

7. Nitrous Oxide and Halocarbons Group

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7.1. CONTINUING PROGRAMS

7.1.1. FLASK SAMPLES

Air samples continued to be collected in pairs during 1990 and analyzed for CFC-12, CFC-11, and N_2O concentrations. Samples were collected from the CMDL baseline stations BRW, MLO, SMO, and SPO with the addition of Niwot Ridge (NWR), Colorado (see Section 7.1.2) and Alert, North West Territories (ALT). Higher pressure pumps (3 atm) were deployed at BRW, MLO, and SMO in late February to early March so that sufficient sample volume would be available for both the LEAPS and flask projects. NWR received the pump in July. SPO personnel used the new pump in 1989 and continued its use during 1990. ALT will be upgraded in 1991.

The new automated flask-analysis system was tested extensively throughout the year. Intercomparisons of flask and calibration tank results were made between the new and old GC systems. The two systems gave consistent results with no systematic differences. Routine flask analyses with the new system should begin in 1991.

The time series of monthly mean N_2O concentrations has been extended another year in Figure 7.1. Likewise, updated CFC-12 and CFC-11 data are shown in Figures 7.2 and 7.3.

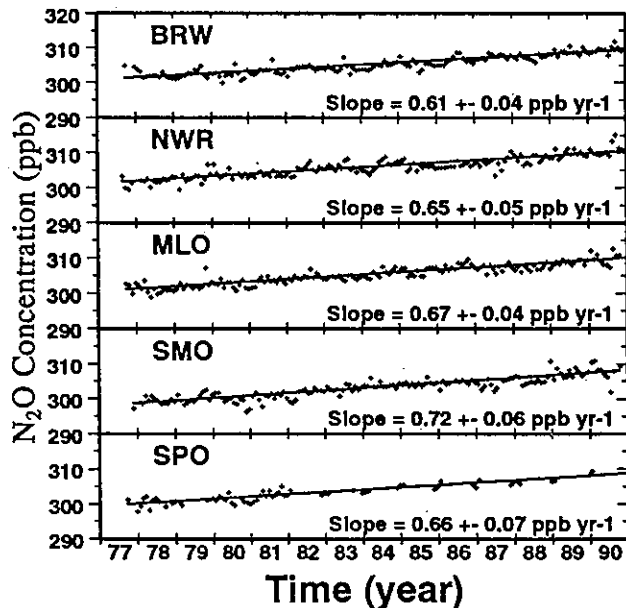


Fig. 7.1. Monthly mean concentrations of N_2O (CO_2 and H_2O corrected) from the CMDL flask sample network. The trends and 95% confidence intervals are also shown.

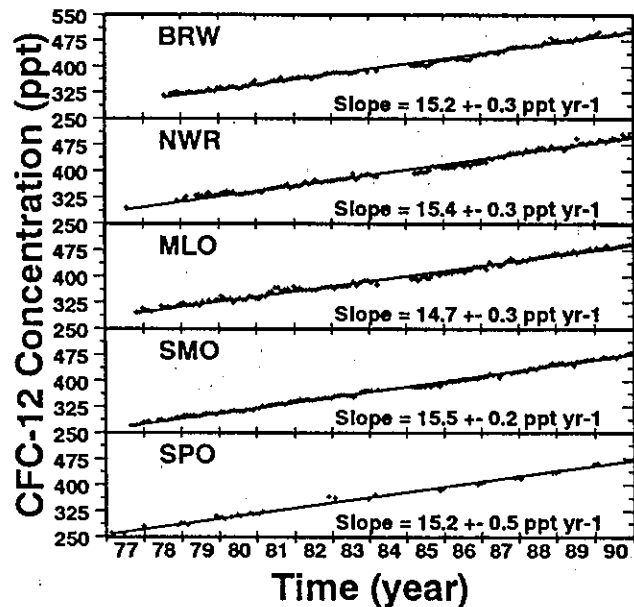


Fig. 7.2. Monthly mean dry concentrations of CFC-12 from the CMDL flask sample network. The trends and 95% confidence intervals are also shown.

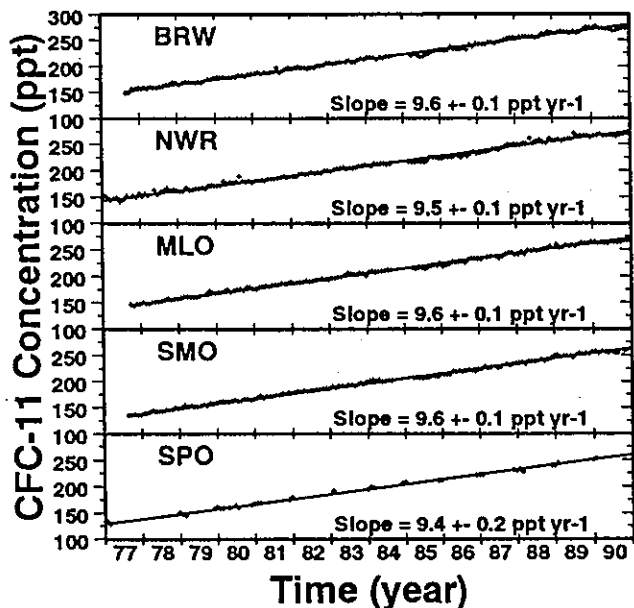


Fig. 7.3. Monthly mean dry concentrations of CFC-11 from the CMDL flask sample network. The trends and 95% confidence intervals are also shown.

ALT flask sample concentrations, which have now been measured for 3 years, are plotted in Figure 7.4. The incidence of inconsistencies between flask pairs decreased considerably at ALT in 1990.

The long record of BRW data has been analyzed for seasonality by removing the trend and fitting a locally weighted spline to the residuals. CFC-12, CFC-11, and N_2O all exhibit the same seasonal cycle (Figure 7.5) with higher concentrations in the November-February period and lowest values during May through August. This is typical of many pollutants measured in the Arctic Basin. A cold stable air mass develops in winter, bounded by the arctic front, with limited loss mechanisms from advection, mixing, deposition and photochemistry. Concentrations grow from periodic injection of polluted air masses originating at midlatitudes.

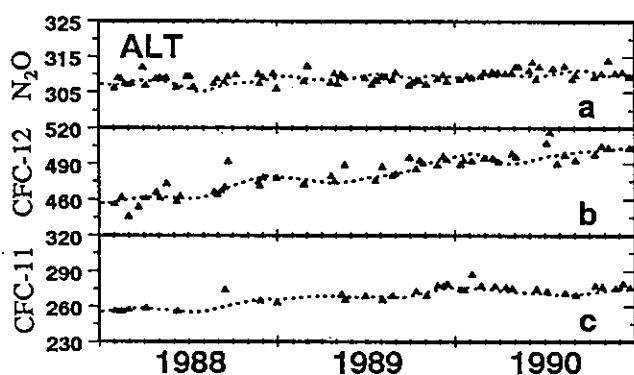


Fig. 7.4. Flask sample concentrations for (a) N_2O , (b) CFC-12, and (c) CFC-11 at Alert, North West Territories. The dashed lines are spline fits to corresponding BRW flask sample data, for comparison.

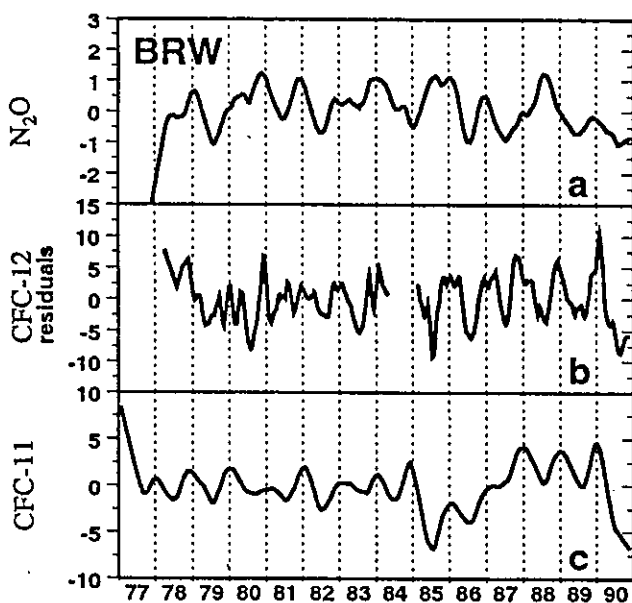


Fig. 7.5. Spline fit showing seasonal variability in the residuals of (a) N_2O , (b) CFC-12, and (c) CFC-11 flask concentrations at BRW.

7.1.2. RITS CONTINUOUS GAS CHROMATOGRAPH SYSTEMS AT CMDL BASELINE STATIONS

In situ sampling of air continued at BRW, MLO, SMO, and SPO. Twenty-four analyses of N_2O , CFC-12, CFC-11, CFC-113, methyl chloroform and carbon tetrachloride were made every day at each station.

In February a new continuous gas sampling system was brought on line at NWR. The system is a duplicate of the GC systems at BRW, MLO, and SMO. The NWR site provides the group with continuous monitoring of nitrous oxide and halocarbons at the same site used to fill working calibration cylinders. The GC system is located in an air-conditioned unit at site C-1 of the Mountain Research Station, Institute for Arctic and Alpine Research (INSTAAR), University of Colorado. C-1 is located at $40^{\circ}2'N$, $105^{\circ}32'W$ and is at an altitude of 2027 meters (9900 feet). NWR is the group's only interior continental site and provides a unique platform to analyze continental air composition. In addition, it provides a field site for testing hardware and software before installation at other, more remote, sites.

In 1990 significant improvements were made to the GC network. During the first quarter the sampling and analysis frequency was increased to once every half hour. This resulted in a significant improvement in precision, due to the decrease in lag time between sample and calibration runs. The increased frequency was achieved by the addition of an eight-port stream selection valve, which permits two air samples to be analyzed per rotation.

An upgrade of the hard drives at the stations from 15 megabytes to 20 megabytes allowed the addition of new software at each station. This included RITS PLOT, a program developed by the group, and installed at the stations in November. RITS PLOT is a complete package of plotting and database management routines written in HP-BASIC. It calculates preliminary concentrations after every air-sample run and updates a database containing 1 month of concentration values. A key feature of RITS PLOT is that it is accessible by station personnel. With a single keystroke they are able to view the previous month's data and assess the system performance. This should prove invaluable in troubleshooting.

Access to RITS PLOT was made via a new version (v. 5.1) of the NOAA data acquisition software installed in 1990. This allows RITS PLOT to be run without affecting the data collection functions of the system computer. It also has improved error handling capabilities and a routine to store preliminary concentration data in IBM-compatible ASCII format on a 720-kilobyte, 3.5-in. floppy disk for easy transfer to the station PCs. Two 1.44-megabyte data diskettes now provide room for 1216 files. Each diskette is filled with raw chromatographic data approximately every 4 days for return to the Boulder office.

To accommodate the increase in raw data received from the stations, consolidation of the processing programs at the Boulder office was implemented. Ten programs were

consolidated into four: (1) catalog and back-up incoming data diskettes; (2) reprocess raw chromatograms for area and height data; (3) calculate concentration values; and (4) plot data for visual quality control applications. The reduced data is stored on the group's UNIX network hard drive where it is available to all the group for statistical analysis.

The 3.5-year record of daily average N_2O concentrations from the in situ GCs at BRW, MLO, and SMO is shown in Figure 7.6. The annual cycle at BRW can be best seen in the 1990 data set, with a maximum in February and a minimum in August. This also illustrates the improvements brought about by the increased precision due to the higher sampling frequency. During 1989-1990 the annual growth rate was approximately 0.6 ppb yr^{-1} at all stations.

Daily average CFC-12 concentrations are shown in Figure 7.7. The annual increase remained at 19 ppt yr^{-1} for all three stations. CFC-11 daily average concentrations for BRW, MLO, and SMO are shown in Figure 7.8. The CFC-11 data confirm the cyclic nature of CFCs at BRW. Again, the improvements in precision in 1990 are evident, particularly at BRW. CFC-11 measurements from SMO before March 1989 were extremely noisy and have not been plotted. Annual growth rates at BRW, MLO, and SMO were about 7.5 ppt yr^{-1} , which is low compared to the flask data. The study period, however, is short, and experimental and calibration errors are still relatively large. A proper intercomparison of the flask and continuous data is, therefore, not possible at this stage.

Daily average carbon tetrachloride (CCl_4) concentrations are shown in Figure 7.9. The concentrations were nearly constant in 1990.

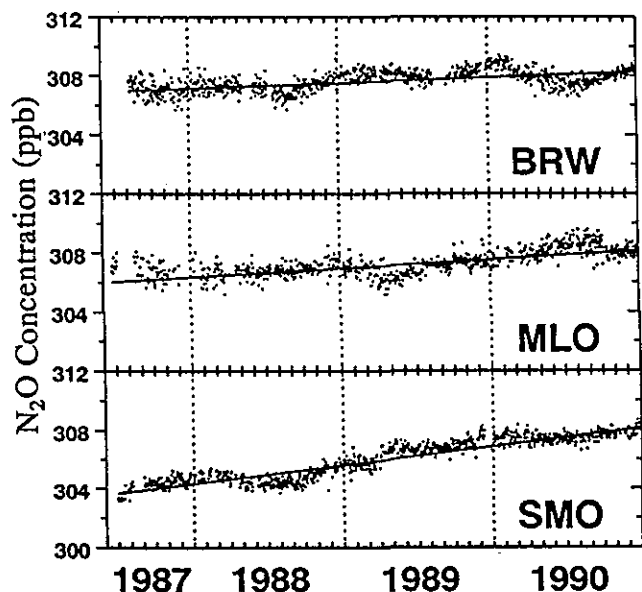


Fig. 7.6. Daily average N_2O concentrations at BRW, MLO and SMO obtained from the in situ GCs. The trends were generated using least squares regression analysis.

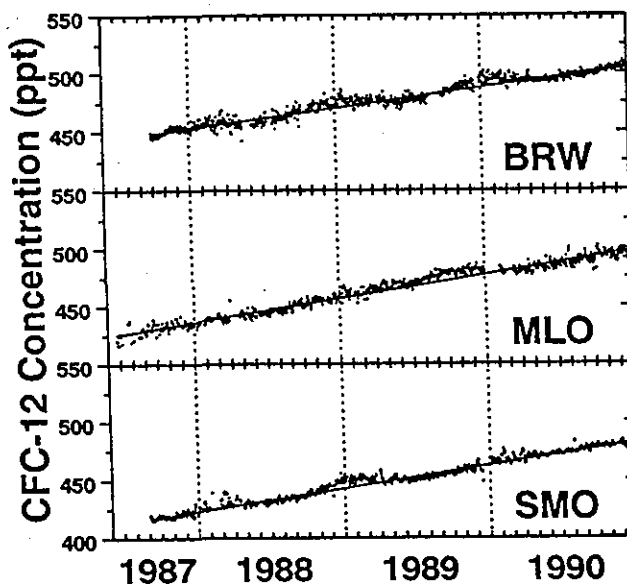


Fig. 7.7. Daily average CFC-12 concentrations at BRW, MLO and SMO obtained from the in situ GCs. The trends were generated using least squares regression analysis.

During 1990 SMO station had a large number of power outages and brownout conditions. The computer equipment that controls the sampling sequence and stores the data was protected by an uninterruptible power supply (UPS). The GCs, because of their high power load, were not protected.

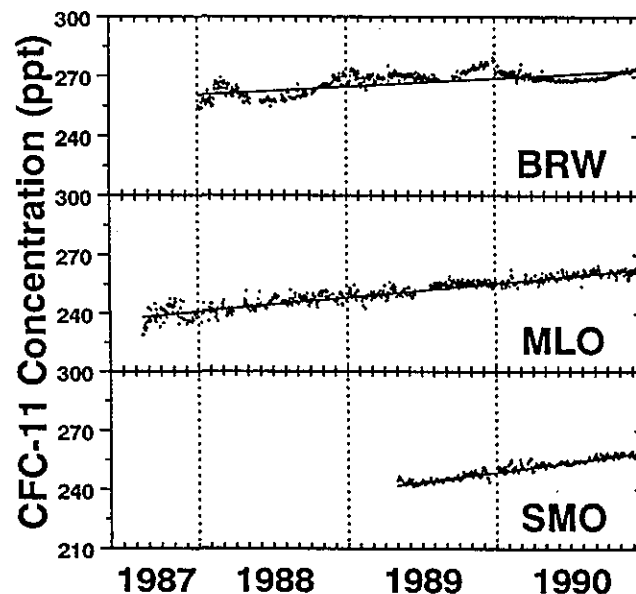


Fig. 7.8. Daily average CFC-11 concentrations at BRW, MLO and SMO obtained from the in situ GCs. The trends were generated using least squares regression analysis.

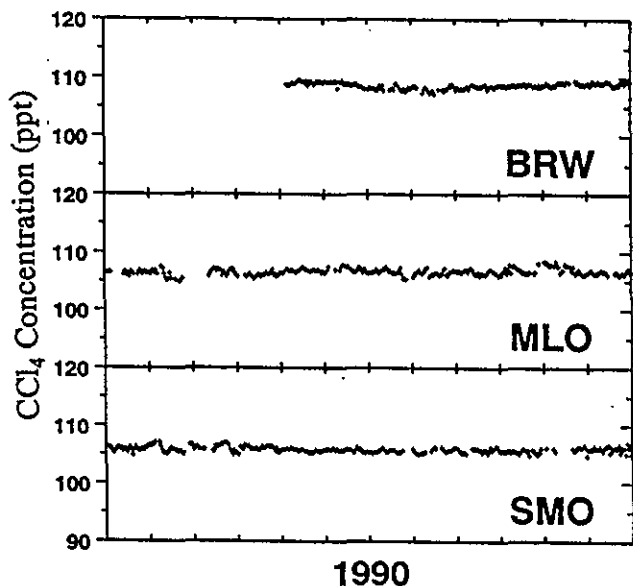


Fig. 7.9. The 1990 daily average carbon tetrachloride (CCl_4) concentrations at BRW, MLO, and SMO obtained from the in situ GCs.

An analysis of the N_2O data shows a diurnal variation (Figure 7.10) that could be due to these variations in line voltage to the GCs. Nine months of data were fitted with a spline to remove trends and seasonality. The residuals were then grouped by hour of the day and the mean and 95% confidence interval calculated. At 0400 GMT (1700 LST), N_2O concentration dropped for a few hours, rose dramatically, then dropped back to normal over the following few hours. This period corresponds to the daily increase in domestic power supply at the end of the working day, resulting in voltage fluctuations observed at the station. In 1991 a large UPS will be installed to condition the GC equipment power and a similar analysis will be done to see if

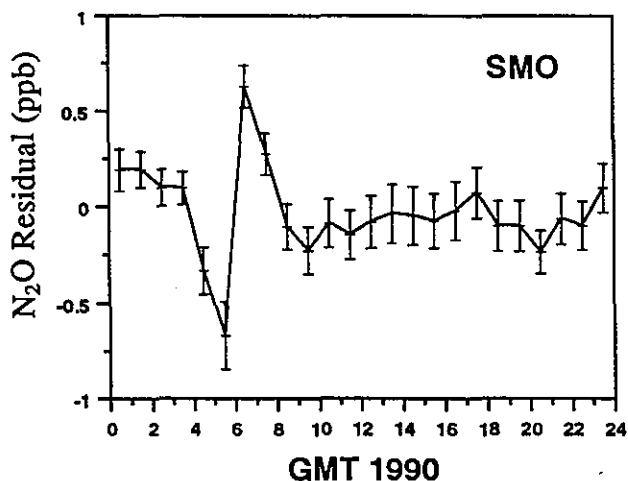


Fig. 7.10. Residual N_2O concentrations at SMO during 1990 averaged for each hour of the day. The bars show the 95% confidence intervals.

the N_2O variation diminishes. Similar variations were not observed in the CFC measurements.

7.1.3. LOW ELECTRON ATTACHMENT POTENTIAL SPECIES

Routine flask sampling and analysis of LEAPS gases began in mid-1989. Despite some instrumental down-time, we now have a relatively continuous record spanning 1.5 years. HCFC-22 measurements began in mid-1990. Procedures have been developed to measure HCFC-22 and the other LEAPS and CFC gases in the same sample by connecting two electron-capture detectors in series and doping the carrier stream with O_2 to 0.2% before the second detector. This enhances the HCFC-22 peak measured by the second detector while the adjacent, and potentially interfering, CFC-12 peak is reduced during passage through the first detector (Figure 7.11). Halon (brominated CFC) measurements have been made without serious problems. Although the data set spans only 1.5 years, some trends are already apparent. Data from the four CMDL observatories show a significant rate of growth for H-1301 (Figure 7.12a). The rate of increase varied among stations from 0.26 to 0.47 ppt yr^{-1} , with a mean of 0.36 ppt yr^{-1} , but the differences between these slopes are only marginally significant, owing to the short amount of time and relatively small number of samples. Mean concentrations at the observatories increased with increasing latitude, indicating the importance of northern hemispheric sources.

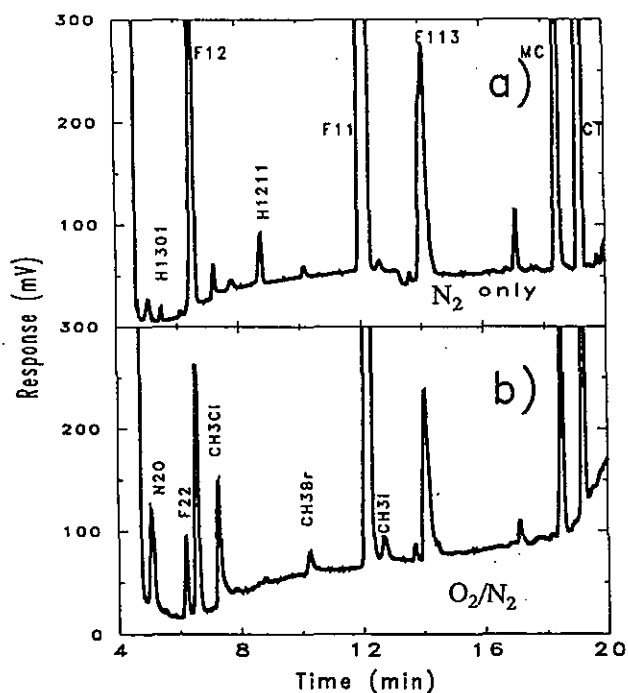


Fig. 7.11. LEAPS chromatograms of air from BRW; (a) N_2 carrier gas (ECD #1), (b) N_2 carrier gas doped with O_2 to 0.2% (ECD #2). The ECDs were connected in series.

H-1211, unlike H-1301, showed little or no growth at the four observatories during this period, and the latitudinal gradient was not significantly different from zero (Figure 7.12b). Production rates for H-1211 did not decline during this time, although release rates may have slowed in response to international control agreements and environmental considerations [Halon Research Institute, 1989]. A longer sampling record is required to determine accurately whether or not there are indeed temporal and latitudinal variations in both H-1301 and H-1211.

7.1.4. GRAVIMETRIC STANDARDS

A total of 36 primary calibration standards were prepared during 1990 for use in the RITS, LEAPS, and special projects. A summary is given in Table 7.1. The total number of primary standards on the NOAA inventory was 223 at the end of 1990. Of these, 122 were prepared in our own standards laboratory. Twenty-five cylinders were filled

with air at Niwot Ridge during the year and analyzed for use as secondary standards at the field sites and in the laboratory.

7.2. SPECIAL PROJECTS

7.2.1. ALTERNATIVE HALOCARBON MEASUREMENTS

It is anticipated that by the year 2000 most CFCs will have been phased out, partly by substitution with two alternative families of compounds: HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons). Both break down more rapidly in the atmosphere, and therefore have lower ozone depletion and global warming potentials. Apart from HCFC-22, which is already in production, the "alternative halocarbons" are not currently present in the atmosphere. They present a three-fold challenge to their analysis: very low atmospheric concentrations for at least the next two decades, poor sensitivity with the electron capture detectors (ECDs) that NOAA presently uses to routinely measure CFCs, and similar physical properties to the CFCs that they replace, making their chromatographic separation difficult in some cases.

Beginning in October 1990, we began work to develop techniques for alternative halocarbon measurements and concentration of air samples using adsorbent traps. Initially we are focussing on HCFC-22, HCFC-123, and HFC-134a. We have been unable, as yet, to obtain standards for HCFC-141b, another important alternative halocarbon candidate.

GC/Mass Spectrometer Analysis

An HP 5971A GC interfaced to a mass spectrometer detector (GC/MS) was purchased by the NOAA group to address some of the difficulties involved in measuring alternative halocarbons in the atmosphere. This instrument can sensitively detect a much wider variety of compounds than the ECD. For example, HFC-134a contains no chlorine atoms and, therefore, has almost no ECD response. HCFC-22 does contain chlorine atoms, but is weakly electrophilic and is two to three orders of magnitude less sensitive by ECD than CFC-12. Sensitivity of the GC/MS, however, is nearly equivalent for HFC-134a, CFC-12 and HCFC-22 (Figure 7.13a). HCFC-123, a proposed replacement for CFC-11, is also sensitively detected by GC/MS and can be easily separated from CFC-11 (Figure 7.13b). By collecting 1-10 dm³ of air for a single analysis we expect to be able to detect <1 pptv of alternative halocarbons such as HFC-134a in air. This will be accomplished by either cryogenically concentrating air contained in cylinders or by using adsorbent tube pre-concentration techniques.

The GC/MS can be operated in either a full scan mode, with a wide range of compound sensitivity, or in a highly selective "single ion mode" (SIM). SIM enables quantification of coeluting compounds and also provides greater sensitivity for the selected species. Although the

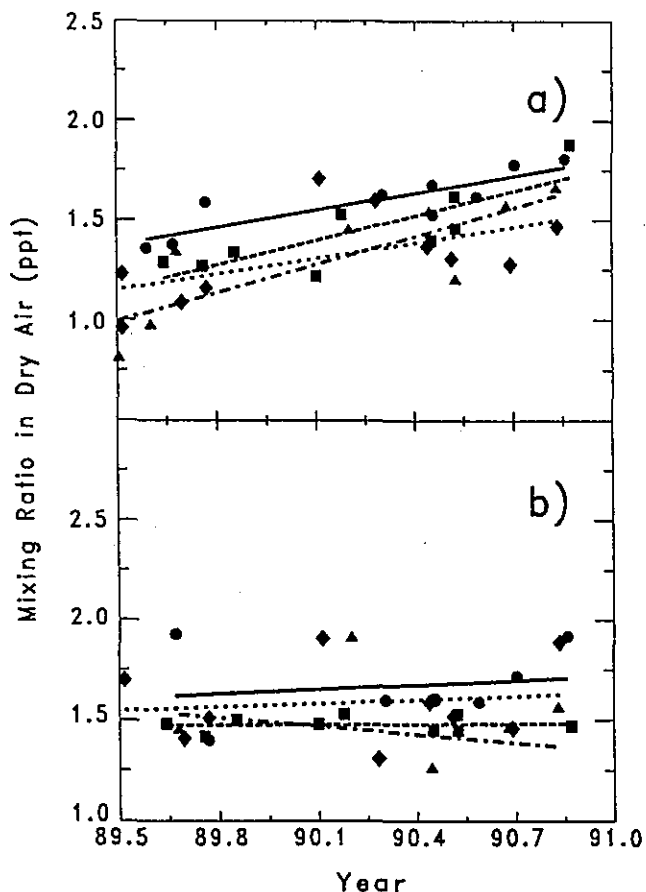


Fig. 7.12. Concentration trends in (a) H-1301 and (b) H-1211 at CMDL observatories from mid-1989 through 1990. The mean slope for all H-1301 measurements is 0.36 ppt y⁻¹. The mean slope of the H-1211 measurements does not differ significantly from zero. Stations are identified as follows: BRW, circles and solid line; NWR, squares and dashed line; MLO, triangles and broken dashed line; SMO, diamonds and dotted line.

Table 7.1. Summary of Gravimetric Standards Prepared in 1990

Compounds	Quantity	Concentration Range	Prepared for
N ₂ O	6	ppm, ppb	NOAA/RITS
CFC-12	2	ppt	NOAA/RITS
CFC-11	2	ppt	NOAA/RITS
CFC-11, CH ₃ CCl ₃ , CCl ₄	7	ppm, ppb, ppt	NOAA/RITS
C ₆ F ₁₂ , C ₇ F ₁₄ , C ₈ F ₁₆ , C ₉ F ₁₈	4	ppm, ppb, ppt	NOAA/ARL
CFC-11, CFC-113, CH ₃ CCl ₃ , CCl ₄	5	ppt	NOAA/RITS
CFC-11, CFC-12, CFC-113, CH ₃ Cl, CH ₃ CCl ₃ , CCl ₄	3	ppt	NOAA/RITS
CFC-11, CFC-113, CH ₃ CCl ₃ , CCl ₄	6	ppb, ppt	NOAA/RITS
Halon-1301	1	ppt	NOAA/LEAPS

compounds presently under study have been successfully separated chromatographically, SIM may prove invaluable for other alternative halocarbons.

Because of its wide-range sensitivity and ability to identify unknowns from their ion spectra, the GC/MS will also prove useful in checking our gravimetric standards for purity. It will also be used to investigate contamination problems with sample and standard tanks; for example, acetaldehyde has been identified as a contaminant in one of our gravimetric standards, possibly originating from a sealing compound in the pressure fittings.

Adsorbent Tube Pre-Concentration

A large number of materials, including chromatography packing materials, carbon molecular sieves, and activated carbons, have been screened for their potential use as adsorbents to concentrate CFCs and alternative halocarbons

from large volumes of air. This presents a significant challenge since the compounds we wish to collect are considerably more volatile, and therefore less easy to trap, than compounds normally collected with adsorbent tubes. We now have several alternative designs for multi-stage traps (see example in Figure 7.14). After sampling, trapped compounds are desorbed by heating the tube while backflushing with nitrogen. The compounds are then cryogenically reconcentrated at the head of a GC capillary column for analysis.

Adsorbent tubes offer a number of advantages over flask sampling. Due to their small size we will be able to produce a hand-portable microcomputer-controlled 32 tube sampler and desorber. Designs have also been made for an automatic aircraft sampler-desorber-GC analyzer. Tubes can be used to concentrate greater volumes: as much as tens of dm³ compared with approximately 2.5 dm³ for the largest flasks used in our sampling network. This is valuable where detection of ultra-low concentrations is required, or where less sensitive techniques such as GC/MS are employed.

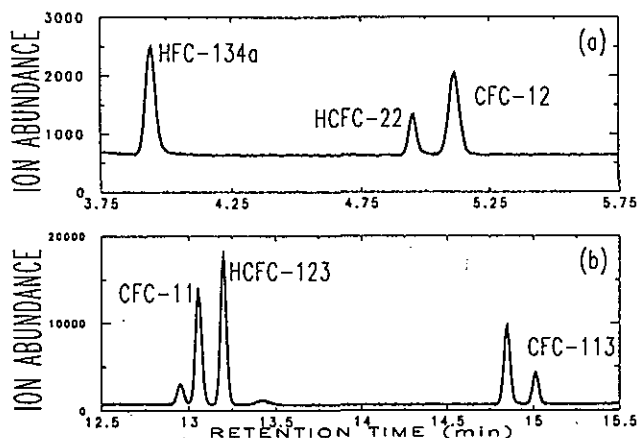


Fig. 7.13. Reconstructed selected ion chromatograms of (a) HFC-134a (1.3×10^{10} dm³), HCFC-22 (1.1×10^{11} dm³), and CFC-12 (2.4×10^{11} dm³), and (b) HCFC-123 (1.0×10^{10} dm³) and CFC-11 (1.0×10^{10} dm³). Sample volumes are vapor phase volumes at STP.

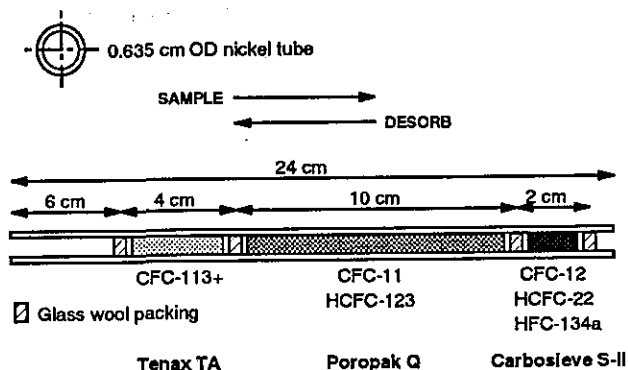


Fig. 7.14. Example of three-stage adsorbent trap designed to collect key CFCs, HCFCs and HFCs with high efficiency from 15 dm³ of air at a flow rate of 50 cm³ min⁻¹, and desorb all trapped compounds within 5 minutes at 220°C.

Most compounds are very stable on the adsorbents and, since the entire tube is desorbed, wall losses should not be a problem; thus some of the artifacts that plague flask samples may be overcome. The adsorbents selected are hydrophobic and other gases such as CO₂, which may cause cryo-trapping and analytical problems, are not collected. Tubes also extend the practical limits to in situ GC cryo-trapping; to directly cryo-trap the same amounts of air could take more than an hour of instrument time and undoubtedly lead to peak broadening, sample loss, and column plugging.

It is planned to send the portable tube sampler to the baseline observatories and on aircraft and ocean-cruise missions. On return it will be interfaced to the GC/MS and/or GC/ECD. Specialized ECD techniques will need to be developed, including oxygen doping, halogenation reactions, and multiple columns, to improve HCFC sensitivity and separation. In the long term, we look to placing real-time GC systems in the field to measure alternative CFCs.

7.2.2. SOVIET-AMERICAN GAS AND AEROSOL EXPERIMENT (SAGA III)

The SAGA III cruise, from February to April 1990, began in Hilo, Hawaii, and crossed the equator seven times between 20°N and 15°S before ending in Singapore. Automated in situ measurements of N₂O, CFC-11, CFC-113, CH₃CCl₃, and CCl₄ in the atmosphere and surface water were made at 40-minute intervals. The main objectives were to evaluate the spatial and temporal variability of trace gases across the inter-tropical convergence zone (ITCZ), trace the zonal movement of the ITCZ, determine halocarbon saturation anomalies and assess their use in calculating air-sea transfer coefficients, measure the flux of N₂O from equatorial waters, and compare the results at stations sampled in 1987, an El Niño year.

The most significant findings were that CH₃CCl₃ and CCl₄ were undersaturated in surface seawater for almost the entire cruise. Until now the ocean has not generally been considered to be a sink for these gases. The air-sea fluxes we calculated (Figure 7.15) are supported by recently published rates of hydrolysis for the two compounds [Gerken and Franklin, 1989; Jeffers et al., 1989]. Our results indicate that 5-11% of atmospheric CH₃CCl₃ and 16-35% of CCl₄ are lost to hydrolysis and mixing in the world oceans [Butler et al., 1991]. This finding is particularly significant to model calculations of tropospheric OH concentration based on the lifetime of CH₃CCl₃, since it is presently assumed that CH₃CCl₃ is lost solely by reactions in the atmosphere. This suggests that current estimates of mean global OH concentration are about 5-11% too high. This in turn implies that estimates of the atmospheric lifetimes of some important atmospheric compounds that are removed by tropospheric OH, such as CH₄, CO, non-methane hydrocarbons (NMHCs), HCFCs, and HFCs, are longer than previous estimates by about 5-11%, increasing their global warming or ozone destruction potentials by the same amount.

The utility of CH₃CCl₃ and CFC-11 as tracers of atmospheric circulation was demonstrated on this cruise.

Both compounds indicated that the width of the ITCZ varied from 2° to 20° of latitude, depending upon major atmospheric circulation patterns (Figure 7.16). The concentrations were also used to identify an intrusion of northern hemispheric air as far south as 14°S. This was later identified from satellite photographs as having been associated with a large storm system moving southward.

As expected, N₂O was supersaturated in equatorial surface waters, with highest saturation anomalies in the east Pacific (Figure 7.17). N₂O was found to be the most sensitive chemical tracer of upwelling, in agreement with the findings of SAGA II [Butler et al., 1988, 1989]. It was also noted that atmospheric N₂O increased in response to higher saturation anomalies in the underlying water, implying either stratification within the marine boundary layer or the presence of a shallow, stable surface layer retarding vertical mixing. This is consistent with observations of CO₂ during SAGA II where atmospheric CO₂ was found to be lower over highly undersaturated waters during surface inversion conditions. One notable exception to this occurred around day 58, when atmospheric N₂O increased with the intrusion of northern hemispheric air mentioned earlier.

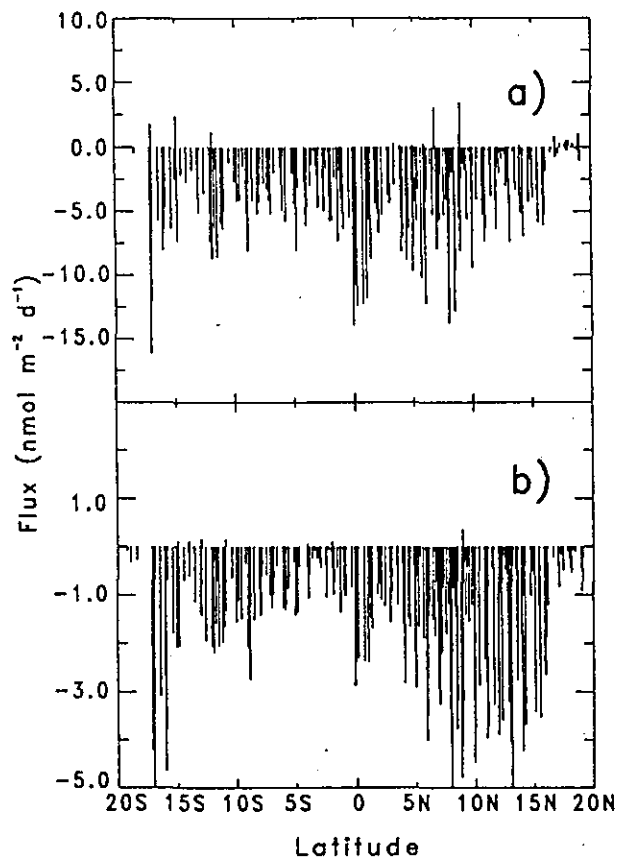


Fig. 7.15. Fluxes of (a) CH₃CCl₃ and (b) CCl₄, calculated from saturation anomalies and instantaneous air-sea transfer velocities from SAGA III, and plotted as a function of latitude. The mean flux of CH₃CCl₃ was 3.2 nmol m⁻² d⁻¹ and for CCl₄ was 0.95 nmol m⁻² d⁻¹.

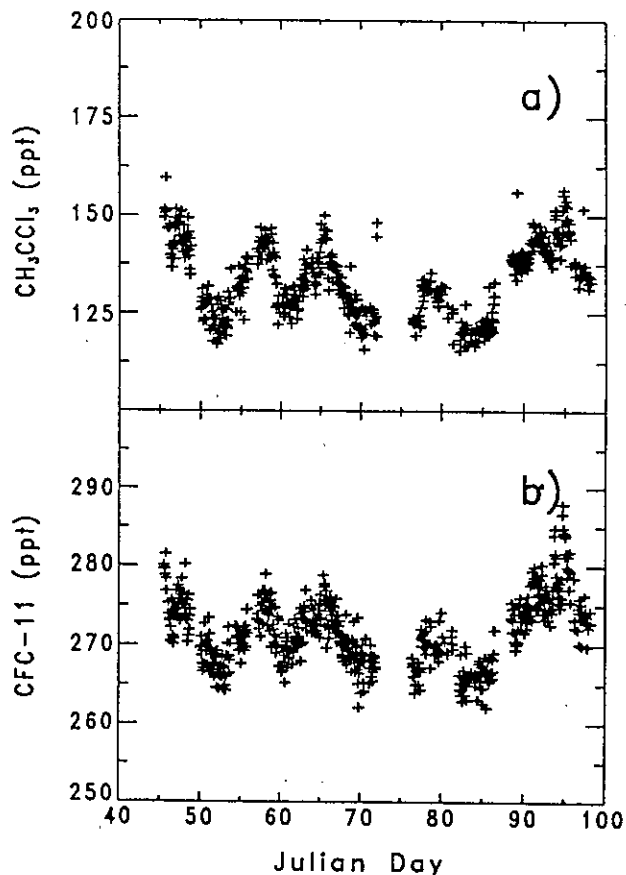


Fig. 7.16. Atmospheric dry mixing ratios of (a) CH_3CCl_3 and (b) CFC-11 during SAGA III, showing the transition between northern and southern hemispheric air masses.

7.2.3. AIRBORNE CHROMATOGRAPH FOR ATMOSPHERIC TRACE SPECIES (ACATS)

One of the recommendations of the National Global Climate Change Program [GCRP, 1989] is that more measurements be made of vertical profiles of atmospherically significant trace gases. Such measurements are required as input to increasingly sophisticated and detailed atmospheric models used to predict potential global climate change. Expanding our measurements of trace gases to vertical profiles has therefore become one of the major goals of the RITS program at NOAA. In the NOAA group this is being implemented for N_2O and halocarbons by collecting flask samples for later analysis and by installing real-time GC analysis systems in aircraft. For aircraft such as the NASA ER-2 and for future pilotless drones (e.g. the Condor) with flight times of 8 hours or more, an airborne GC has the advantages of higher time resolution (up to 2 minutes per sample), smaller bulk and weight on a per-sample basis, no flask artifacts from wall losses and contamination, and immediate availability of analytical results. The greater spatial and temporal resolution achieved by the high sampling frequency may help resolve such issues

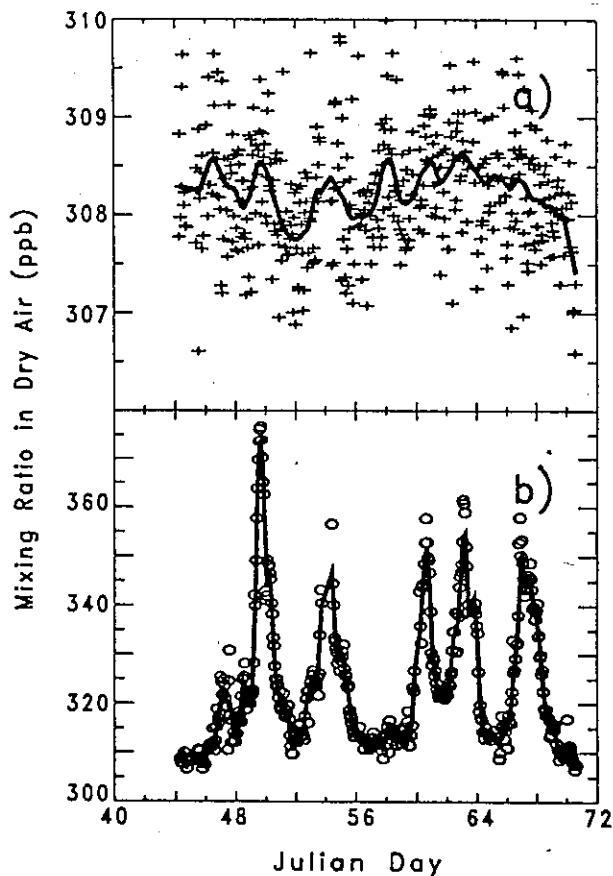


Fig. 7.17. N_2O gaseous mixing ratios in the (a) atmosphere and (b) surface water for the entire cruise. Data are fitted with a locally weighted statistical smoothing (LOWESS) function [Cleveland, 1988].

as whether the polar vortex is a static or dynamic processor for ozone depletion [Albritton *et al.*, 1991].

Some of the capabilities of an airborne GC were demonstrated during flights sponsored by the California State Board of Air Quality over the San Joaquin Valley and San Jose-San Francisco metropolitan area during August 1990. The aim of the study was to examine the influence of human activities and the role of the ocean in transport of pollution into and out of the San Joaquin Valley. Northern California is one of the top ten areas of the world for the release of CFC-113, a solvent used in the production of semiconductor circuits and metal degreasing.

A commercial GC was modified for aircraft operation (Figure 7.18) to measure CFC-11 and CFC-113 once every 3 minutes. The system pressure was regulated to be unaffected by changes in cabin and ambient pressure. The most prominent feature on all flights was the high concentration of CFC-113 over San Jose ("Silicon Valley"), a major producer of semiconductor circuit boards and chips (Figure 7.19). There was also a distinct change in CFC-113 concentrations on crossing the coastline, with values over the ocean lower by about 5-10%.

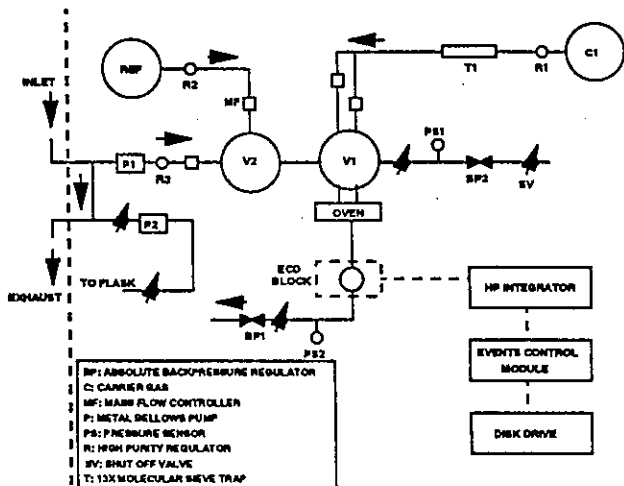


Figure 7.18. Schematic diagram of airborne gas chromatograph.

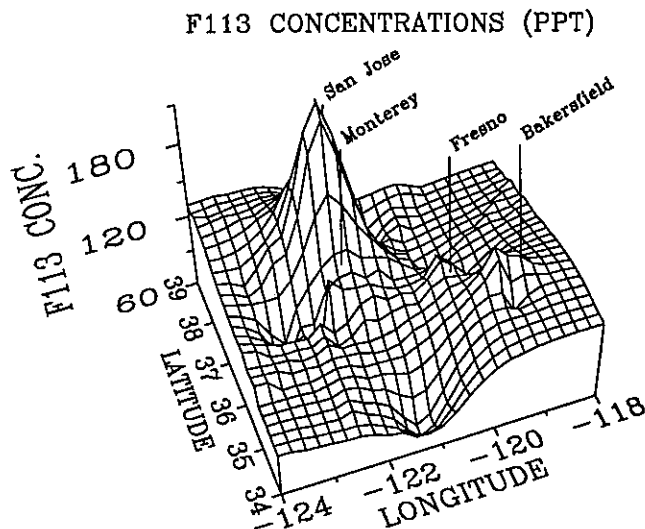


Figure 7.19. Three-dimensional display of concentration levels of CFC-113 (in ppt) over northern California measured from an airborne GC on August 22.

7.3. REFERENCES

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