

8. NITROUS OXIDE AND HALOCARBONS GROUP

8.1 Continuing Programs

ORGANIZATION

The NOAA Group was created in July 1986 as a result of the reorganization of the Trace Gases Group under the RITS initiative and the arrival of the new group chief in Boulder. The chief is a former NBS employee with expertise in gas standard preparation, EC-GC, and IR spectroscopy. A CIRES research associate joined the group at the same time as leader of special projects (KOROLEV cruise and LEAPS, discussed below).

CONTINUOUS AND FLASK NETWORK (CFN)

Weekly collection of air samples in 0.3 L flasks from BRW, NWR, MLO, and SMO continued as in the past; station personnel at SPO exposed flasks only during January, November, and December 1986. These air samples were analyzed for halocarbons CCl_3F (F-11) and CCl_2F_2 (F-12), and N_2O using EC-GC at the Boulder laboratory. Figure 1 presents the flask data for F-11, F-12, and N_2O from BRW, NWR, MLO, and SMO. Estimated secular trends and standard deviations (at the 95% confidence level, C.L.) are also presented.

The Shimadzu Mini-2 GC at SPO measured N_2O , F-12, and F-11 in situ twice a week. SPO flask data are combined with the in situ GC data in fig. 2. N_2O data for 1986 were excluded from fig. 2, because of excessive drift of the N_2O signal. A new detector and gas sample valve will be sent on the 1987 mid-winter drop to fix this problem.

Latitudinal profiles of F-12 and F-11 using annual mean flask data are presented in fig. 3 for 1977-1986 from the GMCC baseline stations and NWR. The increases in the growth rates of F-11 and F-12 at all stations between 1985 and 1986 are probably the result of switching to a new calibration tank whose calibration is drifting with time. This tank was last calibrated against OGC's scale in 1985. An intercomparison is planned with OGC in late 1987, which may resolve this change in growth rate.

The new RITS automated GC and data processing system was installed at SMO in June and BRW in October. Representative data for F-12 daily means from the RITS GC at SMO are compared with flask data in fig. 4. It is planned that MLO will receive its system in early 1987 and SPO late next year. Using an HP model no. 5890 GC, Nelson Analytical interface, HP9816 computer, HP9133 hard disk, and printer, the system measures air concentrations of N_2O , F-12, F-11, methyl chloroform (CH_2CCl_3), and carbon tetrachloride (CCl_4) every 2 hours. Commercially prepared calibration gases in 29.5-L aluminum high-pressure cylinders were found to be contaminated with 1,1,2-trichlorotrifluoroethane (F-113), making quantitation of CH_2CCl_3 impossible. Also, low concentrations of CCl_4 (about 30 ppt) were found to be unstable in the untreated aluminum cylinders; CCl_4 completely disappeared after 6 months. Changes will be made in 1987 to correct these problems.

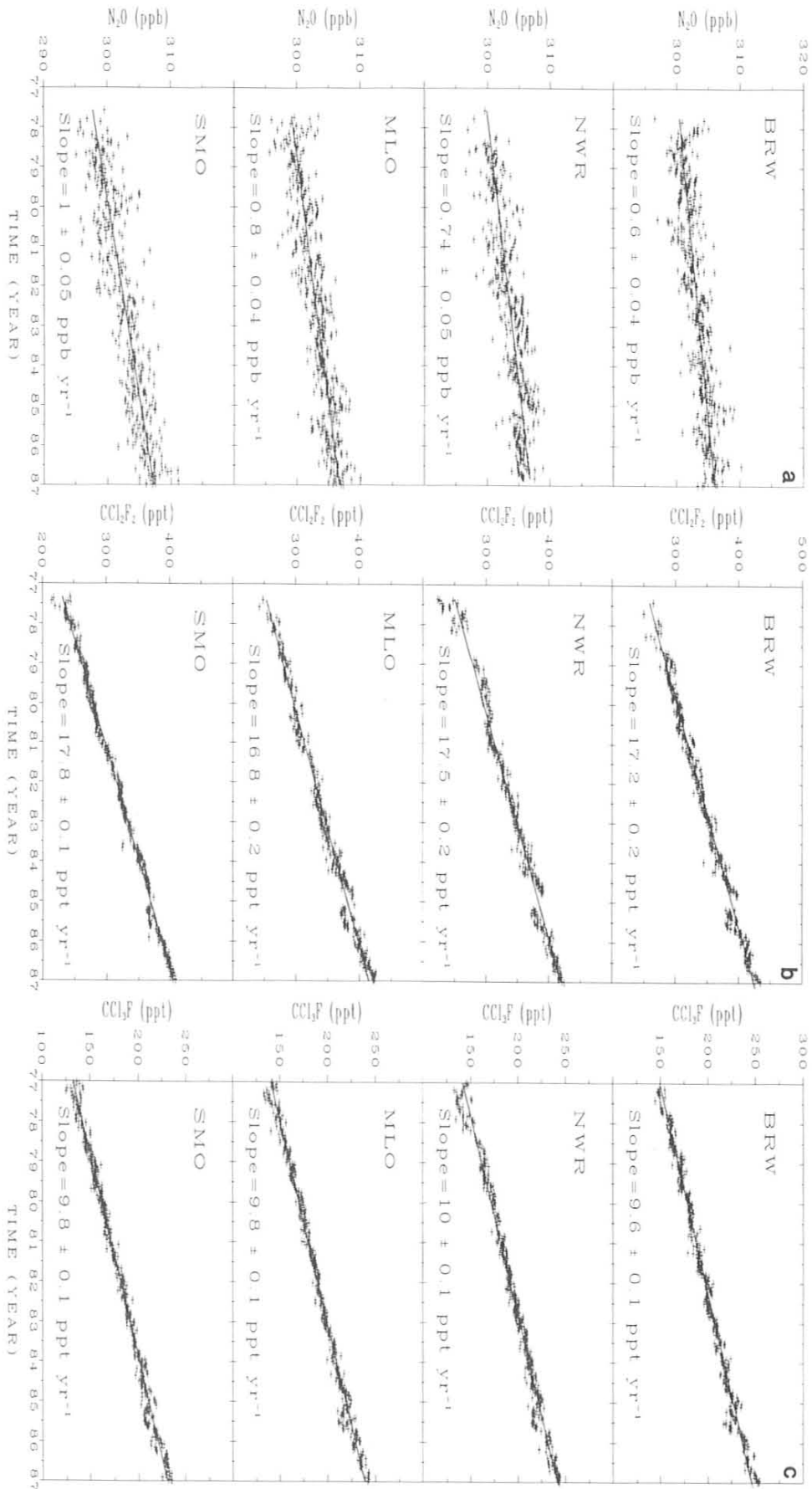


Figure 1. ---Growth rates of (a) N₂O, and halocarbons (b) F-12 and (c) F-11 at BRW, NWR, MLO, and SMO for 1977-1986. The growth rates and their standard deviations at the 95% confidence level (C.L.) are also presented.

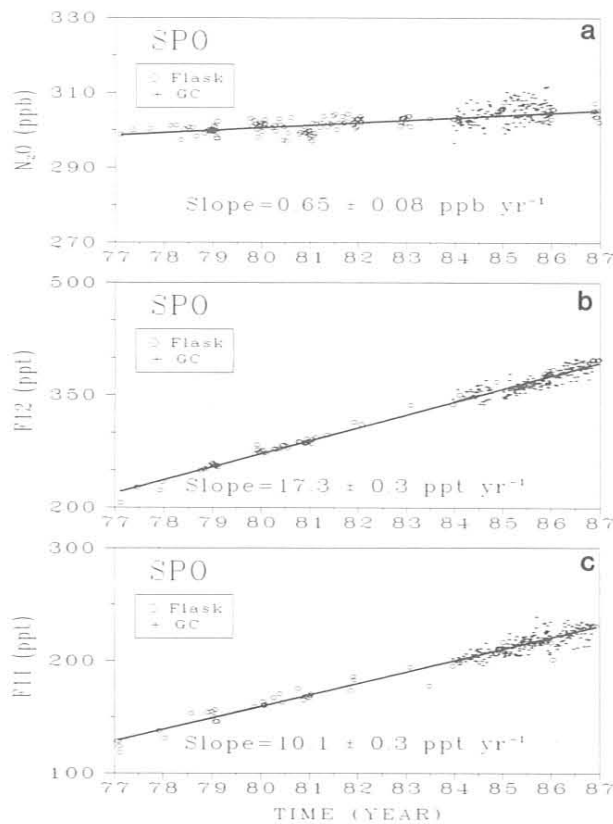


Figure 2.--Growth rates of (a) N_2O , and halocarbons (b) F-12 and (c) F-11 at SPO for 1977-1986. Crosses denote in situ GC results and ovals indicate flask samples analyzed in Boulder. The growth rates and their standard deviations at the 95% C.L. for the combined data sets are also presented.

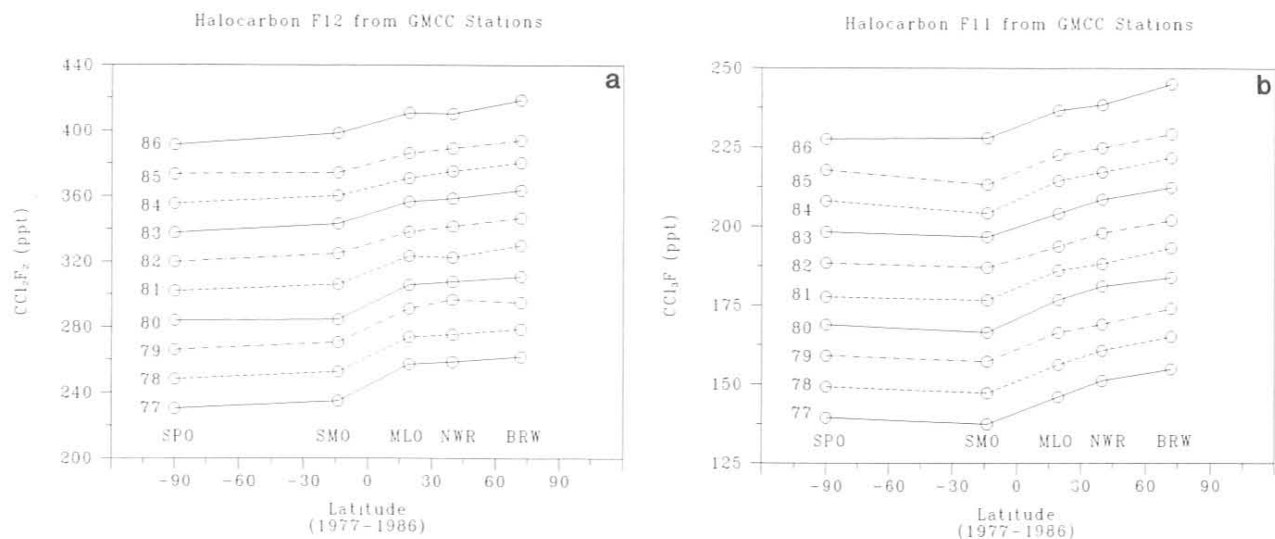


Figure 3.--Latitudinal profiles of (a) F-12 and (b) F-11 using annual mean flask data are presented for 1977-1986 from the GMCC baseline stations and NWR.

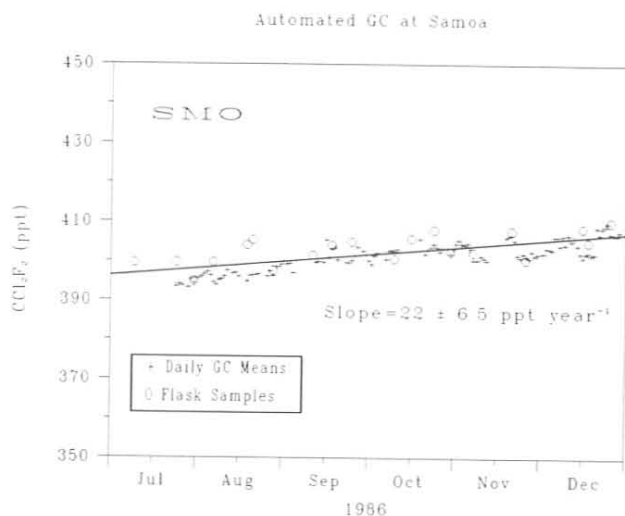


Figure 4.--F-12 daily means (+) from the RITS GC at SMO compared with flask samples (o) that were analyzed in Boulder. The growth rate and its standard deviation at the 95% C.L. for the combined data sets are given.

LOW ELECTRON ATTACHMENT POTENTIAL SPECIES (LEAPS)

The NOAA Group has received incremental RITS funding to begin measuring some of the "minor" atmospheric halocarbons. Specifically, plans are to develop or adapt techniques to investigate F-22 (CHClF_2), F-113 ($\text{CCl}_2\text{F}-\text{CClF}_2$), Halon-1211 (CBrClF_2), and Halon-1301 (CBrF_3). Although currently low in concentration, these halocarbons have been introduced into the atmosphere in much greater quantities in recent years, and their atmospheric lifetimes are long. These gases are involved in the radiative budget of the Earth's atmosphere, and all appear to be increasing in concentration at alarming rates. As with most halocarbons, they also may be important in the chemistry of the stratosphere. This is especially true of the brominated species, as stratospheric bromine is 10 times more effective than chlorine in removing ozone. These gases have been historically difficult to measure by EC-GC techniques because of their low electron affinity, their low atmospheric concentration, or both. Hence, they have been designated as LEAPS gases. Physical data are outlined in table 1. Information for table 1 came from Braker and Mossman (1980), Weast and Ostle (1979), L'Air Liquide (1976), and WMO (1986).

Table 1.--Properties of LEAPS Gases

Halocarbon	Formula	Boiling point (°C)	Atmospheric concentration (ppt) (year)		Residence time (years)	Annual increase %	Sources*
F-22	CHClF_2	-40.8	52	1980	75	11.7-25	1,2,3,6
F-113	$\text{CCl}_2\text{F}-\text{CClF}_2$	47.7	32	1985	90	10	5
Halon-1211	CBrClF_2	-4.0	1.5	1984	25	20	4
Halon-1301	CBrF_3	-57.8	1.0	1984	110	30	1,2,3,4

*1 = Refrigerant; 2 = freezing; 3 = air conditioning; 4 = fire extinguishing; 5 = solvent; 6 = intermediate in polymer chemistry.

GRAVIMETRIC STANDARDS

NOAH received RITS incremental funding in 1986 to develop an independent scale for the absolute gas calibration of RITS gases using gravimetric techniques. Since there are no standards available for many of the LEAPS gases, NOAH must prepare these standards. A standards laboratory complete with high-accuracy analytical balances will be installed in 1987. The NBS N₂O SRM which was developed and prepared by the Group Chief of NOAH, is currently being used for the absolute calibration of N₂O. NOAA personnel prepared a series of gravimetric standards for CH₄, F-11, F-12, CH₂CCl₃, and CCl₄ at NBS in the spring of 1986. The new CH₄ gravimetric standards compare better than ±1% with the NBS SRM, the most commonly used standard for atmospheric methane studies. The halocarbon standards are being used for our automated RITS GC. However, the OGC scale is still being used for F-11 and F-12 for continuity with the flask program until intercomparisons can be made with other international standards.

8.2 Special Projects

PLANS FOR JOINT U.S.-U.S.S.R. RESEARCH IN 1987

Planning was begun for a joint U.S.-U.S.S.R. research cruise aboard the research vessel AKADEMIK KOROLEV, to take place May-August 1987. The expedition, SAGA II, will involve the measurement of atmospheric and dissolved trace gases along a transect from Hawaii to Kamchatka, then down the 160°E meridian from about 45°N to 45°S, around Australia, up to Singapore, and back along the equator to Hawaii. The work will be conducted in conjunction with the Carbon Cycle Group of GMCC, as well as participants from NOAA/PMEL, OGC, SIO, University of Washington, Washington State University, and University of Hawaii. It is anticipated that GMCC will be able to obtain considerable valuable information on a number of gases along this route. The gases to be measured are N₂O in the atmosphere, in the surface water, and at depth, and F-11, F-12, CO₂, and CH₄ in the atmosphere and surface waters. In addition, we plan to collect flask samples along the 160th meridian for subsequent analysis of CCl₄, CH₂CCl₃, CO₂, CH₄, and perhaps the LEAPS gases as well.

Our objectives are (1) to test our new, highly precise technique for measuring N₂O under rigorous operating conditions, (2) to test a new automated headspace sampler for measuring dissolved N₂O, (3) to compare the latitudinal, atmospheric gradients obtained from these data with those indicated from our station sampling network, (4) to detect any sharp interhemispheric gradients of N₂O, F-11, F-12, CO₂, or CH₄ near the equator, (5) to evaluate the fluxes of these gases from the sea surface to the atmosphere along this transect, and (6) to observe any signals that may be associated with the recent ENSO event. We also hope to intercalibrate some of our measurements with those of the Soviets as well as other US participants on the cruise.

FOURIER TRANSFORM INFRARED ARCHIVE PROGRAM

The total atmospheric content of a strong IR absorbing gas is required to determine the "greenhouse effect" of a particular species. Although ground-based measurements of these species give a reliable temporal indication of the

total atmospheric content, a vertical profile must either be assumed or measured using expensive balloon or aircraft studies in order to calculate the total gas concentration in the atmosphere. It is possible with new computer technology and instrumentation to measure the "column density" or the total concentration above a site using an FT-IR spectrometer at a resolution (0.12 cm^{-1} or better) sufficient to resolve possible overlapping IR absorption lines of interfering species. The measurement of the column density involves tracking the sun, using it as an IR source at various zenith angles, yielding atmospheric path lengths between 10 and 70 km with a ground-based FT-IR spectrometer coupled to a cooled (70 K) IR detector. Many of the RITS gases, including O_3 , CO_2 , CH_4 , CO , N_2O , F-12, and F-11, have been observed using this technique to precisions of a few percent. A great many IR absorbing lines have not been identified in solar spectra, and archiving spectra can be used to establish a baseline for future molecules not analyzed by GMCC (e.g., hydrocarbons, oxides of nitrogen, heavier halocarbons). It is also possible to measure the greenhouse effect directly by observing warming trends on night-time emission of atmospheric IR lines.

A proposal was written by the NOAA, ARM, and Carbon Cycle Groups in GMCC to start this research. This proposal received partial support from the Director's Office of ERL to purchase a used FT-IR spectrometer with a maximum resolution of 0.06 cm^{-1} from NBS in Gaithersburg, MD. Plans are to field test this instrument in an observatory on the roof of RL-3 in Boulder. After successful tests, the plan is to move the instrument to MLO where both the water vapor content and atmospheric pressure broadening are lower.

8.3 References

- Braker, W., and A.L. Mossman, 1980. Matheson Gas Data Book, 6th ed. Matheson Gas Products, Secaucus, NJ, 711 pp.
- Weast, R.C., and M.J. Astle (eds.), 1979. CRC Handbook of Chemistry and Physics, 59th ed. CRC Press, Inc., West Palm Beach, FL.
- L'Air Liquide, 1976. Encyclopedie des Gas. Elsevier/North-Holland, New York, 1150 pp.
- WMO (World Meteorological Organization), 1986. Atmospheric ozone 1985. WMO Global Ozone Research and Monitoring Project, Report No. 16. Vols. 1-3, Geneva, Switzerland.