

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
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AERONOMICA ACTA

A - N° 334 - 1988

CHANGES IN STRATOSPHERIC OZONE : OBSERVATIONS AND THEORIES

by

Guy BRASSEUR and Paul C. SIMON

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

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FOREWORD

This document is the text of two conferences presented before the "Deutsche Gesellschaft für Chemisches Apparatewesem, Chemische Technik und Biotechnologie e.V." (DECHEMA) association in Frankfurt (FRG) in December 1987 and during the study-days on "Air pollution and its effects on the environment" in Padua (Italy) in April 1988. The text will be published in the proceedings of the meetings.

AVANT-PROPOS

Ce document constitue le texte de deux conférences présentées devant la société "Deutsche Gesellschaft für Chemisches Apparatewesem, Chemische Technik und Biotechnologie e.V." DECHEMA à Francfort (RFA) en décembre 1987 et aux journées d'étude sur "Air pollution and its effects on the environment" à Padoue (Italie) en avril 1988. Le texte sera publié dans les comptes-rendus des réunions.

VOORWOORD

Dit document vormt de tekst van twee voordrachten die gegeven werden voor de vereniging "Deutsche Gesellschaft für Chemisches Apparatewesem, Chemische Technik und Biotechnologie e.V." (DECHEMA) te Frankfurt (BRD) in december 1987 en tijdens de studiedagen over "Air pollution and its effects on the environment" te Padua (Italië) in april 1988. De tekst zal gepubliceerd worden in de verslagen van de vergaderingen.

VORWORT

Dieses Dokument ist der Text von zwei Vorträgen präsentiert für die "Deutsche Gesellschaft für Chemisches Apparatewesem, Chemische Technik und Biotechnologie e.V." (DECHEMA) Vereinigung in Frankfurt (BRD) im Dezember 1987 und während der Studientage über "Air pollution and its effects on the environment" in Padua (Italien) im April 1988. Der Text wird publiziert werden in den Berichten der Tagungen.

CHANGES IN STRATOSPHERIC OZONE : OBSERVATIONS AND THEORIES

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Abstract

The ozone abundance in the stratosphere is predicted to vary as a consequence of increasing emissions of trace gases such as the chlorofluorocarbons, methane, nitrous oxide, carbon dioxide, etc... The paper reviews available observations used to derive a possible ozone trend over the last decade. Model simulations of ozone changes are also considered. A particular attention is devoted to the spectacular ozone depletion observed over Antarctica especially during springtime. Several theories presented to explain this remarkable and unexpected phenomena are reviewed. Recent observations show unambiguously that elevated amounts of ClO are present over Antarctica in the lower stratosphere during springtime. It is believed that the release of active chlorine is activated by the presence of polar stratospheric clouds.

Résumé

La concentration de l'ozone dans la stratosphère est affectée par l'émission de constituants tels que les halocarbones, le méthane, l'hémioxyde d'azote, le dioxyde de carbone, etc. dans la troposphère. Ce travail présente et analyse les observations disponibles permettant de déterminer les changements de l'ozone stratosphérique pendant les dix dernières années. Les simulations à l'aide de modèles numériques sont également considérées. Une attention particulière est portée sur la diminution importante de l'ozone au-dessus du continent Antarctique au printemps. Les théories présentées pour expliquer ce phénomène sont revues. Les observations récentes montrent une quantité élevée de ClO dans la stratosphère inférieure pendant le printemps en Antarctique. La présence des nuages polaires stratosphériques semble expliquer la présence de chlore chimiquement actif à des altitudes inférieures à 22 km.

Samenvatting

De ozonconcentratie in de stratosfeer wordt getroffen door de emissie van minderheidsbestanddelen zoals chloorfluorkoolstoffen, methaan, distikstofoxide, koolstofdioxide enz. in de troposfeer. Dit werk onderzoekt de beschikbare waarnemingen die toelaten de veranderingen in het stratosferisch ozon te bepalen tijdens de laatste tien jaar. Simulaties met behulp van numerieke modellen worden eveneens in beschouwing genomen. Bijzondere aandacht wordt geschonken aan de belangrijke ozonvermindering boven Antarctica tijdens de lente. Verscheidene voorgestelde theorieën om dit opvallend en onverwacht verschijnsel uit te leggen, worden herzien. Recente waarnemingen tonen ondubbelzinnig een grote hoeveelheid ClO in de lage stratosfeer boven Antarctica tijdens de lente. De aanwezigheid van polaire stratosferische wolken schijnt de aanwezigheid van chemisch actieve chloor uit te leggen op minder dan 22 km hoogte.

Zusammenfassung

Die Ozonkonzentration in der Stratosphäre wechselt durch die Emission von Minoritätsgasen wie Chlorfluorkohlstoffen, Methan, N_2O , CO_2 ... in der Troposphäre. Diese Arbeit untersucht die verfügbare Beobachtungen die zulassen die Veränderungen im stratosphärischen Ozon zu bestimmen während des letzten Jahrzehntes. Simulationen mit der Hilfe von numerischen Modellen werden auch betrachtet. Besondere Aufmerksamkeit wird gewidmet an der wichtige Ozonverringerung über Antarktis während des Frühlings. Verschiedene präsentierte Theorien zur Erklärung dieses auffallenden und unerwarteten Phänomenes werden revidiert. Rezente Beobachtungen zeigen unzweideutige grosse Quantitäten ClO in der geringen Stratosphäre über Antarktis während des Frühlings. Die Anwesenheit von polarer stratosphärischer Wolken scheint die Anwesenheit von chemischem aktivem Chlor zu erklären auf geringerer Höhe als 22 km.

1. INTRODUCTION

Ozone, which protects the biosphere from harmful solar ultraviolet radiation and plays a key role in the radiative budget of the middle atmosphere, is present in the atmosphere from the surface to as high as 100 km altitude. The peak density of this chemical constituent is located near 25 km altitude in the tropics and 18 km at high latitude. The transmission of solar radiation in the 200-310 nm region is determined in large part by the ozone column density, which corresponds, for standard pressure and temperature conditions, to a highly absorbing layer with a thickness of only 2.5 to 4.5 mm (250 to 450 Dobson).

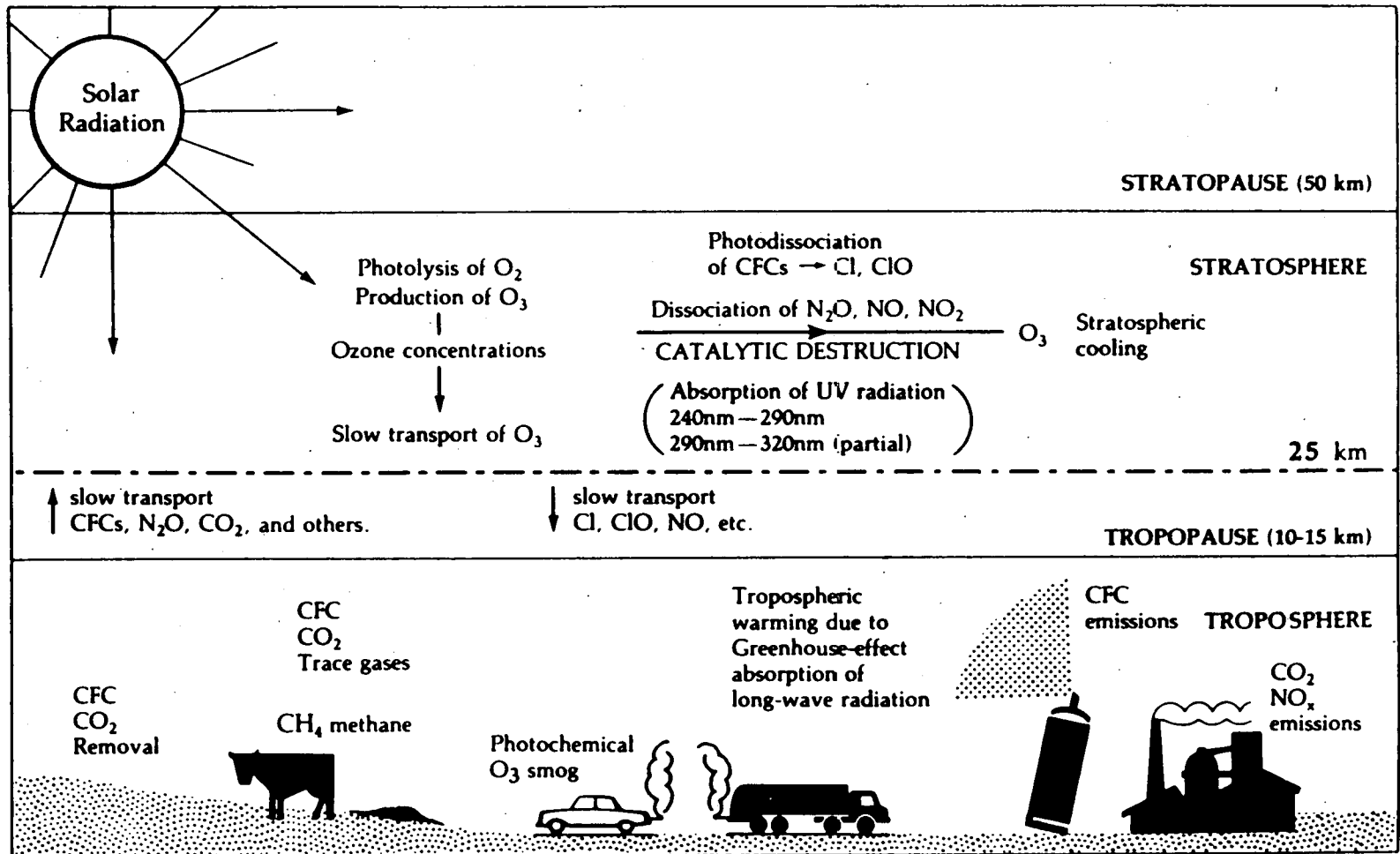
Ozone is produced by the action on molecular oxygen of solar ultraviolet radiation at wavelength shorter than 242 nm. Its destruction by recombination with atomic oxygen is catalyzed by the presence of different radicals belonging to the families of hydrogen (H, OH, HO₂), nitrogen (NO, NO₂), chlorine (Cl, ClO), bromine (Br, BrO), etc... The relative contribution of these radicals to the ozone loss varies with altitude; in the mesosphere (50-85 km), the most efficient processes are due to the hydroxyl radicals while in the stratosphere (15-50 km), the most important destruction agents for ozone are the nitrogen oxides. The effects of chlorine are the largest near 40 km altitude (under conditions prevailing outside the polar regions). Recent measurements have shown that the chlorine chemistry is substantially modified in the cold stratosphere over Antarctica in spring.

Increases in the atmospheric concentration of methane, nitrous oxide and the chlorofluorocarbons (CFCs) are expected to modify the density of the active radicals affecting the ozone amount. Some of these compounds are released in the atmosphere as a result of agricultural and industrial activity. Because of the relatively long lifetime of these species (see Table 1), a large fraction of these molecules penetrate in the stratosphere, where their destruction leads to the formation of ozone destroying radicals. Active chlorine is for example released in

TABLE 1.- Main characteristics of chemical species released in the atmosphere 1980 conditions.

Species	Typical mixing ratio at the surface	Total atmospheric mass (10^6 Tonnes)	Approximate lifetime (yrs)	Recent growth rate (%/yr)	Ozone depletion efficiency relative to CFC-11*
CO ₂	340 ppmv	2.1 x 10 ⁶		0,2-0,5	-
CH ₄	1.6 ppmv	4 183	8	1-2	-
N ₂ O	300 ppbv	2 170	170	0.25	-
CH ₃ Cl	700 pptv	5.27	1	0	-
CCl ₄	100 pptv	2.44	70	0-3	1.06
CH ₃ CCl ₃	100 pptv	2.09	8	6-9	0.10
F-11 (CFC1 ₃)	170 pptv	3.74	70	5-8	1.0
F-12 (CF ₂ Cl ₂)	285 pptv	5.65	140	5-8	1.0
F-113 (C ₂ F ₃ Cl ₃)	22 pptv	0.67	100	10-20	0.78
F-22 (CHF ₂ Cl)	64 pptv	0.92	20	12	0.05
Halon 1301 (CF ₃ Br)	~ 1 pptv	0.02	100	rapid	11.4
Halon 1211 (CF ₂ ClBr)	~ 1.5 pptv	0.03	20	20	2.70

* according to LLNL one-dimensional model.



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Fig. 1.- Selected physical and chemical processes impacting on ozone densities and climatic processes (from Miller and Mintzer, 1986).

the stratosphere from the photodissociation of the CFCs. These gases of anthropogenic origin as well as carbon dioxide, a constituent partly produced by combustion processes, are also radiatively active in the infrared and therefore contribute to the "greenhouse" effect of the atmosphere. An increase in carbon dioxide, a molecule without chemical action on ozone, leads to a warming of the troposphere (0-15 km) and of the Earth's surface (greenhouse effect) and to a cooling of the stratosphere (larger emission to space of radiative energy) and, through this temperature change, reduces the loss rate of ozone above 30 km and consequently enhances its concentration in the upper stratosphere. A change in the ozone density also modifies the depth of penetration of solar ultraviolet radiation and the related stratospheric heating rate. Figure 1 illustrates the most important processes affecting both the ozone distribution and climate.

The study of the ozone response to perturbations of natural and anthropogenic origin requires a detailed understanding of chemical, radiative and dynamical processes occurring simultaneously in the atmosphere. The most recent models account for the most important couplings between these processes. These models are the only tools presently available to predict the effects of perturbations in the future. They are used to identify the relative importance of different atmospheric processes and to validate theory against available observations.

The protection of the ozone layer is a major concern since this layer shields the biosphere against harmful UV-B (290- 320 nm) and UV-C (200-290 nm) radiation. Abiotic ultraviolet radiation is strongly absorbed by the DNA molecules of living cells and alters reproductive processes of these cells. A well-known example is the relation between UV-B exposure and human skin cancer although other biological effects could lead to even more important consequences. The global warming at the Earth's surface expected from increasing levels of chemical compounds in the atmosphere could produce major climatic changes with substantial environmental consequences.

The purpose of this paper is to review the most recent studies dealing with possible trends in the stratospheric ozone density. These investigations involve ground-based and satellite observations as well as model simulations. It is indeed important to estimate if observed ozone and temperature variations over periods of the order of a decade can be explained by increasing levels of trace gases measured in the atmosphere. A particular attention will be given to the specific problem of the dramatic decrease in springtime ozone over the Antarctic continent. This phenomena, which was not predicted by any model, is not yet entirely understood, although several theories have been proposed. These theories will be reviewed, critically analyzed and confronted to recent atmospheric measurements.

2. CLIMATOLOGY OF OZONE

Observations of ozone reveal that the mean total ozone content increases with latitude with the most pronounced latitudinal gradient in late winter and early spring (Fig. 2). The spatial distribution is significantly different in the two hemispheres. Ozone, which is produced by the action of solar radiation on molecular oxygen essentially in the upper stratosphere at mid- and low latitudes, is transported downwards and towards higher latitudes by the stratospheric meridional circulation, which is particularly strong during winter when planetary waves propagate and dissipate in the stratosphere. Ozone therefore accumulates at high latitude during winter and the total column density reaches a maximum value in early spring. Because of hemispheric differences in orography, the strength of the planetary waves (which are produced by the wind flow over large mountain ranges) is weaker in the Southern than in the Northern hemisphere and the meridional eddy flux of ozone and heat is significantly lower in the austral than in the boreal regions. The presence of a strong and undisturbed polar vortex over Antarctica in winter explains the low ozone content and the relatively cold temperature (about 10K lower than in the Arctic region) at the South Pole as well as the presence of a warm zonal belt near 60 degrees South

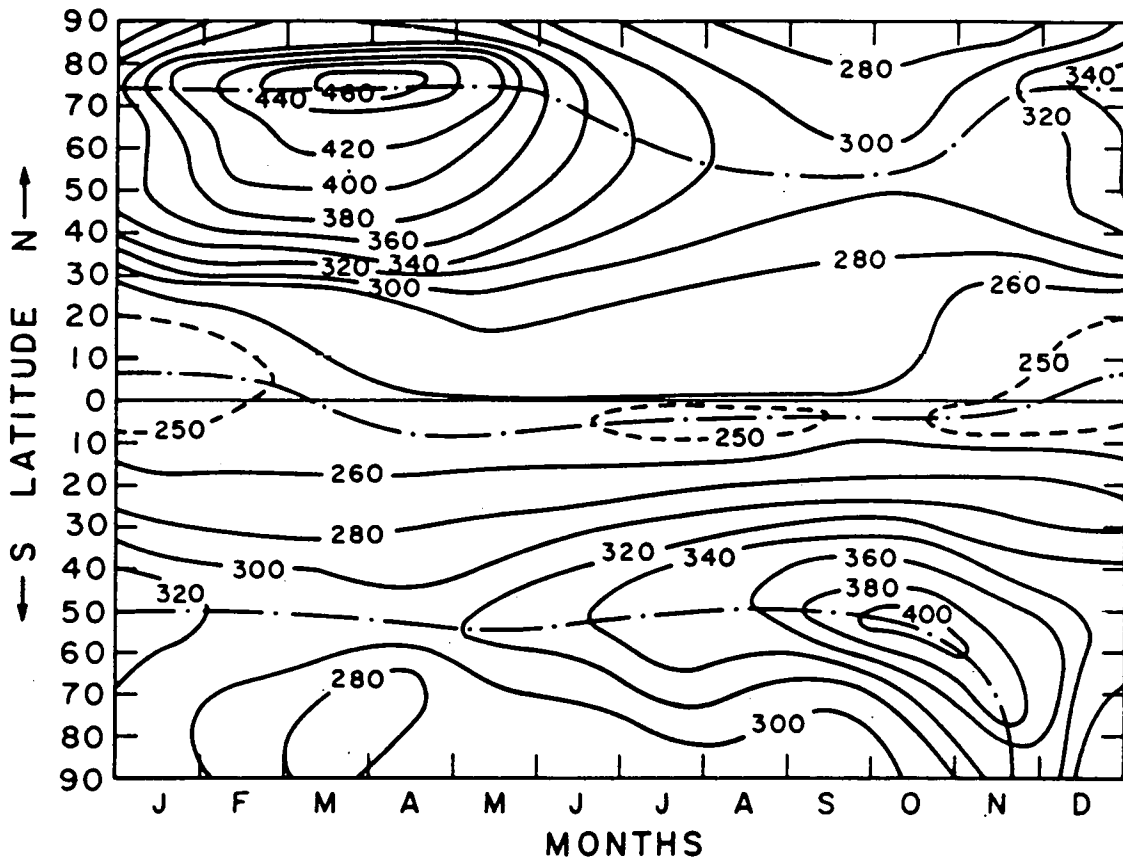


Fig. 2.- Ozone column abundance (Dobson units) as a function of latitude and month (from London, 1980).

with high ozone content. This morphology is important for explaining the observed ozone hole over Antarctica and shows how dynamics produces the conditions allowing for a rapid chemical ozone destruction in this region.

The temporal and geographical variations of ozone are also influenced by meteorological conditions near the tropopause, and by annual, semi-annual and quasi-biennial oscillations in wind and temperature in the stratosphere changes in the solar ultraviolet emission associated with the 27-day rotation period of the Sun and the 11-year cycle affect ozone above 30 km altitude.

3. OZONE MODELING

Atmospheric modeling of the chemical constituents has now reached the stage where it can reproduce with reasonable agreement the "natural" atmosphere with some exceptions such as ozone in the upper stratosphere and mesosphere, where calculated densities are underestimated by 20 to 30 percent compared to observed values. The most realistic models handle more than 100 chemical and photochemical reactions and 40 active species. Photochemistry is initiated by the penetration of solar radiation, which is governed by ozone and molecular absorption and multiple scattering. The transport of the species depends on the circulation which is driven essentially by wave drag associated for example with Rossby and gravity waves breaking. Dynamics is also closely related to deposition of radiative energy mainly controlled by the presence of molecules like ozone, molecular oxygen, carbon dioxide and water vapor.

Numerical models are currently used to predict the possible changes in stratospheric ozone density and temperature during the next decades. These models are based on plausible scenarios for the increasing density of perturbing gases in the future. These scenarios are highly uncertain, so that a large number of plausible cases have to be considered. For example, in the model shown in Figure 3, the densities of CO_2 , CH_4 and N_2O are assumed to increase by 0.5, 1.0 and

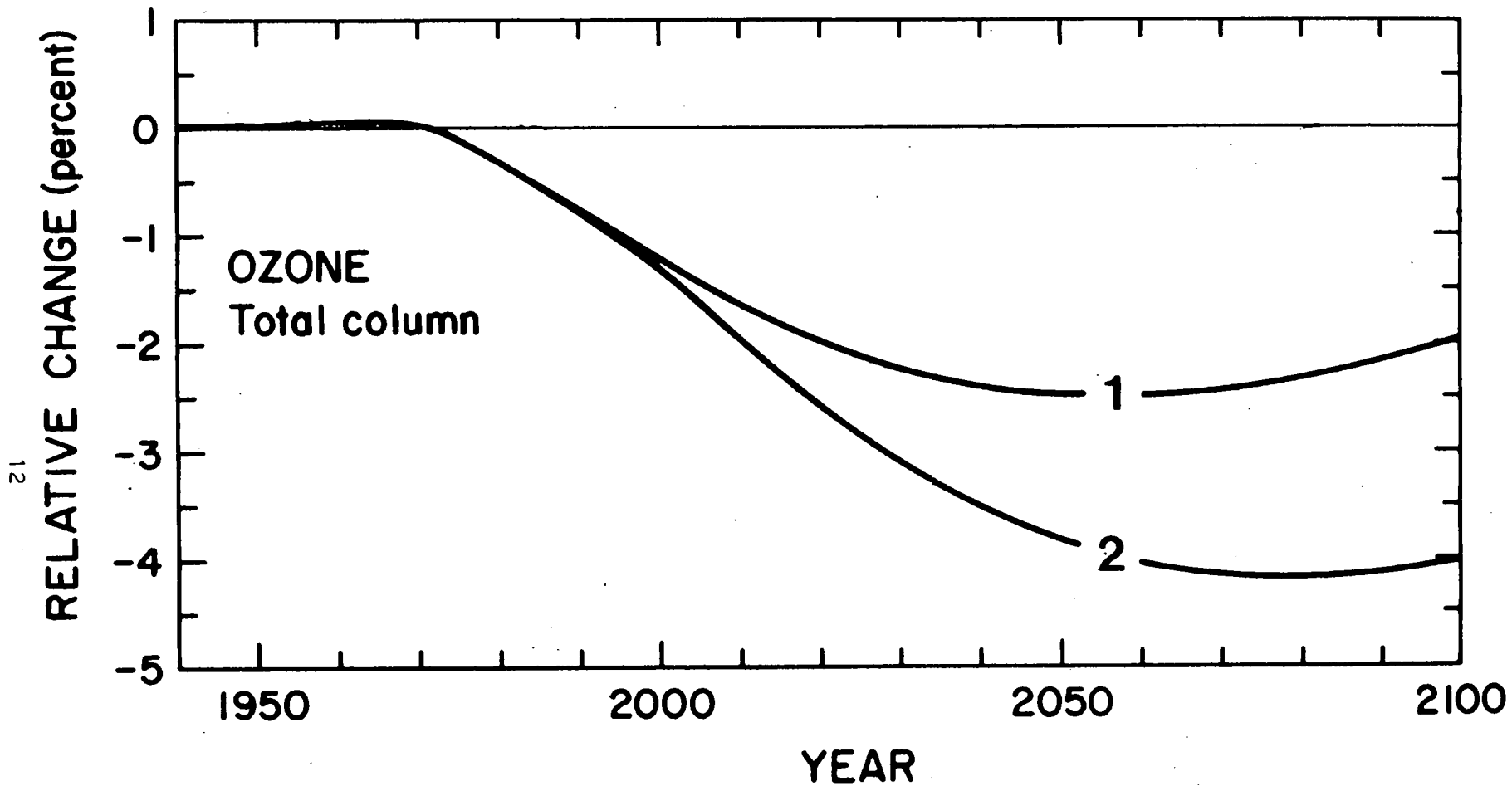


Fig. 3.- Change in the ozone column abundance relative to 1940 predicted by the chemical-radiative-transport one-dimensional model of Brasseur (1987). For conditions, see text.

0.25 percent per year respectively. Trends in CFC-11 (CFCl_3), CFC-12 (CF_2Cl_2), and CFC-113 ($\text{C}_2\text{F}_3\text{Cl}_3$) are based on historical emissions until 1985 and on prescribed scenarios for the future. In case 1, a constant emission at the 1985 level is assumed for CFC-11 and CFC-12. In case 2, a 3 percent growth, with a capacity cap of 1.5 times the 1985 level, is specified for the production of CFC-11 and CFC-12. In both cases, the emission of CFC-113 is assumed to increase by 6 percent per year with an upper limit equal to the production of CFC-11. The change in the ozone column abundance calculated for these conditions by a one-dimensional chemical-radiative-transport model is characterized in both cases by a decrease until the second half of the 21st century, essentially as a result of an increasing amount of chlorine in the stratosphere. The slow recovery predicted after the 2050-2080 time frame results from the assumed rapid growth in the methane concentration. The trend in the methane density is poorly understood and could be reduced in the future. Its effect is to enhance the ozone amount in the troposphere and consequently to partially compensate the reduction of the ozone column resulting from the effect of chlorine compounds in the stratosphere near 40-45 km altitude. At these heights, the model predicts ozone reductions of 60 to 75 percent and temperature decreases of 25 to 30 degrees by year 2040. An increase of tropospheric ozone is expected but its magnitude will depend on the release rate of nitric oxide and carbon monoxide at the surface, depending on the level of pollution at the Earth's surface. This ozone increase is thus expected to be smaller in the Southern than in the Northern hemisphere. A warming of the surface is also predicted in the future with a magnitude which evolves as a function of the scenario for the release of the "greenhouse" gases and of the mean timescale for heat exchanges with the ocean.

Calculations based on two-dimensional models show that the response of the atmosphere is variable with latitude and season. The change in the ozone column resulting from a doubling of CO_2 (to be achieved in the second half of the 21st Century) or from an increase in the chlorine concentration from 2.0 to 6.6 ppbv is shown as a function of latitude in Figure 4. In both cases, the change is largest at high

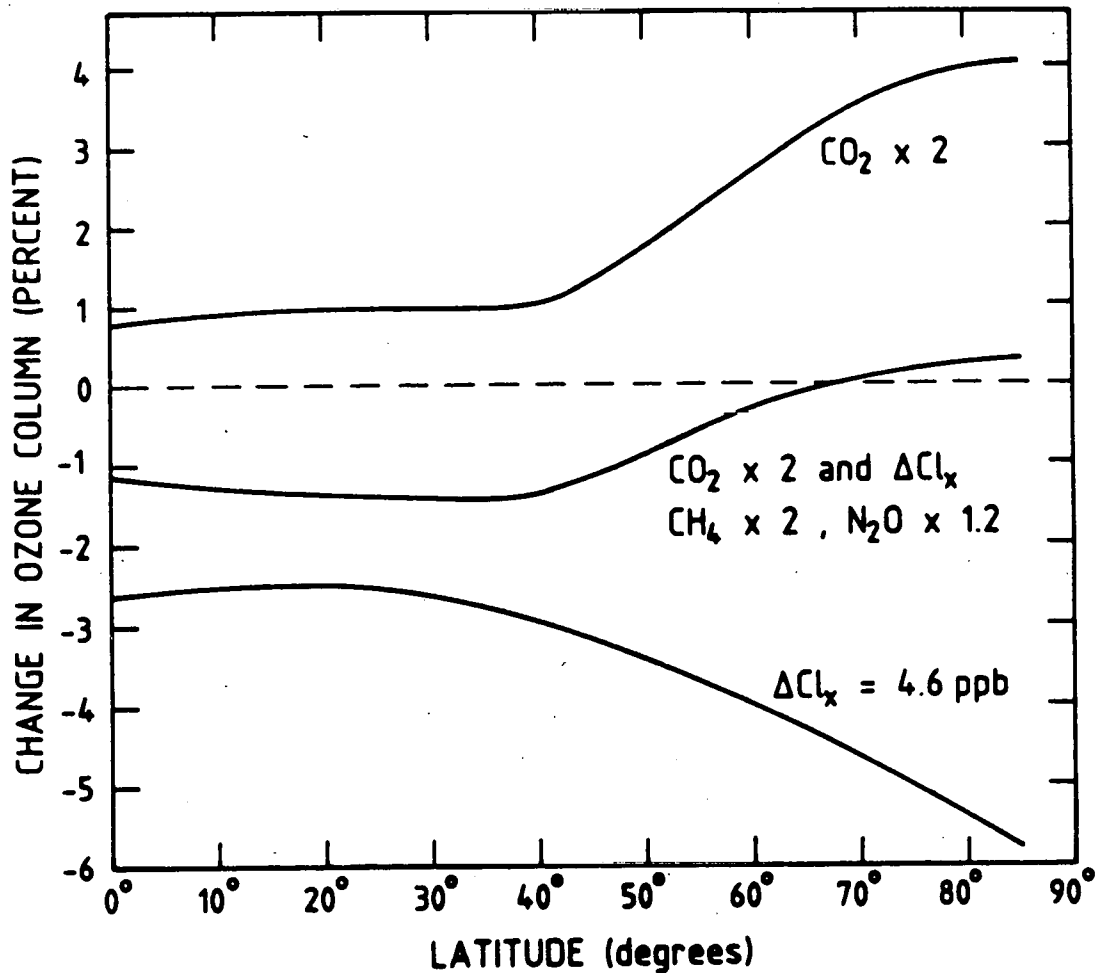


Fig. 4.- Percentage change of the ozone column density as a function of latitude calculated for different perturbations. Upper curve : Effect of a doubling of CO_2 . Lower curve : Effect of an increase of 4.6 ppbv in the chlorine abundance. The change due to the latter effects as well as doubling in CH_4 and a 20 percent increase in N_2O is shown by the third curve.

latitude. The mean ozone depletion due to the effects of the CFCs is a factor 2-3 larger at the pole than in the tropics. The response to CO_2 is also more pronounced near the polar cap than near the equator. This situation results from a complex interplay between chemical, radiative and dynamical effects. For example, the efficiency of chlorine for destroying ozone in the upper stratosphere depends on the concentration of methane, which converts active chlorine (Cl) into the reservoir. Since methane is less abundant at high latitudes than in the tropics, where its injection into the stratosphere takes place, the chlorine catalytic cycle leading to the destruction of ozone is most efficient at high latitudes. Moreover, since the circulation is directed downwards over the pole in the winter hemisphere, air with depleted ozone will be transported from the upper to the lower stratosphere and produce a maximum reduction in the column abundance at high latitude at the end of the winter season. When all perturbations are treated simultaneously, the latitudinal dependence of the change in the ozone column is reduced but the quantitative values are scenario dependent.

Finally, Figure 5 shows a simulation of the ozone and temperature variations calculated for the period during which operational satellite data are available. The densities are assumed to increase between 1979 and 1986 from 335.5 to 344 ppmv for CO_2 , from 1.62 to 1.70 ppmv for CH_4 , from 305 to 310 ppbv for N_2O , from 170 to 220 pptv for CFC-11, from 290 to 418 pptv for CFC-12, and from 110 to 174 pptv for CH_3CCl_3 . The solar irradiance is assumed to vary over the solar cycle (from peak to peak) by a factor 2 at Lyman α (121.6 nm), 15 percent in the Schumann-Runge bands region (180-200 nm), 9 percent at 205 nm and 3 percent at 260 nm.

4. OZONE TRENDS

Total ozone content

Monitoring of total column ozone has been performed for more than 30 years by means of the ground-based Dobson network. The determination from these observations of a long-term trend is difficult to achieve

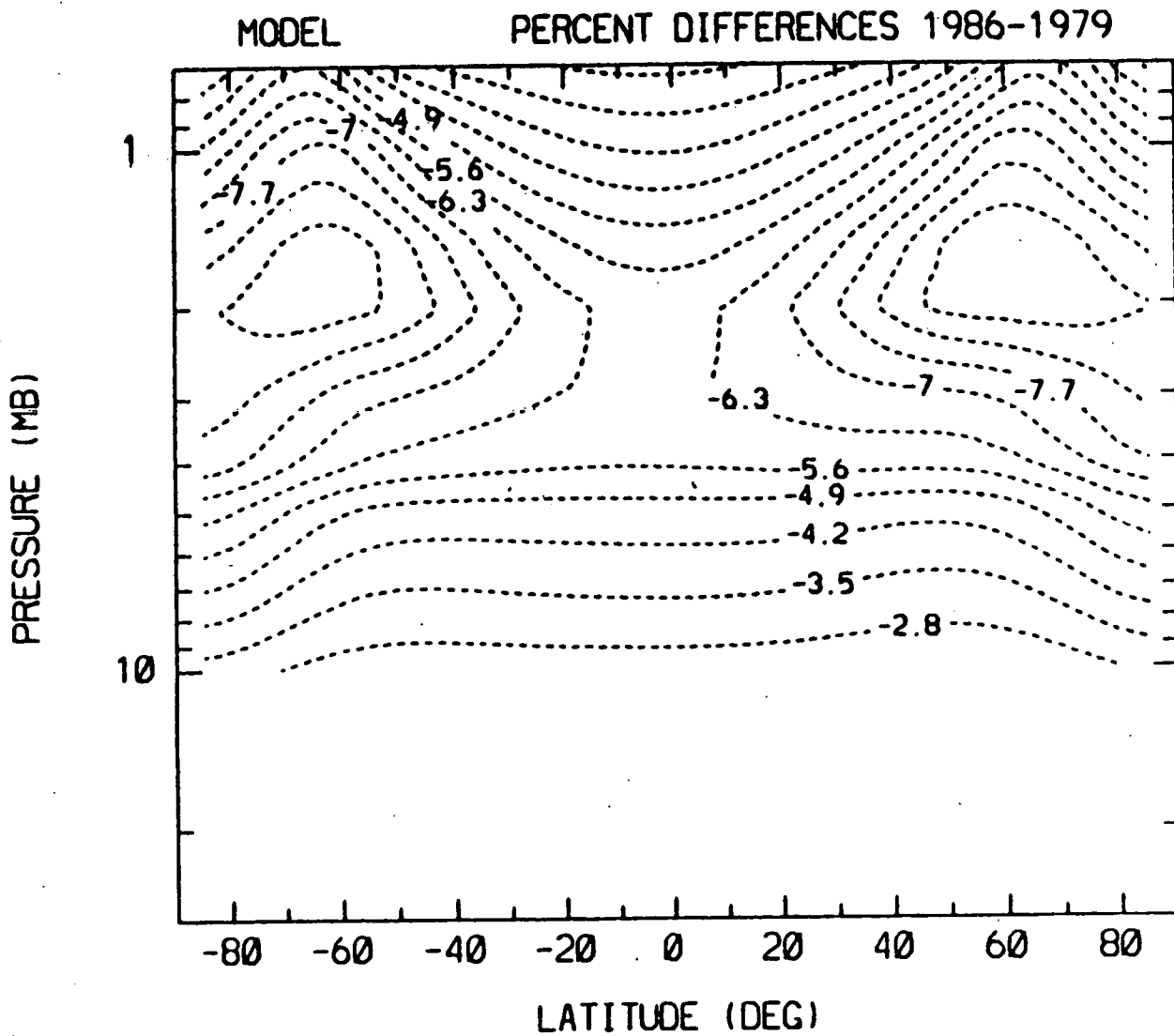


Fig. 5.- Meridional distribution of the percent difference in ozone density between 1979 and 1986 (seasonal variation removed) in the upper stratosphere (about 30 to 50 km altitude).

because of the poor geographical coverage of the ground-based instruments. For instance, observations are predominantly concentrated in the mid-latitudes of the Northern hemisphere leading to oversampling with respect to the equatorial zone and the Southern hemisphere. An analysis of the Dobson data shows that, after the effects of the dynamical oscillations and the solar cycle are removed, the residual (negative) trend in total ozone for the 1970-1986 time period is of the order of 2-3 percent at mid- and high latitudes in the Northern hemisphere.

Monitoring from space provides very good latitude coverage; it has been started in the 1970's with Nimbus 4 and Nimbus 7 satellites. The later, with the Solar Backscatter Ultraviolet (SBUV) spectrometer and the Total Ozone Mapping Spectrometer (TOMS), is providing continuous data since November 1978. The main problem and consequently the origin of controversies about the trends derived from these data is the degradation of the diffuser plate used when looking towards the Sun (and possible aging of both spectrometers). For the last 7 years of SBUV observations, Reinsel et al (1988) quote a linear trend of $- 0.74 \pm 0.26$ percent per year. This figure, when SBUV data are corrected for negative drift between SBUV and Dobson data, is reduced to $- 0.35 \pm 0.28$ percent per year.

Global trends in total ozone from TOMS, reported by Bowman (1988) from 1979 through 1986, show a linear decrease of 1.0 percent per year at mid-latitude with a strong latitude dependence. This instrument shares the same diffuser plate as SBUV. Consequently those trends cannot be supported because the model of the diffuser plate degradation, used to correct the data, is not unique and could introduce some artificial changes in the derived ozone abundance. If nevertheless the satellite data are normalized to the Dobson network, the trend between 65°N and 65°S is estimated to be only $- 0.36$ percent per year. Figure 6 shows the time-latitude distribution of the change in the ozone column between the late 70's and present, obtained after correction for instrument drift.

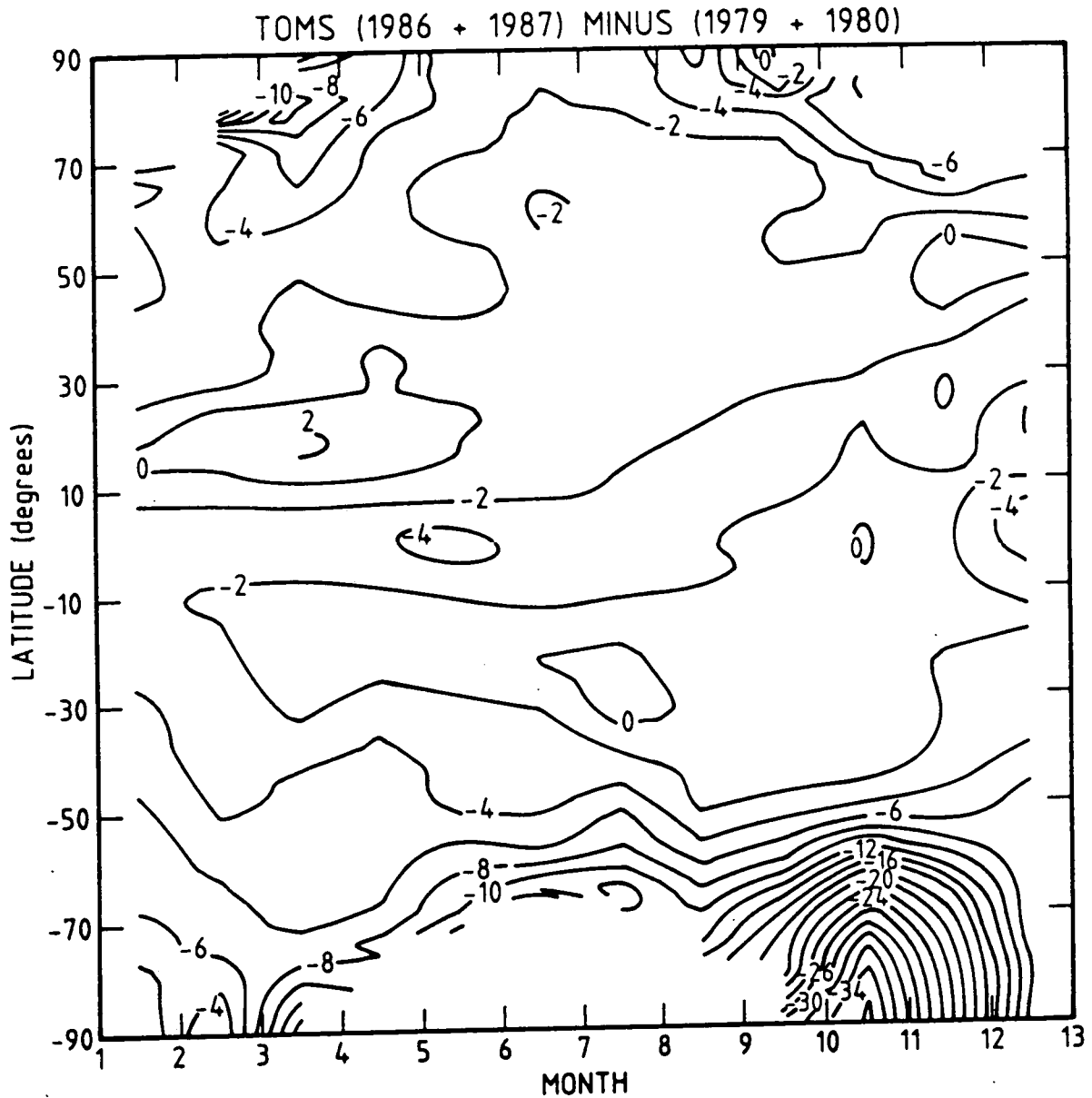


Fig. 6.- Changes in the ozone column abundance between a reference value (average of 1979 and 1980) and a final value (average of 1986 and 1987), as a function of latitude and time of the year. The changes expressed in percent are deduced from TOMS data corrected for drift using the observations from the ground-based Dobson network. The data of 2 consecutive years have been averaged to avoid any signature of the quasi-biennial oscillation observed in the atmosphere (Stolarski, personal communication).

The ozone reduction is of the order of 1-2 percent at the equator but generally increases with latitude. A clear hemispheric asymmetry is visible. The particular case of the South Pole region in September to November will be discussed in section 5.

Vertical profile

The ground-based Umkehr technique provides the vertical distribution of ozone together with the Dobson instrument at a limited number of stations and consequently with a poorer geographical coverage than ground-based total column ozone network. This method is very sensitive to aerosol loading in the stratosphere which shows strong time dependence, as it did for example in 1982 with the El Chichon eruption. The determination of an accurate trend in ozone as a function of height, based on this technique requires therefore a careful analysis.

Recent satellites, including Nimbus 7, the Stratospheric Aerosol and Gas Experiments (SAGE I and II), and the Solar Mesosphere Explorer (SME) have provided time series of observations by means of various instruments and different techniques. Ozone decreases of 20 percent near 50 km altitude from 1978 to 1985 have been reported on the basis of SBUV data for which, as indicated earlier, instrument drift is a major concern. This trend is not confirmed either by both SAGE I and II observations lasting respectively from 1979 to 1981 and from 1984 to present or by SME data from 1982 to 1986. These three satellite observations are based on very different methods (solar occultation for SAGE and limb scattered light measurement from SME). Both data sets basically show no change near 50 km. SAGE observations suggest however a possible decrease of ozone around 40 km at mid-latitudes with a maximum value of -3 ± 3 percent over the same time period. These numbers however need to be confirmed by further analyses.

Natural changes

Both the total column and the vertical distribution of ozone are affected by natural changes induced in the atmosphere by solar variation

or related to the quasi-biennial oscillations (QBO). The later have a period of about 26 months. Solar irradiance variations affect ozone with a period of 27 days (rotation period of the Sun) and 11 years (solar activity cycle)

Long-term trend ozone analysis based on observations starting in late 1978 have to take into account the ozone response to solar activity during the declining phase of solar cycle 21. According to model calculations, these changes ($- 0.20 \pm 0.13$ percent per year over the seven year period - Reinsel et al., 1988) are of the same magnitude as total ozone trends deduced from corrected satellite observations. It is therefore difficult to distinguish between anthropogenic and solar variability effects during this short period of time. Both effects are, in addition, most pronounced in the upper stratosphere near 40 km altitude.

5. ANTARCTIC OZONE

Observations

In 1985, scientists of the British Antarctic Survey (Farman et al., 1985) reported that the ozone column measured in October over the scientific station of Halley Bay (76°S, 27°W) had gradually decreased by about 40 percent between 1979 to 1984 (Fig. 7). These results were based on ground-based observations obtained by means of a Dobson spectrometer. Farman suggested that this trend could have been produced by chlorine compounds of anthropogenic origin. Subsequently, satellite data available since 1979 were reanalyzed. They showed that the ozone hole is formed in early September and lasts until November, and that it extends over essentially the entire Antarctic continent. They also confirmed the Dobson measurements (Stolarski et al, 1986) as well as other ground-based data obtained for example from both the Japanese scientific station located at Syowa (69°S, 40°E) (Chubachi and Kajiwara, 1986) and the American station at the South Pole (Komhyr et al., 1986). Finally, the satellite measurements showed that the decrease in ozone is

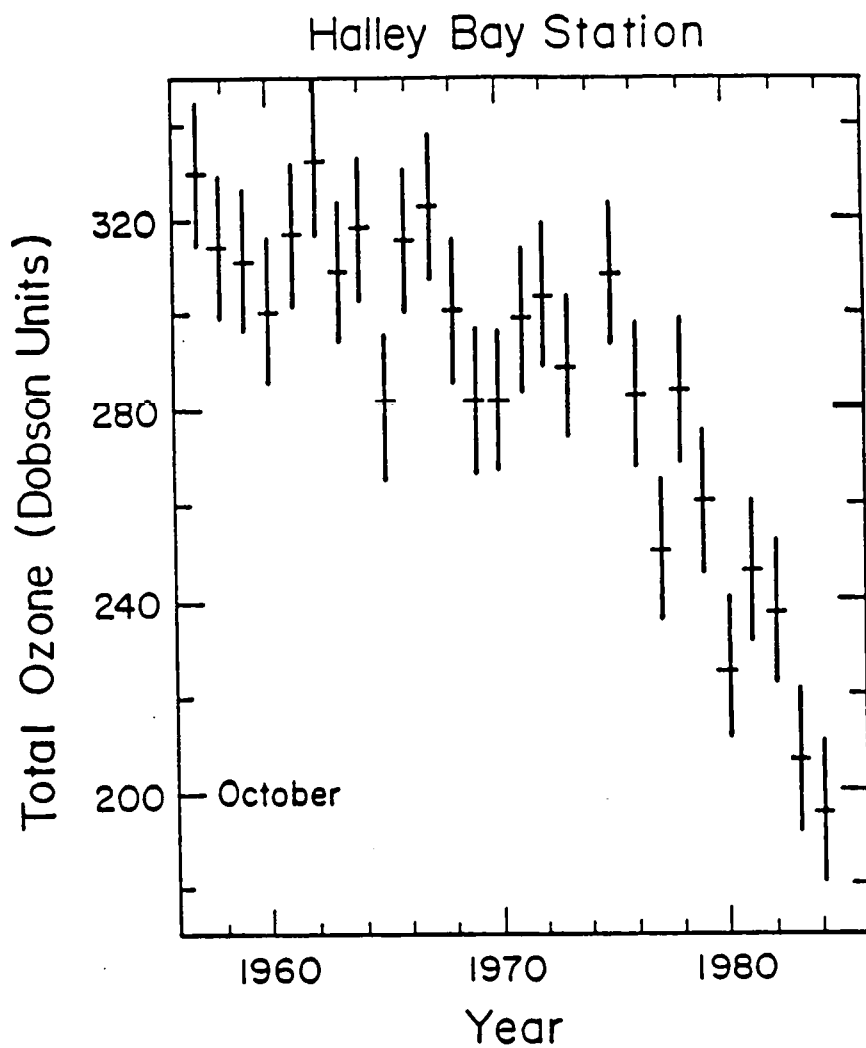


Fig. 7.- Monthly mean total ozone observed at Halley Bay (76°S, 27°W) in October, since 1957 (from Farman et al., 1985).

not entirely confined in the polar vortex but extends to latitudes near - 45°S but with smaller amplitudes. The most recent data analysis suggests that since 1979, Antarctic ozone has noticeably been perturbed all the year round (see Fig. 6).

A first campaign was organized by the United States to perform coordinated measurements at the U.S. station of McMurdo in spring 1986 and a second took place in August and September 1987 during which, in addition to the Mc Murdo's observations, measurements were taken from two airplanes flying from Punta Arenas (Chile) into the polar vortex at 12 and 18 km altitude respectively. During this campaign, the lowest value of ozone total column measured so far was recorded (about 150 Dobson).

The first campaign confirmed the recurrence of the "ozone hole". Hofmann et al (1987) reported ozone profile measurements made from McMurdo in 1986 showing that the altitude of the ozone depletion was ranging from 12 to 22 km. Unusual chlorine and nitrogen concentrations were revealed by comparison with mid-latitude conditions. For example, observations showed very low abundances in NO_2 (Mount et al, 1987; Solomon et al, 1987a) and large amounts of ClO in the lower stratosphere, near 20 km (De Zafra et al, 1987). For the first time, OC10 molecules were detected (Solomon et al, 1987b), confirming the importance of chlorine chemistry in the polar vortex.

Measurements performed during the polar night at the South pole station (Komhyr et al, 1986) do not show such a dramatic ozone depletion, which seems to confirm that solar radiation is required to produce the ozone hole. Furthermore, measurements made by Dobson (1968) at Halley Bay using the moon as a light source confirm that the total ozone abundance at this station (280-300 Dobson) remains at similar levels from late January to late October. Actually, seasonal variations were always present with a minimum at springtime and a maximum value in December but with much higher springtime minima than those observed since the end of the 70's. Other atmospheric parameters such as the

temperature also exhibit seasonal variations but there is no evidence that these affect ozone over Antarctica, even if recent observations have demonstrated a correlation between total ozone and the 50 mbar temperatures in October (Labitzke, 1987).

The second campaign confirmed the previous findings. An example of ozone profiles obtained from balloon soundings at Halley Bay is given in Figure 8. The ClO abundances at the highest latitude, around 18.5 km were found 100-500 times greater than those observed at mid-latitudes, with maximum values between 0.5 and 1 ppbv at 18.5 km and a steep decrease towards lower altitudes. The stratospheric vortex was also found to be highly denitrified as well as dehydrated. The abundance of BrO of a few pptv was observed around 18 km altitude and was decreasing at lower levels. Very low values of CFC-11 and 12, CH_3CCl_3 and N_2O were also measured.

An important feature is the apparently more frequent occurrence of stratospheric clouds in both winter polar regions observed by the SAM II experiment on board Nimbus 7 satellite since late 1978 (McCormick et al, 1982). The presence of these clouds, illustrated by the optical depth measured at 1 micron, is noticeable in June-September 1979 with similar signatures repeated each year (Fig. 9). The same data also show a noticeable minimum in October, every year. Additional measurements are needed to understand the processes involved in the formation and disappearance of these clouds. Their importance is justified by their potential role in releasing gaseous active chlorine from chlorine reservoirs.

Theories

Different theories have been suggested to explain the increasingly stronger springtime ozone minimum over Antarctica. Some of these theories invoke natural fluctuations while others suggest a perturbation effect linked to industrial activity.

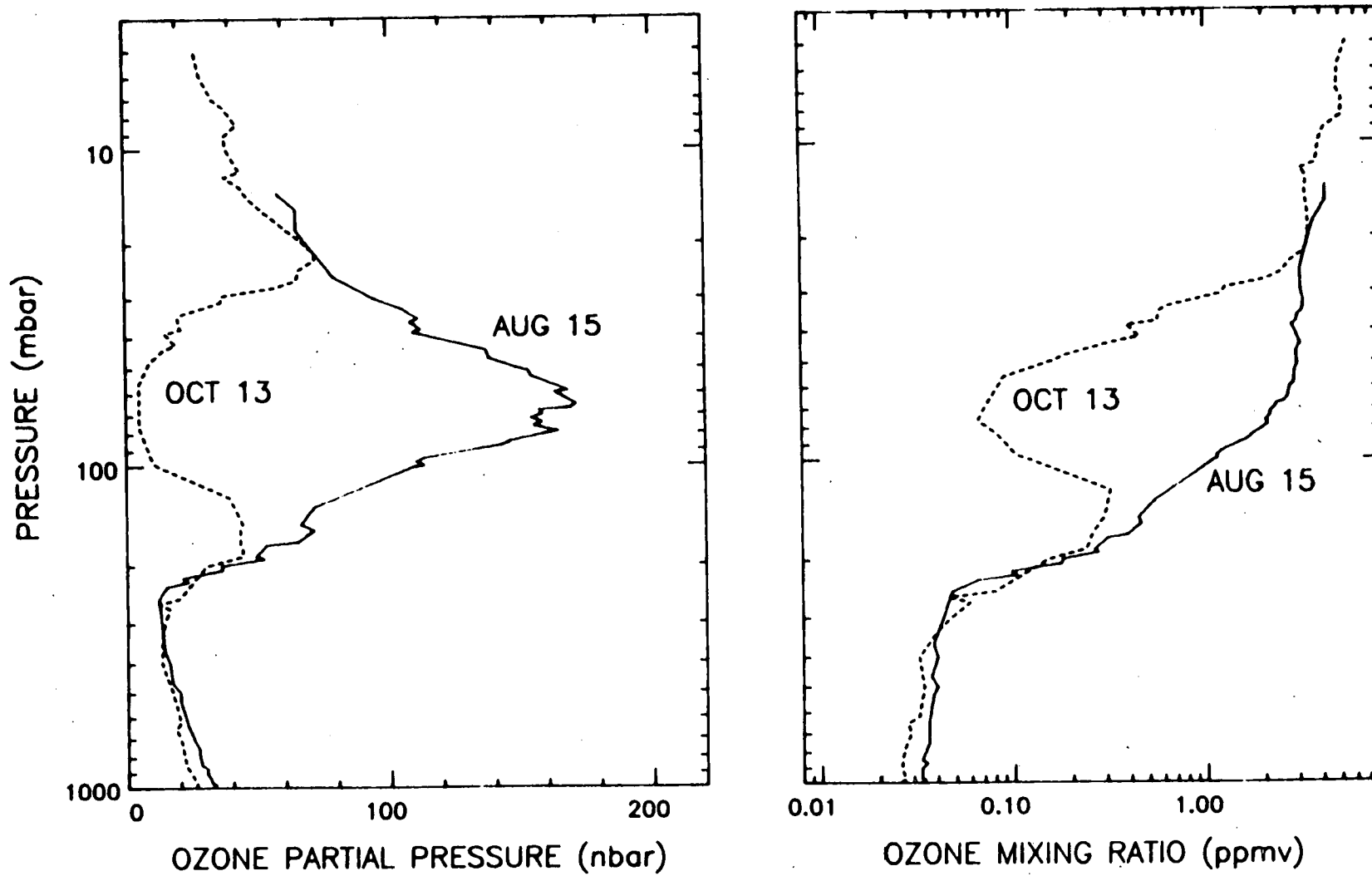


Fig. 8.- Vertical distribution of the ozone partial pressure (nbar) and volume mixing ratio observed at Halley Bay station on August 15, 1987 (high values) and October 13, 1987 (low values) respectively (Farman, personal communication, 1987).

SAM II (1 μ m) POLAR STRATOSPHERIC OPTICAL DEPTH

October 1978 - September 1986

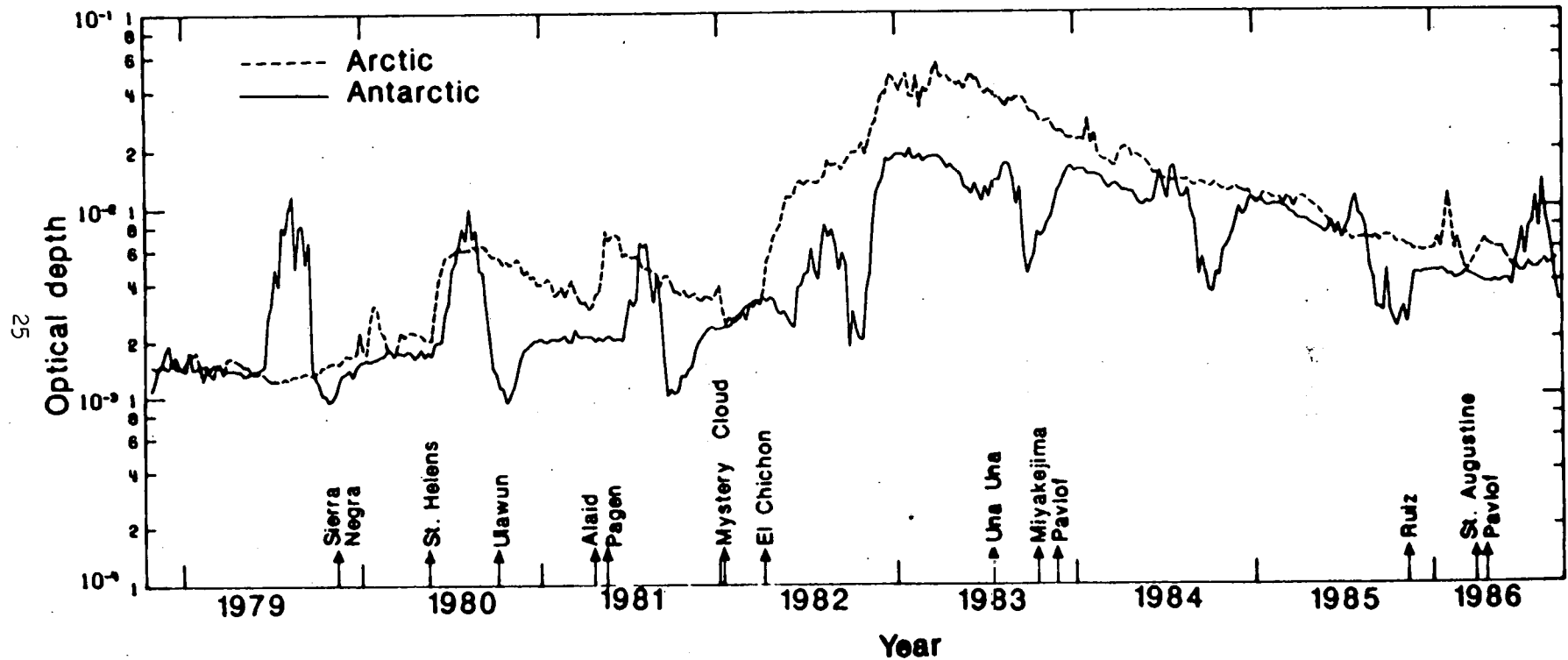


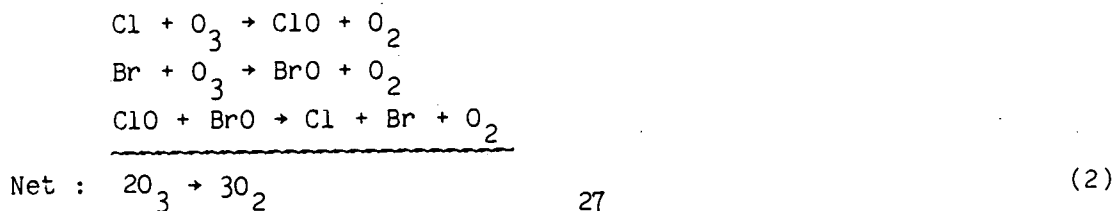
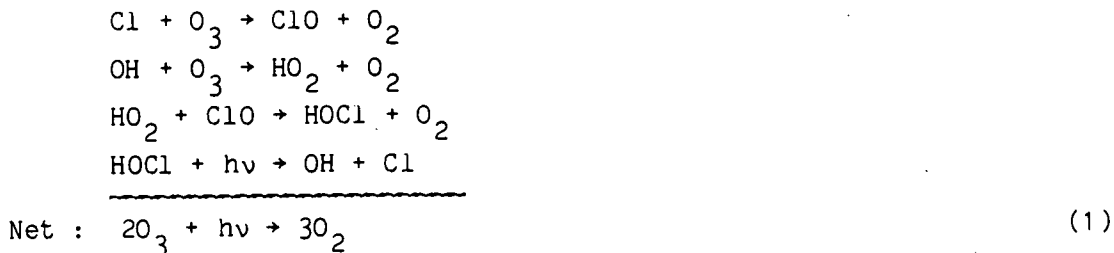
Fig. 9.- SAM II weekly-averaged Polar stratospheric optical depth at 1 μ m over the Arctic and Antarctic regions from October 1978 to September 1986 (from McCormick and Trepte, 1987).

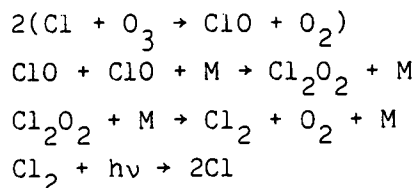
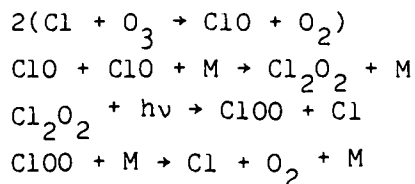
Among the first type of explanations, a theory (Tung, 1986) suggests that the strength of planetary wave activity could have been reduced over the last decade eventually as a result of changes in the sea water temperature. This effect would bring the Southern hemisphere closer to radiative equilibrium conditions with reduced poleward and downward transport of ozone and heat, the formation of upwelling after the return of the Sun at high latitude in spring and the later appearance of the final polar warming, Mahlman and Fels (1986). The ozone depletion in the lower stratosphere would then be produced by intrusion of tropospheric air which is known to be poor in ozone. This mechanism, if real, should also introduce relatively high levels of gases such as N_2O , CH_4 or CFCs which are produced at the Earth's surface and are therefore most abundant in the troposphere. The recent measurements made over Antarctica clearly show that the density of these gases in the polar vortex is particularly low. This observation suggests that the net vertical transport over the polar region is directed downwards rather than upwards in winter and early spring. Thus, dynamics cannot explain by itself the formation of an ozone hole but meteorology nevertheless plays an important role by setting up the special conditions required for some chemical processes to happen. Meteorology is also controlling the termination phase of the ozone decrease in late spring. It is also interesting to note that the August and September temperatures show little changes over the 1979-1986 period, suggesting little dynamical variation during the last decade. The cooling observed since 1979 in the lower stratosphere in October and November (after the occurrence of the ozone depletion) should be attributed, at least in part, to a reduction in the absorption of solar radiation by ozone and in the related diabatic heating.

Another theory invokes the effect of solar activity (Callis and Natarajan, 1986). Nitrogen oxides, which efficiently destroy ozone in the stratosphere when solar radiation is present, are produced in the thermosphere (above 85 km) by ionospheric processes. The production of NO_x at these levels, which is controlled by the intensity of extreme ultraviolet radiation, is highly dependent on solar activity. Large

amount of nitrogen oxides were produced during the solar maximum period in the late 70's and early 80's. If NO_x is transported downwards in the winter polar region by the general circulation, and if it reaches the lower stratosphere in fairly large amount by the end of the winter, it could efficiently destroy ozone as the Sun returns over Antarctica. Observations of different nitrogen compounds indicate however that the lower stratosphere is highly denitrified so that this theory has to be rejected. Furthermore, a recent analysis of NO_2 data indicates that, if there has been an increase in NO_2 between 1979 and 1986, it is too small to explain the dramatic change in ozone observed over this period. Finally, the most substantial ozone change in spring is recorded in a layer below 22 km or so, while the action of nitrogen oxides would be noticeable also above this level, where the ozone decrease, if any, is significantly smaller than in the lower stratosphere.

Other theories suggest that the formation of the ozone hole is related to the release in the atmosphere of increasing amounts of chlorofluorocarbons. The link between the rapid destruction of ozone below 20 km and the emissions of the CFCs is not straightforward since at these heights, active chlorine is, in principle, rapidly transformed into chlorine reservoirs such as HCl and ClONO_2 , without effect on ozone. If under special conditions prevailing in the lower stratosphere over Antarctica, these reservoirs could be destroyed by some mechanisms to be identified (and discussed hereafter), ozone could be removed in a couple of weeks by several catalytic cycles, provided that the level of ClO would reach about 1 ppbv. Possible cycles are





The second of these cycles, to be efficient over Antarctica, requires BrO to be present in the polar vortex. Observations made in September 1987 in the region of the ozone hole indicate that the amount of BrO is not larger in the vortex than outside the vortex. However observations of OClO over the station of McMurdo, Antarctica, in September 1986 and 1987, with levels 50 times larger than expected under mid-latitude conditions, suggest that Bromine monoxide could play a certain role. Indeed, if our understanding of the chlorine chemistry is correct, OClO is produced by the following reaction



and accumulates during nighttime. During daytime, OClO is photodissociated in the visible and its concentration decreases. The photochemistry of OClO is entirely different from that of ClOO. This form of chlorine oxide is believed to be produced by photodissociation of the Cl₂O₂ dimer. Anyhow, the observation of elevated levels of OClO over Antarctica provides an important indication that the amount of ClO is extremely high in the polar vortex at the end of the winter and that the inactive chlorine reservoirs are probably destroyed in late August and early September. Indeed, observations made in late September 1987 from the NASA ER-2 aircraft indicate that the mixing ratio of chlorine monoxide at 18.5 km altitude is a factor of 100 larger within the region

of very low ozone than at mid-latitudes. The measured density of ClO at 18.5 km (about 1 ppbv) is sufficiently large to explain the destruction of ozone at this height, if our current understanding of the chlorine dimer catalytical cycles (3) and (4) is correct. The abundance of ClO seems to decrease rapidly below 18 km, suggesting that other processes (including a vertical downward transport) could be involved.

As indicated earlier, the chlorine theory requires significant amounts of active chlorine to be liberated from the reservoirs (HCl and ClONO₂). It also requires low levels of NO_x to avoid the transformation of ClO into ClONO₂. Several ways to destroy the chlorine reservoirs have been suggested. These explanations are constrained by the fact that the proposed mechanism should operate only in early spring, primarily in the lower stratosphere over Antarctica as opposed to other altitudes, latitudes and time of the year, i.e., in a stable region with temperatures lower than about 200 K. Crutzen and Arnold (1986) have noted that the condensation of nitric acid (HNO₃) could condense into small particles, as soon as the temperature of the lower stratosphere decreases below about 205 K. Ice crystals can start forming only below 191 K. A polar stratospheric haze with small HNO₃.H₂O and HNO₃.3H₂O particles should thus be formed in the lower stratosphere at temperatures between 205 and 191 K, while, below this latter temperature, together with HNO₃, H₂O and HCl would also freeze. The largest particles, which form the so-called polar stratospheric clouds (PSCs), are expected to be removed from the stratosphere by gravitational sedimentation. This mechanism may contribute to remove NO_x and H₂O from the lower stratosphere (if N₂O₅ is converted into HNO₃ by heterogeneous reactions on the surface of ice particles). As nitric acid is removed from the gas phase, the abundance of the OH radicals, which are destroyed essentially by HNO₃ in the lower stratosphere, is expected to be significantly enhanced. OH is very efficient in destroying HCl and producing active chlorine. When HNO₃ is again released to the gas phase by evaporation at higher temperature, active chlorine is transformed back into HCl and ClONO₂ and the ozone decay slows down. Figure 10 shows a model simulation of density of the chemical species at 18 km from

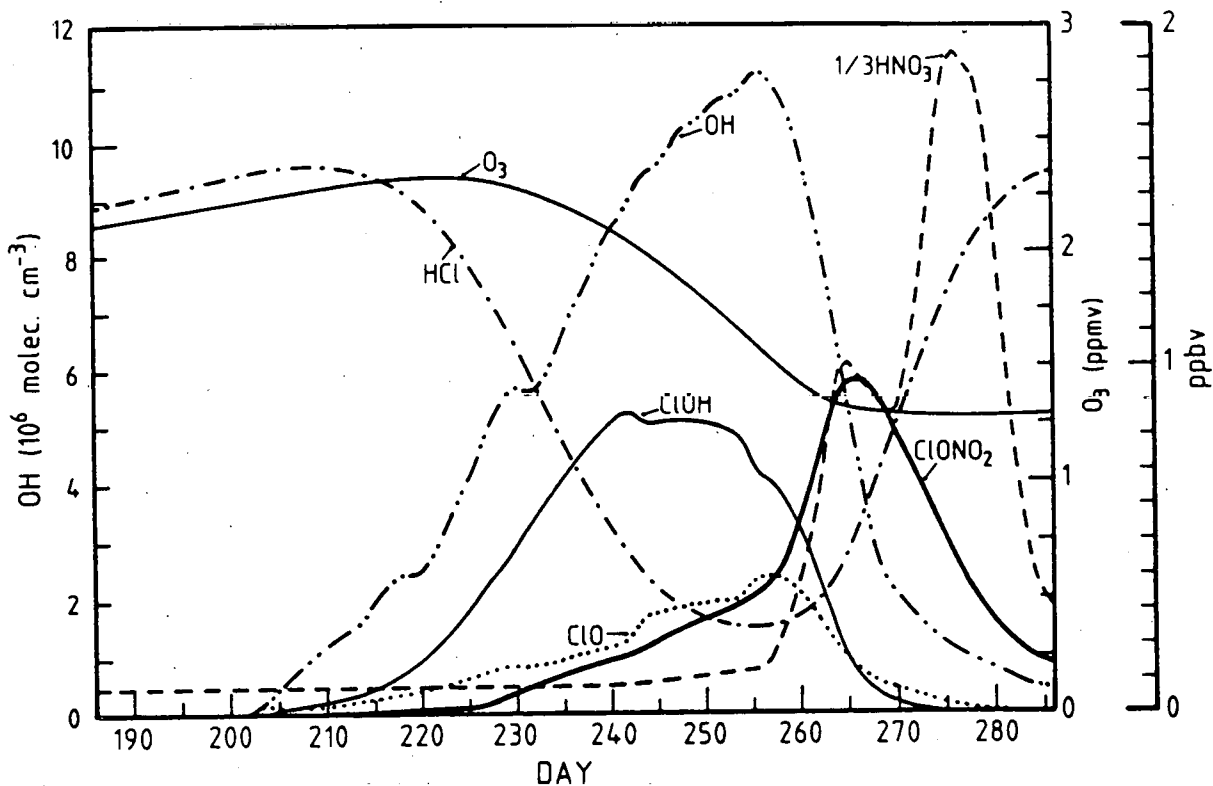


Fig.10.- Chemical developments at 18 km from day 185 (July, 5) to day 285 (October, 15) in 1986. Left hand scale : OH concentrations in units of 10^6 molecules cm^{-3} ; right hand scales : volume mixing ratios of O_3 (ppmv) and for ClO, HNO_3 , ClONO_2 , ClOH and HCl (ppbv) for the temperature sequence measured by Hofmann et al (1987) at McMurdo (78°S) in Antarctica. The small bumps in the curves indicate the times when daylight hours change discontinuously in the program (from Crutzen et al, 1988).

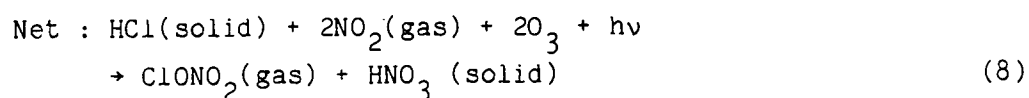
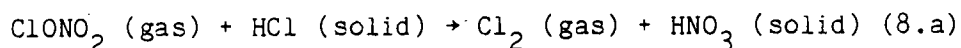
July, 5 to October, 15, 1986 based on the theory expressed by Crutzen and Arnold (Crutzen et al., 1988). The significant increase in OH to a density as high as 10^7 cm^{-3} and the resulting decrease in HCl and ozone are clearly visible. Also, the enhancement in the ClO and HOCl abundance can be noticed. A detailed quantitative study of this mechanism is required to establish if it can entirely explain the observed springtime polar ozone trend and if it would account for the rather sudden appearance of the ozone hole after 1979.

Solomon et al. (1986) were the first to point out that the formation of the ozone hole in spring could be associated with the presence of polar stratospheric clouds which are produced and observed in winter (McCormick, 1987). They suggested that the following reactions occur heterogeneously on the surfaces of ice particles :



The efficiency of these reactions however are expected to be small since the probability for two gaseous phase molecules to collide on an aerosol surface is low. Molina et al. (1987) as well as Wofsy et al. (1988) have shown that the reaction of atmospheric HCl with ClONO_2 is considerably enhanced in the presence of ice particles. In fact, at low temperature, HCl molecules dissolve in ice crystals and the probability for a reaction of gas phase ClONO_2 with dissolved HCl to occur at the surface of the solid particles is of the order of 5 to 10 percent at about 200 K for an HCl mole fraction between 3.5×10^{-3} and 1×10^{-2} . Nitric acid which is produced by this reaction, remains in the condensed phase (so that this process contribute to the denitrification of the stratosphere), while Cl_2 is released in the gas phase on a time scale of a few milliseconds. The chlorine molecule is then photodissociated into 2 atoms which react immediately with ozone molecules. The reaction of ClONO_2 with ice (H_2O) has a collision efficiency of about 2 percent at 200 K and produces HOCl in the gas phase on a time scale of minutes.

Wofsy et al. (1988) have shown that solid solutions of HCl in H₂O ice with a mole fraction of (2.0 - 3.5) 10⁻² will form in the stratosphere between 193 and 190 K and that condensation of small quantities of water vapor leads to nearly complete removal of HCl (and HNO₃) from the gas phase. The following cycle will transform HCl into ClONO₂ and NO₂ (in the gas phase) into HNO₃ (in the condensed phase).



So far, this mechanism has little effect on ozone. However, if the initial HCl number density (before onset of condensation) is equal or larger than half of the NO_x density (NO_x being the sum of nitrogen oxides readily converted to NO₂), the last reaction in this cycle (reaction 8.d) will no more be possible due to exhaustion of NO_x. At this stage, ClO accumulates and ozone is being efficiently destroyed by cycles (1) to (4). Thus, during polar night, when stratospheric clouds are present, preexisting HCl condenses into ice particles and reaction (8.a) depletes gas phase ClONO₂, producing gaseous Cl₂. As the Sun returns over Antarctica, Cl₂ is photolyzed and NO_x depleted, producing first ClONO₂ molecules and later ClO radicals. It is interesting to note that the initial density of HCl is a key factor in this scheme. According to Wofsy et al., the sudden onset of the Antarctic ozone depletion in the late 1970's could reflect the growth of HCl density beyond a threshold equal to half the NO_x abundance.

In conclusion, the formation of an ozone hole in spring over Antarctica seems to be closely linked to the presence of polar stratospheric clouds. These are observed in the altitude range where a large fraction (eventually more than 90 percent) of ozone is depleted in

September. The details of the clouds formation are not yet fully understood and an extensive program in the area of heterogeneous chemistry is urgently needed. Dynamics creates the conditions for the winter temperature to become sufficiently low for clouds to be produced. The polar vortex is quasi isolated from the rest of the stratosphere. Although the ozone hole seems to be particular to conditions prevailing near the South pole, it is important to determine if the processes involved could play a role in other regions of the world and if large ozone reductions could be produced at present or in the future, for example, in the Arctic region. It is also necessary to determine if the region of large ozone reduction could become wider or deeper and to what extent the air with low ozone could be diluted towards lower latitudes and affect the entire Southern hemisphere. If the theory in which the ozone hole is linked to increasing abundances of chlorine is proved to be correct, it can be stated that the springtime hole over Antarctica should be persistent over several decades, even if the release in the atmosphere of chlorofluorocarbons was dramatically reduced. This is a direct consequence of the long atmospheric lifetime (about 100 years) of the CFCs. On the other hand, the ozone column abundance in the hole is not expected to further decrease in a substantial way because in the region, where the depletion mechanisms are important, almost all of the ozone is already destroyed each spring. It is nevertheless crucial to determine if the extent in altitude and latitude of the PSCs remains unchanged from year to year.

6. CONCLUSIONS

The ozone abundance in the atmosphere is predicted to change as a result of increasing concentrations of trace gas such as methane, nitrous oxide, carbon dioxide and the chlorofluorocarbons. Model calculations show that stratospheric ozone and temperature should be significantly reduced in the future if present growth in the abundance of these source gases, mainly as a result of anthropogenic activity, is extrapolated to the next century. Ozone and temperature in the troposphere are expected to increase. Analyses of data provided by ground-

based instruments indicate that total ozone has decreased by as much as 2 percent since 1970. During the 1979-1986 period, during which satellite measurements were made on a continuous basis, the observed ozone reduction in the upper stratosphere by anthropogenic effect is believed to be comparable to the ozone decrease expected from the reduction in solar activity over this period. Quantitative values are subject to controversy because of instrument degradation, leading to large uncertainties in current observations.

Over the Antarctic continent, the springtime ozone column has been reduced by about 50 percent since 1979. The processes leading to this ozone hole are not yet fully understood. Recent measurements however suggest that, in the presence of polar stratospheric clouds, active chlorine is released in the gas phase and destroys efficiently ozone in the lower stratosphere.

The protection of the ozone layer requires limitations in the emission of the chlorofluorocarbons. Even the recent protocol on the protection of the ozone layer, signed in Montreal, Canada, in September 1987 is applied by most countries, the amount of active chlorine in the stratosphere should reach 6 to 7 ppbv in year 2050 as opposed to 2.5 to 3.0 ppbv at present. Therefore despite regulations recently adopted, ozone and temperature are expected to be modified in the future, as a result of human activities.

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