

issn 0065-3713

I N S T I T U T D ' A E R O N O M I E S P A T I A L E D E B E L G I Q U E

3 - Avenue Circulaire
B - 1180 BRUXELLES

AERONOMICA ACTA

A - N° 359 - 1991

Spring polar ozone behavior

by

A.C. AIKIN

B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

3 - Ringlaan
B - 1180 BRUSSEL

FOREWORD

This report summarizes our understanding of the springtime behavior of polar stratospheric ozone as of mid-1990. Ozone changes each spring since 1979 have clearly established for the first time that man-made chlorine compounds influence stratospheric ozone. Long before important advances in satellite and in situ investigations, it was Dobson's decision to place a total ozone measuring spectrometer at Halley Bay in Antarctica during the International Geophysical Year and subsequent continuous monitoring which led to the discovery that ozone was being destroyed each spring by chlorine processed by polar stratospheric clouds.

Many unresolved scientific issues remain, and the report identifies some of the most important problems. That the decline of polar spring ozone was unforeseen underscores our lack of understanding of the situation. The problem has many nonlinear aspects, which may lead to unforeseen effects on stratospheric ozone. It is important to continue and broaden scientific investigation in this exciting area.

AVANT-PROPOS

Ce rapport est un résumé de notre compréhension actuelle, en mi-1990, du comportement printannier de l'ozone stratosphérique antarctique. Les changements en ozone, mesurés chaque printemps depuis 1979, ont pour la première fois établi clairement le fait que les composés chlorés d'origine anthropogénique influencent l'ozone stratosphérique. Même si les investigations par satellite ou in situ avaient subi des progrès non-négligeables, c'est Dobson qui a décidé l'installation à Halley Bay en Antarctique d'un spectromètre pour mesurer le contenu total en ozone pendant l'Année Internationale de Géophysique et depuis lors en continu. C'est ainsi qu'on a découvert que chaque printemps l'ozone est détruit par le chlore provenant de réactions avec les nuages stratosphériques polaires (PSC's).

Plusieurs aspects scientifiques ne sont pas résolus, et ce rapport identifie quelques-uns des problèmes les plus importants. Le fait que la diminution de l'ozone au printemps polaire n'était pas prévue, souligne que la situation n'est pas suffisamment bien comprise. Le problème contient plusieurs aspects non linéaires, ce qui peut produire des effets imprévus sur l'ozone stratosphérique. Il est donc important de continuer et d'élargir la recherche scientifique dans ce domaine particulièrement intéressant.

VOORWOORD

Dit rapport geeft een overzicht van het gedrag van ozon in de polaire stratosfeer tijdens de lente, zoals dit momenteel, half 1990, begrepen wordt. De ozon veranderingen elke lente vanaf 1979 hebben voor het eerst duidelijk aangetoond dat de chloor verbindingen van antropogene oorsprong het ozon in de stratosfeer beïnvloeden. Ondanks belangrijke vorderingen in satelliet- en in situ waarnemingen, heeft Dobson het initiatief genomen om een spectrometer te installeren in Halley Bay in Antarctica voor het meten van de totale ozon abundantie. Waarnemingen tijdens het Internationaal Geofysisch Jaar en daaropvolgende continue observaties hebben geleid tot de ontdekking dat tijdens elke lente ozon vernietigd wordt door chloor na reactieprocessen met PSC's (polaire stratosferische wolken).

Vele wetenschappelijke vragen blijven onopgelost; dit verslag stelt enkele van de belangrijkste problemen in het daglicht. Het feit dat de vermindering van ozon in de polaire lente niet voorspeld was onderstreept dat de situatie slecht begrepen is. Het probleem vertoont veel niet-lineaire aspecten die tot onvoorziene effecten op stratosferisch ozon kunnen leiden. Het is daarom belangrijk het wetenschappelijk onderzoek over dit opwindend onderwerp voort te zetten en uit te breiden.

VORWORT

Diese Arbeit fasst zusammen wie gegenwärtig das Verhalten des Stratosphären Ozons im Frühjahr verstanden werden kann. Es ist eindeutig erwiesen, dass die Frühjars Änderungen im Ozon seit 1979 durch anthropogene Chlor Verbindungen verursacht werden. Lange bevor Satelliten und In-Situ Untersuchungen gemacht wurden, entschloss Dobson ein Spektrometer zur Messung des totalen Ozon Gehaltes in Halley Bay in der Antarktic während des internationalen Geophysikalischen Jahres zu installieren, und die kontinuierlichen Messungen seit dieser Zeit führten zur Entdeckung dass Ozon jedes Frühjahr durch Chlor Prozesse in polaren Stratosphären Wolken zerstört wird.

Eine Reihe von ungelösten wissenschaftlichen Fragestellungen verbleiben, und die gegenwärtige Arbeit identifiziert einige der wichtigsten Probleme. Die Tatsache dass die Abnahme im polaren Ozon während des Frühjahrs nicht vorrausgesehen wurde, weist darauf hin, wie wenig die Situation verstanden wird. Das Problem hat viele nicht-lineare Aspekte die zu unvorsehbaren Effekten im Stratosphären Ozon führen können. Es ist daher wichtig, dass auf diesem anspruchvollen Gebiet die wissenschaftlichen Untersuchungen weiter geführt und ausgedehnt werden.

SPRING POLAR OZONE BEHAVIOR

by

A.C. AIKIN

Abstract

The general spring behavior of Antarctic and Arctic total ozone within their respective polar vortices can be explained in terms of heterogeneous reactions of chlorine and nitrogen reservoir compounds on polar stratospheric cloud particles. Ozone loss rates for the Arctic are estimated to be between 0.3 and 1% per day during the spring, with the proportion due to ClO_x amounting to 75%, BrO to 15%, and HO_x to 10%. Ozone depletion is no more than 4 to 8%. The situation in the Antarctic is complicated by uncertainties in ozone and ClO amount. There may be an additional mechanism required to explain ozone depletion at the cloud level, but there is agreement at the level of the experimental uncertainties. Ozone loss is also observed above the polar stratospheric cloud level, implying another mechanism, either chemical or dynamical. Formation of ozone-destroying odd nitrogen above the cloud level is still an open question.

In the Arctic, ozone can be depleted with reactions on nitric acid-based clouds, so that the lower temperatures required for water ice clouds are not a prerequisite. In general, warmer temperatures that prevent cloud formation and a less stable vortex lead to much less ozone depletion in the Arctic than the Antarctic.

There is strong evidence that tropospheric forcing within or just outside the vortex leads to adiabatic cooling, with resulting cloud formation. During such events ozone-poor tropospheric air is transported into the stratosphere. In the Arctic this can result in the transport of long-lived hydrocarbons. Subsequent reactions lead to the formation of HCl , reducing the effect of Cl . There is also production of HO_2 , which accelerates ozone loss due to chlorine. These events are observed as small areas of large and rapid ozone depletion. Ozone-poor air from these regions can propagate to lower latitudes, as can the air from within the vortex, when it disintegrates in late spring.

Data from the BUV ozone-measuring instrument on the Nimbus 4 satellite indicate the existence of October, 1970 Antarctic ozone of only 250 DU. This is the evidence of the existence of ozone loss with only CH_3Cl and low concentrations of CFCs as chlorine sources.

Résumé

Le comportement général des colonnes totales d'ozone au printemps en Antarctique et en Arctique dans leurs vortex respectifs, peut être expliqué en termes de réactions hétérogènes entre, d'une part, les réservoirs de composés chlorés et azotés et, d'autre part, les particules dans les nuages stratosphériques polaires. On estime que les vitesses de perte d'ozone au printemps dans l'Arctique sont de l'ordre de 0.3 à 1% par jour avec la proportion due au ClO_x montant jusqu'à 75%, celle due à BrO jusqu'à 15% et celle due à HO_x jusqu'à 10%. La diminution de l'ozone reste inférieure à 4 à 8%. La situation dans l'Antarctique est plus compliquée par suite des incertitudes dans les abondances d'ozone et de ClO . Il est possible qu'il faille un mécanisme supplémentaire pour expliquer la diminution de l'ozone à l'altitude des nuages, mais on est en accord en ce qui concerne les erreurs expérimentales. La perte d'ozone est également observée au-dessus de l'altitude des PSC, ce qui implique un mécanisme supplémentaire de caractère chimique ou dynamique. La génération au-dessus du niveau des nuages d'azote impair détruisant l'ozone est toujours une question ouverte.

Dans l'Arctique, l'ozone peut être détruit par réactions avec les nuages riches en acide nitrique, de sorte que les températures plus basses requises pour la formation des nuages composés de cristaux de glace ne sont pas une exigence. En général, dans l'Arctique, les températures plus élevées qui empêchent la formation des nuages et le vortex moins stable conduisent à une perte d'ozone moins importante que dans l'Antarctique.

Il existe de solides preuves que ce sont les forces troposphériques à l'intérieur ou à la limite du vortex qui génèrent un refroidissement adiabatique, avec comme résultat, la formation de nuages. Pendant ces événements, l'air troposphérique pauvre en ozone est transporté dans la stratosphère. Dans l'Arctique, ceci peut mener à un transport d'hydrocarbures de longue durée de vie. Les réactions suivantes produisent la formation de HCl qui réduit l'effet du Cl . Il y a aussi production de HO_2 qui accélère la perte d'ozone due au chlore. Ces événements sont observés au sein de petites régions où la diminution d'ozone est importante et rapide. L'air de ces régions, pauvre en ozone, peut se propager vers les latitudes moyennes, de même que l'air de l'intérieur du vortex au moment de sa désintégration à la fin du printemps.

Les données de l'instrument BUV pour mesurer l'ozone à partir du satellite Nimbus 4 montrent l'existence d'une quantité d'ozone de seulement 250 DU en octobre 1970 en Antarctique. Ceci met en évidence qu'une diminution d'ozone peut se produire avec comme seules sources de chlore CH_3Cl et de basses concentrations de CFC.

Samenvatting

Algemeen kan het gedrag van de totale ozon abundantie in de noord- en zuidpoolgebieden tijdens de lokale lente en binnen de respectieve polaire vortices, verklaard worden in termen van heterogene reacties van chloor- en stikstof reservoir verbindingen op polar stratospheric cloud (PSC) deeltjes. Men schat dat de snelheid waarmee ozon afneemt tijdens de lente in het noordpoolgebied ligt tussen 0.3 en 1% per dag; daarvan zou 75% te wijten zijn aan ClO_x , 15% aan BrO en 10% aan HO_x . De ozon vermindering bedraagt niet meer dan 4 tot 8%. De situatie in Antarctica is ingewikkelder tengevolge van onzekerheden in de abundanties van ozon en ClO . Misschien is een extra mechanisme vereist om de ozon vermindering ter hoogte van het wolkendek te verklaren maar binnen de experimentele onzekerheden bestaat er overeenstemming. Het feit dat ozon vermindering ook waargenomen is boven het niveau van de PSC's impliceert dat een ander mechanisme, van chemische of dynamische aard, in het spel is. De vorming van oneven stikstof verbindingen boven het niveau van de PSC's die ozon zouden vernietigen blijft nog steeds een open vraag.

In het noordpoolgebied kan ozon vernietigd worden door reacties op PSC's die voornamelijk bestaan uit salpeterzuur, zodat de lagere temperaturen die nodig zijn voor de vorming van PSC's bestaande uit ijskristallen niet vereist zijn. Over het algemeen in het noordpoolgebied, in vergelijking met Antarctica, geven de hogere temperaturen, die de vorming van de PSC's voorkomen, en de minder stabiele werveling (vortex) aanleiding tot minder ozon vernietiging.

Het is duidelijk bewezen dat de krachten vanuit de troposfeer, binnen of net buiten de vortex, adiabatische afkoeling veroorzaken met bijgevolg vorming van PSC's. Zulke gebeurtenissen gaan gepaard met aanvoer van troposferische lucht die arm is aan ozon in de stratosfeer. In het noordpoolgebied kan dit het transport van lang-levende koolwaterstoffen tot gevolg hebben. Daaropvolgende reacties leiden tot de vorming van HCl , dat het effect van Cl vermindert. Anderzijds is er produktie van HO_2 , dat de vernietiging van O_3 door Cl versnelt. Deze gebeurtenissen worden herkend als kleine gebieden met een belangrijke en snelle Ozon vermindering. Zowel ozon-arme lucht uit deze gebiedjes als volumes lucht uit de vortex, op het moment van zijn desintegratie laat in de lente, kunnen zich bewegen naar lagere breedtegraad.

Ozongegevens gemeten door BUV aan boord van de Nimbus 4 satelliet wijzen op een hoeveelheid ozon van slechts 250 DU boven Antarctica in oktober 1970. Ze vormen het bewijs voor het optreden van ozon vernietiging met enkel CH_3Cl en lage CFC concentraties als bronnen van chloor.

Zusammenfassung

Das allgemeine Verhalten des Ozon Gehaltes im Frühjar über der Arktik un Antarktisc, innerhalb der entsprechenden polaren Vorticex Winde, kann auf Grund der heterogenen Reaktionen zwischen Chlor un Stickstoff Reservoir Molekülen und polaren Wolken Teilchen in der Stratosphäre erklärt werden. Ozon Velust Raten in der Arktik sind im Frühjar schätzungsweise zwischen 0.3 und 1% pro Tag; die Anteile sind für ClO : 75%, BrO : 15%, HO₂ : 10%. Der Ozon Verlust ist nich über 4 bis 8%.^xIn der Antarktik, ist^xdie Situation komplizierter wegen der Ungenauigkeiten im Ozon und ClO Gehalt. Ein zusätzlicher Mechanismus könnte notwendig sein um den Ozon verlust in Wolkenhöhe zu erklären, obwohl die Übereinstimmung innerhalb der experimentellen Ungenauigkeiten ist. Ozon wird auch oberhalb der Stratosphären Wolken beobachtet, was darauf schliessen lässt dass noch ein anderer Mechanismus am Werk ist, entweder chemischer oder dynamischer Art. Die Bildung von ungeradem Stikstoff, der Ozon oberhalb der Wolken zerstreuen könnte, ist noch eine offene Frage.

In der Arktik, kann der ozon Gehalt duch Reaktionen in Stickstoffsäure hältigen Wolken reduziert werden, so dass keine Notwendigkeit mehr besteht für die niedrigen Temperaturen in Wassereis Wolken. Die wärmeren Temperaturen die eine Wolken Bildung verhindern, und ein weniger stabiler Vortex führen im allgemeinen zu einer viel geringeren Ozon Enleerung in der Arktik als in der Antartik.

Die Beobachtungen weisen darauf hin, dass die troposphärischen Anregungsprozesse innerhalb oder gerade ausserhalb des polaren Vortex zur adiabatischen Abkühlung führen und Wolken bilden. In diesen Processes wird ozon-arme troposphärische Luft in die Stratosphäre befördert. In der Arktik führt das zum Transport von langlebigen Wasserkohlenstoffen. Die nachfolgenden Reaktionen führen zur Bildung von HCl und einer Reduzierung des Cl Effektes. Wasser wird auch produziert und das beschleunigt den Ozon Verlust durch Chlor. Diese Vorgänge werden in kleinen Gebieten beobachtet wo der ozon Verlust sehr schnell abläuft. Ozon-arme Luft aus diesen Gebieten kann sich bis in die niederen Breiten ausbreiten, und das gleiche gilt auch für die Luft innerhalb des polaren Vortex wenn dieser sich im späten Frühjar auflöst.

Die Daten von den BUV Ozon Messungen am Nimbus 4 Satelliten zeigen 250 DU für das Antarktisk Ozon im Oktober 1970. Das gilt als Beweis dafür dass der Ozon Verlust nur durch CH₃Cl erfolgt und durch die niedrigen Konzentrationen von CFCs als Chlor Quelle.

INTRODUCTION

Dobson (1966) established the first Antarctic ozone measuring station during the International Geophysical Year, 1957-1959. Two important findings of these early observations were that there was less ozone in the Antarctic spring than in the Arctic and that a decrease in total ozone occurred during early spring. These results have been largely ignored, but gain important significance with the recent discovery of the spring ozone depletion labeled the "ozone hole". The term "ozone hole" was originally coined by Deutsch (1969) to describe a large ozone decrease, which was observed over Boulder, Colo., in conjunction with a volcanic event in 1964.

In reference to the Antarctic ozone hole Farman et al (1985) observed that, in spring time, total ozone over Halley Bay, 76°S, 27°W had been decreasing each year since 1979. The decrease was attributed to the increase in atmospheric free chlorine caused by the rising level in chlorofluorocarbons. Confirmation of this change in total ozone came from measurements at the Sowy Station, 69°S, 40°E (Chubachi, 1984) (Chubachi and Kajiwara, 1986), and by total ozone measurements from a satellite (Stolarski et al, 1986). The satellite observations established that the region of ozone depletion encompassed the entire Antarctic continent and was associated with the polar winter vortex in stratospheric circulation.

Figure 1 illustrates the total ozone in October as observed above Halley Bay, Antarctica. Measurements are expressed in Dobson units (1 DU = 1 milliatm cm of ozone). Relative to the years before 1979 there has been a progressive decline in total ozone. In 1987 only half the ozone was present. Alternate years have more ozone.

This is true over entire data set. The strength of the polar vortex has been postulated as the cause of this effect. While direct correlation with a particular phase of the equatorial stratospheric quasi-biennial oscillation in winds and temperatures is not evident, there

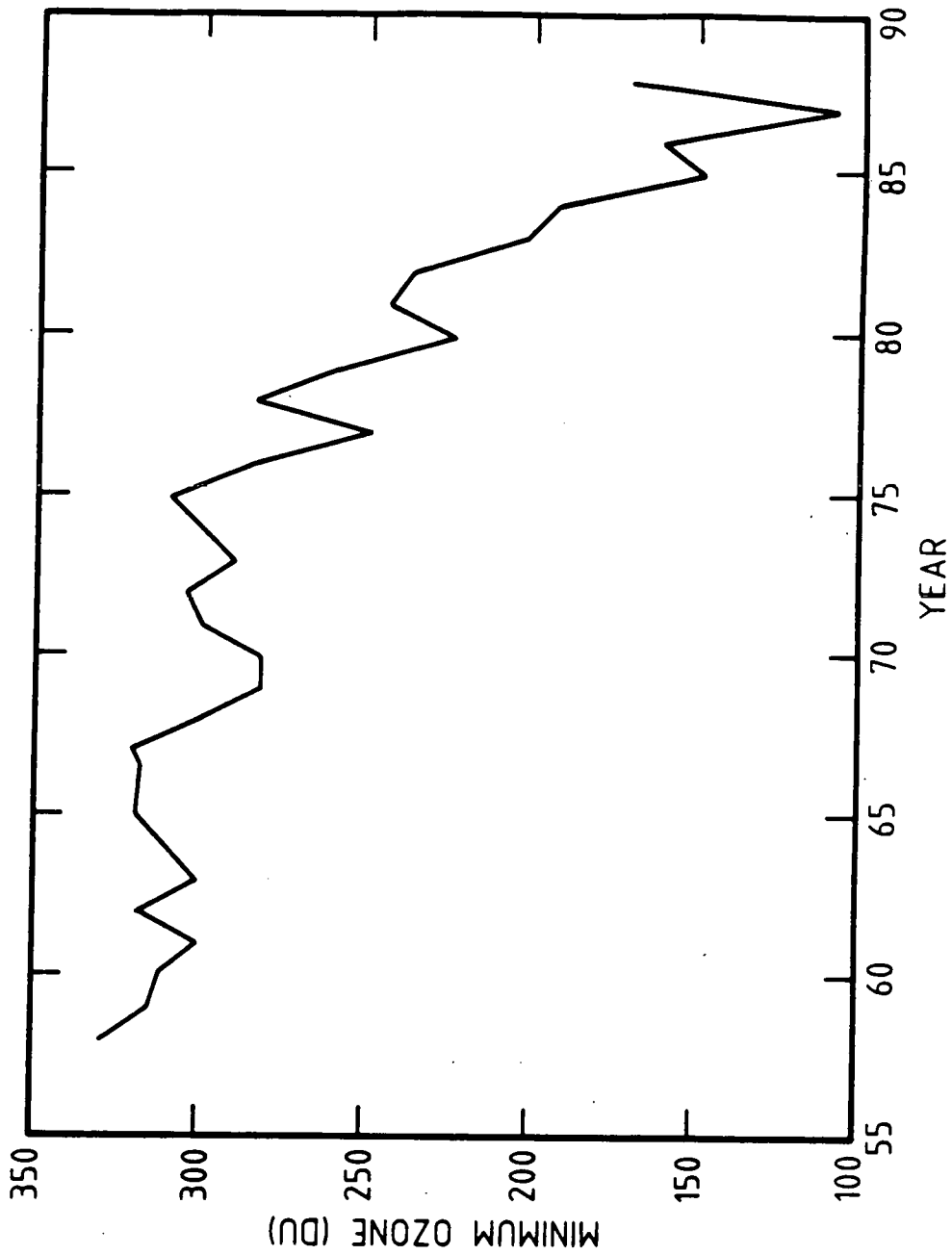


Fig. 1.- Total ozone at the minimum as a function of time for Halley Bay, updated to include recent years (adapted from Farman et al, 1985).

is correlation with the mid-latitude form of this behavior (Lait et al, 1989).

Maps of the total ozone for the years 1985 to 1989 are shown in Figure 2. These maps give the average total ozone amounts for October as a function of latitude and longitude, where information is displayed on a polar plot with colors representing different ozone amounts. The lowest ozone amounts are at latitudes near the south pole, with rough longitudinal symmetry. North of 55°S, ozone loss is in general not observed. An analysis of corresponding winds and temperatures shows a very strong correlation with the southern polar vortex. This vortex is characterized by a very strong counterclockwise circulation with winds that are as great as 55 m s⁻¹ and temperatures as low as 180°K. This circulation confines polar air within the vortex during the winter and early spring until the vortex disintegrates. During this period there is very little mixing of lower latitude air, which has often been exposed to sunlight. Confirmation of the circulation can be obtained by calculating the trajectories on an isentropic surface. Such a surface is obtained by using potential temperature for the vertical coordinate. Examples of such trajectories are found in a paper on miniholes by McKenna et al (1989). Miniholes are small regions of enhanced ozone depletion imbedded within areas equatorwards of the vortex where little loss occurs.

HETEROGENEOUS REACTIONS ON POLAR STRATOSPHERIC CLOUDS AS A HYPOTHESIS
FOR OZONE LOSS

The temporal behavior of the total ozone during spring is unique. In August and early September the ozone amount is nearly constant. Beginning in mid-September there is a decline in total ozone, with a minimum reached in mid-October. This is followed by a rise coinciding with the breakup of the polar vortex. As the sun returns in November, there is a rise in the total ozone. This is illustrated in Figure 3,

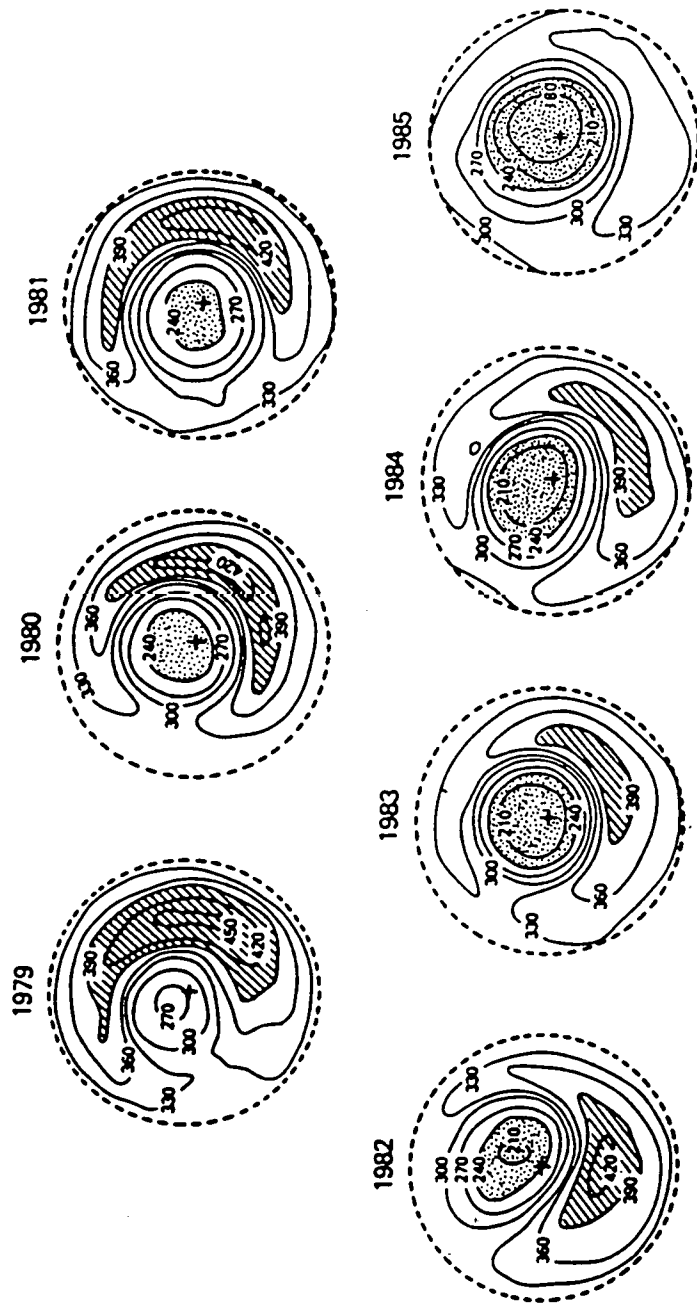


Fig. 2. - Maps of total ozone for the years 1979-1985 based on satellite ozone measurements using the TOMS instrument (from Stolarski et al, 1986).

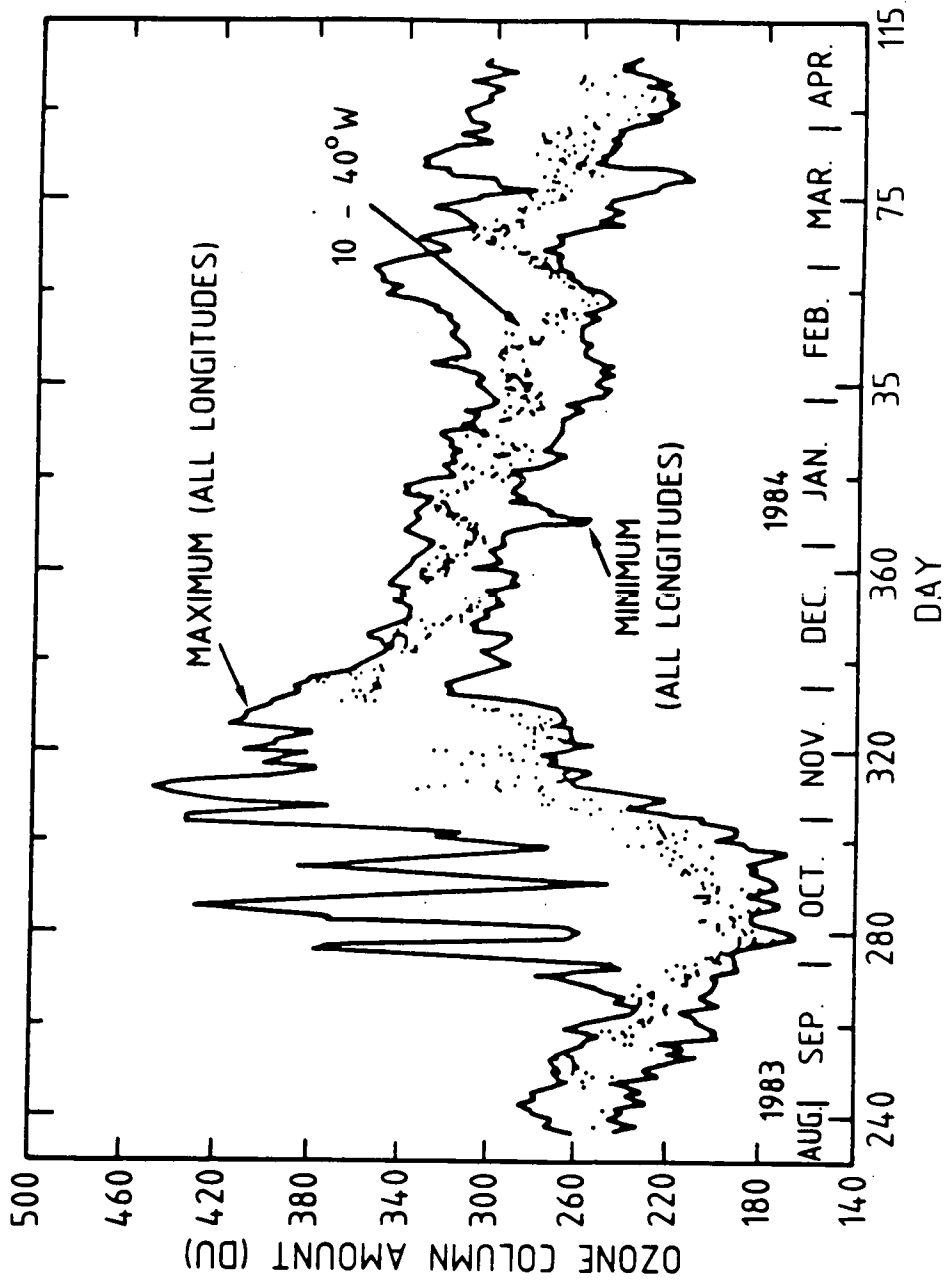


Fig. 3.- The time behavior of total ozone (from Stolarski et al, 1986).

which is based on satellite data. The breakup of the polar vortex carries ozone-poor air to lower latitudes. Such events may be harmful to sea plankton and other life because of the increased UV-B radiation. The temporal total ozone behavior in early spring for solar zenith angles greater than 75° must be modified due to a correction which must be applied to TOMS for large solar zenith angles based on ground-based total ozone measurements at twilight (Pommereau et al, 1989). This correction has the effect of giving a steeper decline in early spring and shifting the ozone depletion, as seen on maps, towards the sunlit areas.

Direct ozone measurements, using balloon-borne instruments, show that the altitude region where the greatest ozone depletion occurs coincides with the maximum ozone mixing ratio and the polar tropopause (Hofmann et al, 1987, 1989).

In the Antarctic, tropopause temperatures may be as low as 180°K , allowing the formation of clouds at this level. These polar stratospheric clouds are readily visible from the ground and have been observed for nearly a century. They have been mapped by a satellite-borne occultation instrument (McCormick et al, 1982). Figure 4 illustrates a series of plots showing the temporal behavior of temperature and the extinction ratio for altitudes of 14, 16, 18, 20, 22 and 24 km (McCormick et al, 1989a). The extinction ratio is the total amount of observed extinction relative to the extinction when gas absorption and Rayleigh scattering is removed. The highest extinction ratios are observed in June, July and August when temperatures are a minimum, the optimum conditions for cloud formation. Laboratory experiments on vapor pressure versus temperature for water-nitric acid vapor mixtures show that the temperatures required for particle formation are several degrees Kelvin higher for the nitric acid mixture than for a pure water mixture (O.B. Toon et al, 1989a; Crutzen and Arnold, 1986).

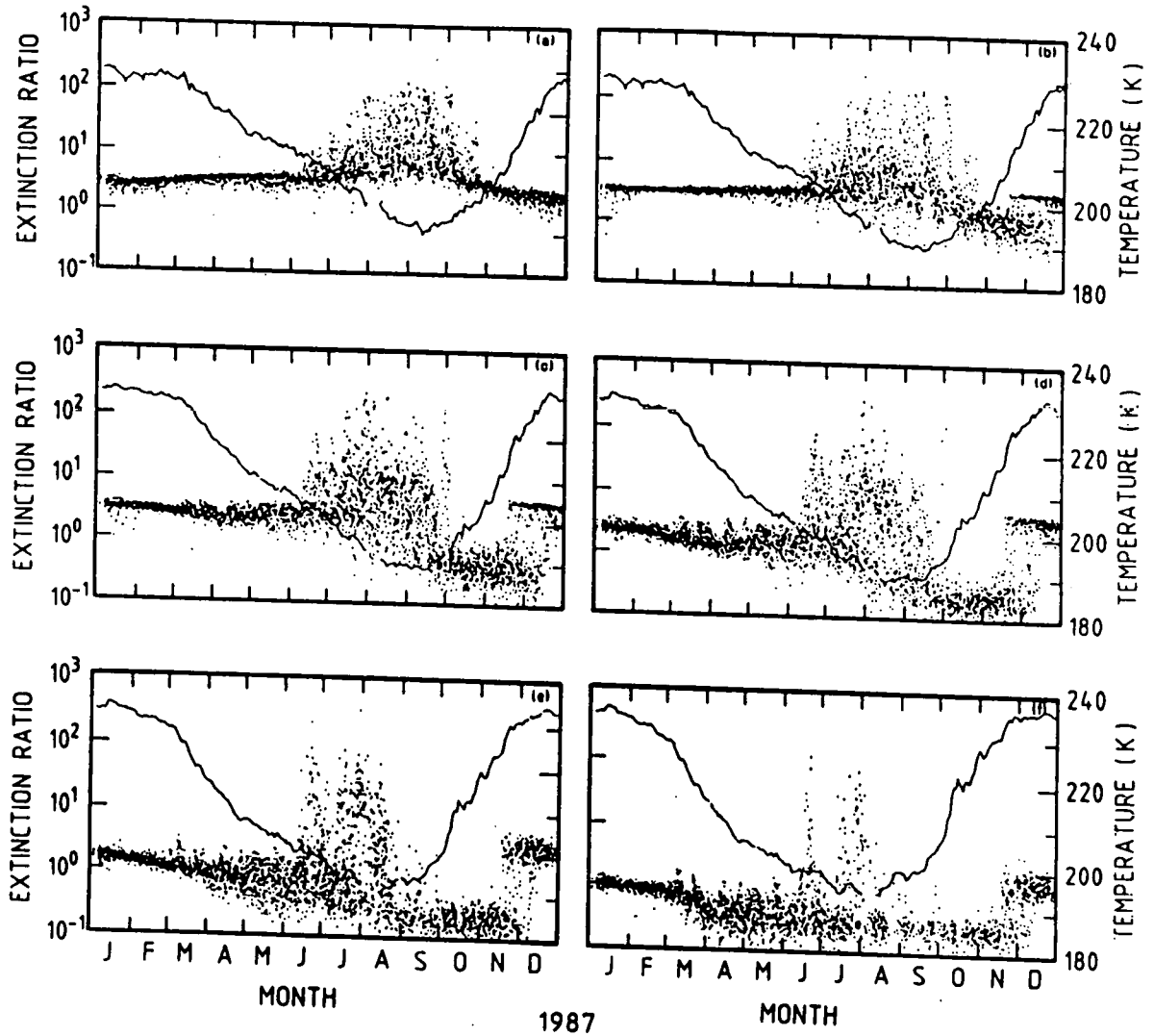


Fig. 4.- Temporal behavior of temperature and extinction ratio for several different altitudes (from McCormick et al, 1989).

- (a) 14 km
- (b) 16 km
- (c) 18 km
- (d) 20 km
- (e) 22 km
- (f) 24 km

Therefore two forms of polar stratospheric clouds (PSCs) are possible, type I, consisting of nitric acid trihydrate and type II, consisting of pure water ice. Growth for type I begins at 188°K at 30 mb and 192°K at 50 mb (Poole and McCormick, 1988). Figure 4 shows that PSCs are more frequent at lower altitudes than at 22 or 24 km.

The observational evidence that has emerged on the lower stratosphere ozone altitude distribution is summarized in Figure 5. Two ozone amount versus height profiles are shown for 28 August and 16 October (Hofmann et al, 1987). Notice the maximum reduction in October ozone relative to the amount in August occurs at the height of maximum O_3 partial pressure, which nearly coincides with the polar tropopause where the clouds are formed. These observations, coupled with the ozone temporal behavior and laboratory results on heterogeneous reactions involving chlorine and nitrogen species, form the basis of the ozone depletion theory. The ozone decrease is so large that it cannot be accounted by the conventional gas phase chemistry.

Heterogeneous reactions involving stratospheric particles have been considered in the past in conjunction with the Junge layer of stratospheric aerosols, which occurs at lower latitudes and is composed of sulfuric acid-water particles. Cadle et al (1975) postulated that ozone photochemistry could be modified by such processes. However, in general such reactions have been ignored, since it was thought that the accommodation coefficients were small and, except in the case of volcanic eruptions, there didn't appear to be sufficiently large stratospheric particle densities to support a significant ozone reduction. The uniqueness of the Antarctic ozone decrease, the presence of polar stratospheric clouds, and recent laboratory results changed the situation, resulting in the proposal that heterogeneous reactions on cloud particles were responsible for the observed ozone loss (Solomon et al, 1986).

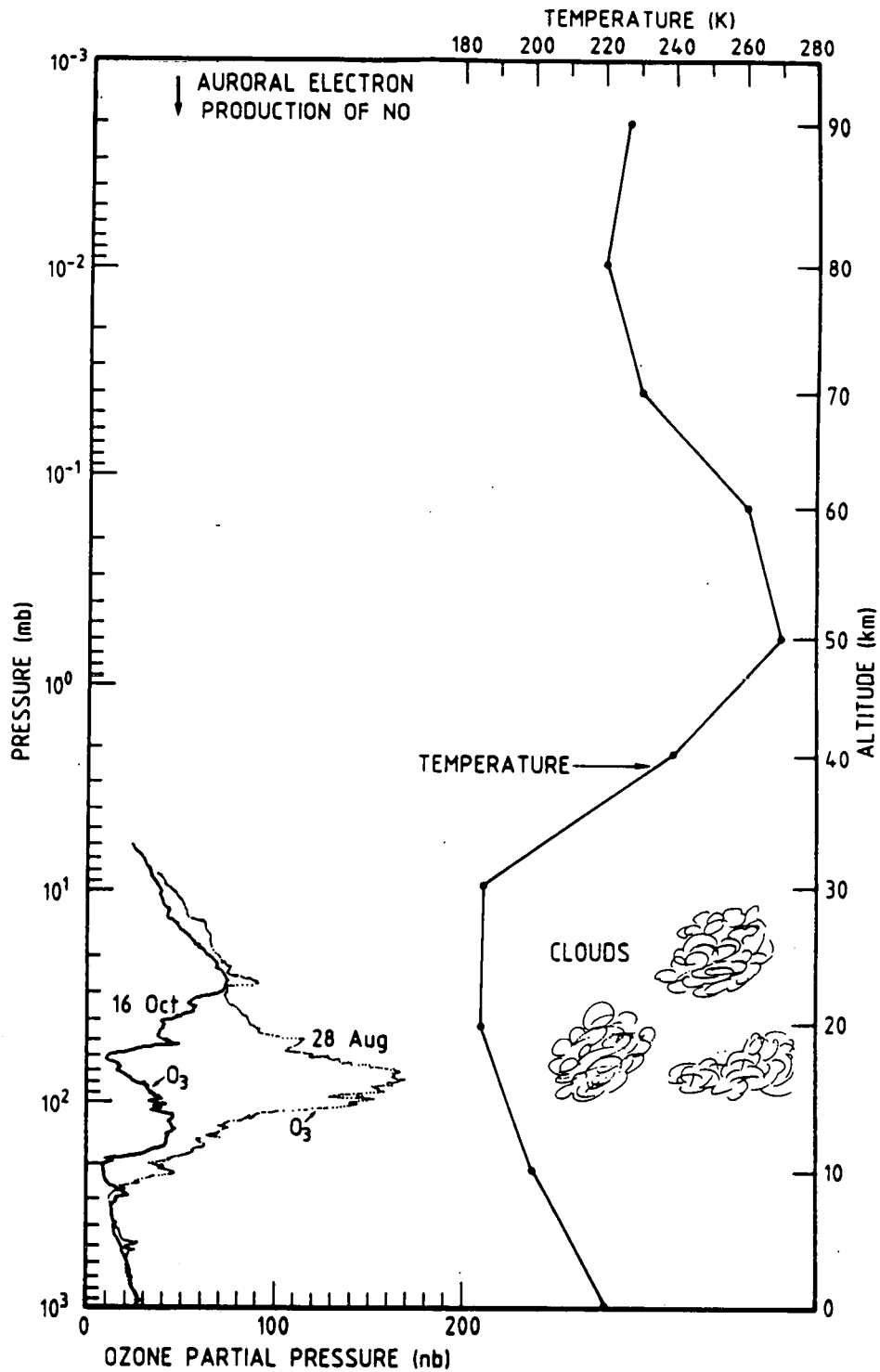


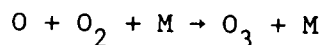
Fig. 5.- Schematic showing the interrelationship of clouds, polar temperature structure, and ozone loss.

The formation of type I clouds effectively denitrifies the atmosphere as far as the nitrogen reservoir species nitric acid is concerned. Ozone destruction is considered in terms of catalytic cycles. Each of these cycles has chemical species, which serve as reservoirs for the reactive component responsible for ozone destruction. In the case of the nitrogen cycle, nitric acid is the long-lived reservoir. A shorter lived species, which is also a reservoir, is nitrogen pentoxide. Laboratory studies have shown that both of these species can be incorporated into ice particles (Tolbert et al, 1987, 1988). This is one element of the theory of ozone reduction by cloud particles. The other essential event is the inclusion of HCl, the reservoir for chlorine, into the clouds.

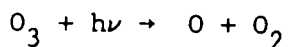
Ozone formation is initiated by molecular oxygen photodissociation



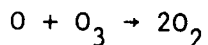
followed by



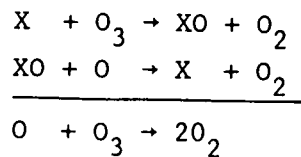
While photodissociation of ozone occurs, odd oxygen is not destroyed



The destruction of odd oxygen occurs through the reaction

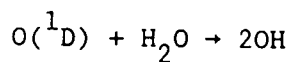
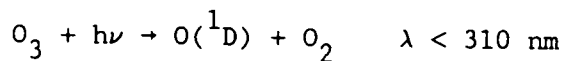


Ozone is mainly destroyed by several additional catalytic cycles, the basis of which is the reaction set

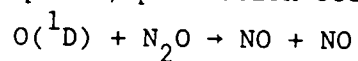


where X = OH, NO, Cl, or Br.

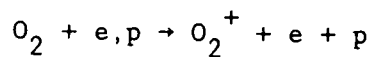
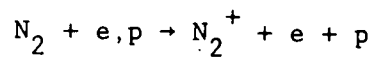
The production of odd hydrogen in the stratosphere occurs by the sequence



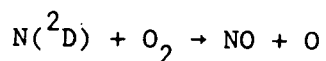
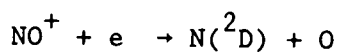
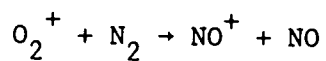
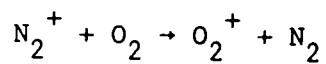
There are a variety of processes for the production of NO. In the stratosphere, production occurs primarily by



If energetic electrons or protons are precipitated, then ionization occurs

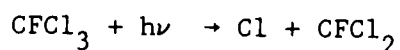
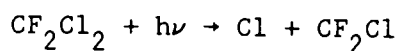


followed by the ion-molecule reactions

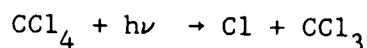
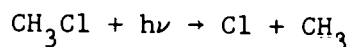


In the stratosphere and most of the mesosphere the excited state of N is quenched, i.e., below 85 km, the reaction proceeds in the ground state. The region where most of the energy responsible for the aurora is deposited is above 85 km.

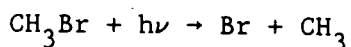
Chlorine originates mostly with the stratospheric photodissociation of the CFCs



and some contribution from other compounds

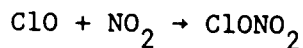


Similarly, bromine production is due to

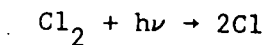


The intermediary in the chlorine catalytic cycle is ClO.

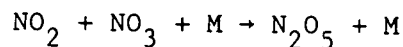
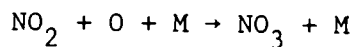
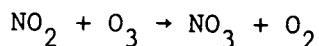
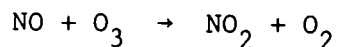
An important temporary storage reservoir for ClO and, to a certain degree, NO₂, both intermediaries of the chlorine and nitrogen cycles, is chlorine nitrate



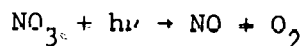
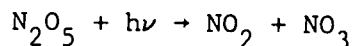
The basis of the heterogeneous reaction theory for ozone removal in the Antarctic spring is the permanent removal of odd nitrogen species and the transformation of odd chlorine reservoirs into Cl₂, a species which is easily photodissociated to produce Cl :



During the Antarctic winter low temperatures induce the formation of type I polar stratospheric clouds, removing nitric acid, one of the odd nitrogen species. This is important because photodissociation of nitric acid produces nitrogen dioxide, which can remove active chlorine from the lower stratosphere by chlorine nitrate formation. Because of the reaction sequence



the winter stratosphere at high latitudes contains large quantities of N_2O_5 . Under conditions of sunlight



reintroducing odd nitrogen into the stratosphere. Heterogeneous chemistry sticking coefficient measurements by Leu (1988); Molina et al (1987a); and Tolbert et al (1987, 1988) have demonstrated that N_2O_5 is readily lost on ice particles and is incorporated into nitric acid to form type I clouds. When the cloud particles evaporate the nitric acid is rained out of the stratosphere. These processes produce a temporary denitrification and dehydration while ice particles are present and are permanent sources of nitrogen removal. Direct confirmation of this was obtained during the NASA Antarctic aircraft campaign in 1987. Figure 6 illustrates the simultaneous measurement of water, total odd nitrogen,

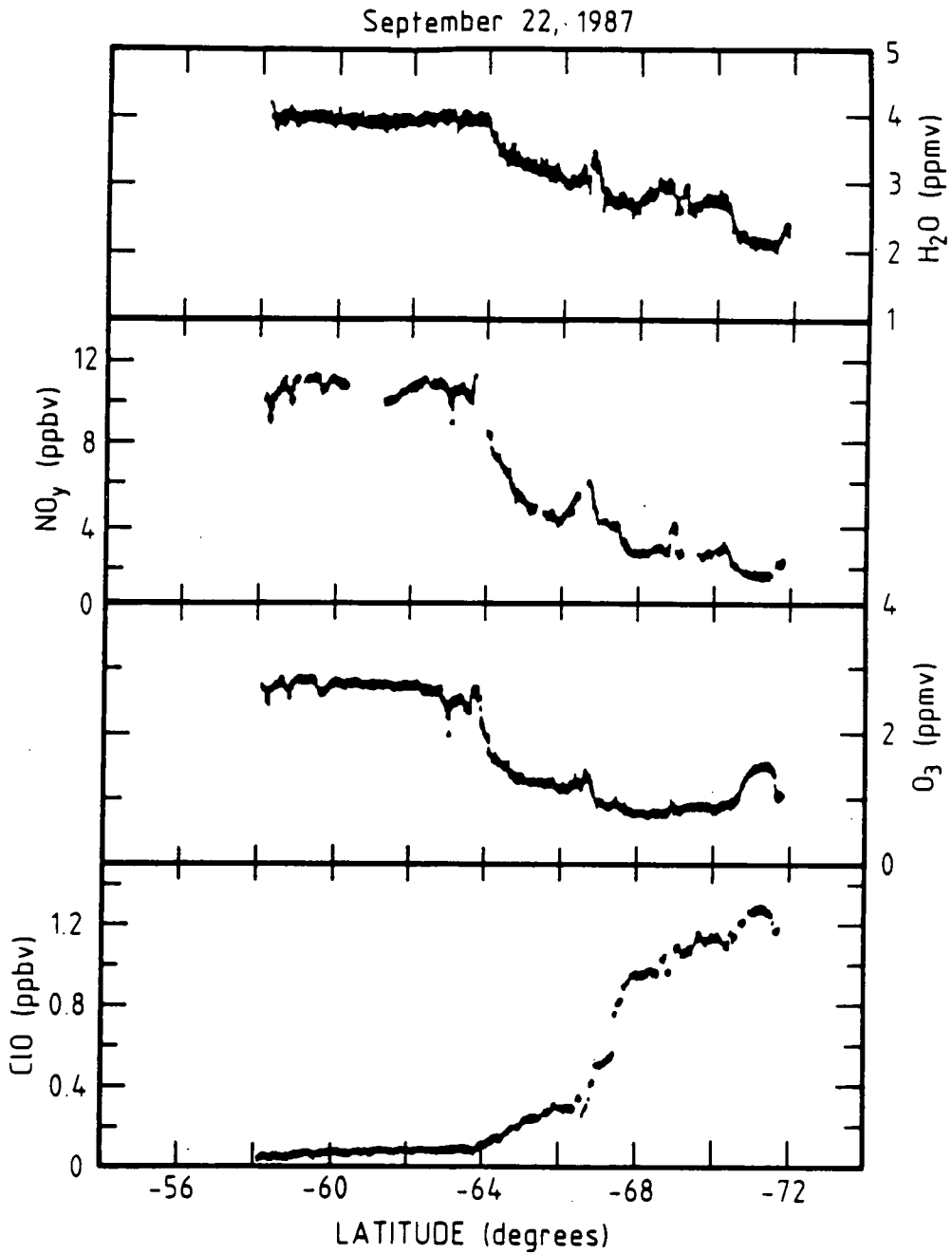
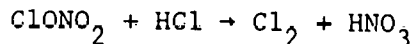


Fig. 6.- Measurements of total odd ozone nitrogen, water, ozone, and chlorine monoxide across the polar boundary. Adopted from Fahey et al (1989).

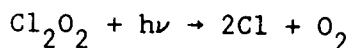
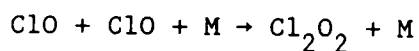
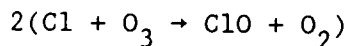
ozone, and ClO as a function of latitude on a constant potential temperature surface. Beginning at 64°S there is a chemically perturbed region where NO_y drops, ozone and water decrease, and the amount of ClO rises (Kelly et al, 1989). Inside this chemically perturbed region, which roughly coincides with the boundary of the polar vortex, the odd nitrogen content is 4 ppb compared to 6 to 12 ppb outside the boundary. The definition of total odd nitrogen is (Fahey et al, 1989)

$$\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HNO}_3 + 2(\text{N}_2\text{O}_5) + \text{HO}_2\text{NO}_2 + \text{ClONO}_2 + \text{aerosol nitrate}$$

Chlorine is removed in the presence of PSCs by reactions within the cloud particle of the form



With the evaporation of the cloud particles Cl_2 is given off and HNO_3 removed by rainout. Photodissociation of Cl_2 produces two chlorine atoms, which interact with ozone. The resulting ClO concentration is large enough that ClO has a significant loss by self reaction to form Cl_2O_2 (Molina et al, 1987b). The entire sequence is



This sequence occurs because of the large amount of ClO that is produced by the reaction of Cl and O_3 . Remember that the 6 ppb of HCl originally present has now been converted to Cl_2 . There are several uncertainties in this reaction sequence, mainly in the exact form of the compound produced by the ClO recombination and in the products of the photodissociation. The entire sequence of events is summarized schematically in Figure 7 (Aikin, 1989).

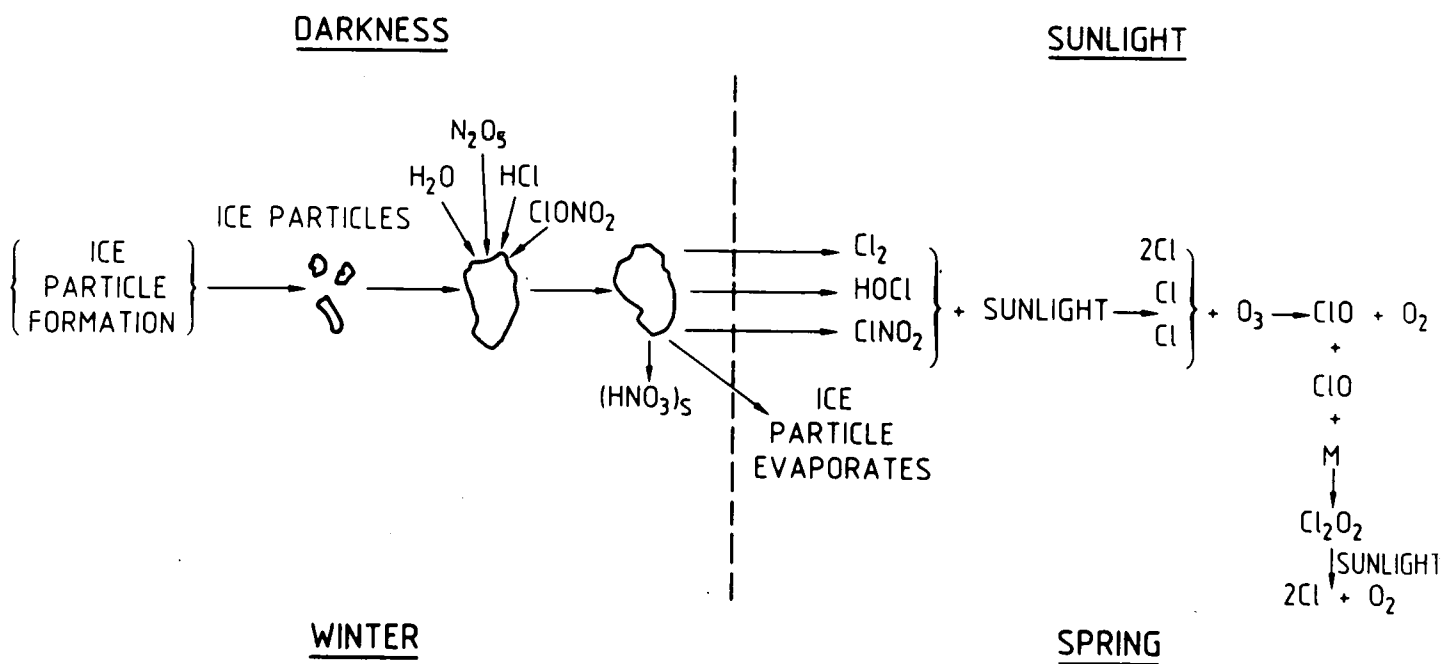


Fig. 7.- A schematic of the sequence of events leading to polar ozone destruction. Adopted from Aikin (1989).

The most dramatic support for this theory is given by the measurement of ClO and O₃ as a function of latitude during an aircraft mission. Figure 8 shows results from a flight on the ER-2 aircraft covering the latitude range 62°S to 72°S on a 450°K isentropic surface for September 1987 (Anderson et al, 1989a). Note the sudden rise in ClO beginning at 68°S, where ClO rises from about 50 ppt at 68°S to 600-650 ppt at 72°S. There is a corresponding drop in O₃ from 2000 ppb at 68°S to 900 ppb at 71°S. In addition, the theory accounts for the observed temporal behavior in total ozone. Nitrogen compounds are depleted, although the evidence is much less dramatic than the observation of ClO.

The changes in column amounts which occur in crossing the boundary from into the vortex are illustrated in Figure 9 (G.C. Toon et al, 1989).

A SIMPLIFIED DESCRIPTION OF THE BEHAVIOR OF ANTARCTIC OZONE IN THE WINTER AND SPRING

Based on the theory and observations presented so far, the ozone hole can be described as follows :

- The effect began in 1979 with the rise in atmospheric chlorine. There was no detectable ozone depletion prior to 1979.
- Ozone depletion is confined within the area defined by the polar vortex. There is no depletion outside this region, although ozone-poor air can be transported to lower latitudes when the vortex disintegrates in the spring.
- The depletion of ozone is confined to the altitude region where polar stratospheric clouds are found. There is no depletion above the clouds.
- Formation of polar clouds of type I and type II leads to the denitrification and dehydration of the lower stratosphere.

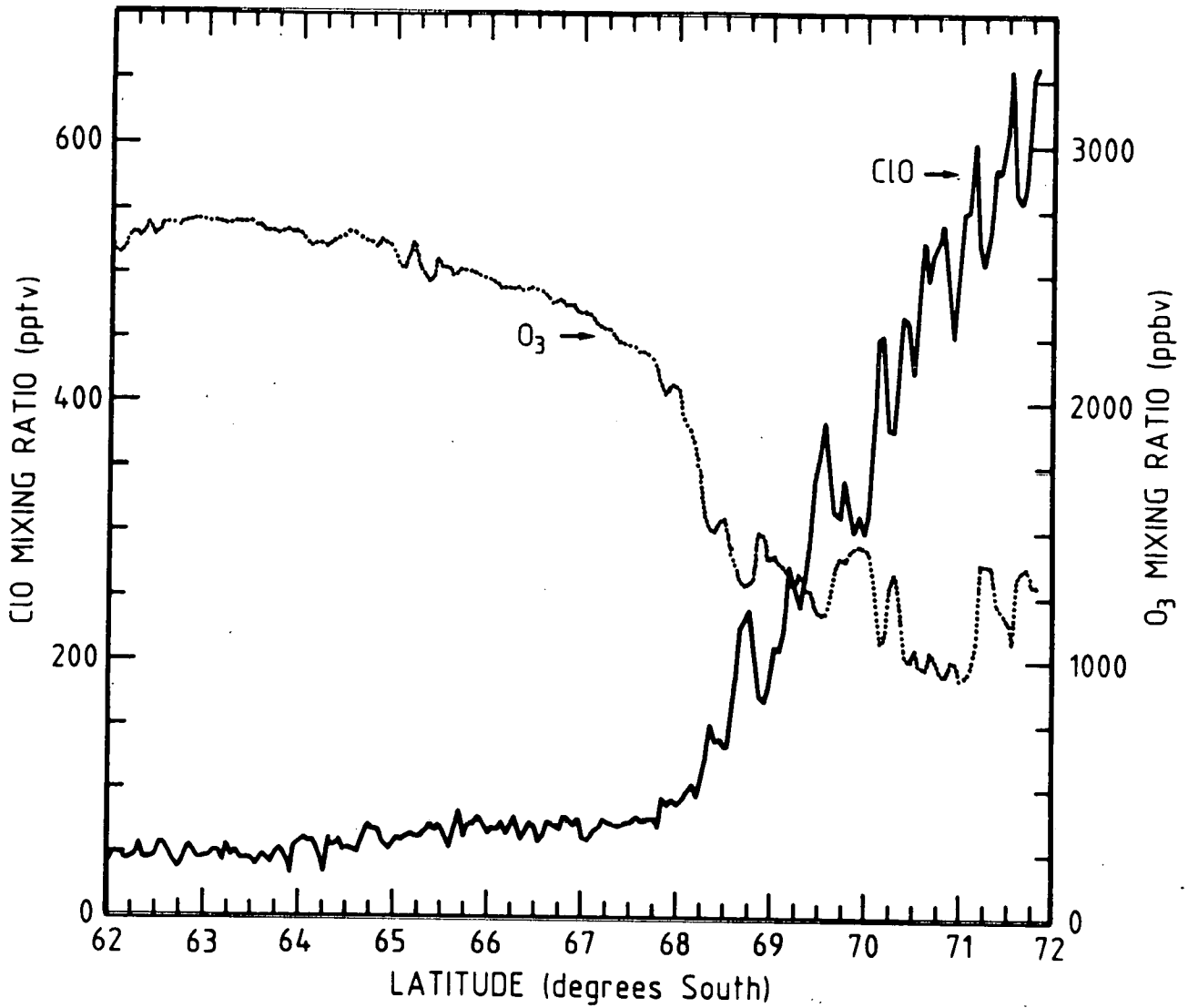


Fig. 8.- Measurements of ozone and ClO during the Antarctic aircraft campaign. Adopted from Anderson et al (1989a).

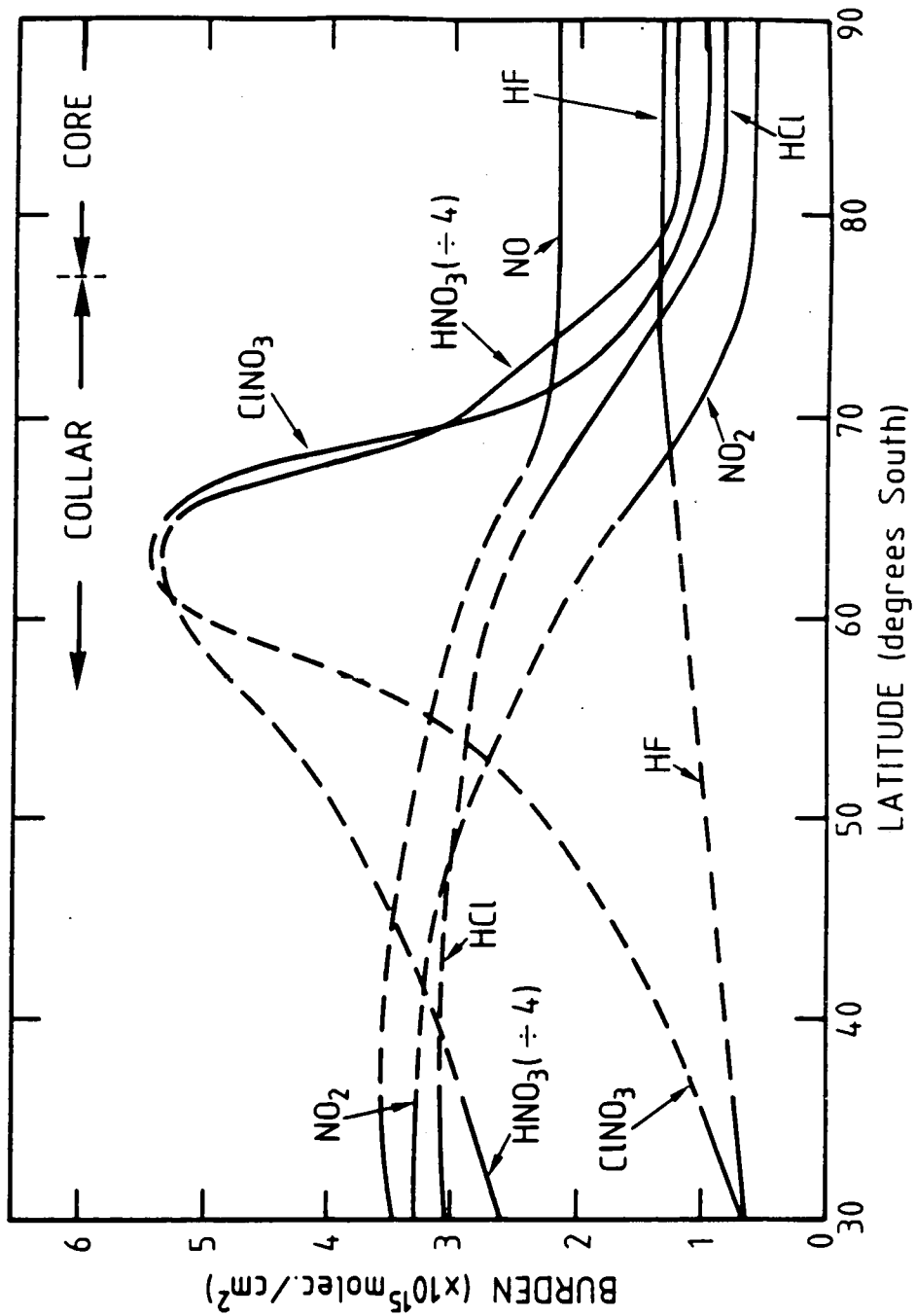


Fig. 9.- Summary of constituent measurements across the polar vortex boundary. Adopted from G.C. Toon et al (1989).

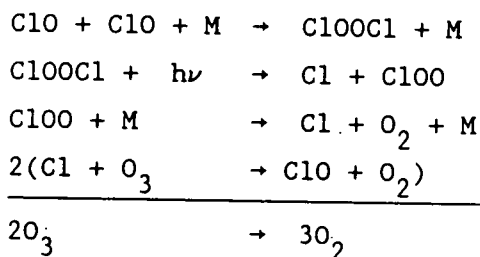
- Heterogeneous reactions with cloud particles remove ClONO_2 and HCl converting these species to Cl_2 and HNO_3 . The Cl_2 is released in the spring as a gas and HNO_3 is rained out.
- Ozone depletion begins in the spring with the release and photo-dissociation of Cl_2 when the sun returns. There is no decrease in O_3 prior to this time.

EVIDENCE THAT THE SITUATION IS MORE COMPLICATED THAN DESCRIBED BY THE THEORY

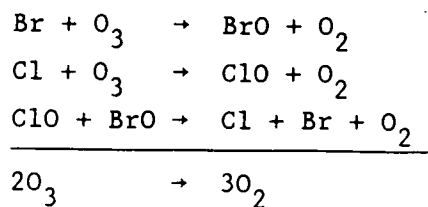
I. The quantitative evaluation of the heterogeneous reaction scheme within the cloud region

The sequence of reactions, which occur when Cl is released into the lower stratosphere, consists of more catalytic cycles than indicated thus far. In fact, the odd hydrogen cycle is not entirely absent, as might be implied by the dehydrated nature of the stratosphere in the vicinity of the clouds. Bromine reactions must be included and methane is destroyed by Cl , producing an additional source of odd hydrogen. In fact, BrO has been detected within the ozone depletion region (Brune et al, 1989).

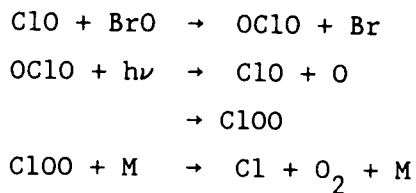
The primary cycle is ClO reacting with itself. This proceeds as



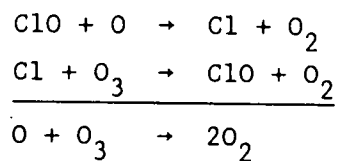
McElroy et al (1986) suggested that bromine may be important



Alternatively

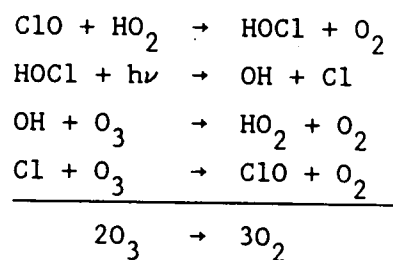


The compound OClO has been observed by monitoring microwave emission as well as absorption in the visible part of the solar spectrum (Sanders et al, 1989). Of course the reaction sequence which governs the destruction of chlorine in the upper stratosphere

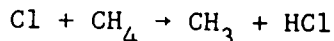


will not be effective owing to the absence of atomic oxygen in the lower stratosphere.

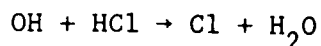
Odd hydrogen is important in the destruction of ClO by the sequence



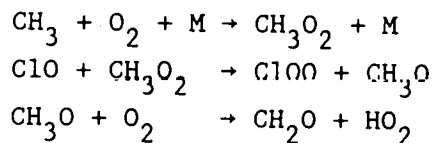
Crutzen et al (1988) suggested that since methane is not depleted in the Antarctic and has nearly equal concentrations in both hemispheres, 1.6 ppm, that methane would both produce HCl by the reaction



and destroy it by enhancing OH, leading to



where OH is a byproduct of the methane oxidation cycle. Additionally, ClO can interact in the cycle



The inclusion of all these cycles in a calculation of the observed ozone depletion and other observed trace species including ClO has been carried out for the AAOE aircraft data set (Anderson et al, 1989a). Results of the calculation show that using all the proposed cycles, the heterogeneous chemistry can account for only between 50% (Anderson et al, 1989b; Ko et al, 1989) and 65% (Salawitch et al, 1989) of the observed depletion. This leaves 50% to be accounted for either by additional mechanisms or by a modification of the cloud particle heterogeneous reaction theory.

Reevaluation of ClO measurements has resulted in greater mixing ratios for this species (Brune et al, 1990). This has the result of minimizing the magnitude of any additional mechanisms for ozone loss. Uncertainties in ozone amount further complicate the situation so there may still be the requirement for additional mechanisms (Salawitch et al, 1990; Yung et al, 1990). However, Brune et al (1990) report that to

the level of uncertainties of the various measured parameters there is agreement between theory and experiment with no additional mechanism required.

II. Early evidence of the ozone polar vortex relationship

Examination of the total ozone data displayed in Figure 2 shows that in October 1979 the total ozone displayed the characteristic pattern with less ozone at the pole than at 55°S. The total ozone at 75°S was 300 DU more than twice the amount currently observed in October. Nevertheless, there is less ozone toward the pole. Figure 10 presents the results of an analysis performed for the first ten days of October 1970, using data from the BUUV ozone instrument on Nimbus 4. The ozone amounts are color coded in the figure, with light yellow representing the least amount of ozone, 250 DU, and light blue the largest amount, 550 DU. The characteristic shape associated with the vortex is displayed in this figure, indicating that the vortex influenced the ozone distribution even at this early date. Comparison with the total ozone amounts in Figure 1 shows that for Halley Bay amounts are within 25 DU of each other.

The vortex has had an effect on stratospheric ozone since 1970. If Dobson's original observations are included as indicators that the vortex influences the southern polar distribution, then there has most likely always been an effect. The cause is uncertain, but temperature is an important parameter. The task is to separate the effects of chemistry, temperature, and ozone redistribution by dynamics. Presumably, both type I and type II clouds were formed in this period, thus the atmosphere is dehydrated and denitrified. Presumably, this depletion is the result of the chlorine present in the stratosphere in 1970. This consisted of 600 ppt of CH_3Cl , which is a naturally occurring compound of nearly constant amount. In addition there would be the contribution from the CFCs already present in the atmosphere in 1970. If another chemical mechanism was involved, what is its identity and does it operate today ?



TOTAL OZONE OCT 1-11,70

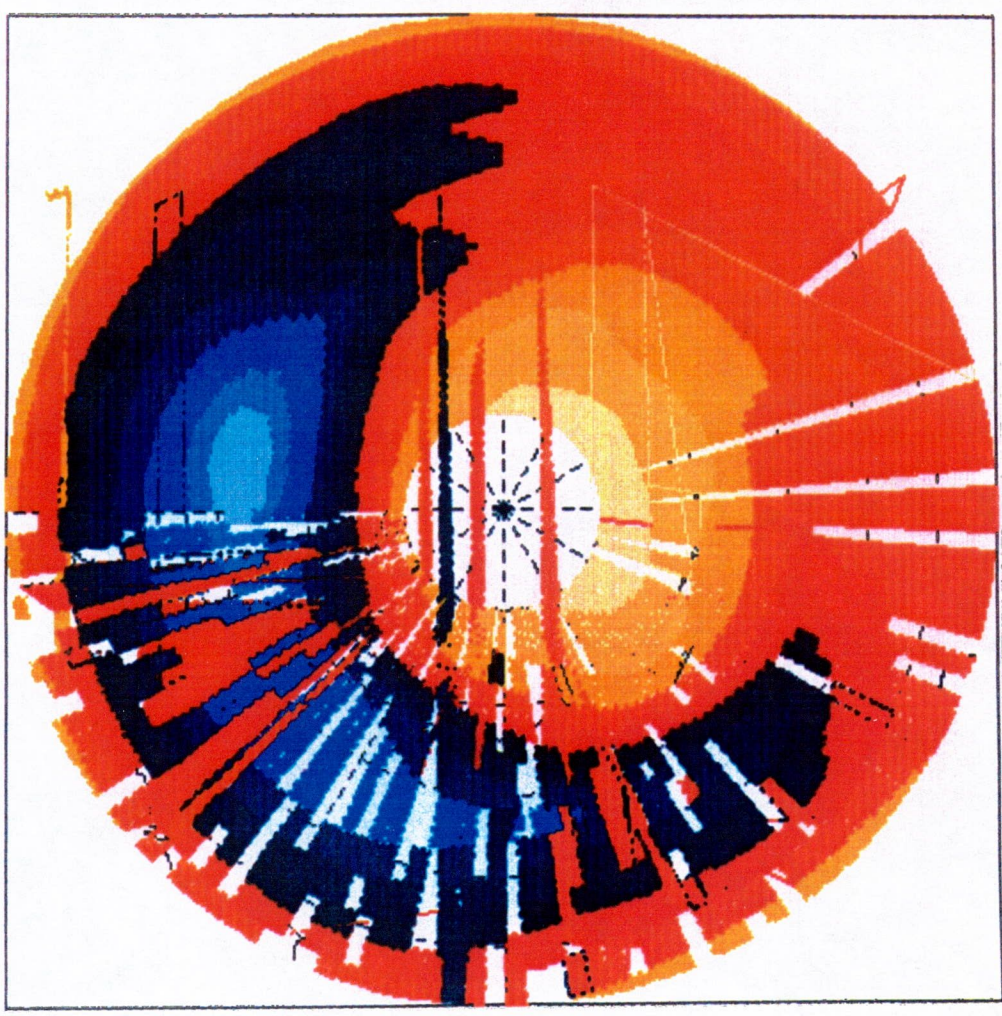


Fig. 10.- The total ozone distribution 1-11 October, 1970. Data is shown on a polar plot and colors indicate the ozone amounts.

III. Ozone reduction above the cloud level

The SBUV data on Nimbus 7 can be used to obtain an altitude profile of the ozone hole in contrast to TOMS, which only measures the total column amount. The stratosphere is divided into four levels as shown in Table I. The lowest level encompasses the 250 to 30 mb pressure level, which is equivalent to 10 to 24 km and encompasses Umkehr layers 2, 3, and 4. The top level corresponds to 0.5 - 2 mb or 43-53 km for Umkehr layers 9 and 10.

Ozone at different levels is presented as the ratio of the ozone value at a particular location and altitude to the area-weighted ozone amount for the particular level. The results are plotted as maps at each level. Figure 11 shows such a map expressed as a south polar to 30°S for the period 1-11 October, 1987. Zero degrees longitude is to the right in each map, which places McMurdo at eight-thirty and Halley Bay at two o'clock. Because of the orbital inclination of Nimbus 7 and the nadir-viewing geometry of the SBUV instrument, there is no information south of 80°S.

The maps show that in addition to the large decrease at low altitudes there is no ozone loss throughout the stratosphere within the vortex. Similar maps for the year 1986 were presented by Aikin and McPeters (1988). Earlier evidence of such high-altitude depletion was presented by Aikin and McPeters (1986), McCormick and Larsen (1986), and more recently, also in map form, by McCormick et al (1989b). The depletion is not uniform with increasing altitude. Therefore a particular location will observe a larger range of altitudes where ozone differences are observed than other sites. This can lead to the mistaken conclusion that ozone change is confined to the altitude region of the polar stratospheric clouds.

TABLE I : Ozone layer structure (altitude based on standard atmosphere).

Umkehr Layers	Pressure (mb)	Altitude (km)
9-10	0.5-2	43-53
7-8	2-8	33-43
5-6	8-30	24-33
2-3-4	30-250	10-24

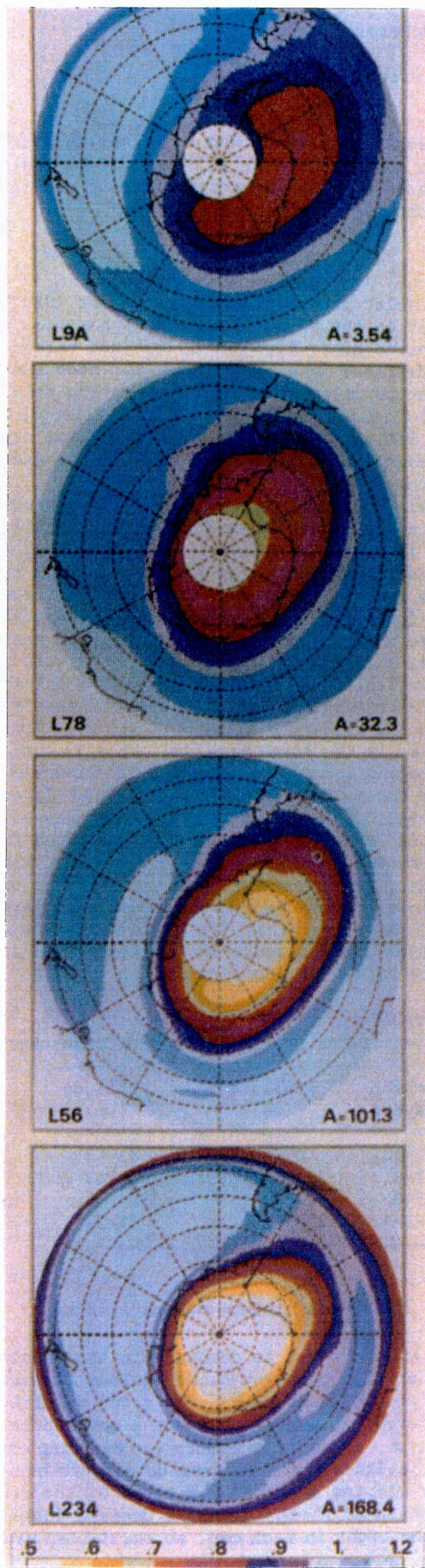


Fig. 11. - Ozone amounts at different levels in the stratosphere for the period 1-11 October 1987. The ozone amounts at the four levels of Table I are plotted on a polar plot as in Figure 10. Amounts are color coded. Adopted from Aikin and McPeters (1988).

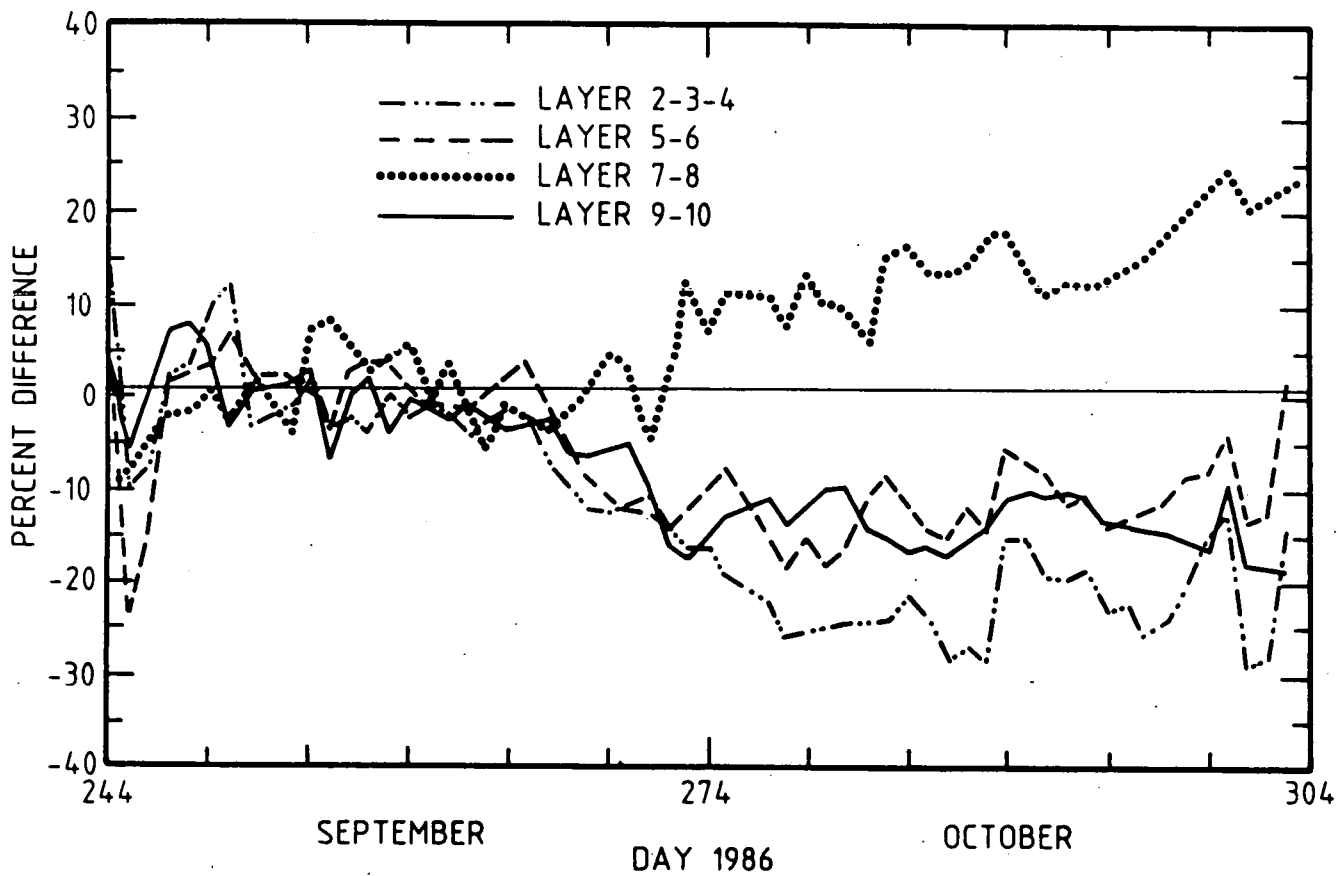
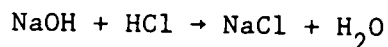


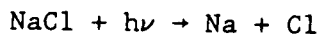
Fig. 12.- Time dependence of ozone at different Umkehr levels for the location of the ozone minimum. Adopted from Aikin and McPeters (1986).

The temporal behavior is of great interest, since it gives important clues on the mechanisms responsible for the ozone behavior. Figure 12 shows the time dependent change of ozone at the location of the ozone minimum (Aikin and McPeters, 1986). The percent difference from early September is plotted against Julian day number for the period September and October 1986. Each of the four levels is shown. With the exception of layer 7-8, corresponding to 33-43 km in the mid-stratosphere, all levels have a characteristic behavior, which consists of little change until late September. After this, ozone declines to a minimum in mid-October. If the time behavior for November had been plotted, a general rise would be seen. This rise is characteristic of the lowering solar zenith angle in late spring.

The increase in ozone in the middle stratosphere may indicate a temperature rise or a partial breakdown of the vortex at this level. The fact that other levels behave like the cloud level may imply a storage mechanism for ozone-destroying species, which does not involve heterogeneous cloud chemistry but nevertheless makes use of a species stored during the course of the polar night. One possibility, suggested by Aikin and McPeters (1986), involves the use of incoming meteoric material to convert HCl, the chlorine reservoir, to an easily photo-dissociated form such as NaCl through reactions of the type

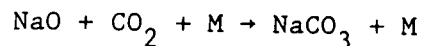


Meteoric material would act to deplete HCl in the upper stratosphere. Other salts are possible, including calcium chloride and magnesium chloride. Photodissociation frees chlorine



and allows Na to recycle, converting more HCl to free chlorine. Finlayson-Pitts et al (1989) showed laboratory data for a high rate of reaction between NaCl in particulate form and gaseous N_2O_5 and HCl.

There are numerous uncertainties associated with this mechanism. Laboratory studies have shown that the formation of sodium carbonate is easily accomplished by the reaction



(Ager and Howard, 1987); it is not known whether this product in the gas phase will react with HCl. Although observations of meteoric species in gas phase have been made for many years, the question of the amount of meteoric material in gas phase relative to the amount in particles is still unresolved, particularly at stratospheric heights. However, the laboratory data indicate that reactions on particulates are fast.

IV. Ozone reduction outside the vortex and during winter

Several results have indicated that ozone reduction may not be confined to the polar vortex and may occur sooner in the winter than indicated by the satellite data or predicted by the heterogeneous reaction theory. Both Chubachi (1984) and Fiocco et al (1989) have reported that during winter ozone declines. Two different techniques have been utilized to arrive at this result. Chubachi employed absorption of moonlight, while lidar was the technique utilized in the Fiocco observations. Proffitt et al (1989) have utilized an airborne instrument to measure ozone in the lower stratosphere between 45° and 75°S latitude. Placing all data on an isentropic surface and performing other corrections shows that ozone is as much as 6% less than normal from 55°S to the edge of the vortex. Since this region is outside the vortex and therefore free of clouds, it is necessary that another mechanism be found to explain the observations.

V. The role of nitrogen oxides at high altitudes

Ionization and subsequent ion-molecule reactions lead to the production of nitric oxide. There can be a variety of sources, including

solar x-rays, which produce large quantities of thermospheric nitric oxide (Nicolet, 1965) and galactic cosmic radiation (Nicolet, 1975) in the stratosphere. One of the largest sources is the ionization resulting from the precipitation of electrons and protons that produces the aurora. Neither solar x-rays nor auroral particles penetrate directly into the stratosphere and galactic cosmic radiation is too small a source to be significant. While it is recognized that diffusion from the thermosphere into the mesosphere is responsible for D region nitric oxide, it is generally believed that the thermosphere is not a significant source of nitric oxide for the stratosphere. Thus the original suggestion by Callis and Natarajan (1986) that the ozone hole was caused by a solar cycle buildup of nitric oxide originating in the thermosphere has been largely rejected.

Protons from particularly large solar flares have energies of 1 to 300 Mev and sufficient flux to create a significant amount of ionization in the mesosphere and upper stratosphere (Reagan et al, 1981). Reduction in upper stratospheric ozone is predicted during such events (Crutzen et al, 1975). An accompanying nitric oxide increase is also observed (McPeters, 1986). However, there are few flares large enough to produce large proton fluxes. Hence this source cannot be considered as a useful candidate on a continuing basis.

Recently it has been noted that the fluxes of high energy electrons, $E > 1$ Mev, within the radiation belts vary considerably, indicating precipitation (Baker et al, 1987; Nagai, 1988). The fluxes are significant and are correlated with the magnetic K_p index, i.e., large increases in K_p result in precipitation of electrons from the belt. Figure 13 shows the measured flux as a function of time together with a K_p dependent model (Nagai, 1988). Direct evidence of the effect of such precipitation on the atmosphere has been lacking. Using the partial reflection technique, von Biel (1989) has detected numerous

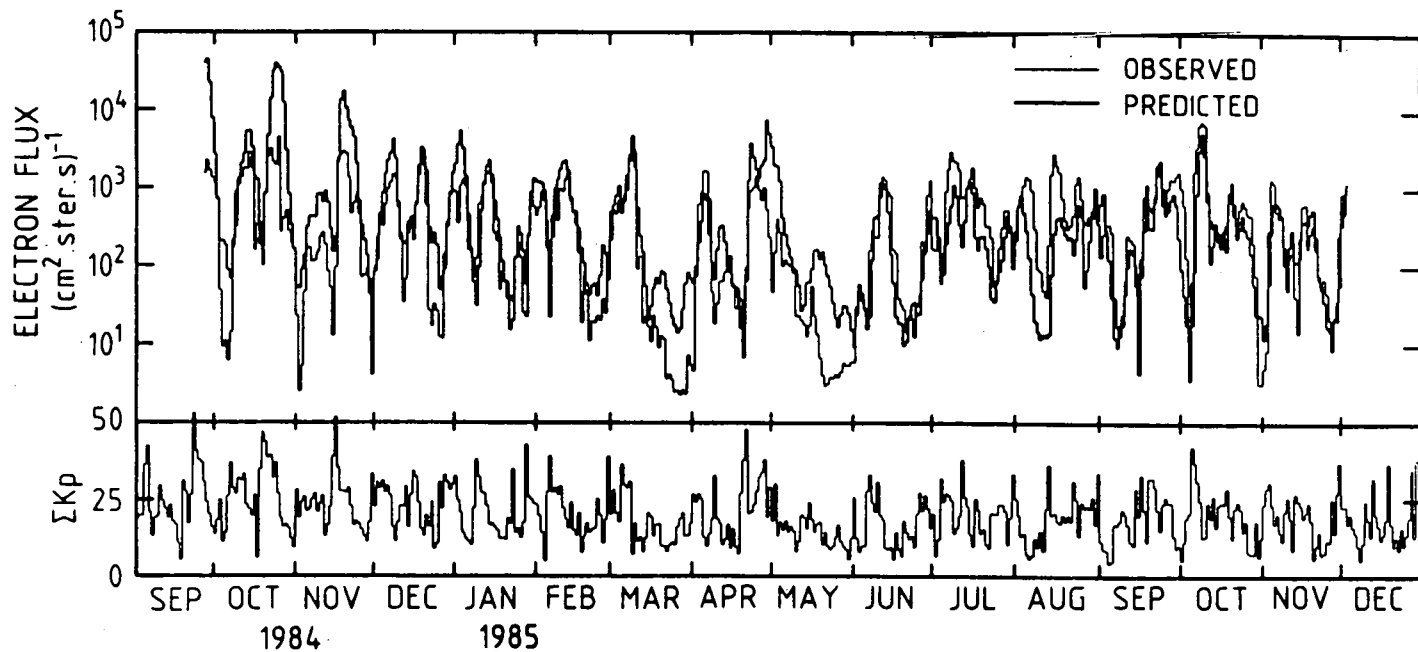


Fig. 13.- Variation of energetic electron fluxes as a function of time.
 Adopted from Nagai (1988).

events during all seasons when the electron density is significantly enhanced at altitudes as low as 40 km above Scott Base in Antarctica, 90°S. Sample profiles are shown in Figure 14. Due to the formation of negative ions, very few electrons normally exist at these low altitudes. In order to maintain such densities an extraordinary amount of electron precipitation must be present. Figure 15 gives the amount required based on an assumed equilibrium between production and loss for positive ions, electrons, and negative ions. The relationships employed are

$$N_+ = N_- + N_e = N_e (1 + \lambda)$$

$$\lambda = N_- / N_e = a(O_2)^2 / d$$

$$q = N_e^2 ((H\lambda)(\alpha_D + \lambda\alpha_i))$$

The symbols have the following meanings :

- a attachment coefficient of electrons to O_2
- d detachment coefficient of electrons from negative ions
- α_D dissociative recombination coefficient
- α_i positive ion negative ion recombination coefficient
- q ion pair production function
- N_- negative ion density
- N_e electron density
- N_+ positive ion density

For comparison purposes the ion pair production function for other high-latitude sources is also presented. Auroral electrons have their peak ionization above 90 km and have almost no effect below 70 km. The polar cap absorption event (PCA) is due to solar protons. One of the largest events occurred on 12 November 1972. A peak ion pair production of $5 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ occurred between 35 and 40 km. The effect of this event was observed on high-latitude ozone data (Heath et al, 1977; McPeters et al, 1981). High-energy electrons are estimated to have a flux of

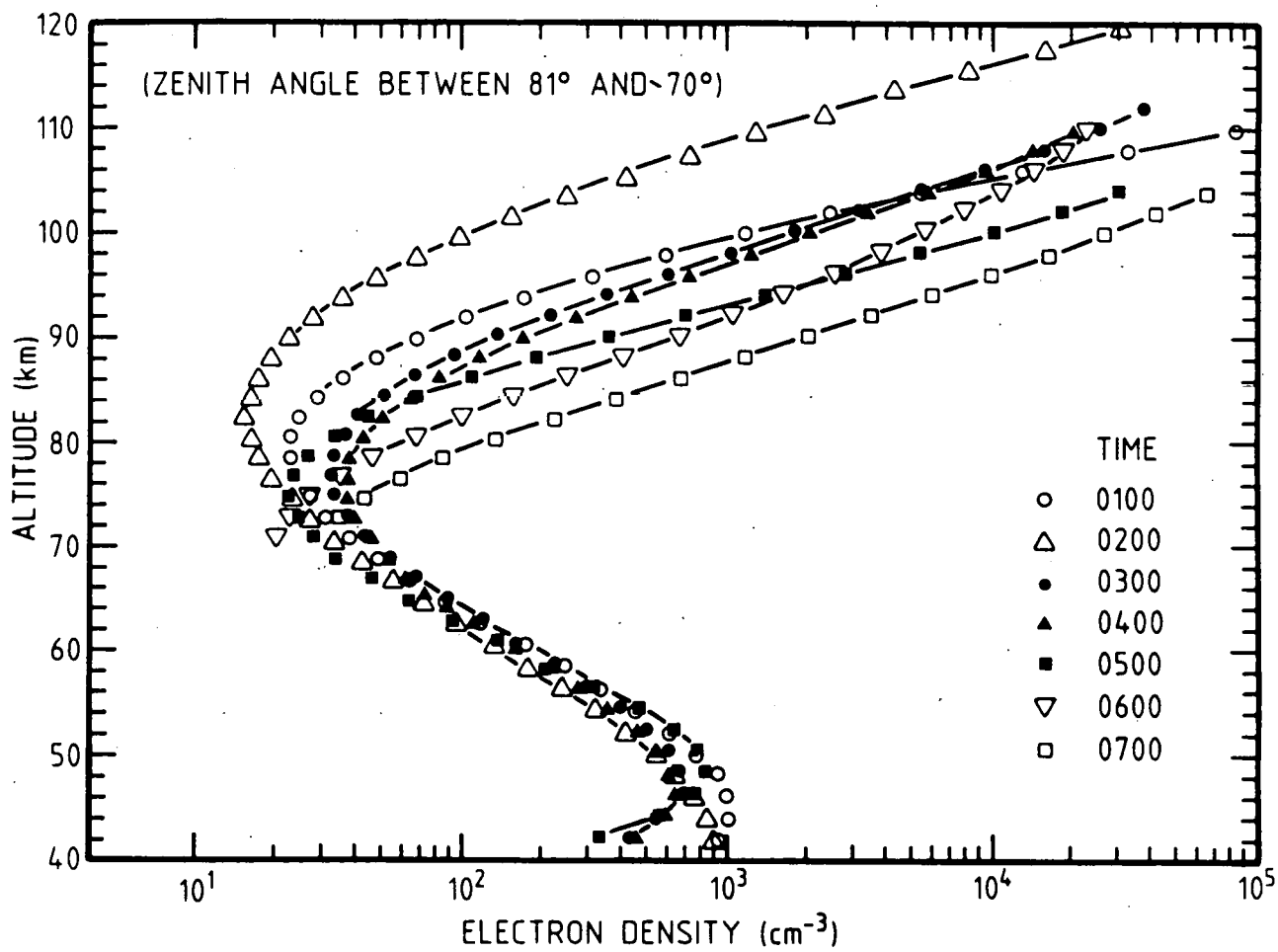


Fig. 14.- Electron density profiles as measured at Scott Base, Antarctica. Adopted from von Biel (1989).

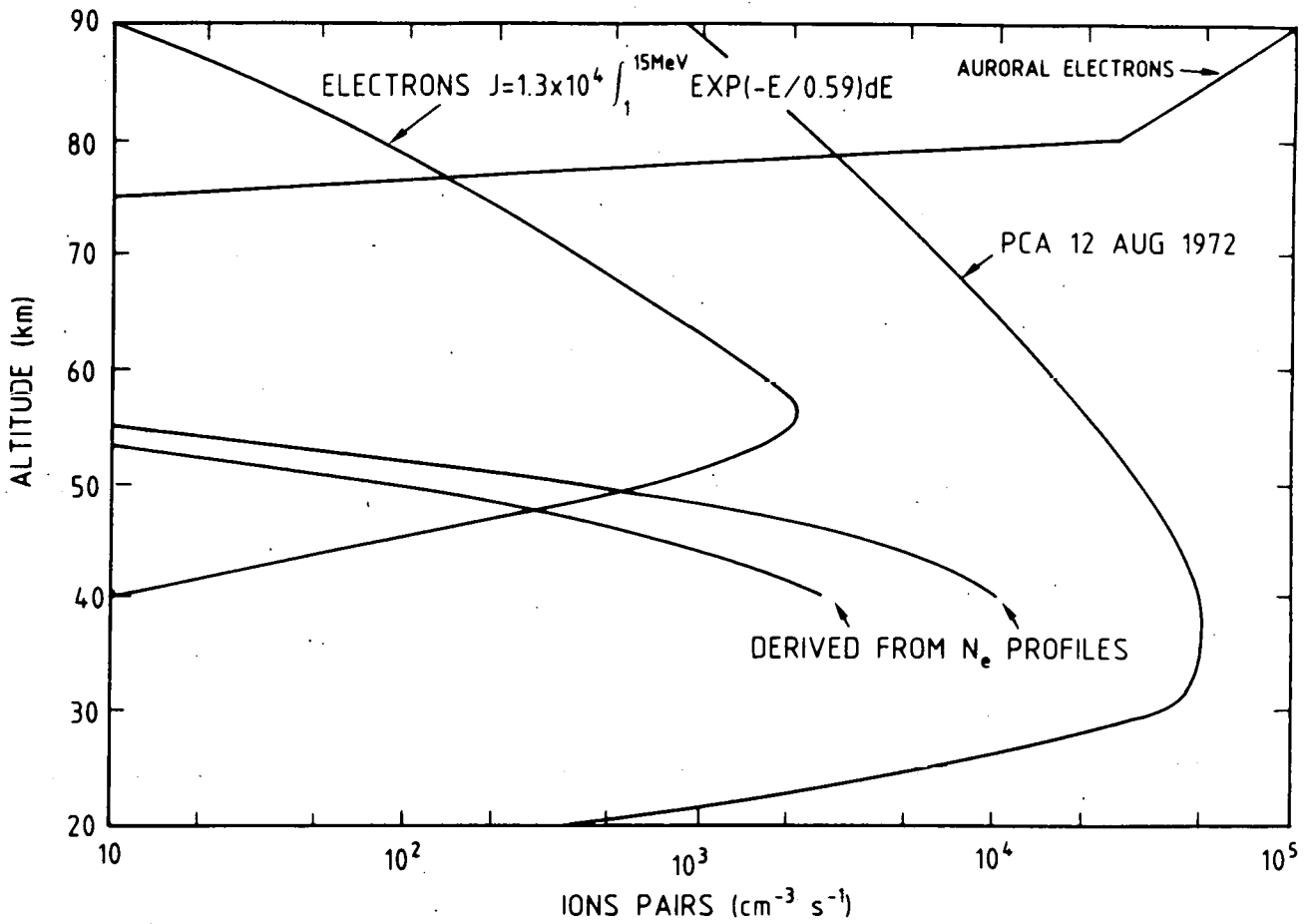


Fig. 15.- Ion pair production functions for different classes of events, including observed electron density enhancements.

$$J = 1.3 \times 10^4 \int_1^{15\text{Mev}} \exp(-E / 10.59) dE \text{ cm}^{-2} \text{ s}^{-1}$$

(Baker et al, 1987). This results in a peak ion pair production of about $2 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ centered between 55 and 60 km. At 40 km the ion pair production function is $10 \text{ cm}^{-3} \text{ s}^{-1}$ and because of bremsstrahlung this same value applies at altitudes as low as 25 km. The q values derived from the electron density profiles have a value of $10^5 \text{ cm}^{-3} \text{ s}^{-1}$ at 40 km. This exceeds the PCA peak by a factor of 2, so that such events should be detectable in the SBUV data set. Such a correlation study is in progress. No information on the ion pair production is available below 40 km.

The frequency of such events as recorded with the partial reflection sounder is quite large. During the period November 1983 to January 1986, some months had frequency of occurrence rates as high as 26%. The period November 1983 to July 1984 showed more than 15% for all months. The frequency of occurrence is lowest in the winter and spring months, usually less than 5%.

It is possible that these electron density enhancements represent the result of high-energy electron precipitation. However, the connection has not yet been established. The net effect of such events on the stratospheric odd nitrogen concentration is also unknown. It appears that at certain times there should be enhanced odd nitrogen and reduced ozone.

Direct evidence of odd nitrogen enhancement in the polar atmosphere below 50 km at times other than during SPEs is sketchy. Callis and Natarajan (1986) reported doubling in the NO_2 amount between 1979 and 1984, but there is some problem of intercalibration between instruments on the SAGE spacecraft from which the measurements were conducted. The AAOE campaign reported no enhanced odd nitrogen and, in

fact, a denitrified atmosphere. Ground-based measurements of column NO_2 show a doubling in column amounts during the spring from days 250 to 280. This is just the period when the ozone is showing its largest decrease. McElroy et al (1988) modeled the NO_2 column for the winter and spring under the assumption of no input odd nitrogen flux and a fixed lower limit, which would be set by denitrification.

Because of the large reaction rate between N_2O_5 and cloud particles it is difficult to imagine odd nitrogen as being significant in ozone depletion at the cloud level. It may be involved at higher altitudes. The relativistic electron effects need to be investigated in this regard.

ARCTIC OZONE BEHAVIOR

The continent-wide ozone hole observed in the Antarctic has never been detected in the Arctic. Meteorological differences between the Arctic and Antarctic may be the largest contributing factor, but there are important chemical differences. The Arctic polar vortex is neither as stable nor as intense as the Antarctic vortex. Although temperatures are slightly higher, PSCs are present (Browell, 1989). Enhanced ClO is observed, but not as consistently as it is observed in the Antarctic (Brune et al, 1988, 1989).

During the NASA Arctic mission of 1989 (AASW), no direct measurement was made of ozone loss. However, several estimates of the rate of ozone loss have been made. Schoeberl et al. (1990) used measured N_2O , O_2 and H_2O data to estimate that a descent velocity of 0.1 cm/s existed inside the vortex and that ozone was being lost at the rate of 0.4% per day. A loss rate of 1%/day is calculated by McKenna et al. (1989) on the basis of ClO measurements and a photochemical model including heterogeneous chemistry. Salawitch et al. (1990) estimate 0.3% per day. The total estimated loss is 12% of the total ozone over a

40-day period. For loss due to heterogeneous reactions ClO-ClO chemistry accounts for 75%, with the remainder being divided between ClO-BrO and HO_x. In the case of HO_x loss may be greater than 10%.

Reevaluation of ClO measurements taken during the Antarctic ozone campaign shows that ClO was underestimated by 50% (Brune et al., 1989, 1990). This leads to much better agreement between calculated and observed ozone loss. Measurements and theory are now within 25%. For both the Arctic and Antarctic, O₃ loss due to Cl reactions is estimated to be 75%, with 10% due to HO_x and the remainder to the effects of bromine.

MINIHOLES INDICATING RAPID OZONE DEPLETION

On several occasions the TOMS instrument detected areas of 10^6 km² or less, where total ozone decreased by 60% during 24 to 48 hours. These regions are termed "miniholes". They are extremely intriguing because they cannot be explained in the conventional way with the heterogeneous chemistry acting on a single air parcel. The holes do not move around the south pole with the velocity of normal air parcels. Instead, they are nearly stationary regions, which meander and gradually merge with one another (Krueger, 1988, 1989). They are associated with the appearance of high-altitude clouds. Two explanations for the origin of these clouds have been put forward. Both involve the intrusion of low-ozone tropospheric air into the stratosphere. Tropospheric anticyclones are the origin of the disturbance in one theory (McKenna et al., 1989). The movement of the tropospheric jet over the mountains of the Antarctic peninsula gives rise to vertical motion and adiabatic cooling in the second theory (Cariolle et al., 1989). In both cases, tropospheric air is raised into the lower stratosphere. This results in sufficient cooling to create stratospheric clouds.

The anticyclone remains nearly fixed in position, so that stratospheric air parcels will be processed through the region of enhanced polar stratospheric clouds. However, the combination of heterogeneous chemistry and low ozone is probably still insufficient to account for the entire depletion. Wofsy et al. (1990) suggested that falling water ice cloud particles during such events would attain a coating of nitric acid trihydrate, thereby preventing evaporation of the cloud particles and enhancing the removal of HNO_3 .

They are also observed in the northern hemisphere. A strong event was observed during early February 1990 over Scandinavia. Temperatures in the 12 to 20 km region decreased sufficiently to create water ice clouds. Ozone was observed to decrease to 160 DU, half the total amount. The decrease occurred within 24 hours. The low ozone air parcel split into two parts, one of which moved to southern Europe with 230 DU. The other drifted over the U.S.S.R. (Pommereau et al., 1990). This event occurred outside the polar vortex and was associated with an anticyclonic forcing of air from the troposphere. Of course there is a ridge of mountains along Scandinavia, which was at the edge of the event.

HYDROCARBONS IN THE ARCTIC

The presence of light molecular weight hydrocarbons in the Arctic is one other important difference between the conditions in the Antarctic and Arctic. In addition to methane, which is found with nearly equal mixing ratios over most of the globe, the northern hemisphere contains significant quantities of ethane, acetylene, and propane. The amount increases with latitude in the northern hemisphere and decreases with latitude in the southern hemisphere (Rasmussen and Khalil, 1989). A seasonal variation is observed, with larger concentrations in winter and spring. Figure 16 summarizes the latitudinal variation of ethane for each of the four seasons (Blake and Rowland, 1986). Tropospheric concentrations of ethane are between 2 and 3 ppb at high latitudes in winter and spring.

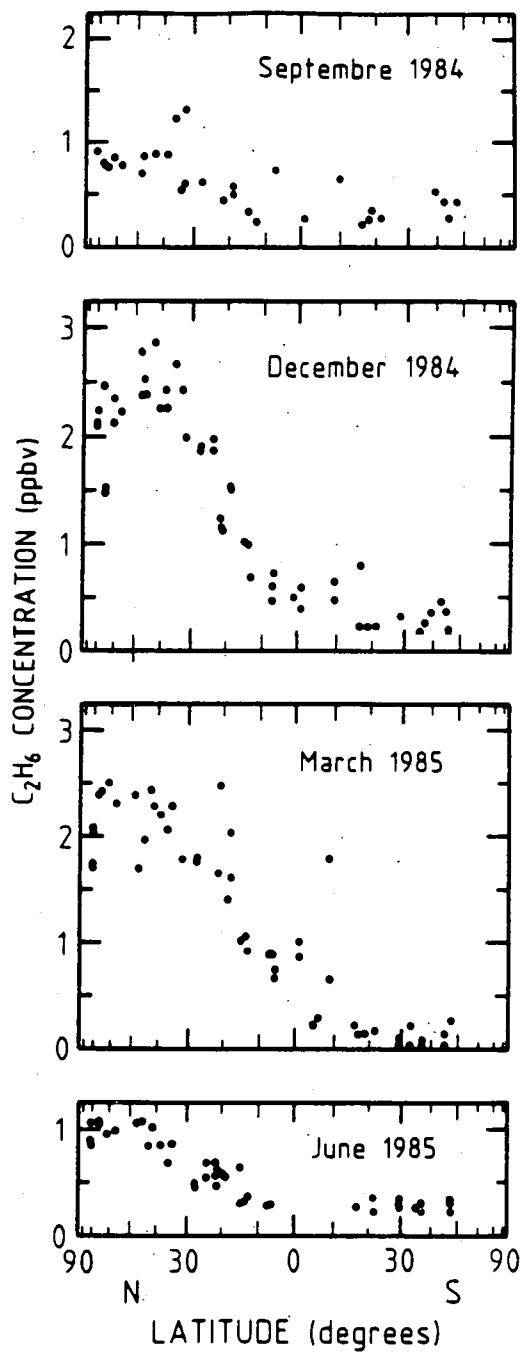
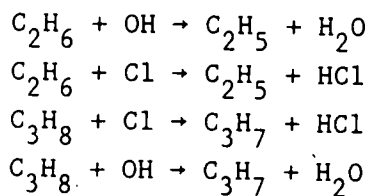
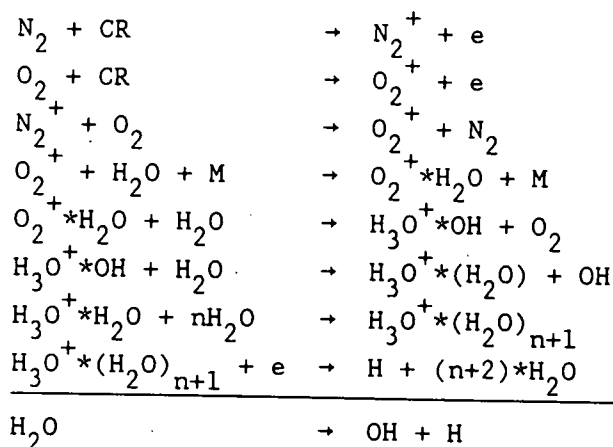


Fig. 16.- The latitudinal variation of ethane for each of the four seasons. Adopted from Blake and Rowland (1986).

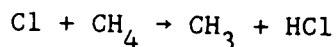
Like methane these compounds have a photochemical lifetime which is determined by their reaction with OH and Cl. The reaction rate between OH and ethane, C_2H_6 , and to a certain degree propane, C_3H_8 , is low enough to allow these species to penetrate into the stratosphere where they are destroyed by the larger concentrations of Cl and OH. The reactions for destruction are



In the winter polar atmosphere, with little or no sunlight, OH is produced by cosmic radiation through the reaction set

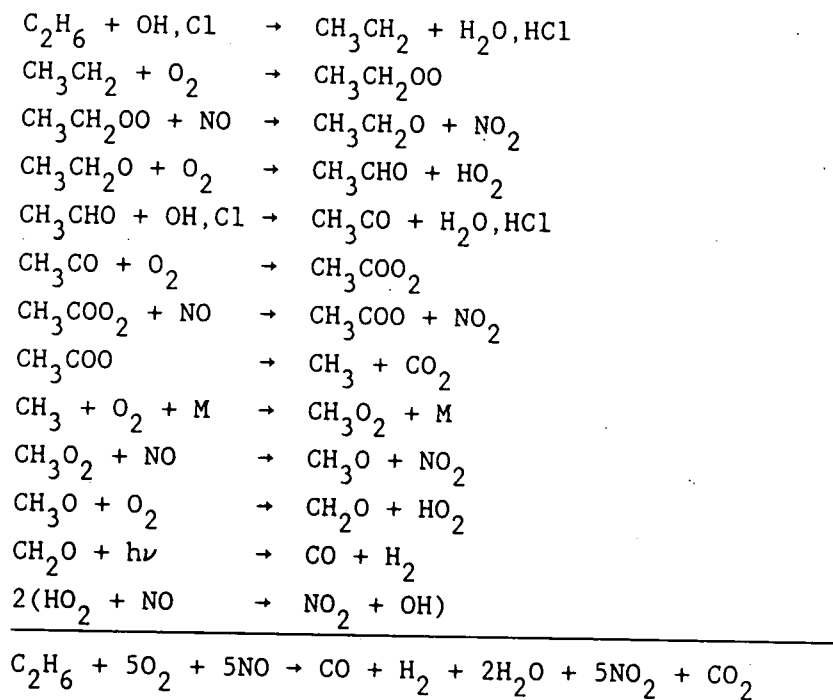


Thus at a time when the tropospheric concentrations of ethane and propane are the highest the chemical lifetimes of these compounds are extended in the stratosphere, with only cosmic radiation to produce OH, resulting in a buildup of hydrocarbons over the winter. In the spring, Cl is released by the photodissociation of heterogeneously produced Cl_2 . The impact of Cl is so large because there is no sink for Cl. The only way to remove Cl from its ozone-destroying catalytic cycle is to form HCl. In the Antarctic this is accomplished only by the reaction with methane



Ethane and propane offer another channel for the formation of the HCl reservoir molecule. Figure 17 gives the ratio of chlorine loss to the sum of hydrocarbons and methane compared to methane alone as a function of altitude. The combined loss is a factor of 10 greater at 14 km and becomes negligible above 24 km.

The situation is complicated because of the presence of the oxidation cycle for the hydrocarbons. The result of this oxidation process is to produce odd hydrogen species which can destroy ozone. However, this depends on other factors such as the action of nitrogen oxides and, in the Arctic spring, the action of chlorine compounds. In the normal atmosphere ethane is broken down by the reaction sequence (Aikin et al, 1982)



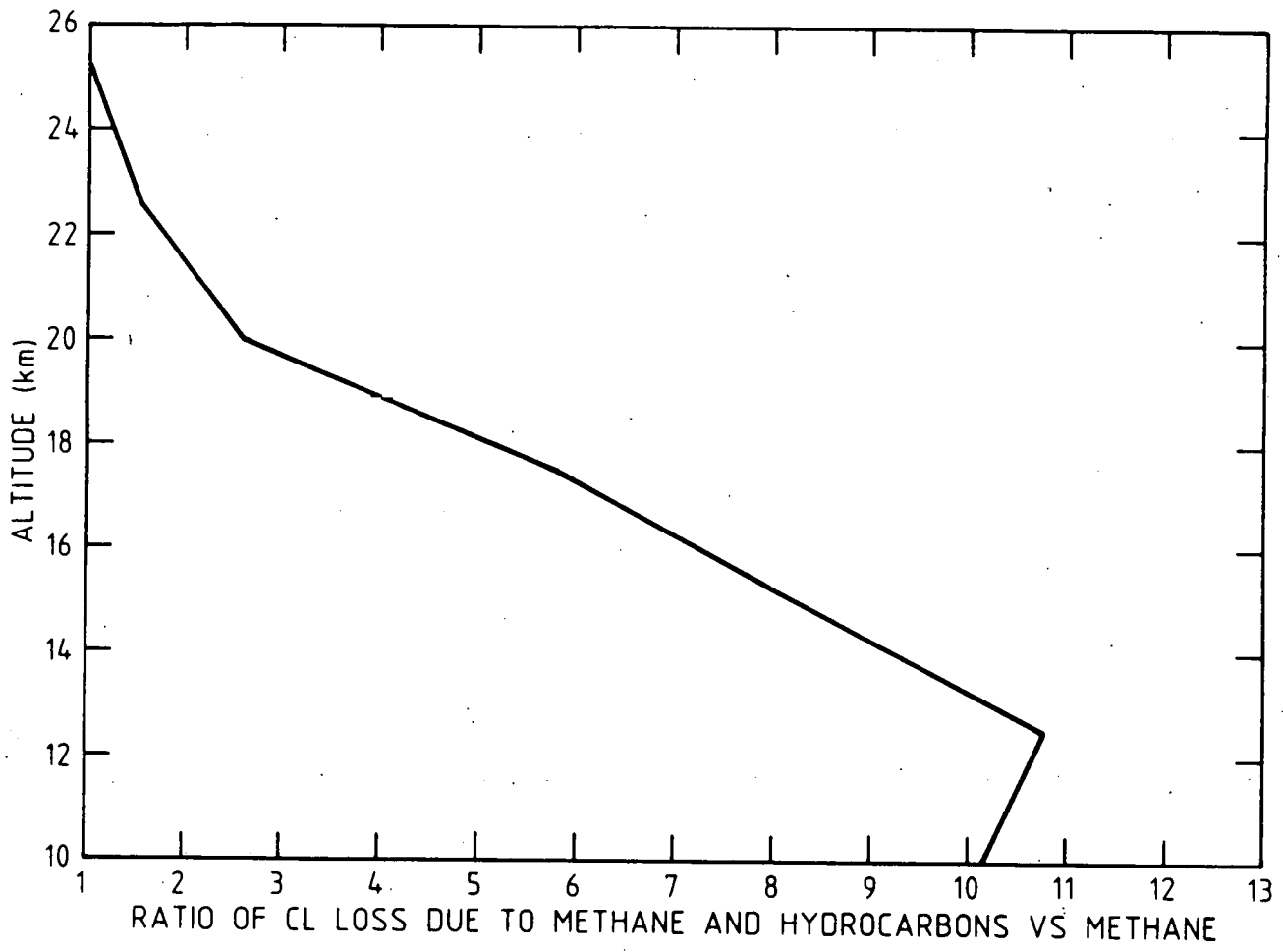
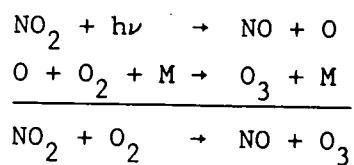
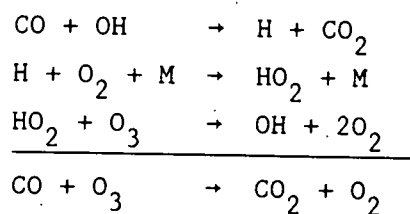


Fig. 17.- The ratio of chlorine loss when hydrocarbons are included versus methane alone.

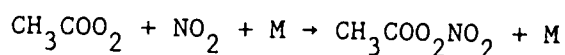
There are two competing processes affecting ozone. Nitrogen dioxide photodissociation leads to ozone formation by



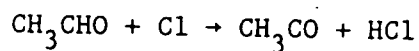
Loss of ozone can occur through



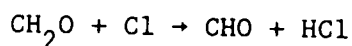
Also, with sufficient NO_2 and cold enough temperatures the cycle is interrupted by the formation of peroxyacetylnitrate, PAN, by the reaction



The rate of thermal dissociation of this compound is directly proportional to temperature. There is also the possibility of PAN destruction by OH and Cl, so that PAN is another avenue for removing Cl from the atmosphere. PAN has been observed in the spring Arctic stratosphere in varying amounts from 60 to 130 ppt (Bottenheim and Gallant, 1989). In addition to OH destruction of acetylhyde, CH_3CHO , it can be destroyed by Cl



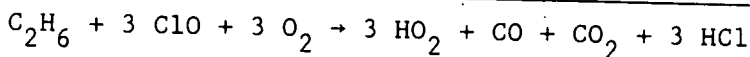
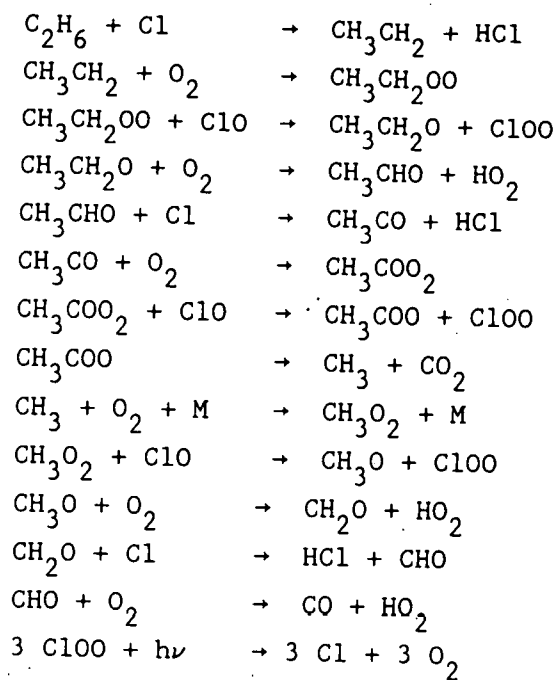
Also the oxidation of the hydrocarbons leads to the formation of formaldehyde, which can also destroy Cl by the reaction



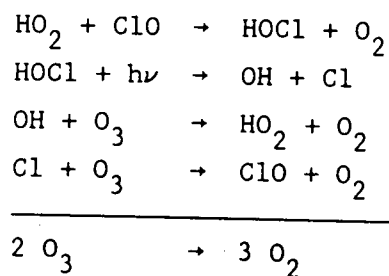
The reaction set may also be affected by ClO, which may replace NO as an agent to remove oxygen from different intermediates.

The higher temperatures encountered in the Arctic lead to important chemical differences. The presence of hydrocarbons also changes the situation in a unique manner. The primary effect of higher temperatures is to prevent the formation of polar stratospheric clouds, which are the surfaces for heterogeneous reactions. For example, Fahey et al (1990) report that during the winter 1989-1990 temperatures were -85°C at a pressure level of 50 mb. This is low enough to create polar stratospheric clouds composed of nitric acid ice, but not cold enough to form water ice clouds. Observations verify that the atmosphere was not dehydrated and was in fact denitrified. The denitrification measurement was based on a NO chemiluminescence measurement where all active nitrogen species are converted to NO and then detected. The species PAN is not mentioned as one of those species which are detected in this manner, so it is possible that a large concentration of PAN could be interpreted as a low NO_y measurement. In either case there is less NO_2 available to react chemically.

The abundance of ClO is also enhanced. This was measured by Brune et al (1988) during the Arctic winter 1987-1988 and also during the Arctic winter 1989-1990 (Fahey et al, 1990; Brune et al, 1990). Brune et al (1988) attribute the enhanced ClO to a denitrified atmosphere, which prevents the formation of ClONO_2 due to the absence of NO_2 . In such a situation the ethane oxidation cycle will follow a different path from the one depicted above. Oxygen removal steps involving NO and PAN formation using NO_2 will be absent. Instead, by analogy with the ClO, CH_3O_2 reaction, determined in the laboratory as rapid (Simon et al, 1989), ClO will react with various products to form ClOO. The complete reaction scheme is



In this way ethane acts to remove ClO and Cl, forming HCl, an inactive chlorine species. However, this apparently beneficial reaction sequence also produces HO₂, which reacts with ClO through the sequence



In this way ozone is destroyed by the presence of the additional hydrocarbons. The final outcome depends on the relative rates of the different reactions, so a detailed calculation is required. However, on at least one occasion during the 1989-1990 winter, total ozone as low as 165 DU was observed (Pommereau et al, 1990), indicating that ozone loss over limited areas does occur.

One interesting point is that if temperatures are not low enough to initiate denitrification, then PAN formation is possible, reducing the amount of NO_2 available to form ClONO_2 and raising the concentration of ClO . Therefore the Arctic may be susceptible to enhanced levels of active chlorine even when polar stratospheric clouds are absent.

CONCLUSIONS

Most of the ozone depletion observed in the Antarctic spring can be explained by the theory, in which lower stratospheric nitrogen and chlorine compounds react heterogeneously on polar stratospheric clouds. This results in a denitrification and dehydration in the vicinity of the clouds and a conversion of chlorine nitrate and hydrochloric acid to molecular chlorine. In the spring this species is released and photo-dissociated with the return of the sun.

There are numerous observations of ozone and other parameters which are at a variance with the heterogeneous reaction hypothesis. Ozone depletion has been reported both above the polar stratospheric cloud level and outside the polar vortex. In both of these regions heterogeneous chemistry cannot be invoked. Depletion is observed in data from 1970. The importance of nitric oxides and chlorine in this early time period needs to be investigated. The exact time behavior of ozone during winter and early spring must be quantified.

Possible mechanisms for ozone depletion at altitudes above the cloud level need to be considered. The meteor hypothesis and temperature variations have not been fully explored. The satellite observations of Mev electron precipitation and ground-based observations of enhanced electron density must be correlated and a search conducted for the signature of such events in the ozone data.

The Arctic presents a different situation from the Antarctic. Meteorological conditions are different. The vortex is weaker and does not last as long. This results in a situation where temperatures are higher and there is more opportunity for ozone-rich air to penetrate the vortex. The net result of these factors is less ozone depletion by the heterogeneous reaction mechanism. In addition, the photochemistry is complicated by the presence of low molecular weight hydrocarbons which have a sufficiently long photochemical lifetime to allow diffusion into the lower stratosphere where they react with chlorine species, reducing the impact of chlorine by converting ClO to HCl but increasing the impact of Cl, by producing HO which can free Cl from ClO and by reducing the amount of NO₂ available for ClONO₂ formation.

ACKNOWLEDGEMENTS

This report benefited greatly from useful discussions with P. Aumedieu, R. McPeters and J.-P. Pommereau. Thanks are due to M. De Mazière for assistance in the preparation of the manuscript. The author wishes to thank M. Ackerman and the Institut d'Aéronomie Spatiale de Belgique for hosting him during part of his sabbatical leave from the Goddard Space Flight Center.

REFERENCES

- AGER, III, J.W., and C.J. HOWARD, Rate coefficient for the gas phase reaction of NaOH with CO₂, J. Geophys. Res., 92, 675-678, 1987.
- AIKIN, A.C., J.R. HERMAN, E.J.R. MAIER and, C.J. McQUILLAN, Atmospheric chemistry of ethane and ethylene, J. Geophys. Res., 87, 3105-3118, 1982.
- AIKIN, A.C., and R.D. McPETERS, Meteoric material and the behavior of upper stratospheric polar ozone, Geophys. Res. Lett., 13, 1300-1303, 1986.
- AIKIN, A.C., and R.D. McPETERS, The three-dimensional morphology of the Antarctic ozone minimum, Geophys. Res. Lett., 15, 413-416, 1988.
- AIKIN, A.C., Ozone minimum occurs in Antarctic in the springtime, Earth in Space, 1, 8, 83-85, 1989.
- ANDERSON, J.G., W.H. BRUNE and, M.H. PROFFITT, Ozone destruction by chlorine radicals within the Antarctic vortex : The spatial and temporal evolution of ClO-O₃ anticorrelation based on in situ ER-2 data, J. Geophys. Res., 94, 11465-11479, 1989a.
- ANDERSON, J.G., et al., Kinetics of O₃ destruction by ClO and BrO within the Antarctic vortex : An analysis based on in situ ER-2 data, J. Geophys. Res., 94, 11480-11520, 1989b.
- BAKER, D.N., J.B. BLAKE, D.J. GORNEY, P.R. HIGBIE, R.W. KEBESADEEL, and J.H. KING, Highly relativistic magnetospheric electrons : A role in coupling to the middle atmosphere, Geophys. Res. Lett., 14, 1027-1030, 1987.
- BLAKE, D.R., and F.S. ROWLAND, Global atmospheric concentrations and source strengths of ethane, Nature, 321, 231-233, 1986.
- BOTTENHEIM, J.W., and A.J. GALLANT, PAN over the Arctic : Observations during AGASP-2 in April 1986, J. Atmos. Chem., 9, 301-316, 1989.
- BROWELL, E., paper presented at the Erice School on Quantum Electronics in the Atmosphere, September 1989.

- BRUNE, W.H., D.W. TOOHEY, J.G. ANDERSON, W.L. STARR, J.F. VEDDER and E.F. DANIELSEN, In situ northern mid-latitude observations of ClO, O₃ and BrO in the wintertime lower stratosphere, *Science*, 242, 558-562, 1988.
- BRUNE, W.H., D.W. TOOHEY and J.G. ANDERSON, The gas-phase photochemistry of the polar stratosphere in springtime : Photochemical mechanisms and effects on ozone, *EOS*, 70, 1040, 1989.
- BRUNE, W.H., D.W. TOOHEY and J.G. ANDERSON, The photochemistry of halogens in the wintertime polar stratosphere, *Annals Geophys.*, 295, Special Issue XV General Assembly Copenhagen, 1990.
- CADLE, R.D., P. CRUTZEN and D. EHHALT, Heterogeneous chemical reactions in the stratosphere, *J. Geophys. Res.*, 80, 3381-3385, 1975.
- CALLIS, L.B. and M. NATARAJAN, The Antarctic ozone minimum : Relationship to odd nitrogen, odd chlorine, the first warming and the eleven year solar cycle, *J. Geophys. Res.*, 91, 10771-10796, 1986.
- CARIOLE, D., S. MULLER, F. CAYLA and M.P. McCORMICK, Mountain waves, polar stratospheric clouds, and the ozone depletion over Antarctica, *J. Geophys. Res.*, 94, 1233-11240, 1989.
- CHUBACHI, S., Preliminary result of ozone observation at Syowa Station from February 1982 to January 1983, *Mem. Natn. Inst. Polar Res. (Tokyo). Spec. Iss.*, 34, 13, 1984.
- CHUBACHI, S., and R. KAJIWARA, Total ozone variations at Syowa, Antarctica, *Geophys. Res. Lett.*, 13, 1197-1198, 1986.
- CRUTZEN, P.J., I.S.A. ISAKSEN and G.C. REID, Solar proton events : Stratospheric sources of nitric oxide, *Science*, 189, 457-459, 1975.
- CRUTZEN, P.J., and J. ARNOLD, Nitric acid cloud formation in the cold Antarctic stratosphere : A major cause for the springtime "ozone hole", *Nature*, 324, 651-655, 1986.
- DEUTSCH, H.U., Atmospheric ozone and ultraviolet radiation, pp. 383-415, *Climate of the Free Atmosphere, World Survey of Climatology*, 4, 1969.

- DOBSON, G.M.B., Annual variations of ozone in Antarctica, *Quart. J. Roy. Met. Soc.*, 92, 549-552, 1966.
- FAHEY, D.W., D.M. MURPHY, K.K. KELLY, M.K.W. KO, M.H. PROFFITT, C.S. EUBANK, G.W. FERRY, M. LOEWENSTEIN and K.R. CHAN, Measurements of nitric oxide and total reactive nitrogen in the Antarctic stratosphere : Observations and chemical implications, *J. Geophys. Res.*, 94, 16665-16681, 1989.
- FAHEY, D.W. et al., Observations of denitrification and dehydration in the winter polar stratosphere, *Nature*, 344, 321-324, 1990.
- FARMAN, J.C., B.G. GARDINER and D.J. SHANKLIN, Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interactions, *Nature*, 315, 207-210, 1985.
- FINLAYSON-PITTS, B.J., M.J. EZELL and J.N. PITTS Jr., Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and ClONO_2 , *Nature*, 237, 240-244, 1989.
- FIOCCO, G., W.D. KOMHYR and D. FUA, Is ozone destroyed during the Antarctic winter in the presence of polar stratospheric clouds?, *Nature*, 34, 423-427, 1989.
- HEATH, D.F., A.J. KRUEGER and P.J. CRUTZEN, Solar proton event : Influence on stratospheric ozone, *Science*, 197, 886-889, 1977.
- HOFMANN, D.J., J.W. HARDER, S.R. ROLF and J.M. ROSEN, Balloon-borne observations of the development and vertical structure of the Antarctic ozone hole in 1986, *Nature*, 326, 59-62, 1987.
- HOFMANN, D.J., J.W. HARDER, J.M. ROSEN, J.V. HERFORD and J.R. CARPENTER, Ozone profile measurements at McMurdo Station, Antarctica, during the spring of 1987, *J. Geophys. Res.*, 94, 16527-16536, 1989.
- KELLY, K.K., et al., Dehydration in the lower Antarctic stratosphere during late winter and early spring, *J. Geophys. Res.*, 94, 11317-11357, 1989.
- KO, M.K.W., et al., Implications of AAOE observations for proposed chemical explanations of the seasonal and interannual behavior of Antarctic ozone, *J. Geophys. Res.*, 94, 16705-16715, 1989.

- KRUEGER, A.J., M.R. SCHROEBERL, R.S. STOLARSKI, and F.S. SECHRIST, The 1987 Antarctic ozone hole : A new record low, *Geophys. Res. Lett.*, 15, 1365-1368, 1988.
- KRUEGER, A.J., Antarctic and Arctic total ozone extreme minima, p. 5-9, *Ozone in the Atmosphere*, Ed. R.D. Bojkov and P. Fabian A. Deepak Publishing, 1989.
- LAIT, L.R., M.R. SCHROEBERL and P.A. NEWMAN, Quasi-biennial modulation of the Antarctic ozone depletion, *J. Geophys. Res.*, 94, 11559-11572, 1989.
- LEU, M., Laboratory studies of sticking coefficients and heterogeneous reactions important in the Antarctic stratosphere, *Geophys. Res. Lett.*, 15, 17-20, 1988.
- MCCORMICK, M.P., H.M. STEELE, P. HAMILL, W.P. CHU and T.J. SWISSLER, Polar stratospheric cloud sighting by SAM II, *J. Atmos. Sci.*, 39, 328-331, 1982.
- MCCORMICK, M.P., and J.C. LARSEN, Antarctic springtime measurements of ozone, nitrogen dioxide and aerosol extinction by SAM II, SAGE and SAGE II, *Geophys. Res. Lett.*, 13, 1280-1283, 1986.
- MCCORMICK, M.P., C.R. TREPTE and M.C. PITTS, Persistence of polar stratospheric clouds in the southern polar region, *J. Geophys. Res.*, 94, 11241-11251, 1989a.
- MCCORMICK, M.P., J.M. ZAWODNY, R.E. VEIGA, J.C. LARSEN and P.H. WANG, An overview of SAGE I and II ozone measurements, *Planet. Space Sci.*, 37, 1567-1586, 1989b.
- McELROY, M.B., R.J. SALAWITCH, S.C. WOFYSY and J.A. LOGAN, Reduction of Antarctic ozone due to synergetic interaction of chlorine and bromine, *Nature*, 321, 759-762, 1986.
- McELROY, M.B., R.J. SALAWITCH and S.C. WOFYSY, Chemistry of the Antarctic stratosphere, *Planet. Space Sci.*, 36, 73-87, 1988.
- McKENNA, D.S., R.L. JONES, J. AUSTIN, E.V. BROWELL, M.P. MCCORMICK, A.J. KRUEGER and A.F. TUCK, Diagnostic studies of the Antarctic vortex during the 1987 airborne Antarctic ozone experiment : Ozone mini-holes, *J. Geophys. Res.*, 94, 11641-11668, 1989.

- McPETERS, R.D., C.H. JACKMAN and E.G. STASSINOPOULOS, Observations of ozone depletion associated with solar proton events, *J. Geophys. Res.*, 86, 12071-12081, 1981.
- McPETERS, R.D., A nitric oxide increase observed following the July 1982 solar proton events, *Geophys. Res. Lett.*, 13, 667-670, 1986.
- MOLINA, M.J., T. TSO, L.T. MOLINA and F.C. WANG, Antarctic stratospheric chemistry of chlorine nitrate, hydrogen chloride and ice : Release of active chlorine, *Science*, 238, 1253-1257, 1987a.
- MOLINA, L.T., and M.J. MOLINA, Production of Cl_2O_2 from the self-reaction of the ClO radical, *J. Phys. Chem.*, 91, 433-436, 1987b.
- NAGAI, T., "Space weather forecast" Prediction of relativistic electron intensity at synchronous orbit, *Geophys. Res. Lett.*, 15, 425-428, 1988.
- NICOLET, M., Ionospheric processes and nitric oxide, *J. Geophys. Res.*, 70, 691-701, 1965.
- NICOLET, M., On the production of nitric oxide by cosmic rays in the mesosphere and stratosphere, *Planet. Space Sci.*, 20, 637-649, 1975.
- POMMEREAU, J.P., F. GOUTAIL, H. LE TEXIER and T.S. JORGENSEN, Ozone and nitrogen dioxide monitoring at southern and northern polar latitudes, Proc. 28th Liège International Astrophysical Colloquium "Our Changing Atmosphere", 1989.
- POMMEREAU, J.P., F. GOUTAIL and A. SARKISSIAN, Ozone depletion associated with mountain-wave stratospheric clouds in the Arctic, submitted to *Nature*, 1990.
- POOLE, L.R., and M.P. McCORMICK, Polar stratospheric clouds and the Antarctic ozone hole, *J. Geophys. Res.*, 93, 8423-8430, 1988.
- PROFFITT, M.H., D.W. FAHEY, K.K. KELLY and A.F. TUCK, High-latitude ozone loss outside the Antarctic ozone hole, *Nature*, 342, 233-237, 1989.
- RASMUSSEN, R.A. and M.A. KHALIL, The global distribution and trends of C2-C4 hydrocarbons, *EOS*, 70, 1018, 1989.
- REAGAN, J.B. et al, Effects of the August 1972 solar particle events on stratospheric ozone, *J. Geophys. Res.*, 86, 1473-1494, 1981.

- SALAWITCH, R.J., M.B. McELROY, S.C. WOFSEY and J.H. YATTEAU, Loss of ozone in the polar regions during springtime, *EOS*, 70, 1043, 1989.
- SALAWITCH, R.J. et al, Loss of ozone in the Arctic vortex for the winter of 1989, *Geophys. Res. Lett.*, 17, 561-564, 1990.
- SANDERS, R.W., S. SOLOMON, M.A. CARROLL and A.L. SCHMELTEKOPF, Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica, 4, Overview and daily measurements of NO₂, O₃ and OClO during 1987, *J. Geophys. Res.*, 94, 11381-11392, 1989.
- SCHOEBERL, M.S. et al, Stratospheric constituent trends from ER-2 profile data, *Geophys. Res. Lett.*, 17, 469-472, 1990.
- SIMON, F.G., J.P. BROWN, W. SCHNEIDER, G.K. MOORTGAT and P.J. CRUTZEN, Study of the reaction ClO + CH₃O₂ → Products at 300 K, *J. Phys. Chem.*, 93, 7807-7813, 1989.
- SOLOMON, S., R.R. GARCIA, F.S. ROWLAND and D.J. WUEBBLES, On the depletion of Antarctic ozone, *Nature*, 321, 755-758, 1986.
- STOLARSKI, R.S., A.J. KRUEGER, M.R. SCHOEBERL, R.D. McPETERS, P.A. NEWMAN and J.C. ALPERT, Nimbus 1 SBUV/TOMS measurements of the springtime Antarctic ozone hole, *Nature*, 322, 808-811, 1986.
- TOLBERT, M.A., M.J. ROSSI, R. MALHOTRA and D.M. GOLDEN, Reaction of chlorine nitrate with hydrogen chloride and water at Antarctic stratospheric temperatures, *Science*, 238, 1258-1260, 1987.
- TOLBERT, M.A., M.J. ROSSI and D.M. GOLDEN, Antarctic ozone depletion chemistry : Reactions of N₂O₅ with H₂O and HCl on ice surfaces, *Science*, 24, 1018-1021, 1988.
- TOON, O.B., R.P. TURCO, J. JORDAN, J. GOODMAN and G. FERRY, Physical processes in polar stratospheric ice clouds, *J. Geophys. Res.*, 94, 11359-11380, 1989.
- TOON, G.C., C.B. FARMER, L.L. LOWES, P.W. SCHAPER, J.-F. BLAVIER and R.H. NORTON, Infrared aircraft measurements of stratospheric composition over Antarctica during September 1987, 94, 16571-16596, 1989.
- von BIEL, H.A., An investigation of the Antarctic mesosphere using partial reflections, *Planet. Space Sci.*, 37, 889-897, 1989.

- WOFSY, S.C. et al, Condensation of HNO_3 on falling ice particles : Mechanism for denitrification of the polar stratosphere, Geophys. Res. Lett., 17, 449-452, 1990.
- YUNG, Y. et al, Spatial variation of ozone depletion rates in the springtime Antarctica polar vortex, Science, 248, 721-724, 1990.