Geophysical Monitoring for Climatic Change

No. 3

Summary Report 1974

U.S. DEPARTMENT OF COMMERCE

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

ENVIRONMENTAL RESEARCH LABORATORIES

Geophysical Monitoring for Climatic Change

No. 3

U.S. DEPARTMENT OF COMMERCE
Frederick B. Dent, Secretary

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
Robert M. White, Administrator

ENVIRONMENTAL RESEARCH LABORATORIES
Wilmot N. Hess, Director

GEOPHYSICAL MONITORING FOR CLIMATIC CHANGE NO. 3 SUMMARY REPORT - 1974

John M. Miller, Editor

BOULDER, COLO.
August 1975

DISCLAIMER

The NOAA Environmental Research Laboratories do not approve, recommend, or endorse any proprietary product or proprietary material mentioned in this publication. No reference shall be made to the NOAA Environmental Research Laboratories, or to this publication furnished by the NOAA Environmental Research Laboratories, in any advertising or sales promotion which would indicate or imply that the NOAA Environmental Research Laboratories approve, recommend, or endorse any proprietary product or proprietary material mentioned herein, or which has as its purpose an intent to cause directly or indirectly the advertised product to be used or purchased because of this NOAA Environmental Research Laboratories publication.

CONTENTS

GEOPHYSICAL MONITORING
FOR CLIMATIC CHANGE

NO. 3

SUMMARY REPORT - 1974

1. SUMMARY

The Geophysical Monitoring Program has now reached a major goal. The data output and the subsequent analysis are approaching a balance with the effort expended in establishing the three new observatories. With the completion of the Cape Matatula Observatory in 1975 even more of the Program effort will be focused on the scientific goals of quality data and its interpretation.

A significant contribution to the increased data flow was the successful operation of the mini-computer data system (ICDAS) at the South Pole during 1974 and the subsequent retrieval and processing of the 1974 data tapes. The ICDAS is in partial operation at Mauna Loa Observatory and will be installed in 1975 at both Barrow and Samoa.

Analysis of data from the observatories for 1974 and, where available, for previous years has included ozone, both surface concentrations and total amounts, carbon dioxide, chlorofluorocarbons, and aerosols.

The 1974 carbon dioxide measurements are of particular interest. These data show that the 1973-74 increase in annual concentration is the smallest of the decade dropping at Barrow, Mauna Loa, South Pole, and Cape Matatula (partial 7 month record) from more than 1.5 ppm per year to less than 0.5 ppm per year. It is known that the year-to-year increase is variable and thus it remains to be determined from future data if the small 1973-74 increase was a statistical anomaly or due to physical changes.

Monitoring of the stratospheric aerosol layer has always been an objective of the GMCC program. The lidar system at Mauna Loa has been in intermittent operation since 1973 and scheduled observations were begun in the fall of 1974 shortly before the October eruption of Fuego volcano in Guatemala. The Mauna Loa lidar observations show that the volcano's effluent added major amounts of material to the stratosphere; enhanced backscatter from this material is still being monitored in mid-1975. Analysis of related parameters, including solar aureole and received solar radiation, is

2.2 South Pole

Major additions to the South Pole program during 1973-74 austral summer required relocation of all GMCC systems to one common location compatible with access and sampling requirements.

Original plans called for installation of GMCC equipment in a steel arch building completed buried in the snow at the VLF site approximately 610 meters grid north of the main station complex. However, the space there was inadequate and equipment transfer and installation would be extremely difficult. Therefore, the equipment was installed in the Aurora Tower (fig. 1). The Tower's three immediate advantages were 1) its proximity to main camp, 2) ease of equipment installation, and 3) ease of access by the GMCC station observer. A disadvantage of the Tower was its proximity to surface obstructions which occasionally compromised clean air sampling.

GMCC occupied the two top floors (14.2 sq. meters each). The top floor housed the primary monitoring systems (CO_2, O_3, aerosols) and stores while the floor below contained the data acquisition system and electronics work bench. Doorway access to the outside from the top floor was provided as well as ladder access through several floors from the main undersnow complex.

This location was occupied only during 1973-1974 season; the entire facility was relocated during the 1974-75 austral summer to the new South Pole station site. The details of the new location will be in the next summary report.

Figure 1. Temporary solar radiation platform with the Aurora Tower and the aerosol/gas sampling mast in the background.

2.3 Barrow

Facilities at the Barrow Observatory were improved during 1974 by the addition of a new structure and completion of wiring of the main laboratory building. A 2.5-meter square wooden wanigan, obtained from the Naval Arctic Research Laboratory, was moved to the station site for storage of various shipping containers, flasks for air sampling, and miscellaneous station equipment. Equipment on the roof sampling platform was wired to station power. Power and signal lines leading to the 17-meter tower were supported above the tundra on wooden racks.

The condition of the access road to the station continued to be a problem. The road was usable but severely drifted during the winter months. It became impassable following the spring thaw. After the fall freeze-up, the support contractor at the main laboratory provided a minimal amount of fill gravel and silt capping material and, after some dragging and plowing, the road was improved to a serviceable condition for the winter. During the remainder of the year, the contractor kept the road plowed and clear.

The GMCC vehicle at Barrow, an International crew-cab pick-up, suffered a transmission failure in October, and was out of operation through the end of the year. Substitute transportation was provided by the local contractor.

2.4 Samoa

Three major events during 1974 will help make Samoa the fourth fully operational observatory within the GMCC program. These were the execution of a 20-year land lease agreement, initial construction of the observatory access road, and the award for construction of the observatory building to a local contracting firm.

On August 12 a final agreement was reached between the United States Government and Chief Iuli Togi, local landowner of the proposed observatory site, for use of 0.1 km^2 (26.70 acres) of land. This lease, No. 05-4-022-55, consists of two parcels of land; one, 0.08 km^2 situated north of a boundary line bearing S85°00'E which passes through a concrete monument, with local coordinates X = 300, 192.44 and Y = 316,974.3, and the other 0.02 km^2 consisting of the new observatory access road right-of-way beginning on the Tula-Onenoa Village Road. Reference is made to a Government of American Samoa Survey Print #1530 and accompanying description dated 28 June 1974. Originally access was by an improved trail built by the U.S. Marine Corps in 1941. However, since the trail went through unsurveyed, unregistered communal land, a property ownership dispute over the right-of-way developed between local Samoan landowners. No solution to the dispute could be reached so a new road was constructed east of the trail. This new routing (fig. 2) is also preferable because it has less grade with less chance of mud slides.

In September the pioneer road was blazed through the new right-of-way by the Government of American Samoa-Public Works Department (fig. 3). In December road construction responsibility was transferred to Kong Yung Construction Company. The road consists of a 4-inch compacted coral base paved with asphalt (fig. 4).

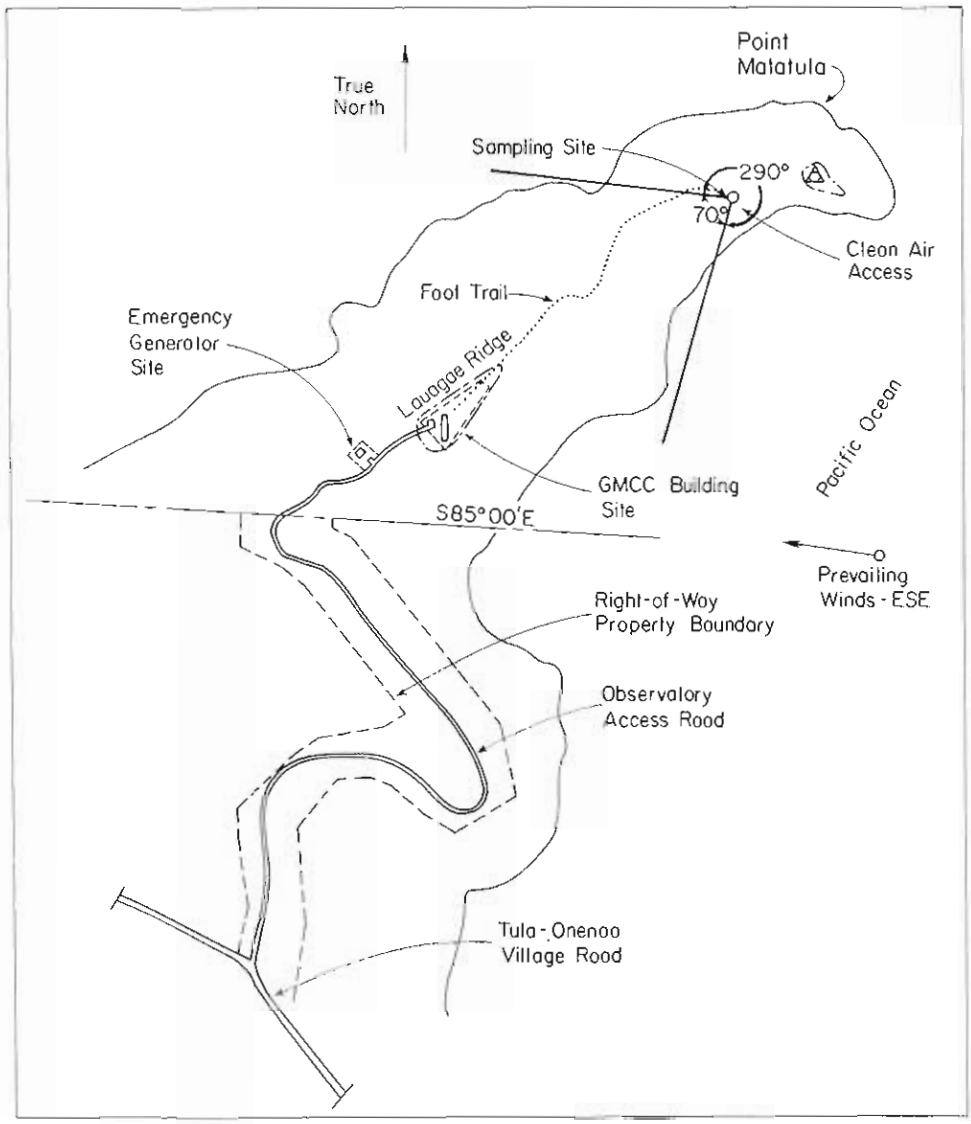

Figure 2. Cape Matatula, American Samoa.

Also in December, Kong Yung was awarded the contract for construction of the observatory building (fig. 5). Construction is expected to commence in April 1975, as soon as the road paving is completed and commercial power is available, and should be completed in August 1975.

The Government of American Samoa agreed to act as our contracting agent during the construction phase of the GMCC program. Thanks are extended to the G.A.S. Public Works Divison and the Office of the Attorney General for their valuable assistance.

Figure 3. Initial road construction, Samoa.

Figure 4. Pioneer road through dense vegetation, Samoa.

Owing to the difficulty of obtaining reliable commercial electric power and the need to protect the scientific instrumentation from the corrosive Samoan environment, we decided to install standby emergency power. A 100-kW diesel unit will meet the power demands for the entire Cape in times of commercial power failure. The generator will be located next to the access road about 110 m down wind from the observatory.

Air sampling is planned at Point Matatula and Lauagae Ridge. The Point is a volcanic promontory almost completely devoid of vegetation, with an elevation of about 25 m above sea level. In 1975 a power line to the Point will be added and a stairway constructed up the very steep hillside. Other additions on the Cape will include a small GMCC remote sampling building and facilities for the first cooperative program with the University of Rhode Island (sponsored by the National Science Foundation). The Rhode Island Group will construct a 19 m air sampling tower and a small instrumentation hut.

Lauagae Ridge has a usable area of about 500 m^2 and an elevation of 77 m above mean sea level. The paved road will terminate on the eastern face of the Ridge and be connected to a foot path leading to the Point.

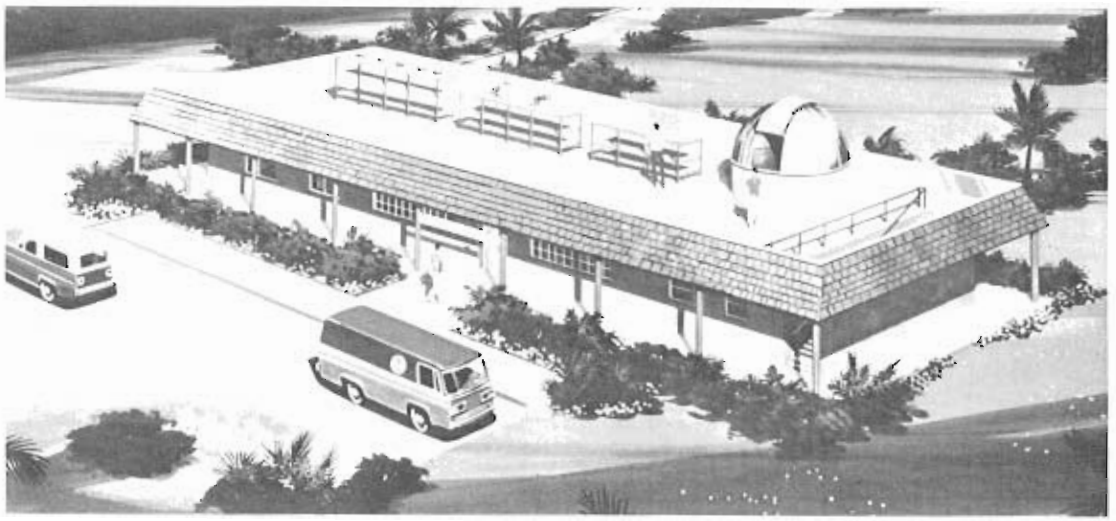

Figure 5. Planned observatory building at American Samoa.

2.5 Planned Stations

2.5.1 West Coast

In June 1974, two 1-year contracts were signed for evaluation of potential GMCC locations along the West Coast of the United States. Depending upon their results and recommendations, we may provide funding for more intensive sampling at one or two sites.

The University of Washington has contracted to study aerosol properties and compositions at three sites having different altitudes and different distances from the coast. Comparing Hurricane Ridge (at 1500 m in the Olympic Mountains), Mt. Octopus (nearer the coast), and Point Grenville (on the coast), the researchers hope to show the advantage of a high-altitude observatory over, or in conjunction with, a low-altitude one. Measurements will be made for three weeks at each site, twice during the year. These measurements include nephelometry, Aitken nucleus counts, surface ozone, meteorology, CO_2 flask samples, and possibly a sunshine switch.

A 1-year contract was awarded to Washington State University to analyse weather data from a north-south strip along the Pacific coast from the Straits of Juan de Fuca to Cape Mendocino, California. Researchers will study wind trajectories, cloud cover (using ERTS satellite photographs), and radiation conditions. They will make three 10-day measurement trips to candidate locations. Their measurements, similar to those of the University of Washington, will also include methane and carbon monoxide.

2.5.2 Bermuda

As in 1973, carbon dioxide flask samples and Gardner condensation nucleus counts were made at High Point, Bermuda, from July to mid-October by Ian Fletcher of the University of Rhode Island. In 1975, samples will be taken only in May and June.

3. OBSERVATORY PROGRAMS

This section is a brief summary of the operating programs and, where relevant, a description of both problems and solutions. The instrument systems used are emphasized.

3.1 Mauna Loa Programs

Several new instruments were added during 1974 to identify and quantify the natural Mauna Loa aerosol. These included a four-wavelength nephelometer to measure the integrated light scattering, a Pollak counter for Aitken nuclei to provide greater sensitivity at low background levels, and an aureole camera to photograph the solar aureole.

A joint ice nucleus program was conducted with Dr. Keith Bigg of the Commonwealth Scientific and Industrial Research Organization (CSIRO) and Mr. Paul Allee of the Atmospheric Physics and Chemistry Laboratory, NOAA. A second program with Dr. Bigg sampled aerosol particles directly on an electron microscope slide for elemental analysis.

Data handling for most continuous monitoring systems was improved with the installation of an acquisition system based on a NOVA 1220 minicomputer. The instruments now feed their data directly to the computer. This allows immediate data check-out which, in turn, provides better equipment adjustment.

Measurements of atmospheric CO_2 continued as in past years at Mauna Loa with an Applied Physics Company infrared analyzer in a cooperative NOAA-Scripps Institution of Oceanography program. In May of 1974, a new URAS-2 CO_2 analyzer system was installed by GMCC with a view toward ultimately replacing the Applied Physics Company instrument for which repair parts are not readily available. It is planned to operate the two instrument systems simultaneously for at least a year in order to obtain a substantial set of comparative data. Current indications are that the two instruments yield CO_2 data that differ by 0.3 ppm on the average. This difference appears to stem from differences in the optical characteristics of the two analyzers.

The original carbon monoxide instrument continued to give difficulty primarily owing to plugging of the phosphorus pentoxide water vapor trap. A new instrument was designed and constructed for installation in 1975.

Table 1 lists all Mauna Loa programs during 1974.

Table 1. Sampling Programs at Mauna Loa

Monitoring Programs	Instrument	Sampling Frequency	Data Record
Gases			
Carbon dioxide	Applied Physics infrared gas analyzer	Continuous	Oct 1958 - present
	URAS-2 infrared gas analyzer	Continuous	June 1974 - present
Surface ozone	Electrochemical concentration cell (ECC)	Continuous	Sept 1973 - present
Total ozone	Dobson spectrophotometer	Discrete	Oct 1957 - present
Fluorocarbons	Evacuated flask	1/week	Sept 1973 - present
Aerosols			
Stratospheric particulates	Lidar	1/week	Apr 1973 - present
Condensation nuclei	Gardner counter	Discrete	Sept 1967 - present
	General Electric counter	Continuous	Sept 1973 - present
	Pollak counter	Discrete	July 1973 - present
Optical properties	Four-wavelength nephelometer	Continuous	Jan 1974 - present
Solar Radiation			
Global spectral irradiance	Ultraviolet radiometer	Continuous	Apr 1972 - present
	Four Eppley pyranometers	Continuous	May 1972 - present
	Eppley bulb-type radiometer	Continuous	Jan 1958 - present
Direct spectral irradiance	Eppley normal incidence pyrheliometer	Continuous	Jan 1958 - present
	Multi-channel pyrheliometer	Continuous	May 1972 - present
Water vapor	Foskett	Continuous	July 1967 - present
Solar aureole	Aureole camera	1/week	June 1974 - present
Meteorology			
Temperature/dewpoint	Hydrothermograph	Continuous	1955 - present
Pressure	Barograph	Continuous	1955 - present
Precipitation	8" raingage	Daily	Dec 1956 - present
	Tipping bucket gage	Continuous	Dec 1956 - present
Winds	Anemometer	Continuous	Dec 1956 - present
Cooperative Programs			
Carbon monoxide-Max Planck Inst.	Chemical reaction with HgO	Continuous	Aug 1973 - present
SO_2, NO_x, NH_3, H_2S-NCAR	Chemical bubbler system	1/ 2 weeks	Mar 1973 - present
SO_2, NO_2 - EPA	Chemical bubbler system	1/ 2 weeks	Aug 1971 - present
Total surface particulates - ERDA	Hi-volume filter	Intermittent	1970's - present
Turbidity - EPA	Dual wavelength sunphotometer	Discrete	1960's - present
Precipitation chemistry-EPA	Misco collector	Discrete	Mar 1973 - present
Rain Sr^{90} - ERDA	Ion exchange column	1/month	Nov 1955 - present
Aerosol particles for analysis - CSIRO	Impactor/precipitator	Discrete	Aug 1971 - present
Surface Tritium - U. of Miami	Molecular sieve	2-day averages	Aug 1971 - present

3.2 South Pole Programs

Table 2 lists GMCC programs sent to South Pole station for 1974 operation together with previously established programs. Continuous CO_2 measurements were not made because the optical detector of the analyzer was damaged by cold exposure during shipment to the station.

Following is a brief review of equipment performance and some of the operational difficulties.

ECC meter. A persistent problem in the ECC (Electrochemical Concentration Cell) meter was a lack of sensitivity evidenced by low readings with respect to the MEC (McMillan Electronics Corporation) analyzer and ozone generator outputs. (Both Regner and MEC ozone generators were available for calibration checks.) Some improvement was realized by not passing air through the SO_2 scrubber housing but connecting the inlet directly to the

Table 2. Sampling Programs at South Pole Station

Monitoring Programs	Instrument	Sampling Frequency	Data Record
Gases			
Surface ozone	Electrochemical concentration cell (ECC)	Continuous	Dec. 1971 - present
	Chemiluminescent meter (MEC)	Continuous	Jan. 1974 - present
Total ozone	Dobson spectrophotometer	Discrete	Dec. 1963 - present
Aerosols			
Condensation nuclei	Gardner counter	Discrete	Dec. 1971 - April 1974
	General Electric counter	Continuous	Jan. 1974 - present
	Pollak counter	Discrete	Jan. 1974 - present
Solar Radiation			
Global spectral irradiance	Four Eppley pyranometers	Continuous during daylight period	Feb. 1974 - present
	Ultraviolet radiometer	Continuous during daylight period	Feb. 1974 - present
Cooperative Programs			
CO_2 sampling - Scripps	Evacuated flasks	1/week	1955 - present
Total surface particulates - ERDA	Hi-volume filter	Intermittent	May 1970 - present
Turbidity - ERDA	Dual wavelength sunphotometer	Discrete	Jan. 1974 - present

air pump. At times, the ozone concentration indicated by the ECC meter was less than 50 percent of the level indicated by the MEC analyzer. A more detailed account of procedures used to improve ECC performance is available in the instrument log for this program.

MEC analyzer. The MEC analyzer performed satisfactorily from mid-March 1974 until station turnover in mid-November. Its operational status was uncertain during late January and early February 1974 because the annual supply of ethylene was lost en route to the South Pole. However, a substitute ethylene supply, obtained in Christchurch, N.Z., by NSF, arrived at South Pole station on the last flight of 1973-1974 summer season (Feb. 16) Although the substitute ethylene was apparently industrial grade and therefore not as pure as specified by the manufacturer, it was used throughout the year with no obvious decrease in instrument performance.

The three instruments available for measuring Aitken nucleus concentrations at the South Pole during 1974 were: 1) a General Electric Condensation Nucleus counter, 2) a Pollak counter and 3) a Gardner counter. The Pollak was most sensitive to low aerosol concentrations. It was used as a standard for comparison with the other instruments. The Gardner, with its shorter condensation tube, was not sensitive enough and its use was discontinued early in the year.

General Electric (GE) Condensation Nucleus Counter. Proper lubrication of the rotary valve is important to performance of the counter, particularly in the extremely dry, cold air at the South Pole. An ambient temperature of >20°C was sufficient for proper lubrication performance.

Initially, air for sampling was obtained from outlets at the base of an air sampling mast. All three instruments sampled ambient air isokinetically. A prehumidifier was used with the GE counter during the first few months of operation; it was later set aside since it produced no significant difference in instrument operation.

During June, it became evident that aerosols were being stripped from air passing through the aerosol sampling stack. As a remedy, Pollak and GE inlet methods were changed. Holes were drilled through the Aurora Tower wall and short lengths of aluminum tubing were inserted to obtain air approximately 30 cm away from the wall at a height of 2.3 m above the snow surface. Similar lengths of tygon tubing (2 m), were then used to route air to the GE and Pollak inlets. This inlet configuration was maintained for the duration of winter and sunrise period until station personnel turnover.

Pollak Counter. Daily observations with the Pollak counter at approximately 0000 GMT and 1200 GMT coincided with radiosonde launches. During the sunrise period, from September 10 through October 1, three to four observations per day were made. The additional observations yielded better resolution of concentration changes during sunrise and also provided a more frequent quality control monitor of the continuous record collected with the GE counter.

Solar Radiation Array. The GMCC solar radiation array was operational during February and March 1974 and from October 2 until turnover in mid-November 1974. It consisted of four Eppley Precision Spectral Pyranometers with QG, GG, OG, and RG filters and an additional UV sensor.

A normal incidence sensor and an Eppley tracking mount were installed on the Aurora tower roof and collected data for part of February, October, and November 1974. A ventilated net radiometer was operational during the entire year.

Thomas Corporation diaphragm pumps directed a jet of air across the sensor domes which kept the domes frost-free in temperatures warmer than approximately -40°C. In temperatures below -40°C, the domes were cleaned daily with ethyl alcohol.

3.3 Barrow Programs

All programs are listed in table 3.

In January a cooperative program of CO_2 flask sampling for the Scripps Institution of Oceanography was initiated on a biweekly basis. The flask sample data are compared with data collected continuously with the UNOR instrument and with the data from the GMCC flask samples.

Four pyranometers with QG, GG, OG, and RG filters and a pyrheliometer were installed in June and data recording commenced on a Leeds and Northrup recorder. A ultraviolet radiometer was added to the system in July.

The cooperative aerosol sampling program conducted by Dr. Fritz Went of the Desert Research Institute, Reno, Nevada, was expanded with the addition of a preferential sampling system. It employs high-volume air filters which operate only when the winds are from the favorable or non-polluted directions. The samples are used for chemical analysis of the organic content of airborne aerosols.

A long-tube, light emitting diode (LED) type Gardner counter was acquired in November, to supplement the normal Gardner counts taken during periods of low Aitken nucleus concentration.

During 1974 preliminary work was completed for the installation of a data acquisition system (ICDAS). Racks were installed and preliminary wiring was completed for electrical power and signal lines to the computer.

3.4 Samoa Programs

A modest program of air sampling and meteorological measurements continued through 1974 as listed in table 4. Only portable battery or spring powered instruments could be used because of the lack of commercial power. Air temperature, relative humidity, and barometric pressure were measured on Laugae Ridge while rainfall, wind speed and direction, and temperature were

Table 3. Sampling Programs at Barrow

Monitoring Programs	Instrument	Sampling Frequency	Data Record
Gases			
Carbon dioxide	UNOR infrared gas analyzer	Continuous	Mar. 1973 - present
	Evacuated glass flask	1/week	Apr. 1971 - present
Total ozone	Dobson spectrophotometer	Discrete	Aug. 1973 - present
Surface ozone	Electrochemical concentration cell (ECC)	Continuous	Mar. 1973 - present
Fluorocarbons	Evacuated flask	1/week	Sept 1973 - present
Aerosols			
Condensation nuclei	Gardner counter	Discrete	Sept 1971 - present
	G.E. condensation nucleus counter	Continuous	May 1973 - present
Solar Radiation			
Global spectral irradiance	Four Eppley pyranometers	Continuous	June 1974 - present
	Ultraviolet radiometer	Continuous	June 1974 - present
Meteorology			
Temperature	Hygrothermograph	Continuous	Feb 1973 - present
Dewpoint temperature	Hygrothermograph	Continuous	Feb. 1973 - present
Pressure	Microbarograph	Continuous	Feb. 1973 - present
Precipitation	8" raingage	Discrete	Feb. 1973 - present
Cloud cover	Observer	Discrete	Sept 1971 - present
Snow cover	Observer	Discrete	Oct. 1974 - present
Wind speed/ direction	Bendix aerovane	Continuous	Feb. 1973 - present
Cooperative Programs			
Turbidity - ERDA	Dual wavelength sunphotometer	Discrete	Mar. 1973 - present
Precipitation chemistry - EPA	Misco collector	Discrete	Sept 1973 - present
Sfc. global radiation - SRBL	Eppley pyranometers	Continuous	Apr. 1973 - present
Total surface particulates - DRI	Hi-volume sampler	Continuous	Oct. 1973 - present
CO_2 sampling - Scripps	Evacuated flasks	1/ 2 weeks	Jan. 1974 - present

measured on Cape Matatula. CO_2, fluorocarbons, and condensation nuclei were measured at both locations. Atmospheric turbidity readings and rainfall collection for precipitation chemistry were carried out at the NWS weather station at Pago Pago International Airport.

A continuing series of malfunctions prevented operation of the National Center for Atmospheric Research sampling system for SO_2, NO_x, NH_3, and H_2S in 1974.

Table 4. Sampling Programs at Samoa

Monitoring Programs	Instrument	Sampling Frequency	Data Record
Gases			
Carbon dioxide	Evacuated glass flask	1/week	July 1973 - present
Fluorocarbons	Evacuated glass flask	1/week	Sept 1973 - present
Aerosols			
Condensation nuclei	Gardner counter	Discrete	June 1973 - present
Meteorology			
Temperature	Hygrothermograph	Continuous	June 1973 - present
Dewpoint temperature	Hygrothermograph	Continuous	June 1973 - present
Pressure	Microbarometer	Continuous	June 1973 - present
Precipitation	Tipping bucket gage	Discrete	June 1973 - present
Wind speed/direction	MRI automated weather station	Continuous	June 1973 - present
Cooperative Programs			
Precipitation Chemistry-EPA	Misco collector	Discrete	Aug. 1973 - present
Turbidity - ERDA, WMO	Dual wavelength sunphotometer	Discrete	Aug. 1973 - present
SO_2, NO_x, NH_3, H_2S — NCAR	Chemical bubbler system	1/ 2 weeks	Oct. 1973 - present

4. MEASUREMENT PROGRAMS

This section provides information on systems qualitatively and quantitatively, and presents representative data collected and analyzed during the year.

4.1 Measurement of Gases

4.1.1 Carbon Dioxide Measurement

The 1974 carbon dioxide data from Mauna Loa Observatory were taken simultaneously with the new URAS-2 analyzer and the Scripps Institution's Applied Physics analyzer. Simultaneous measurement will continue long enough for the data to be correlated.

Computer programs were devised in 1974 for processing the Barrow and Mauna Loa CO_2 analyzer data. These programs permit processing of all data and of data selected on the basis of criteria including instrument zero and span drift, wind speed and direction, humidity, air pollution index, and

data variability. Current effort is directed toward optimizing the application of the data selection criteria. Because final calibrations of the CO_2 reference gases used in the program have not been made, all data obtained to date are provisional.

Provisional monthly CO_2 concentrations determined at Barrow and Mauna Loa are listed in table 5, and plotted in figure 6. All values are expressed in CO_2 ppm index, based on the Scripps Institution of Oceanography Index Scale devised by C. D. Keeling in 1957. Final work on converting CO_2 index values to true concentrations is currently progressing at Scripps, and results are expected to be available in 1975.

Table 5. Provisional Mean Monthly CO_2 Index Values Determined from Analyzer Sampling

1974	Barrow, Alaska	* MLO, Hawaii
January	330.33 ppm	
February	328.86	
March	329.43	
April	330.44	
May	329.28	
June	328.56	324.93
July	324.39	323.95
August	319.84	322.44
September	320.67	321.21
October	323.64	321.29
November	326.13	322.53
December	328.71	323.30

* Measured by the URAS-2 analyzer

The Barrow data plot of figure 6 clearly indicates that the CO_2 concentration is increasing with time, although data are insufficient for computation of a meaningful trend. The large amplitude of the annual cycle at Barrow of 12 ppm peak-to-peak (twice that at Mauna Loa) is also clearly evident.

Another interesting feature of the Barrow CO_2 data is the small variability in the data at times when atmospheric CO_2 concentrations are not particularly affected by plant growth, i.e., from February to June. At such times, standard deviations in mean monthly CO_2 values based on daily means

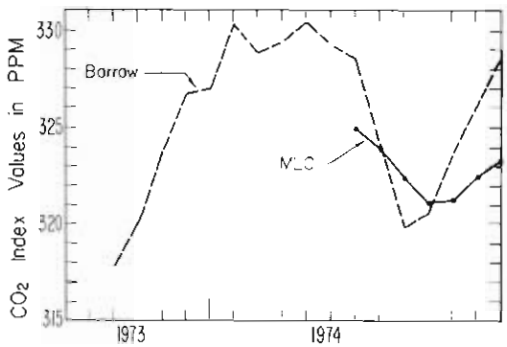

Figure 6. Provisional CO_2 analyzer data from Barrow and Mauna Loa—monthly means.

are generally less than 0.5 ppm, and approach 0.2 ppm for some of the months. In contrast, when the atmosphere in the Arctic is affected by CO_2 uptake by plants, the observed CO_2 data are highly variable, with standard deviations associated with monthly mean CO_2 concentrations ranging from 0.5 ppm to slightly over 2.5 ppm. Figure 7 shows this rapid decrease for July 1974. In contrast, figure 8 shows the increase in CO_2 when biological activity diminishes.

The Barrow data show, also, that during the summer when uptake of CO_2 by biota occurs, rather pronounced diurnal variations in CO_2 can arise. This is illustrated in figure 9 where the amplitude of the diurnal variation is 4 to 5 ppm. Occasionally the amplitude of this oscillation may reach 7 or 8 ppm. This diurnal cycle is not, however, a regular phenomenon; it seems to occur erratically. The data shown, nevertheless, point out some difficulties that occur when one uses a data selection process to obtain optimum quality data. Diurnal variations in CO_2 appear also at Mauna Loa. These are, however, closely linked to the upslope and downslope wind regimes at the observatory. Figure 10 illustrates the effect, where the amplitude of the diurnal cycle is seen to approach 4 ppm.

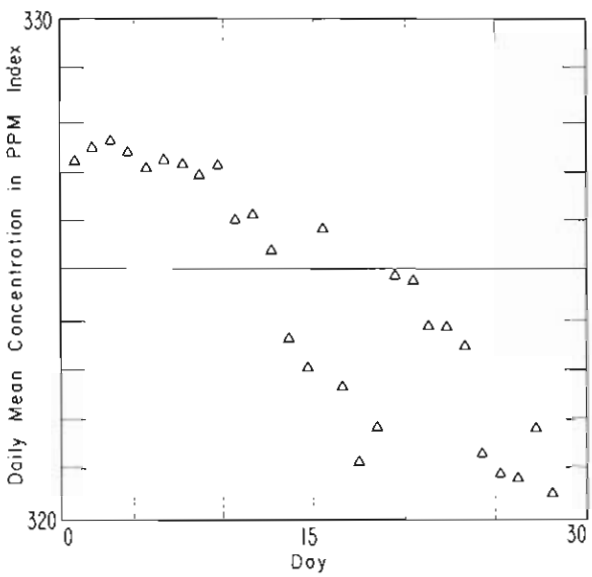

Figure 7. Decrease in concentration values due to uptake of CO_2 by biota, at Barrow, July 1974.

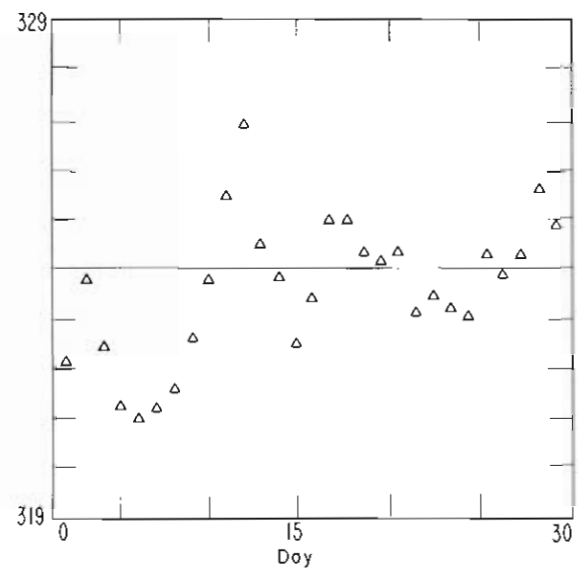

Figure 8. Increase in CO_2 values when biological activity diminishes, at Barrow, October 1974.

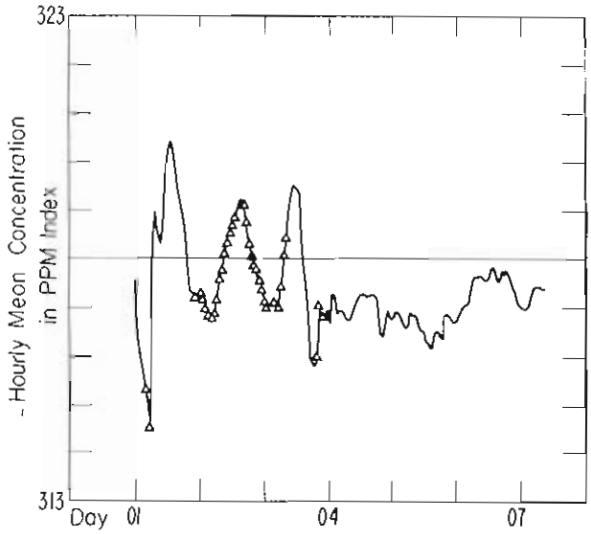

Figure 9. Diurnal variations in atmospheric CO_2 observed at Barrow, Alaska, August, 1973.

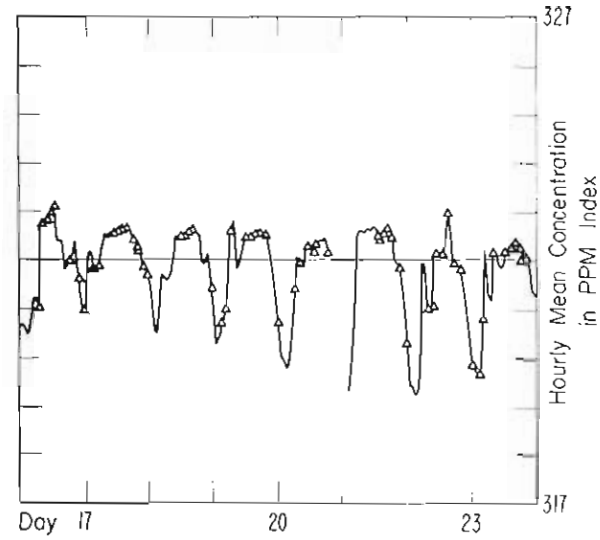

Figure 10. Diurnal variations in atmospheric CO_2 observed at Mauna Loa, Hawaii, August, 1974.

Atmospheric CO_2 concentrations were also monitored by flask sampling throughout 1974 at Barrow, Alaska, and Cape Matatula, American Samoa. A similar program, of short duration, was conducted in Bermuda from July to October. In general, four samples were obtained each month at weekly intervals at the stations, each sample comprising air contained in a pair of ½-liter glass flasks. A complete set of data was, however, not obtained since in many instances data from paired flasks did not agree sufficiently closely owing to improper sampling or, possibly, contamination. To improve the quality of future data, a new technique is under development whereby flask pairs will be filled simultaneously with air entering the flasks via a long sampling tube. At stations with CO_2 analyzers, flask sampling systems will be built into the analyzer plumbing so that air passing through the CO_2 analyzer air sampling line will simultaneously flush and fill the flask pairs. This technique will also allow the calibrations of station CO_2 analyzers to be compared with the calibration of the Boulder analyzer that is used for CO_2 flask sample analyses.

Provisional monthly mean flask sample CO_2 index values are given in table 6. Plots of the Barrow and Samoa data, including data obtained prior to 1974, are shown in figure 11. Here, again, a striking feature of the plots is the large difference between the annual cycle peak-to-peak amplitude that occurs at a high latitude station like Barrow and that which is observed in near-equatorial Samoa.

Sufficient Barrow flask data are available for the computation of the secular trend in CO_2. As shown in figure 12, the rate of increase of atmospheric CO_2 at Barrow is 1.36 ppm/year. The rate is derived from a least squares fit of a trend line to data from which the annual cycle has been removed. For comparison, similar data obtained at ocean station "Charlie" in

Table 6. Provisional Mean Monthly CO_2 Index Values Determined from Flask Sampling

Year Month	Barrow 71°N 156°W			Bermuda 32°N 64°W			Samoa 14°S 170°W		
	No. of Samples	Mean Conc. Index	σ	No. of Samples	Mean Conc. Index	σ	No. of Samples	Mean Conc. Index	σ
1974									
January	2	329.67	0.94				5	325.61	0.91
February	1	331.28	-				2	324.68	0.48
March	1	330.44	-				1	325.07	-
April	1	329.90	-				3	324.76	0.67
May	1	330.06	-				3	324.77	0.82
June	1	330.80	-				2	324.46	0.08
July	3	324.84	4.42	5	324.89	0.76	2	324.87	1.17
August	4	318.23	0.74	3	322.71	0.20	4	325.07	1.67
October	5	324.22	2.78	6	323.04	0.56	3	325.53	0.11
November	3	327.02	1.27				2	325.82	2.35
December	5	328.77	2.16				3	324.29	1.32

the Atlantic, and Niwot Ridge, Colorado, are shown. At Niwot Ridge, the secular rate of increase of atmospheric CO_2 is 1.14 ppm/year based on data obtained from February 1968 to January 1973. Adding to the plot another year's data, which appear to be less reliable than previous data, increases this value to 1.23 ppm/year. Ocean station "Charlie" data, on the other hand, yield a significantly lower trend value of only 0.84 ppm/year. Whether this result is characteristic for observations made at an ocean station as compared with observations made on land is yet to be determined.

4.1.2 Total Ozone Measurement

Total-ozone measurements were continued at twelve stations in the U.S. during 1974 (table 7). Since modernization of most of the instruments (as described in GMCC Summary Report 1973), very few data have been lost because of instrument malfunctions.

Calibrations. Work was completed in the spring of 1974 in electronically modifying and recalibrating Green Bay Dobson spectrophotometer No. 58. This instrument was recalled to Boulder late in 1973 because of general deterioration in its performance. Final calibration of the instrument had to be delayed until the spring when the sun was high enough in the sky to allow for accurate calibration data to be obtained.

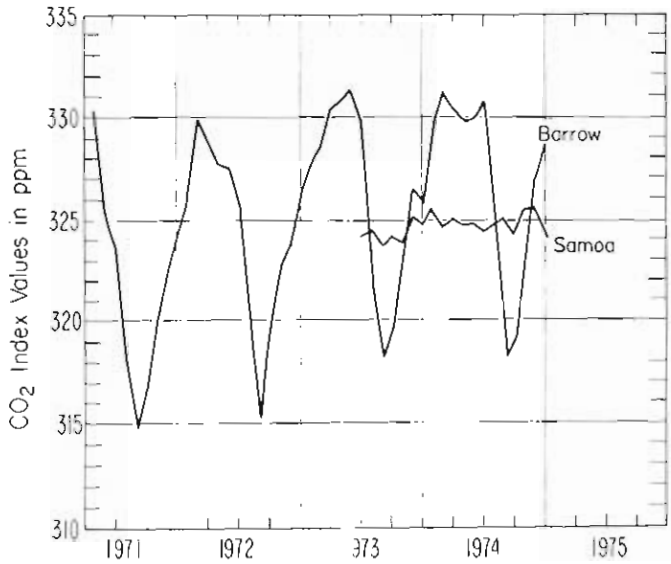

Figure 11. Barrow and Samoa CO_2 flask data—provisional monthly means.

Also electronically modified and calibrated during 1974 was Dobson spectrophotometer No. 91, which belongs to the National Center for Atmospheric Research (NCAR) in Boulder, Colorado. This instrument is not used in the U.S. total-ozone network but is operated at NCAR on an intermittent basis.

A major breakdown of Huancayo, Peru, instrument No. 87 occurred during November and December 1974. This is the only spectrophotometer in use in our network that has not been electronically modernized. A special effort will be made during 1975 to modify the electronics of this instrument, and to recalibrate it by comparison with our reference spectrophotometer No. 83. Huancayo is a very useful station for trend analysis since ozone variations there are small, and it is located at a latitude where the quasi-biennial oscillations are minimal. For this reason Huancayo represents an excellent "baseline" station that should be carefully monitored.

International Comparison of Dobson Spectrophotometers. The highlight of the year's activity in the total-ozone program was the U.S. participation in an international comparison of total-ozone measuring instruments held at Belsk, Poland (fig. 13). This activity was recommended in 1972 by the International Ozone Commission (IOC) of the International Association of Meteorology and Atmospheric Physics (IAMAP). The primary purpose of the comparisons was to ensure the comparability of ozone measurements made in the global network

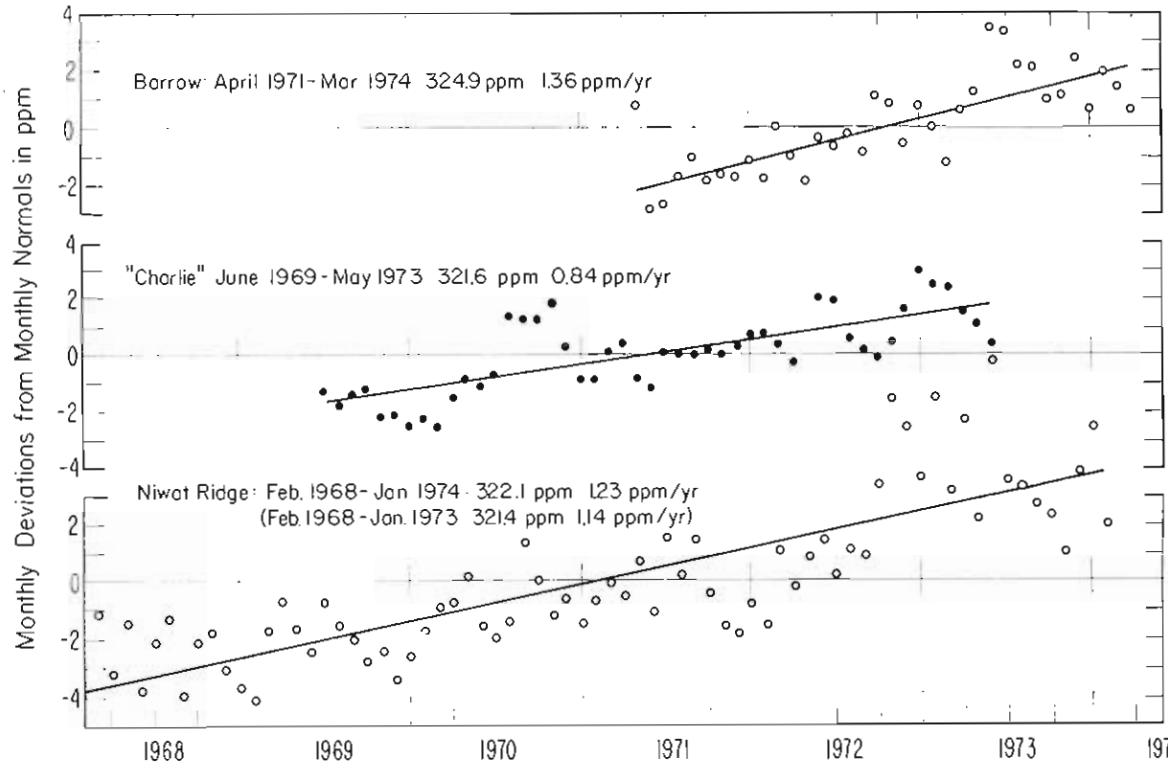

Figure 12. Secular increases of atmospheric CO_2 determined from flask sampling at Barrow, station "Charlie," and Niwot Ridge.

Table 7. U. S. Dobson Ozone Spectrophotometer Stations

Station	Period of Record	Inst. Ser. No.	Agency
Bismarck, N. D.	010163 - Present	33	NOAA-ARL
Caribou, Maine	010163 - Present	34	NOAA-ARL
Green Bay, Wisc.	010263 - Present	38	NOAA-ARL
Tallahassee, Fla.	060273 - Present	58	Fla. State U.
Mauna Loa, Hawaii	010264 - Present	63	NOAA-ARL
Wallops Island, Va.	070167 - Present	72	NOAA-ARL
Barrow, Alaska	080273 - Present	76	NOAA-ARL
Nashville, Tenn.	010163 - Present	79	NOAA-ARL
South Pole	120563 - Present	80	NOAA-ARL
Boulder, Colo.	090166 - Present	82	NOAA-ARL
White Sands, N.M.	010572 - Present	86	Dept. of Army
Huancayo, Peru	021464 - Present	87	NOAA-ARL

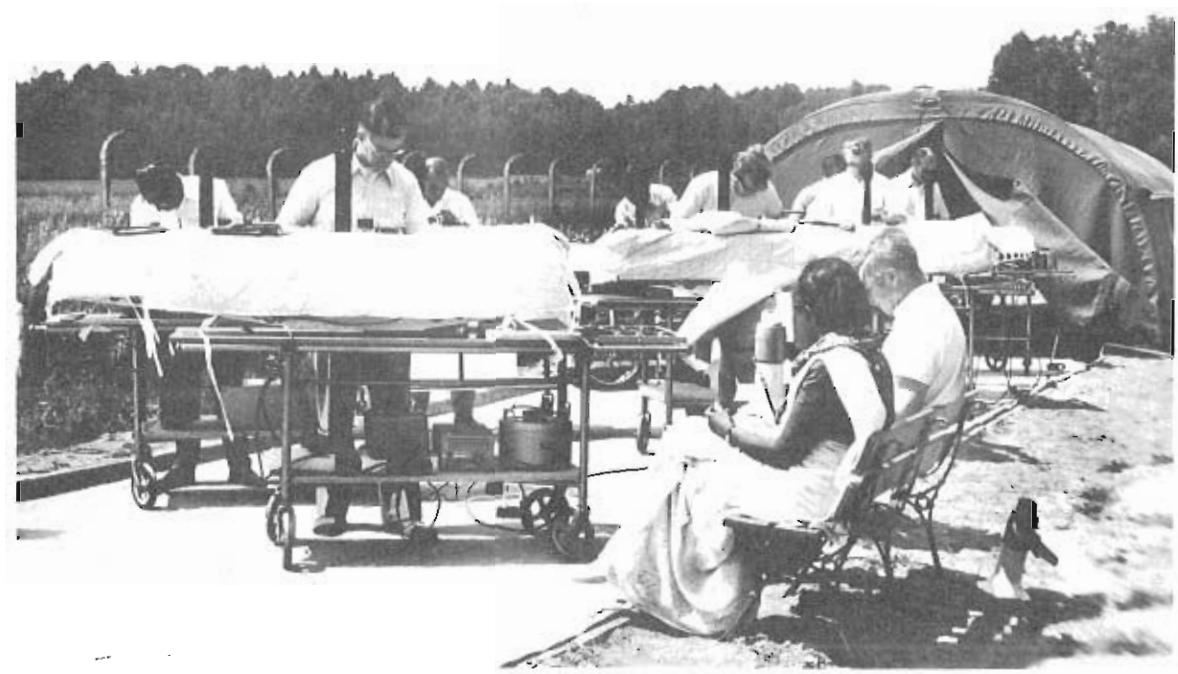

Figure 13. International comparison of Dobson ozone spectrophotometers at Belsk, Poland.

of total-ozone measuring stations. Although it is now possible to obtain from satellites global data of total ozone, high quality ground observations of total ozone are still necessary because their high accuracy and their long-term continuity provide controls on the satellite data. Thus, ozone measurements at the ground, made with Dobson ozone spectrophotometers, still remain the primary basis of all accurate measurements of atmospheric total ozone.

At the invitation of the Institute of Geophysics of the Polish Academy of Sciences, the international comparison of ozone instruments, held from June 24 to July 7, 1974, brought together representatives from the United States, Canada, United Kingdom, German Democratic Republic, Poland, Switzerland, Egypt, Hungary, India, Soviet Union, Romania, and France. The meeting was sponsored jointly by the International Ozone Commission and the World Meteorological Organization, and conducted by the Institute of Geophysics under the direction of Professor C. D. Walshaw and the honorary chairmanship of Professor G. M. B. Dobson. All arrangements were made by the Polish Organization Committee under the chairmanship of Dr. A. Losiowa. Ten Dobson spectrophotometers and three filter instruments (two Soviet M-83 models, one French Vassy filter ozonometer) were compared.

Simultaneous observations were obtained on six days using as many as nine Dobson instruments in one of the sessions. Although the meteorological observing conditions were variable, the data quality was good enough to allow

the elimination of large differences in calibrations (mainly in the extra-terrestrial constant N_0) found among the instruments. It was agreed to regard U.S. ozone spectrophotometer No. 83 as the standard for the true value of N_0. The N-value corrections determined for the various instruments to reduce their calibration levels to that of the U.S. spectrophotometer are given in table 8.

Table 8. Dobson Ozone Spectrophotometer N-Value Corrections

Inst. No.	ΔN_C	ΔN_A	ΔN_D
41	+0.006	+0.002	-0.014
64	-0.012	+0.084	-0.024
77	-0.003	-0.017	+0.006
83	0	0	0
84	+0.016	+0.046	-0.010
96	-0.031	-0.054	-0.056
101	-0.007	+0.001	-0.017
108	-0.012	-0.015	-0.040
110	-0.023	+0.018	-0.033
112	-0.025	-0.030	-0.006

Participants considered the meeting to have been most successful not only in the achievement of the basic object, but also in the valuable exchange of experience between the different countries.

Data. Figure 14 shows plots of mean monthly total-ozone amounts determined at the U. S. station network during 1974. The vertical bars in the plots are standard deviations associated with the means, and represent the natural variability in data as well as observer and instrument errors.

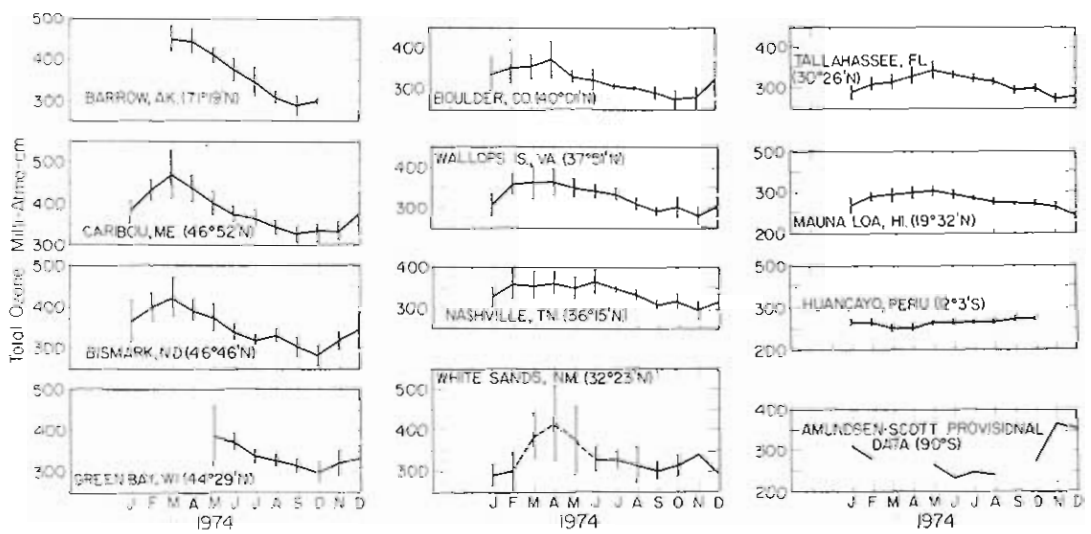

Figure 14. Mean monthly total ozone with standard deviations for U.S. Dobson ozone spectrophotometer network.

Of increasing importance is the question of global trends in atmospheric total ozone. In recent years, concern has been expressed within the scientific community about possible ozone destruction by NO emitted from supersonic jet transports (or atomic bomb explosions) which could lead to an increase in solar ultraviolet radiation at ground level with possible detrimental effects on life. More recently, partial destruction of the Earth's protective ozone shield by fluorocarbons has become an issue. At the present time, observations made with Dobson spectrophotometers offer the most reliable means of measuring secular changes in atmospheric total ozone.

The increase in total ozone that occurred in the Northern Hemisphere during the 1960's (see, e.g., GMCC Summary Report 1972) appears to have ended during 1970. Figure 15 shows total-ozone trend lines fitted to data obtained from 1970 to 1974 at seven stations in the U.S. network. Note that decreases in total ozone have occurred at all stations, with the computed rates of decrease ranging from 1.0% per decade at Huancayo, Peru, to 11.2% per decade at Bismarck, North Dakota. Caution must be exercised, however, in attributing a cause to the observed decreasing ozone amounts. It is not yet possible to separate effects of natural phenomena (e.g., small temporal variations in solar ultraviolet energy output) from possible changes due to man's activity.

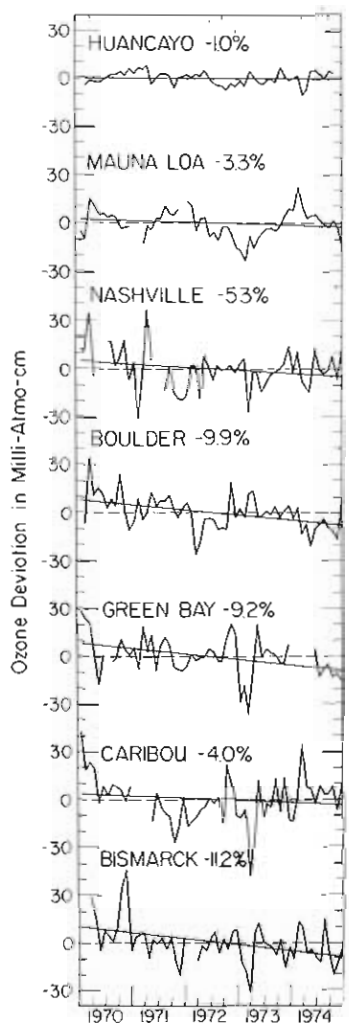

Figure 15. Mean monthly total ozone deviations from monthly normals. Linear trends have been fitted to the data. Percentages are decreases since 1964.

4.1.3 Surface Ozone

Continuing surface ozone measurements at Barrow, Alaska; Mauna Loa, Hawaii; South Pole station, Antarctica, have begun to give a picture of the surface ozone distribution at clean air locations in three distinctly different parts of the world. Surface ozone distribution at these locations is summarized in the following section. A description of improvements in instrumentation and plans for the future are also included.

Data Summary. The most easily detected variation in the surface ozone data is the annual cycle. The average variations at four stations are depicted in figure 16. Although the observations cover a period of less than 2 years at Barrow, Boulder, and Mauna Loa, the qualitative features of this variation are probably correct. At Barrow and South Pole maximum ozone occurs in the

winter and the minimum in the summer. A phase shift appears in the Mauna Loa and Boulder data compared with the high latitude station data, with the maximum at these two locations occurring in the spring, and the minimum in the autumn. (The Mauna Loa data actually indicate an ozone minimum in summer, but the results obtained to date are provisional).

The annual variation in surface ozone at Mauna Loa is very nearly in phase with the total-ozone variation. At Boulder the maximum in total ozone preceeds that in surface ozone by about 1 month. At Barrow, on the other hand, the maximum in surface ozone occurs 3 months before that in total ozone, indicating that at the higher latitudes represented by Barrow, direct transport of ozone from the stratosphere above to the troposphere below is probably not the main determiner of the surface ozone distribution. In the Southern Hemisphere at South Pole station, the maximum in surface ozone also precedes that in total ozone by 3 to 4 months, although at South Pole the maximum in surface ozone occurs later in the winter than at Barrow.

An important feature of surface ozone, observed at stations where local pollution occurs, is the diurnal variation with an early morning minimum and an afternoon maximum. The maximum results when ozone is produced photochemically in polluted air; the minimum is due to chemical and catalytic destruction of ozone at night by pollutants such as NO and various particulate materials. An example of such diurnal variations is shown in figure 17.

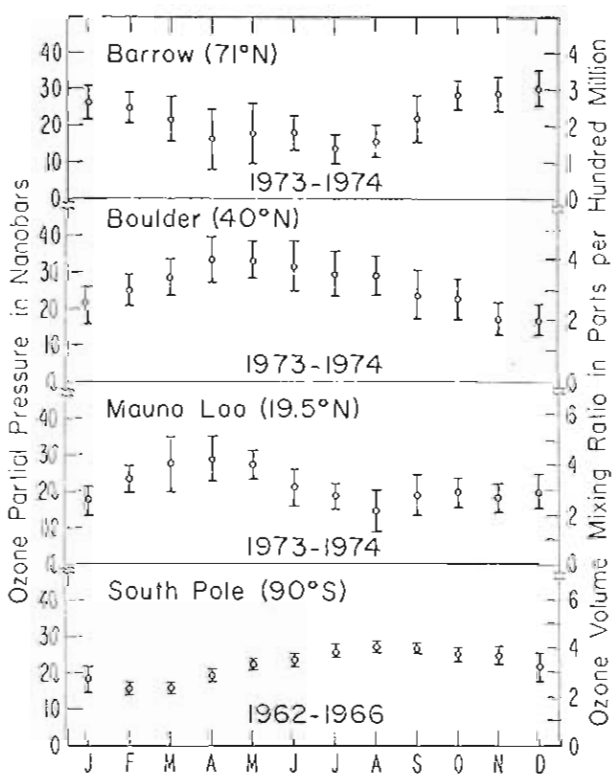

Figure 16. Surface ozone annual cycles at Barrow, Boulder, Mauna Loa, and South Pole.

Diurnal variations in total ozone also occur at Mauna Loa (fig. 18). The variations here, however, result from two distinct wind regimes which daily bring air from different sources to the observatory. During daytime, upslope winds predominate, bringing air to the observatory whose ozone content has been partially depleted by passage over rocks and vegetation. Night air at the observatory generally arrives from above the trade wind inversion, and since its downslope trajectory takes it only a relatively short distance over rock, the destruction of ozone within it is minimal. The Barrow and Antarctica stations reveal a noteworthy lack of diurnal variations (figures 19, 20, and 21). Note that the vertical scales are greatly expanded compared with the vertical scales of figures 18 and 19. The very small diurnal variations at Barrow during December to August and at Eights station during December to February are possibly artifacts of the observations rather than real variations.

At all of the non-Antarctic stations there are also day-to-day variations during all seasons of the year associated with changing weather systems. At the Antarctic stations the late spring and summer months show day-to-day variations in connection with breakdowns in the strong, low-level temperature inversion.

Equipment. With the advent of a computerized data acquisition system at South Pole Observatory a need for an updated version of the electrochemical concentration cell (ECC) ozone meter became apparent. A modernized ECC meter has been built and tested which provides a computer-compatible data signal, an improved air pump, a computer-controllable zero switching capability, and which can be mounted in an instrument rack. This meter is to be installed at all of the observatories in 1975.

During 1974 a chemiluminescent type of ozone meter was used at South Pole in addition to the ECC meter. This instrument uses the principle of

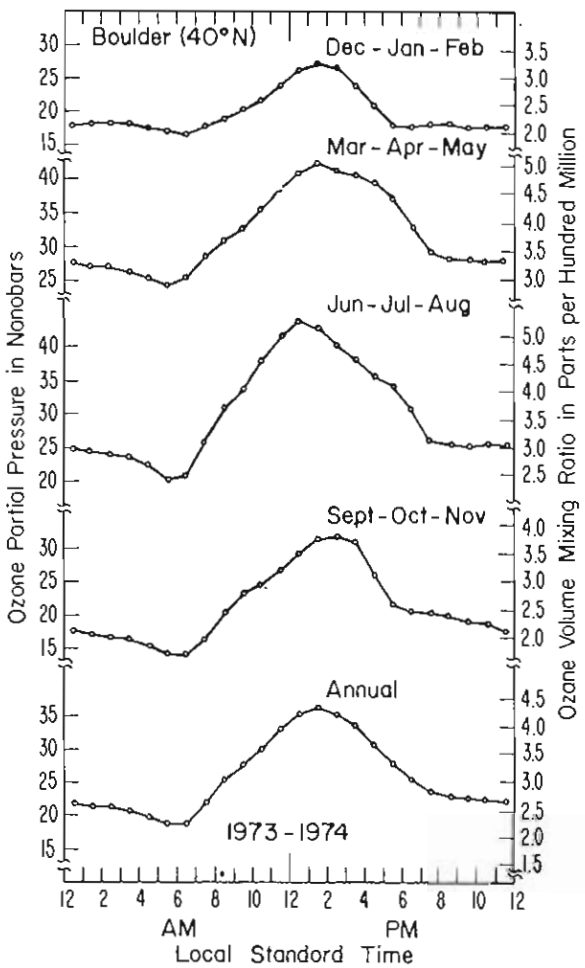

Figure 17. Diurnal plots of Boulder surface ozone data—seasonal and annual averages.

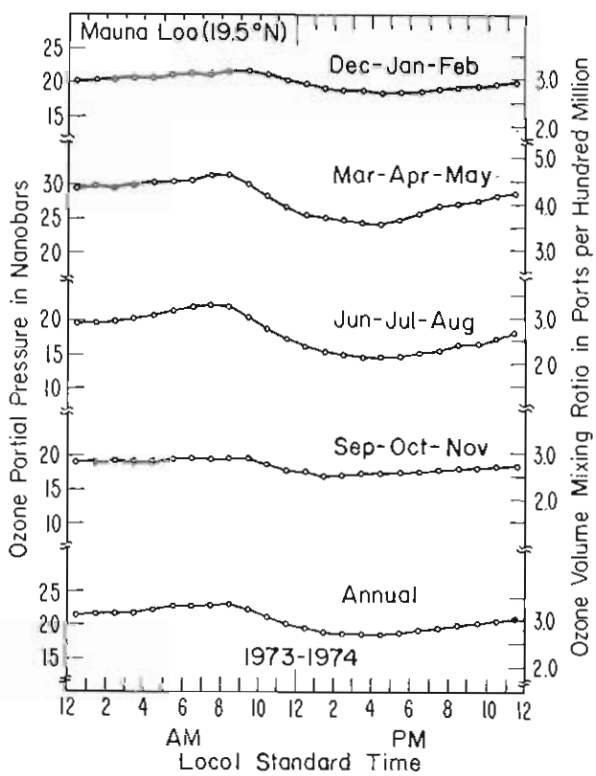

Figure 18. Diurnal plots of Mauna Loa surface ozone data—seasonal and annual averages.

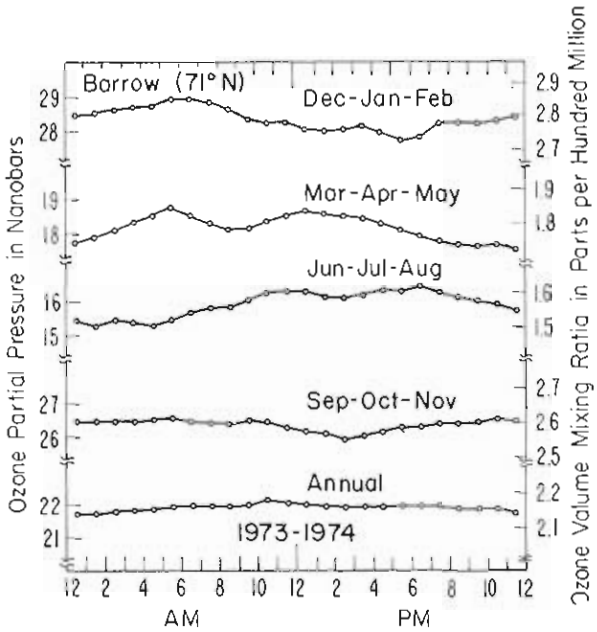

Figure 19. Diurnal plots of Barrow surface ozone data—seasonal and annual averages.

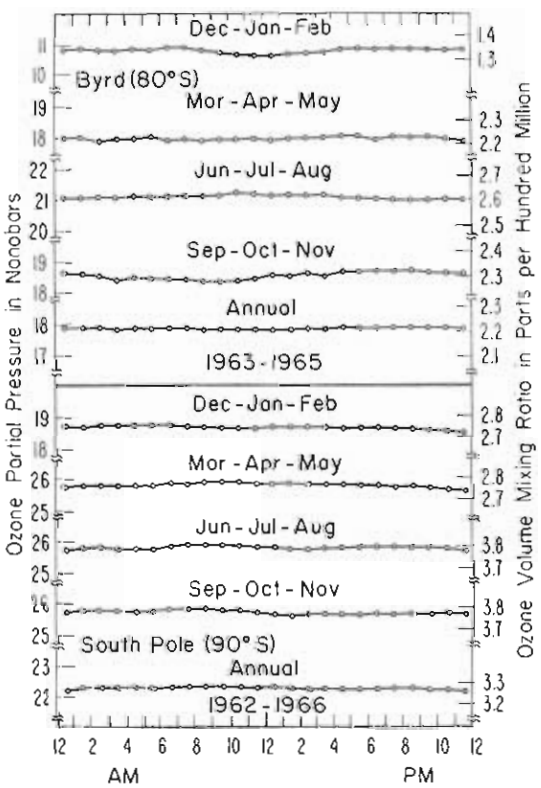

Figure 20. Diurnal plots of Byrd and South Pole surface ozone data—seasonal and annual averages.

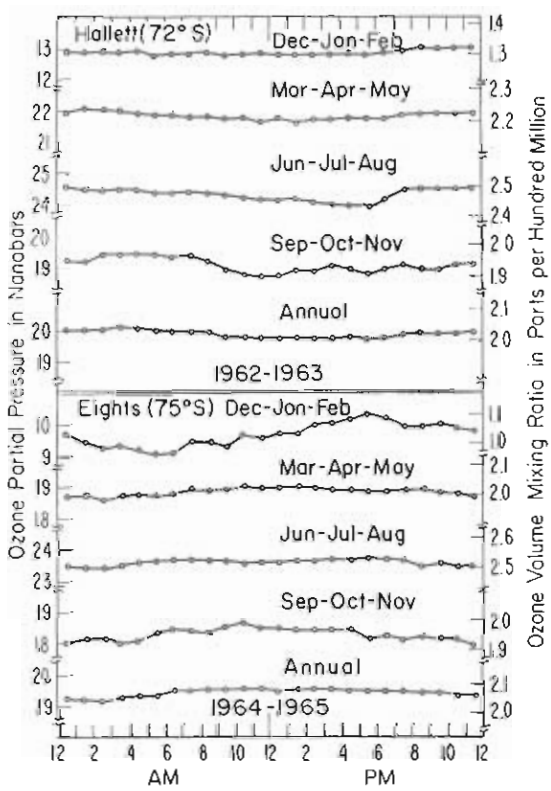

Figure 21. Diurnal plots of Hallett and Eights surface ozone data—seasonal and annual averages.

photometric detection of the chemiluminescence resulting from the flamless reaction of ethylene gas with ozone (fig. 22). Air and ethylene are drawn into a Pyrex reaction chamber that contains an optically flat window mounted at the end of a photomultiplier tube. If any ozone is present in the sample air stream, the ethylene and ozone produce a flamless reaction emitting photons which are dtected by the photomultiplier tube. The signal is amplified by an electrometer; and the output signal is directed to signal conditioning and buffer amplifiers. The entire photomulitplier tube assembly and electrometer are contained by a thermoelectrically cooled housing to minimize short- and long-term signal drafts due to temperature drifts in the photomultiplier dark current.

The sensitivity of the chemiluminescent ozone meter is approximately 1 nanobar (0.1 pphm). The instrument is specific to ozone since the common atmospheric pollutants do not interfere. However, it does not measure ozone absolutely. To obtain an absolute measure of the ozone amount, the instrument is made to sample twice daily a known concentration of ozone provided by a calibrated ozone generator. The measured zero of the meter is also checked at the time of the calibration.

Plans. During 1975 it is planned not only to place updated ECC meters at our observatories but also to deploy Dasibi ultraviolet absorption ozone photometers at the GMCC sites.

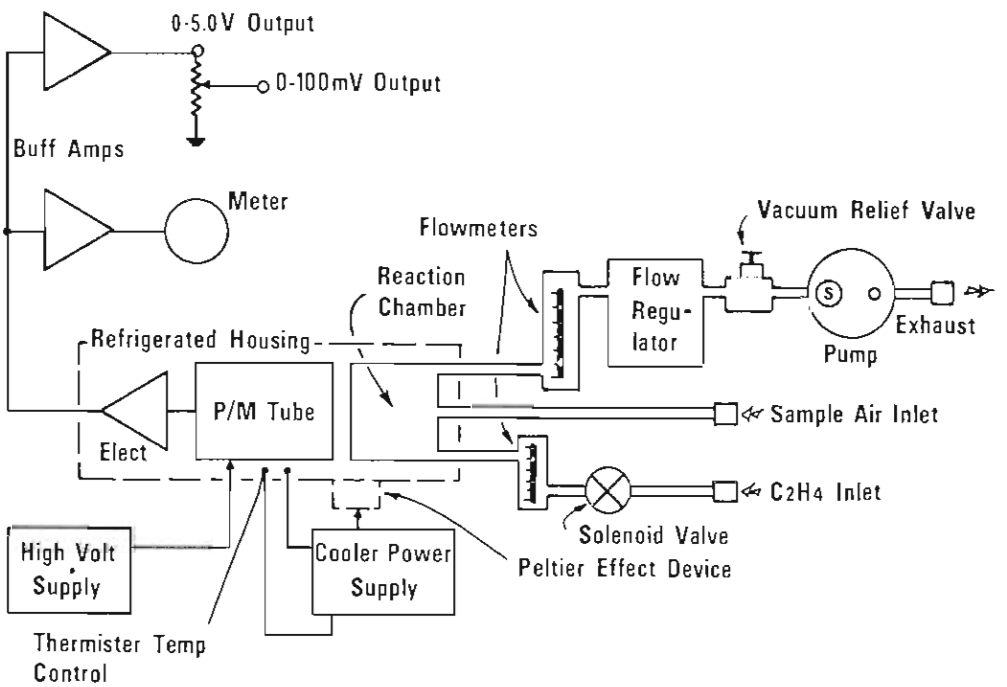

Figure 22. Block diagram of chemiluminescent ozone meter.

4.1.4 Halocarbon Studies

A number of activities in this field have involved several components of the Air Resources Laboratories in addition to GMCC. However, only GMCC activities will be reported here.

Freon-11 (CCl_3F)

Program. The major change of the Freon-11 program has been the relocation of the preparation and analysis phases from Idaho Falls to the Techniques and Standards Group in Boulder, Colorado. The flask program initiated in September 1973 was continued through 1974. Evacuated stainless steel flasks were used to sample surface ambient air at Barrow, Alaska, Mauna Loa, Hawaii, and Cape Matatula, American Samoa. The flasks were prepared at the Air Resources Laboratory Field Research Office at Idaho Falls, Idaho, and airmailed to the sampling stations. Station personnel exposed the flasks and returned them to Idaho Falls for Freon-11 analysis. The analysis setup using an Electron Capture Gas Chromatograph was presented in the GMCC Summary Report No. 2, 1973.

Some special short-term sampling, in which pairs of flasks were exposed simultaneously for observation of coincidence in the sampling techniques, was performed at Cape Matatula, Mauna Loa, and South Pole.

Equipment. A new chromatographic system is to be installed at Boulder, Colorado. Major equipment orders for the following were placed in late 1974 and will be installed in 1975:

(1) Hewlett-Packard 5713A Electron Capture Gas Chromatograph

(2) Hewlett-Packard 3380A Reporting Integrator

(3) Tylan Corp. Mass Flow Controller FC-200

Because the Electron Capture Chromatograph's detector contains the radionuclide Ni-63, it was necessary to procure a nuclear license covering the quantity of radiation that would be handled. An amendment to the current NOAA-ERL license has been submitted to the Nuclear Regulatory Commission for approval.

Because of the high risk of leaks contaminating evacuated flasks during transport, it seems advisable to pressurize the flasks prior to shipping them to the stations and to flush and repressurize them with sampled air for return and analysis. A prototype flask pressurizing unit has been designed and is under construction and testing.

Data. Freon data for 1974 are tabulated in tables 9-12. Proper data interpretation must include a decision that a sample is truly "background air" or that it contains local or transient contamination. The usual method of data selection is based on meteorological information. If the wind direction is within a chosen "clean air" quadrant, the sample is assumed to be contamination free. If, however, the wind is coming from a direction outside the quadrant, the sample is considered contaminated and is eliminated from the data record. The use of wind direction is a direct although incomplete method of determining the representativeness of a Freon sample. Trajectories provide a

Table 9. Barrow Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 3	160.5	5.9	157.8	5.0
16	94.5	6.2	47.9	5.1
Feb 1	95.2	3.1	38.4	1.4
Mar 21	95.1	1.3	90.3	1.2
30	91.5	5.4	21.7	2.7
Apr 25	112.4	4.1	141.7	12.3
May 8	167.5	4.8	135.0	32.2
Jun 15	5986.0	72.0	15.3	0.7
Jul 2	111.1	13.2	61.5	3.6
9	381.3	15.2	60.9	3.1
31	133.3	8.2	75.1	2.0
Aug 20	114.1	7.9	77.3	4.3
Sep 10	122.0	4.0	101.5	3.3
17	103.2	3.4	96.1	2.3
24	MF		45.5	3.2
Oct 1	MF		42.2	2.6
11	MF		34.6	2.9
22	195.8	11.1	13.6	1.8
Nov 11	159.7	9.3	98.1	4.5
20	141.4	10.7	24.2	1.1
Dec 3	132.2	4.2	ND	
18	150.3	7.8	102.1	7.8
28	142.3	6.2	24.0	1.7
31	147.2	2.0	ND	

MF = equipment malfunction
ND = not detected

more reliable basis for judgment, but these are not yet available. Low wind speed is also an indication of variable wind flow and possible contamination.

A selection criterion was determined for the samples based on local conditions at each station. For all the stations, if the Freon-11 value exceeded 200 ppt, it was excluded as being contaminated. Also, if the wind velocity was below 2.2 m/sec (5 mph), the value was deleted. The "clean air" quadrant for Barrow, Alaska was chosen to be 320-360, 0-170 degrees; for Samoa, 300-360, 0-130 degrees. Mauna Loa, Hawaii, presents a unique problem since the observatory is in the center of the island with cities on the coast

Table 10. Cape Matatula Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 2	159.9	4.8	84.4	1.9
11	108.4	4.5	75.7	5.6
19	71.8	2.0	66.8	2.0
26	72.8	4.3	83.4	10.0
30	80.3	2.6	115.8	3.3
Feb 9	78.0	2.6	65.4	4.4
Mar 25	115.9	4.7	68.8	5.8
Apr 4	2640.1	196.1	91.9	3.5
4	1053.9	84.5	78.7	2.1
13	6546.1	414.4	101.5	2.5
13	3034.5	117.9	78.8	4.6
24	1463.7	359.4	422.2	211.6
24	4933.0	664.1	411.9	320.4
27	171.9	4.9	111.6	10.4
May 4	103.6	13.1	164.5	89.2
15	112.8	29.7	91.7	4.7
28	140.7	3.7	92.7	7.1
Jun 12	101.7	4.4	89.9	2.2
Jul 24	161.8	13.5	99.7	8.4
Sep 14	MF		60.8	4.2
25	MF		51.8	7.2
Oct. 2	248.7	20.2	90.3	4.3
10	159.8	9.7	100.3	6.6
19	76.8	3.3	92.2	2.2
26	129.0	8.9	97.6	5.2
Nov 3	157.1	16.4	99.2	11.1
Dec 10	121.8	6.0	100.1	4.8
20	1579.0	110.0	104.9	6.3
30	143.2	7.6	94.2	3.2

MF = equipment malfunction

on all sides. The samples were taken during the daytime generally at the time of upslope winds and so no selection was made based on a "clean air" quadrant. Aitken nucleus readings were taken concurrent with the flask sampling and these showed normal levels for most conditions.

After data were selected, both linear and semi-log least squares regression fit were determined. The 1974 semi-log regressions are graphically

Table 11. Mauna Loa Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 16	86.5	6.5	75.6	3.0
25	87.5	5.1	192.1	17.6
Feb 2	82.4	5.2	ND	
8	101.9	2.6	47.6	6.0
15	98.6	2.3	ND	
22	80.8	1.3	83.4	2.1
Mar 1	61.7	2.7	49.7	0.8
11	96.3	5.3	78.8	7.3
15	97.5	2.2	19.6	3.3
19	5792.7	183.3	11.8	0.6
19	156.9	4.0	ND	
19	5244.0	110.2	4.5	0.8
19	117.8	10.4	ND	
19	121.8	7.6	ND	
19	107.2	2.5	ND	
21	126.9	14.5	ND	
21	126.7	9.8	ND	
29	73.3	1.6	54.2	1.5
Apr 5	88.0	9.9	49.3	5.8
12	107.8	2.5	ND	
19	139.5	2.5	166.6	10.7
May 3	120.3	12.0	273.1	269.6
17	131.9	15.2	111.7	35.8
23	131.1	9.8	121.1	17.0
Jun 7	122.0	14.7	142.3	27.0
21	108.9	10.0	ND	
28	150.9	25.4	97.6	2.8
Jul 5	143.2	4.5	ND	
Sep 6	89.8	4.3	ND	
13	95.2	3.0	ND	
20	125.9	2.9	108.9	3.4
30	MF		ND	
Oct 4	MF		54.2	3.9
11	MF		ND	
18	149.5	13.1	ND	
25	164.3	9.1	ND	
Nov 1	161.9	5.0	103.8	2.7
9	147.3	6.9	65.5	3.8
15	204.1	15.0	ND	
Dec 6	131.3	3.4	ND	
13	145.3	3.1	62.5	3.0
20	147.8	6.3	113.5	2.8
27	150.0	1.3	58.0	5.5

MF = equipment malfunction; ND = not detected < 5 ppt

Table 12. South Pole Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 14	61.9	3.1	ND	
14	182.9	7.7	ND	
20	142.0	4.4	53.7	1.4
20	89.3	2.9	28.0	1.6
Feb 5	99.7	4.2	ND	
5	149.9	3.4	50.4	4.2

ND = not detected < 5 ppt

presented in figures 23-25. The regression results for the entire period for both procedures are shown in table 13. We prefer the linear regression results until we have ore data to indicate the best approach.

Coincidence sampling at Mauna Loa on March 19 and 21 shows large deviations in some cases and good agreement in others. Samoan coincidence samples obtained on April 4, 13, and 24 were all highly contaminated. Antarctica coincidence samples had large deviations. This has raised the question of the appropriateness of the sampling technique.

Instrument Performance. There is wide scatter in the data for the past year. This can be attributed to three causes:

(1) Variations in actual atmospheric Freon concentration at the time of sampling.

(2) Imperfect sampling because of absorption, chemical reaction, vacuum flask leaks, sampling hookup leaks, inadequate cleaning, etc.

(3) Subtle changes in the detector response of the analytic equipment (gas chromatograph) due to temperature variations, carrier flow rate changes, carrier gas contamination, inadequate calibration, etc.

Many things affect the operation of the gas chromatograph. Good documentation of their effect has not been possible because of the lack of standard gases with which comparisons of response to controlled variations could be made. With a new chromatographic system, a pressurizing sample system, and renewed efforts in standard gas production, many variables will be eliminated and higher quality data produced.

Cooperative Program – Adrigole, Ireland

The cooperative program with Dr. J. E. Lovelock for measurement-analysis of CCl_3F and CCl_4 continued with 1974 at Adrigole, Ireland. Beginning in November 1973 the observation frequency was increased to 4 per day at 0000,

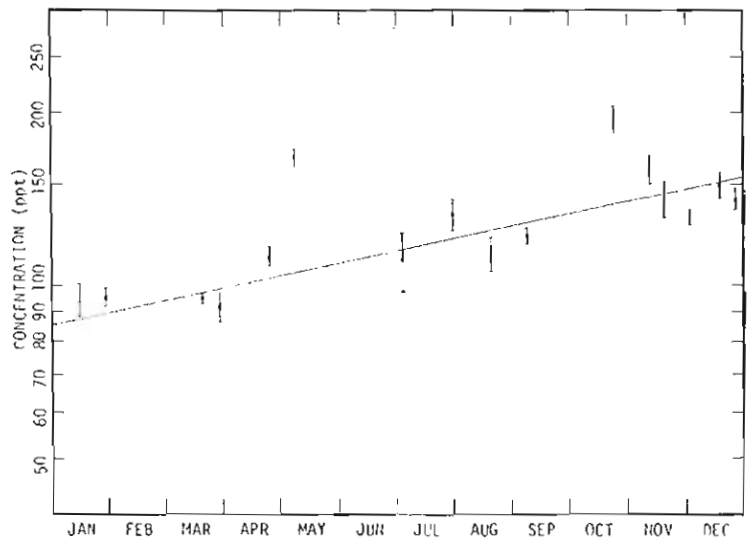

Figure 23. Semi-log regressions of selected Freon-11 data from Barrow, Alaska, 1974.

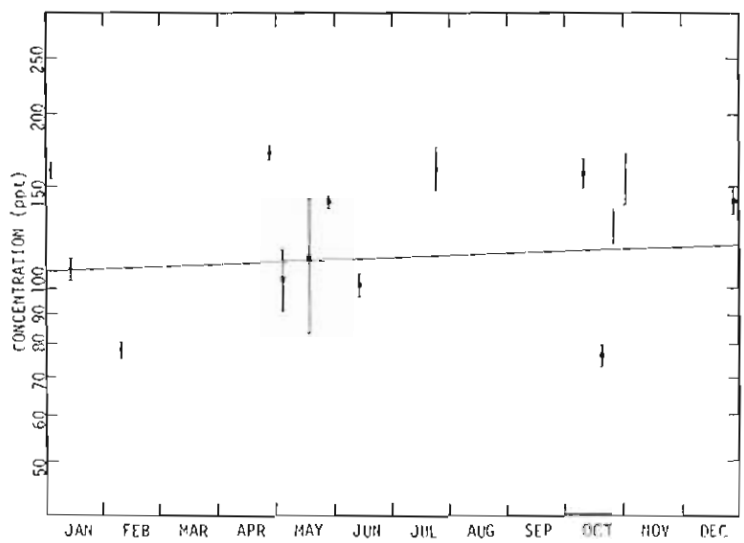

Figure 24. Semi-log regressions of selected Freon-11 data from Cape Matatula, Samoa, 1974.

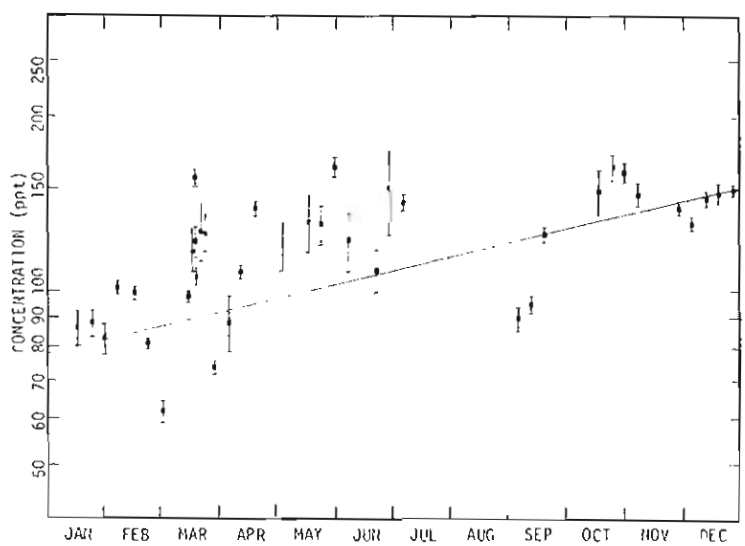

Figure 25. Semi-log regressions of selected Freon-11 data from Mauna Loa, Hawaii, 1974.

Table 13. Concentrations and Growth Rates of Freon-11 Derived From Regression Analyses of Selected Data, September 1973-December 1974.

Linear Regression	1 January 1974	31 December 1974	Change
Barrow, Alaska	89.9 pptv	144.4 pptv	+54.5 pptv
Cape Matatula, Samoa	98.0 pptv	121.1 pptv	+23.1 pptv
Mauna Loa, Hawaii	87.3 pptv	143.9 pptv	+56.6 pptv
Average	91.7 pptv	136.5 pptv	+44.7 pptv

Semi-log Regression	1 January 1974	31 December 1974	Change
Barrow, Alaska	86.5 pptv	151.6 pptv	+65.1 pptv
Cape Matatula, Samoa	96.5 pptv	126.6 pptv	+30.1 pptv
Mauna Loa, Hawaii	83.8 pptv	146.3 pptv	+62.5 pptv
Average	88.9 pptv	141.5 pptv	+52.6 pptv

0600, 1200, and 1800 Greenwich Meridian Time. These essentially continuous data were obtained for 9 months. (Data are not available for March, April, and May 1974).

Meteorological trajectories extending backwards in time and space for 10 days are being calculated for each observation. These data are being used to identify source regions and trends in the halocarbons. A sample of a complex trajectory set for June 26, 1974 is shown in figure 26. In addition, statistical correlations were prepared to reveal any diurnal trends. None was found. Hence the entire body of data can be pooled to form daily and monthly averages.

Unstratified data indicate an increase in CCl_3F concentrations of more than 30% to near 110×10^{-12} parts per part of air. A similar or even larger increase in CCl_4 may have occurred but the data for this compound require further study.

4.2 Measurement of Aerosols

4.2.1 Mauna Loa Ruby Laser Radar (Lidar) System

The lidar system measures atmospheric scattering properties in the upper atmosphere that have climatic importance. These lidar data supplemented with other measurements such as solar aureole, skylight, and spectral transmission form an integral system that can be used to monitor cirrus clouds, changes in the Junge layer strength, and injection of particles by volcanic activity that could lead to changes in the stratospheric albedo.

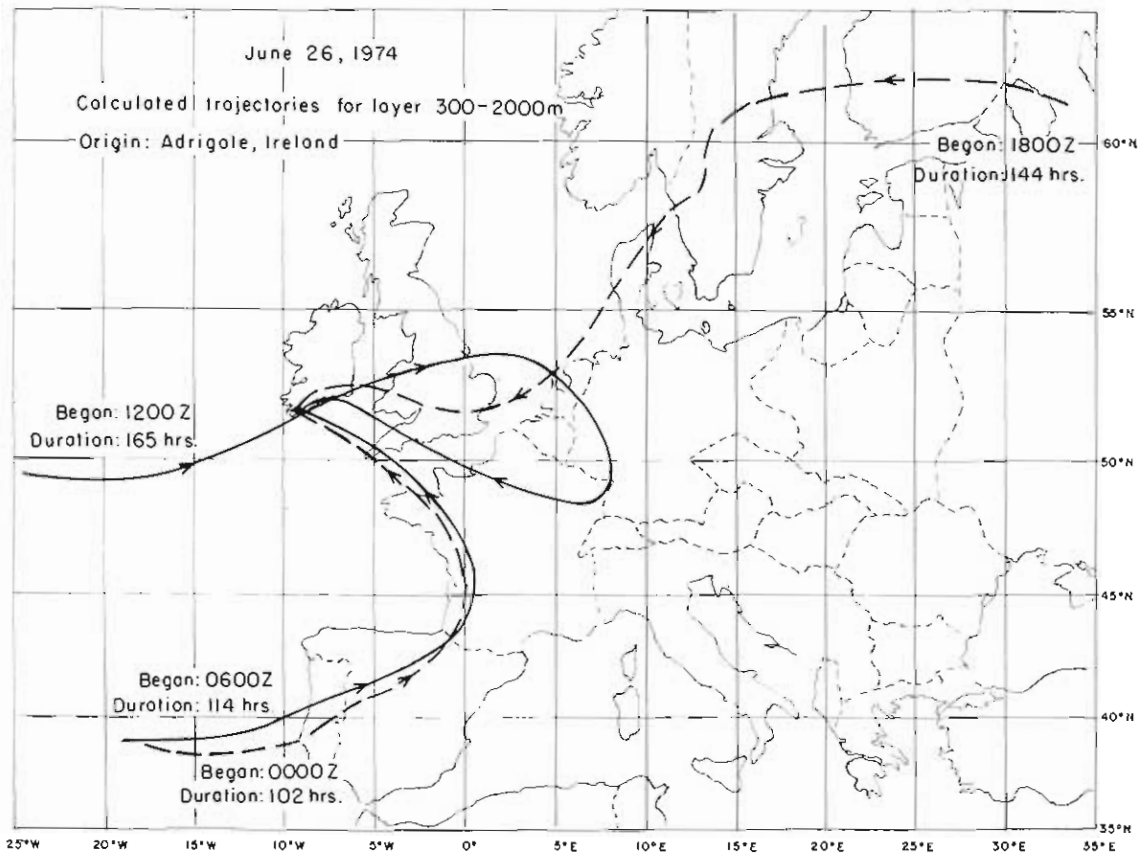

Figure 26. Sample complex trajectory set.

Properties that can be deduced directly are

(1) Profiles of relative atmospheric reflectivity coefficient.

(2) Height, thickness, and reflectivity coefficient of atmospheric aerosol and cirrus cloud layers.

(3) Height of cloud base.

Properties that can be roughly calculated are

(1) Profiles of aerosol number density.

(2) Extinction coefficient of aerosol layers.

System Description. Figure 27 shows the lidar processing electronics in the Mauna Loa computer room. The lower unit is an interface with the 61-M transmission cable from the lidar dome. The upper unit is the NOVA minicomputer. Current electronic configuration and programming require about 15 sec to transfer and store the data from a single shot into the minicomputer.

The Tektronix graphics display unit and teletypewriter are shown in figure 28. The graphics unit has been programmed to display the profile of scattering ratios for a series of shots as a function of altitude. The teletype

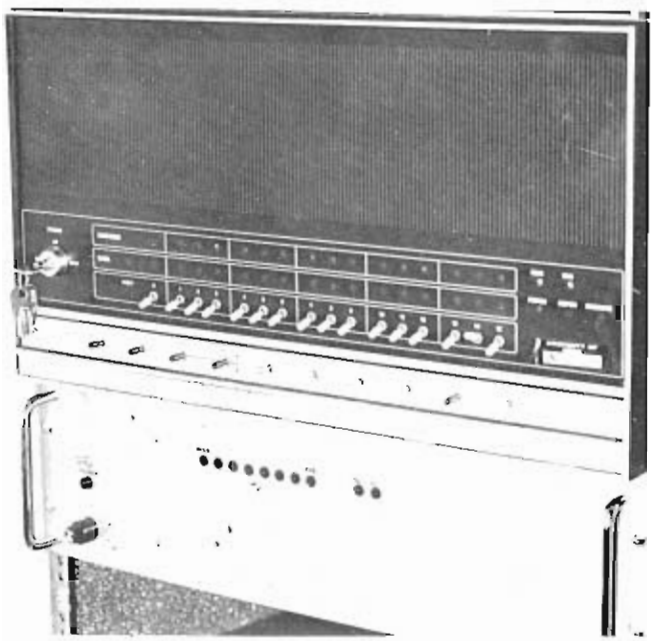

Figure 27. NOVA minicomputer and NOAA interface unit in Mauna Loa computer room, February, 1975.

Figure 28. Tektronix graphic terminal and NOVA teletype in Mauna Loa computer roon, February, 1975.

gives a listing of the Rayleigh and non-Rayleigh backscatter coefficients, the scattering ratio, and the Rayleigh extinction coefficient as a function of height for each series of shots. This is the primary data output from the system. Graphics from the Tektronix unit allow the tabulated data to be interpreted visually.

The CAMAC* system described here will be implmented during 1976. The standardized CAMAC crate and associated modules are located in the lidar dome (fig. 29). The large crate has capacity for 25 individual electronic modules running from left to right across the front of the crate. The power supply control, metering, and the air intake filter are located across the bottom of the crate. In slot 24 and 25 is a double width Type A-1 crate controller. This module accesses the remaining 23 modules under control of the NOVA computer and allows the utmost in flexibility in reading data from each of the 23 modules. Using the CAMAC concept, it is possible to change the control of sophisticated electronic instruments, such as the lidar, by simply changing the minicomputer program.

Figure 30 is a recent photograph of the lidar head in the dome. Above the laser head on the left is the collimator installed during 1974 to reduce

* CAMAC (Computer-Aided Measurement and Control) is a standard system for interfacing a computer to electrical instruments, data acquisition systems, computer peripherals or even dissimilar computers. It is both an actual written standar or a set of specifications and the embodiment of this standard in equipment.

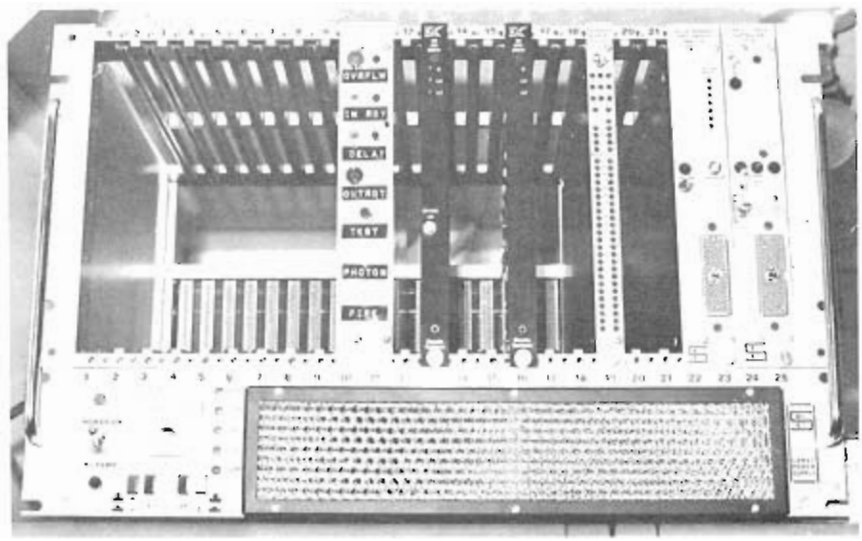

Figure 29. CAMAC crate and modules in Mauna Loa lidar dome, February, 1975.

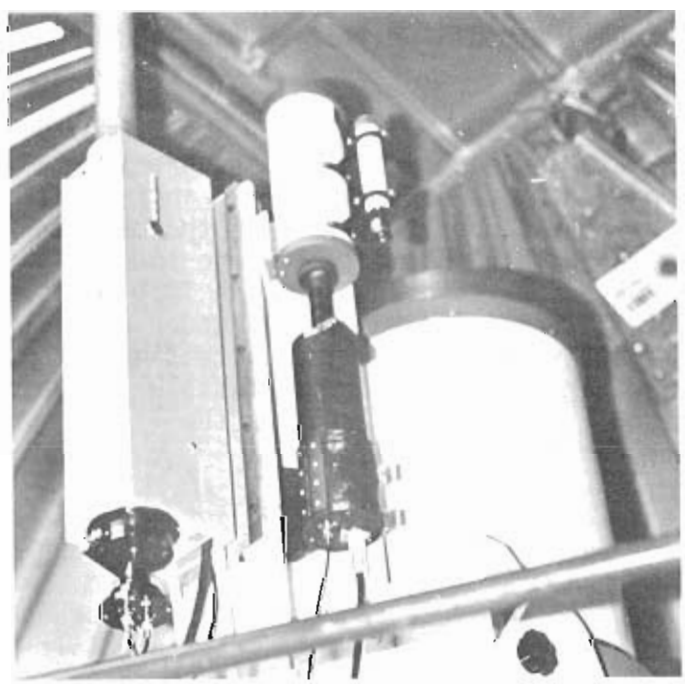

Figure 30. Mauna Loa lidar head, February, 1975.

the background light occurring in the dome at the time of each laser shot. The 10-cm diameter reflecting telescope with phtomultiplier tube is in the center, and on the right is the 40-cm diameter long range telescope.

The electronics console in the lidar dome is shown in figure 31. It consists of a Dumont dual beam oscilloscope (used to monitor the signal return from each lidar shot). Below this is an interface to match the one in the computer room. This unit interfaces the 61-m cable to the Biomation transient digitizer and the digital voltmeter that is used to provide relative laser output. Provision is made to display the number of shots performed during a series. Below this unit is a modulator control panel to generate an electronic signal that reduces the gain of the photomultiplier tube for the first 60 μsec or so, thus preventing saturation of the photomultiplier tube by the near field laser return. At the bottom is the Biomation model 8100 transient digitizer. This unit takes the return signal from the photomultiplier tube and digitizes it to an accuracy of about ½ percent of full scale. This process is repeated 10 times each μsec over a period of about 200 μsec. The results are stored in a buffer memory in the unit. The high voltage power supplies are used to power the photomultiplier tube.

Hardware Development. In January 1974 the flashlamp of the lidar broke and damaged a feed-through connector. Although a new lamp was ordered and installed, some redesign for easier installation was warranted.

The minicomputer and Biomation transient digitizer were connected to the lidar so that the data could be automatically processed. This new addition tremendously improved the data quality compared with that obtained previously

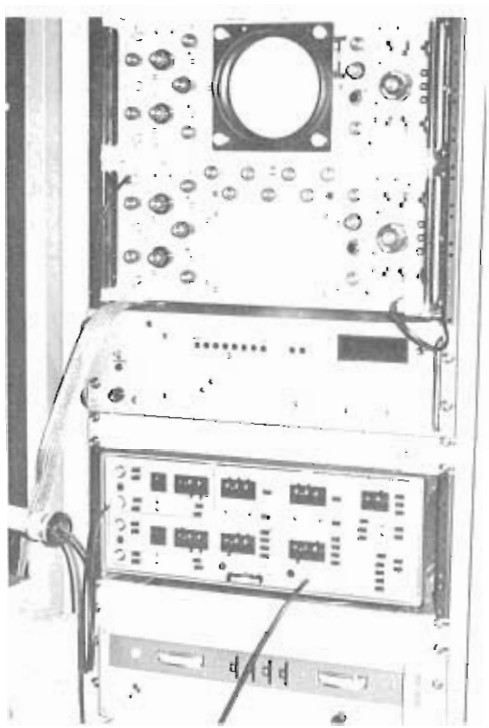

Figure 31. Lidar electronics console in Mauna Loa lidar dome, February, 1975.

from manual reduction of Polaroid photographs. It also permits a more frequent data collection schedule (now once per week) and reduces any random errors in the data.

A gain switch amplifier was built as designed by Jim Spinhirne of the University of Arizona, Engineering Dept. This unit compresses the dynamic range of the lidar return signal so that each lidar shot can give a profile of the atmosphere from 5 to 25 km. This change greatly enhances the usability of the lidar system.

1974 Results. Cumulative results of the vertical profiles from early 1973 to the present are shown in figure 32. The data are the non-Rayleigh backscatter (NRB) measured in units of $10^{-9}m^{-1}Ster^{-1}$. Each datum point is a monthly average of 3 or 4 individual evening observation periods from the region 17–19 km MSL. Data are now obtained at approximately 300-m intervals so that each point represents the average of several range intervals. The data show apparent natural variability of the backscatter coefficient; for example, during late 1973 and early 1974 monthly averages varied by a factor of 2. This indicates that short term probing of the stratospheric aerosol can be substantially different from the long term average. There is some evidence of cyclic behavior, but the data record is still too short to be conclusive. There is a downward trend in the values until October of 1974. This presumably indicates the stratosphere was still in the process of cleaning itself from previous dust injections. The abrupt increase in October is now believed to have been caused by an injection of dust into the stratosphere by the Fuego volcano in Guatemala (14.29N, 90.52°W). Monitoring continues to determine the vertical spreading and the change in NRB with time. Results are being reported periodically (Fegley and Ellis, 1974, 1975a,b,c, and d).

Hilo upper air data, used to check for deviation of the atmospheric temperature profile from the U.S. Standard Tropical Atmosphere, are now archived at the observatory and have proved useful in interpreting the lidar returns.

Figure 33 shows data for the 19–21 km layer, which has been strongly influenced by the October injection. Note that the backscatter is continuing

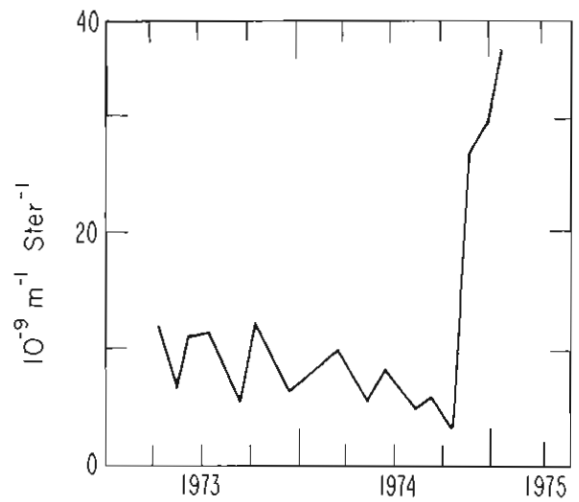

Figure 32. Monthly average of the non-Rayleigh backscatter coefficient over the 17–19 km regions above Mauna Loa Observatory from spring 1973 to the present. Vertical axis is non-Rayleigh part of the back scatter coefficient in units of $10^{-9}m^{-1}Ster^{-1}$.

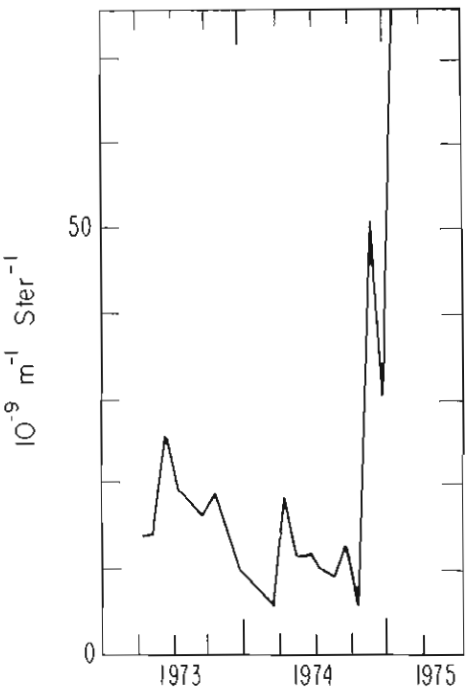

Figure 33. Non-Rayleigh backscatter coefficient for the 19–21 km region.

to increase. This is in contrast to the steadily decreasing backscatter previous to October 1974. The stratospheric cloud has been present generally in the 19.5–20 km region; hence its effect is greatest in this layer.

The 21–23 km MSL layer also shows the generally decreasing trend from 1973 through fall of 1974 (fig. 34). There is a slight increasing trend after this date not easily seen in the graph because of the incursion of the stratospheric cloud layer into the 21-km region. There are also no obvious cycles present in the data. The natural variability of the measurements seems to be quite large.

The measurements from the 23–25 km layer are shown in figure 35. The average backscatter coefficient at 23–25 km appears to be slightly higher

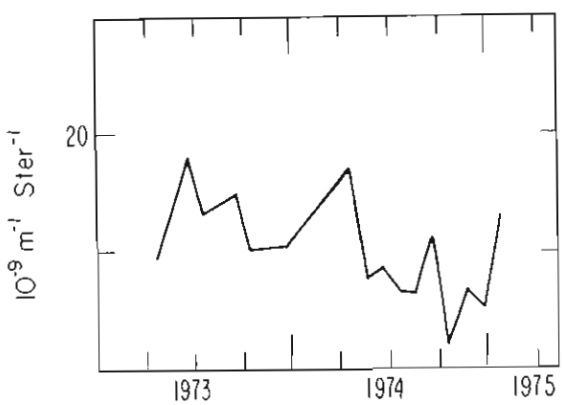

Figure 34. Non-Rayleigh backscatter coefficient for the 21–23 km region.

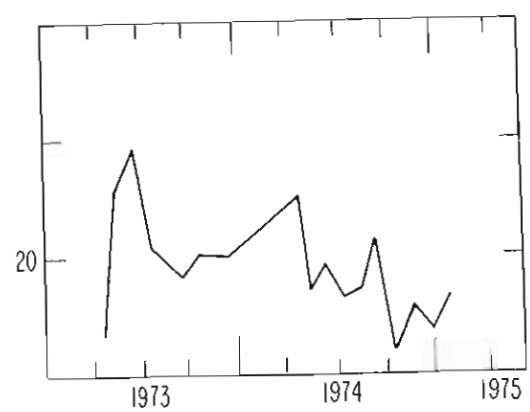

Figure 35. Non-Rayleigh backscatter coefficient for the 23–25 km region.

than that for 21–23 km. There is an apparent slight downward trend. To date, the October injection has not had any apparent influence upon this region.

Since only 20 shots per series are integrated, there is rather large scatter in the data above 25 km, and therefore these data are omitted. When the lidar is completely automated, a large number of shots for each series can be integrated to reduce the scatter. Measurement can then be extended to even higher levels. A photon counting system will also assist in this goal.

Figure 36 is a plot of the integral of the backscatter coefficient throughout the depth of the stratospheric cloud that appeared in October 1974. Weekly values are shown rather than monthly averages. Several interesting features emerge: (1) an apparent increase in the average total layer backscatter since the original volcanic eruption, and (2) the appearance of two major peaks, early November 1974 and mid-February 1975. If the source of this cloud was the Fuego volcano, then one could interpret the original peak as the arrival of the main dust cloud from the volcano a couple of weeks after the primary eruption. The second major peak in February 1975 is more puzzling. New Zealand's Mount Ngauruhoe erupted on February 19, 1975, but it is most unlikely this material could have reached Mauna Loa so quickly. There is an apparent 3-week cycle in the data. This may be the circulation of the main volcanic cloud around the globe with an appropriate 3-week transit time. It is interesting to note that during the two main peaks, the layer backscatter approached the value of 10^{-3} $Ster^{-1}$, indicating that the total amount of solar radiation reflected by the layer back to space may have approached ½ percent of the incident radiation.

During 1974, two series of horizontal profiles were taken across the saddle, the area between Mauna Loa and Mauna Kea. The first, summertime, data series showed the aerosol concentration was not uniform across the 40-km pathlength. The data taken late in the year showed a relatively uniform aerosol concentration. It would be of interest to know how representative short period samples of the aerosol concentration at the observatory ground level are.

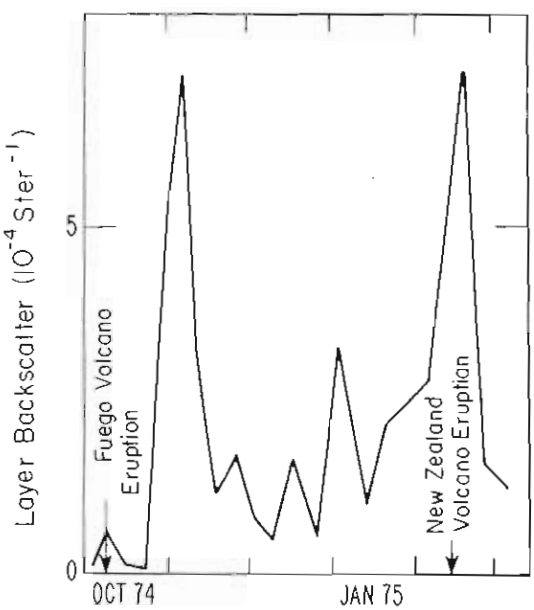

Figure 36. Total backscatter of the 1974 stratospheric dust cloud above Mauna Loa Observatory.

In 1975 attempts will be made to monitor several new parameters using the Mauna Loa lidar system. These include:

(1) Relative profiles of ozone to 25 km, using a tunable UV laser.

(2) Relative profiles of the hydroxide radical, using a tunable UV laser.

(3) Relative profiles of temperature, using the ruby lidar.

4.2.2 Measurement of Surface Aerosols at Mauna Loa

Aitken Nuclei. Gardner counter SN 826 was operated hourly at Mauna Loa throughout 1974. Figure 37 shows monthly averages of the 1000, 1100, 1200, 1300, 1400 LST observations. The error bars give the standard error of the mean ($\sigma/\sqrt{n}$). Because the 1000 LST observation is most representative of clean or background conditions, it is shown as a shaded dot for each month. The 1200 LST (noon) observation is indicated by an "n". The normal upslope-downslope difference is clearly evident for each month as shown by the large increase in the afternoon. Furthermore, the first 6 months show generally erratic results with fairly high background values. The high February readings are a result of local contamination by volcanic activity. The last 6 months of the year show more consistent results with clean background concentrations of about 300-350 CN/cm^3. These concentrations are near the lower limits of sensitivity of the standard Gardner counter.

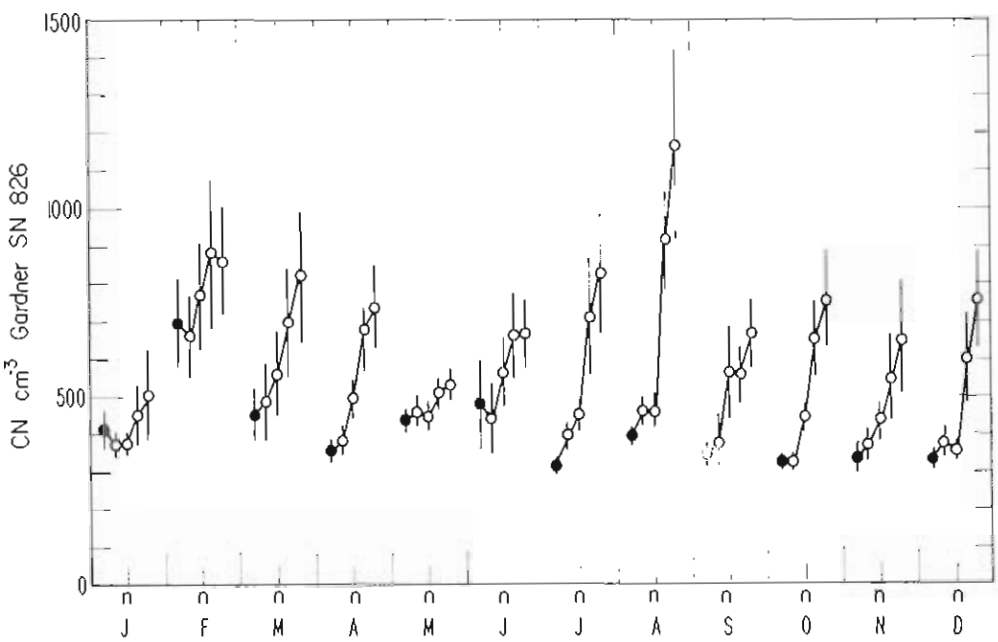

Figure 37. Hourly means of condensation nuclei in each month of 1974 at Mauna Loa Observatory, measured with Gardner counter SN 826, for 1000, 1100, 1200, 1300, and 1400 LST. The shaded dots indicate the 1000 LST means; n indicates the 1200 LST (noon) mean. Vertical bars give standard errors about the mean (S.E. = $\sigma/\sqrt{n}$).

The long-tube Gardner counter is a more sensitive version of the standard Gardner counter, using a fog tube 60 cm long and a light emitting diode (LED) as its light source. Because the concentrations at background monitoring stations are likely to be near the lower threshold of the standard Gardner, the more sensitive long-tube instrument is being adopted at all GMCC stations.

Figure 38 gives a calibration curve obtained for long-tube instrument SN 912, now in use at Samoa. In addition to the NiCr aerosol calibration, a lengthy comparison was made between this instrument and Pollak SN 13 on MLO ambient aerosol. The ambient aerosol measurements lie to the right of the laboratory NiCr aerosol data. This displacement most likely arises from differences in aerosol size distributions. Assuming that the Pollak counter, having large diameter orifices in the plumbing, gives the true reading for all aerosol distributions, the Gardner counter probably has few or no internal losses for the very small NiCr aerosol but some losses for the larger ambient aerosol. Because of these performance differences, a Pollak counter will be located at each GMCC station to provide on-site calibration.

Pollak counter SN 13 was operated hourly at Mauna Loa June— December 1974. Figure 39 shows monthly averages of nucleus concentration in a format similar to figure 37. Again, the diurnal trend is evident with high afternoon concentrations. Unfortunately the Pollak was not operated during the first half of the year so it was not possible to verify the more variable results obtained with the Gardner counter during that period. However, the last half of the year shows a trend toward smaller concentrations during

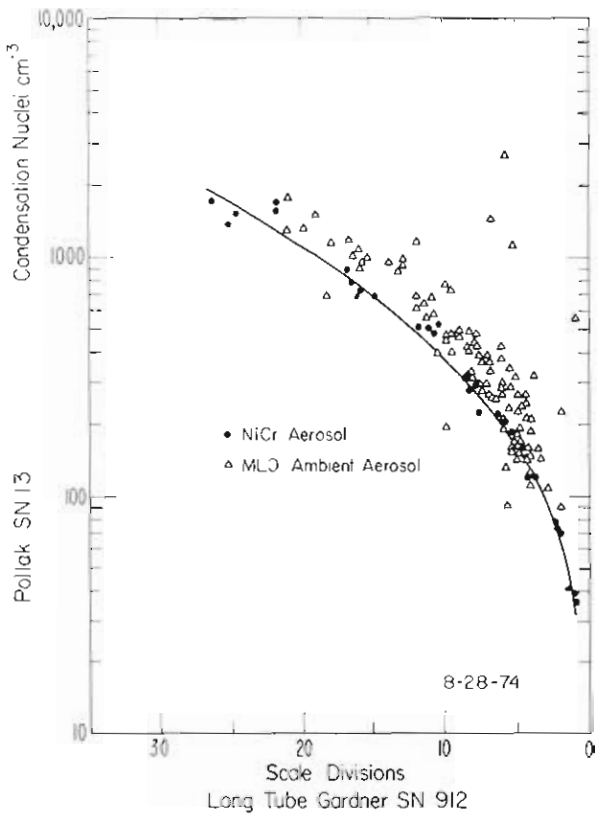

Figure 38. Calibration of long-tube Gardner counter SN 912 with Mauna Loa Pollak No. SN 13. Black dots indicate calibration points obtained using NiCr aerosol generated from a hot wire. Triangles indicate comparisons made on ambient aerosol at Mauna Loa observatory.

morning observations. The more sensitive Pollak counter shows a pronounced downward trend of background nucleus values to below 200 CN/cm^3 for November and December 1974.

Figure 40 shows the annual averages of both the Gardner and Pollak counter data. Again the diurnal trend is evident with high afternoon values. The Pollak counter concentrations are significantly lower, primarily because the Pollak data span only the last half of the year, but also because of the counter's superior sensitivity. The standard error bars are quite small since many data form each average.

The General Electric condensation nucleus counter suffered from maintenance problems and produced no data in 1974. In June, 1974, the Mauna Loa GE counter was shipped to the University of Washington for modification using more advanced electronics. This modification should produce a more reliable and more sensitive instrument for use in 1975.

Nephelometry. In January 1974, a four-wavelength nephelometer was installed at Mauna Loa Observatory. This instrument is designed to measure integrated light scattering over all scattering angles from about 7° to 175°, simultaneously at 450, 550, 700, and 850 nanometers (nm). The simplified diagram in figure 41 shows the mechanical construction. A 150-W halogen-iodine projection lamp is used to illuminate the sample volume through which passes a continuous flow of sample air. A rotating filter wheel in front of the photomultiplier tube, along with suitable timing and multiplexer circuitry, allows the light scattering signal at the four wavelengths to be stored

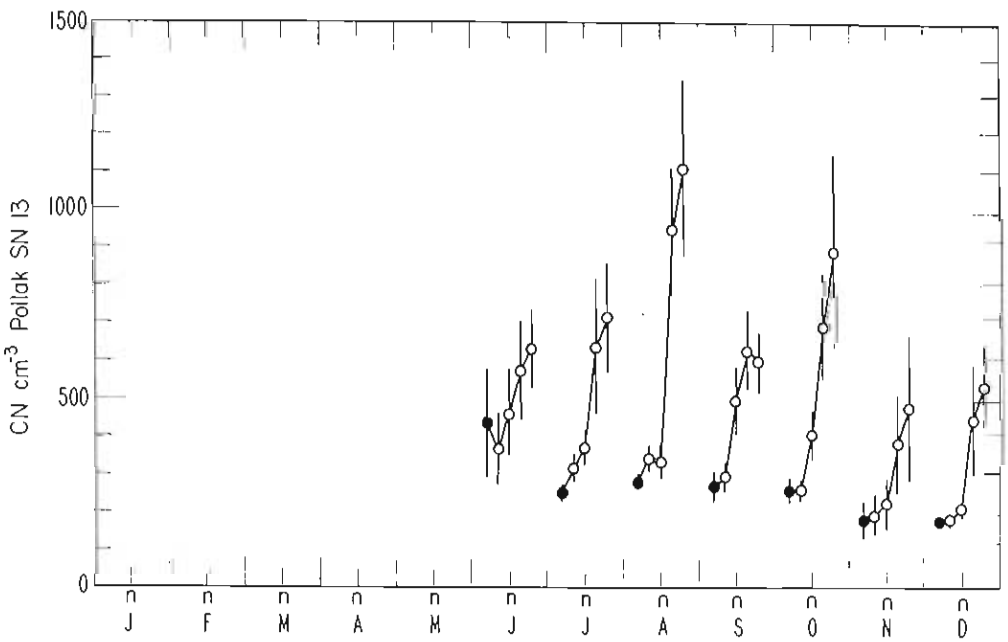

Figure 39. Hourly means of condensation nuclei at Mauna Loa in months for which data are available, measured with Pollak counter SN 13. (See legend, fig. 37.)

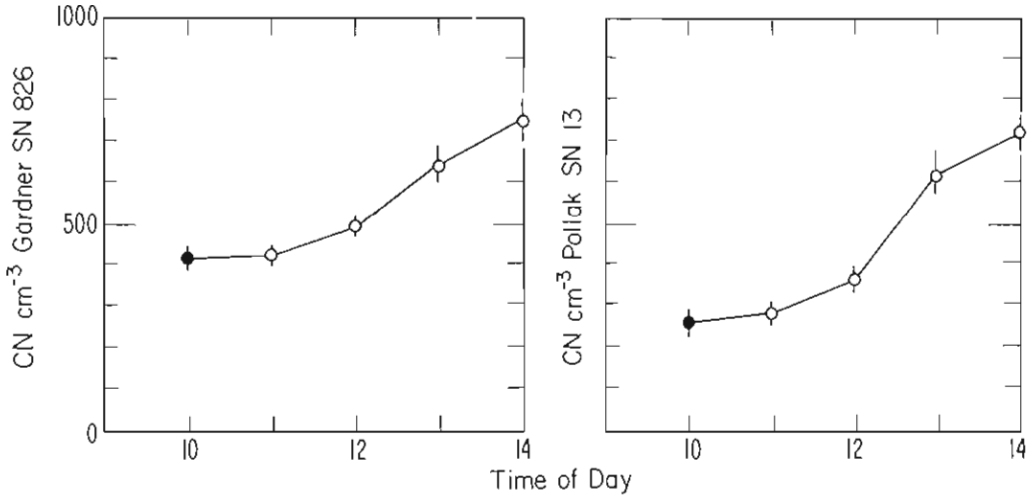

Figure 40. Hourly means of condensation nuclei for 1974 measured with Gardner counter SN 826 and Pollak counter SN 13. Vertical bars give standard errors about the mean (S.E. = $\sigma/\sqrt{n}$).

in four separate digital counters. These signals are then processed electronically to provide continuously available analog signals of light scattering. A block diagram of the electronics is shown in figure 42. A more detailed description of the instrument and a discussion of some preliminary data have been published (Bodhaine and Mendonca, 1974).

An important capability of the four-wavelength nephelometer is the measurement of b_{sp}, the light scattering of aerosols, as a function of λ, the wavelength of light. This relationship is ordinarily expressed as $b_{sp} = C\lambda^{-\alpha}$ where C is the constant, and α is the Ångstrom exponent. Furthermore α is related to ν, the slope of the aerosol size distribution, by $\alpha = \nu - 3$. Therefore, the four-wavelength nephelometer provides a three-segment

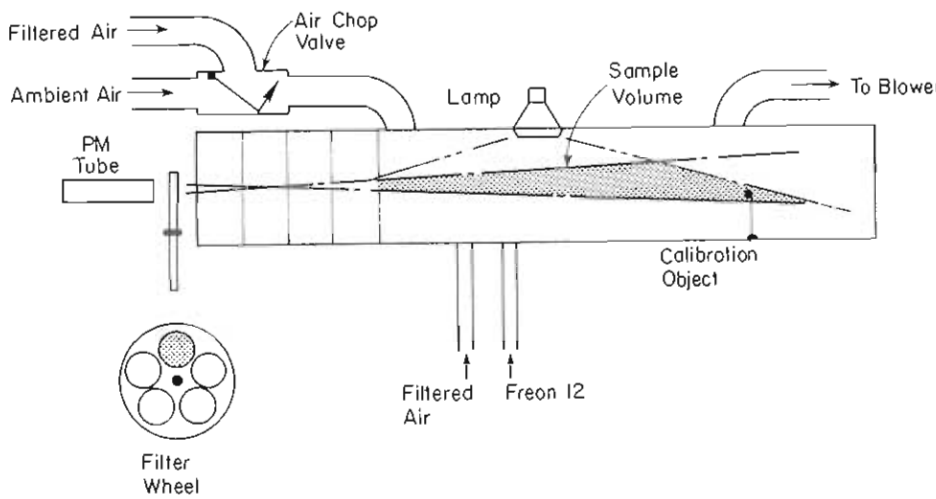

Figure 41. Mechanical arrangement for the Mauna Loa four-wavelength nephelometer.

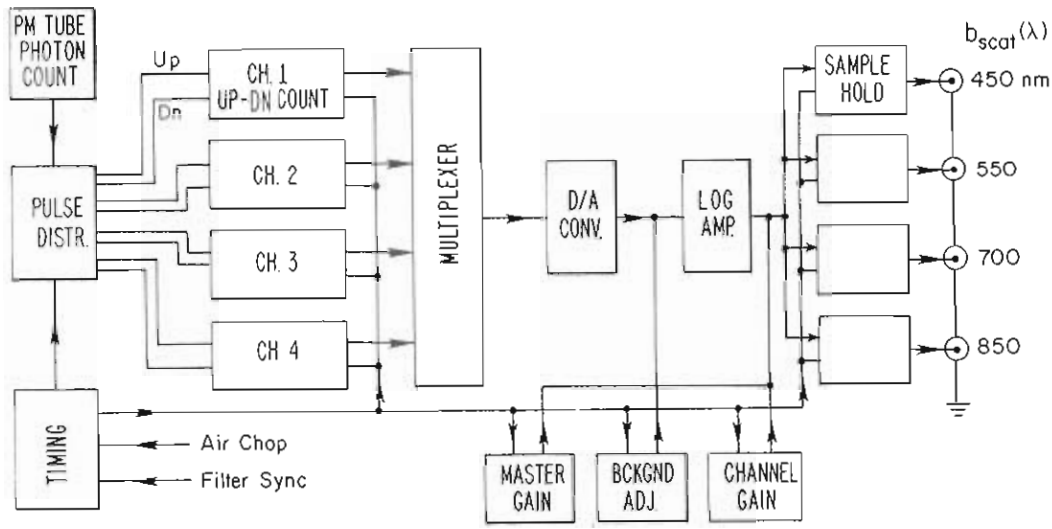

Figure 42. Electronic block diagram of the Mauna Loa four-wavelength nephelometer.

approximation to the Ångstrom exponent which then provides information on the aerosol size distribution.

The 1974 hourly data for the four-wavelength nephelometer have been averaged to produce hourly values. In an effort to provide nighttime data representative of background conditions, the data were screened on the basis of relative himidity to define "upslope-downslope" days.

Figure 43 shows averages of hourly data for the year 1974. The diurnal trend is obvious; more important for background measurements is the clean

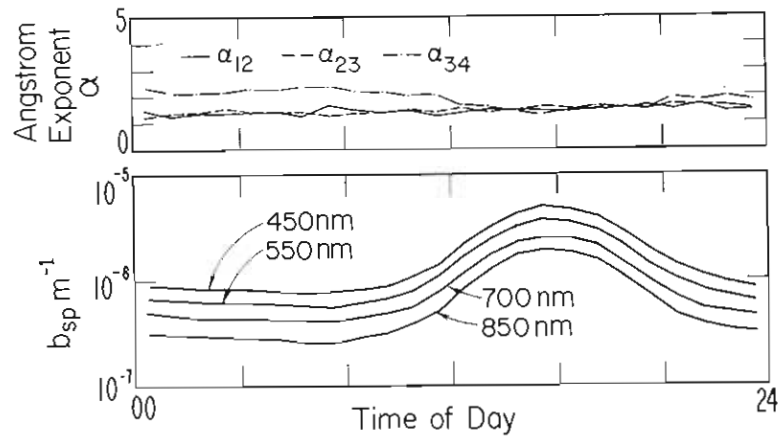

Figure 43. Annual averages of hourly data from the Mauna Loa four-wavelength nephelometer on the 127 upslope-downslope days in 1974. a_{12} is derived from 450 and 550 nm light scattering, a_{23} from 550 and 700 nm, and α_{34} from 700 and 850 nm.

early morning period with the cleanest time of day occurring just before sunrise, about 0700 hours. The Ångstrom exponent remains at about $\alpha = 1.4$ throughout the day except for α_{34} (706–850 nm) which increases to about 2.2 during the night, suggesting a depletion of larger sized particles. The difference in light scattering between night and day is about one order of magnitude for the whole year. All averages are geometric (or logarithmic) averages and the standard errors amount to approximately 30 percent of the distance between adjacent channels. To maintain clarity in the graphs, standard errors are not plotted. In general, the raw data show excellent correlation among the individual channels ($R \simeq 0.97$) and adjacent channels never cross.

Figure 44 gives hourly averages for selected months of data taken on "upslope-downslope" days only. All months show the usual diurnal effects. March shows unusually high light scattering values because of local volcanism. Note the high values of α, indicating a preponderance of smaller-sized particles. On the other hand, May shows high light scattering but low α, indicating larger-sized particles. The second half of the year shows a general downward trend in light scattering during clean conditions, although the afternoon peak remains at approximately the same level throughout the year. The time of day of minimum light scattering generally follows sunrise; i.e., it is later during winter and earlier during summer. For the individual months, because of small sample sizes (e.g., only 3 days in December), standard errors are quite large, of the order of the distance between adjacent wavelengths. Again the raw data show excellent correlation among individual channels (which maintain fairly constant separation).

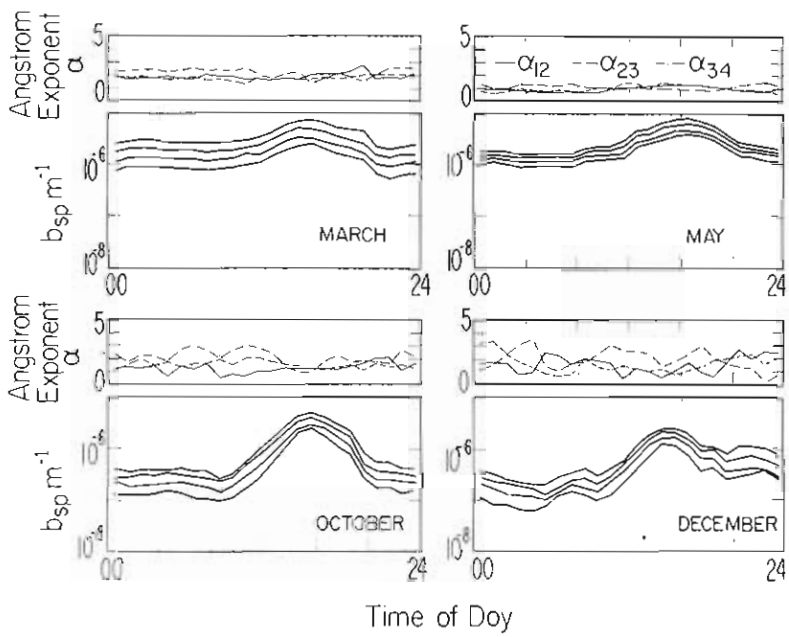

Figure 44. Monthly averages of hourly data from the Mauna Loa four-wavelength nephelometer on upslope-downslope days. a_{12} is derived from 450 and 550 nm light scattering, a_{23} from 550 and 700 nm, and α_{34} from 700 and 850 nm.

Figure 45 shows the annual trend of light scattering data. Each point is the geometric mean of the 0300 to 0400 LST hourly average for *all days* of each of the 12 months of record. No data screening was performed. The shaded symbols plotted at June 30 show annual means. The generally erratic behavior during the first half of the year is again apparent (shown also by $\bar{\alpha}$), while more consistent values of light scattering and $\bar{\alpha}$ are obtained for the last half of the year. The values of $\bar{\alpha}$ plotted on this graph are the averages of α_{12} (450–550 nm) and α_{23} (550–700 nm) for each month.

Calibration of the Nephelometer. The four-wavelength nephelometer is absolutely calibrated by filling the instrument with Freon-12 and adjusting for the known scattering coefficients given in table 14. An absolute calibration is performed monthly. In addition, the nephelometer has a built-in calibration object which may be rotated into the sample volume to check for instrumental drift. This relative calibration is performed weekly. The value of the calibration object is measured each month at the time of a Freon calibration.

In general, the four-wavelength nephelometer has exhibited excellent stability throughout the year with no perceptible change in stability, linearity, or in the value of the relative calibration object.

Data Reduction. Data for 1974 were reduced manually directly from the strip chart record by an equal area interpolation technique to obtain hourly averages, ending at the hour, and plotted at the midhour point. In November, the nephelometer was interfaced with the Mauna Loa data acquisition system and the same hourly averages were obtained automatically. A comparison showed the manual and computer results to be equivalent. Therefore, the faster and easier automated system is used to process the data. Strip chart records are used only during computer downtime.

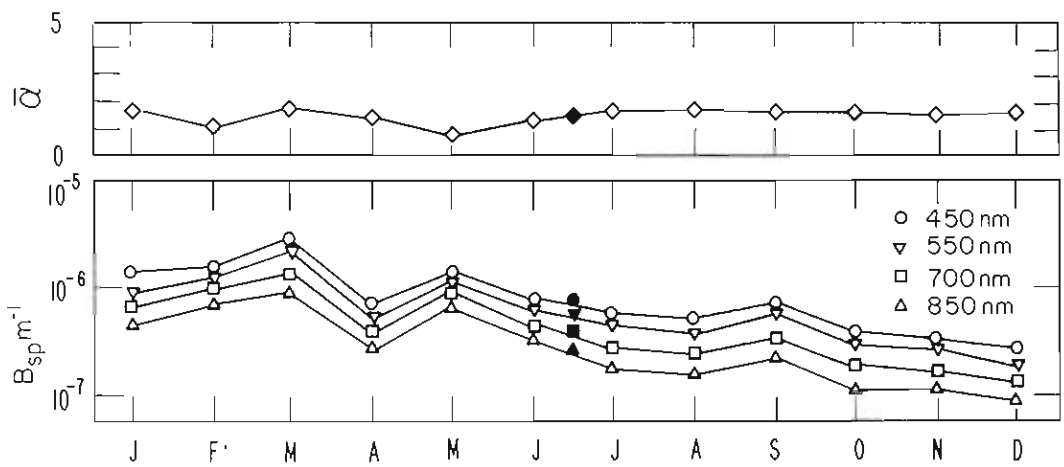

Figure 45. Monthly means of light scattering and Ångstrom exponent for the 0300–0400 LST averages at Mauna Loa observatory for 1974. All data were used. $\bar{a}$ *is the average of* α_{12} *and* α_{23}.

Table 14. Known Scattering Coefficients.

	b_{sg}(Freon 12)	b_{sg}(Air)
450 nm	3.00×10^{-4} m^{-1}	0.200×10^{-4} m^{-1}
550 nm	1.36×10^{-4}	0.086×10^{-4}
700 nm	0.50×10^{-4}	0.032×10^{-4}
850 nm	0.24×10^{-4}	0.014×10^{-4}

Plans. The Mauna Loa four-wavelength nephelometer has shown good reliability and sufficient sensitivity for use at Mauna Loa. During 1975 the instrument may be further automated for calibration and averaging under microprocessor control.

Cloud Condensation Nuclei. Eventually cloud condensation nuclei may be monitored routinely by GMCC. Now, however, there is not an instrument available suitable for long-term, unattended operation. A short series of CCN measurements has been performed at Mauna Loa with a manually operated thermal diffusion chamber modeled after one built by Allee (1971); the results are shown in figure 46.

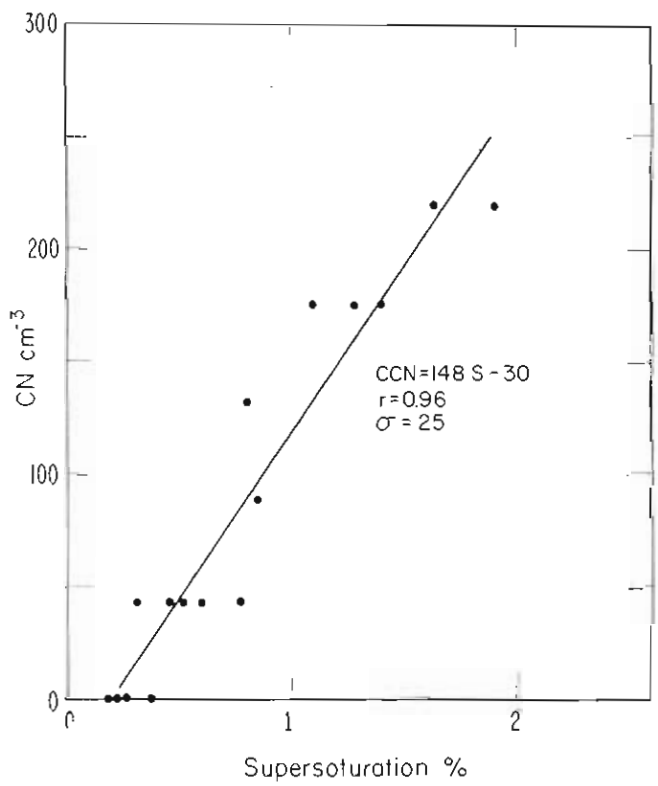

Figure 46. Cloud condensation nuclei at Mauna Loa observatory on Jan 17, 1974, from 1300 to 1328. Measurements were taken during upslope wind conditions.

Ice Nuclei. It may also be necessary to monitor ice nuclei routinely in the GMCC program. However, there is no general agreement among investigators as to how best to measure ice nuclei. Some preliminary work has been done at Mauna Loa during June—September, 1974 in cooperation with Dr. Keith Bigg of CSIRO, Australia, and with Mr. Paul Allee of Atmospheric Physics and Chemistry Laboratory, NOAA. Samples were taken by the membrane filter technique and were developed by the thermal diffusion chamber technique. Dual volume samples were taken, separated according to daytime or nighttime, and screened for upslope-downslope conditions. Bigg used the standard static chamber development technique whereas Allee allowed saturated air to circulate past the developing filters. Results are compared in figure 47. The upslope conditions are richer in ice nuclei. The dual volume effect is apparent, and filters developed at -20°C show about an order of magnitude or so more nuclei than filters developed at -15°C. However, the -15°C development temperature is probably more representative of cloud process temperatures at this latitude.

4.2.3 Condensation Nucleus Measurements at Barrow

Condensation nucleus concentrations have been measured at or near the Barrow, Alaska, observatory since September 1971. Single daily observations were made until February 1973, when the observatory became operational. Since that time nucleus data have been taken hourly during the day, 6 days a week.

Figure 48 shows the average condensation nucleus concentrations and wind direction frequencies at the observatory for each of eight wind sectors. The prevailing winds are from the northeast. Winds from north, northeast, east, and southeast are defined here as "clean air" directions. Wind directions

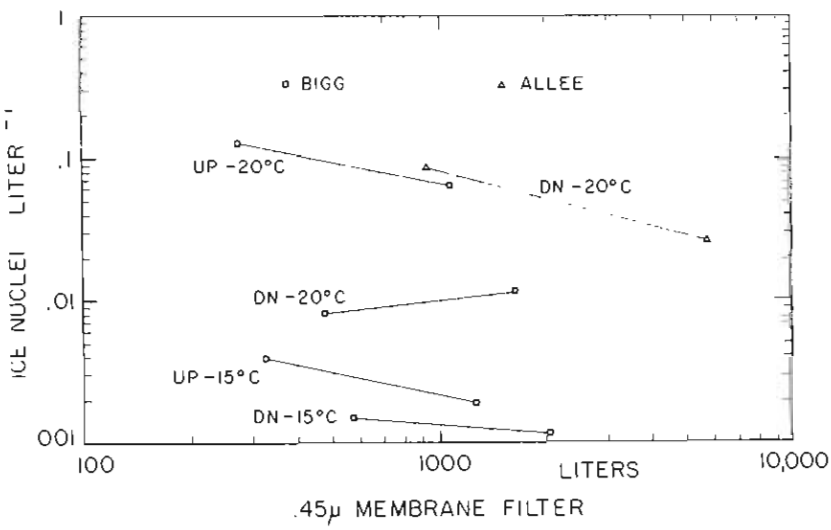

Figure 47. Ice nuclei at Mauna Loa observatory, June-September, 1974, upslope-downslope days only. All samples were taken on 0.45 μm membrane filters. Filters were analyzed by Bigg and by Allee.

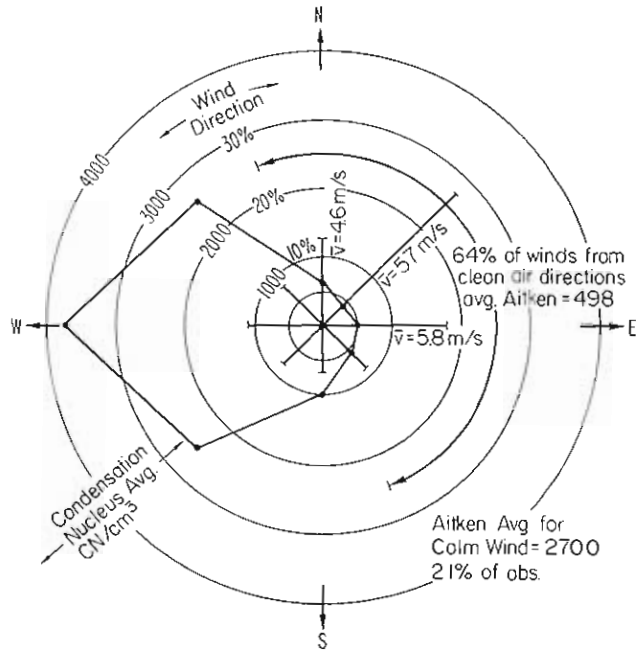

Figure 48. Barrow wind rose and condensation nucleus averages for period from March 1973 through February 1975.

having the lowest nucleus concentration averages are associated with trajectories that pass over the Arctic Ocean. These wind directions provide the best selection of background sampling conditions. The average of the most recent 2 years of data measured by Gardner counter SN 1098 is 498 CN cm^{-3} for these directions.

The average condensation nucleus concentrations since the beginning of record are given in table 15. The averages are for the "clean air" directions only. The data for the winter months (November through January) for 1971 and 1972 are not considered to be completely representative because of the sampling location and the probability of contamination.

Table 15. Monthly Condensation Nucleus Averages (cm^{-3}) For Wind Directions in the Clean Air Sector (N-SE).

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1971									355	338	493	503
1972	480	685	1132	397	348	869	1378	755	575	383	4267	504
1973	4352	344	1205	292	340	399	1497	675	367	354	260	273
1974	291	751	577	299	246	455	700	709	250	283	274	206
1975	787	716										

The percentage of winds from the "clean air" sector (north to southeast through east) during observation times is illustrated at the top of figure 49. Clean-air directions have occurred from 28 percent to 93 percent of the time for a particular month. This frequency reflects the potential percentage of time background air exists at the observatory. Many of the lower percentages occur during months of higher-than-average median condensation nucleus concentrations. In the bottom portion of figure 49, the solid line connects monthly median values of hourly averaged nucleus concentrations for clean air fetches for 42 successive months. The dotted line connects monthly median values of the hourly averaged nucleus concentrations using all wind directions. During March and July the tabulated nucleus concentrations were high; for longer periods around May and November concentrations were low. The reason for these variations has not yet been identified.

Figure 50 is a log normal distribution plot of condensation nucleus concentration data for 2 years (March 1974 - February 1975; cf. fig. 49). The data are separated into two classes, one representing all wind directions and the other representing "clean air" wind directions only. Below 500 CN cm^{-3}, the distributions have different slope which may indicate that a background aerosol does indeed exist at levels below 500 CN cm^{-3}. Note also that the median values are much smaller than the average values. The average 2-year nucleus count for all wind directions is 1256 CN cm^{-3} compared with the

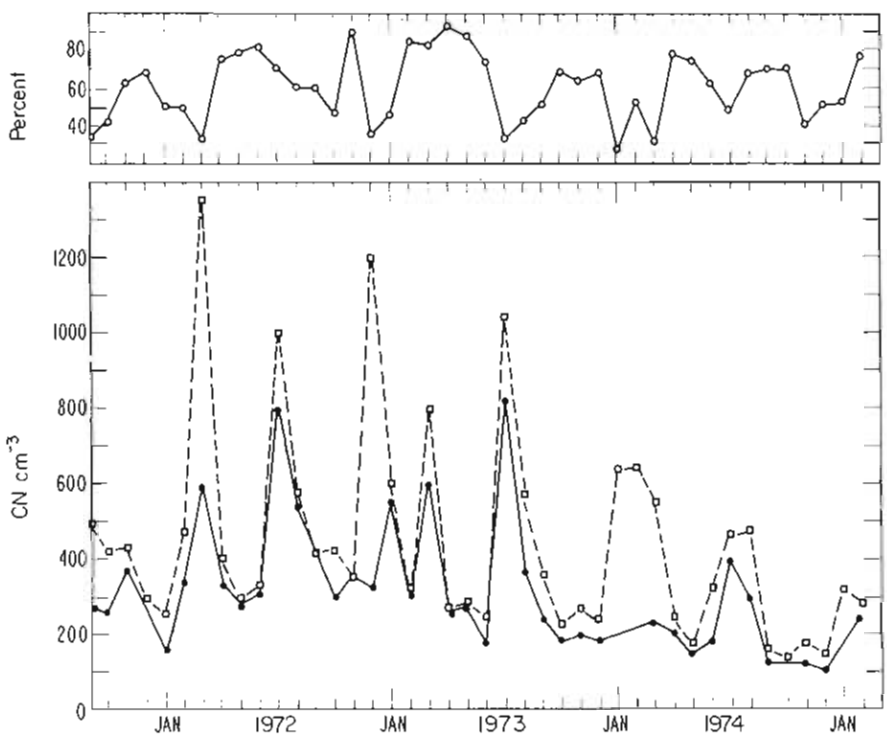

Figure 49. Barrow condensation nucleus concentrations. Above: Percentage of time wind came from clean air sector during observation. Below: Monthly median values for clean air directions (solid line) and for all directions (dotted line).

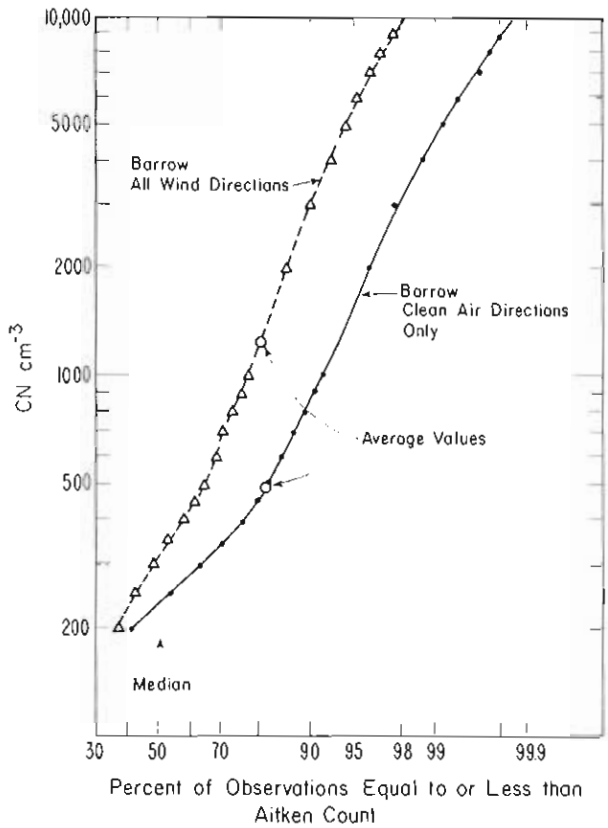

Figure 50. Log normal plot of Barrow condensation nucleus concentration for period from March 1973 through February 1975.

median value of 315. This skewness of the distribution of measurements means that there are frequent conditions when background air flow exists at the observatory compared with relatively few cases with high condensation nucleus concentration.

4.2.4 Condensation Nucleus Measurements at Cape Matatula

Data were collected from February through December with a Gardner condensation nucleus detector, model CN with incandescent light source. The mean concentration (cm^{-3}) for this period was 351 ± 58. Nucleus counts remained at the lower threshold of the short tube Gardner counter all year with no obvious sources of local contamination even during the few periods of land breeze (although no statistical significance can be attached to the latter because of the small number of observations).

Figure 51 shows a sampling wind rose with mean nucleus counts for all wind directions. Figure 52 shows the seasonal condensation nucleus variation; Figure 53 shows the diurnal variation. The high monthly values for November and December were due to increased dust and engine exhaust resulting from road construction during this period.

In December an improved long tube Gardner counter with a light emitting diode (LED) was placed in operation. Simultaneous readings were taken on Lauagae Ridge to obtain a correlation between the short-tube and LED instruments. The mean December nucleus concentration (cm^{-3}) for the LED model was

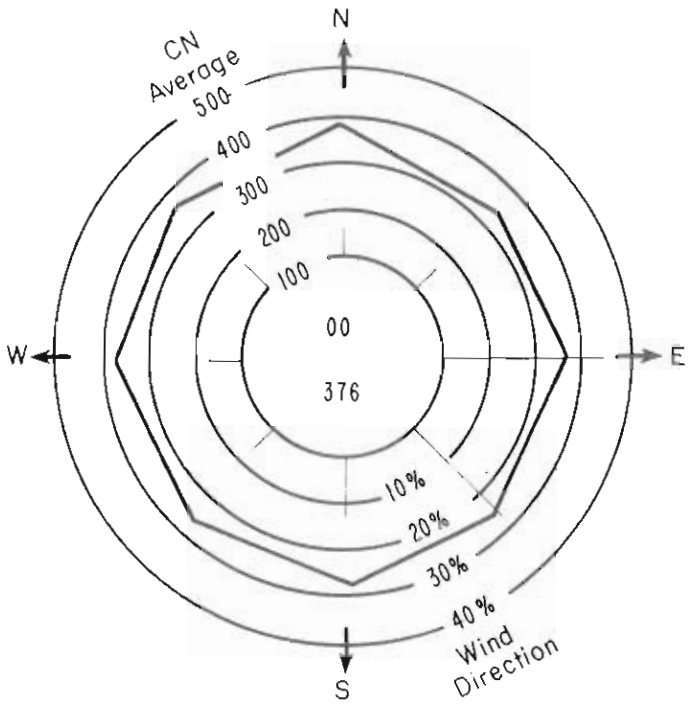

Figure 51. Average condensation nucleus count for 197[illegible] at Cape Matatula and sampling wind rose.

219 ± 66; the short-tube model averaged 487 ± 83. The new LED model is more accurate in the lower range than the older short tube model, so the true mean value measured in Samoa for 1974 may be considerably lower than 351 CN cm^{-3}.

This comparison of the two instruments will continue for several months until a good statistical correlation can be derived.

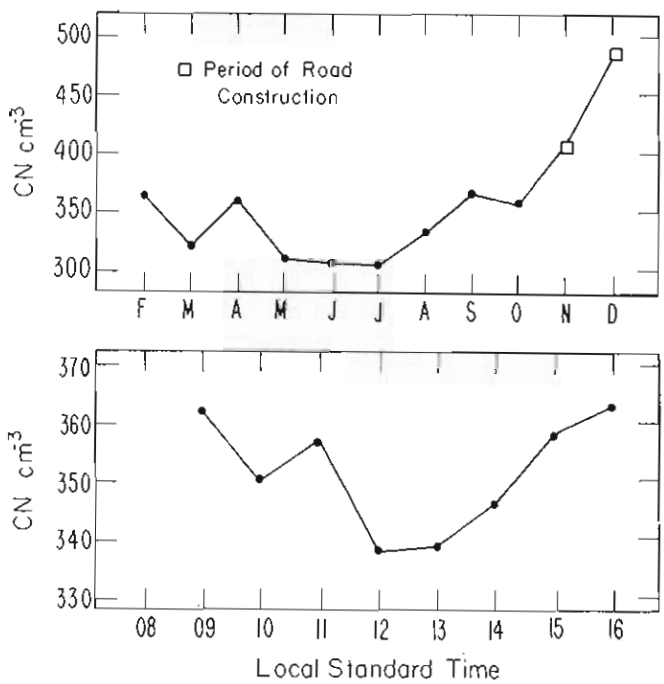

Figure 52. Seasonal variation of condensation nuclei at Cape Matatula in 1974.

Figure 53. Diurnal variation of condensation nuclei at Cape Matatula in 1974.

4.2.5 Measurement of Surface Aerosols at South Pole.

As part of the 1974 GMCC program at South Pole station, Antarctica, a Pollak Counter (Ser. No. 15, BGI Corp., Boston, Mass.) was used for daily monitoring of Aitken nucleus concentration. Observations were made daily at 0000 GMT and 1200 GMT, during uncontaminated wind situations. Prevailing winds at the South Pole are grid NE. Since the instrument was located in the Aurora Tower, on the upwind side of the station complex, contaminating winds were infrequent.

Air was sampled directly through the building wall using a length (1.3m) of Tygon tubing. This inlet configuration was used from June 24, 1974 until November 11, 1974 when replacement personnel assumed station operation. The daily aerosol counts for August, September, and October, obtained at 0000 and 1200 GMT, are shown in figure 54. Also shown are hourly averaged temperature, wind speed, and direction during the time periods in which observations were made.

The Pollak Counter accuracy at low concentrations provided an opportunity for monitoring low Aitken counts encountered at the geographic South Pole. Concentrations of approximately 20 CN cm^{-3} were not uncommon during the winter months. In addition to the low concentrations measured during the winter, concentrations measured during onset of sunrise and austral summer are of interest. This period was characterized by much greater day-to-day variability plus higher concentrations. During the sunrise period, from September 10 through October 1, three to four observations per day were made. The additional observations yielded better resolution of concentration changes during sunrise and also provided a more frequent quality control monitor of the continuous record collected with the General Electric counter.

Figure 55 shows the log normal distribution of measurements taken from July 1 through November 10, 1974. The abscissa represents the percentage of observations made that give particle concentrations at or below the corresponding ordinate value. Note that the median value for measurements made in this period is about 31 CN cm^{-3}.

4.3 Meteorology

4.3.1 Mauna Loa Meteorology

The meteorological instruments used at Mauna Loa Observatory for atmospheric monitoring are listed in table 16. The instruments for Kulani Mauka on the east slope at 2.6 km MSL are listed in table 17. That observing site has been an extension of the observatory since 1963.

Weather 1974. The year was characterized by a severe drought in the eastern section of the island. Sugar crop losses were high. The effects of the drought were felt at the observatory from June 6 to September 1 when Mauna Loa had only 60 percent of the average precipitation for that part of the year. The total for the year was 592.33 mm or 118 percent of the long

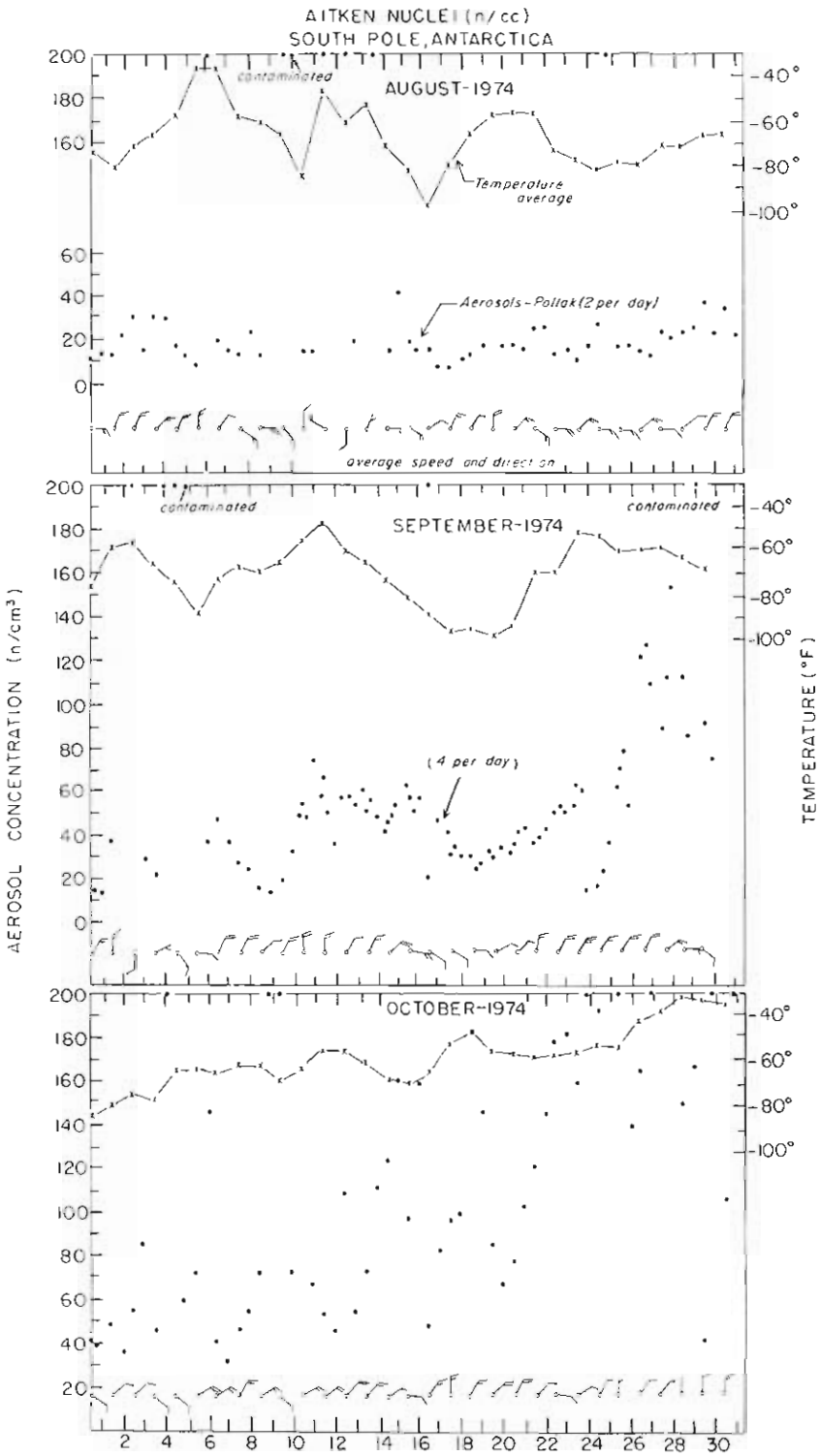

Figure 54. Average condensation nucleus concentrations at South Pole, Antarctica.

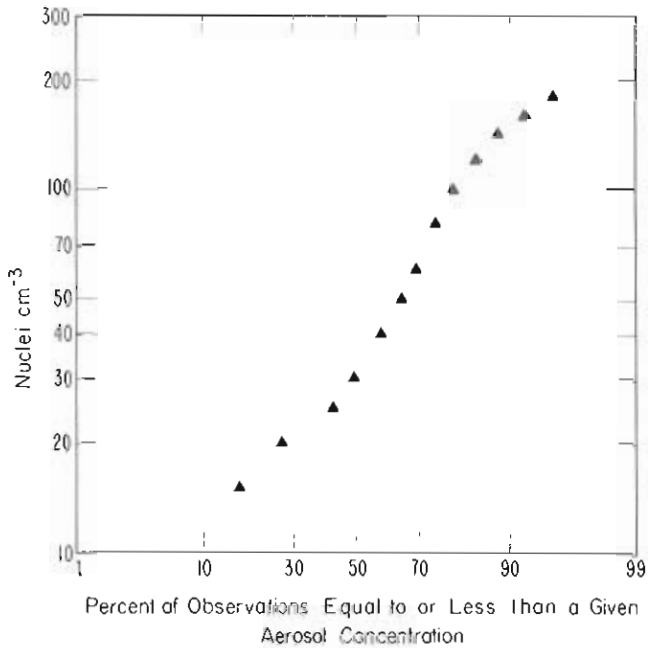

Figure 55. Log normal plot of South Pole aerosol concentration July 1-November 10, 1974.

term yearly average. Figure 56 shows the monthly amounts of precipitation and the number of days having 0.25 mm or more. Table 18 lists the monthly departures from the long term averages of precipitation and temperature.

The monthly variations in temperature at the observatory are given in figure 57. February was the coldest month and August the warmest. There was an unusual amount of high cloudiness throughout the year, especially in the spring. Only two months did not experience freezing temperatures and 96 days had temperatures at or below 0°C. The coolness of the year is reflected in the departure of temperatures from the long term averages; every month the average maximum was below normal. The departures of the yearly average maximum temperature and the yearly average minimum from the 13-year average were -3.6°C and -0.5°C, respectively.

The trade wind regime, within which easterly component flow persists 95 percent of the time (regardless of vertical motion), and the anti-trade regime together constitute the most prevalent wind direction patterns at the observatory. In figure 58 the wind direction data have been plotted as a function of these two dominant fetches. The frequency of westerly and easterly flow is approximately equal during winter and spring; otherwise the trade wind regime is most common at the observatory. However, there are times when no set pattern is observed at the observatory and no diurnal wind direction variation (north for daytime and south for nighttime) is established. The mildness of the climate at the observatory is shown by the relatively small number of days during which 1-hr average wind speed exceeds 10 m/sec.

Table 16. Meteorological Instruments Used for Atmospheric Measurements at Mauna Loa Observatory.

Measurement Instrument	Type		Operation Period From	To
Pressure				
Barograph	NWS - G210C (ser #1318)		12- 9-56	Present
Mercury Barometer	Ser. # 723		12- 9-56	Present
Wind				
Aerovane & recorder	NWS 141-1 (Bendix) + 120		8-15-59	Present
Aerovane	NWS F010, F005		12- 9-56	8-15-59
Aerovane	NWS F-431		8-15-59	Present
Anemometer	NWS F-102		12- 9-56	Present
Recorder	NWS F-315 (Esterline Angus)		8-14-57	Present
Precipitation				
Tipping bucket	NWS D120		12- 9-56	Present
8 Inch	NWS D100		12- 9-56	Present
Weighing gage	NWS D110		12- 9-56	2-66
Fog collector	U. of Hawaii construction		11 - 73	Present
Temperature				
Max & Min	NWS - C102, C122		12- 9-56	Present
Psychrometer	NWS - H031		12- 9-56	Present
Hygrothermograph	NWS - 110		12- 9-56	Present
Thermister	Science Assoc. Mod. # 172		11 - 70	Present
Humidity				
Infrared hygrometer	Local construction		7-15-67	Present
Hygrothermograph	NWS 110		12- 9-56	Present
Dew point	Science Assoc. Mod. # 172 "Dew Cell"		11 - 70	Present
Solar Radiation				
NIP & HI (Epply)	NWS - A100 & A110	NIP	10- 2-57	Present
		HI	12- 9-57	Present
Surface Observations				
Daytime	NWS Aviation Hourlys of Temp. Press., Wind, RH, Cloud Cover, Visibility, Precipitation, Remarks		7- 1-58	12-31-70
Minimum of one daily observation of above parameters			1- 1-71	Present

Table 17. Meteorological Instruments Used for Atmospheric Measurements at Kulani Mauka.

Measurement Instrument	Type	Operation Period From	To
Precipitation			
Eight Inch Raingage	NWS D100	1-1-63	Present
Weighing Raingage	NWS D110	2 - 66	Present
Fog Collector	U. of Hawaii construction	11- 73	Present
Temperature			
Max & Min	NWS C102, C122	1-1-63	Present
Hygrothermograph	NWS 110	1-1-63	Present
Humidity			
Hygrothermograph	NWS 110	1-1-63	Present

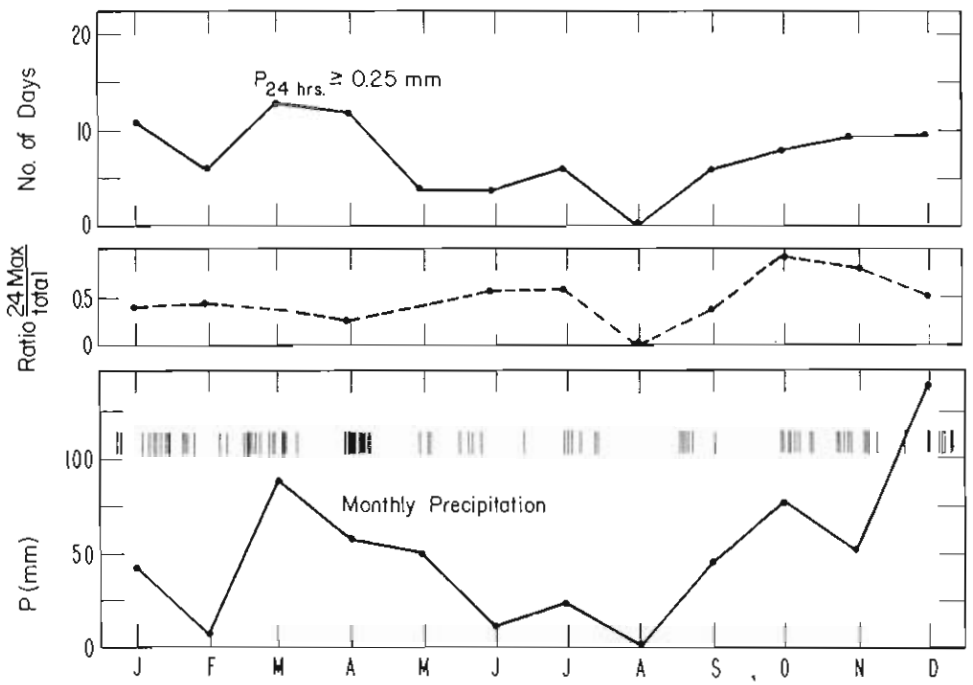

Figure 56. Precipitation at Mauna Loa (mm) in 1974. The vertical bars are the days when precipitation occurred.

Figure 59 is a plot of hourly averages of wind speed and direction 0301-0400 LST throughout the year. The air flow during optimum clean air conditions at the observatory is shown. The absence of upslope flow throughout the year is to be noted.

Figure 60 shows the frequency of diurnal variation of surface moisture. This dominates any annual trends observed at the observatory. Two-hundred sixty-one days had at least one hourly average of relative humidity ≤ 20 percent; 57 days had one hourly average relative humidity of 100 percent, and 208 days had a diurnal regime of low nighttime-high daytime relative humidity.

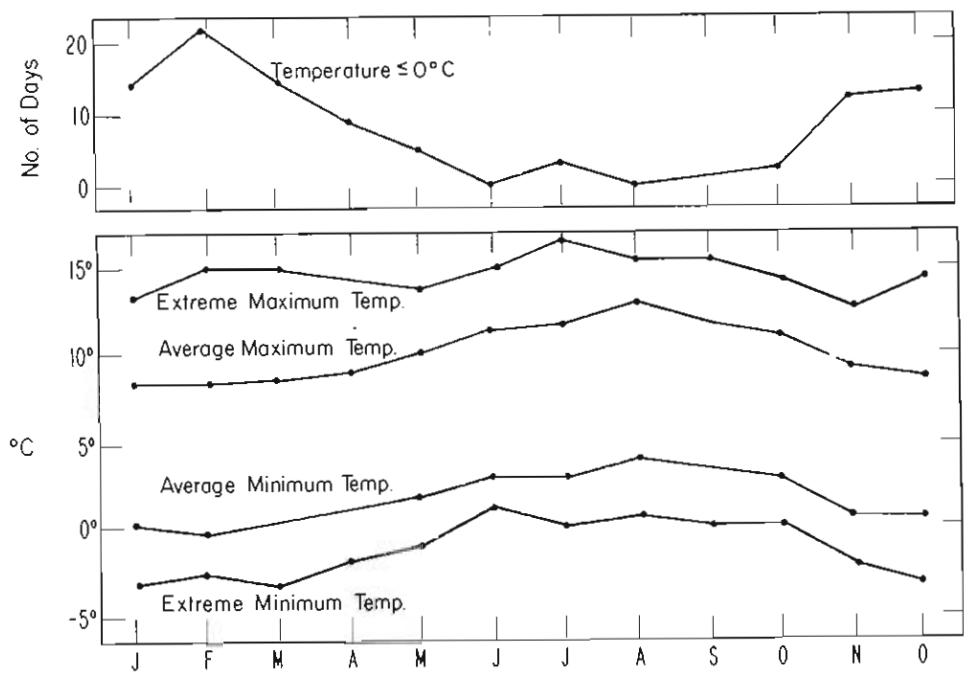

Figure 57. Temperatures at Mauna Loa Observatory in 1974. The number of days that had freezing temperatures is plotted above.

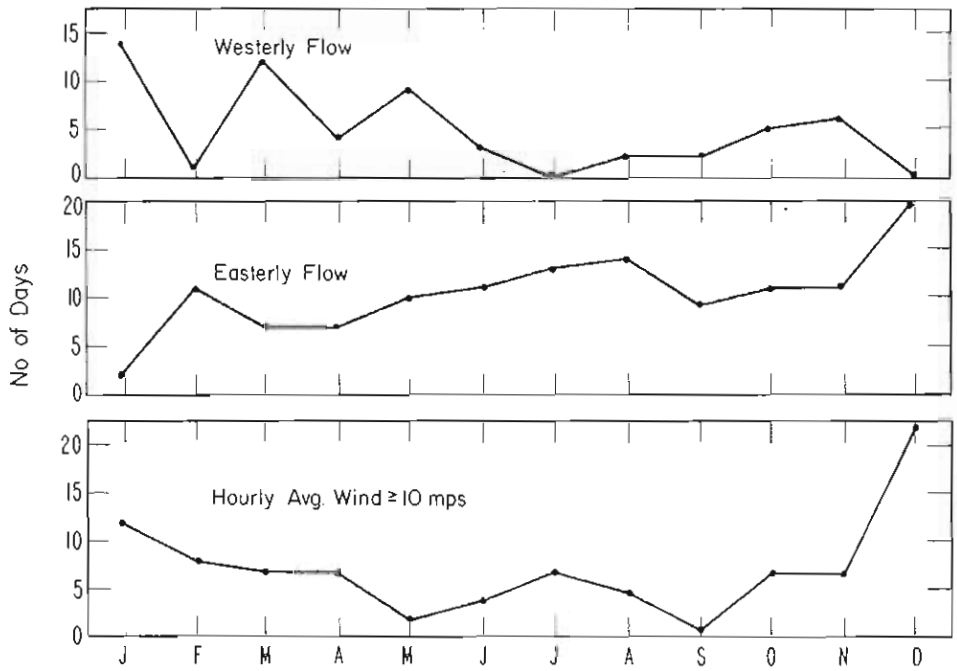

Figure 58. Wind direction and speed at Mauna Loa Observatory in 1974.

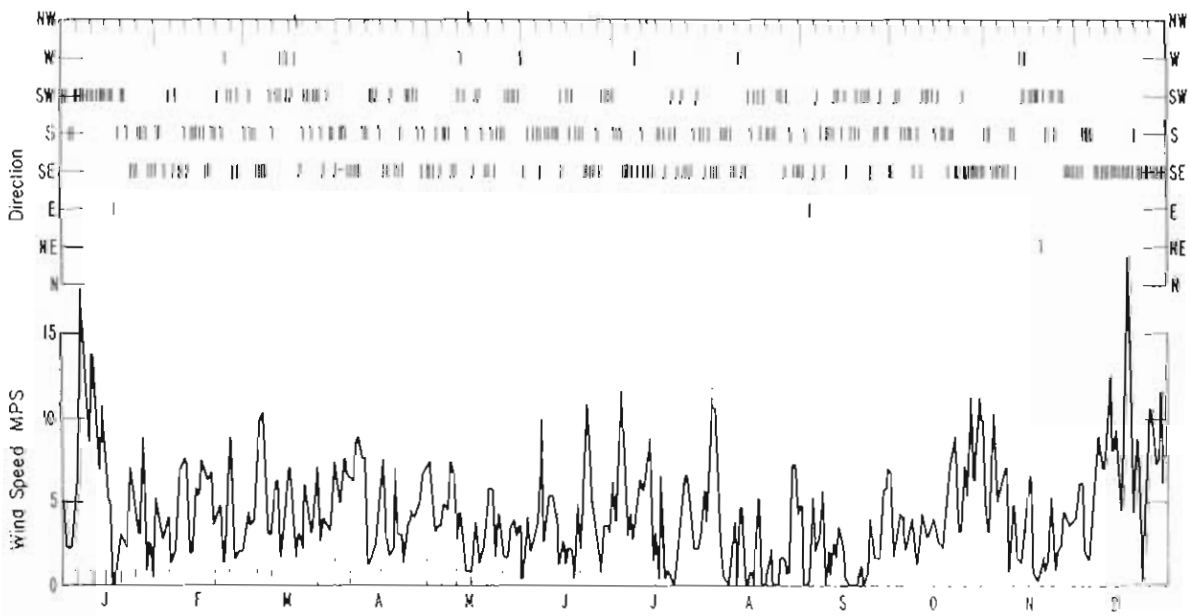

Figure 59. The 1974 average wind speed and direction for the hour ending at 0400 LST at the Mauna Loa Observatory. Note the gentle speeds and the absence of the upslope direction during clean air conditions.

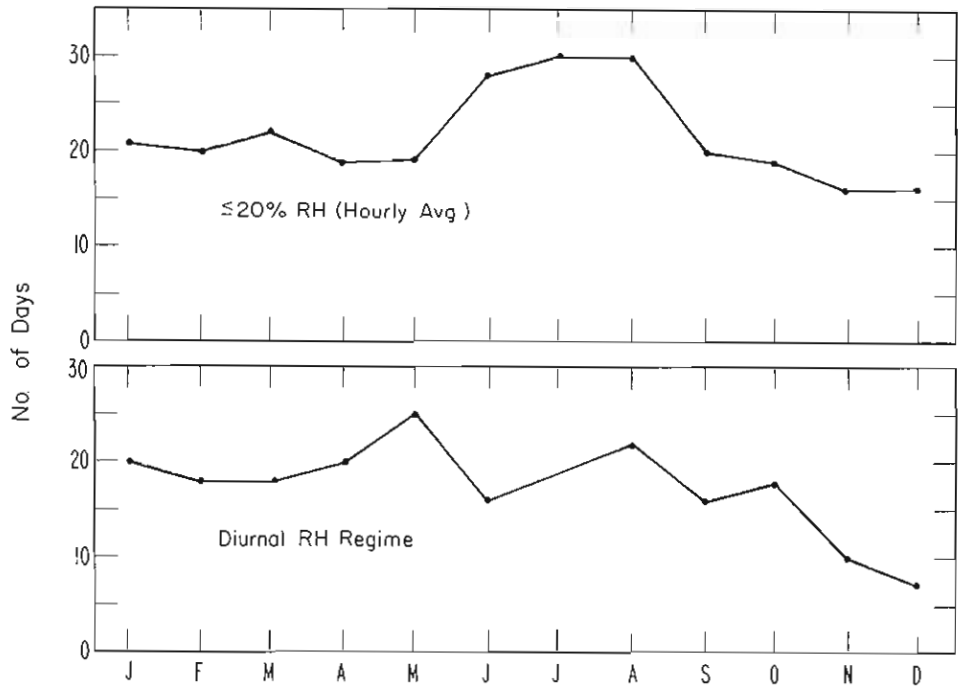

Figure 60. Relative humidity (percent) at MLO in 1974. The diurnal regime is an increase in RH of +45% or more in the afternoon from an initial low in RH of ≤ 20% in the morning to a return of RH ≤ 20% in the night.

Hilo Rawinsonde Data. A pilot program was started in September to evaluate upper air soundings taken at the Hilo Airport, 55 km northeast of the Mauna Loa Observatory, for use in interpreting other data measured at Mauna Loa. Three sets of data were computer processed from the rawinsonde soundings: (1) twice daily computations of total precipitable water above the elevation of Mauna Loa (2) computations of the gradient (850 mb) and jet stream (250 mb) wind layers; (3) tabulations of daily temperature inversions and moisture cutoffs in relation to the height of the observatory.

Figure 61 shows the plot of precipitable water above the elevation of Mauna Loa. Synoptic trends as well as day-to-day variations are frequent and pronounced. The average precipitable water for this period is about 2.2 mm. On days when there is a strong low-level temperature inversion the precipitable water content can fall to below 1.0 mm.

The plot of the cutoff temperature inversions as determined from the NWS Hilo soundings is shown in figure 62. A cutoff temperature inversion is defined as one where the mixing ratio drops from about 6 to 10 g kg^{-1} to ≤ 2.0 g kg^{-1} across the inversion layer. Such inversions separate a moist sub-inversion layer from a drier upper tropospheric air mass and inhibit extensive vertical mixing. These inversions generally form below the elevation of the observatory and act as a barrier to the upward transport of more turbid marine air past the observatory.

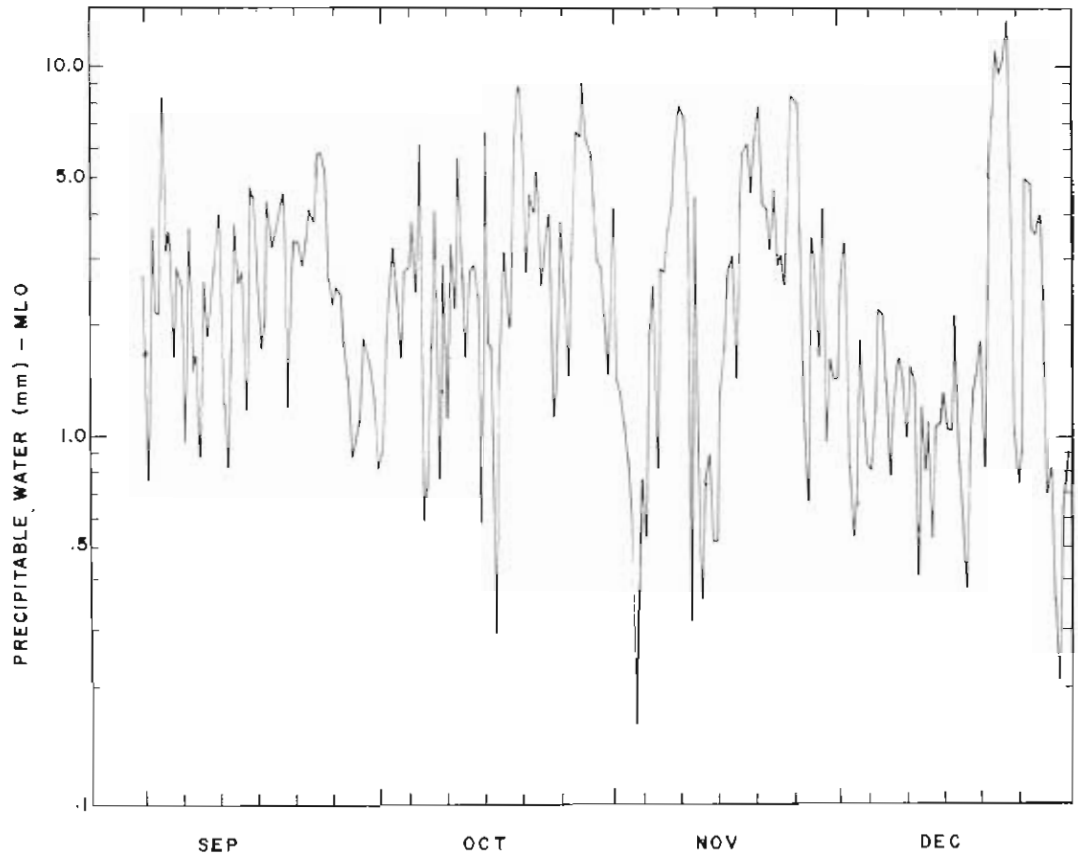

Figure 61. Total precipitable water above Mauna Loa Observatory elevation in 1974. Values computed from NWS Hilo rawinsonde observations, twice daily, approximately 55 km upwind of the observatory. The average for the whole period is 2.2 mm but daily fluctuations are pronounced. Trends corresponding to long term synoptic condition are evident in the periods Oct 25-Nov 10 and Nov 25-Dec 25.

Table 18. Departure of 1974 Precipitation and Temperature from a 13-Year Average (1958-1970) at Mauna Loa Observatory.

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Precipitation percent of 13-year average												
104	20	188	115	105	71	80	0	94	212	121	306	118
Temperature: difference from 13-year average maximum °C												
-3.1	-3.3	-3.0	-3.6	-4.1	-5.5	-4.1	-1.3	-3.3	-2.9	-3.7	-2.5	-3.6
Temperature: difference from 13-year average minimum °C												
+1.6	-1.2	-0.1	+0.2	-1.0	-1.7	-1.0	+0.5	-0.2	-0.4	-2.0	-0.3	-0.5

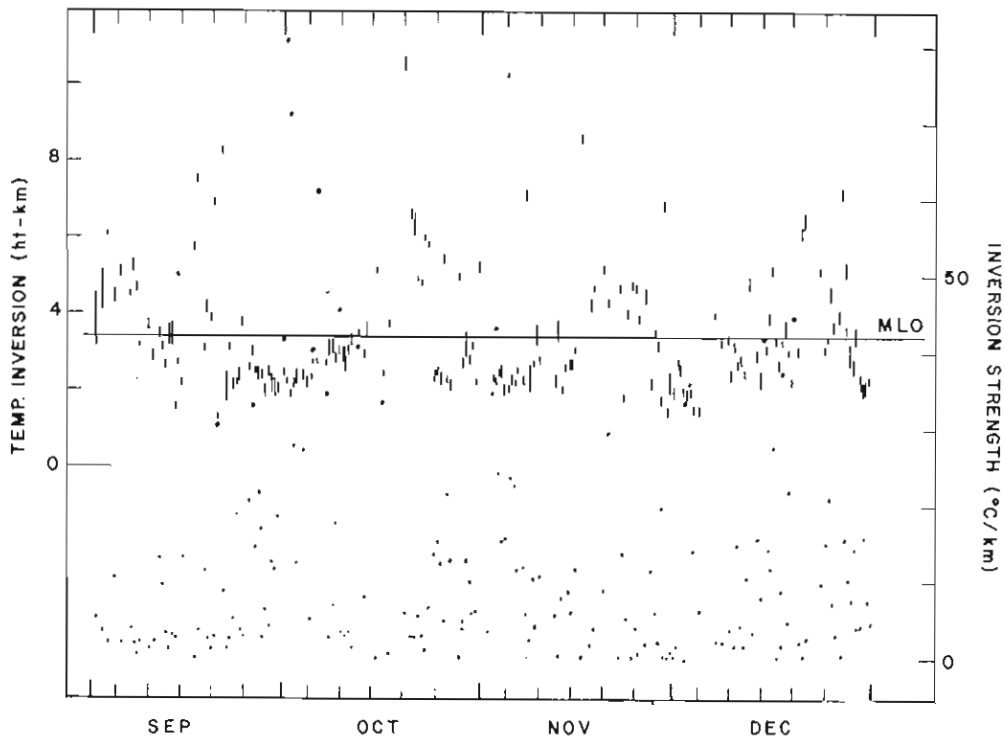

Figure 62. Cutoff temperature inversions as determined from the NWS Hilo rawinsonde data, twice daily in 1974. The mixing ratio decreases across the cutoff temperature inversion from 6 to 10 g/kg to ≤ 2.0 g/kg. Note the position of the inversion below the elevation of the Mauna Loa Observatory where it acts as a barrier to vertical mixing. Read vertical lines on temperature inversion scale; read dots on inversion strength scale.

Figures 63 and 64 are plots of the gradient and jet stream wind layers. In both cases there is significant daily variability in the height and thickness of the layers. The gradient wind layer is less persistent than the jet stream layer. Its direction is predominantly from the east and represents the trade wind regime. The upper extent of the gradient wind layer just reaches the elevation of the observatory.

The jet stream wind layer is more persistent, thicker, and has a striking bimodal direction frequency. It is either from the west or the northeast. It frequently extends down to within 1.5 km of the elevation of the observatory. The northeast directions observed are the results of upper level synoptic low pressure systems and represent periods of downward vertical transport rather than zonal transports from the east.

Summary. Colder than usual maximum temperatures and more days with temperatures below 0°C characterized the weather at the observatory during 1974. The summer months were dry but the yearly precipitation was above average.

Computer processing of NWS Hilo rawinsonde data for the latter part of the year showed the precipitable water content above the observatory to

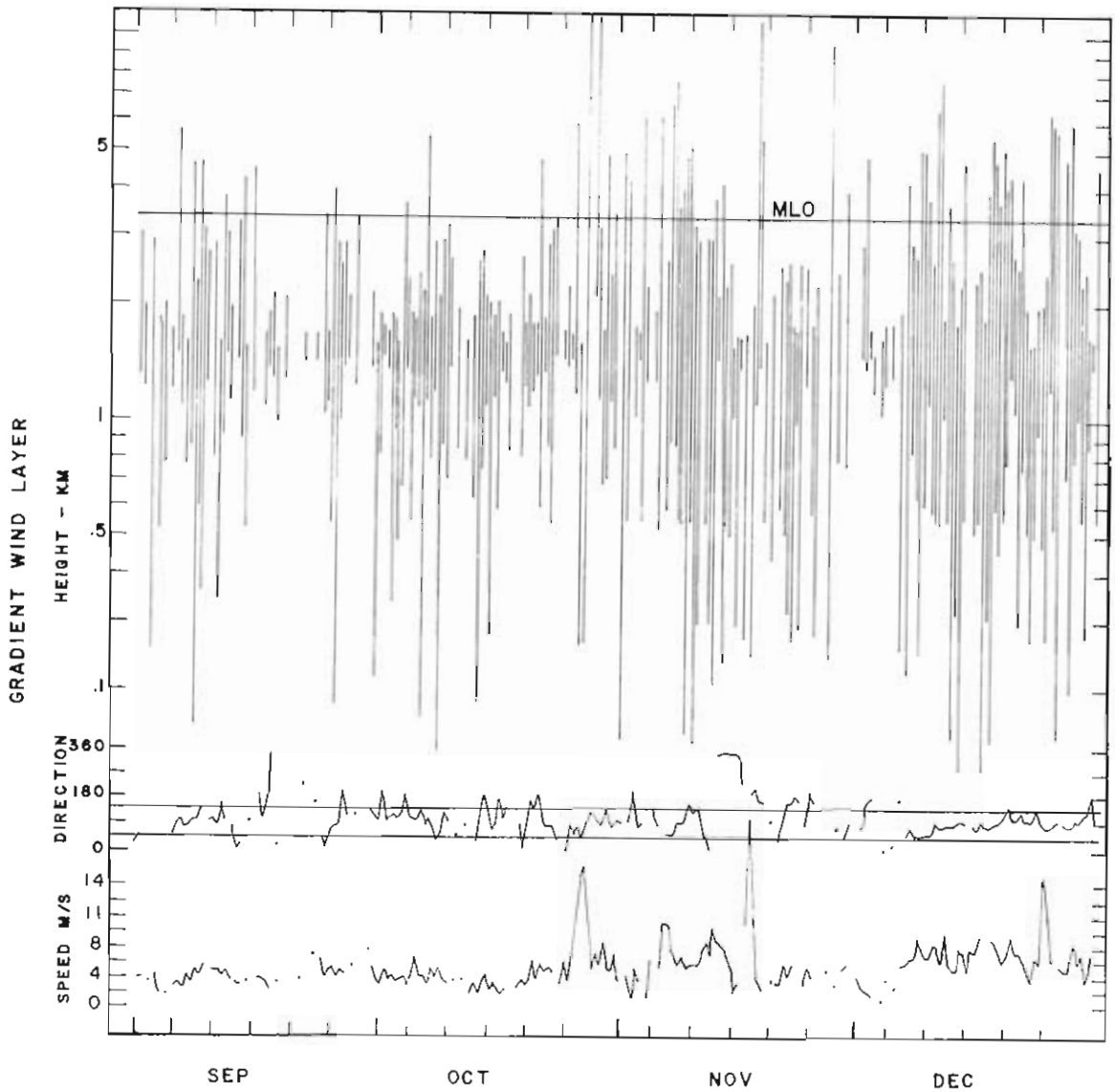

Figure 63. The gradient wind layer (850 mb) as plotted from NWS Hilo 1974 rawinsonde data, 55 km upwind of Mauna Loa Observatory. The vertical bars show the height and thickness of the layer. Wind speed and direction are averages of the whole layer. Note the elevation of the observatory in relation to the top of the gradient wind layer.

average about 2.2 mm but with great variability. It also showed the vertial extent of the trades to be just at the height of the observatory, with a cut-off temperature inversion embedded in the trades at about 0.8 km below the elevation of the observatory. A deep westerly flow persists above the observatory and frequently extends down to the height of the mountain top. This steady upper level flow provides a constant replenishment and circulation of upper tropospheric air over the observatory for geophysical benchmark monitoring.

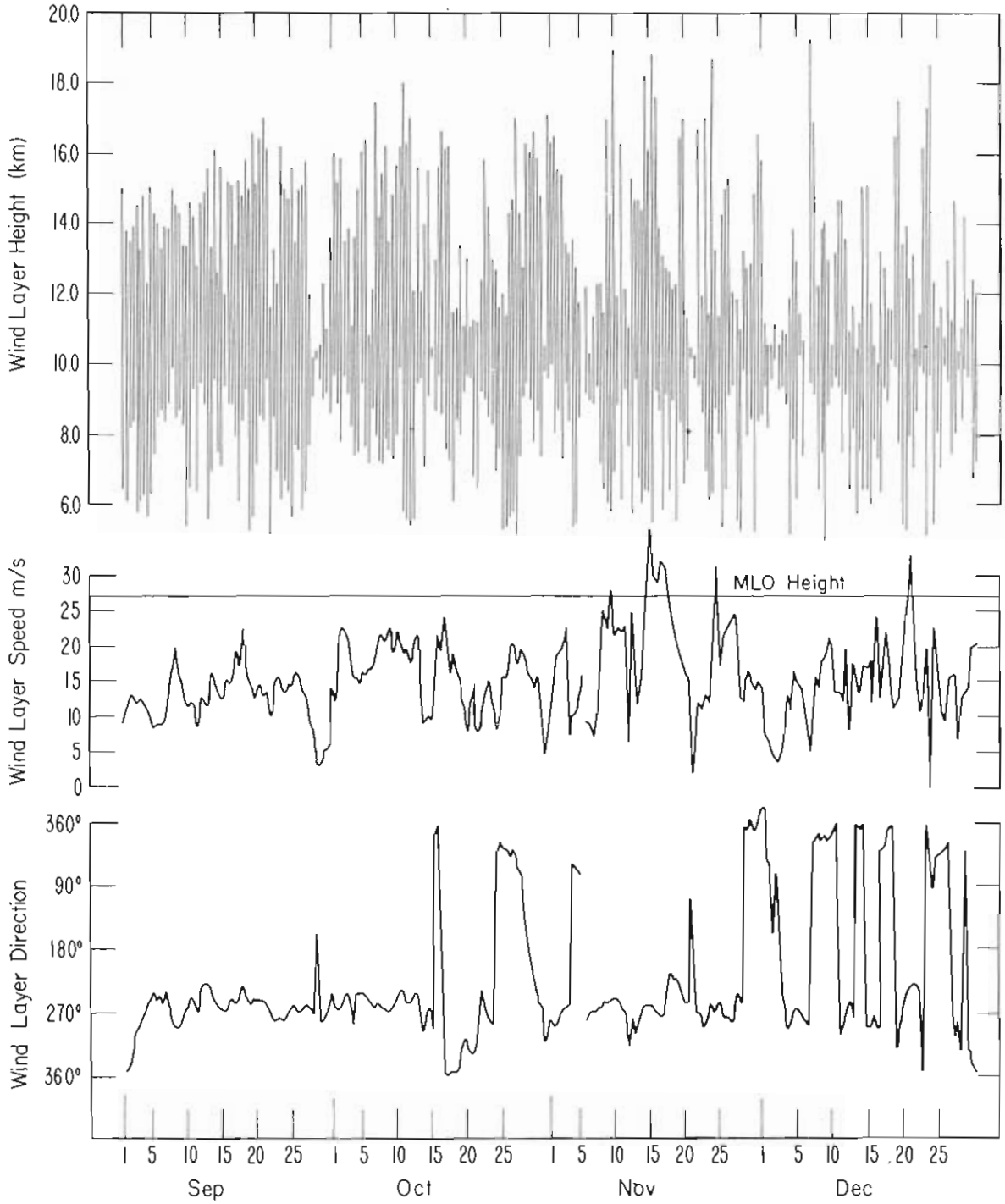

Figure 64. The jet stream wind layer (250mb) as plotted from NWS Hilo 1974 rawinsonde data. The vertical bars show the height and thickness of the layer. Wind speed and direction are averages of the whole layer. Note the bimodal direction of the layer and the downward extent to 5 km or about 1.5 km above the elevation of the observatory.

4.3.2 Barrow Meteorology

The topography surrounding Barrow is very flat and offers no wind barriers. Temperature inversions are therefore weak because of mixing of radiationally cooled air and no drainage of cold air. The sea is covered by ice from November to June. Average daily temperatures above 0°C occur in June, July, August, and September. Temperatures during 1974 ranged from 19°C to - 46°C. Transition between winter and summer seasons is rapid. The sun remains below the horizon from November 18 to January 24, and remains above the horizon from May 10 to August 2. Maximum cloudiness averaging almost 9/10 sky cover occurs in the summer when the sun is always above the horizon and the nearby ocean surface is free of ice. In the fall, cloudiness gradually decreases to winter and spring season averages of 4/10 and 5/10 sky cover. Wind speed averages show small variations both in seasonal and diurnal time periods; fall months are the windiest. Likewise the wind direction changes only slightly on a monthly basis, summer having increased southerly winds (fig. 65).

4.3.3 Samoa Meteorology

Cape Matatula climatological data for 1974 are summarized in table 19. The seasonal variation of air temperature was only 2.3°C, about one-third the diurnal variation. Relative humidity averaged over 90 percent on the Ridge and total yearly rainfall on the Point was only 179.2 cm. NWS WSO at the airport recorded 197.79 cm for the year and all-time monthly record minimum precipitation amounts were reported for July, August, September, and October.

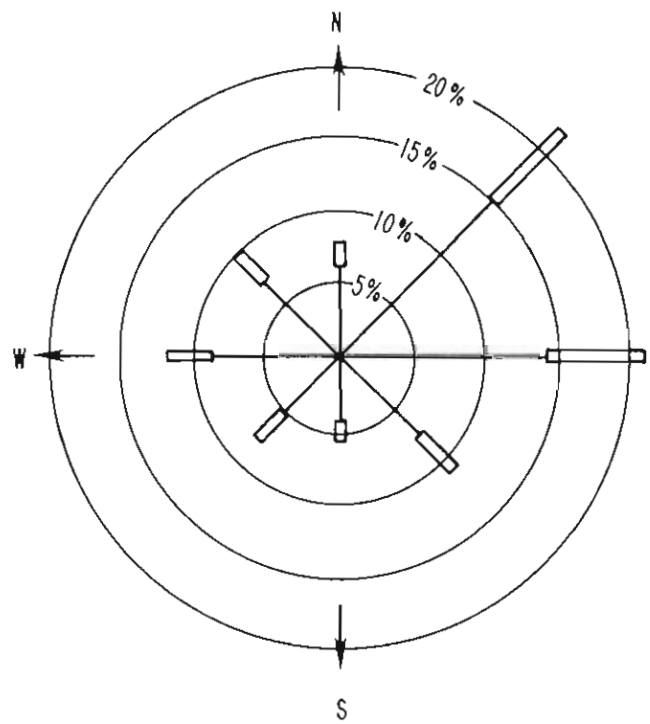

Figure 65. Barrow Observatory wind rose for 1974, from 24 hourly readings per day. Enlarged portions of spokes indicate winds ≥ 6.7 m sec^{-1}

Table 19. 1974 Climatology for Cape Matatula, American Samoa.

Month	Air Temperature (°C) Mean Daily Max	Mean Daily Min	Monthly Mean	Precip (cm) Monthly Total	RH (%) Monthly Mean	Winds (mps) Resultant Vector Speed	Dir	Zonal	Merid-ional	Monthly Mean	*Sky Cover (No. of Days) Clear	Ptly Cldy	Cldy
Jan	30.4	24.1	26.7	20.19	90.2	3.6	05	-2.6	-2.5	5.0	0	13	18
Feb	30.6	24.2	26.8	14.43	87.9	NIS	NIS	NIS	NIS	NIS	0	7	21
Mar	28.0	23.1	25.1	14.15	92.2	-	-	-	-	-	0	10	21
Apr	30.4	24.7	27.0	20.22	85.6	-	-	-	-	-	0	11	19
May	29.9	23.9	26.2	19.48	88.2	-	-	-	-	-	4	14	13
Jun	29.7	24.4	26.3	15.98	92.8	-	-	-	-	-	0	14	16
Jul	30.6	24.7	26.5	3.43	88.4	-	-	-	-	-	2	21	8
Aug	30.6	23.7	26.2	3.66	92.2	-	-	-	-	-	6	25	0
Sep	32.1	24.5	27.1	6.60	92.0	6.8	14	-3.9	5.5	7.6	5	23	2
Oct	32.3	24.4	27.4	7.65	92.3	6.5	15	-3.6	5.4	7.2	1	22	8
Nov	31.5	24.5	27.1	24.43	95.5	0.6	26	-0.6	0.1	5.5	0	8	22
Dec	30.1	24.9	27.0	28.98	95.6	0.6	13	-0.4	0.4	2.8	1	11	19
Year	30.7	24.3	26.7	179.20	90.1	3.2	14	-2.1	2.5	6.2	19	179	167

*From NWS-WSO Tafuna
NIS = Not in service

Winds on Matatula Point had a mean speed of 6.2 m sec^{-1} with a resultant vector of 3.2 m sec^{-1} at 140°, and were slightly diminished in comparison with 1973 values. Figure 66 shows direction frequencies and mean wind speeds to eight compass points. Table 20 lists mean diurnal variations of air temperature, humidity, pressure, and winds. Of interest to the GMCC program of air sampling is the constancy of the easterly trades. Mean hourly resultant vectors deviated from 140° only 21 percent of the time. Zonal wind components were very stable with a range of only 1 m sec^{-1} over the 24-hour period. Meridional components had a somewhat higher diurnal variation with a range of 1.4 m sec^{-1}.

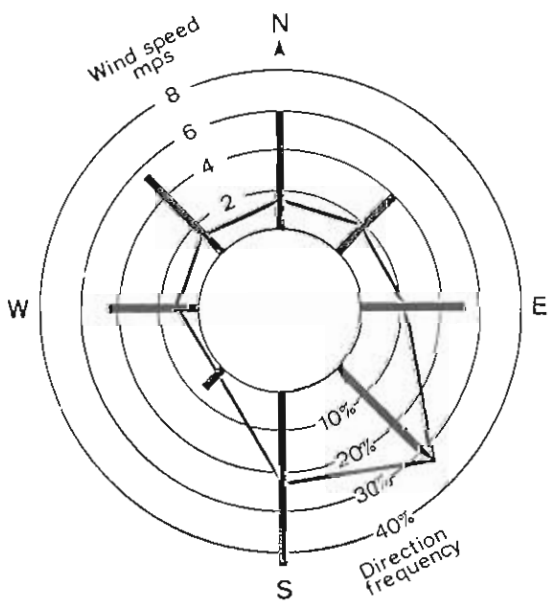

Figure 66. Surface wind rose for Cape Matatula, 1974. Bars give wind speed and polygon represents direction frequency.

Table 20. Diurnal Variations of Meteorological Parameters Measured in Samoa.

Hour	Air Temp (°C)		RH	Station Pressure		Winds (mps)		Resultant Vector	
LST	Point	Ridge	(%)	(mb)	Mean Speed	Zonal	Meriod-ional	Speed	Dir
01	27.1	25.2	96.3	1002.7	6.2	-2.4	3.1	3.9	14
02	27.0	25.1	96.5	2.2	6.1	-2.2	3.0	3.7	14
03	26.9	25.0	96.7	1.9	6.1	-2.3	3.0	3.8	14
04	26.9	24.9	96.7	1.8	6.5	-2.2	3.0	3.8	14
05	26.9	24.9	96.7	2.0	6.4	-2.2	2.9	3.7	14
06	27.0	24.9	96.6	2.5	6.4	-2.1	2.9	3.6	14
07	27.6	25.3	96.3	3.0	6.4	-2.1	3.1	3.8	15
08	27.9	26.1	94.3	3.5	6.5	-2.2	2.8	3.6	14
09	28.0	27.2	89.9	3.9	6.5	-2.2	2.5	3.3	14
10	28.3	28.2	86.4	3.9	6.3	-2.0	2.0	2.8	13
11	28.3	29.0	83.6	3.6	6.1	-2.0	1.9	2.7	13
12	28.6	29.5	81.6	3.1	6.1	-1.9	1.7	2.5	13
13	28.8	29.8	79.7	2.5	5.9	-1.8	1.7	2.5	13
14	28.7	29.7	79.4	2.0	6.0	-1.7	1.8	2.4	14
15	28.6	29.4	80.1	1.6	6.1	-1.7	1.9	2.5	14
16	28.4	28.7	82.1	1.5	6.1	-1.6	2.2	2.7	14
17	28.2	27.9	85.7	1.6	6.0	-1.7	2.0	2.7	14
18	27.9	26.7	90.9	2.0	6.0	-1.9	2.2	2.9	14
19	27.5	25.9	94.7	2.5	5.9	-1.6	2.6	3.0	14
20	27.4	25.6	95.5	2.9	6.1	-2.0	2.5	3.2	14
21	27.3	25.5	95.8	3.3	6.2	-2.1	2.5	3.3	14
22	27.3	25.4	95.7	3.5	6.2	-2.5	2.5	3.5	14
23	27.3	25.3	96.0	3.4	6.2	-2.6	2.8	3.8	14
24	27.2	25.3	96.2	1003.1	6.1	-2.3	2.7	3.6	14
Mean	27.7	26.7	91.0	1002.7	6.2	-2.1	2.5	3.2	14
N	2424	6861	6859	6708	2424	2424	2424	2424	

Harmonic Analysis. To describe the diurnal variation of meteorological parameters, a harmonic analysis was performed on surface pressure, temperature, and wind data. Table 21 contains diurnal and semidiurnal mean amplitudes and phase angles for 1974.

Figure 67 shows a harmonic dial for the determination of the solar-induced atmospheric tide in surface pressure. The diurnal oscillation had an amplitude of 0.28 ± 0.03 mbar with a phase angle of 352 ± 6° (where ± values indicate probable error). The semidiurnal wave had an amplitude of 1.03 ± 0.02 mbar with a phase angle of 154 ± 1°. Maximum value in the diurnal wave occurs at 0633 LST, and maximum value in the semidiurnal wave occurs at 0952 and 2152 LST. An error analysis using the method of Chapman (which states dial vectors must be at least three times the radius of probable

Table 21. Harmonic Analysis of Pressure, Temperature, and Wind Data From Cape Matatula for 1974.

MONTH	PRESSURE VARIATION DIURNAL A_1	DIURNAL θ_1	SEMIDIURNAL A_2	SEMIDIURNAL θ_2	TEMPERATURE VARIATION DIURNAL A_1	DIURNAL θ_1	SEMIDIURNAL A_2	SEMIDIURNAL θ_2
JAN	-	-	-	-	2.38°C	246°	0.80°C	64°
FEB	0.22mb	17°	1.07mb	147°	1.81	236	0.67	43
MAR	0.25	356	1.10	160	0.96	243	0.62	55
APR	0.26	1	1.06	155	2.05	245	0.85	55
MAY	0.40	341	1.01	152	2.20	244	0.97	60
JUN	0.26	335	0.96	151	1.72	249	0.85	65
JUL	0.43	359	0.98	149	2.34	242	1.14	55
AUG	0.46	343	1.05	154	2.85	245	1.17	55
SEP	0.20	345	1.04	155	3.07	244	1.19	52
OCT	0.26	342	1.11	155	3.36	253	1.20	70
NOV	0.31	357	1.00	159	2.58	251	0.93	66
DEC	0.13	16	0.95	154	1.62	251	0.47	71
1974 MEAN	0.28	352	1.03	154	2.24	246	0.90	59

MONTH	ZONAL WIND VARIATION DIURNAL A_1	DIURNAL θ_1	SEMIDIURNAL A_2	SEMIDIURNAL θ_2	MERIDIONAL WIND VARIATION DIURNAL A_1	DIURNAL θ_1	SEMIDIURNAL A_2	SEMIDIURNAL θ_2
JAN	84cm/s	273°	15cm/s	289°	50cm/s	121°	20cm/s	103°
SEP	27	200	16	315	69	79	37	232
OCT	40	156	13	261	52	17	39	269
NOV	43	263	18	350	90	49	24	317
DEC	34	251	25	28	114	4	7	261
1974 MEAN	34	244	12	332	58	44	15	261

NOTE: A represents amplitude and θ represents phase angle in degrees.

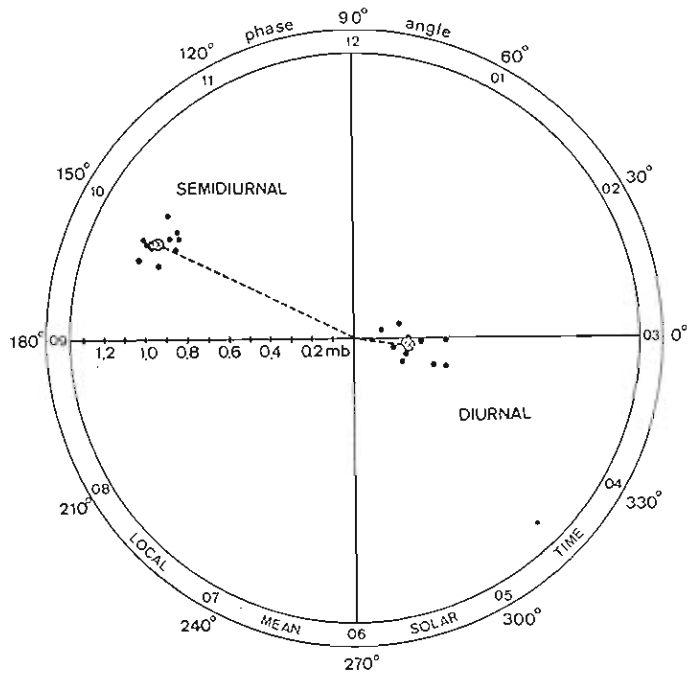

Figure 67. Harmonic dial for solar tidal variation of surface pressure at Cape Matatula. Dots represent monthly determinations; crosses, surrounded by probable error circles, represent mean values for 1974. Probable error circles for each of the monthly values are $\sqrt{11}$ times larger than the probable error circle for the mean.

error circles) shows that results obtained are statistically significant. The harmonically synthesized wave quite accurately describes the pressure oscillation, if the latter is represented by values averaged over a long period of time. The mean absolute deviation between the synthesized wave and actual hourly data for 1974 is only 0.0002 mbar.

Figure 68 shows a harmonic dial for the determination of the atmospheric tide in air temperature. The diurnal oscillation had an amplitude of 2.24 ± 0.16°C with a phase angle of 246 ± 4° and the semidiurnal wave had an

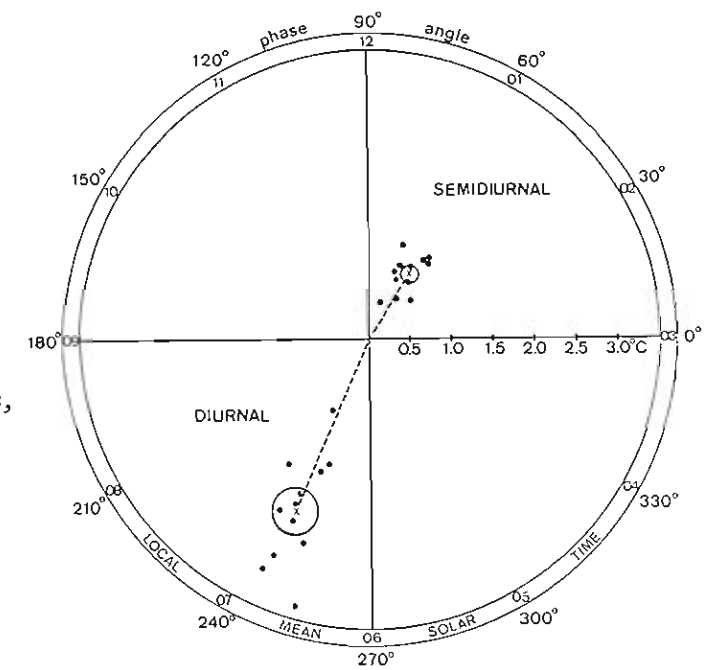

Figure 68. Harmonic dial for solar tidal variation of air temperature at Cape Matatula. Dots represent monthly determinations; crosses, with corresponding probable error circles, represent the mean for 1974. Probable error circles for each of the monthly values are $\sqrt{12}$ larger than the probable error circle for the mean.

amplitude of 0.90 ± 0.06°C with a phase angle of 59 ± 4°. Maximum value in the diurnal wave occurs at 1335 LST and maximum amplitude in the semidiurnal wave occurs at 0101 and 1301 LST. The temperature determination also meets Chapman's criterion for significance.

Figure 69 shows harmonic dials for zonal and meridional tidal winds. The determination is not significant because the ratio of amplitude to probable error is less than 3. The determination should be strengthened by more data. Figure 70 shows the path traced out by the wind vector over the period of 24 (or 12) hours. The path of an airborne particle due to these oscillations is similar in form and orientation to the ellipses.

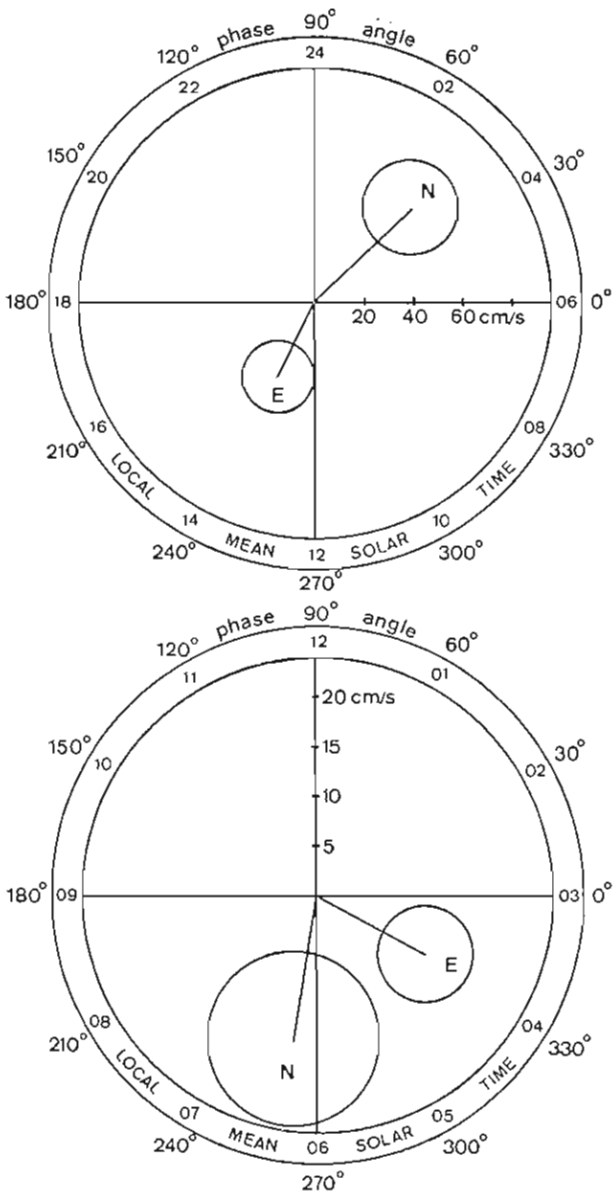

Figure 69. Twelve- and 24-hour harmonic dials (with probable errors circles) for annual mean solar-induced variations of zonal (E) and meridional (N) wind components at Cape Matatula.

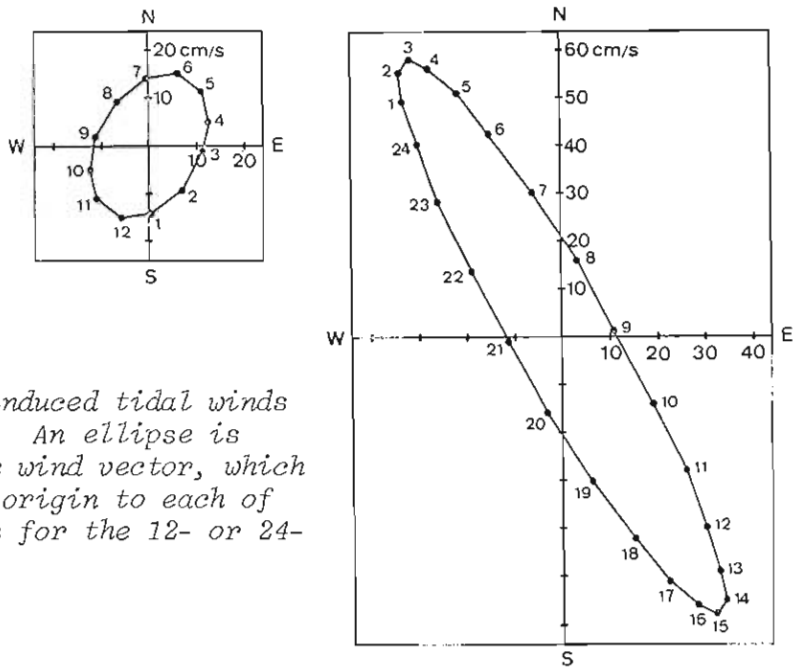

Figure 70. Solar induced tidal winds at Cape Matatula. An ellipse is traced out by the wind vector, which extends from the origin to each of the numbered dots for the 12- or 24-hour period.

4.3.4 GMCC Trajectory Program.

The GMCC (air parcel) trajectory program was initiated this year for Barrow, Adrigole (Ireland), Bermuda, and Ithaca (N.Y.). The trajectories were computed using the Regional-Continental Scale Trajectory Program developed by the Air Resources Laboratory (Heffter, Taylor, and Ferber, 1975). At each station 5- or 10-day backward trajectories were computed for monthly periods (fig. 71). Mauna Loa, Samoa, and the South Pole were not covered by the data base for 1973 and 1974, but are expected to be included in the new data base established in January 1975.

The minimum requirements for trajectory computations are winds at two levels within the layer of interest and two locations separated by not more than 150 nautical miles. For the GMCC stations, the heights usually chosen were 300-1500 m above average terrain height. Wind data were obtained from two sources: (1) the observed winds (at 00Z, 06Z, 12Z, and 18Z) as reported by the global upper air station network, and (2) the daily analyzed winds (00Z and 12Z) from the NMC Northern Hemisphere octagonal grid (1966 grid points) at 1000, 800, 700, and 500 mbar levels. The observed winds are always taken in preference to the analyzed winds, the latter being used only when station data are lacking. The results of the computations are displayed as a listing of trajectory end points for selected durations (usually every 24 hours) within the 5- or 10-day period and as a plot of individual trajectories (usually every 6 hours) on Mercator or polar stereographic map projections.

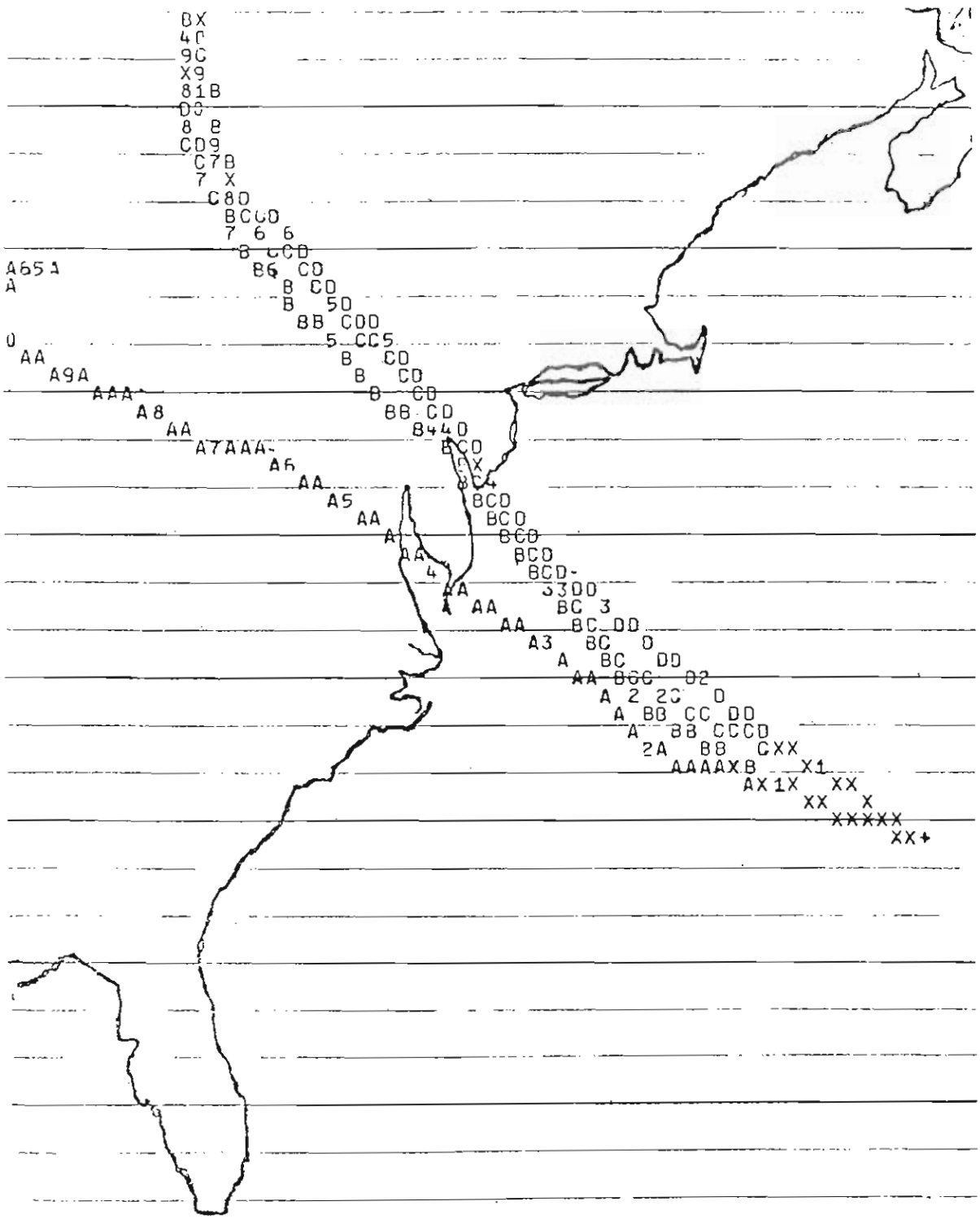

Figure 71. Examples of 5-day back trajectories to Bermuda for May 6, 1974. A, B, C, and D represent 0000, 0600, 1200 and 1800 Greenwich Mean Time respectively. Numbers 1, 2, etc., represent points 6, 12, etc., hours back in time.

Considerable difficulty with the computational system on the CDC 6600 resulted from a rather complex computational scheme being supported by an erratically performing magnetic tape system. This situation should improve with the new system being formulated on the IBM 360.

4.4 Measurement of Solar Radiation

4.4.1 New Field Instruments

Another multichannel radiometer was received from the manufacturer in 1974. A summary of the instrument properties is given in table 22.

Table 22. Multichannel Radiometer (No. 4759) Calibration Summary, According to Manufacturer.

Channel	Thermopile No.	Calibration $mV/mWcm^{-2}$	Impedance (ohms)
1	12719P3	0.660	1244
2	12720P3	0.239	1210
3	12726P4	0.144	524
4	12725P4	0.156	567
5	12447P4	0.199	605
6	12418P4	0.167	563
7	12419P4	0.157	582
8	12420P4	0.155	559
9	12713N3	0.0759	726
10	12715N3	0.0738	739
11	12718N3	0.0783	742
12	12716N3	0.0743	776
13	12717N3	0.0862	840

4.4.2 Field Stations and Instruments Received

Barrow, Alaska. In June 1974, five pyranometers and a UV radiometer were installed at Barrow along with an L&N strip chart recorder and a Smithsonian blower system. Table 23 lists the calibrations and glass filters used on the installed pyranometers. UV radiometer serial no. 12348 is also in operation at Barrow. Some of the July and August data were lost because of a faulty L&N recorder.

Table 23. Barrow Pyranometer Arrray.

Serial No.	Filter	Eppley calibration $mV/mWcm^{-2}$	GMCC calibration $mV/mWcm^{-2}$
12263	Quartz	0.0957	0.0958
12264	OG1	0.1058	0.1065
12265	GG22	0.0983	0.0991
12266	Quartz	0.1068	0.1070
12267	RG8	0.0965	0.0965

Mauna Loa, Hawaii. Early in 1974, pyranometer 10154 (quartz) developed moisture condensation problem. On March 21, 1974, a new pyranometer (serial number 12617F4) replaced the old instrument. The Eppley calibration constant is 0.0794 $mV/mWcm^{-2}$ and GMCC calibration is 0.0787 $mV/mWcm^{-2}$ ± 0.8 percent.

On June 9, 1974, a new multichannel radiometer (serial no. 4758) was installed to replace the old multichannel unit. Because of problems with the digital voltmeter in the Hewlett-Packard data acquisition system, the instrument was not on line until September 11, 1974. Most of the radiation data in the meantime were lost.

South Pole. A multichannel radiometer (serial No. 4757) was shipped to the South Pole for installation in January 1975. Only the broadband channels are to be operational.

4.4.3 Data Processing and Analysis

Initial processing of the Mauna Loa radiation data tapes began in February 1974. The first step in the processing began with the conversion of the Mauna Loa raw data tapes to standardized edited tapes. This process assured that a number of problems with the raw data tapes (e.g., parity errors, clock errors, changing of channel order) were eliminated. This work was completed by the National Bureau of Standards for the Mauna Loa tapes through June 1974.

Much effort was given to analysis of the processed data. The hourly integrals and Ångstrom turbidity coefficients were the primary parameters for study. For the hourly integrals, the diffuse component (obtained by subtracting the direction radiation from the global radiation) in many cases early in the morning became negative. This situation could arise from (1) radiation scale differences between the pyrheliometer and pyranometer, or (2) poor cosine response to the pyranometer. It will be necessary to check both possibilities.

Even greater problems were encountered in trying to analyze the multichannel radiometer data to obtain values of the Ångstrom turbidity coefficients (α and β). Although computer programs were checked by comparison with manual calculations and with published values of all calculated quantities, calculated α and β values were inconsistent. This error is probably instrumental, specifically: (1) The glass channels cannot be calibrated self-consistently to better than about ± 1.0 percent although a calibration self-consistency of ± 0.1 percent is needed: (2) Internal reflections between the glass protective cover, glass filters, and inner glass protection are not known accurately and are not measured. Calculations of these quantities to better than ± 0.5 percent is difficult and facilities to measure them are not yet available: (3) Thermal control on the radiometers is very poor, allowing calibration constants to vary over a range of ± 1 percent and allowing an unknown and varying amount of thermal radiation to strike the thermopiles. Lack of thermal control makes data interpretation difficult. Facilities to check the thermal response are also not yet available.

Because of the difficulties described, design of a replacement system to correct the problems is under way. Note that the criteria necessary for long-term geophysical monitoring are about one order of magnitude more stringent than is customary in routine radiometry.

4.4.4 Other Solar Radiation Measurements.

The Advanced Applications Flight Experiment (AAFE) and Solar Energy Experiment (SEE). A proposal to measure the solar total irradiance (the so-called solar constant), entitled "Total Solar Irradiance Measurement Experiment for AAFE," was submitted to the Advanced Applications Flight Experiment program of NASA-Langley in June 1974.

The AAFE proposal covered the justification for this type of measurement and its relation to climatic change, defined the accuracy needed for success of the experiment (± 0.1 percent), covered the means of measurement which is a modification of the National Bureau of Standards laser calorimeters, described the sources of error and showed by references to work in the published literature how the ± 0.1 percentage accuracy could be achieved, and included information on testing, management, budgeting, and method of publication.

Although the proposal received favorable and often enthusiastic comments, it was not funded. A similar proposal to NASA entitled "Solar Energy Experiment" (SEE) was also not funded. Efforts to initiate this important program are continuing.

Earth Energy Budget Study. A new study of the Earth energy budget both for the present and for the last ice age (18000 BP) was made. For the present-day case, models with the ground-based determinations of cloud cover and satellite determinations of cloud cover were calculated and compared. Although the information obtained in the computer runs of the models is too vast to tabulate here, the major conclusions are: (1) The global mean albedo of 29.4 percent for the satellite cloud cover model is lower than most previous theoretical estimates and in accord with satellite observations. Most of the difference in albedo occurs in the tropical regions where more

radiation is reaching the Earth's surface and being absorbed. (2) Total global cloud cover is 44.1 percent, or 9.1 percent less than previous estimates. In the tropical regions (30°S-30°N), it is 16.2 percent less. (3) Total evaporation and precipitation of 98.9 $cmyr^{-1}$ agrees better with Budyko (1963) than the value determined with the ground-based cloud climatology does. The zonal distribution of precipitation in the satellite climatology model agrees favorably with Meinardus (1934) whereas the ground-based climatology model does not agree nearly as well. (4) The transequatorial fluxes of water vapor are in better agreement with previous aerological studies such as those of Kidson et al. (1969) or Oort (1971).

Similar models have been reconstructed for the last ice age. Major conclusions from these models, for the Northern Hemisphere only, are: (1) Global annual albedo is 31.7 percent (28.5 percent in present). (2) Annual mean surface temperature of 279°K (288°K in present) with the greatest seasonal drop in temperature in winter (-11.6°K) and least in summer (-4.6°K). (3) Precipitation is 85.3 percent of the present amount and decreases north of 30°N and increases slightly south of this latitude. (4) The solar constant must be reduced by at least 1.2 percent ± 0.2 percent to achieve global radiation balance. The value 1.2 percent is a lower limit since the ice-snow albedo feedback is greater in the Northern Hemisphere than in the Southern Hemisphere. Finally, it should be noted that the calculated overall cloud cover is slightly less than today's and that there is more cirrus, particularly in the northern latitudes over the ice sheets.

Publication of these results is planned for 1975.

Gate Pyranometer Comparison. Two Eppley model-2 pyranometers (serial numbers 10155 and 12616) participated in the GATE pyranometer comparison in April.

4.4.5 Corrections to Last Year's Summary Report

The last five items on table 16 of GMCC Summary Report 1973 should read as given in table 24 of this report. In table 23 of Summary Report 1973, the

Table 24. Manufacturer's Calibration Data for Pyranometers Corrected From Table 16, Summary Report 1973.

Serial No.	Dome Calibration ($mV/mWcm^{-2}$)	Sun Calibration ($mV/mWcm^{-2}$)	Applicable Temp. (°C)*	Impedance at 23°C
12616F3	0.0790	0.0797	15°	700
12617F3	0.0806	0.0813	15°	650
12618F3	0.0765	0.0773	15°	700
12619F3	0.0785	0.0795	15°	700
12622F3	0.0932	0.0947	15°	650

*For sun calibration.

calibration constant of channel 12, multichannel 4757, should be 0.0690 $mV/mWcm^{-2}$. All the multichannels in that table are based upon Ångstrom 2272, not Ångstrom 2202 as stated.

4.4.6 Ultraviolet Radiation Measurements in the Erythema Spectrum

Measurements of irradiance in the erythema spectrum continued throughout 1974 at Bismarck, North Dakota, and Tallahassee, Florida, with the spectrophotometric dosimeter instrumentation described in GMCC Summary Report 1973. Some difficulty was experienced at Bismarck in instrument calibration drift owing to a gradual deterioration in performance of a high voltage power supply. After replacement of the power supply in June, the calibration drift problem was eliminated. Observations at Tallahassee continued with no major problems during 1974 except for a 52-day period in late summer and autumn when the dosimeter was inoperative because of damage by lightning.

The GMCC erythema spectrum irradiance measurements program was terminated at Bismarck in December 1974. The Tallahassee program will be terminated in April 1975. Processing of data is continuing and is expected to be completed by about June 1975. Meanwhile, data analysis at the NOAA Air Resources Laboratory, Silver Spring, Maryland, is continuing (Machta et al., 1975). A preliminary finding is that the percentage change of erythemal ultraviolet radiation to percentage change in total ozone varies between 1.5 and 2.0, depending on solar elevation.

4.5 Precipitation Chemistry

The World Meteorological Organization (WMO) has defined a baseline observatory as a remote measuring site where, at a minimum, carbon dioxide, turbidity, and the chemistry of precipitation are determined. Junge (1973), in a review of regional and baseline observation concepts, stated that the WMO made a very important decision in monitoring sulfur, nitric oxides, and ammonia not by their concentrations in air but by their concentrations in precipitation. In establishing a precipitation chemistry program within GMCC, certain advantages and disadvantages must be recognized.

Advantages.

(1) Simplicity and reliability of precipitation analysis as compared with other measurements.

(2) Integration over a considerable portion of the lower troposphere due to washout and rainout; hence, more representative values.

(3) Less influence of local pollution on the chemistry of precipitation than on other measurements.

Disadvantages.

(1) Occasional insufficiency in both the quantity and frequency of precipitation.

(2) Difficulty in distinguishing between chemical analyses of precipitation from different storm or shower types.

(3) Difficulty in avoiding dry fallout in arid zones.

Long-term monitoring of precipitation chemistry, as required for baseline work by the WMO, is an important part of any global monitoring program. However, as simple as this may seem, establishing permanent programs for both a baseline and regional monitoring network for precipitation chemistry in the United States has been difficult. Lack of long-term programs and technical problems in the collection and analysis of precipitation samples have hindered quality work in this area. In past efforts, many of the possible sources of error have not been evaluated for network operations. As a result the validity of the data is questionable.

GMCC's mission to establish and maintain the United States baseline network includes precision measurement of precipitation chemistry. To monitor precipitation, the following actions are being taken:

- Establishment and evaluation of collection sites at and near GMCC observatories.
- Standardization of collection techniques using both bulk and open-close collectors.
- Analysis of the samples locally by specific ion techniques and simple wet chemistry. (Samples will also be analyzed at a central laboratory under a cooperative program with the Environmental Protection Agency (EPA) and the Energy Research Development Administration (ERDA)).
- Simple statistical evaluation of the data to include interpretation in terms of air trajectories and other meteorological parameters.

4.5.1 Locations of Precipitation Chemistry Collection Sites

Collection sites around a given GMCC observatory must be chosen with care. Each location is to be as clear as possible of all sources of contamination such as buildings, roads, people, towers. The Mauna Loa, Barrow, and Samoa station sites all must be evaluated in terms of their own topography and micro-climatology.

Mauna Loa. Because of its unique location, this observatory presents a wide spectrum of precipitation regimes from which precipitation can be collected for analysis. The following sites have been established by the Mauna Loa staff.

Site 1. University of Hawaii (GMCC Hilo office) at 300 m MSL. A tipping bucket rain gage is used to determine the rain amounts. The average amount of precipitation is 3760 mm per year.

Site 2. Kulani Mauka at 2530 m MSL level. This site is situated on a lava field devoid of vegetation. A tipping bucket gage is used for determining precipitation amounts. The annual rainfall is 820 mm.

Site 3. This site is located 10 meters from the Mauna Loa Observatory building at an elevation of 3400 MSL. Other collection areas will be tested in and around the observatory. Besides the tipping bucket gage, there is a full complement of meteorological measurements available to use in the evaluation of the precipitation data. The annual rainfall is 304 mm.

Other sites may be chosen on the island to better define elevation effects on the chemistry of the precipitation.

Barrow. In contrast to Hawaii, Barrow is located in an Arctic environment and may be appropriately termed a "desert" (114 mm/yr^{-1}). An attempt to collect precipitation with a Misco collector has not been successful because the extreme weather conditions at the site affect the operation of the collector. A pilot program has been established to collect snow for pH analysis at four sites around the observatory.

Samoa. Because the observatory facilities on Cape Matatula have not been completed, monthly samples are being collected in an open-close gage at the Pago Pago International Airport where the annual precipitation averages 3175 mm.

Beginning in 1975, collection sites will be established within the observatory grounds. Potential instrument placement would include an open-close collector near the observatory and another at the sampling site farther out on Cape Matatula. Other sites will be established to test the variation of precipitation and its chemistry.

Washington, D.C. Although Washington is not a part of the baseline observatories, the collection of precipitation locally is useful as a testing program in establishing methods of analysis and collection before they are used at GMCC observatories. The present network consists of six sites.

4.5.2 Methods of Collection

The four methods currently used in GMCC to collect precipitaton for chemical analysis are: manual, bulk, open-close, and wet-dry. The last three methods are being evaluated under a NOAA grant at Cornell University (Galloway and Likens, 1975).

Manual. This method is used only at Barrow. Wide-mouth plastic bottles (250 ml) are pushed into the snow at designated sites around the observatory. The sample is then allowed to melt and a pH determination is made.

Bulk. The bulk collector, which consists of a plastic funnel and collection bottle, is being used at Mauna Loa and will eventually be used at Samoa. Samples are collected at least once weekly although ideally sampling should be made on an event-by-event basis to prevent dry deposition. In Washington, the Taylor 10-cm diameter plastic rain gage is used as a collector.

Open-close. The Misco collector is now used at all sites from which samples are sent to EPA for analysis. This collector is shown in figure 39 of Summary Report 1972.

Wet-dry. The Health and Safety Laboratory (HASL) collector will be used at Mauna Loa on an experimental basis. Samples will be returned to the HASL for analysis.

Table 25 lists precipitation collectors in GMCC.

Table 25. Precipitation Collectors in GMCC.

	MLO	BRW	SMO	DC
Manual	---	4	---	--
Bulk funnel	5	---	---(4)*	--
Plastic rain gage	---	---	---	5
Misco	2	1	1 (2)	1
HASL	1	---	---(1)	--

*Parentheses indicate planned for 1975.

4.5.3 Method of Analysis

Because of the unknown effects of long storage and shipment times, a modest program of on-station analysis is being attempted.

pH. The measurement of pH in precipitation is probably one of the easiest measurements to make. Its importance has been discussed extensively in the literature. pH measurements are made at Mauna Loa (5 per week), Barrow (4 per week) and Washington metropolitan (6 per storm). An Orion 401 and a Fisher electrode are used by GMCC staff in the measurement.

Specific ion electrode. There has been a rapid improvement in the ability to measure low concentrations of ions in water by the use of specific ion electrodes. Though pH has been measured for years by this technique, other electrodes have just been developed that will measure many more ions found in water samples. These new techniques are being evaluated for possible application to precipitation chemistry at the baseline sites.

Table 26 is a list of specific ion electrodes that have been developed by the Orion Company to measure low concentrations in a solution. It is hoped that each of these electrodes can be evaluated later at the GMCC observatories. Current plans are to work closely with the Naval Research Laboratory in Washington, D.C. to develop the techniques of low level measurements, beginning with fluoride. References for these techniques are presented in Warner and Bresson (1973) and Harriss and Williams (1969).

Table 26. Specific Ion Electrodes To Be Tested At GMCC Sites.

	Type	Detection Limit (mg/l)	Best Wet Chemical Detection Limits (mg/l)	Low Values at Clean Sites (mg/l)
Ammonia	gas sensing	0.018	0.01	0.1
Cadmium	solid state	0.011	0.001	0.03
Calcium*	liquid membrane	0.40	0.005	0.09
Chloride*	liquid membrane	0.355	0.01	0.1
Fluoride*	solid state	0.002	----	0.001
Lead	solid state	0.021	0.005	0.05
Nitrate	liquid membrane	0.62	0.01	0.2
Potassium	liquid membrane	0.39	0.01	0.05
Sodium*	glass	0.002	0.005	0.13
pH*	combination electrode	0.01 (pH unit)	0.01 (pH unit)	----

* Most promising for GMCC studies.

Wet chemistry. Some initial on-station wet chemistry will be attempted at Mauna Loa in conjunction with the Crop Log Laboratory and the University of Hawaii at Hilo.

EPA-ERDA analysis. EPA monthly composite samples collected at Mauna Loa, Barrow, and Samoa are sent to the Quality Assurance and Environmental Monitoring (QAEM) Laboratory at Research Triangle Park, N.C. Table 27 gives the constituent limits of detection and methods of analysis.

Table 27. The Constituents, Limits of Detection, and Methods of Analysis In the EPA-NOAA Precipitation Chemistry Program.

Constituent	Detection Limit (mg/1)	Method
pH	(0.01 pH unit)	Electrode
SO_4	1.0	Colorimetric
NO_3	0.2	Hydrozine reduction
NH_4	0.1	Sodium phenolate/hypochloride
Cl	0.1	Colorimetric
F	0.04	Specific electrode
Ca	0.01	Atomic absorption
Cu	0.01	" "
Fe	0.03	" "
K	0.04	" "
Mg	0.002	" "
Mn	0.02	" "
Na	0.02	" "
Ni	0.05	" "
Pb	0.05	" "
Zn	0.02	" "

ERDA. The Health and Safety Laboratory of ERDA plans a pilot program to measure Pb, Ni, Ce, V, pH, SO_4, Cl and NO_3 at the Mauna Loa and Samoa observatories.

4.5.4 Past Precipitation Chemistry Data

Mauna Loa. The island of Hawaii has been the site of many investigations of cloud physics and precipitation. Included in some of these projects has been analysis of the precipitation. Unfortunately, much of this work has never been published; even the published literature is already difficult to obtain.

In the first such project, Project Shower in 1954, Eriksson (1957) collected samples along the road leading to the observatory. Plastic-coated pineapple cans were used as collecting vessels. Table 28 shows measurements made by the Stockholm laboratory on selected samples.

The Public Health Service–NCAR network (1960-1966) maintained an open-close gage (Wong type) at the Mauna Loa Observatory. Except for a metals analysis done by Lazrus et al. (1970), the data have never been published. The metals data (1966-1967) published by Lazrus show the following concentrations averaged over a 6-month period: Pb–3g/ha/mo, Zn–5g/ha/mo, Cu–0g/ha/mo, FE–0g/ha/mo, Mn–0g/ha/mo, and Ni–2g/ha/mo.

Table 28. Precipitation Chemistry Values Measured During Project Shower.

Height Above Sea Level in feet	Distance from Sea in km	Prec. in mm	mg ℓ^{-1} Na	K	Mg	Ca	NH_3-N	NO_3-N	Cl	SO_4-S	pH
1325	6.3	18.9	1.28	.10	.41	.41	.06	<.01	2.43	.29	5.2
1725	8.1	19.8	1.16	.09	.34	.35	.06	<.01	2.03	.26	5.2
2100	9.7	19.8	.80	.10	.35	.30	.06	<.01	1.61	.20	5.2
2700	12.4	18.6	.58	.06	.23	.15	.06	<.01	1.12	.21	5.4
3680	15.9	15.9	.27	.05	.21	.12	.06	<.01	.53	.11	5.5
5550	29.3	6.6	.19	.04	.15	.18	.06	<.01	.28	.08	5.7
30	1.0		5.46	.37	.92	.47	.08	.05	9.63	.64	4.8
1620	7.6		3.80	.19	.87	.67	.08	.05	6.87	.53	4.9
2630	12.3		2.09	.14	.51	.44	.07	.05	4.62	.29	4.9
4080	19.4		.98	.09	.60	.49	.07	.02	2.49	.27	5.0
5330	25.8		.40	.06	.41	.27	.06	<.01	1.12	.10	5.2

Another group of measurements was made at the University of Hawaii during the late sixties by Duce et al. (1969), Seto et al. (1969) and Woodcock et al. (1971). Sodium, chloride, and iodide were measured in precipitation samples throughout the island. Most of the data were interpreted in terms of ratios to chloride.

Naval Research Laboratory scientists collected samples of precipitation on the island of Hawaii during the summer of 1970 and analyzed them for potassium, fluoride, chloride, and carbon dioxide. Swinnerton et al. (1971) and Wilkniss and Bressan (1972) have reported on these results.

Another short program of precipitation chemistry at Mauna Loa was completed by H. J. Simpson (1972). His purpose was to compare these values with aerosol collection and analysis values. Table 29 summarizes his data for 1970-1971.

The most recent precipitation chemistry measurements were performed by Kratky et al. (1974). These researchers tried to correlate reduced acidity of the precipitation on the Kona side of the island with the reduction in the tomato crop. Their precipitation chemistry measurements are shown in table 30.

Barrow. Duce et al. (1966) measured bromine, iodine, and chlorine in Barrow snows. Since these measurements were performed, no known collection and analysis of precipitation has been made in the area except under the GMCC program.

Samoa. There have been no known precipitation chemistry measurements at Samoa except those performed under GMCC.

Table 29. Precipitation Chemistry Data Collected by Simpson (1972) On Hawaii.

Sample Number	Collection Date	Collection Location	Na	K	µg/l Ca	Hg	Pb	Cu	Zn
C1	11/24-25	Cloud Physics (Hilo)	780	180	100	120	3.8	2.6	30
G2	9/11-12	Glenwood	1420	220	160	170	5.8	3.6	50
G3	11/20-21	Glenwood	500	80	40	30	5.0	9.2	120
K4	2/11-16	Kumukahi	15000	1150	1840	2700	3.2	---	210
ML5*	11/20-21	Mauna Loa	8	10	3	1	5.0	>30	1080
ML6*	11/25	Mauna Loa	7	10	4	0.5	5.0	>30	150
ML7	12/2	Mauna Loa	200	110	370	50	7.4	6.6	80
ML8	12/2-16	Mauna Loa	30	30	20	4	11.3	7.3	70
ML9	1/15	Mauna Loa	20	10	10	6	3.2	3.6	10
ML10	2/1	Mauna Loa	10	10	5	3	3.4	3.4	10

*These samples were collected in a standard rain gage (brass) and thus have contaminated Cu and Zn values.

GMCC data EPA-NOAA. Descriptions of the monthly samples collected at Mauna Loa, Barrow, and Samoa during 1974 in cooperation with EPA will be published in *Atmospheric Turbidity and Precipitation Chemistry for the World, 1974.*

Values of pH of the precipitation collected from October to December 1974 at Mauna Loa are shown in figure 72. Because the rain chemistry program was initially a test program, the samples that were collected in metal containers were probably biased. That is, the measured pH values of samples collected in metal containers were probably higher than those of samples collected in plastic containers. The values indicated as "fog" were collected

Table 30. Analysis of Rainwater From Kona District Where Tomato Disease Symptoms Appeared (Kratky, et al., 1974).

pH	4.0
H^+ (meg)	0.107
Cl (meg)	0.038
SO_4 (meg)	0.090
Total cations (meg)	0.109
Total anions (meg)	0.123

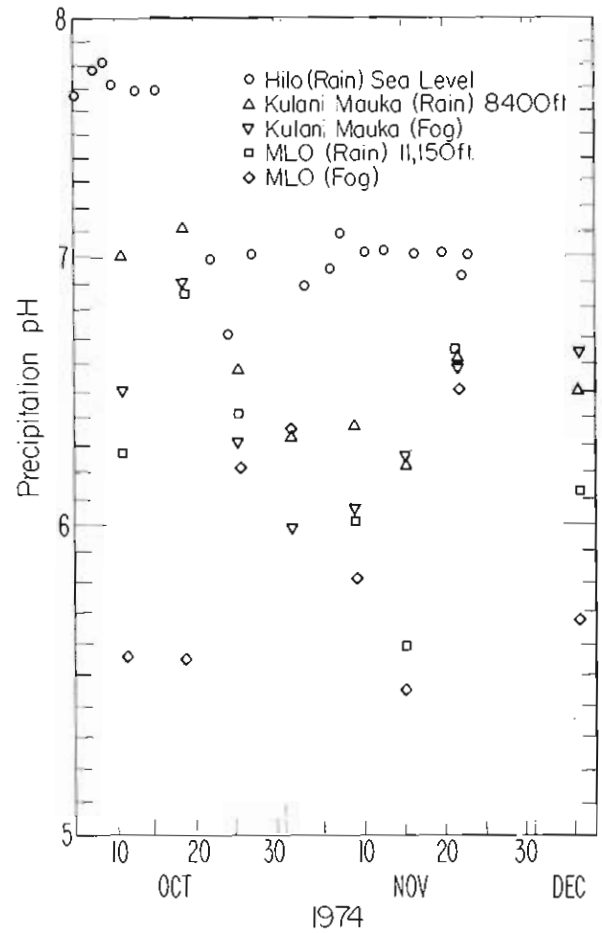

Figure 72. Precipitation pH on Hawaii. Since collections were made in metal gages values must be interpreted as provisional.

in the metal fog collector described in GMCC Summary Report 1972. It is interesting to note a decrease in relative pH values with increasing elevations on Mauna Loa.

An example of the pH data collected in the Washington, D.C., areas is shown in figure 73. Unfortunately, no comparison can be made between Mauna Loa and Washington because of the different materials used in the collection (plastic vs. metal).

Plans. The GMCC precipitation chemistry program's main goal is to develop on-site measurement capability to avert the problem of storage and shipment. The pH measurement will be extended to include conductivity and other ions of interest in precipitation. A further goal is to automate collection and analysis of precipitation on a real time basis.

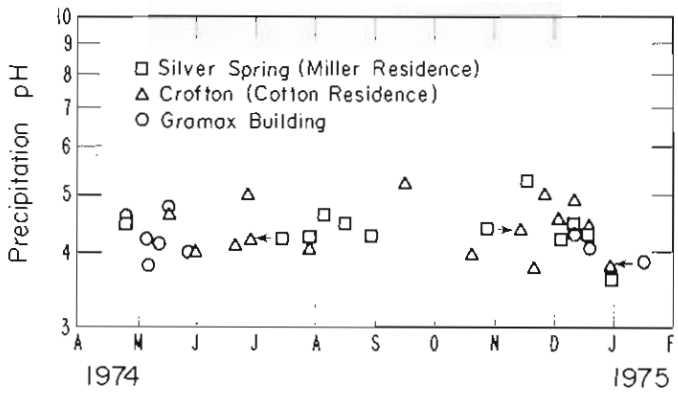

Figure 73. Precipitation pH in Washington, D.C. area.

4.6 Cooperative Programs

4.6.1 Summary of Programs

In 1974 Mauna Loa Observatory participated in the following cooperative programs:

Measurement of Sr^{90}, ERDA
Total surface particulate matter, ERDA
Surface Tritium concentration, Univ. of Miami
Atmospheric extinction-turbidity, EPA/WMO
Carbon monoxide concentration, Max Planck Institute
Precipitation collection for chemical analysis, EPA
Fog concentration, Univ. of Hawaii, Hilo
Surface SO_2 and NO_2 concentration, EPA
Surface SO_2, NO_X, NH_3 and H_2S, NCAR
Ice nucleus measurements, CSIRO (Australia)

The cooperative programs at Barrow Observatory in 1974 were:

Surface global radiation, Smithsonian Radiation Biology Laboratory
Precipitation collection for chemcal analysis, EPA
Atmospheric extinction-turbidity, EPA/WMO
Total surface particulates, Desert Research Institute
Carbon dioxide flask sampling, Scripps Institution of Oceanography

Cooperative programs at Samoa Observatory in 1974 were:

Precipitation collection for chemical analysis, EPA
Atmospheric extinction-turbidity, EPA/WMO
Surface SO_2, NO_X, NH_3 and H_2S, NCAR

Cooperative programs at South Pole Observatory in 1974 were:

Carbon dioxide flash sampling, Scripps Institution of Oceanography
Total surface particulates, ERDA
Atmopheric extinction-turbidity, ERDA/WMO
Condensation nucleus concentration, State Univ. of New York

All the cooperative programs with the exception of the two following were operated successfully during 1974. Data records have been forwarded to the respective investigators for analysis.

4.6.2. Unsuccessful programs

Carbon Monoxide. The Mauna Loa cooperative program for carbon monoxide operated for about 3 months during mid-year after Dr. W. Seiler of the Max Planck Institute, Mainz, F.R.G., installed new equipment. The method, calibration, and system description are the same as those given in GMCC Summary Report 1973. A new freezer unit to act as a cold moisture trap was installed to replace the chemical drying agents. Because of uncertainties in the calibration data and the loss of calibrating gases, nearly all of the data collected during the year have little value. Carbon monoxide values in the upslope flow are near 0.08 ppm and in the downslope flow near 0.07 ppm but again, caution should be exercised in attaching any significance to these values. A new instrument is being constructed for installation in 1975.

Surface SO_2, NO_x, NH_3 and H_2S measurements. The National Center for Atmospheric Research (NCAR) sampling system for SO_2, NO_x, NH_3 and H_2S measurements suffered from a variety of instrumental problems at both Mauna Loa and Samoa during 1974. In February two samples were taken and analyzed at Mauna Loa. However, the power supply module later failed and was not repairable. From March through November difficulties included a defective timer unit, faulty batteries and charger, and burned out electronics, each one making the system inoperative. In late November NCAR personnel connected their bubbler sampling system to main station power, thus doing away with the faulty batteries and charger. They also replaced two defective pumps and a timer unit. A normal sampling routine was resumed in December.

A continuing series of instrument malfunctions and a faulty tape recorder prevented operation of the Samoa NCAR sampling system in 1974. In October the 10-meter sampling tower used to support the bubbler system was dismantled and removed from Lauagae Ridge so that site preparation for construction of the observatory building could begin.

4.7 Data Acquisition System

4.7.1 Hardware

The configuration of the Instrument Control and Data Acquisiton System (ICDAS) changed little during the year. In all it was a time of detailed testing and evaluation. In January, a complete data system was installed at the South Pole station. A second system, installed in June at the Mauna Loa

Observatory to process lidar data, is being modified to perform as a central data system as well.

Between the purchase of equipment for the South Pole ICDAS and the purchase of the Mauna Loa system, the vendor of the digital clock used in the former system went out of business. A replacement clock (Chrono Log Series 70,000) was purchased, tested, and found to meet the two important specifications: 1) Time stability of 1×10^{-6} per week; and 2) 90-min standby power. The clock issues for each digit a binary coded decimal (BCD) that can be read by the computer. It displays the day of the year, the hour, minute, and second. A new interface board had to be constructed for this clock.

A second modification to the ICDAS was the addition of an array of terminal strips, mounted in a drawer, to allow easier access to the multiplexer. Each channel of the mutliplexer is initiated in this way. Thus, while providing a good electrical contact, it is also a flexible input mode that can be changed with little difficulty.

Although not all the interface circuitry was completed, all major components of the ICDAS in the prototype station at the Technique and Standards Group (T&SG), Boulder, were purchased and tested. The system is expected to be finished early in 1975.

A moving head disk was purchased during the year to facilitate generation of a new operation code. It will serve as the core of the data reduction center where tapes returning from the stations will be certified.

4.7.2 Software

The software of the ICDAS consists of three major components. The system by which the tape drive is used as a program storage device is known as the System Tape Operating Software (STOS). The main operating system is divided into two parts: The first is the Peripheral Access Subroutine Software (PASS); the second is the Basic Operating System Software (BOSS), which is written in the interactive language (BASIC). Both PASS and BOSS reside in the core with the BASIC compiler.

A new version of STOS has been composed. This routine moves core image records from the magnetic tape recorder to the computer or from core to tape. All contents of core are transferred and blocked into files. The new routine follows the bootstrap instructions given in the manufacturer's operating manual. All system tapes use the sample bootstrap procedure; all are self-contained. Although the read/write routine must reside in core at all times, it uses only 48 core locations.

Testing of PASS in the preparation of the ICDAS for installation at Mauna Loa Observatory uncovered deficiencies in the handling of the error routines in the tape/write routine, and in the speed of the multiplexer/digitizer routine. The latter was corrected by transferring the autoranging function from BASIC code to machine language. Now it is necessary to specify only the starting channel number, the number to be digitized, and the destination of the data. The routine tests for overflow and adjusts the gain

accordingly. It will digitize more than 400 channels per second. The problems with the tape/write routine were more difficult to solve. They were finally resolved by rewriting the entire tape drive control routine. In the process, a facility to skip records was added along with a "read" subroutine. It is now possible for the operator at the station to read back any part of a data tape to check its validity.

When the data tapes recorded in Antarctica were replayed in the T&SG Laboratory, an interesting failure was detected. External signal noise had been triggering the write head while the tape was positioned and waiting. The processor interpreted the stray signals as bad record gaps, and where they occurred, did not access the data correctly. The software was corrected and should not affect future recordings. The data were extracted by reading the tapes backward. Additional processing routines were also written.

The work on BOSS was limited to refining the set of instructions used at South Pole and writing a set of statistical routines to perform the comparison of a standard radiation device with other instruments at the T&SG, Boulder. The mean and standard deviation of the ratio of the test instrument to the standard instrument and the correlation coefficient are computed.

5. RESEARCH PUBLICATONS

5.1 Mauna Loa Observatory Publications

Bodhaine, B. A. and R. F. Pueschel, 1973: Sources of seasonal variations in solar radiation at Mauna Loa, *J. Atmos. Sci.* 31:840-845.

Bodhaine, B. A. and B. Mendonca, 1974: Preliminary four-wavelength nephelometer measurements at Mauna Loa Observatory, *Geophys. Res. Letters* 1:119-122.

5.2 Techniques and Standards Group Publications

Hanson, K., E. Flowers, G. Herbert, D. Hoyt, P. Kuhn, S. Manabe, R. Pueschel, and L. Stearns, 1974: Environmental Research Laboratories Radiation Programs-Requirements and Recommendations, NOAA Tech. Rept. ERL 300-OD 12, 22 pp.

5.3 Air Resources Laboratories Publications

Turner, C. P. (ed), 1974: Solar Energy Data Workshop, November 29-30, 1973, prepared for National Science Foundation by NOAA-ERL, NSF-RA-N-74-062, pp 218.

Pack, D. H., 1974: Measurement of atmospheric pollution, *WMO Bulletin* 23:64-65.

6. REFERENCES

Bodhaine, B. A., and B. G. Mendonca (1974): Preliminary four-wavelength nephelometer measurements at Mauna Loa Observatory, *Geophys. Res. Letters*, 1:119-123.

Budyko, M. I. (1973): *Atlas Teplovogo Balansa Zemnogo Shara* (Atlas of Heat Balance of the Earth's Surface), Moscow, Glavanaia Geofiz. Observ., 69 pp. plus charts.

Duce, R. A., J. B. Seto, and J. T. Mayero (1969): Variation of sodium and chloride concentrations with rainfall intensity in Hawaiian trade wind showers, *Pacific Science* 23:483-495.

Duce, R. A., J. W. Winchester, and T. W. VanNahl (1966): Iodine, bromine and chlorine in winter aerosols and snow from Barrow, Alaska, *Tellus* 18:238-248.

Eriksson, E. (1957): The chemical composition of Hawaiian rainfall, *Tellus* 9:509-520.

Fegley, R. W. and H. T. Ellis (1974): Long term laser radar monitoring of stratospheric aerosols at Mauna Loa Observatory", Presented at the 1974 International Laser Radar Conference in Sendai, Japan, September 3-6, 1974.

Fegley, R. W. and H. T. Ellis (1975a): Lidar observations of a stratospheric cloud layer in the tropics, *Geophys. Res. Letters*, 2:139-141.

Fegley, R. W. and H. T. Ellis (1975b): Optical effects of the 1974 stratospheric dust cloud, *Applied Optics*, 14:1751-1752.

Fegley, R. W. and H. T. Ellis (1975c): Monitoring of a stratospheric dust cloud using lidar, Presented at the Spring Conference of the Optical Society of America in Anaheim, CA, March 17-21, 1975. Available from the Optical Society of America.

Fegley, R. W. and H. T. Ellis (1975d): Lidar monitoring of the 1974 stratospheric dust cloud, Presented at the AGU-AMS Annual Meeting in Washington, D. C., June 16-19, 1975.

Galloway, J. and G. E. Likens (1975): Calibration of collection procedures for determination of precipitation chemistry. Presented at the First International Symposium on Acid Precipitation and the Forest Ecosystem, Columbus, Ohio, sponsored by the U.S. Dept. of Agriculture Forest Service and the Ohio State University.

Harriss, R. C. and H. H. Williams (1969): Specific-ion electrode measurement of Br, Cl and F in atmospheric precipitation, *J. Appl. Met.* 8:299-301.

Heffter, J. L., A. D. Taylor and G. J. Ferber (1975): A regional-continental scale transport, diffusion, and deposition model. *NOAA Technical Memorandum ERL-ARL 50.*

Junge, C. E. (1973): The requirements of the world meteorological organization for measurement of atmospheric pollutants, *Special Environment Report No. 3*, Observation and Measurement of Atmospheric Pollution, WMO No. 369:1-10.

Kidson, J. W., D. G. Vincent, and R. E. Newell (1969): Observational studies of the general circulation of the tropics: Long-term mean values, *Quart. J. Roy. Met. Soc.*, 95:258-287.

Kratky, B. A., E. T. Fukunaga, J. W. Hylen and D. T. Nakano (1974): Volcanic air pollution: Deleterious effects on tomatoes, *Journal of Environ. Quality* 3:138-140.

Lazrus, A. L., E. Larange and J. P. Lodge (1970): Lead and other metal ions in the United States precipitation, *Environ. Sci. and Tech.* 4:55-58.

Machta, L., G. Catton, W. Hass and W. Komhyr (1975): Erythemal ultraviolet solar radiation and environmental factors, unpublished report to CIAP, DOT.

Meinardus, W. (1934): Die Niederschlagsverteilung auf der Erde, *Meteor. Z.*, 51:345-350.

Oort, A. H. (1971): The observed annual cycle in the meridional transport of atmospheric energy, *J. Atmos. Sci.*, 28:325-339.

Seto, Y. B., R. A. Duce and A. H. Woodcock (1969): Sodium-to-chlorine ratio in Hawaiian rains as a function of distance inland and elevation, *J. Geophys. Res.* 74:1101-1103.

Simpson, H. J. (1972): Aerosol and Precipitation Chemistry at Mauna Loa Observatory, *NOAA Technical Report ERL 248-APCL 24*, 56 p.

Swinnerton, J. W., R. A. Lamontagne and V. J. Tennenbaum (1971): Carbon monoxide in rainwater, *Science* 172:943-945.

Warner, T. B. (1972): Ion selective electrodes properties and uses in sea water, *Marine Tech. Soc. J.* 6:24-33.

Warner, T. B., and D. J. Bresson (1973): Direct measurement of less than 1 ppb fluoride, in rain, fog and aerosols with an ion-selective electrode, *Anal. Chim. Acta* 63:165-173.

Wilkniss, P. E. and D. J. Bressan (1972): Fractionation of the elements F, Cl, Na, and K at the sea-air interface, *J. Geophys. Res.* 77:5307-5315.

Woodcock, A. H., R. A. Duce and J. L. Moyers (1971): Salt particles and raindrops in Hawaii, *J. Atmos. Sci.* 28:1252-1257.

7. GEOPHYSICAL MONITORING STAFF

7.1 Director's Office

*Donald H. Pack, Director, GMCC
*Gerald F. Cotton, Statistician
*John M. Miller, Research Meteorologist
*James A. Watkins, Executive Assistant

7.2 Techniques and Standards Group

*Walter D. Komhyr, Chief
Arija Bottomley, Clerk
*Robert Grass, Physicist
Rudy H. Haas, Mathematician
Joyce Harris, Programmer
*Thomas B. Harris, Meteorological Technician
*Gary A. Herbert, Research Meteorologist
*Douglas V. Hoyt, Physicist
Milton S. Johnson, Electronic Technician
Colleen McAvoy, Secretary
*Sam Oltmans, Physicist
*Thayne Thompson, Physicist
Emerson Wood, Lt., NOAA Corps

7.3 Analysis and Interpretation Group

Kirby Hanson, Chief
*Charles P. Turner, Research Meteorologist

7.4 Mauna Loa

7.4.1 DIRECTORS of Mauna Loa Observatory

Jack C. Pales, 1958-1963
Howard Ellis, 1963-1966
Lothar H. Ruhnke, 1966-1968
Howard Ellis, 1968-1970
Rudolf F. Pueschel, 1970-1972
Ronald Fegley, 1972-present

7.4.2 Mauna Loa Observatory Staff

*Ronald Fegley, Director
*Howard Ellis, Physicist
John F. S. Chin, Physicist
*Bernard Mendonca, Research Meteorologist
Mamoru Shibata, Electronic Technician
Alan M. Yoshinaga, Analytical Chemist
*Barry A. Bodhaine, Research Physicist
Judith B. Periera, Secretary

7.5 Barrow

*Larry Westerman, Station Chief

7.6 Samoa

*Vernon T. Rumble, Station Chief

7.7 South Pole

*Donald W. Nelson, Station Chief

---

*Contributors to the Summary Report.

APPENDIX A. RADIATION SENSOR HISTORY AT MAUNA LOA OBSERVATORY

All the pyranometer and pyrheliometer data sent to the National Climatic Center by MLO were processed with the same two-channel Honeywell Brown recorder. The recorder's input compensators were always set with a precision potentiometer so that half scale range was achieved with a millivoltage stated on the sensor as required to represent one Langley.

When sensors were not changed during a year, the recorder was checked at least twice and was never found to be in significant error. However the compensator settings were not recorded.

Only three pyranometers have been used to obtain data. We still have two of them, one of which is in use. Both require terminal calibration.

Eppley instrument 3201 was first calibrated on May 8, 1957, at 2.32 millivolts/Langley. It received its terminal correction on July 17, 1973 at 2.06 millivolts/Langley. It provided data from Mauna Loa for the following periods:

Oct 27, 1957 – Jan 26, 1960
Apr 13, 1960 – Feb 23, 1961
Apr 19, 1961 – Aug 7, 1961
Oct 4, 1961 – Jun 24, 1962
Jul 27, 1962 – Dec 7, 1962

Pyranometer #1825 has a calibration constant of 2.43 millivolts/Langley. We do not have a record of the date it was calibrated. This sensor was used during the following periods:

Dec 8, 1962 – Feb 23, 1965
Jul 1, 1974 – present

Pyranometer #1833 has a calibration constant of 1.95 and was in use from Feb 24, 1965 to June 30, 1974.

The pyrheliometer history appears in table A.1.

Table A.1. Pyrheliometers Used at Mauna Loa

Instrument Number	Calibration Constant	Date of Calibration	Date On Line	Date Off Line	Terminal Calibration
3107	2.01	10-2-57	1-1-58	7-19-58	Defective Seal
2724	2.09	10-11-57	7-20-58	12-31-58	2.12
2119	2.08	4-9-58	1-1-59	3-6-59	In use later
2725	1.98	12-4-58	3-7-59	7-23-59	Defective Seal
2119	2.08	4-9-58	7-24-59	7-23-59	In use later
3844	2.10	4-20-60	10-1-60	1-2-62	Broken leads
3843	2.00	5-24-61	1-3-62	1-24-62	2.00
2119	2.08	6-1-61	1-25-62	7-10-62	2.11
3287	2.04	10-6-61	7-11-62	2-5-65	In use later
2119	2.11	9-15-62	2-22-65	3-21-68	2.14
3287	2.04	7-20-59	3-21-68	10-1-68	2.02
2119	2.14	9-24-68	10-1-68	4-11-70	2.06
3287	2.02	2-27-69	4-17-70	11-26-71	2.09
2119	2.06	6-9-70	11-26-71	6-15-73	In use later*
3287	2.09	2-16-72	6-15-73	7-30-74	On shelf
2119	2.06	6-9-70	7-30-74	Present	

*was not recalibrated.

APPENDIX B. CCl_3F (FREON-11) and CCl_4 (CARBON TETRACHLORIDE) CONCENTRATIONS IN THE TROPOSPHERE

Introduction

This is adapted from a report prepared by D. H. Pack for the Interdepartmental Committee on Atmospheric Sciences.

Its purpose is to collect all available concentration data on chlorofluorocarbons and to estimate their change with time. Only two such compounds have been adequately measured, both in frequency and geographical distribution, to permit even a crude estimate of their global concentration and history. These are CCl_3F (Freon-11) and CCl_4 (carbon tetrachloride). A few sets of simultaneous measurements of CCl_2F_2 (Freon-12 or F-12) and Freon-11 have been made. From ratios it is possible to estimate the Freon-12 levels based on the more numerous F-11 observations.

Data Base

It is not possible to present all of the original concentration data on the compounds of interest. In many cases the data were extracted from graphs in published papers or from those provided privately. Often there were too many individual determinations of concentration to make it practical to list them all. In such instances the averages, standard deviations, and the number of concentration measurements that went into these statistics have been included. All concentration data are given in parts per trillion by volume (pptv—one part per trillion equals 1 part in 10^{12} parts of air).

The data have been divided in four ways. First they have been divided into "clean" and "urban" categories. Since the urban values can easily reach four or five times the clean air values, they could both dominate and distort the data averages. Figure B.1 is a concentration versus time plot of all of the Freon-11 data. Note that in all years for which there are sufficient data to calculate the standard deviations these are invariably much larger for the "urban" than for the "clean" data and in fact the deviation can be used as a criterion in evaluating the effects of nearby sources on data. Typical values for F-11 variability in "clean" air range from 3 to about 6 pptv depending on the length of time the sampling continues; urban-contaminated samples have standard deviations from 15-20 pptv to more than 400 pptv, depending on how close the sampling point was to the source of the material.

A second division has been made in terms of the latitudinal gradients. For this purpose only the four oceanographic cruises provide unambiguous separation between the time change in concentration and any latitude difference. Figures B.2 and B.3 present these data.

The third category includes only data that have been taken at the same point over a long enough time and in sufficient numbers to provide a time history of the concentrations over a year or more. There are only two such data sets, that of Lovelock at Adrigole, Ireland, where a continuous, automatic gas chromatograph has operated since May 1973 and that derived from the

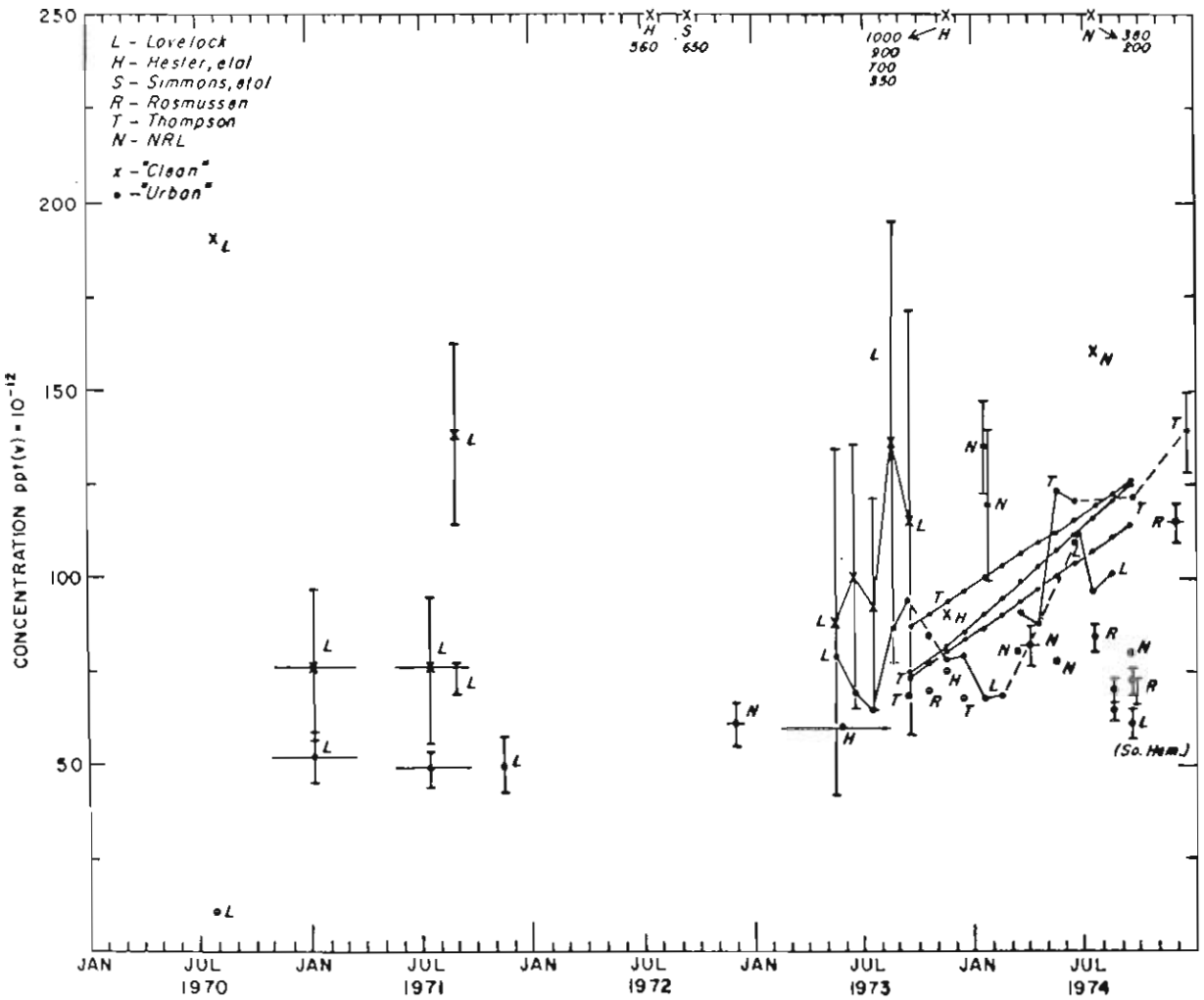

Figure B1. Time history of CCl_3F (Freon-11) concentrations. Continuous series are connected by lines. Vertical bars are ± one standard deviation. o represents "clean air" samples; X represents "urban" samples. Letter code identifies analyst of samples.

weekly flask samples taken since September 1973 by NOAA's Geophysical Monitoring for Climatic Change Program (GMCC) at Point Barrow, Alaska, Mauna Loa, Hawaii, and Cape Matatula, American Samoa.

A final category includes data for the Southern Hemisphere. Since the primary source of Freon-11 is in the Northern Hemisphere, measurements should be less affected by transitory conditions. In this connection, a most valuable series of observations is now being made in Antarctica by Dr. Rei Rasmussen. These will produce the first useful data from this area. (Unfortunately, the flask samples taken by GMCC in Antarctica during January 1974 were all apparently contaminated and are unreliable.)

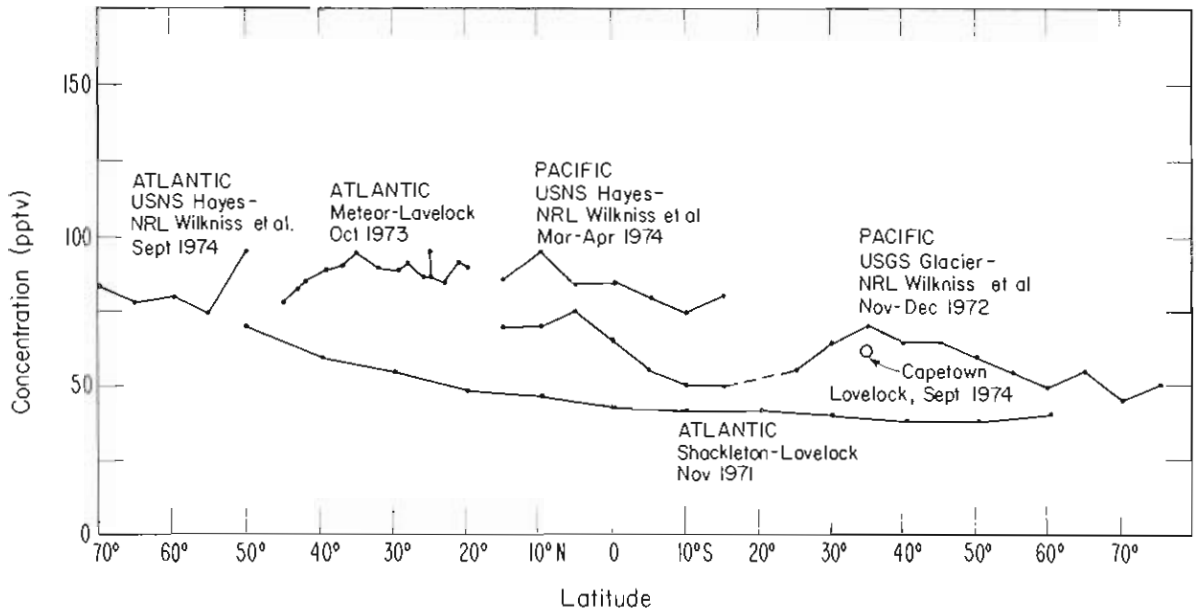

Figure B2. CCl_3F data from oceanographic cruises.

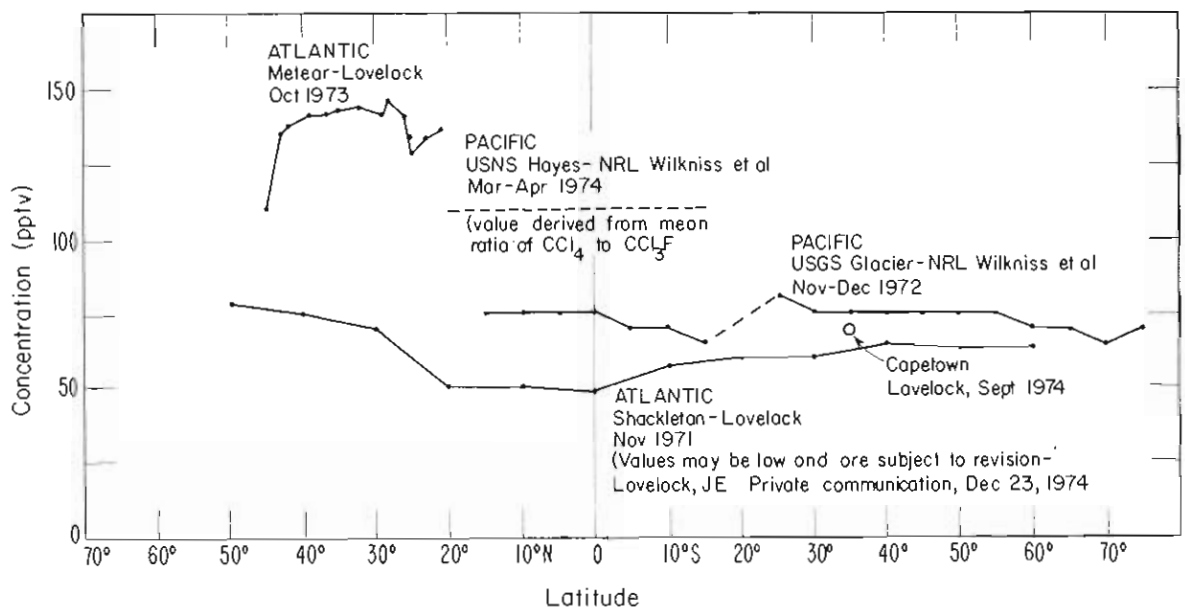

Figure B3. CCl_4 data from oceanographic cruises.

Carbon tetrachloride concentration data (figs. B.3 and B.4) are even more scarce than those for Freon-11. The earliest available observations are by Lovelock in 1971 and the only continuous time series is also based on Lovelock's data from Adrigole. (The GMCC flask data are extremely erratic, quite often below the chromatograph's threshold of detection. It is believed that CCl_4 is destroyed in the flasks by action with simultaneously collected water vapor which later condenses. The values are not used in this report.)

CCl_2F_2 (Freon-12) condensation data are confined to a few sets of measurements by Hester and one by Grimsrud and Rasmussen. Two sets were definitely urban, having been collected in Los Angeles, California, and vicinity in July 1972 and February 1973. The aircraft data of Hester and the aircraft and surface data of Grimsrud and Rasmussen near Pullman, Washington, are probably from "clean" samples. However, the ratio of Freon-12 to Freon-11 is similar in all cases.

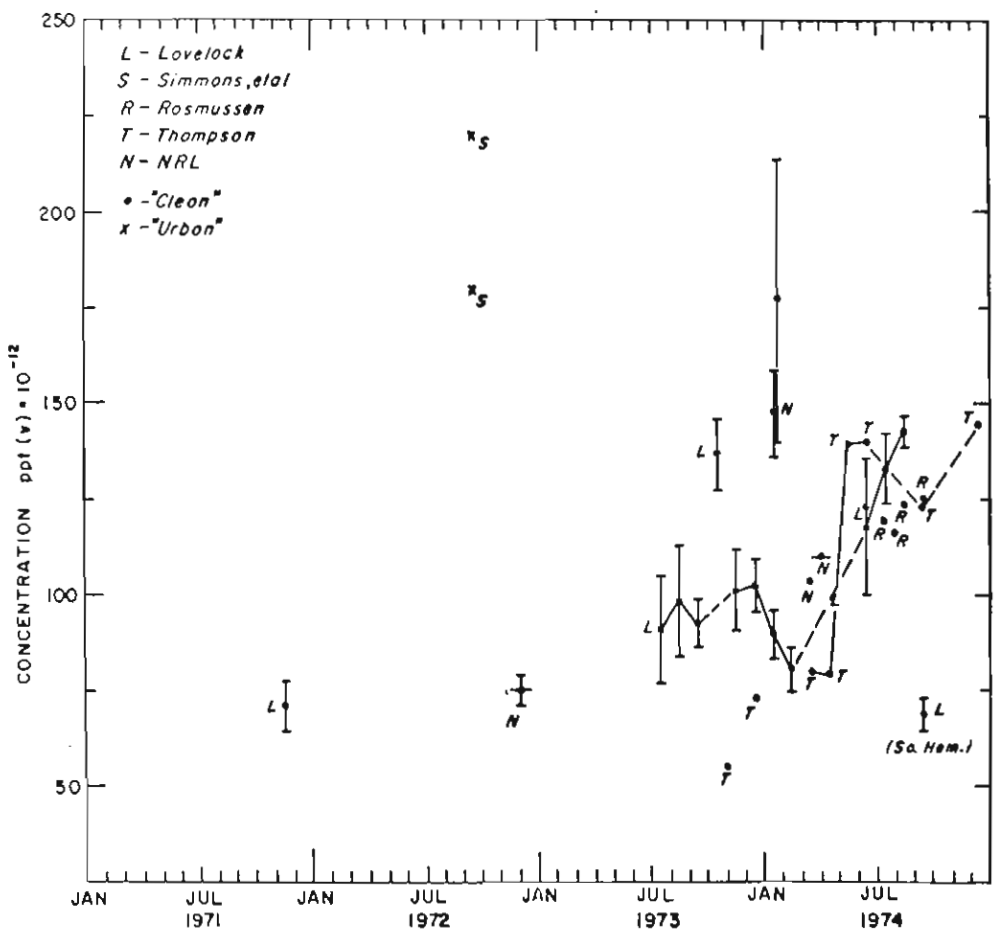

Figure B4. Time history of CCl_4 (Carbon tetrachloride) concentrations. Symbols are as in figure 2.

Discussion

It became obvious in the process of assembling these data that a direct comparison of concentration values made by different investigators at different times, in different places, using different instruments, was very difficult. Indeed, if the operating conditons of the electron capture gas chromatograph are permitted to vary significantly, a single investigator's data may not be comparable between data series. Additionally, fluorocarbon sources within a few hundred miles may or may not be advected to the sampling point by the wind, thus providing a further potential for data variability. The concentrations in the Southern Hemisphere are 27 to 61 percent lower than those of the Northern Hemisphere. The Northern Hemisphere, which is the primary source region, has Freon-11 values near 99 pptv in 1974 compared with values between about 60 pptv (Lovelock, Capetown) and 78 pptv (Wilkniss, 5-15°S) measured in the Southern Hemisphere.

Tables B.1 through B.5 summarize the data. In table B.1 all the "clean" observations are averaged together except for the Adrigole and GMCC data. The annual increase of 87 percent for 1970-71 is based on very few data. In fact, omission of the earliest value of 10 pptv measured during technique development would change the value to 12 percent for that period. There were no Freon-11 data suitable for background estimates in the Northern Hemisphere in 1972. The change between 1971 and 1973 is 26 percent and one could evaluate this change as a 13 percent increase in 1971-1972 and in 1972-1973.

For the 1973-1974 data we have three independent estimates. The Adrigole data show an increase between the summer seasons (June-August) of 1973 and 1974, on the average, of 47 percent. Note, however, the large variability for the individual months.

From the GMCC program we have a full 12 months of data between September 1973 and September 1974 but for three different locations. The composite increase for the three observatories is 45 percent. The 1974 average concentration values for the three data sets-107, 113, and 99 pptv-are not dissimilar. The mean for all data sets (ignoring the number of data points in each) is 106 pptv for a total variation of only 14 percent among the three data sets.

Table B.2 summarizes the less numerous CCl_4 data. There are two problems. Since the data are few, any conclusions are subject to challenge. Also, the data show an increase of the same order as that for Freon-11. However, no anthropogenic source of carbon tetrachloride has been put forward although it is hard to imagine a natural source that would generate such a continuing and relatively uniform growth since 1971.

Table B.3 contains the oceanic cruise data. The data are scattered in time and space but, while numerous on a particular cruise, provide relatively few numbers relative to the space covered.

The Freon-12 values have been briefly discussed (table B.4). The ratio value of about 1.7 can be used with the data of table B.1 and B.3 or figure B.2 or B.3 to estimate Freon-12 concentration.

Table B.1. CCl_3F "Average" Concentration and Change.

Northern Hemisphere Data

Year	Avg. (pptv)	Change Between Years	
1970	31		
1971	58	1970-71	87%
1972	72	1971-72	24%#
1973	73	1972-73	1%#
1974	99*	1973-74	36%

*Exclusive of Adrigole and NOAA GMCC data.
#Only Wilkniss "Glacier" data available in 1972.

Adrigole Data

	1973 Avg. (pptv)	1974 Avg. (pptv)	Change Between 1973-74
June	68	122	79%
July	65	97	49%
August	87	101	16%
Average	73	107	47%

NOAA GMCC Data

	Sep 1973 Avg. (pptv)	Sep 1974 Avg. (pptv)	Change Between 1973-74
Point Barrow	74	114	54%
Mauna Loa	73	125	71%
American Samoa	87	100	15%
Average	78	113	45%

Finally, table B.5 compares the only other known estimate of growth rate with that made here. Considering all the variables, variations, and possible sources of error, the two estimates are remarkably similar. (It must be remembered that Pack had more and later data.)

Table B.2. CCl_4 "Average" Concentration and Change.

Northern Hemisphere Data

Year	Avg. (pptv)	Change Between Years	
1970	---		(No Data)
1971	71		---
1972	75	1971-72	6%#
1973	103	1972-73	37%#
1974	125*	1973-74	21%

*Exclusive of Adrigole data.
#Only Wilkniss "Glacier" data available

Adrigole Data

	1973 Avg. (pptv)	1974 Avg. (pptv)	Change Between 1973-74
June	82	119	45%
July	91	133	46%
August	99	144	45%
Average	91	132	45%

Table B.3. Oceanographic Cruises - Average Data.

Date	Latitude	CCl_3F	Annual % Change	CCl_4	Annual % Change
		Northern Hemisphere			
Nov 1971	40°N-10°N	53	--	61	--
Nov-Dec 1972	15°N-50°N	72	36	75	23
Oct 1973	45°N-20°N	89	29	140	104
Mar-Apr 1974	20°N- 5°N	89	0	119*	-15
Sep 1974	80°N-50°N	80	-10	--	--
		Southern Hemisphere			
Nov 1971	0-60°S	40	--	59	--
Nov-Dec 1972	25°S-75°S	57	43	73	24
Mar-Apr 1974	5°S-15°S	78	28	104*	32

*Derived from reported CCl_4/CCl_3F ratio of 1.34.

Table B.4 CCl_2F_2 (Freon-12) Data.

Date	Concentration pptv	Ratio CCl_2F_2/CCl_3F	Location
Jul 1972	700	1.43	Surface, Los Angeles
Feb 1973	450	1.74	Surface, Los Angeles
May 1974	130	1.67	Central U.S., 21,000 and 40,000 feet
Nov-Dec 1974	230	1.80	Surface and 4-12,000 ft, Pullman, Washington

Table B.5. CCl_3F Concentration Estimates vs. Time

	Wilkniss 1975	Pack	% Difference
1970	--	31	
1971	50	58	16
1972	61	**	--
1973	--	73	--
1974	80	99	24

** Two few data. Only "clean air" data are from the NRL Southern Hemisphere cruise.

Conclusions

1. The available data show an unequivocal increase in CCl_3F concentrations and, by implication of the relatively constant ratio of Freon-12 to Freon-11, an increase in Freon-12.

2. From the few aircraft data, the Freons and carbon tetrachloride appear to be uniformly mixed throughout the Northern Hemisphere troposphere.

3. The Freon growth rate appeared to be about the same as the production rate until 1973-74. At that time, the growth rate appeared to be at least twice the production rate. Only additional data can determine if this is real or a data artifact.

4. There appears to be an increase in CCl_4 almost as large as for the Freons. At present the reality of the increase, and most of all the probable cause, is in doubt.

Recommendations

1. Immediate development of an interchangeable calibration method for the Freon and carbon tetrachloride measurements. Accepted and certified reference gases in the 50-100 pptv range for exchange between laboratories may be the quickest method.

2. Establishment of four to six additional "continuous" sampling programs in "clean" locations. At least two of these should be in the Southern Hemisphere. Sampling could use the continuously operating chromatographic technique used by Lovelock at Adrigole (if the requisite talent is available) or frequent flask sampling (at least one flask per week) for central laboratory analysis.

☆ U.S. GOVERNMENT PRINTING OFFICE 1975 - 677-347/1213 Reg. 8