

8. Nitrous Oxide and Halocarbons Group

T.M. THOMPSON (Editor), J.W. ELKINS, J.H. BUTLER, B.D. HALL, K.B. EGAN, C.M. BRUNSON,
J. SCZECHOWSKI, AND T.H. SWANSON

8.1. CONTINUING PROGRAMS

8.1.1. FLASK SAMPLES

The flask air-sampling program continued at BRW, NWR, MLO, SMO, SPO, and ALT as usual throughout the year, with only two minor changes. Larger 1-L flask pairs were pressurized monthly beginning in March at BRW, NWR, MLO, and SMO to meet the larger sample requirements of the LEAPS project. In November, personnel at SPO began using a higher pressure pump (3 atm) to fill flask pairs during their summer sampling period. All CMDL stations will convert to this higher pressure pump in early 1990 to provide sufficient sample amounts for both the LEAPS and flask projects.

The automated flask analysis system was completed according to the original design. However, extensive tests showed some problem areas and the need for redesign. The redesign was completed, and implementation and tests will continue into 1990.

Two calibration gas tanks, T3088 and 62631, were intercompared with standards maintained by the OGIIST in Beaverton, Oregon. This work was done in late April.

Preliminary monthly mean N₂O, CFC-11, and CFC-12 concentrations measured at BRW, NWR, MLO, SMO, and SPO during 1989 are listed in Table 8.1. Figure 8.1 shows monthly mean N₂O data for these stations for 1977-1989. The annual N₂O increase is approximately 0.2% at all the sites. BRW data exhibit a weak annual cycle. This cycle is more apparent in the continuous GC record.

CFC-12 and CFC-11 monthly mean concentrations are plotted in Figures 8.2 and 8.3. For the 1977-1984 period, the annual increase for each is less than it is for the 1985-1989 period. It appears that the source strength of these two halocarbons is increasing. The ratio of CFC-12 to CFC-11 concentrations has shown no significant change during the 13-year period, and therefore usage of the two gases is increasing proportionately.

N₂O, CFC-11, and CFC-12 data for ALT continued to be erratic; results from flask pairs did not match well. Actual flask pair averages are shown in Figure 8.4. BRW and ALT data compare favorably on average.

8.1.2. RITS CONTINUOUS GAS CHROMATOGRAPH SYSTEMS AT CMDL BASELINE STATIONS

In-situ sampling of air continued at BRW, MLO, and SMO. Eight analyses were made each day for N₂O, CFC-12, CFC-11, CFC-113, methyl chloroform (1, 1, 1-trichloroethane), and carbon tetrachloride. At SPO, these gases were sampled and analyzed 12 times per day [Elkins *et al.*, 1988].

In January 1989 processing of the chromatographic data began for both peak area and peak height. Concentrations based on peak height are sometimes more precise, yielding less scatter in the data. Small peaks such as those of methyl chloroform and carbon tetrachloride are prone to precision problems, especially if other substances are not chromatographically resolved from them. Processing programs were written to retrieve pre-1989 chromatograms and determine peak heights. A SMO peak-height data base

TABLE 8.1. Monthly Mean Concentrations in 1989 of N₂O (ppb by mole fraction in dry air), CFC-12 (ppt), and CFC-11 (ppt) From Air Samples Collected in Flask Pairs at BRW, NWR, MLO, SMO, and SPO

1989	N ₂ O					CFC-12					CFC-11				
	BRW	NWR	MLO	SMO	SPO	BRW	NWR	MLO	SMO	SPO	BRW	NWR	MLO	SMO	SPO
Jan.	308.5	308.8	308.1	305.9	307.1	459.5	453.6	453.7	437.4	427.4	274.6	269.6	266.6	260.4	
Feb.	309.7	311.5	309.1	309.0		460.0	455.8	447.4	440.5		276.7	270.9	264.3	257.1	
March	307.8	308.4	308.6	307.9		460.8	447.0	450.9	435.0		278.3	267.7	265.6	258.9	
April	309.2	309.4	309.7	306.5		461.6	455.3	454.1	437.8		278.5	270.8	269.6	258.4	
May	309.4	310.6	308.8	306.5		463.1	459.1	452.8	440.6		276.6	271.1	268.8	258.7	
June	308.7	311.6	309.4	308.5		459.8	461.4	461.9	432.2		275.6	272.4	270.2	254.2	
July	310.9	309.8	308.4	306.6		468.1	475.4	453.8	443.1		279.1	285.7	268.4	258.9	
Aug.	309.3	311.5	309.3	309.2		464.1	468.3	458.4	442.3		274.9	277.1	271.3	263.3	
Sept.	309.0	310.0	309.7	308.2		467.1	467.5	460.6	445.2		277.6	279.6	273.7	262.1	
Oct.	308.4	310.6	309.7	306.9		471.0	464.2	464.1	448.4		283.5	275.9	273.8	263.5	
Nov.	310.4	309.6	308.4	307.8		477.1	470.8	467.2	448.1		290.0	280.7	272.2	263.8	
Dec.	309.4	309.4	309.5	308.0	308.2	478.1	468.1	459.7	451.6	445.7	288.2	276.7	276.3	266.2	259.8

These data are provisional, pending final calibration.

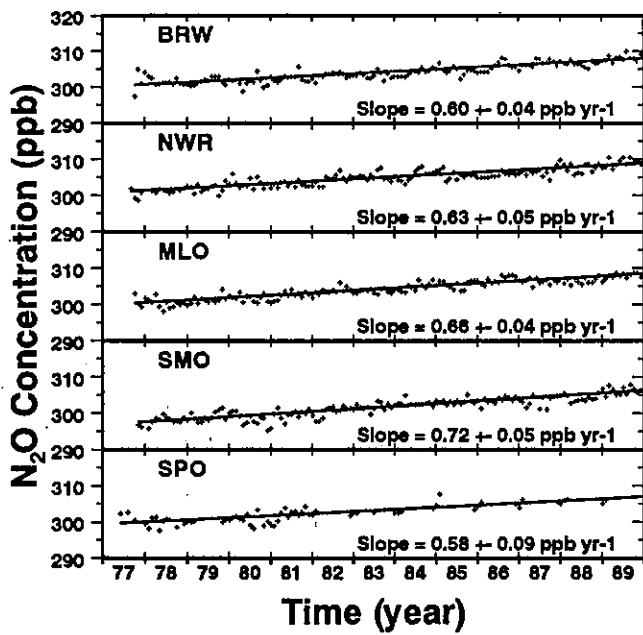


Fig. 8.1. Monthly mean concentrations of N_2O (CO_2 and H_2O corrected) from the CMDL flask air sample network. The trends and 95% confidence intervals are also shown.

was created using these programs. Other station peak-height data will be similarly obtained in 1990.

In April the BRW system was modified so that all three columns could be backflushed. MLO and SMO systems were previously modified in 1988. Precision has been improved because of this change.

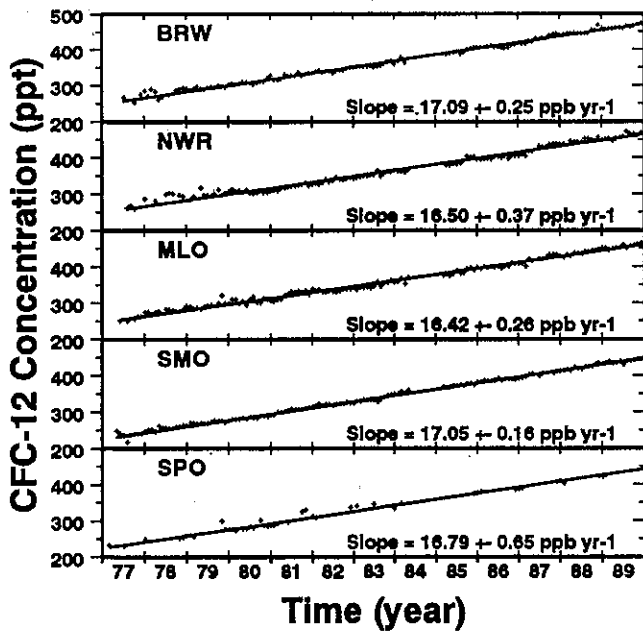


Fig. 8.2. Monthly mean dry concentrations of CFC-12 from the CMDL flask air sample network. The trends and 95% confidence intervals are also shown.

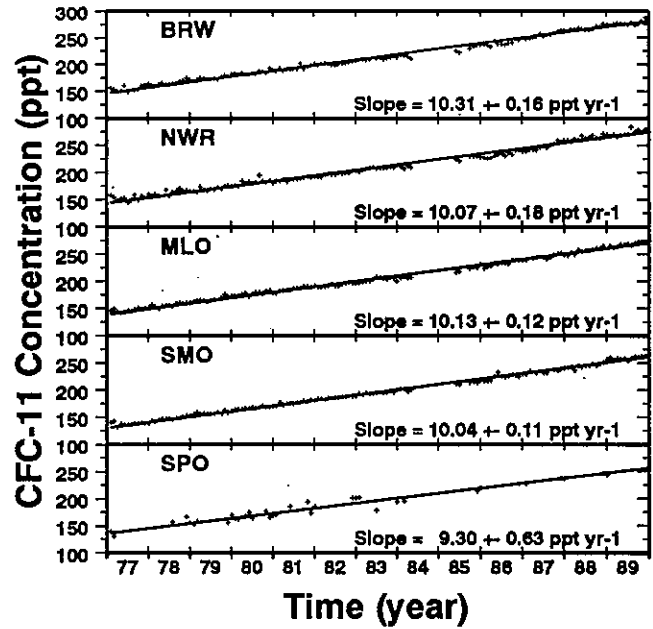


Fig. 8.3. Monthly mean dry concentrations of CFC-11 from the CMDL flask air sample network. The trends and 95% confidence intervals are also shown.

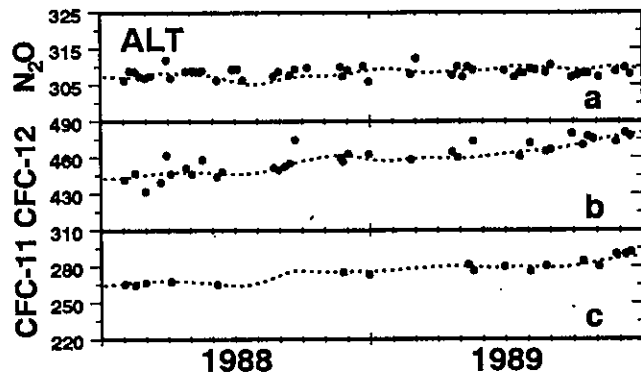


Fig. 8.4. Flask sample concentrations for (a) N_2O , (b) CFC-12, and (c) CFC-11 at Alert observatory, Canada. The dashed lines are spline fits to corresponding BRW flask sample data, for comparison.

In June a new operations manager was hired to oversee the operation of the equipment at the field sites, provide support when equipment or software failures occur, and supply expendables like carrier gas, paper, and disks.

Version 4.2 of the software was completed and tested. This revision changes the way gas is sampled at the field sites. Previously the order of analyses was (1) calibration gas 1, (2) calibration gas 2, and (3) outside air. Now the order is (1) calibration gas 1, (2) outside air sample 1, (3) calibration gas 2, and (4) outside air sample 2. This increases the number of times air is sampled from once every

3 hours to once every 2 hours for hourly analyses. Another change incorporated in the software is storing data using two floppy disk drives instead of a single floppy drive and an emulated disk in RAM.

Both software changes also required hardware changes. In October, an eight-port stream selection valve replaced the old six-port valve at BRW. A dual high-density (1.5 Mbyte) floppy drive was installed. These same hardware and software changes will be made at the other sites in early 1990.

A new RITS GC system, incorporating the new software and hardware, was set up and tested in Boulder. This equipment will be moved to NWR in early 1990 to complete the in-situ measurement program. All flask sites except ALT will then have GC's.

Because of increased data processing needs, an HP340 workstation was purchased with a 330-Mbyte hard disk. This is the first acquisition toward the move to a group computer network.

The 2.5-year record of daily average N_2O concentrations from the in-situ GC's at BRW, MLO, and SMO is shown in Figure 8.5. The annual cycle at BRW has a February maximum and an August-September minimum similar to the periods of the maximum and minimum observed in CO_2 concentrations at BRW. Data for SMO in 1988 appear to be cyclic, but the cycle is not repeated. Because N_2O has a seasonal cycle and is growing at a small rate, it is difficult to establish an annual growth rate with only 2 years of data. The calculated growth rate of atmospheric N_2O concentration for 1988-1989 at BRW is about 0.6 ppb yr^{-1} . However, the MLO record for N_2O shows little growth because of the short record period and larger experimental error in the 1987 data.

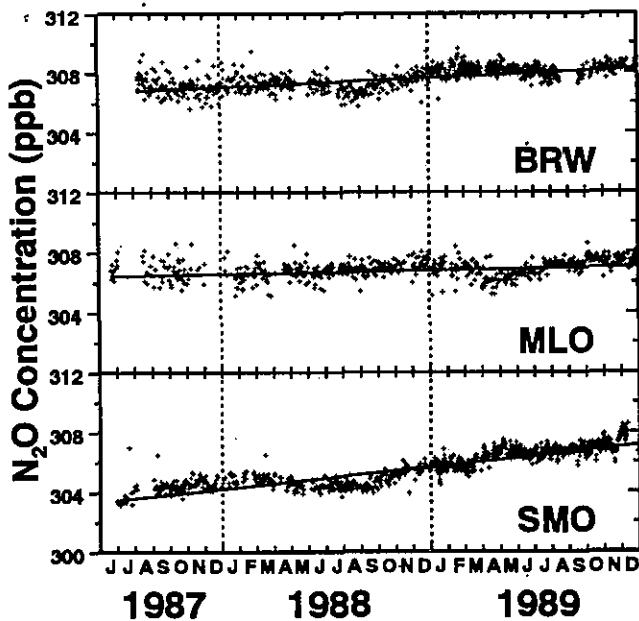


Fig. 8.5. N_2O daily mean concentrations at BRW, MLO, and SMO obtained from the in-situ RITS GC's. The trends were generated using least squares regression analysis.

The growth rate at SMO during 1988-1989 is about 1 ppb yr^{-1} . This value is higher than at other stations and may be the result of calibration gas problems associated with calibration gas tank changes in 1988.

Daily mean CFC-12 concentrations derived from the gas chromatograph measurements are shown in Figure 8.6. The annual increase is about 19 ppt yr^{-1} during 1988-1989 for all three stations. This result confirms observations from flask data during the past few years.

Carbon tetrachloride concentration at our sampling sites appears to have been steady during the past 2 years, in the range of 100-110 ppt. As an example, SMO data are shown in Figure 8.7.

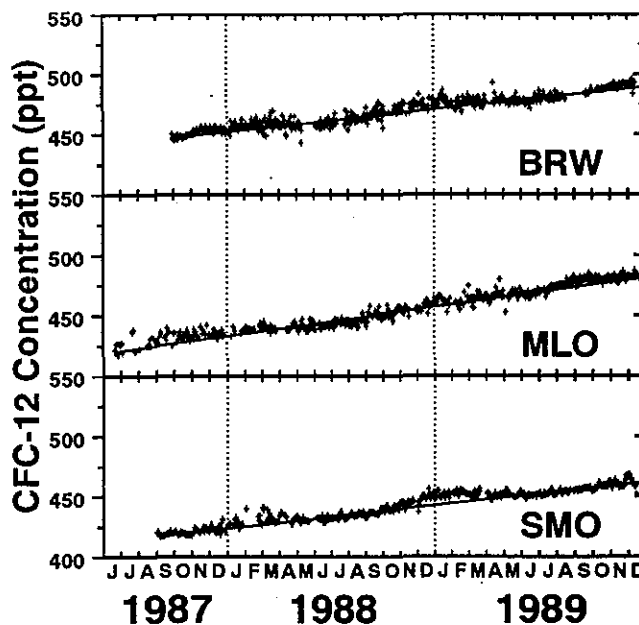


Fig. 8.6. CFC-12 daily mean concentrations at BRW, MLO, and SMO obtained from the in-situ RITS GC's.

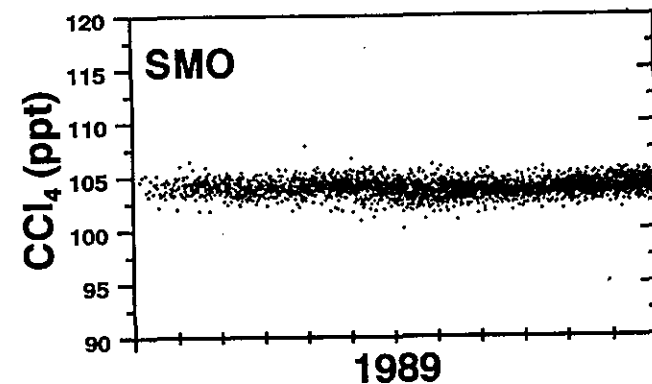


Fig. 8.7. SMO CCl_4 concentrations from the in-situ RITS GC. The air was sampled every 3 hours.

Quantization of methyl chloroform still remains a problem because of an unknown contaminant in some of our calibration gases.

8.1.3. LOW ELECTRON ATTACHMENT POTENTIAL SPECIES

Although formal flask sampling for LEAPS gases began in March, a number of changes were made throughout the year in the sampling and analysis of LEAPS gases. By November, one of the main problems limiting these measurements was resolved when the old flask pump at SPO was replaced with a new sampling pump capable of filling flasks to a gauge pressure of 3 atm. The same type of pump will be installed at the other CMDL stations early in 1990. Contamination tests have shown the pumps to be clean and not a source of CFC-113, a commonly used cleaning agent. Analytical columns were changed as the GC was optimized for the various measurements. Initially, gases were separated with a 0.53 mm x 50 m methyl-silicone column, which was changed in August to a 0.53 mm x 25 m Poraplot Q column, and was ultimately replaced by a 0.32 mm x 10 m Poraplot Q column. The Chrompack cryotrap was modified extensively to allow for the direct measurement of samples from flasks and to improve overall sensitivity of the measurements.

Insufficient data are available to calculate atmospheric trends of the LEAPS gases from flask air samples collected at the CMDL stations. However, flask samples collected from over the Pacific Ocean during the RITS-89 cruise (January-April) on the NOAA ship *Discoverer* were analyzed for H-1301, H-1211, and CFC-113, as were five 8-L flask air samples remaining from the SAGA II cruise (May-July 1987) in the West Pacific and East Indian Oceans. Growth rates for these gases (Table 8.2) were estimated both by considering the differences between 1987 and 1989 measurements and by evaluating the latitudinal gradients (Figure 8.8). These estimates are only preliminary; they are based on small data sets, representing only two "snapshots" in time. Also, the northern hemispheric CFC-113 values from the 1989 cruise were affected by urban contamination

TABLE 8.2. Estimated Annual Growth Rates for LEAPS Gases, Calculated from RITS-89 and SAGA II (1987) Data

Gas	Method 1	Method 2
H-1301	25.7%	23.6%
H-1211	4.4%	10.8%
CFC-113	10.1%	

Data are shown in Figure 8.8. Method 1 involves direct calculations of the average difference between samples collected between 30°S and 40°N on both cruises. Method 2 involves calculations based on the measured latitudinal gradient, a relative production of 20:1 for the two hemispheres, and an assumed interhemispheric exchange time of 1 year [see *Butler et al.*, 1989].

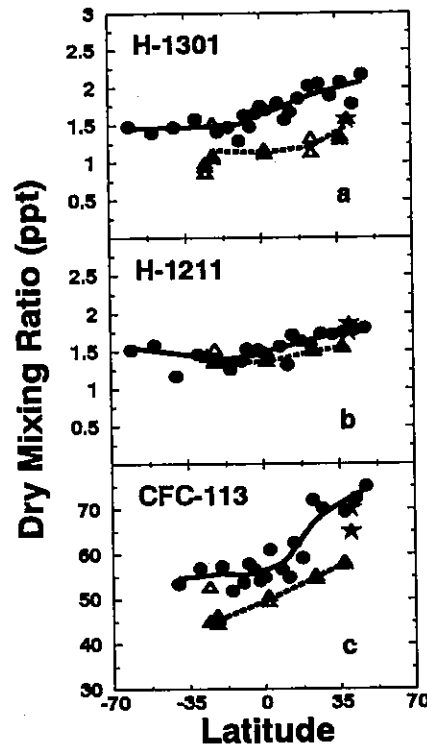


Fig. 8.8. Dry mixing ratios versus latitude in degrees for (a) H-1301, (b) H-1211, and (c) CFC-113, measured in flask air samples collected during SAGA II in 1987 (triangles) and the RITS cruise of 1989 (circles), and in air from a cylinder filled at NWR in 1988 (stars). Estimated growth rates are given in Table 8.2.

as the ship proceeded along the California coast during a period of strong offshore winds. The growth rates for H-1301 calculated by either method agreed well, but there is a discrepancy in results for H-1211. This discrepancy should be resolved when more data from our stations become available.

Sample concentrations of the LEAPS gases to date have been determined by response ratio to CFC-12 compared with the same ratio for a cylinder of NWR air (Scott cylinder SRL-K-009288, Aculife-5-treated steel, filled November 1988 at NWR). However, a detailed evaluation of the response curves for gravimetrically prepared standards shows that the response of the halons, and to a lesser extent CFC-113 and CFC-12, is nonlinear (Figure 8.9). Consequently, the LEAPS GC will be modified further in 1990 to allow measurement of exact sample volume so that nonlinearities in the response can be evaluated. This will lead not only to more accurate results but also much better precision.

8.1.4. GRAVIMETRIC STANDARDS

A principal goal for 1989 was the development of independent calibration scales for all RITS gases. CFC-113,

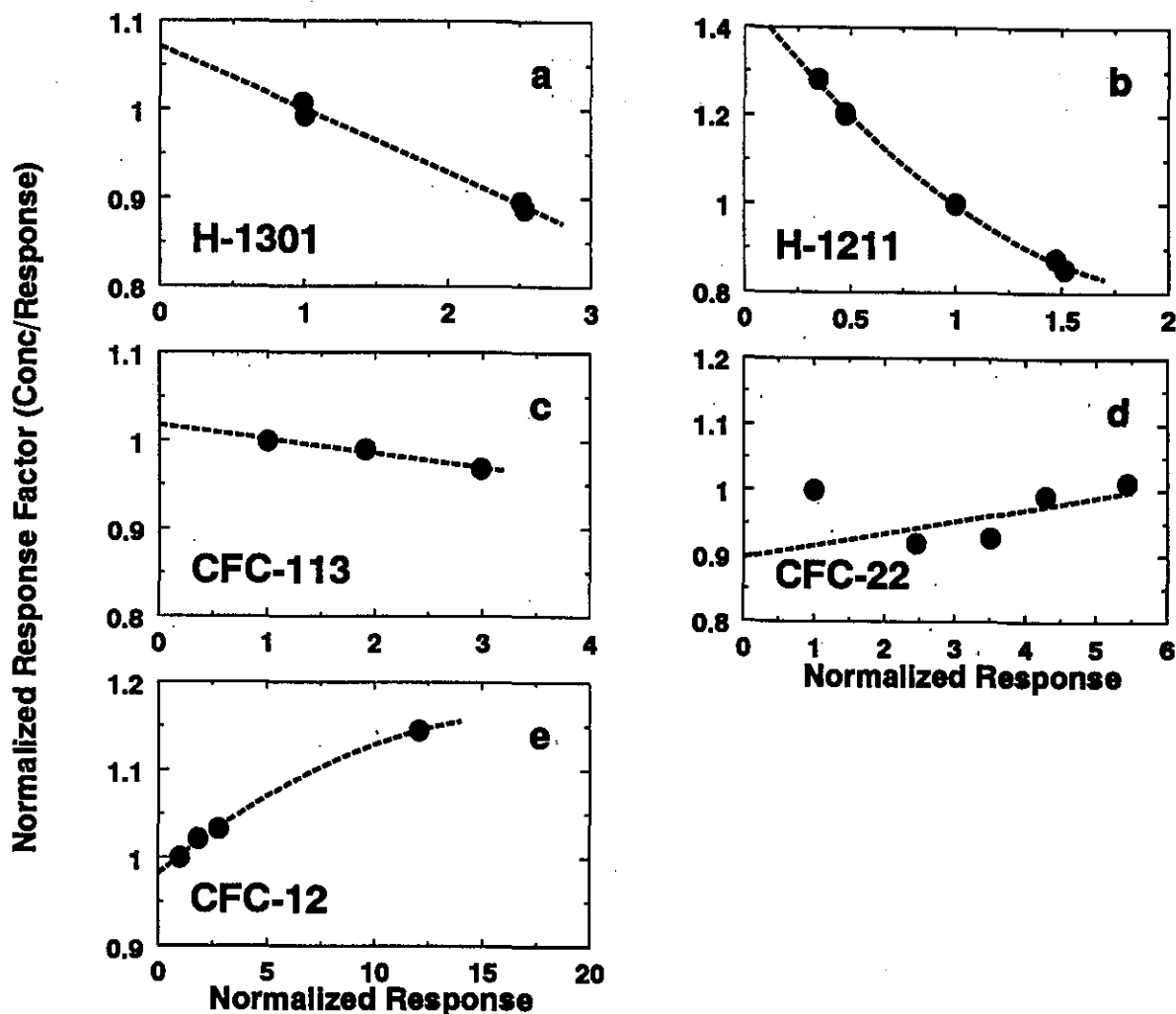


Fig. 8.9. Response curves for (a) H-1301, (b) H-1211, (c) CFC-113, (d) CFC-22, and (e) CFC-12. The data show that nonlinearities in the detector response should be considered in measuring these gas concentrations. (Although CFC-12 is not a LEAPS gas, it is used to estimate sample volume for the LEAPS measurements.) A horizontal plot for the response factor is indicative of a true linear response of the detector to the compound being analyzed.

CH_3CCl_3 , and CCl_4 have proved to be the most difficult to quantify. Several measures were taken to improve our ability to prepare accurate standards at the part per trillion level. Aluminum transfer tubes were Aculife-treated to minimize adsorption and surface reactions during the transfer step for CH_3CCl_3 and CCl_4 . Specially cleaned valves containing as little CFC-113 as possible were purchased and tested.

The gravimetric standards prepared in 1989 are shown in Table 8.3. The CFC-113 standards were prepared in both Aculife-treated aluminum cylinders and 33-L stainless steel cans to investigate possible valve contamination, and a calibration curve (Figure 8.10) was prepared. No valve bias was observed within experimental error. CMDL participated in an intercomparison in which flask air was analyzed for CFC-113. Our result was 36% higher than

that of OGIST (Table 8.4).

Another goal for 1989 was to replace calibration standards at the CMDL observatories and to obtain standards for use during cruises and in the laboratory. This was accomplished by filling several Aculife-treated aluminum tanks and 33-L stainless steel cans with NWR air. These working standards were carefully calibrated using our gravimetric standards. Two each of the new working standards were installed at BRW, MLO, and SMO observatories. These new standards should eliminate CFC-113 contamination problems and help resolve minor discrepancies in results obtained among stations.

Standards support for various other projects continued as in the past. As indicated in Table 8.3, standards were prepared for the LEAPS project, special RITS projects, and the CMDL Carbon Cycle Group.

TABLE 8.3. CMDL Gravimetric Standards Prepared in 1989

Set	Compounds in Cylinder	No. of Cylinders	Range	Project
1	CFC-11, CFC-113, CH ₂ Cl ₂ , CCl ₄	2	ppb, ppt	NOAA/RITS
2	N ₂ O	2	ppb	NOAA/RITS
3	N ₂ O, CO ₂	4	ppb	NOAA/RITS
4	N ₂ O, CO ₂	7	ppm	NOAA/RITS
5	CFC-113, CFC-11	6	ppb, ppt	NOAA/RITS
6	H-1301	2	ppm, ppb	NOAA/LEAPS
7	H-1211	1	ppt	NOAA/LEAPS
8	CFC-22	2	ppm, ppb	NOAA/LEAPS
9	CO	8	ppm, ppb	NOAA/CC

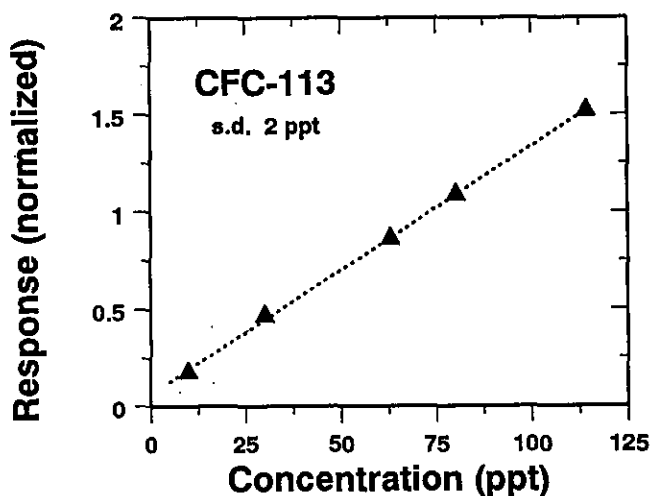


Fig. 8.10. The normalized calibration curve for CFC-113. It is linear in the 10-120 ppt range and has a residual standard deviation of about 2 ppt.

TABLE 8.4. Comparison of Concentration Scales for CFC-113 from CMDL and OGIST

	CFC-113, ppt	Standard Deviation, ppt
NOAA	69.9	1.9
OGIST	51.0	0.6

8.2. SPECIAL PROJECTS

8.2.1. RITS DISCOVERER CRUISE

Atmospheric and surface water N₂O, CFC-11, CFC-113, methyl chloroform, and CCl₄ were measured aboard the

NOAA research ship *Discoverer* on the RITS-89 cruise from February to April 1989. Dissolved N₂O at depth was also measured. The cruise track extended south from 47°N to 60°S along 110°W and then returned northward along 140°W (Figure 8.11). The purpose of the cruise was (1) to measure the interhemispheric gradient of these trace gases in the atmosphere, (2) to quantify the ocean's effect on these trace gases in the surface waters, (3) to measure the biological rate for production of dissolved N₂O, and (4) to compare these measurements to those from CMDL observatories. Surface waters near the equator were found to have N₂O supersaturations as high as 140%. Results from this cruise indicate that previous estimates for the global production of N₂O may have underestimated the strength of the ocean source, which could be as high as 30% of the total natural source.

8.2.2. FT-IR SPECTROMETER ARCHIVE PROJECT

Working in collaboration with scientists at NOAA/NSO, CMDL scientists from the CC and NOAA Groups restarted FT-IR spectrometric observations in January 1989 at Kitt Peak, Arizona (30°N, 112°W), which had been terminated in 1985. The purpose of resuming the observations was to compare trace gas concentrations derived from the FT-IR spectrometer observations with values determined from flask air samples collected at the nearest CMDL site, NWR (40°N, 105°W). The sun is tracked at Kitt Peak by a solar telescope, and its beam is directed into an FT-IR spectrometer. Trace gases present in the atmosphere absorb incoming solar IR radiation. Concentrations of trace gases can be determined by measuring integrated areas of absorption lines and comparing these measured values to published line-strength data. *Wallace and Livingston* [1990a, b] have reanalyzed CO₂, CH₄, N₂O, and CO spectra obtained at Kitt Peak during 1979-1985 using the diatomic lines of oxygen as an internal standard to yield average atmospheric concentration values for these gases.

Spectroscopic CO₂ measurements made at Kitt Peak during 1978-1989 yield a mean growth rate of 0.49% per year

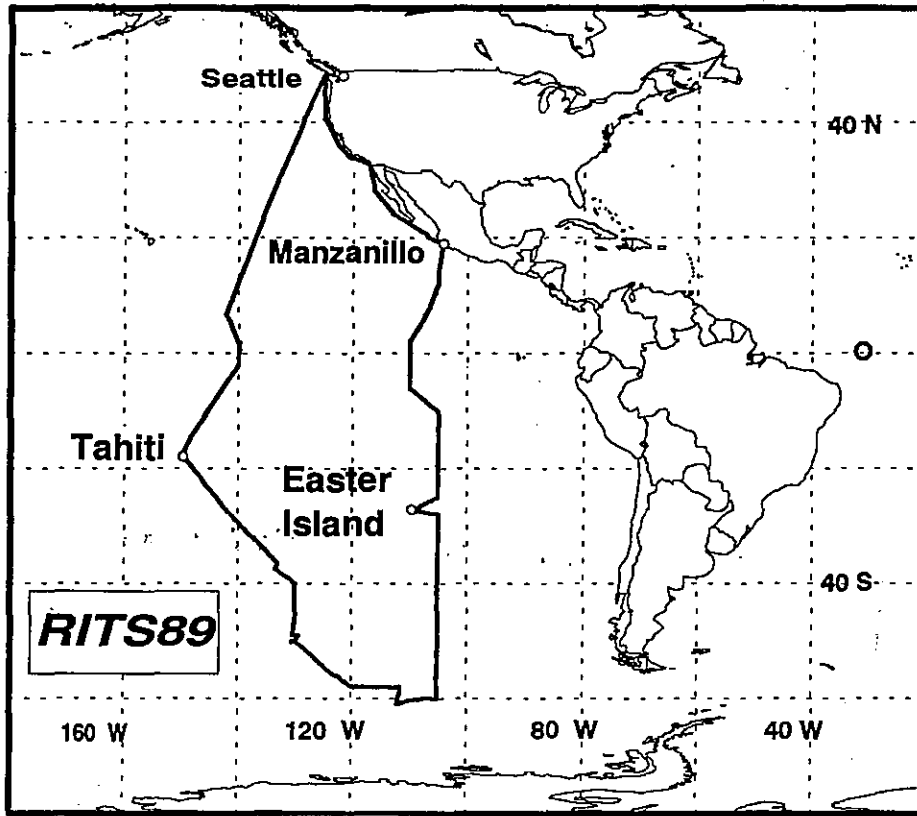


Fig. 8.11. Cruise track of the RITS expedition in the eastern Pacific Ocean.

whereas NWR flask air-sample data yield a mean CO_2 growth rate of 0.48% (Figure 8.12a). There is a difference of ~10 ppm between the scales of the two measurement techniques, perhaps due to errors associated with the absolute line strengths or to differences in the features of the vertical profiles of O_2 and CO_2 . A similar comparison of CH_4 concentrations also shows a bias in the measurements

(~60 ppb), as well as a difference in growth rates that is not statistically significant. Data from Kitt Peak yield a growth rate of 1.01% per year compared with 0.76% per year for the NWR data (Figure 8.12b). Although the NWR CH_4 flask record began in 1983, air in cylinders was collected at NWR between 1977 and 1979, and was recently analyzed for CH_4 . Including these new data and assuming a linear growth for

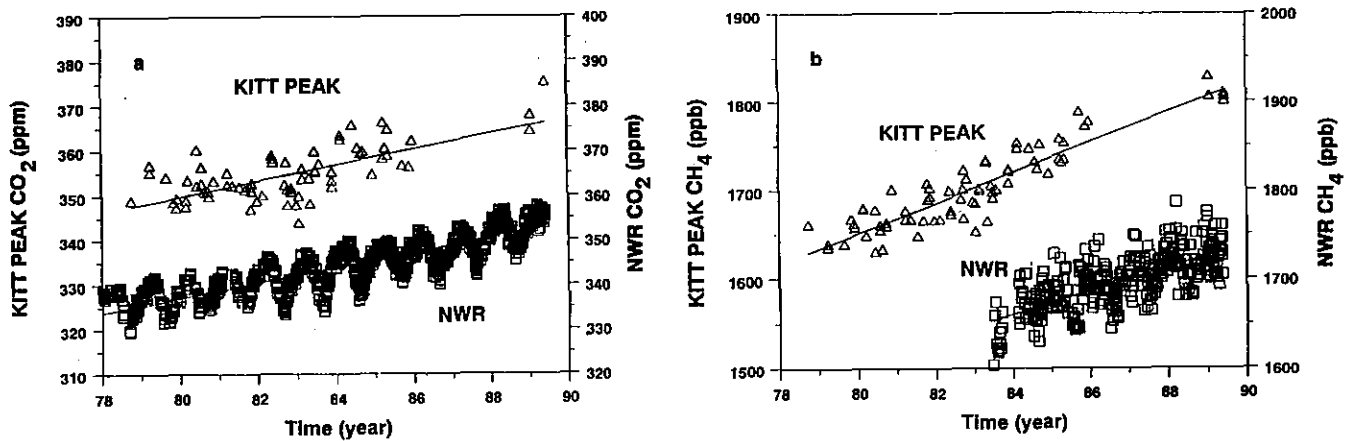


Fig. 8.12. Comparisons of CMDL flask sample data from NWR (squares) with NSO data derived from IR spectra measured at Kitt Peak, Arizona (triangles) (a) CO_2 and (b) CH_4 .

the complete NWR record gives a calculated growth rate of ~1% per year, in good agreement with the spectrometric record.

In early 1991 a CMDL FT-IR spectrometer will be moved to the fifth floor of the building in Boulder. Operation of the spectrometer and archiving of spectra will begin in the summer of 1991 to complement observations made at Kitt Peak.

8.2.3. AIRBORNE GAS CHROMATOGRAPH

Testing of a Shimadzu Mini-2 gas chromatograph continued aboard the NOAA King Air research aircraft. Tylan mass flow controllers were used to maintain a steady carrier gas flow rate. In February N_2O was measured in coal-fired power plant plumes near Miami, Florida. N_2O was also measured in the Pawnee Power Plant plume near Brush, Colorado (Figure 8.13) on July 28. Although data obtained during the flight were not as precise as station data, we did not detect parts per million levels of N_2O in the plumes, and it was therefore concluded that combustion is a minor source of atmospheric N_2O . During the flight in the Pawnee Power Plant plume, air samples were collected in 500 mL airbags for subsequent analyses. Before the flight, the stability of N_2O in the airbags was examined over the course of 24 hours. The airbags proved to be a reliable and inexpensive method of collecting air samples for quick N_2O analysis. Flue gas samples were also collected at the power plant.

High variability in the N_2O in-situ flight data was attributed to changes in the ECD cell pressure. Because the ECD sensitivity increases with decreasing atmospheric pressure, an absolute backpressure regulator was subse-

quently installed on the ECD outlet to maintain a constant cell pressure. Two flights were then made over eastern Colorado on September 7 and 8 during which CFC-11 was measured with the in-situ GC, and flask air samples were collected. With use of both the backpressure regulator and Tylan mass flow controllers, on-board CFC-11 measurements improved; results agreed with flask sample CFC-11 concentrations as well as with the CFC-11 value obtained at our sampling site at NWR (Figure 8.14).

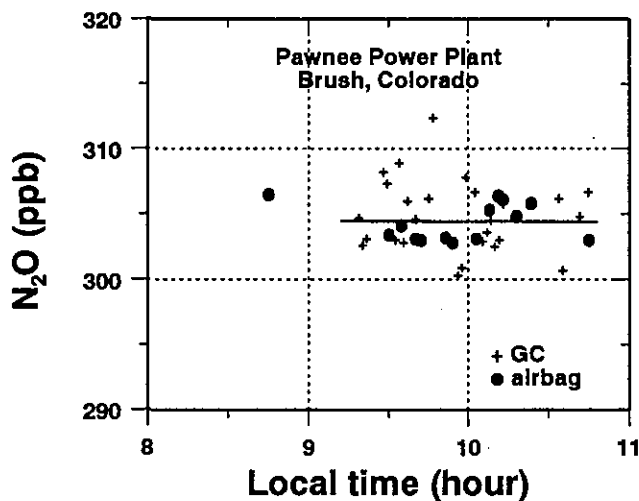


Fig. 8.13. Concentrations of N_2O in the plume at the Pawnee Power Plant, Brush, Colorado, on July 28, 1989, derived from in-situ GC (pluses) and airbag sample (circles) measurements aboard the NOAA King-Air aircraft.

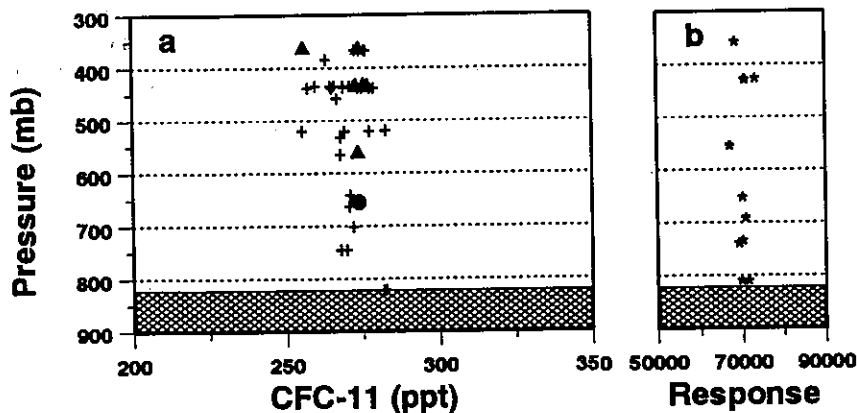


Fig. 8.14. CFC-11 concentrations measured over central Colorado September 8 and 9, 1989, aboard the NOAA King-Air aircraft. (a) Aircraft CFC-11 data obtained from in-situ GC measurements (pluses) and from flask air samples (triangles) are compared with NWR flask sample data (circle). (b) The relative response (peak height) of the in-situ GC while a gas standard was analyzed during the flight. The relative standard deviation for measuring CFC-11 in the standard during the flight was better than 3.0%.

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