

Seventy years of ozone research

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Introduction

Seventy years ago Fabry and Buisson¹ published their measurements which proved beyond doubt that the short wavelength cut-off of the solar spectrum in the UV-B region was the unique consequence of the absorption by atmospheric ozone, and, at the same time, they provided a method to observe the total amount of ozone in the atmosphere quantitatively. This marked the starting point of a development which moved atmospheric ozone after many varying views to the centre of our present concerns about the destructive influences of man's activities on his environment.

Discovery of the basic properties of the ozone layer

In the same decade Dobson² developed the instrument which opened the possibility for systematic observations of total ozone, the Dobson spectrophotometer, which, after a full redesign³ and a further improvement, has stayed the basic tool for such observations until the present day. Only recently another instrument, using modern technology, the fully automated Brewer⁴ spectrophotometer, has come into regular use at a number of stations. With a small network which Dobson organized in 1926 he detected⁵⁻⁷ the high latitude maximum and the tropical minimum of total ozone and the pronounced seasonal variation in middle and high latitudes with a spring maximum and a fall minimum. He also found relatively rapid short time variations connected with weather.

In the early thirties a relatively reliable determination of the vertical centre of gravity of the ozone layer became possible by ground-based zenith sky light measurements with the Dobson spectrophotometer, using the so-called Umkehr effect, discovered by Götz⁸. Applying rather laborious calculations Götz *et al.*⁹ showed that the ozone maximum in mid-latitudes was situated between 20 and 25 km, in contrast to previous

assumptions which put it at around 50 km, at the height of the warm layer, just detected from the anomalous propagation of sound¹⁰ and the observation of shooting stars¹¹. This result was confirmed in the same year by Regener and Regener¹² who flew a small automatic spectrograph on a radiosonde balloon to 30 km. Systematic observations of the vertical distribution of atmospheric ozone were, however, not available before the late fifties and early sixties.

In 1930 Chapman¹³ explained by a simple photochemical theory, the existence of a stratospheric ozone layer, exhibiting a sharp maximum, relying on the photodissociation of molecular oxygen by wavelengths shorter than 242 nm. In the forties this theory was put on a quantitative basis by Dütsch¹⁴, Schröer¹⁵ and Craig¹⁶. It was found that the observed ozone distribution was produced by simultaneous action of photochemical and transport processes, the latter dominating in the lower part of the stratosphere where the photochemical relaxation time was long. Within the accuracy with which the ozone distribution, especially in the vertical, and the photochemical parameters were known, rather satisfactory agreement between theory and observation could be obtained. It was realized that, at least with a further improved knowledge of its distribution, ozone could be used as a tracer for stratospheric circulation, while it became, however, clear that in contrast to early speculation at the time when Dobson² started his research, there was no direct influence of ozone on weather.

Advances in the observational knowledge

The discovery that ozone was a useful tracer led to a new effort on the observational side, particularly promoted by Dobson, using the IGY which initiated a marked forward step in ozone measurements². The considerable extension of the Dobson spectrophotometer network showed, among other things, a pro-

nounced asymmetry between the hemispheres in the high latitude total ozone regime, indicating differences in stratospheric circulation (a mid-latitude spring maximum in the Southern hemisphere instead of the polar maximum in the North, Figure 1). A considerable longitude dependence of total ozone was also detected with maxima over Eastern North America and East Asia and to a lesser extent over Central Europe, all of them connected to quasi-stationary troughs in the upper tropospheric flow, in agreement with the already known transient ozone-weather relationship.

In the late fifties and early sixties also more or less regular measurements of the vertical ozone distribution were started. A world network on the basis of the Umkehr method evolved, with centralized profile retrieval at the World Ozone Data Center of WMO, established at Toronto, Canada, where the computer method developed by Mateer and Dütsch¹⁷ was employed. These data showed clearly¹⁸ that the high latitude spring maximum of the total amount was largely a consequence of the seasonal variation of ozone in the lower stratosphere, i.e. at the level of the ozone maximum, while low concentrations at these altitudes were found over the tropics. In the middle stratosphere, however, a tropical maximum was shown all the year round, and above this, in the upper stratosphere, a tropical minimum was again observed (Figure 2a,b). These findings were later largely confirmed by more accurate measurements using direct methods and satellite observations (Figure 2c,d). It was further demonstrated that not only measurements in the UV-

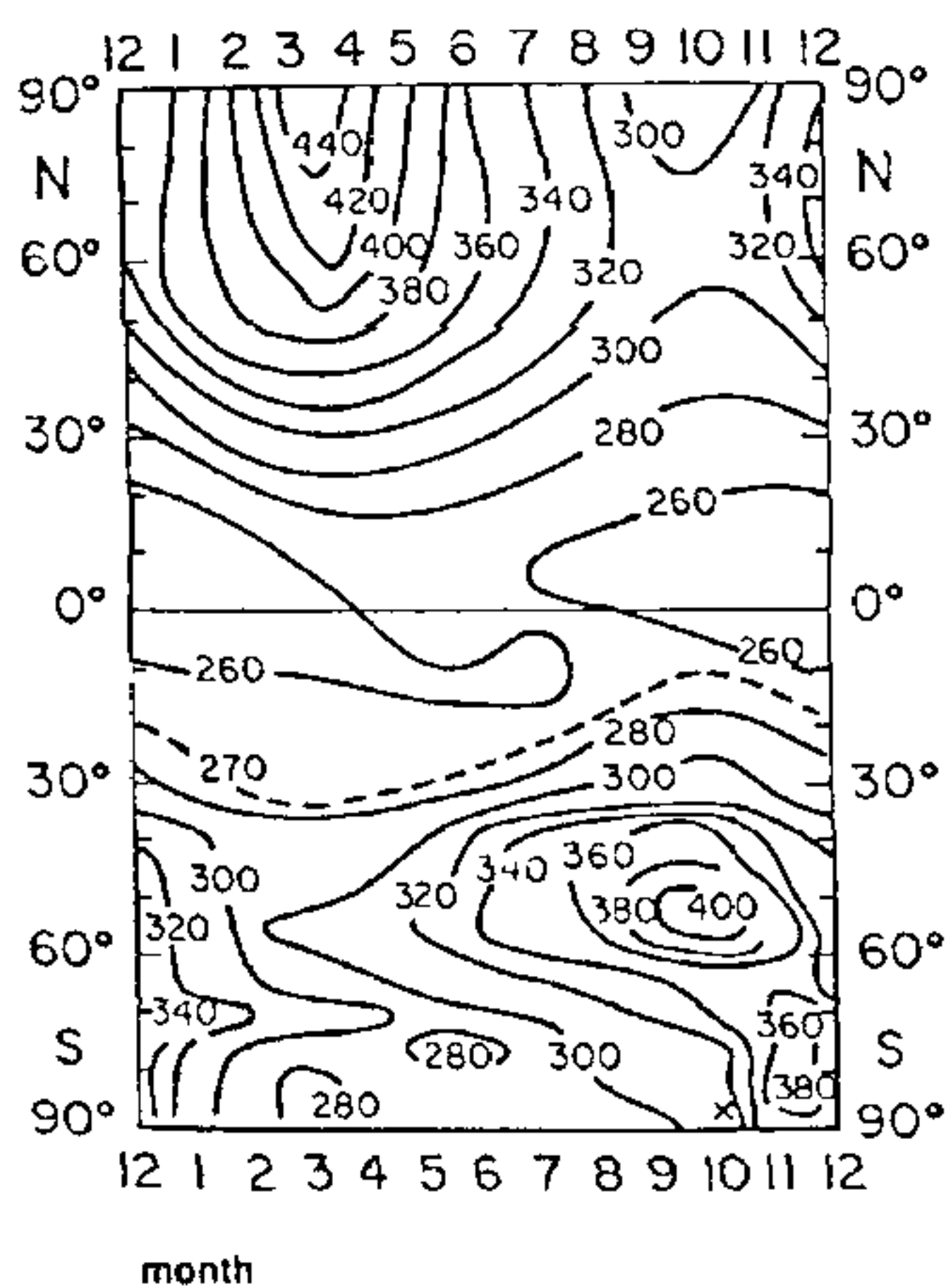


Figure 1. Total ozone as a function of latitude and season as known around 1965. Isolines in Dobson Units (DU) = 10^{-3} cm pure ozone at NTP.

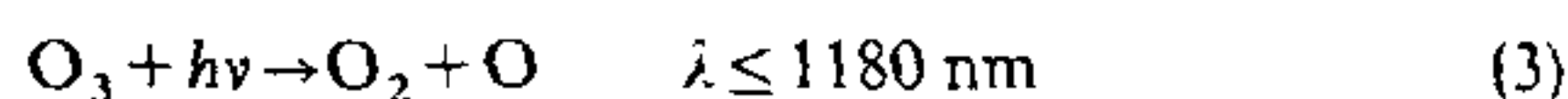
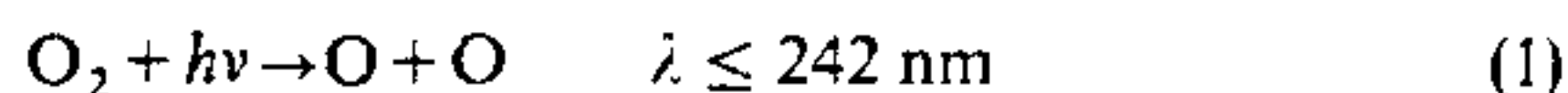
spectrum, but also in the infrared spectrum taken from the ground could yield information on the vertical ozone distributions¹⁹.

Balloon-borne ozone sondes came also into more or less regular use: optical²⁰, chemiluminescent²¹ and electrochemical instruments²²⁻²⁴. Only the latter has survived until the present and thus provide the basis for trend calculations. Also observations with rocket-borne ozone sondes²⁵ became possible, extending the measurements into the mesosphere.

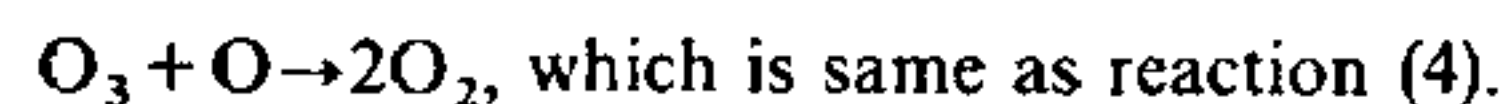
The improved knowledge of the ozone distribution, particularly in the vertical, together with better laboratory data on chemical kinetics and absorption coefficients, as well as improved knowledge of the solar UV-spectrum indicated that results from the classical Chapman photochemistry could not anymore be brought into full agreement with the observations. New ideas about much more involved chemical processes in the stratosphere, which began to evolve in the mid-sixties and developed further until the present, were therefore easily accepted. They gave the ozone research a new dimension because they indicated possible destructive anthropogenic influences on the ozone layer.

The modern photochemical theory

The simple Chapman model



was successively complemented by ozone-destroying catalytic processes, mainly produced by the radical groups HO_x (ref. 26), NO_x (ref. 27, 28) and ClO_x (ref. 29), as e.g.



Each such cycle accelerates reaction (4).

The radicals are produced, according to Figure 3, from the so-called source gases, which are rather stable molecules, such as H₂O, N₂O, chlorofluorocarbons (CFCs), CH₃Cl, CH₄ and others, by reactions with electronically excited O(¹D) atoms which are a product of reaction 3, if $\lambda \leq 310$ nm, by reactions with the OH radical or through photodissociation by UV radiation, mostly of the same wavelengths which

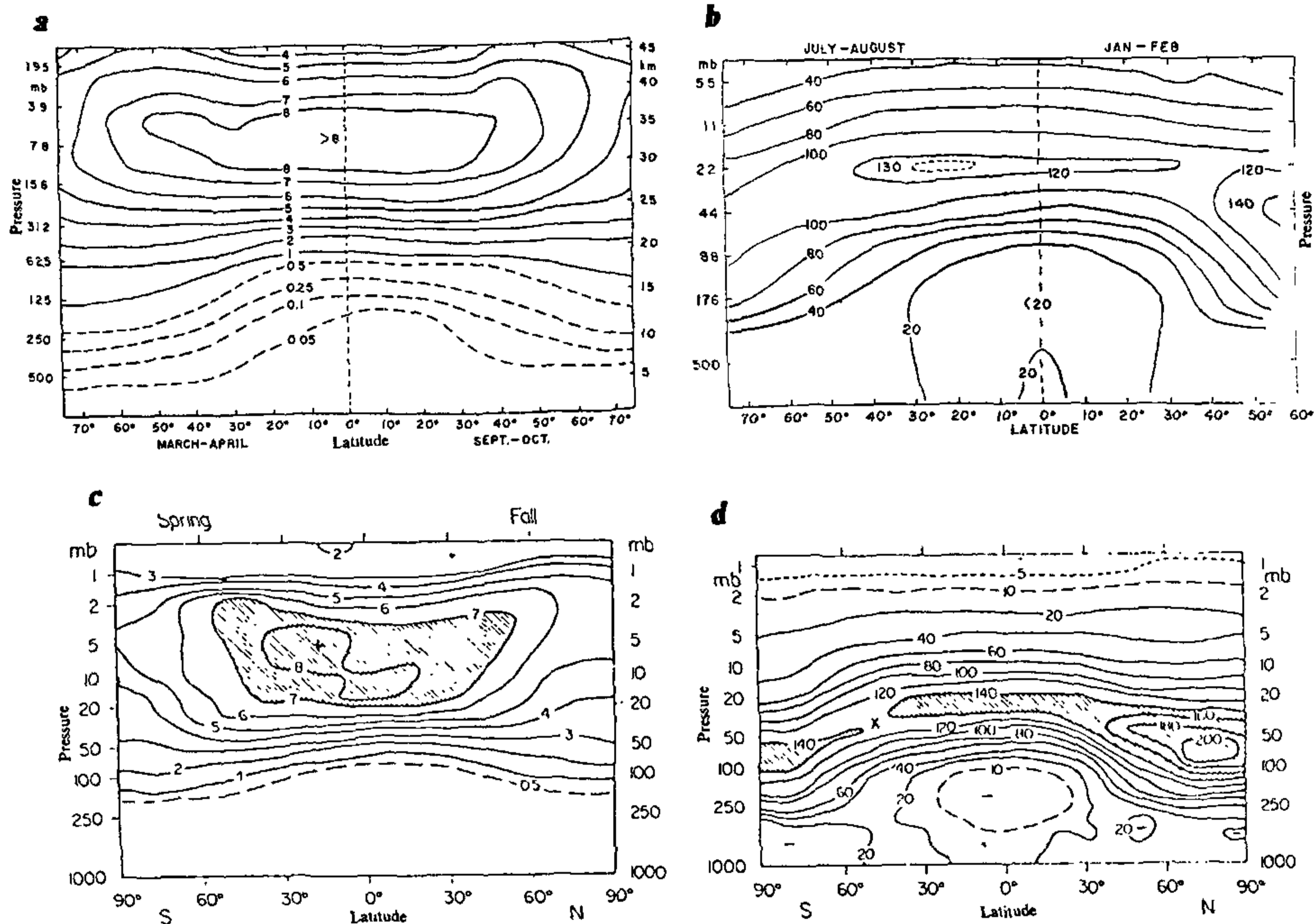
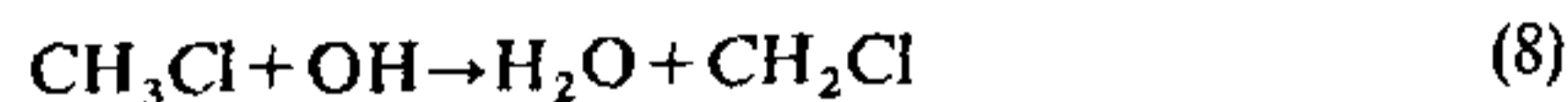


Figure 2. *a*, Latitude/height cross section of the ozone/air mixing ratio in ppmV around the equinoxes for the Northern hemisphere (from Umkehr observations before 1964). *b*, Latitude/height cross section of ozone partial pressure in nanobar (nb) in the Northern hemisphere in late winter/late summer (from Umkehr observations before 1964). *c*, Latitude/height cross section of ozone/air mixing ratio in ppmV around the equinoxes in both hemispheres based on electrochemical sonde data below 10 mb and on Umkehr and one year of BUV-satellite observations above. *d*, Latitude/height cross section of ozone partial pressure in nb for both hemispheres in February from the same data set as in Figure 2c.

yield ozone via reaction 1 ($\lambda \approx 210$ nm). Examples are:



followed by the rapid decay of the radical CH_2Cl , producing a free Cl atom



also followed by further disintegration of the radical CFCl_2 , producing more chlorine atoms. These reactions occur predominantly in the stratosphere, some of them already in the troposphere as e.g. reactions 7 and 8. The radical production from the source gases is, with the exception of the HO_x group, irreversible; however, the radicals are transferred, mostly by reactions among each other, into molecules of a rather reactive type,

such as e.g. HNO_3 , HCl , ClONO_2 , but which do not destroy ozone; these processes are reversible and lead to an equilibrium state between the radicals and the molecules, which are called reservoir species (Figure 3), because radicals are easily produced from them. There are no further reactions removing reservoir species and radicals from the stratosphere, and there is no cleaning of this layer by precipitation processes; therefore, unlimited growth of radical and reservoir gas concentrations is only prevented by the return of stratospheric air parcels to the troposphere where these substances are washed out (Figure 3). All this means that a calculation of the stratospheric ozone content is only possible with rather involved computer models combining a complex chemistry (more than 100 simultaneous reactions) with rather involved transport processes: the source gases are entering the stratosphere through the tropical tropopause and are carried polewards while the described chemical processes are going on.

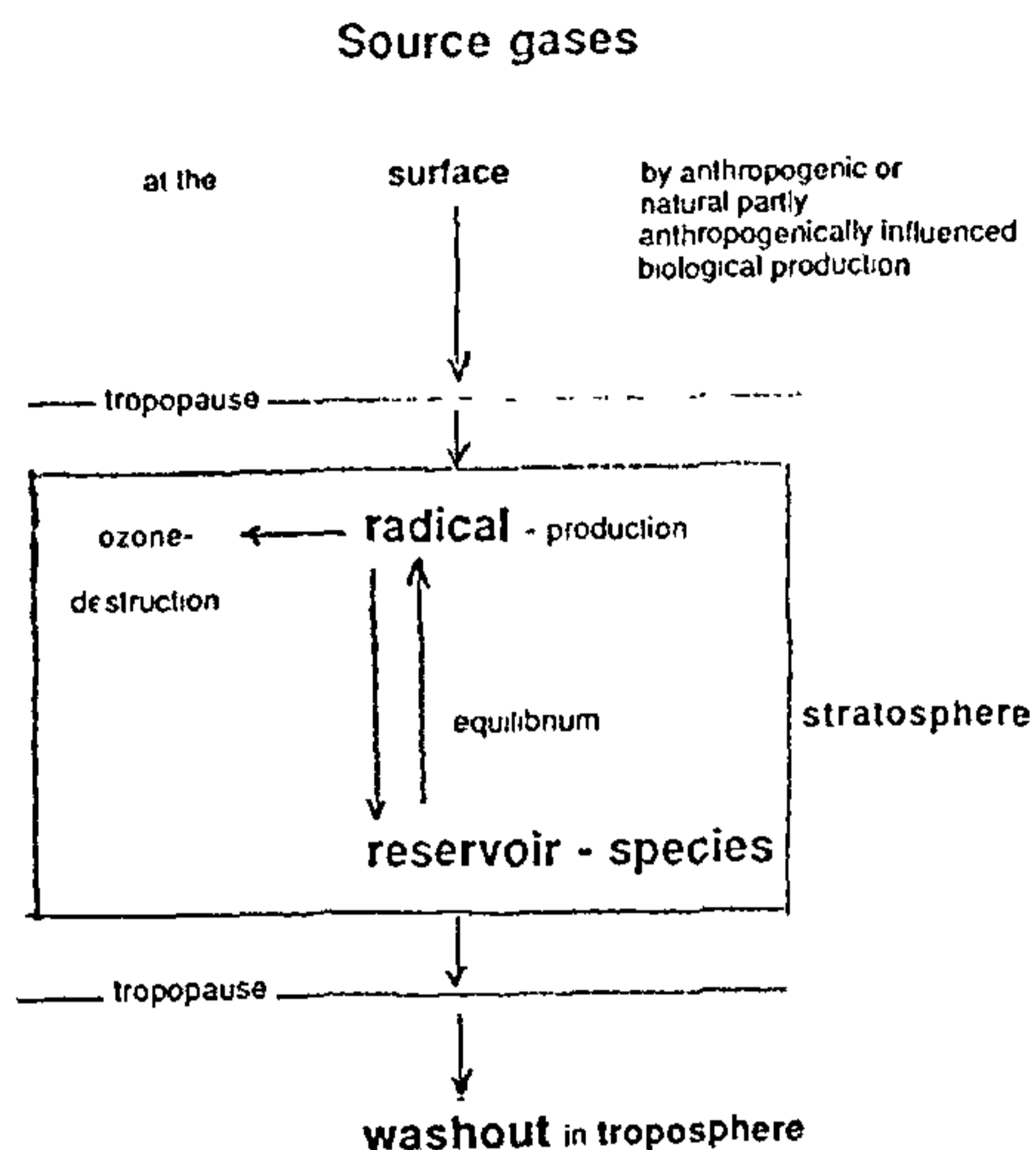


Figure 3. Scheme of the modern photochemistry coupled with transport processes.

The possibility of anthropogenic damage to the ozone layer

While most of the source gases are of natural origin, many of them produced by biological processes, some are of purely anthropogenic nature as e.g. the CFCs; also the biological production is, to various extents, influenced by man. By this the concentration of ozone-active radicals is increased. It was thus realized that there is a growing probability of damage to the ozone layer by man's activities. Already in the early seventies there

was much concern about the consequences of the NO_x -radical-output into the stratosphere by supersonic transport^{30,31}. Since the discovery of the CFC-problem³² in the mid-seventies, ozone destruction by active chlorine (ClO_x) has become the dominating question. While the knowledge on the involved chemistry was further developing, the model predictions were strongly fluctuating³³ (Figure 4a). Considering also all the other anthropogenically produced changes in the atmospheric trace gas system, e.g. growing N_2O and CH_4 -content and rising CO_2 -level, leading to a cooling of the stratosphere, the forecasts seemed finally to settle on a relatively low-loss value for total ozone (Figure 4b). Therefore the concerns calmed somewhat down although considerable changes in the vertical distribution of ozone were predicted³⁴ (Figure 4c).

Satellite observations

The problem of a possibly harmful anthropogenic impact on the ozone layer called for an improved observational watch on a global scale. This became just at that time possible by the use of satellite platforms, applying various types of techniques for observing ozone. Quite successful was—and still is—the measurement of the UV-radiation, backscattered by the atmosphere (BUV-experiment³⁵ on Nimbus 4 and SBUV and TOMS³⁶ on Nimbus 7, the latter has now been working for 13 years). From these observations the total amount of ozone and also the vertical distribution can be derived, using methods similar to those applied in the Umkehr retrieval. While such measurements are confined to the sunlit part of the atmosphere, the use of the infrared upward flux from the atmosphere (TOVS-experiment^{37,38} on NOAA 10 and other satellites) can also yield total ozone during the polar night, which has become of particular interest.

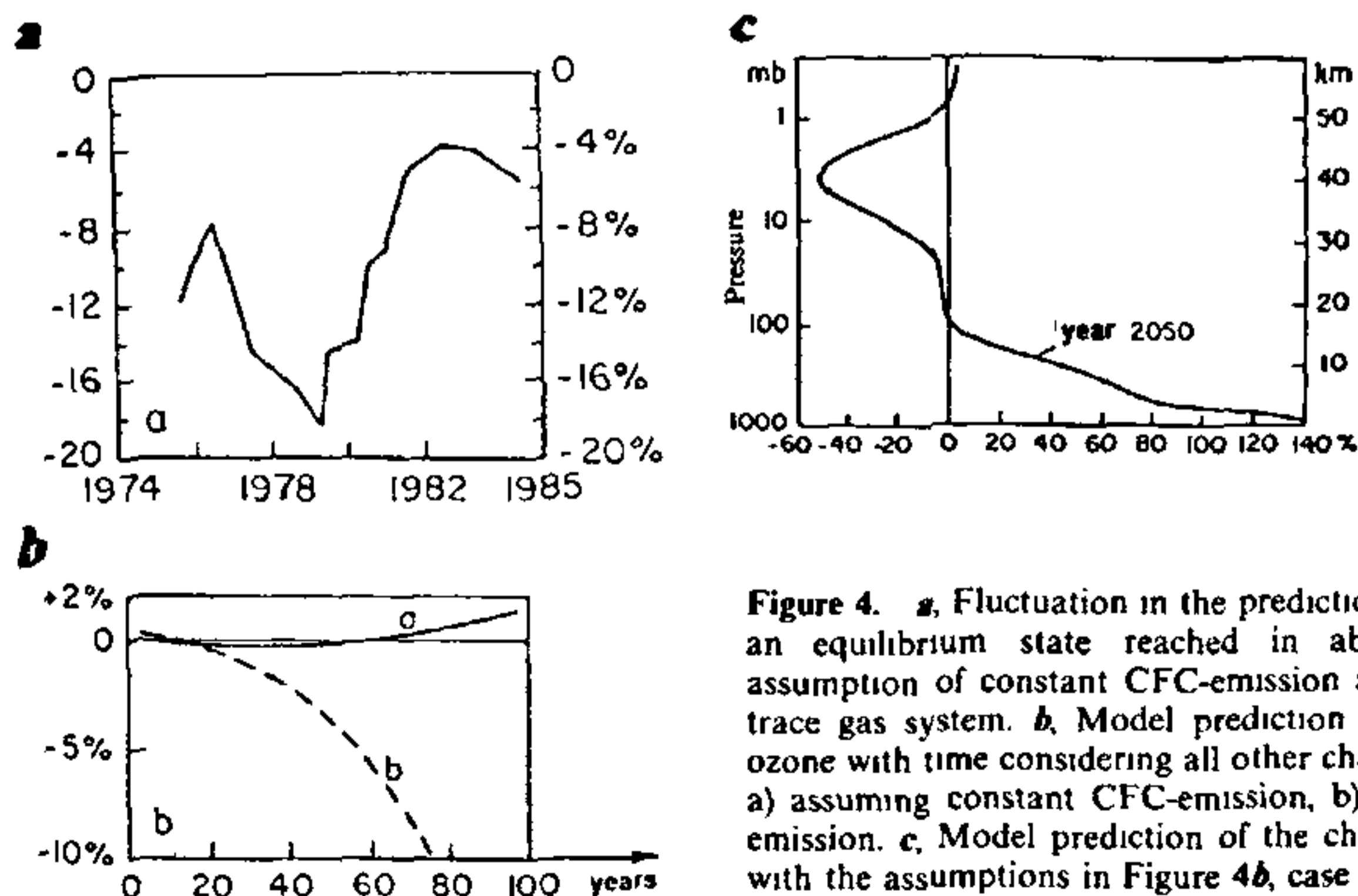


Figure 4. a, Fluctuation in the prediction of total ozone depletion in an equilibrium state reached in about 100 years under the assumption of constant CFC-emission and no other changes in the trace gas system. b, Model prediction of the development of total ozone with time considering all other changes in the trace gas system, a) assuming constant CFC-emission, b) 3% annual increase of this emission. c, Model prediction of the changes in vertical distribution with the assumptions in Figure 4b, case a.

Vertical distributions with a better resolution are provided by the SAGE I and SAGE II experiment³⁹ flown on the Dedicated Explorer Mission and the Earth Radiation Budget Satellite (ERBS) respectively, looking at the sun, rising or setting over the horizon; however, this is limited to a much reduced data coverage. Using infrared emission from the horizon a similarly good vertical resolution could be obtained with a much better data coverage by the LIMS-experiment⁴⁰ on Nimbus 7; the liquid helium-cooled sensor, however, reduced the lifetime to six months. Both, SAGE and LIMS also allow the measurement of the global distribution and its dependence on season of a number of other trace substances—source gases, NO_x and particles—thus giving additional insight into chemical and transport processes. Experiments on the SME satellite⁴¹ yielded together with measurements on the distribution of ozone and other trace gases in the stratosphere and mesosphere also information on the UV spectrum of the sun and its variability.

The 'ozone hole' and the impact of heterogeneous reactions

The results obtained in the early eighties with the best then available models had eased the concerns about the chlorine problem somewhat until in 1985 Farman *et al.*⁴² published the almost-30-year record of total ozone measured by the British Antarctic Survey at Halley Bay (76° S). They found that after a foregoing slow decline, superimposed by the same strong year-to-year fluctuation as known from the Northern hemisphere, the total ozone content in the Antarctic spring had rapidly decreased to very low values since the late seventies (Figure 5), a result which was subsequently confirmed

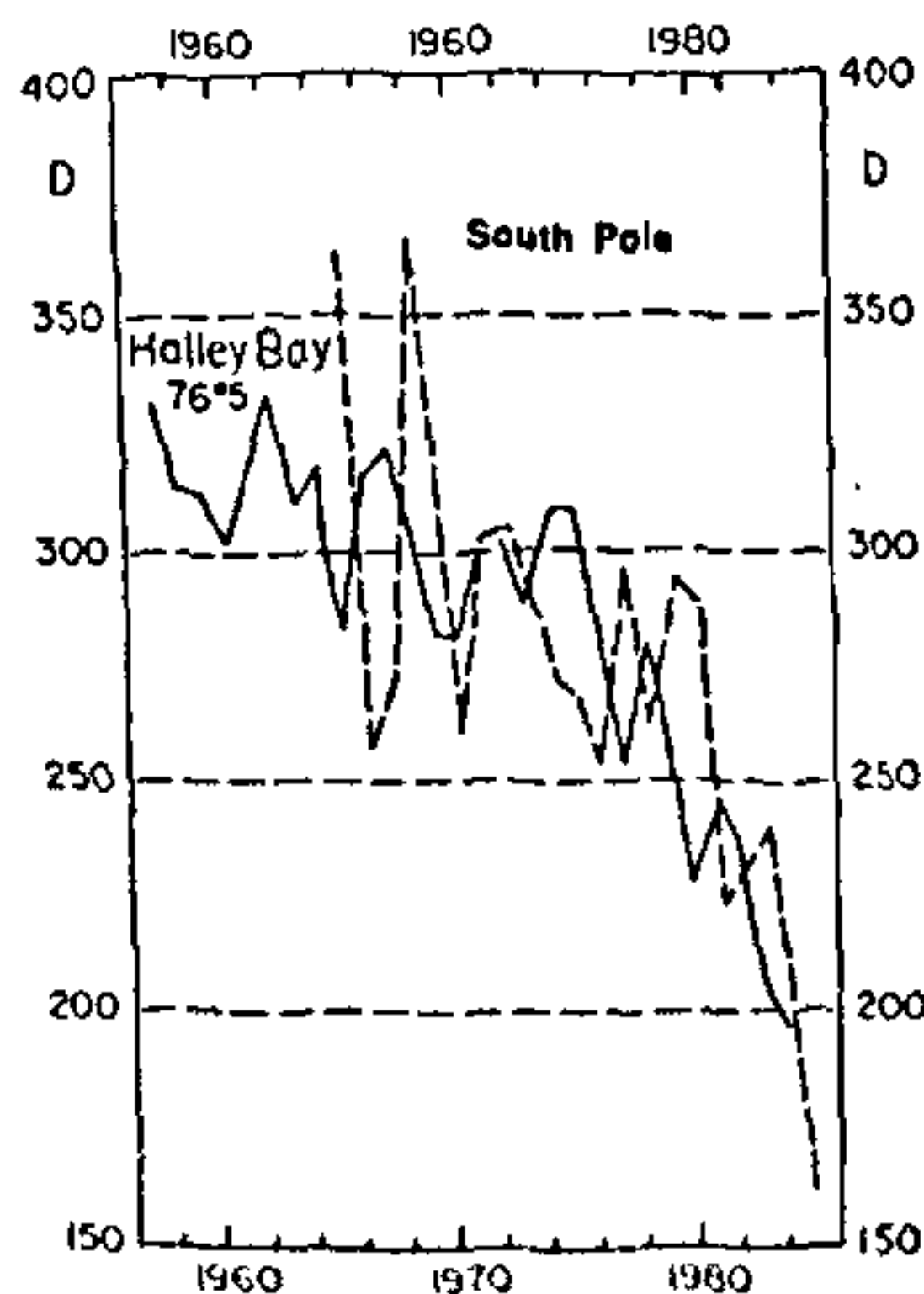


Figure 5. Development of the Antarctic ozone hole, full line record at Halley Bay⁴², dashed line South Pole⁴¹.

by the observational record of the South pole station⁴³ and by satellite measurements⁴⁴ (Figure 6). The phenomenon was, not quite correctly, called the Antarctic 'ozone hole'. It was found that this 'hole' formed each year after the return of the sun at the end of the polar night. Farman *et al.*⁴² had indicated that the development of the phenomenon occurred parallel to the increase of the atmospheric chlorine content, produced by the emission of CFCs, and had thus suggested that mankind was responsible. Measurements of the vertical distribution within the ozone hole (Figure 7) shed first some doubt on this explanation, because the main ozone decline was found in the lower stratosphere. According to model calculations (Figure 4c), ozone destruction by the catalytic ClO_x-cycle

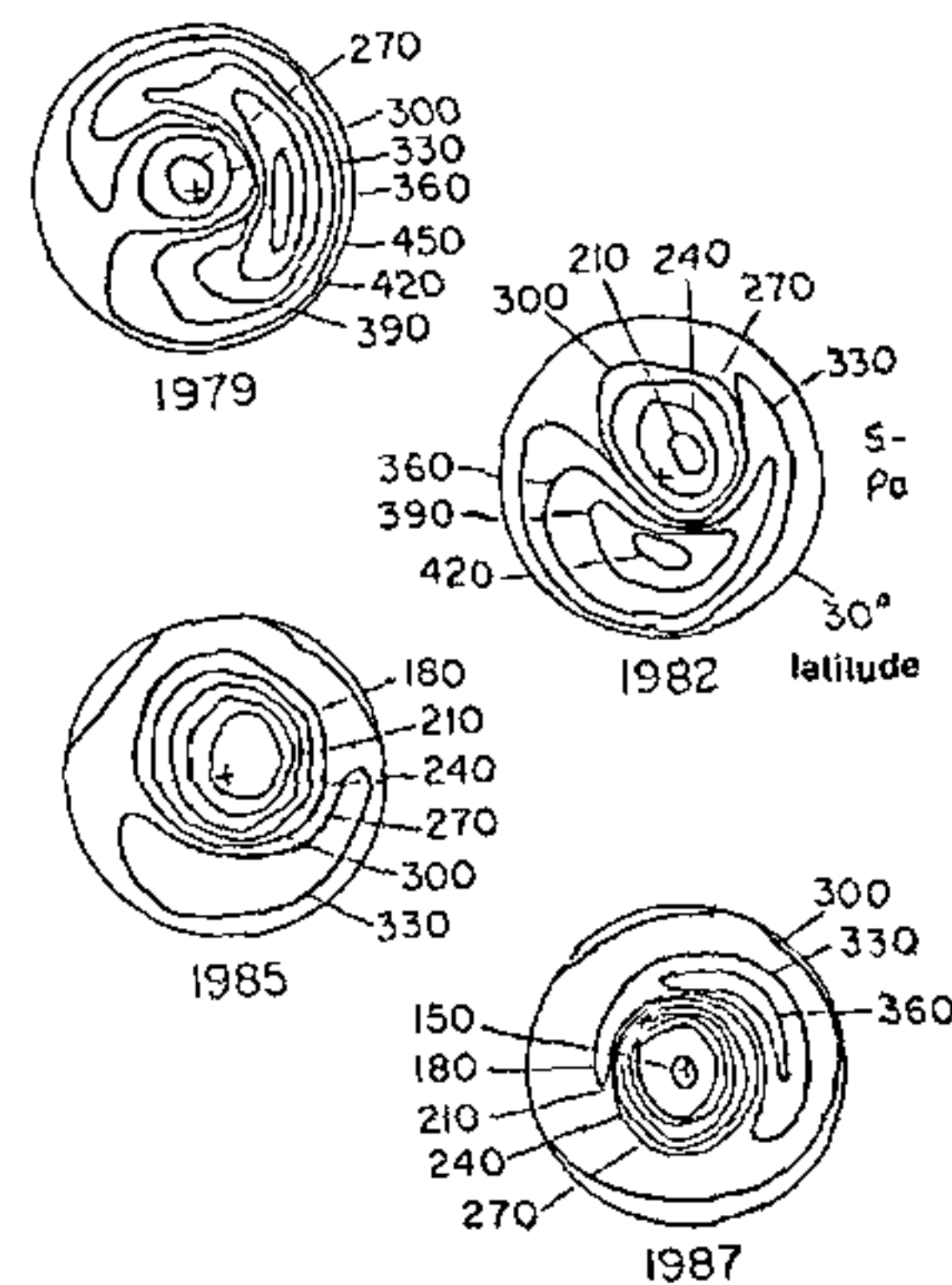


Figure 6. Development of the ozone hole as revealed by satellite observations⁴⁴. Isolines of October mean values between South Pole and 30° S in DU.

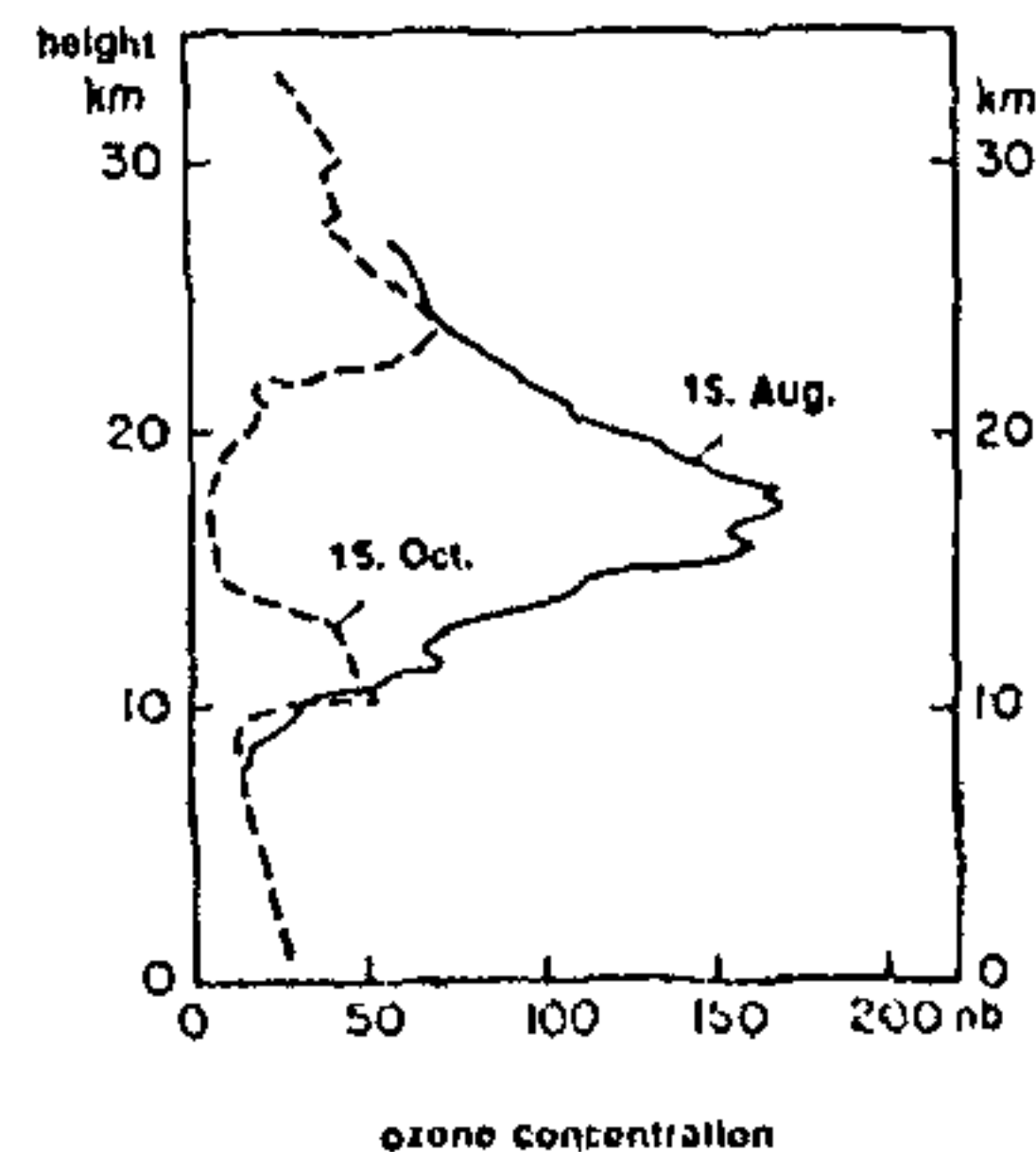


Figure 7. Vertical distribution at McMurdo, 78° S near the end of the polar night (15 August) and on 15 October 1987 close to the maximum development of the ozone hole.

SPECIAL SECTION: OZONE

(reactions 5 + 6) is very slow in the lower stratosphere, because the concentration of atomic oxygen needed for reaction (6) is very small there (10^5 times smaller than in the upper stratosphere), where the models predicted the main loss. It was not possible either to explain the observed rapid disappearance of ozone in the lower stratosphere (Figure 7) by a change in stratospheric circulation, i.e. in the ozone transport from the tropical source region to the Antarctic. Undoubtedly an active destruction by hitherto unknown processes was going on.

These processes had to be linked to a specific property of the Antarctic lower stratosphere; this is its very low temperature during and at the end of the polar night (below -80°C). Such a low temperature has two consequences:

1. On the meteorological side it produces, due to the more rapid decrease of pressure with altitude in the cold region, a very intense circumpolar vortex. Modern dynamical meteorology suggests⁴⁵ that such a feature, once formed, is almost, although not completely, impermeable to air, e.g. an enormous closed chemical reaction chamber is formed over the Antarctic continent.

2. On the physico-chemical side the low temperatures lead to surprising processes. First of all clouds are forming in the otherwise largely cloud-free stratosphere—the so-called polar stratospheric clouds (PSC)⁴⁶. They consist of fine ice-crystals, which are below 80°C , a mixture of H_2O and HNO_3 (ref. 47); below -85°C also larger pure water ice crystals are produced. This leads to heterogeneous chemical reactions; thus processes become possible which do not exist or are very slow in the pure gas phase, which only had been taken into consideration in the current models.

N_2O_5 which is formed during polar night from NO_2 in the presence of ozone can react with water in the ice-crystals⁴⁷:



Nitric acid is at these temperatures frozen out, leading to an increased density of the PSCs which accelerates the heterogeneous processes. Gaseous NO_x thus rapidly disappears from the PSC regions.

In addition, reservoir species, e.g. ozone-inactive forms of chlorine compounds, are heterogeneously reacting on the solid surfaces, where also HCl may be incorporated.

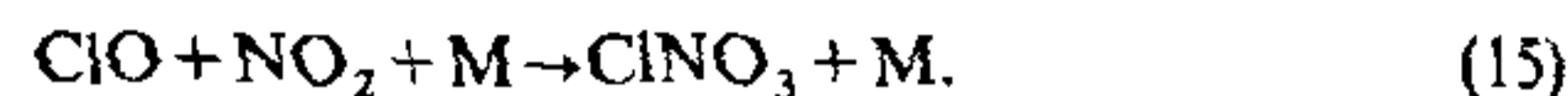


The so produced new chlorine compounds are still reservoir substances, e.g. not reacting with ozone. They are, however, much less stable than ClONO_2 and HCl

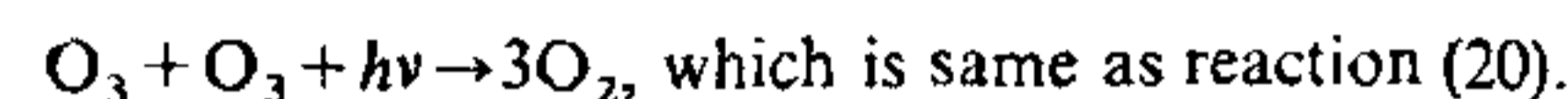
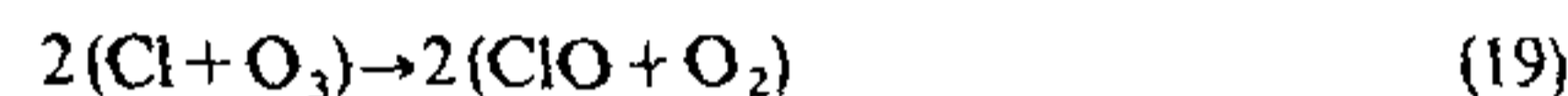
and are easily dissociated by sunlight into active chlorine after the return of the sun at the end of the polar night, thus leading to the observed rapid ozone hole formation:



In a 'normal' lower stratosphere these radicals would be after conversion to ClO (reaction (5)) rapidly transformed back into ClONO_2 by reaction with NO_2 .



In the Antarctic vortex, this is, however, not possible because NO_x has already disappeared via reaction 10. The active chlorine concentration is thus rapidly growing, leading to a new kind of ozone destroying catalytic cycle which is independent of atomic oxygen⁴⁸.



This cycle depends on high ClO concentrations, because the speed of the dimer (ClOOC) formation (16) is proportional to the square of the ClO , i.e. active chlorine content.

The rising concentration of BrO_x in the stratosphere⁴⁹ which is still only some per cent of the ClO_x -content and is produced from the anthropogenic halons; such as CFCl_2Br , used in fire extinguishers, and from CH_3Br , gives rise to another catalytic cycle which would work more rapidly than that described above if BrO_x and ClO_x -concentrations were equal.



The new theoretical concept of ozone destruction on the basis of heterogeneous reactions has been substantiated by the results of the two American Antarctic ozone expeditions⁵⁰ in 1986 and 1987. Simultaneous observations of the vertical ozone distribution by the SAGE satellite system at the same latitude inside and outside the polar vortex, i.e. inside and outside the 'closed' reaction chamber (Figure 8), showed a 'normal' vertical distribution outside, the typical ozone hole

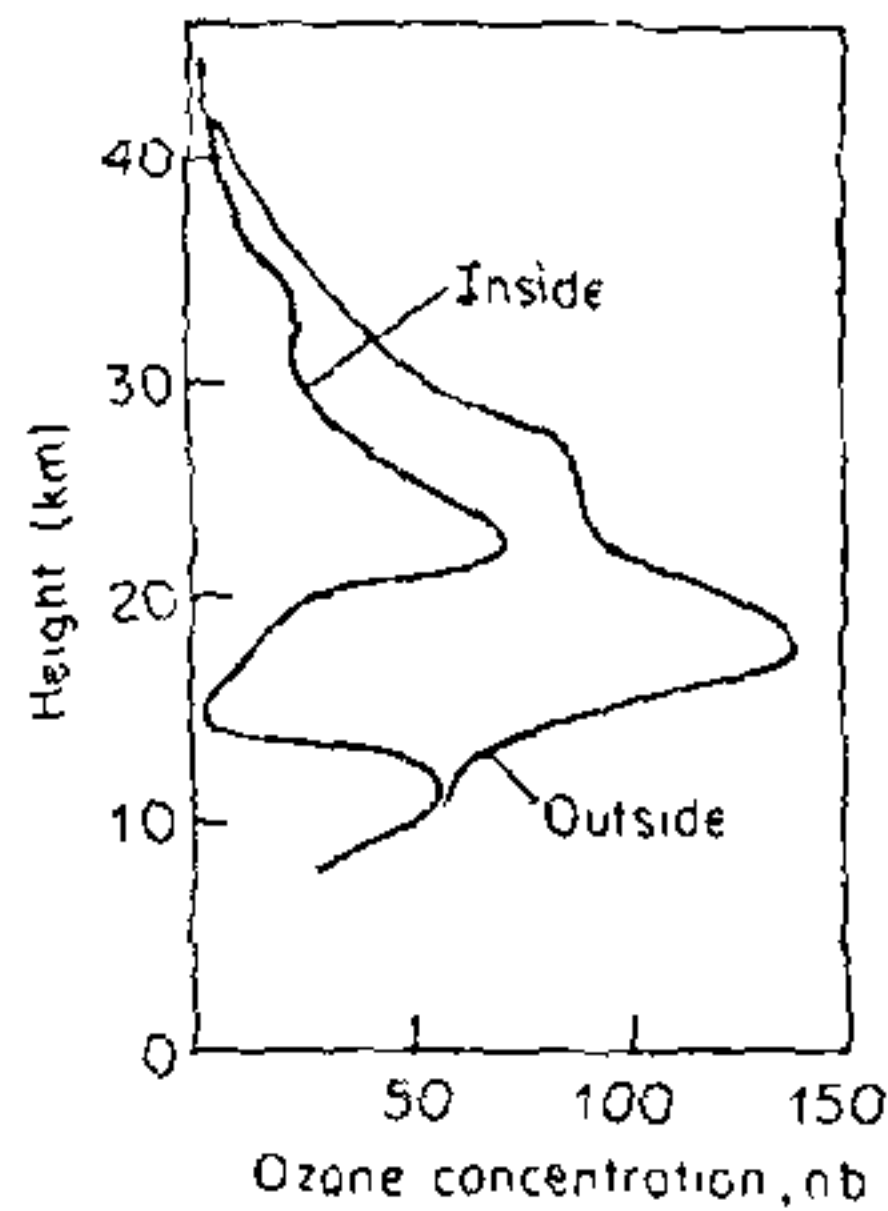


Figure 8. Simultaneous observation of the vertical ozone distribution inside and outside the polar vortex at the same latitude by the SAGE satellite system.

profile inside the vortex. Such observations were possible because of the often asymmetric position of the vortex (Figure 8) with respect to the pole. Penetration flights with an ER-2 airplane at ≈ 18 km showed inside the vortex an at least 100 times higher ClO mixing ratio than outside⁵¹, HNO₃-containing aerosol (crystals) was found and the NO_x-values were very low inside the vortex. On the basis of specific reaction rate measurements⁵² it could be shown that the ClO-dimer cycle destroys ozone under the measured ClO-concentration (2 ppb) at the observed speed ($\approx 2\%$ per day).

Although these facts leave no doubt that the ozone hole is a consequence of the increased stratospheric chlorine content produced by CFC emissions, stratospheric circulation plays an important role too. First of all, the smaller stratospheric poleward heat transport in the Southern hemisphere, compared to its Northern counterpart, is responsible for the low temperatures, leading to PSCs and thus to the described heterogeneous chemistry. Further the 'ozone hole' showed, at least until 1988, considerable year-to-year fluctuations (Figure 9)⁵³. Presumably this variability is connected with the quasi-biennial oscillation (QBO) of the tropical stratospheric winds which is known to influence high latitudes also, particularly in the Southern hemisphere. The direct circulation impact may be increased by feedback mechanisms: low temperatures reinforce ozone destruction by heterogeneous reactions; ozone loss decreases the radiative heating by this gas and thus lowers the temperature further. The last three years (1989-91) produced, however, very strong 'ozone holes' in a row. In 1991 total ozone values as low as 108 DU were reported provisionally; which means not more than 1/3 of the mean values observed in October 30 years ago; the three-year sequence of very strong ozone 'holes' might shed some doubt on the concept of the QBO influence; but possibly it may show that at

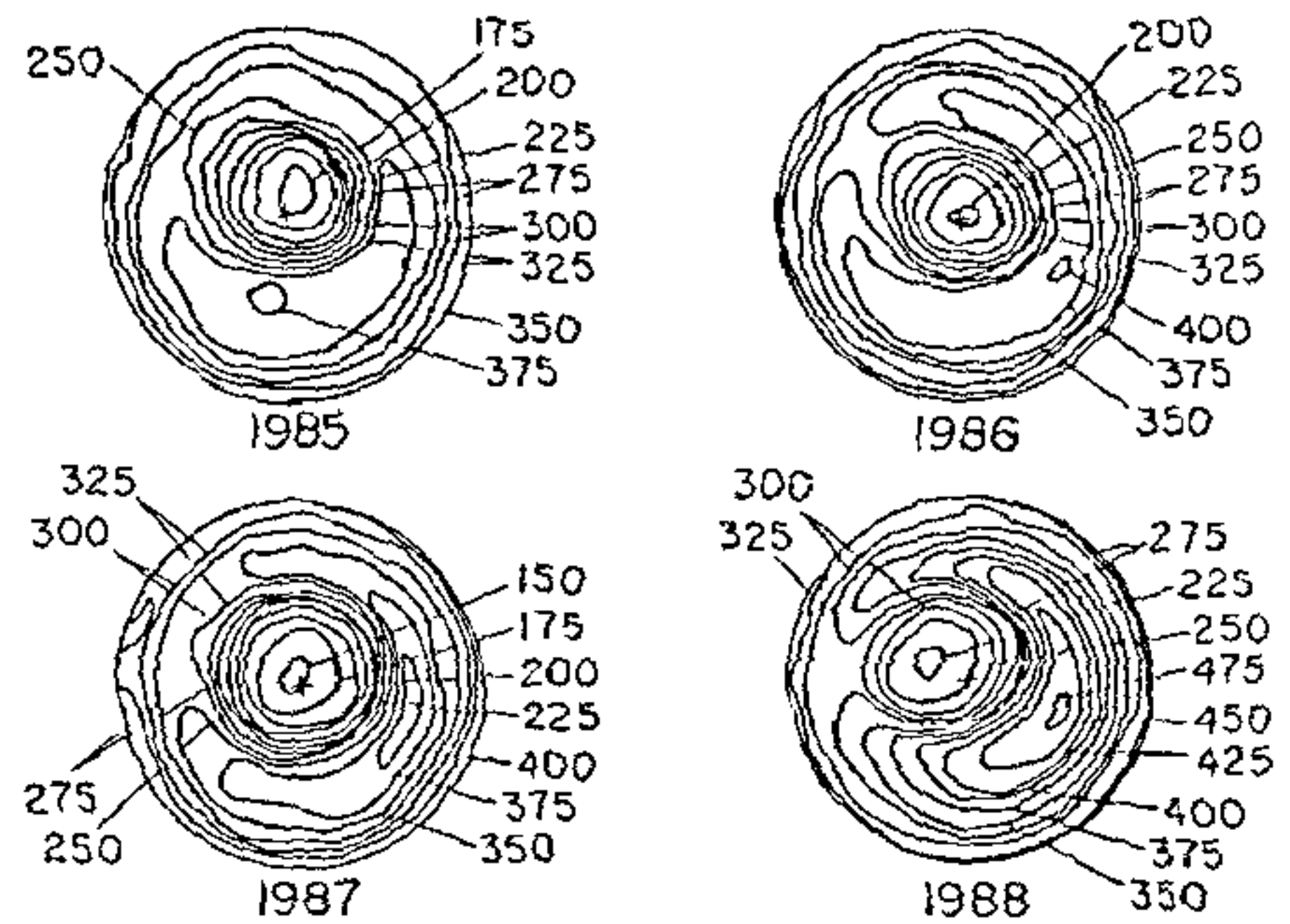


Figure 9. Biennial variation of the ozone hole between 1985 and 1988. Isolines of total ozone mean values for October from satellite observations between South Pole and 20° S.

present chlorine levels in the stratosphere the chemistry is fully dominant.

Hemispheric consequences of the Antarctic ozone destruction

Although the ozone-poor airmasses of the Antarctic 'ozone hole', are to a large extent, contained within the circumpolar vortex, the ozone-destroying processes in that region influence the ozone regime of the whole Southern hemisphere. Already during the time of the closed vortex the exchange processes are not completely zero, leading to some ozone reduction in the surroundings; but particularly in the transition period from the winter to the summer time circulation, when the vortex is broken up, its ozone-poor air can reach lower latitudes. This means that the winter/spring time loss in the Antarctic influences the ozone budget of the whole hemisphere. This effect is clearly indicated by the satellite measurements of the TOMS experiment on Nimbus 7 which shows at 45° S since 1979, a decrease of over 5% in the annual mean total ozone amount.

Trends and unexpected changes in the vertical distribution in the Northern hemisphere

In order to obtain a reliable interpretation of the changes in the ozone layer introduced by the CFC-emissions, long observational records, including also times in which the anthropogenic influence should have been negligible, are needed. Satellite observations which yield the important worldwide and continuous data coverage are in reliable, i.e. comparable form, available only for the last 12 years and are to some extent even then disturbed by instrument degradation.

SPECIAL SECTION: OZONE

The latter problem could be largely solved by comparison with the data of the ground-based Dobson spectrophotometer network although this network is not global, but rather concentrated in the Northern hemisphere. It seems that on the basis of this comparison, a method could be developed⁵⁴ which will allow future degradations to be corrected using satellite data themselves. Nevertheless parallel observations with the ground-based instruments will keep their importance also in future.

This is particularly true for those stations which carry a long record. A 'global' network of such stations with, as mentioned above, a quite inhomogeneous regional distribution, exists only since the IGY and is largely concentrated in Europe, North America, India and Japan with only scattered stations in the Southern hemisphere, particularly operating in Australia and in the Antarctic region—the latter led to the discovery of the 'ozone hole'.

An almost twice as long, practically continuous record is available from Arosa, Switzerland, started in 1926 by Paul Götz⁵⁵. Undoubtedly the use of single station observations for trend calculations can be misleading because of the pronounced weather influence on the ozone distribution (a consequence of ozone transport). Using the temperature record of the free troposphere given by a mountain top station at 2500 m altitude this bias can be at least partly removed⁵⁶. The Arosa record (Figure 10) shows a small, statistically not significant rise of total ozone until 1970, superimposed by strong year-to-year fluctuations, and thereafter a highly significant decrease of more than 2% per decade. The slight increase before 1970—if it means anything—could be a consequence of 1) rising tropospheric ozone due to air pollution, 2) stratospheric cooling because of the CO₂ increase, and/or 3) the CH₄ increase, reducing the ozone effect of ClO_x, at that time a product of natural CH₃Cl.

For the period of strong ozone decrease regular ozone soundings (3 times per week) at Payerne,

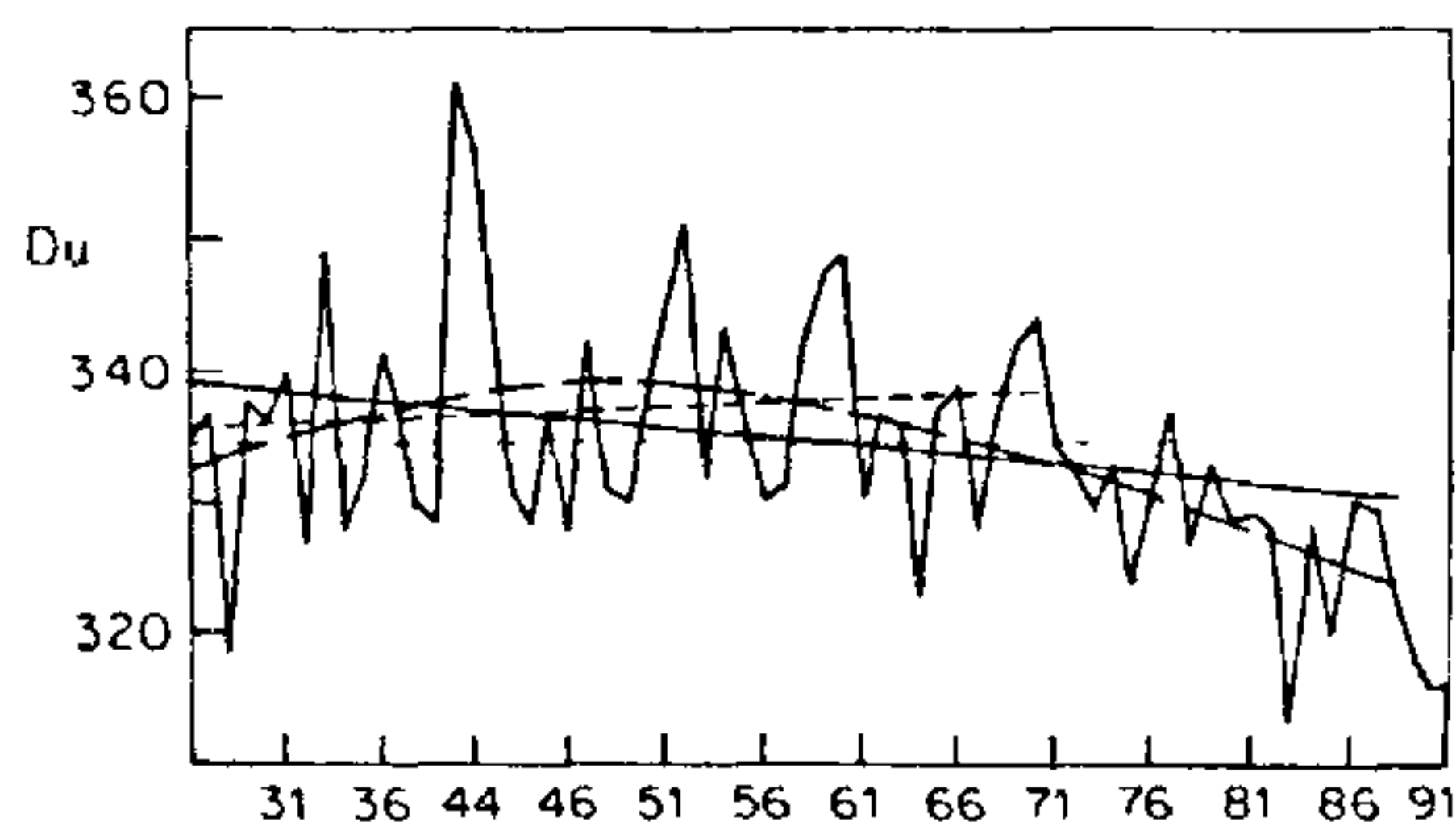


Figure 10. Arosa total ozone record with regression lines for the whole period, for 1926-70 and 1970-90 and with best fit by a parabola

Switzerland (since 1967) and Umkehr measurements at Arosa (since 1956), extending the data set into the upper stratosphere, are also available. They give the surprising result, that the main ozone loss has occurred in the lower stratosphere at and just below the level of the ozone maximum (Figure 11). This corresponds to the loss level in the Antarctic ozone hole region and is also at odds with expectations from the current models using homogeneous gas phase chemistry (Figure 4c). The negative trend reaches between 50 and 70 mb over 7% per decade (Table 1). The decrease predicted by homogeneous gas phase models in the upper stratosphere with a maximum around 40 km, is, however, confirmed by the Umkehr record if the new retrieval algorithm of Mateer and DeLuisi⁵⁷ is applied⁵⁸. This negative trend is not much smaller (around 6%, Figure 11) than that observed in the lower stratosphere, but contributes only little to the total ozone loss.

Table 1 also shows that the ozone decrease between 100 and 20 mb has been strongly accelerated during the eighties and reached 16% per decade between 70 and 50 mb. The total stratospheric loss (above 200 mb) during this period was 7% of the total amount; 40% of this loss was, however, compensated by the growing tropospheric ozone content produced by the rising air pollution.

The seasonal differences in the trends (Table 1) suggest that the ozone destruction between 100 and 30 mb is largely a wintertime phenomenon which persists into summer and fall because there is no photochemical reformation at these levels. The wintertime loss is, however, slowly reduced by transport processes. In the lowest part of the stratosphere, where the trend is not significant due to the dominating weather influence, its sign is even partly reversed in autumn.

The results of the one-station record of Arosa are

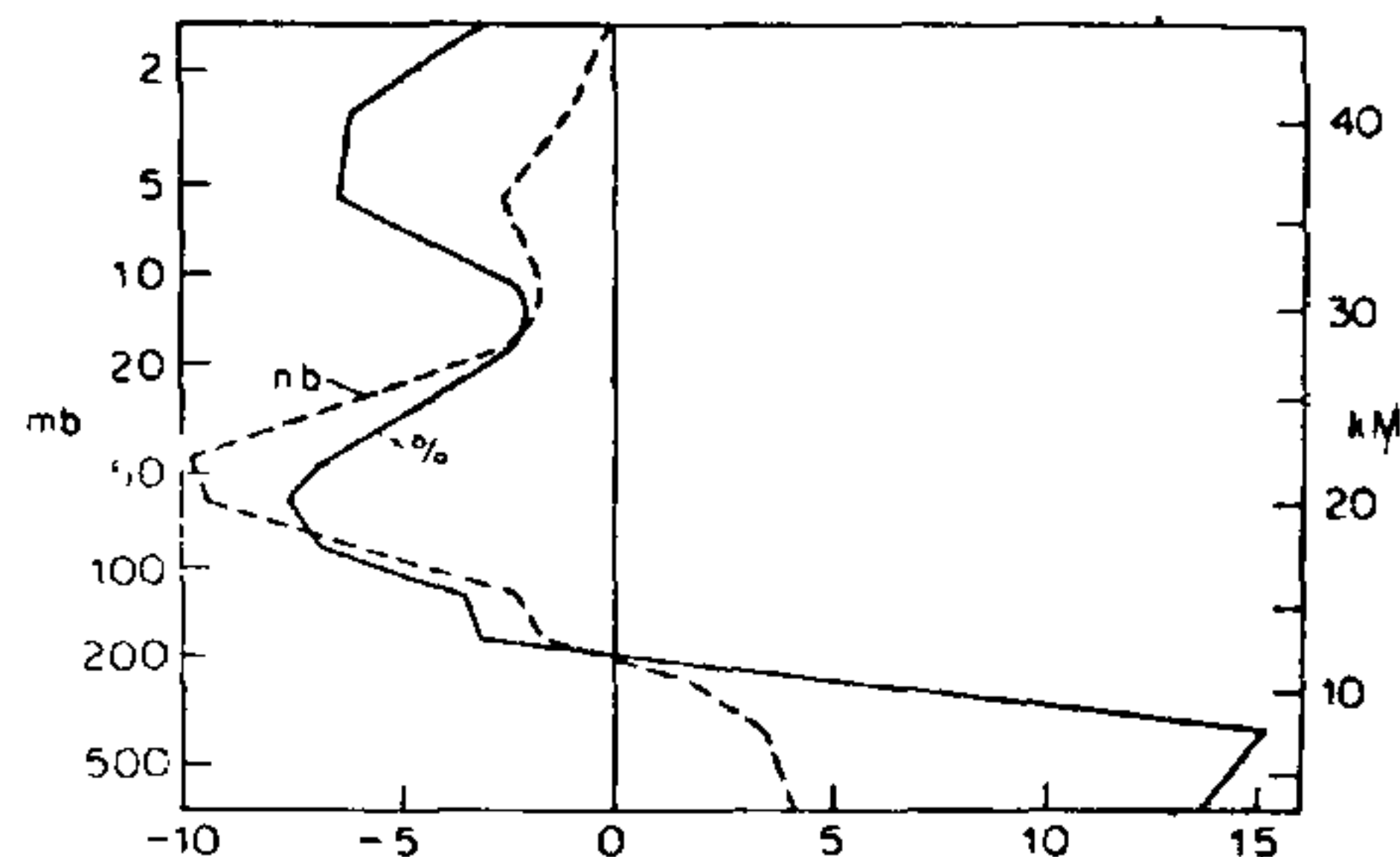


Figure 11. Trends 1967-90 at different levels over Switzerland; relative trend in %, full line and absolute trend in nb, dashed line; below 15 mb from soundings at Payerne, above 15 mb from the Arosa Umkehr record.

Table 1. Trends; percentage change per decade

Whole year	Total ozone	950-500	500-300	300-200	200-150	150-100	100-70	70-50	50-40	40-30	30-20	20-15	15-12	12-10
1967-90	-2.2	13.8	15.2	5.3	-3.2	-3.5	-6.8	-7.5	-6.9	-5.4	-3.2	-1.2	-0.2	0.1
1979-89*	-3.7	30.1	27.1	11.8	4.0	-1.2	-6.2	-16.1	-12.7	-10.6	-9.0	-5.0	-2.6	-0.9
1967-90														
Wintert†	-3.6	14.1	15.8	3.3	-5.1	-6.4	-9.1	-8.8	-7.7	-5.5	-4.2	-2.8	-2.0	-0.8
Summer**	-1.5	13.8	15.0	2.3	-4.7	-1.6	-5.5	-6.7	-7.2	-5.7	-2.4	-0.2	1.7	1.3
Autumn‡	-1.1	13.4	15.3	8.9	5.5	1.8	-3.2	-5.6	-5.1	-4.4	-2.4	-0.6	0.8	1.0

*In this short period 1990 was omitted because the consequences of an instrumental change could not yet have been fully corrected; †December through April; **May through August; ‡September through November.

with respect to the most recent development well in line with the (corrected) data from TOMS⁵⁹. These also show a strong winter time decrease of total ozone in Northern mid-latitudes (over 8% per decade) from January through March. A compilation of different data sources⁶⁰ indicates for the period December through March an ozone depletion per decade of 5.6% at 45°N while the corresponding losses for summer (May-August) and for fall (September-November) are only 2.9 and 1.7% respectively. At 45°S, however, the decreases are more equally distributed over the year and are smallest (4.4%) in spring (at the time of the maximum development of the Antarctic ozone hole) against 5.2% in summer and 6.2% in winter.

Possible causes of the Northern mid-latitude ozone depletion

While a clear connection is indicated between the ozone depletion in Southern mid-latitudes including its seasonal variation and the Antarctic 'ozone hole' through its influence on the hemispheric ozone budget the corresponding depletion in the North and particularly its height distribution is at first rather puzzling, because no comparable 'ozone hole' has so far been seen in the Arctic. This latter fact is not surprising because the mean winter temperature in the North polar lower stratosphere is at least 10° higher than in the Antarctic due to the stronger meridional heat flux.

Therefore the formation of PSCs and by this the occurrence of heterogeneous chemistry is much less frequent; also the polar vortex is less stable than over the Antarctic. Nevertheless as two Arctic ozone expeditions have shown^{61,62}, there is a formation of PSCs and disturbed chemistry on a regional scale for only some weeks in each case; this leads to the development of so-called 'mini-holes', i.e. rather localized ozone depletion. Because of the more vigorous meridional circulation in the Northern hemisphere stratosphere the associated vortices are relatively rapidly broken up and the produced ozone-poor air is

transported to lower latitudes, decreasing there, by this mixing process, the mean ozone values. Such a mini-hole could be followed in February 1990 on its way from Scandinavia to Europe⁶³. Figure 12 shows the ozone variation (at different levels) during its passage over Switzerland; it also depicts the enormous variations which can happen within a few days due to the combined action of horizontal transport and vertical motion.

With a mini-hole also its chemically perturbed air is carried to lower latitudes and ozone destruction may, under increased solar irradiation, yet continue for some time. ClO measurements—unfortunately still rather spotty—have demonstrated an increase of active chlorine in Northern mid-latitudes during winter⁶⁴, this is in line with the observed maximum ozone depletion in this season.

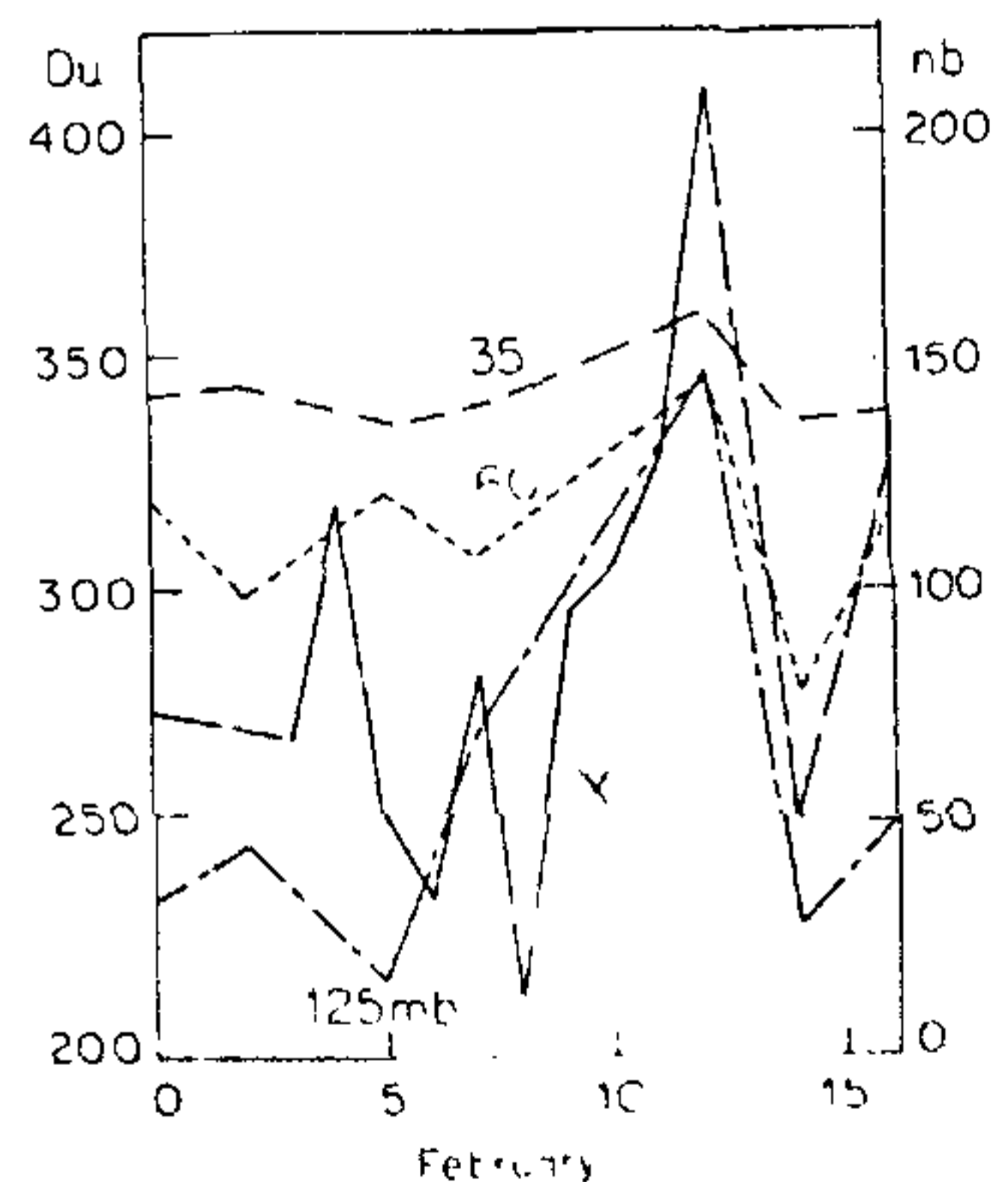


Figure 12. Variation of total ozone at Arosa in the first half of February 1990, the minimum of 213 DU, a value never before reached at this time of the year, marks the passage of the 'mini-hole', dashed parts of the curve: missing data. There is no sounding on the 8th, the variability is mediocre at 60 mb, relatively small at 35 mb and maximum at 125 mb where the weather type fluctuations are very marked.

Laboratory measurements⁶⁵ demonstrate that a conversion of N_2O_5 and thus NO_3 into HNO_3 and a production of active chlorine may occur heterogeneously also at the surface of sulphuric acid droplets (which contain some water) in the stratospheric aerosol layer (Junge layer around 20 km). This could also lead to an increased ClO_2 -level and thus to *in situ* ozone destruction in mid-latitudes. The ozone loss at these latitudes by the action of advected polar or by *in situ*-produced ClO_2 , as well as an ozone decrease by mixing with ozone-depleted (mini-hole) air from the Arctic, would all occur around 20 km and are thus consistent with the observed—at first surprising—maximum negative trend at about that level (Table 1). It is not yet clear, how the combination of the mentioned processes in depleting Northern mid-latitude ozone works and what their percentage contribution is. This must be further investigated, because the observed surprisingly big negative trend at these latitudes is one of the main concerns.

The different seasonal distribution of the ozone depletion and its higher annual mean value in Southern mid-latitude compared to the North (minimum in spring at the time of the maximum development of the Antarctic ozone hole) is largely a consequence of the different circulations. During spring the ozone-poor air is, to a large extent, contained within the vortex; in summer it is mixed to lower latitudes; the low winter value, largely in the absence of mixing from the Antarctic, may also here indicate the importance of the *in situ* heterogeneous processes and might thus support the hypothesis about their importance for the Northern hemisphere. However, before we have increased knowledge on the distribution of ClO_2 , NO_3 and HO_x radicals, i.e. on the chemical processes at different levels and latitudes, this is rather speculative.

Another still open question is the possibility of secular changes in stratospheric circulation and thus in the transport processes. The fact that the TOMS data show no ozone depletion over the equator or rather a small, but insignificant increase, may indicate that ozone transport from the tropical source regions to higher latitude has recently somewhat decreased and that some, probably small, part of the loss at higher latitudes could also be due to such a change. However, because of the simultaneous transport of ozone and trace substances, such qualitative reasoning may be misleading. It will only be possible to interpret future changes in the ozone layer reliably if a coupled chemistry-transport model, including complete heterogeneous chemical processes, becomes available.

In the meantime, a big step forward in our understanding of the processes governing the changes in the ozone layer is expected from the data of the Upper Atmospheric Research Satellite (UARS) launched by NASA in September 1991 (ref. 66). The experiments

on board of this spacecraft should provide a simultaneous picture of the stratospheric wind field and of the distribution not only of ozone, but also of a considerable number of other trace gases together with measurements of the incoming chemically active solar UV-radiation. This information will also be helpful in the construction and testing of the above mentioned models.

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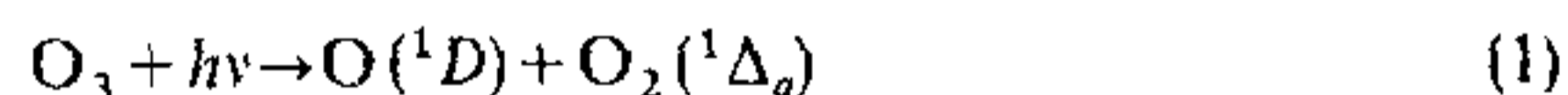
Laboratory studies of the photochemistry of ozone

R. P. Wayne

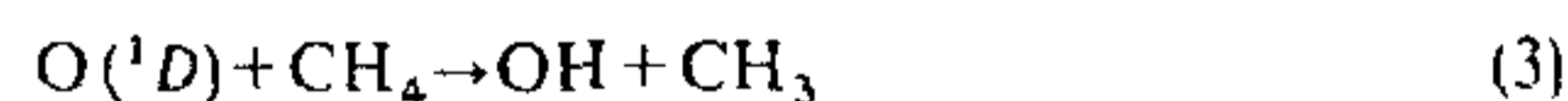
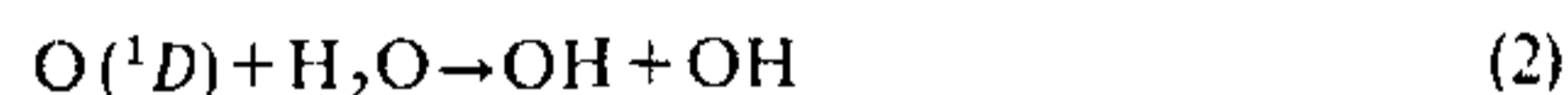
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Introduction

Ozone is a minor constituent of the earth's atmosphere, but one that plays a disproportionately important part in atmospheric physics and chemistry¹. Atmospheric ozone absorbs solar radiation strongly, and consequently influences the temperature structure and dynamics of the stratosphere. There is a powerful interrelation between circulation and other meteorological phenomena, the radiation field and stratospheric chemistry. One outstanding feature, of course, is the relationship between the absorption spectrum of ozone and the protection of living organisms from unattenuated solar ultraviolet radiation. Because ozone has a positive enthalpy of formation, reactions involving the molecule have a tendency to be exothermic and thermodynamically favoured, and reaction rates are often high. If ozone absorbs radiation, the energy of the system is further elevated and yet other reactions become accessible. In particular, at wavelengths shorter than about 310 nm, ozone is photodissociated by ultraviolet radiation, and two excited fragments are formed



in a large proportion of the photodissociation events. The excited atomic fragment is able to participate in key reactions such as



which generate radicals, especially OH in the stratosphere and the troposphere, and NO in the stratosphere. With excited atomic oxygen the reactions are fast, but with ground-state oxygen they are too slow to be of importance. The radicals themselves are of paramount significance in the atmosphere. Indeed, in daytime tropospheric chemistry, many transformations involve the OH radical, and it is difficult to postulate sources of this radical that do not start with the photodissociation of ozone.

Not only is the atomic fragment of the ultraviolet photodissociation of ozone electronically excited, but so