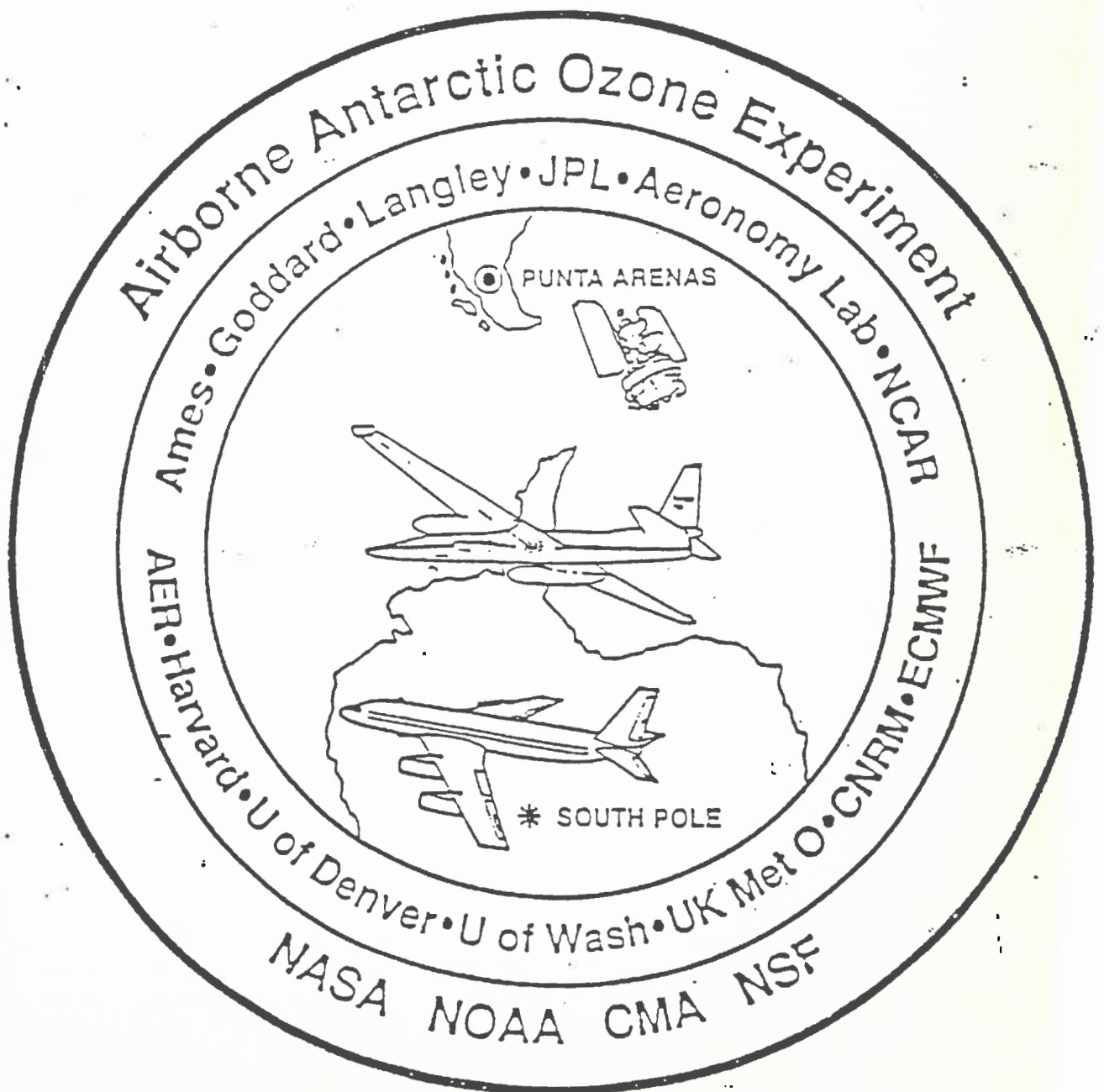


National Aeronautics and Space Administration  
National Oceanic and Atmospheric Administration  
National Science Foundation  
Chemical Manufacturers Association

## Fact Sheet

Initial Findings from  
Punta Arenas, Chile  
September 30, 1987



# Antarctic Ozone

## INITIAL FINDINGS FROM PUNTA ARENAS, CHILE

This statement has been prepared by the scientists who went to Punta Arenas, Chile to study the Antarctic ozone hole. This summary represents the views of the scientists themselves and not necessarily those of the cosponsoring organizations. The findings that will be presented are preliminary. Under normal circumstances, scientists studying such a complex scientific issue would take many months to years to disclose their initial findings. However, the issue of ozone perturbation is one of justifiable public concern, and hence the public should be kept abreast of the current scientific thinking. It is in this spirit that we would like to share our provisional picture of the Antarctic springtime ozone hole. Furthermore, this will help to stimulate the scientific inquiry and debate that can only lead to an improved and timely understanding of the phenomenon. A much more complete and final interpretation of our findings will be forthcoming after a planned intensive series of scientific meetings and the submittal of a group of scientific papers to the peer review process. This procedure will occur within the next six months.

### Description of Goals and Objectives of the Mission

Three basic theories have been proposed to explain the observed decrease in spring-time Antarctic ozone that has been occurring since the late-1970's. One class of theories suggest that the hole is caused by the human activity of loading the atmosphere with chlorinated and brominated chemicals. Chlorofluorocarbons (CFC's) and Halons are contributing increasing levels of chlorine and bromine to the atmosphere. These compounds could then efficiently destroy stratospheric ozone in the Antarctic environment because of the special geophysical conditions that exist in this region of the atmosphere, i.e. a contained polar vortex (an isolated air mass), cold temperatures, and the presence of polar stratospheric clouds. A second class of theories suggests that there have been changes in the circulation of the atmosphere, which now transports ozone-poor air into Antarctica. A third theory postulates solar and cosmic ray induced, periodically enhanced abundances of oxides of nitrogen, which can cyclically destroy ozone.

The NSF-coordinated expedition to the McMurdo station in Antarctica last year was exceptionally successful in increasing our understanding of the Antarctic ozone hole. In conjunction with other experiments, this ground based effort demonstrated the recurrence of the ozone hole, the altitude over which ozone was depleted, that chlorine and nitrogen chemistry was highly perturbed relative to that observed at mid-latitudes, and that the solar cycle theory is an unlikely explanation. However, the McMurdo data were insufficient to distinguish adequately between the relative contributions of the first two classes of theories. Therefore, the goal of the present airborne campaign is to improve our understanding of the relative contributions of these, and possibly other, mechanisms to the formation of the Antarctic ozone hole.

One of the key environmental issues is whether the ozone depletion observed in Antarctica will always be localized in and around Antarctica, or whether it is a precursor of future global changes. A longer term objective of this campaign is to be able to provide information relevant to answering this question.

## **Participants, Sponsors, and Foreign Government Support**

The campaign was coordinated by the National Aeronautics and Space Administration (NASA) and cosponsored by NASA, the National Oceanic and Atmospheric Administration (NOAA), the National Science Foundation (NSF), and the Chemical Manufacturers Association (CMA). In addition, the British Meteorological Office (BMO) provided a significant contribution to the project.

Scientists, engineers, and other personnel from Harvard University, University of Denver, University of Washington, University of Colorado, National Center for Atmospheric Research, Jet Propulsion Laboratory, NASA Ames Research Center, NASA Langley Research Center, NASA Goddard Space Flight Center, NOAA Aeronomy Laboratory, the British Meteorological Office, the European Center for Medium Range Weather Forecasts (ECMWF), Centre Nationale Recherches Meteorologiques, and Atmospheric and Environmental Research, Inc. participated in this campaign. Dr. J. C. Farman of the British Antarctic Survey kindly made available Halley Bay ozonesonde data. Scientists from both Chile and Argentina were also involved.

Key participants in this campaign were also the flight and ground crews of NASA, Lockheed, and Northrop, who flew and maintained the ER-2 and DC-8 research aircraft under very challenging conditions. Research and Data Systems provided the necessary telecommunication links and support.

The Chilean government hosted the airborne campaign, which was based out of Punta Arenas. The Chilean Air Force supplied the facilities and logistical support. The Chilean Antarctic Institute provided advice regarding the study area. In addition, invaluable assistance was provided by the Direccion General De Aeronautica Civil, and the National Meteorologic Service of Chile.

Other countries also helped: Panama, Costa Rica, Peru, and Ecuador cooperated with the overflights necessary for the transit from the United States to Chile. The government of Argentina offered alternate landing fields for the aircraft as they returned from their Antarctic missions. The National Meteorological Service of Argentina furnished data from Marambio. Lastly, the government of New Zealand assisted with the transcontinental Antarctic flight by the DC-8 that was part of the return to the United States.

## **Description of Campaign**

The Airborne Antarctic Ozone Campaign succeeded in making 12 flights of the high altitude ER-2 aircraft, and 13 flights of the DC-8 medium altitude aircraft over Antarctica. The ER-2 typically operated at geometric altitudes relative to sea level between 12.0 and 18.7 km and flew to 72 degrees South along the Palmer Peninsula. The DC-8 operated at altitudes up to about 10 km and with its long range capability was able to reach the South Pole on several occasions, and is currently returning to the United States via New Zealand after crossing the Antarctic continent. The project had available to it Total Ozone Mapping Spectrometer (TOMS) images of the total ozone column of the southern hemisphere within a day of observation and of the orbits passing over the region of the Antarctic peninsula within 2 to 4 hours of observation. Aerosol and cloud extinction data were also available from the Stratospheric Aerosol Measurement (SAM II) and Stratospheric Aerosol and Gas Experiment (SAGE II), with the latter providing ozone measurements as well. Twice daily analyses and forecasts of winds and temperatures up to 30 mb, 22 km, for three days

ahead, were provided by the BMO in chart form, plus forecasts of the trajectories of air parcels on surfaces along which air masses move. Photochemical modelling along these trajectories was done using the aircraft observations. The ECMWF provided once a day analyses and forecasts up to 30 mb for 10 days ahead. A small theory team assisted the experimental scientists with the interpretation on a day to day basis. This approach was possible because of the availability of rapid data reduction facilities and an extensive, dedicated international telecommunications network.

Detailed lists of the participants, a discussion of the theories being addressed, the approach taken in the tests of these theories, and a description of the apparatus involved are given in the Airborne Antarctic Ozone Experiment Plan (NASA and NOAA, July 1987). Copies are available on request from NASA Ames Research Center or NASA Headquarters.

### **Data obtained from the ER-2 and DC-8 instrumentation**

The spatial and temporal distribution of a large number of relatively short-lived chemical constituents that participate in chemical reactions that affect the abundance of ozone were measured from both the ER-2 and DC-8. Instruments aboard the ER-2 resulted in measurements of the distributions of ozone ( $O_3$ ), chlorine monoxide radical (ClO), bromine monoxide radical (BrO), total odd nitrogen ( $NO_y$ ), nitric oxide (NO), and water ( $H_2O$ ) in the vicinity of the aircraft at altitudes ranging from 12 to 18 km above the Earth's surface, well into the altitude region where ozone is undergoing depletion. Instruments aboard the DC-8 measured the abundances of  $H_2O$  and  $O_3$  in the vicinity of the aircraft, the vertical distribution of  $O_3$  for approximately 10 km above the aircraft, and the total column amounts of  $O_3$ , hydrochloric acid (HCl), chlorine nitrate (ClONO<sub>2</sub>), chlorine dioxide (OCIO), BrO, hydrofluoric acid (HF), NO, nitrogen dioxide (NO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), as well as a number of other constituents, above the aircraft altitude.

Additionally, the temporal and spatial distributions of long-lived chemical tracers and dynamical variables were measured in order to understand atmospheric motions. These included measurements of nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>), chlorofluorocarbons 11 (CFCl<sub>3</sub>) and 12 (CF<sub>2</sub>Cl<sub>2</sub>), carbon tetrachloride (CCl<sub>4</sub>), and methylchloroform (CH<sub>3</sub>CCl<sub>3</sub>). In-situ measurements of all of these species were made from both the ER-2 and DC-8, and column measurements of most from the DC-8. The size distribution, abundance, and composition of particles was determined by instrumentation aboard the ER-2, as well as the vertical distribution of aerosols from 12 to 28 km by the DC-8 lidar, in an effort to understand the role of heterogeneous processes. Additionally, atmospheric pressure, temperature, lapse rate, and winds were measured aboard the ER-2 to determine the state variables and dynamical structure of the atmosphere.

The project had regular ozone sonde data available from the Palmer station, the Halley Bay station, the South Pole station, and McMurdo. These define the vertical distribution of ozone at points not routinely covered by the flight tracks. Ozonesondes were launched at special times from Palmer and the South Pole to coincide with aircraft overflights of those locations.

The analyses of some of these data sets have not yet been completed, either because of the lengthy data reduction procedures required or because of the sheer volume of raw data acquired. An example of the latter is the meteorological data set, whose initial analyses had the primary goal of forecasting the flight conditions. Furthermore, many of the analyses of the chemical data sets are clearly only preliminary, to be refined by recalibration checks and more sophisticated re-analyses available at the home laboratories. As a consequence, the initial picture summarized below cannot be a balanced, complete, and final one.

## Results and their relationship to theories

The processes controlling the abundance and distribution of ozone in Antarctica are complex and intertwined. However, given the successful nature of this campaign, we are now in a position to start to more fully appreciate the exquisite balance between the meteorological motions and the photochemistry. We will present our preliminary scientific findings as answers to a series of posed scientific questions that are relevant to public policy.

### *1) Did the springtime ozone hole occur over Antarctica in 1987?*

Yes. TOMS satellite, balloon ozonesonde, and both ER-2 and DC-8 aircraft measurements of ozone showed that the springtime ozone decrease occurred again this year. TOMS showed the spatial extent of the phenomenon is continental or greater in scale and revealed the temporal change in the total column of ozone. The abundance of ozone in August and September of 1987 was lower than any previous year at all latitudes south of 60 degrees. In mid-September of this year column ozone was approximately 15% lower at both 70 and 80 degrees south than the values observed in the lowest previous year of 1985. The balloon-sonde data demonstrated that ozone was depleted in the altitude region between approximately 13 and 24 km at Halley Bay, and 15 and 24 km at Palmer. Ozone trends observed at Halley Bay and at Palmer are quite similar, with an approximate 50% decrease observed from mid-August to mid-September near 18 km. The upward looking lidar aboard the DC-8 observed more than a 50% decrease in O<sub>3</sub> at 77 to 90 degrees south between 14 and 19 km, during September, but no discernible trend between 12 and 14 km. There was also evidence from the lidar data of a decrease in O<sub>3</sub> up to 23 km. The in-situ ER-2 instruments observed changes consistent with this picture.

The TOMS data showed that ozone did not simply change monotonically with time, but in some instances changed dramatically over large spatial scales in the matter of only a day or so. One example of such a rapid change in ozone is demonstrated by the TOMS data for September 4-6 over the Palmer Peninsula and Weddell Sea. Changes of greater than 25 Dobson units (DU) in one day were observed over large regions (3 million square km). The ozone sonde data from Halley Bay and the DC-8 lidar data showed that, during this event, the ozone was depleted over a wide altitude range, from about 14 to 23 km.

### *2) Does the evidence indicate that both chemical and meteorological processes are responsible for the ozone hole?*

The weight of observational evidence strongly suggests that both chemical and meteorological mechanisms perturbed the ozone. Additionally, it is clear that meteorology sets up the special conditions required for the perturbed chemistry.

### *3) Was the chemical composition of the Antarctic stratosphere observed to be perturbed?*

Yes. It is quite evident that the chemical composition of the Antarctic stratosphere is highly perturbed compared to predictions based on currently accepted chemical and dynamical theories. The present findings are consistent with the observations made last year from McMurdo. The distribution of chlorine species is significantly different from that observed at mid-latitudes, as is the abundance and distribution of nitrogen species. The amount of total water within some regions of the vortex is significantly lower than anticipated.

Since late August the abundance of the chlorine monoxide radical within the polar chemically perturbed region has been elevated by a factor of more than 100 relative to that measured at mid-latitudes at the highest altitude at which the ER-2 was flown, about 18.5 km. However, the abundance of ClO was observed to decrease rapidly towards lower altitudes. At the highest flight levels, the abundance of ClO at local solar noon ranged between 0.5 and 1 ppbv for the last month of the campaign. While we have no data at higher altitudes, the observed increase in the abundance of ClO from lower altitudes, coupled with the observed low column abundances of HCl, suggests that the ClO abundance may increase somewhat at altitudes above 18 km. In addition to the steep decrease in ClO abundance at lower altitude, the abundance of ClO was also observed to decrease dramatically outside of the chemically perturbed region.

Chlorine dioxide, OClO, which is most likely formed in a reaction sequence involving the ClO radical, was observed both day and night at highly elevated concentrations compared to those at mid-latitude. The preliminary analyses of these observations are consistent with measurements made from McMurdo last year. The column content of hydrochloric acid, HCl, which is one of the major chlorine reservoirs at mid-latitudes, is very low within the chemically perturbed region reaching column contents below  $1 \times 10^{15}$  molecules per  $\text{cm}^2$ . In addition, the column amount ratio of HCl/HF within the chemically perturbed region decreased significantly from a normal mid-latitude value of 4 to a value less than unity. While chlorine nitrate was observed, the data have yet to be fully analyzed thus precluding a statement at this time about its abundance.

The bromine monoxide radical has been observed at concentrations of a few pptv within the chemically perturbed region of the vortex at the flight levels of the ER-2. The abundance of BrO decreases at lower altitudes. However, because the observed concentrations are close to the detection limit of the instrument, little more can be said about the altitude dependence. The low measured abundances of BrO, coupled with our current lack of understanding of the ClO + BrO reaction means that we cannot currently assess the significance of this mechanism for ozone reductions at the ER-2 flight levels.

The ER-2 observations of the abundance of odd nitrogen, which is the sum of all nitrogen-containing reservoir and radical species, show, like total water, very low values within the chemically perturbed region of the vortex, indicating that the atmosphere has been denitrified, as well as dehydrated. Abundances of  $\text{NO}_y$  of 8-12 ppbv were observed outside the chemically perturbed region, while abundances of 0.5 to 4 ppbv were observed inside the chemically perturbed region. A similar large change was observed for one of the nitrogen components, i.e. nitric oxide, NO. In addition, some of the  $\text{NO}_y$  observations suggest that  $\text{NO}_y$  component species are incorporated into polar stratospheric cloud (PSC) particles and nitrate was observed in the particle phase on some of the filter samples and on some of the wire impactor samples taken in the chemically perturbed region of the vortex. The column measurements of nitric oxide, nitrogen dioxide, and nitric acid made from the DC-8 exhibit a strong decrease in the abundance of these species towards the center of the vortex. These low values of nitrogen species are contrary to all theories requiring elevated levels of nitrogen oxides, such as the the proposed solar cycle theory.

#### *4) How do the observed elevated ClO abundances support a chemical role in the formation of the ozone hole?*

There is no longer debate as to whether ClO exists within the chemically perturbed region near 18 km at abundances sufficient to destroy ozone if our current understanding of the chlorine-ozone catalytic cycle is correct. The rate of decrease in ozone during the month of

September at the highest altitudes at which the ER-2 was operated during this campaign is consistent with simultaneously observed concentrations of ClO. However, our present understanding of key chemical reaction rates and photodissociation products within the catalytic process is incomplete. Thus, laboratory studies are urgently needed. It is essential to define the rate of ClO dimer ( $\text{Cl}_2\text{O}_2$ ) formation and the photolysis products of dimer decomposition because only one of several possible routes leads to ozone destruction. Once the results of ongoing laboratory studies become available, these in-situ ClO data will allow the chemical mechanism to be quantitatively defined and its consequences better understood.

There is another line of observational evidence consistent with ozone destruction by chlorine catalysis. In the month of August, a consistent positive correlation between ClO and  $\text{O}_3$  was observed. By the middle of September, as the ozone concentration was dropping at ER-2 altitudes, a strong anti-correlation developed between ClO and  $\text{O}_3$ . The anti-correlation was usually present on both large and small scales within the chemically perturbed region.

There are observations that are not entirely consistent with these chemical arguments. For example, based on preliminary data from this year and data from last year from McMurdo, the observed diurnal behavior of OClO, is difficult to rationalize with the present chemical mechanisms, particularly in light of the new observations that the abundances of BrO are low at ER-2 flight altitudes.

*5) Can the elevated abundances of ClO inside the chemically perturbed region of the vortex be explained?*

Significant progress was made. Observational data that air within the chemically perturbed region of the vortex is dehydrated and that the  $\text{NO}_y$  abundances are very low are consistent with theories that have been invoked whereby the chlorine reservoir species,  $\text{ClONO}_2$  and HCl, can react on the surfaces of polar stratospheric clouds to enhance the abundance of active chlorine species, i.e. ClO. The observations also support the picture that the abundance of  $\text{NO}_y$  is low because odd nitrogen can be removed from the atmosphere by being tied up in ice crystals, which can then gravitationally settle to much lower altitudes. Low abundances of  $\text{NO}_y$  are needed to prevent the rapid reconversion of ClO to  $\text{ClONO}_2$ . This picture is further supported by the observations of low column abundances of HCl, by occasional observations of high levels of nitrate found in the ice particles, and by the visual and lidar observations of high cirrus and polar stratospheric clouds.

One observation which is currently difficult to understand is the sharp decrease in the abundance of ClO at lower altitudes. This could be due to a lack of understanding of either the abundance or partitioning of  $\text{ClO}_y$ , or to dynamical effects. Lack of observations of reactive hydrogen containing radicals, hydroxyl (OH) and hydroperoxy ( $\text{HO}_2$ ) currently prevents an assessment of their role in the conversion of chlorine reservoir species to ClO.

*6) How do the observations support a meteorological role in the formation of the ozone hole?*

There were instances of rapid large scale changes in total ozone where meteorology appears to have been the controlling factor. One such event occurred over the Palmer Peninsula on September 5. Over a period of 24 hours total ozone as observed by TOMS decreased by 25 DU to below 200 DU over an area of about 3 million square km. Such a rapid decrease is difficult to explain chemically. The origin of that air is not known. It could be either air naturally low in ozone, tropospheric/lower stratospheric, or air in which ozone had been chemically depleted. The feature moved over the Weddell Sea and persisted until

September 16, when it merged with two other regions of low total ozone. Lidar measurements from the DC-8 showed low ozone values and extensive aerosol layers between 14 and 19 km in the region of the TOMS minimum of ozone. This and other similar events evident in the TOMS ozone data and the SAM II PSC data between September 5 and 14 were spatially correlated with deepening surface pressure lows with marked meridional flow from middle to high latitudes at lower stratospheric levels. The detailed meteorological mechanism by which the surface lows produce the low column ozone remains unclear and further analysis is required.

The data offer no support for sustained large scale upwelling. In the restricted region covered by the ER-2, 54 to 72 degrees south latitude and from altitudes of 12.5 to 18.5 km, measurements of CFC-11 and N<sub>2</sub>O which act as tracers of air motions show no evidence of a general increase in abundances above about 14 km during the mission, although there were instances of structure and elevated values.

The meteorology must play a role in the dehydration and denitrification processes. It is crucial to understand whether the necessary low temperatures are maintained radiatively or by ascent, or some combination of both.

*7) Does the complexity of the situation suggest that we need to understand the interplay between meteorology and chemistry?*

Yes. It is clear from our ER-2 flights that the region of dehydrated and denitrified air maintained a sharply defined latitude gradient throughout most of the campaign. On a purely meteorological definition, the vortex edge would be well outside the dehydrated, denitrified region. The meteorological flow must therefore have been such as to maintain a kind of "containment vessel", in which the perturbed chemistry could proceed without being influenced by mixing in more normal stratospheric air from outside or below.

Very low values of CFC-11, CFC-12, CH<sub>3</sub>CCl<sub>3</sub>, and N<sub>2</sub>O were observed at the upper levels of the ER-2 flight track within the "containment vessel". A key question is how these low values are produced and maintained in the chemically perturbed region.

The concept of mixing at the region of sharp latitudinal gradient is important, since it has the potential to supply nitrogen oxides which would tend to decelerate the chlorine chemistry. The meteorology is thus important in the termination phase as well as in the initiation phase.

*8) Can we quantitatively separate the contributions of chemistry and meteorology to the formation of the ozone hole?*

No. The September 5 event illustrates the complexity of the ozone hole, and the difficulty of deriving unambiguous dynamical or chemical signatures. The magnitude and rapidity of the decrease are difficult to ascribe to a chemical cause. Air of low ozone content appears to have been transported into the region. The origin of that air is not known. It could be either air naturally low in ozone, tropospheric/lower stratospheric, or air in which ozone had been chemically depleted.

Another illustration of the difficulty of clearly establishing chemical or dynamical mechanisms is the decreasing trends in ozone in regions of low ClO outside of the vortex whose magnitudes are comparable to those within the vortex. This is evident from an examination of the ozonesonde data from the Palmer station at 64 °S and comparing it to the Halley Bay data at 78 °S, and the DC-8 lidar data. In addition, downward trends of ozone



were observed in the lower altitude region where ClO concentrations were substantially lower than at 18 km.

*9) What are the global implications of the Antarctic ozone hole?*

Until we understand the cause or causes of the spring-time Antarctic hole, we will not be able to address this key question in a responsible manner. Thus, at this time, it is premature for us to speculate on this important topic. However, as we continue to analyze the data that we have acquired and further test and expand the pictures that we have developed, we will be in a better position to address this important question.

*10) When will the data be in a form suitable for use in formulating national and international regulatory policies?*

As noted in the opening paragraph, the schedule for the assimilation and publication of the results is brisk. Peer reviewed publications will appear in 1988. The results from the 1987 ground-based McMurdo campaign will likely appear on about the same schedule. Both sets of these completed conclusions would be the best basis for any possible policy re-evaluations. The major international scientific review scheduled for 1989, which will serve as input to the 1990 policy review of the Montreal Protocol, will have these conclusions available.