additional measurements of the CFCs and their correlations with N_2O allow other tracers to be used to evaluate the effects of ozone depletion.

SPADE Mission

ACATS is a versatile instrument that will be utilized in the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE) and future polar missions like Airborne Southern Hemispheric Ozone Expedition (ASHOE) in 1994. The SPADE mission will provide additional measurements for key components of the prior AASE I and II missions. This year's SPADE test flights and the 1993 SPADE project are components of NASA's HSRP that is in charge of assessing the environmental impact of a projected fleet of supersonic high-speed civil transports. SPADE has two primary scientific objectives: (1) To determine the key chemical processes that affect ozone levels in the parts of the stratosphere that would be most influenced by future stratospheric aircraft. This includes free-radical and heterogeneous chemistry. (2) To estimate the distribution of exhaust effluent in the stratosphere. This involves measurements of a wide range of tracers in the lower stratosphere.

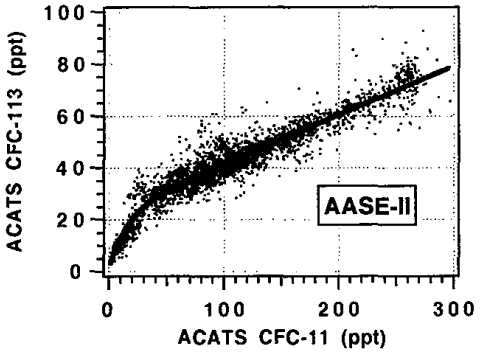

Fig. 5.18. Mixing ratios of CFC-113 versus CFC-11 in ppt for all flights during AASE-2. All data were fit to following equation: CFC-113 = 21.8 + 0.186 CFC-11 - 22.8 $e^{-(0.059\ \text{CFC-11})}$ using least squares techniques. The linear range covers mixing ratios for CFC-11 between 50 and 300 ppt, and CFC-11 is destroyed more rapidly than CFC-113 below mixing ratios of 50 ppt.

ACATS measured CFC-11 and CFC-113 on two of the test flights this November (Figure 5.19). Both of these flights were during the day, lasted about 2 hours, and reached a maximum altitude of 20 km. The flight path on November 9 stayed completely over land, south of the San Francisco Bay area, while the flight on the 12th was mainly over the Pacific coast. The CFC-11 stratospheric mixing ratios for these flights are in good agreement with the previous AASE II data. Similarly, the tropospheric mixing ratios for these flights agree with northern hemispheric station measurements. Unfortunately, the CFC-113 measurements for the flight on November 9 were lost due to contamination, but the data on the 12th also agrees with AASE II and station measurements.

5.2.2. Ocean/Atmosphere Exchange of Trace Compounds

The Ocean Atmosphere Exchange of Trace Compounds (OAXTC) mission was conducted aboard the University of Southern California research vessel *John V. Vickers* between August and October 1992. (Figure 5.20). The main goal of this study was to determine the atmospheric mixing ratio of HCFC-22 and its partial pressure in surface waters of the West Pacific Ocean to assess the possible existence of an oceanic sink for this compound. HCFC-22 is one of the major halocarbons in use today with a growth rate of 7.3% per year and a global mean of around 101.8 ppt [*Montzka et al.*, 1993*a*]. Water column measurements of HCFC-22 were carried out to complement air and surface water determinations to better illustrate its behavior in the ocean. CFC-11, CFC-12, methyl chloroform (CH_3CCl_3), and carbon tetrachloride (CCl_4) were added to these measurements for comparison to similar data that were obtained during previous cruises [*Butler et al.*, 1991] and to data from our network sites. CFC-113 and N_2O were also measured but are not reported here.

Sampling and Analysis

Surface water gases were partitioned with an acrylic seawater equilibrator as done on previous cruises [*Butler et al.*, 1988]. Ambient air and equilibrator headspace were sampled with a two-channel pumpboard. In addition, 27 pairs of flask samples, one each for air and equilibrator headspace, were collected along meridian 165°E for the

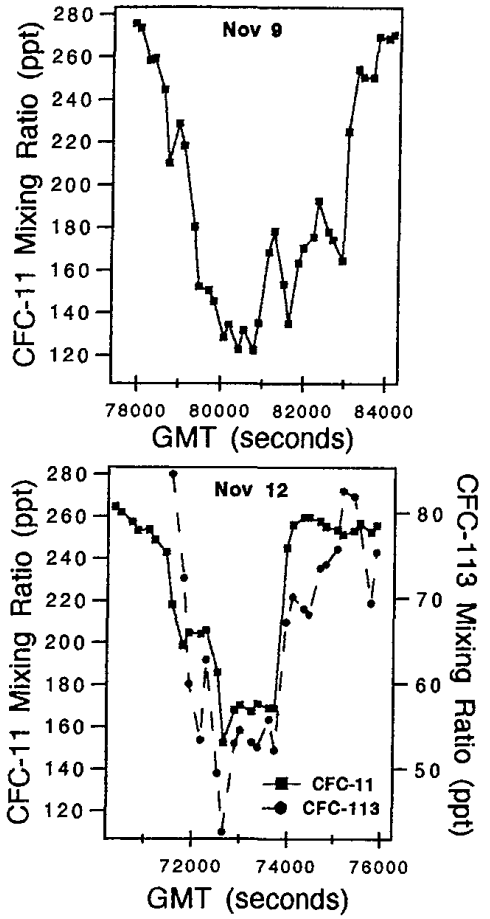

Fig. 5.19. CFC-11 and CFC-113 mixing ratios in ppt by mole fraction for the SPADE test flights on November 9 and November 12, 1992.

determination of gases other than the compounds included in this report and to compare flask data with those from in situ analyses. CFC-12, CFC-11, CH_3CCl_3, and CCl_4 were measured with a custom-designed, three-channel GC. New technology was adapted from our ACATS aircraft projects for the design of this GC to minimize space requirements [*Montzka et al.*, 1992]. In addition to this three-channel GC, we built a fourth gas chromatographic channel for the determination of HCFC-22, using a 35 cm^3 sample loop and a preconcentration step before analysis with an oxygen doped ECD. Most of the data were analyzed with custom

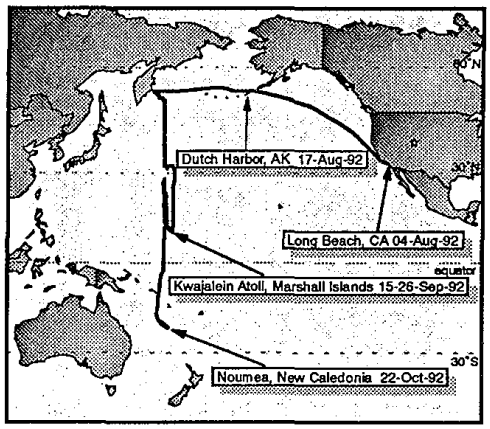

Fig. 5.20. Map with OAXTC cruise track and locations of port stops. A total distance of about 19000 km was covered during this 12-week expedition and about 26000 chromatograms were taken with one datapoint each for air and surface water at 40- to 48-minute intervals.

software *NOAHchrom*, developed in our division, for both integration of chromatograms and advanced database analysis.

CFC-11 and CFC-12

CFC-11 and CFC-12 are anthropogenic halocarbons that have long atmospheric lifetimes and are inert in seawater. Hence, they are very useful as tracers of physical processes. These two halocarbons are also useful in evaluating atmospheric circulation and in determining the effects of physical processes, such as mixing, heating, cooling, and bubble injection, upon air-sea exchange.

CFC-11 behaved predictively in both the atmosphere and the surface water. Apparent large scatter in the latitudinal profile between 55°N and 44°N as well as 28°N and 8°N can be explained in part by air mass movement and temporal variations during the several crossings of these latitudes and must be taken as the expected variability in the mixing ratios of such compounds. CFC-11 mixing ratios did not drop significantly until 30°N and leveled out below 10°S (Figure 5.21). Saturation anomalies were highest in the northern hemisphere where the waters had been subjected to warming throughout the summer. Below 10°S, the saturation anomaly was negative for CFC-11. From cooling alone, one might expect negative anomalies below the equator, but effects of cooling are offset to some degree by air-injection (air bubble dissolution), which tends to supersaturate all gases [*Kester et al.*, 1975].

CFC-12 data show basically the same effects as explained for CFC-11 (Figure 5.22). CFC-12 in seawater is affected only by physical processes, as is CFC-11, so its

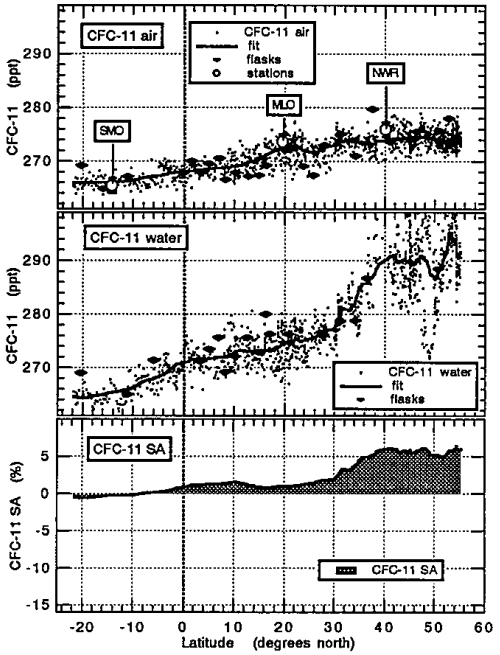

Fig. 5.21. Dry mixing ratios of CFC-11 in the air and the headspace of the sea water equilibrator. The saturation anomaly (SA) is defined as $(MR_{water}-MR_{air})/MR_{air}*100$, with MR=mixing ratio. Solid lines through the data sets (fit) are running means of 51 to 81 data points, as are all saturation anomalies shown here.

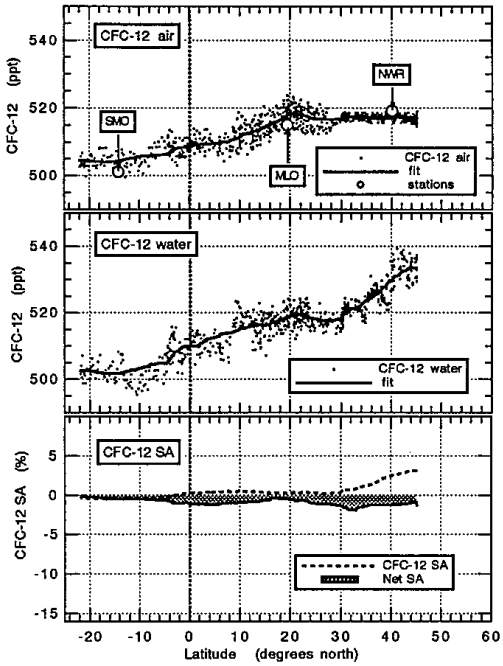

Fig 5.22. Dry mixing ratios of CFC-12 in the air and the headspace of the sea water equilibrator. The *net* saturation anomaly NSA is the saturation anomaly SA according to Figure 5.21, minus the saturation anomaly of CFC-11.

saturation anomaly should not differ substantially from that of CFC-11, and its net saturation anomaly should be near zero. The observed values between 0 and -2% represent the effects of slightly different behaviors of physically controlled gases.

Atmospheric mixing ratios from the in situ measurements of all compounds agreed well with those from flask samples collected on the ship and agreed within one s.d. with data from NWR, MLO, and SMO. Most flask data between 8°N and 30°N were taken on our first of several passes across this region where we observed much lower mixing ratios in both air and surface water because of an influence of southern hemispheric air.

HCFC-22

As with CFC-11 and CFC-12, the mixing ratio of HCFC-22 in the atmosphere decreased with latitude from 30°N (108 ppt) to the equator, where it tended to level off at a value of 98 ppt with latitude (Figure 5.23). This is consistent with recently published results from the CMDL flask sampling network [*Montzka et al.*, 1993*a*]. Data from flasks taken during the cruise extend the dataset of in situ measurements to about 40°N and show an HCFC-22 latitudinal profile that is similar to those of the CFCs. The observed latitudinal gradient for HCFC-22 was on the order of 12 ppt between 40°N and 22°S, and is consistent with a growth rate of about 7% yr^{-1} as reported by *Montzka et al.* [1993*a*].

Although differences in physical properties can explain the observed CFC-11 and CFC-12 anomalies, they cannot explain the differences between HCFC-22 and CFC-11 anomalies. Both the HCFC-22 and CFC-11 anomalies were negative through much of the tropics. Warming and cooling was minimal in these areas at this time and cannot quantitatively explain the observed departures. Dissolution of air bubbles only creates positive saturation anomalies, and the anomaly for HCFC-22 was negative over a wide latitudinal range even before being corrected with CFC-11. Finally, there is some latitudinal dependence of the HCFC-22 net saturation anomaly, which implies a possible temperature-dependent effect. By contrast, the net anomaly for CFC-12 is reasonably constant. Thus, it is also likely

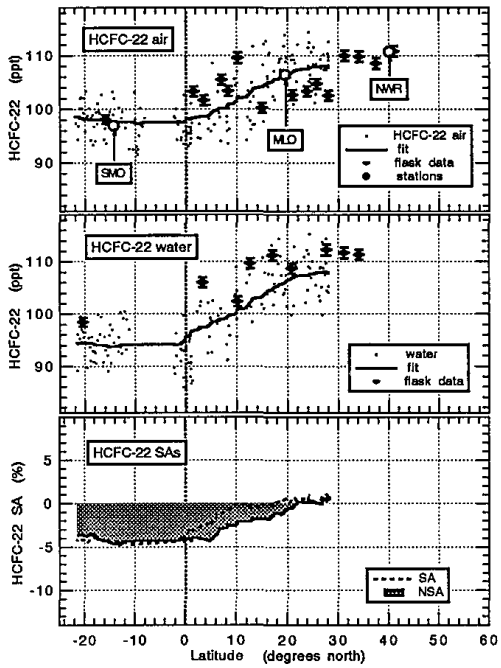

Fig. 5.23. Dry mixing ratios of HCFC-22 in the air and the headspace of the sea water equilibrator, and its saturation anomalies.

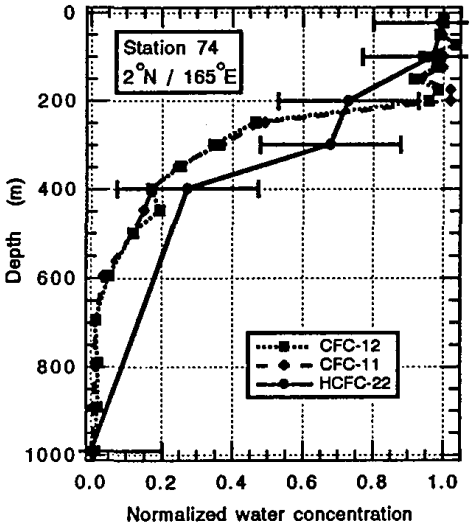

Fig. 5.24. Deep water profiles of HCFC-22, CFC-11, and CFC-12 for a station in the tropics. Water concentrations are normalized to their surface value. Error bars indicate an uncertainty of 15% for the HCFC-22 measurements. Deep water profiles of CFC-11 and CFC-12 were provided by Bullister et al., NOAA/PMEL (private communication, 1993).

hydrolysis, reactions with solvated ions, or even microbial metabolism. The removal rate could be as much as 10 times the published hydrolysis rates, but those rates must be considered only tentative at this time. The removal rate, whatever its cause, corresponds to a partial atmospheric lifetime of 700 years. With an atmospheric lifetime of 13.6 years, this accounts for 2% of all atmospheric losses.

HCFC-22 depth profiles, although somewhat noisy, were similar to those for CFC-11 and CFC-12 (Figure 5.24). At this point, differences in the profiles must be considered insignificant and do not reveal any hard evidence of sub-surface breakdown of HCFC-22. Ratios of surface-water concentrations of the CFCs relative to HCFC-22 were very close to the predicted values, calculated from Henry's solubility law.

Methyl Chloroform

The net saturation anomaly for methyl chloroform is negative almost everywhere except for the region around 30°N where we observed slightly positive values (Figure 5.25). Our data show a significant tropical sink centered that some in situ process is removing HCFC-22 in tropical and subtropical surface waters. This process may involve the equator where upwelling and oceanic breakdown by hydrolysis, and maybe by biological activity, is most intense [*Butler et al.*, 1991].

Our results show a latitudinal dependence of the saturation anomaly for CH_3CCl_3, but no obvious temperature dependence of the calculated flux. The temperature/flux-relationship was confounded by a positive net saturation anomaly between 30°N and 40°N and a negative net anomaly in the higher latitudes. Although these variations are not outside the realm of physical effects, they represent fairly strong fluxes, especially in the higher latitudes, because of the higher wind speeds and higher gas solubilities in those regions. The possible existence of a biological sink might explain negative fluxes at the higher latitudes, but despite their large magnitude, they would not be as great a global contribution as the sink in the tropics, because the coverage of the ocean at higher latitudes is less compared to the ocean in tropical regions.

Carbon Tetrachloride

Although CCl_4 appears slightly supersaturated at the higher north latitudes, its net saturation anomaly is strongly negative at all latitudes (Figure 5.26), which is also consistent with earlier findings by CMDL [*Butler et al.*, 1993]. Laboratory hydrolysis data do not support the loss rate required to sustain the observed saturation anomaly for

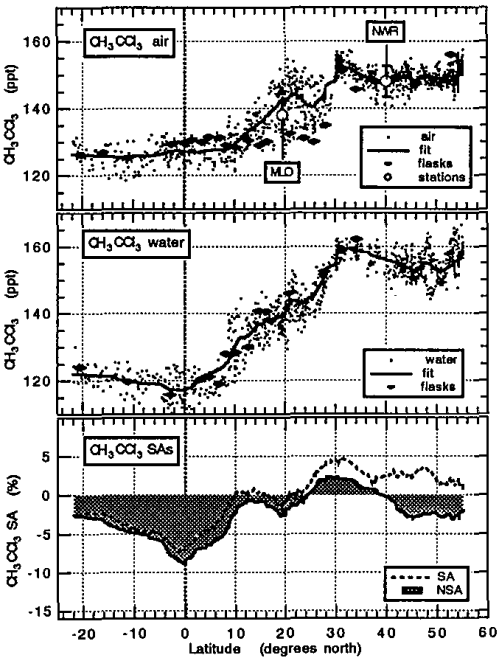

Fig. 5.25. Dry mixing ratios of CH_3CCl_3 in the air and the headspace of the sea water equilibrator, and its saturation anomalies.

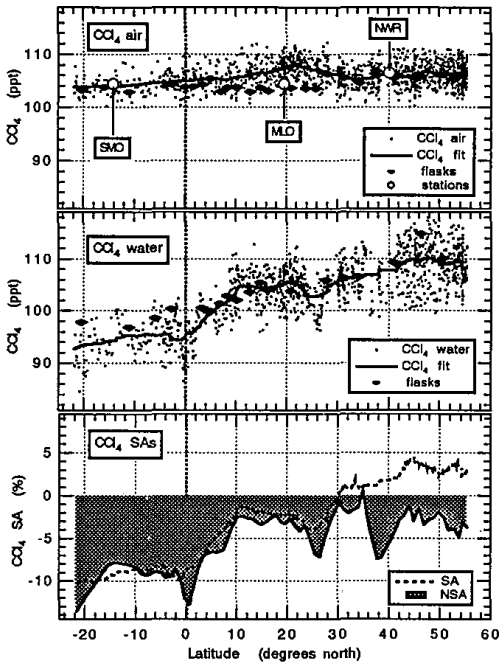

Fig. 5.26. Dry mixing ratios of CCl_4 in the air and the headspace of the sea water equilibrator, and its saturation anomalies.

CCl_4. The highest expected rate of hydrolysis could only give rise to a net saturation anomaly of -0.1%. However, some deep water profiles obtained by investigators on this and other expeditions indicate that CCl_4 is consumed at a depth below the thermocline but near the oxygen minimum.

The flux of CCl_4 from the atmosphere required to sustain the observed saturation anomalies under steady-state conditions represents a partial atmospheric lifetime of around 250 years for loss to the ocean. The best estimate of the global CCl_4 atmospheric lifetime is 40 years, meaning that 16% of the atmospheric CCl_4 is lost to the ocean. This number is a little smaller than the range of values calculated from our other cruises (15-35%), but not outside an expected range of variability. The loss of CCl_4 to the ocean is a significant sink, as it means substantially less chlorine will be delivered to the stratosphere.

5.2.3. Software Development

The NOAH Division has developed a chromatographic interpretation and management system, NOAHchrom, and proved it in 1992 on three separate field missions (AASE II, OAXTC, and SPADE). NOAHchrom runs on Apple Macintosh computers within a commercially available data analysis and presentation application, Igor, by Wavemetrics Corporation. Igor is highly extensible (by virtue of "external operations and functions" written in the "C" programming language, and its own internal programming language), and thus proved to be an excellent platform for the development of a unique system for the interpretation of chromatographic data.

The NOAHchrom package provides a variety of tools for accurate peak integration and subsequent analysis of large data sets. NOAHchrom is essentially a simple database management system designed specifically for chromatographic data: all peak locations, integration results, concentrations, and standard sampling attributes (e.g., chromatogram name and injection time), as well as user-defined (binary) flags and user-defined, quantifiable, sampling attributes (e.g., wind direction, equilibrator temperature) are accessible through the manager. Database searches based on multiple criteria allow the user to define an interesting subset of the entire data set for scrutiny or reprocessing (e.g., find all chromatograms with CFC-11

concentrations greater than 320 ppt and with wind direction between 170-190 degrees, and then reintegrate those peaks using an exponential fit to the baseline). NOAHchrom supports both automatic and manual peak identification and detection. After peaks are located, the user has a variety of integration options: linear or non-linear curve fit to the baseline and an optional curve fit (e.g., Gaussian) to the peak itself. Quality data presentation is accomplished within the Igor application, and thus within NOAHchrom itself, at any stage of data processing.

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