

Preliminary data indicate that vertical backscatter profiles for ice crystals can be obtained for concentrations down to about 0.1 per liter at mean sizes of 400 micrometers. Some preliminary data are given in figures 2 and 3. Figure 2 is a range-corrected lidar return of ice crystals falling out of a cloud layer. The intense signal at about 1,400 meters above the surface is due to the cloud layer. The crystal precipitation can be seen at lower levels.

Figure 3 is a replica of a typical crystal obtained during the event. One "clear sky precipitation" event occurred while we had the equipment running during the summer. Many more events must be studied before conclusions can be drawn about the latter process.

Future plans call for continued measurements at South Pole Station and at other antarctic locations. A significant modification will be added to the lidar to permit discrimination between ice and water cloud particles by a polarization technique.

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## Analysis of halocarbons in Antarctica

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In January 1975 we joined a University of Maryland program studying particulate trace elements in the atmosphere at Amundsen-Scott South Pole Station. The Washington State University team was to determine the concentration and distribution of Freon-11, chloroform, methyl chloroform, and carbon tetrachloride by *in situ* analysis of surface air samples and of air samples collected at different altitudes from aboard U.S. Navy Antarctic Development Squadron Six LC-130 airplane flights. Both compressed air samples and cryogenically enriched air samples also were obtained for more detailed Stateside analysis of trace halocarbons September/October 1975.

and other species in the samples. Further, surface and airborne ozone measurements were made using an instrument employing the chemiluminescence reaction of ethylene with ozone for correlation with the fluorocarbon data.

The halocarbon measurements from fluorocarbon-11 through carbon tetrachloride were made using a Hewlett-Packard 5713A gas chromatograph equipped with a frequency-modulated electron-capture detector set up in the "Skylab" tower at South Pole Station. The sampling and analysis sequence was automated for four analyses per hour. Figure 1 shows raw data for a series of these analyses made on 24 January 1975. Only three peaks—fluorocarbon-11, methyl chloroform, and carbon tetrachloride—were measured in the atmosphere using the instrument's automated mode of operation. Due to an impurity in the carrier gas, a negative disturbance interfered with the resolution-detection of chloroform. The peak heights of fluorocarbon-11 and carbon tetrachloride are labeled in millimeters in the figure. The last analysis shows a chromatogram of the halocarbons in one of nine samples of rural air brought from Pullman, Washington, to the South Pole. These compressed air samples served as secondary standard and as a check on instrument performance compared to its operation in Pullman. The data obtained also provided a statistical check on the stability of the compressed air samples exposed to the rigors of travel to Antarctica. In this sample of Pullman air, five peaks are resolved at a higher concentration than those measured in surface air at South Pole Station. Continuous data were obtained at South Pole Station from 10 through 24 January 1975.

No differences in the level of fluorocarbon-11 or carbon tetrachloride were measured during this study. Data from 16 through 23 January are shown in figure 2 in parallel with measurements for ozone, for radon-222, and for tropopause height at

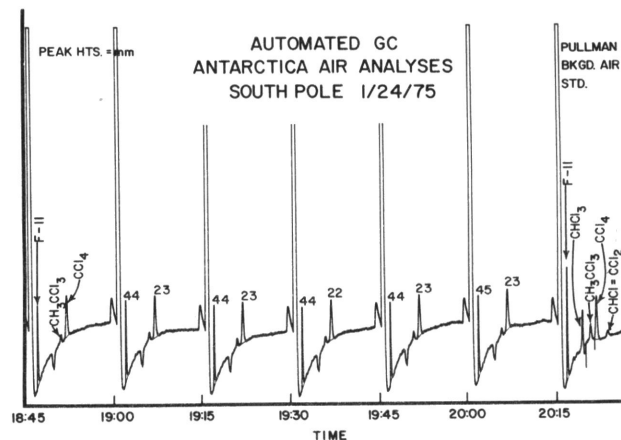


Figure 1.

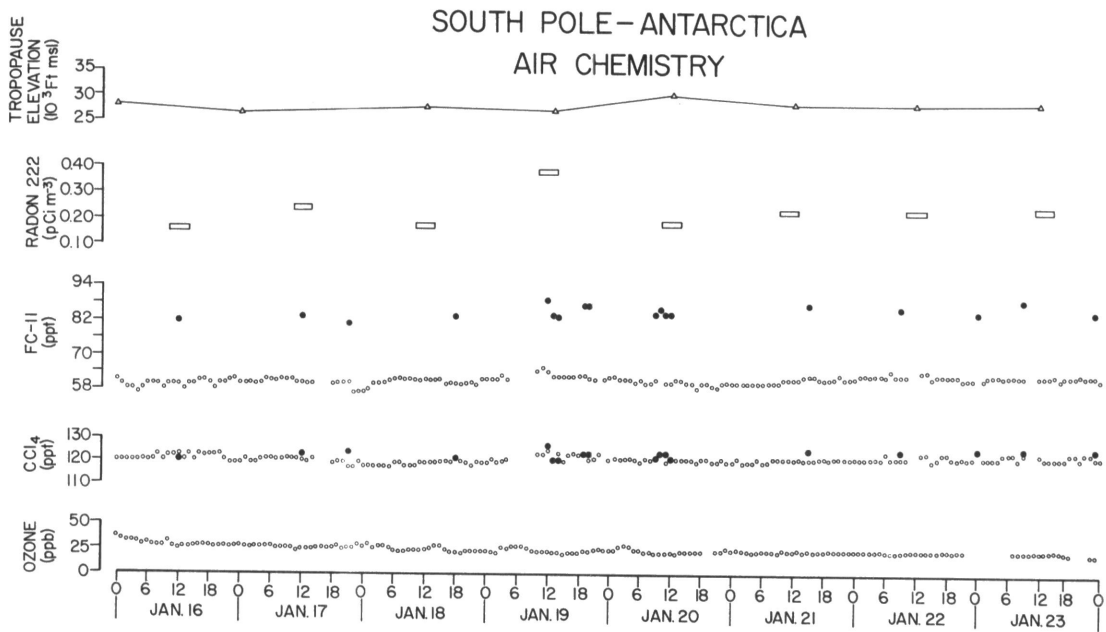


Figure 2.

the South Pole. The average volume concentration of fluorocarbon-11 is 90 parts per trillion. Each open circle in figure 2 is the average of four analyses. The solid circles represent the fluorocarbon-11 measured in Pullman air samples brought to the South Pole. The data provide not only a measure of background level differences between the Northern Hemisphere and the South Pole, but also provide an internal check on the electron-capture/gas chromatograph instrument's stability for measuring these very low trace species. The data indicate that the fluorocarbon-11 level at the South Pole was approximately 30 percent less than the 125 parts per trillion representative of Northern Hemisphere background levels (measured at 45°N. in the eastern agronomic portion of Washington).

The companion analyses of carbon tetrachloride, however, do not show significant differences between South Pole and Northern Hemisphere air samples. Accordingly, this is interpreted to support the suggestion made by Lovelock (1973) that carbon tetrachloride may be of natural origin because of the similar concentrations found in the Northern and Southern Hemispheres during his *Shackleton* cruise in 1972. Alternatively, the equivalent concentration distribution may be a result of carbon tetrachloride use in significant amounts for at least the past 50 years, whereas the use of fluorocarbons has increased rapidly over the past 15 years. The total historical production of fluorocarbons represents about 5 years' worth at current levels. Therefore, we may just be getting a graphic demonstration of the time involved in global dispersion (i.e., between 5 and 30 years).

The daily radon-222 measurements were made by Dr. Zoller and by Willy Maenhaut, University of

Maryland. Their very low, consistent values indicate that the air masses studied during this period had not passed over a large continent for about 2 weeks. Tropopause height also remained very constant during this study time, as did ozone levels. It was anticipated that, when the tropopause subsided, an increase in surface ozone would be measured through the replenishment of surface air with fresher stratospheric air. This phenomenon did not occur until after our fluorocarbon measurements were complete. This is unfortunate, because hindsight suggests that the younger or more directly transported surface stratospheric air would have provided an excellent opportunity to test the limited number of airplane observations. These airborne measurements showed slightly higher (10 percent) fluorocarbon-11 levels and carbon tetrachloride (5 percent, not significant) concentrations in the air mass above the strong surface inversion over South Pole Station during our study period than were measured from the roof of the Skylab tower (height, 18 meters).

Another anomaly in the concentrations measured during our study was in the air samples collected at altitudes of 7,300 and 9,400 meters. No differences in fluorocarbon-11 concentrations were measured in these samples collected above or below the tropopause. Special precautions were taken after these initial observations to verify that both phenomena were real and not due to contaminants in the sampling lines of the airplane or in the containers used to obtain samples. A second flight with the verified sampling apparatus provided similar data that supported the original observation for a reversed gradient of the fluorocarbon-11 concentrations over the South Pole.

Interpretation of the negative surface gradient (concentration increasing with altitude) at first was puzzling since the opposite gradient is observed in the Northern Hemisphere (higher surface background levels relative to upper tropospheric and lower stratospheric concentrations). Also, the lack of any significant difference in the fluorocarbon-11 and carbon tetrachloride levels above and below the tropopause is anomalous compared to the sharp concentration differences measured across the tropopause in the Northern Hemisphere.

The recognized role of the antarctic snow/ice shield as a heat and water sink was considered to determine if trace gases also could be affected in this same manner. To test if the halocarbons were freezing out similar to water vapor, an attempt was made to measure fluorocarbon-11 and carbon tetrachloride values in the air entrained in the wind-blown as well as the sublimated snow deposits. The samples were collected at virgin outdoor sites in 100-milliliter all-glass syringes.

Results from these analyses of fluorochlorocarbons and chlorinated hydrocarbons in the air released from the melted snow are remarkable. Whereas three peaks were typically measured in the free ambient air (figure 1), six to 20 peaks were measured by the electron capture detector in the air released by the melted snow (figure 3). Again, a complete contamination check was performed: washing, heating, and auditing the syringes to determine their contribution of contaminants to static air samples held in the syringes during the time needed to melt the snow. The syringes contributed no halocarbons to the analysis. Subsequent analysis of both subsurface (60-centimeter depth) and surface snows (total of six samples) indicated the same six to 20 peaks of variable intensities.

Snow obtained from 60 centimeters below the surface was packed in an air canister, pressurized in the field with ambient air, and sent to Washington State University. The analysis of air over the melted snow is shown in figure 3. The enrichment ratio of the halocarbons in the snow compared to ambient air ranges from zero in the case of  $\text{CCl}_4$  to 20 to 30 for the other halocarbon species. The enrichment ratios suggest that the ability to form clathrates during the sublimation of water vapor to the snow surface may play a role in the sink mechanism. It is premature to place too much weight on this tentative interpretation, but it is a plausible mechanism. The equivalent chlorine concentration in halocarbons measured in the air at equilibrium above the melted snow water is  $\sim 20$  parts per billion chlorine. In contrast, halocarbons measured in the air equilibrated over sea water are not enriched. This has been reported by Lovelock

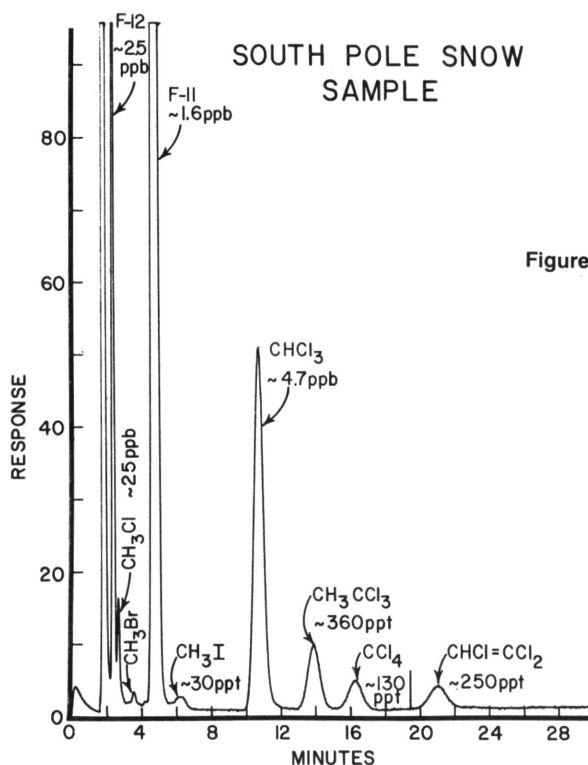


Figure 3.

(1973) and by Wilkniss and Swinnerton (1973), and has been observed in our laboratory.

The entrainment and possible enrichment of the multitude of fluorochlorocarbon and chlorocarbon species in the snow suggest that the antarctic snow and ice pack is scavenging these materials from the atmosphere. The Antarctic's negative gradient for continuously extracting heat from the earth's atmosphere, coupled with the dominant role of *in situ* formation of hoarfrost (snow and ice crystals) through the direct condensation of water vapor at the ground surface, may be enough of a driving force to provide a working mechanism for the entrainment and removal via freezeout of the low levels of trace gases present in the subsiding air masses over Antarctica.

At a time of increasing concern with the composition and chemical behavior of the troposphere, the concentration distribution of trace gases in unpolluted areas of the world has become increasingly important. As a result of technological advances, the distribution and composition of atmospheric trace gases may be affected on a hemispheric if not a global scale. As such, the fluorocarbons are the first exclusively manmade compounds that can be shown to exist everywhere on earth. Since they are believed to be only of human origin, they may serve as the first unequivocal example of man's ability to effect significant changes in the atmosphere and, through it, the climate.

There is a need to more systematically quantify the phenomenon of enriched concentrations of halocarbons and other trace gases in antarctic snow and ice, especially for snow-ice samples that date from the 19th century to the present. The immediate goal of our work is to establish a halocarbon concentration profile for troposphere-stratosphere polar regions; this requires geophysical investigation of the role of polar atmospheric and precipitation processes for removing trace gases, especially chlorofluorocarbons. Thus we may better understand how these processes affect possible manmade changes in the chemistry of the atmosphere and in the earth's climate through the inadvertant accumulation of chlorofluorocarbons in the troposphere-stratosphere.

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## Advanced Technology Satellite-1 experiment at South Pole Station

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The National Aeronautics and Space Administration's (NASA) dual air density (DAD) program begins in November 1975 with the launch of two polar-orbiting Explorer satellites, A and B, with an apogee of 1,500 kilometers and a respective perigee of 350 and 700 kilometers. The satellites are equipped with mass spectrometers to simultaneously measure various constituents in the upper atmosphere.

The polar atmosphere's complexity makes the South Pole area of prime interest. Measurements from these satellites will be telemetered to ground equipment and recorded on magnetic tape at Amundsen-Scott South Pole Station. NASA needs to receive this DAD data as soon as possible for

reduction at Langley Research Center, Langley, Virginia.

To relay DAD satellite data from the South Pole to Langley Research Center, NASA has installed equipment at South Pole Station to interface with Advanced Technology Satellite-1 (ATS-1). ATS-1 is at 149°W.; although considered synchronous, it has developed a figure-eight deviation from sub-satellite point due to sun and moon magnetic effects. In June 1975 the southern swing of this figure eight was about 7°S., which gave a look angle from South Pole Station of about -1.8° elevation. The figure-eight continues to elongate at a rate of 0.01° per month.

The first transmission attempt from South Pole Station through ATS-1 was in January 1975 with a look angle of -2.3° elevation. The system was tested again in May 1975 with a look angle of -1.9°. Although both tests were negative, we are optimistic that further testing in the fall of 1975 will succeed when ATS-1 reaches an elongation of about -1.5°.

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## New equipment for radio-echo sounding

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In 1973 the National Science Foundation, the Scott Polar Research Institute (SPRI), and the Technical University of Denmark (TUD) established a cooperative program to improve radio-echo sounding techniques in Antarctica. Responsibility for developing and constructing a new 60-megahertz radar based on previous equipment developed by SPRI and TUD (Evans and Smith, 1969; Christensen *et al.*, 1970) was assigned to TUD.

The work by TUD consisted of constructing an antenna system and two complete sets of radar electronics. The antenna system is a linear array of four dipoles suspended under the wing of an LC-130 Hercules airplane flown by U.S. Navy Antarctic Development Squadron Six (VXE-6). The system operates at 60 megahertz with a peak power of 10 kilowatts, a mean power of 250 watts, and a good match in the bandwidth of 50 to 70 megahertz (voltage standing wave ratio less than 1.6). The dipoles