

# DEPLETION OF STRATOSPHERIC OZONE RESULTING FROM GLOBAL GASEOUS POLLUTION

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## ABSTRACT

*The possible depletion of the stratospheric ozone layer has become an issue of international importance. The primary concern is based on the possible inhibition of its functioning as a life protecting ultraviolet shield and the adverse biological and climatological effects that might result from this. There is, however, still considerable scientific uncertainty concerning this issue. It is against this background that an appraisal is given of the current state of knowledge regarding the potential for depletion of stratospheric ozone by global gaseous pollution and the attendant environmental effects. Special reference is made to the SA research effort that will make an important contribution towards understanding the tropospheric/stratospheric processes which play a role in the formation and destruction of ozone.*

## EKSERP

*Die moontlike uitdunning van die stratosferiese osoon laag het 'n kwessie van internasionale belang geword. Die hoofrede tot kommer is die moontlike verhinderende van dié laag se funksionering as beskermende skild teen ultraviolet straling en die nadelige biologiese en klimatologiese effekte wat hierdeur kan ontstaan. Daar bestaan egter nog heelwat wetenskaplike onsekerheid hieroor. Dit is teen hierdie agtergrond dat 'n beskouing van die stand van kennis ten opsigte van die potensiaal vir die uitdunning van stratosferiese osoon deur globale gasagtige besoedeling en die begeleidende omgewingseffekte gegee word. Daar word ook verwys na die SA navorsingspoging wat 'n belangrike bydrae sal maak tot begrip van die troposferiese/stratosferiese prosesse wat 'n rol in die vorming en vernietiging van osoon speel.*

## 1. INTRODUCTION

For many decades, air pollution was generally considered as a local problem, closely associated with man's industrial activities and urban living patterns. Consequently, large-scale effects with great potential for changing the air environment were neglected because of more immediate demands for solving problems on the local scale. However, increasing realisation of the more global aspects of the problem has been emerging, largely because of the rapid expansion of population and industrial development.

Today, there is general concern that pollution of the atmosphere due to man's activities can cause irreversible changes in the environment on a global scale. This concern stems from general belief that man-made pollutants can disturb many of the natural pathways for cycling trace substances with resulting adverse effects on world climate, human health and the environment. One such effect, the 'greenhouse' effect, is predicted to cause a world-wide atmospheric temperature increase due to the absorption of infrared radiation emitted by the earth by increasing amounts of carbon dioxide and other trace gases arising from combustion and industrial processes. This will, in turn, cause a change in the world's rainfall pattern which will have important implications for food production and also cause a rising of ocean levels with attendant detrimental effects on the ecology and economy of coastal zones. Another effect is the partial destruction of the stratospheric ozone layer by aerosol propellants (chlorofluorocarbons) which is predicted to cause an

increase in ultraviolet radiation intensity at the earth's surface with resulting adverse effects on man and his environment.

Recent discussions on the protection of the stratospheric ozone layer by a group of UNEP experts resulted in a draft convention which called for international co-operation as regards

- undertaking systematic observations and research on the ozone layer to better understand and assess the effects of human activities on this layer and the attendant effects on human health
- taking legislative measures and harmonizing policy to control, limit, reduce or prevent human activities that have or are likely to have adverse effects on the ozone layer.

No agreement has, however, been reached by these experts on a protocol which is designed to limit and control global emissions of chlorofluorocarbons (CFCs). There appear to exist two points-of-view. The Toronto group (USA, Canada, Norway, Finland, Sweden and Switzerland) supports a banning of at least 80% of non-essential CFC use and a reduction of CFC production, whereas the ten member countries of the European Economic Community support a less drastic curtailment of CFC use and production and intend further action only if scientific evidence justifies it.

It is against the background of the above sketched developments that this paper will give an appraisal of

the present state of knowledge regarding the potential for depletion of stratospheric ozone resulting from global gaseous pollution and the attendant environmental effects. Also, special reference will be made to the South African research effect in this regard.

## 2. PROCESSES THAT DETERMINE THE OCCURRENCE OF OZONE IN THE TROPOSPHERE AND THE STRATOSPHERE

In order to obtain the necessary perspective on the stratospheric ozone depletion issue, it will first be necessary to briefly discuss the physical and chemical processes that determine the occurrence of ozone in the troposphere and the stratosphere.

### 2.1 Occurrence of ozone in the troposphere

Ozone is a natural constituent of the troposphere, with downward transport of ozone-rich stratospheric air and photochemical production from naturally occurring nitrogen oxides and volatile organic compounds as the main sources, and surface removal as the main sink. Enhanced levels of ozone are formed photochemically from emissions of nitrogen oxides and volatile organic compounds which result from fossil fuel combustion (See Appendix A : Formation of ozone in the troposphere). Exposure to enhanced levels

of ozone poses a risk to human health and it has lead to significant yield reductions in many crops in the USA. Moreover, it is currently thought that ozone in combination with other pollutants ( $\text{SO}_2$  and  $\text{NO}_x$ ) has played a role in the destruction of millions of hectares of coniferous forests in Central Europe and North America.

Presently, it is predicted that a doubling of the concentration of tropospheric ozone will occur over the course of the next century with an attendant increase in the surface temperature of the earth by nearly  $1^\circ\text{C}$ . This is comparable with the effect expected from doubling the carbon dioxide content of the atmosphere by the middle of the next century.

### 2.2 Occurrence of ozone in the stratosphere

The primary processes which determine the concentration of ozone in the stratosphere are presented schematically in Figure 1. Stratospheric ozone is formed by reactions which occur following the photolysis of oxygen. It is removed by reactions catalyzed by species such as Cl, NO, OH and Br (See Appendix B : Elementary reactions which determine the concentration of stratospheric ozone) as well as by photolysis. The abundance of these species in the stra-

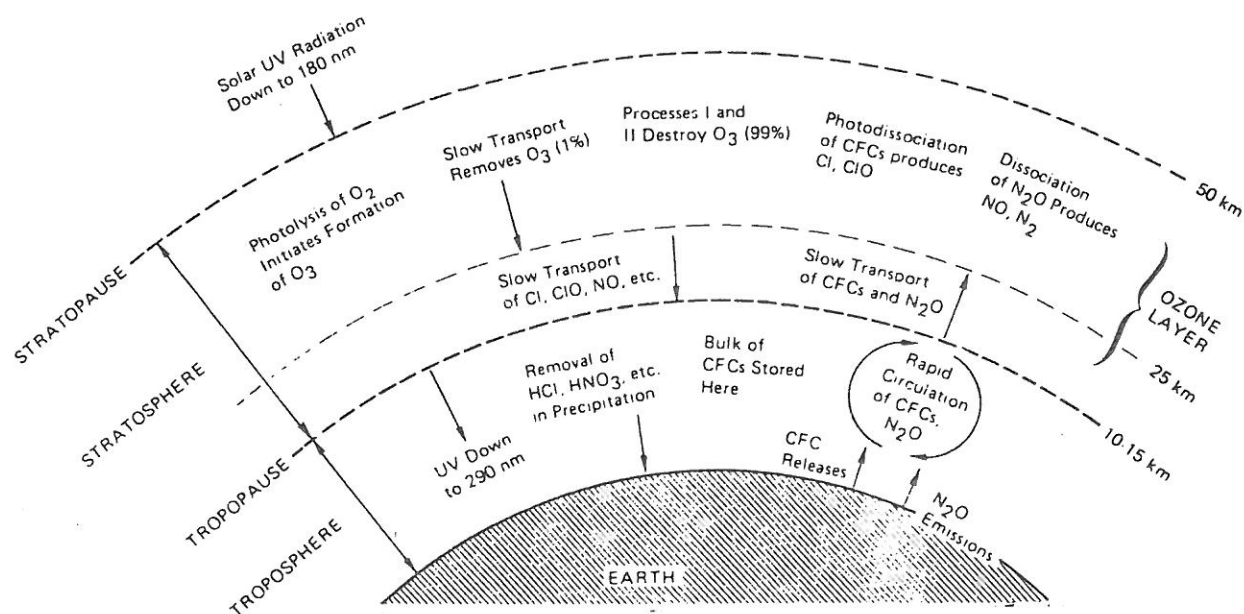
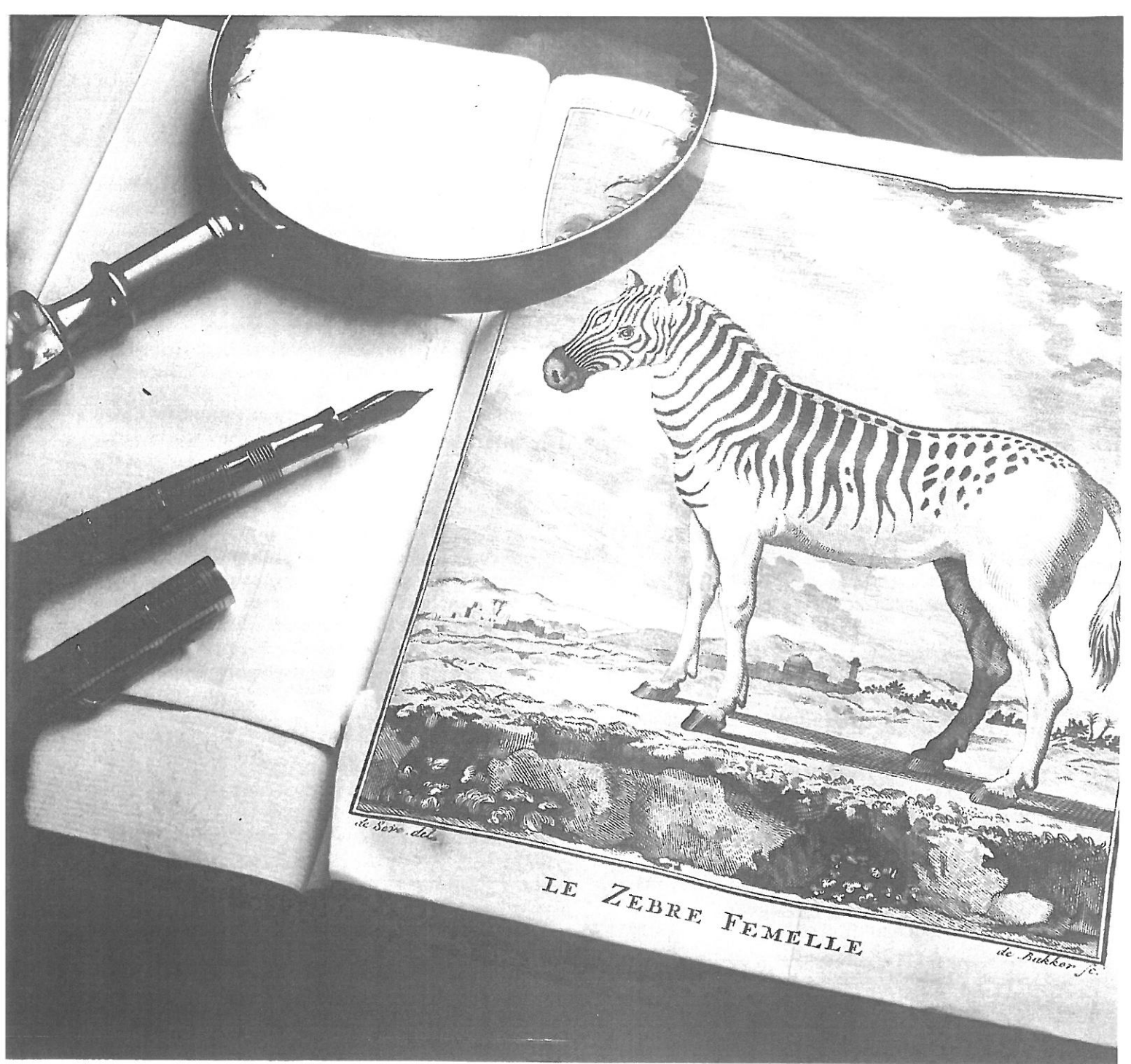


FIGURE 1. Representation of processes that determine the concentration of ozone in the stratosphere (Source : See Reference 13, 'LITERATURE CONSULTED')



An early engraving of the extinct zebra in the Africana Library.

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tosphere depends on supply from the troposphere of compounds such as CH<sub>4</sub>, N<sub>2</sub>O, CFCS and CH<sub>3</sub>Br which are produced by industry and/or by natural functions of the biosphere.

It is anticipated that, because of increasing atmospheric pollution (notably by CFCS), the concentration of ozone in the stratosphere may decrease. This is in contrast to the situation in the troposphere where ozone is increasing. A dual dilemma therefore appears to exist in that the natural processes in both the stratosphere and the troposphere are being disturbed and associated with detrimental effects. These disturbances do not 'compensate' one another because the attendant change in the vertical distribution of ozone would eventually climatic consequences that might be substantial.

### 3. PREDICTIONS REGARDING THE REDUCTION OF STRATOSPHERIC OZONE

Predictions regarding the extent of reduction of stratospheric ozone due to manmade releases of notably

CFCS have ranged widely over the past decade. This warrants a closer examination.

In 1983 a total stratospheric ozone reduction of 2–4% was predicted to occur by late in the next century. Previous estimates of total stratospheric ozone reduction made in 1982 and 1977 were 5–9% and 15–18%, respectively. These revisions in estimates were due to improvements in the knowledge of atmospheric chemistry kinetics as well as better measurements of trace gases which were 'fed' into the relevant atmospheric photochemical models.

It was, however, gradually realised that besides CFCS, other trace gases also play an important role in setting the concentration of stratospheric ozone and that this had to be taken into account to allow a realistic assessment of the depletion of stratospheric ozone. For example, the results in Table 1 show that a doubling of carbon dioxide concentration is estimated to cause an *increase* in total ozone that is comparable to the *decrease* expected to result from the presence of CFCS. This is because the stratosphere will be cooled by the increased levels of carbon dioxide which, in turn, will slow the rate of chemical reactions that destroy ozone.

TABLE 1  
SENSITIVITY OF TOTAL STRATOSPHERIC OZONE TO PERTURBING INFLUENCES  
(Source: See reference 13, 'LITERATURE CONSULTED')

Trace gas and magnitude of perturbation	Typical estimate of stratospheric ozone change (%) <sup>*</sup>	Atmospheric lifetime (years)	Principal mode of pollutant removal
CFC-11 and -12 (1980 release rates)	-2 to -4	50 - 150	Photolysis of CFCS in middle stratosphere
Other halocarbons (2 ppbv Cl <sub>x</sub> increase)	~ -1	1 - 15	Decomposition of tropospheric chlorocarbon reservoir by reaction with OH
Subsonic aircraft (2 x 10 <sup>9</sup> kg NO <sub>2</sub> /yr @ 12 km)	~ + 1	< 1	Conversion to nitric acid and removal to surface
N <sub>2</sub> O (20% increase by 2050)	~ -4	100	Photolysis in stratosphere
CH <sub>4</sub> (doubling)	~ + 3	10	Reaction with tropospheric OH
CO <sub>2</sub> (doubling)	+ 3 to + 6	?	Uptake by oceans, sediment and biosphere

\*NOTE: Estimated using one-dimensional atmospheric photochemical models



It is estimated that when the uncertainties in the atmospheric photochemical models which incorporate the effects of CFCS as well as trace gases such as carbon dioxide, nitrous oxide and methane are taken into account, the resultant total stratospheric ozone change over the next century could range between an increase of a few percent to a decrease of as much as ten percent. It should be pointed out that up to now most of the stratospheric ozone depletion assessments have been done with relatively simple one-dimensional atmospheric photochemical models which do not adequately represent the complex three-dimensional atmosphere.

The ultimate test of the ozone depletion theory will reside in the detection of long-term trends in total ozone concentration. Detailed analyses of ozone concentrations for 1970–1980 have not produced any discernible trend in the total amount of ozone in the atmosphere. The apparent inconsistency between observation and theory could be due to a number of factors, i.e.

- ‘noise’ in the data obtained and uncertainties of the theoretical predictions
- incorrect predictions of ozone depletion
- masking of ozone depletion by other manmade or long-term natural trends.

Recent advances on time series analysis have, however, brought the possibility of early detection of trends within our reach. Moreover, steps are being taken to implement proper calibration techniques to ensure reliable satellite observations of long-term trends in total ozone.

Our understanding of the dynamics and chemistry of the stratosphere has developed considerably over the past decade, but there are still many remaining uncertainties. However, there is reason to believe that advances will be made because of improvements that are envisaged in remote sensing technology that will enable a better insight into the dynamics and chemistry of stratosphere and also because of promising progress in the development of three-dimensional atmospheric photochemical models.

#### 4. ENVIRONMENTAL EFFECTS RESULTING FROM THE REDUCTION OF STRATOSPHERIC OZONE

It is anticipated that if stratospheric ozone decreases, more solar ultraviolet radiation, in the ultraviolet-B range, will penetrate to the earth's surface and into surface waters with attendant adverse effects to human health, agricultural production and fisheries.

With regard to human health it seems to be well-established that an increase in solar ultraviolet-B will lead to an increased incidence of non-melanoma skin cancers which are rarely fatal. There are several indications that sunlight may be one of the causative factors of malignant melanoma, but it is presently not proved whether ultraviolet-B is involved. It is however, of relevance to point out that life on earth is exposed to daily solar fluxes ranging from  $0,05 \text{ W/m}^2$  in the northern temperate regions to  $0,2 \text{ W/m}^2$  in the tropics, yet there are no indications that natural ecosystems in the higher irradiated regions are in any way limited by ultraviolet radiation.

With regard to plants, crops and other vegetation as well as maritime life, the effects from increased ultraviolet-B radiation is even less well understood and major uncertainties remain about why some plants are more susceptible than others. One possible explanation is that some plants have evolved a resistance to ultraviolet-B exposure by producing compounds in their leaves that absorb the ultraviolet-B before it reaches the chlorophyll.

Numerous exposure experiments have so far been made under artificial laboratory environments, exposing selected micro-organisms as well as animal and plant tissues to ultraviolet-B radiation. The situation has, however, been reached where experiments are needed under real environmental conditions to enable a realistic assessment of the effects of ultraviolet-B radiation on ecosystems.

#### 5. THE SOUTH AFRICAN RESEARCH EFFORT TOWARDS ASSESSING THE POTENTIAL FOR DEPLETION OF STRATOSPHERIC OZONE

The SA atmospheric scientific community realised, in view of the many uncertainties concerning depletion of the stratospheric ozone layer, that there was a need, inter alia, for obtaining reliable information on the long-term trends and behaviour of ozone and other important trace gases in the troposphere and the stratosphere/mesosphere (middle atmosphere). Consequently, the local research effort is focussed on addressing this need. This effort is co-ordinated and supported financially by the National Programme for Weather, Climate and Atmosphere Research (NPWCAR).

##### 5.1 Studies of the troposphere

Since 1976/77 a number of important trace gases that might be causing global climatic change have been continuously monitored in maritime air by the CSIR at a specially equipped global background monitoring station at Cape Point. Up to now invaluable data have been obtained which

supplement those obtained at other global background stations which are part of the international Global Environmental Monitoring System. Some of the results obtained are reflected in Table 2. It follows from these that

- the annual mean ozone levels cluster around 21 ppbV. This is comparable with levels recorded at the South Pole. Although there is some variability in ozone abundance from year to year no apparent long-term trend is as yet observed at Cape Point.
- the halocarbons, F-11, and CCl<sub>4</sub>, which are potential destroyers of stratospheric ozone, have maintained steady annual growth rates which over the last five years amounted to 8,5 pptV and 3,5 pptV, re-

spectively. These are considerably lower than the annual growth rates of 11,5 pptV (F-11) and 6,0 pptV (CC14) which had been recorded for the two year period, 1979-1981. This may indeed be as a result of the control measures which were adopted by countries in the Northern Hemisphere. It is also of interest to mention that the F-11 levels recorded at Cape Point are comparable with those reported for the South Pole.

- methane (CH<sub>4</sub>) appears to exhibit a regular increase which is consistent with observations made elsewhere in the world. Atmospheric methane is of importance because it is second only to carbon dioxide as an absorber of infra-red radiation.

TABLE 2  
MEAN ANNUAL CONCENTRATIONS OF TRACE GASES AS MEASURED AT CAPE POINT  
(Source: See references 22 and 23, 'LITERATURE CONSULTED')

Year	O <sub>3</sub> (ppbV)*	F-11 (pptV)**	CC1 <sub>4</sub> (pptV)	CH <sub>4</sub> (ppmV//)	CO (ppbV)	N <sub>2</sub> O (ppbV)
1979	21	-	-	-	65	-
1980	18	173	139	-	68	-
1981	26	182	142	-	68	-
1982	20	192	145	1,56	67	-
1983	22	198	149	1,57	73	296,2
1984	21	207	153	1,59	70	296,8
Average annual growth rate	-	8,5	3,5	0,02	1	0,6
	-	8,5	3,5	0,02	1	0,6

- \* ppbV: parts per billion by volume
- \*\* pptV: parts per trillion by volume
- // ppmV: parts per million by volume

Besides the monitoring of trace gases, a study is being made at Cape Point of the CH<sub>4</sub>-OH-CO atmospheric reaction cycle from which it will hopefully be possible to derive the tropospheric OH radical density. The OH radical plays an important role in atmospheric chemistry in that it controls the rate at which many trace gases such as HCl, H<sub>2</sub>S, SO<sub>2</sub>, CH<sub>3</sub>CCl<sub>3</sub>(F-11) and NH<sub>3</sub> are oxidized and removed from the atmosphere. These reactions have far-reaching environmental/climatic consequences. The oxidation of F-11 by OH, for example, limits the impact which this manmade trace gas has upon stratospheric ozone.

## 5.2 Studies of the middle atmosphere

A project has recently been initiated by Rhodes University to study the composition as well as the physical and chemical processes of the middle atmosphere, because these are currently considered to have an impact on terrestrial climate. The measurement of species such as stratospheric ozone, aerosols and nitrogen oxides will receive high priority.

In addition to getting important local expertise in observing, processing and using such information, this work will benefit from being linked to

other similar investigations such as those co-ordinated under the international SCOSTEP/Middle Atmosphere Programme.

## 6. CONCLUSION

The potential depletion of stratospheric ozone has become an issue of international importance. Countries like the USA, Canada, Sweden and Norway have already banned the use of CFCS as propellants in aerosol products. The European countries, however, have adopted a less drastic attitude in applying control measures in view of the lack of sufficient scientific evidence.

The present situation in the RSA is that its share in the world market in terms of the production of CFCS and products containing aerosol propellants is negligible. Current contribution to CFC (F-11 and F-12) world

production is estimated at about 1%, whereas production of products containing aerosol products is estimated to be only about 4% of that of the USA. Consequently, there is not sufficient justification as yet to introduce control measurements in the RSA either on the production of CFCS or on their use as propellants in aerosol products.

The local scientific and user communities are nevertheless well aware of the urgency for obtaining reliable information on the long-term trends and behaviour of ozone and other relevant trace gases in the troposphere and the stratosphere in order to ultimately allow a realistic assessment of the potential for depletion of stratospheric ozone. The local research currently carried out under the auspices of the NPWCAR will make an important contribution towards understanding the tropospheric/stratospheric processes which play a role in the formation and destruction of ozone.

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FORMATION OF OZONE IN THE TROPOSPHERE  
(Source: See reference 8, 'LITERATURE CONSULTED')

Ozone is formed by the reaction:



Where M denotes a third body.

Most of the atomic oxygen is formed by photodissociation of nitrogen dioxide:



Nitric oxide reacts with ozone, regenerating  $\text{NO}_2$ :



The concentration of ozone can reach levels of adverse effects, if other species can convert NO to  $\text{NO}_2$  in competition with ozone in reaction (3): These other species are peroxy radicals ( $\text{RO}_2$ ):



The peroxy radicals are formed by degradation of volatile organic compounds. Among the most important reactions are attack by the hydroxyl radical and addition of molecular oxygen, as shown for alkanes:



The natural concentration level of OH is partly sustained by the photolysis of ozone and reaction with water vapor:



During pollution episodes there is a net OH production in the daytime hours, and the concentration may be up to a factor of ten higher than the natural background.

Aldehydes are important intermediate species in the reaction chains. They are formed by degradation of hydrocarbons, or directly emitted to the atmosphere. Aldehydes dissociate by solar radiation and are thus important sources of radicals. PAN can be formed from acetaldehyde in reaction with OH:

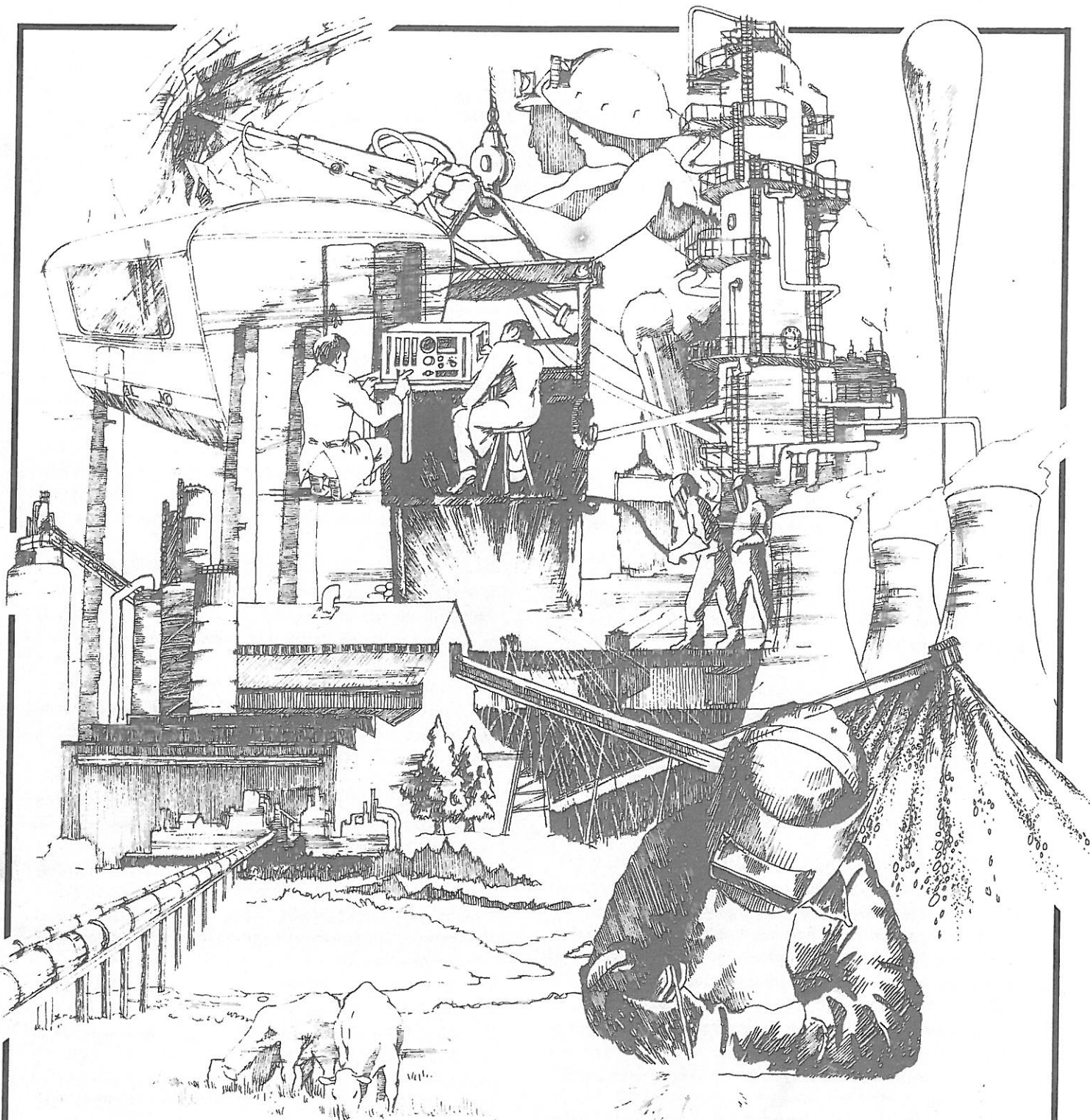


The more complex reaction schemes show in detail how the organic molecules are degraded, how the nitrogen compounds are oxidized, and how the various intermediate species are produced and consumed.

ELEMENTARY REACTIONS WHICH DETERMINE THE CONCENTRATION OF STRATOSPHERIC OZONE

(Source : See reference 2, 'LITERATURE CONSULTED')

1.  $O(^1D) + N_2 \rightarrow O(^1P) + N_2$
2.  $O(^1D) + O_2 \rightarrow O(^1P) + O_2$
3.  $O(^1D) + N_2O \rightarrow NO + NO \rightarrow N_2 + O_2$
4.  $O(^1D) + CH_4 \rightarrow OH + CH_3$
5.  $OH + CH_4 \rightarrow CH_3 + H_2O$
6.  $OH + CO \rightarrow CO_2 + H$
7.  $CO + O + M \rightarrow CO_2 + M$
8.  $O(^1D) + H_2O \rightarrow OH + OH$
9.  $O(^1D) + H_2 \rightarrow OH + H$
10.  $O + OH \rightarrow O_2 + H$
11.  $H + O_3 \rightarrow OH + O_2$
12.  $OH + O_3 \rightarrow HO_2 + O_2$
13.  $HO_2 + O_3 \rightarrow OH + 2O_2$
14.  $O + H_2O_2 \rightarrow O_2 + H_2O \rightarrow OH + HO_2$
15.  $H + H_2O_2 \rightarrow H_2 + HO_2 \rightarrow OH + H_2O$
16.  $H + HO_2 \rightarrow H_2 + O_2 \rightarrow OH + OH$
17.  $H + O_2 + M \rightarrow HO_2 + M$
18.  $OH + OH \rightarrow H_2O + O$
19.  $O + HO_2 \rightarrow OH + O_2$
20.  $OH + H_2 \rightarrow H_2O + H$
21.  $O + H_2 \rightarrow OH + H$
22.  $OH + H_2O_2 \rightarrow HO_2 + H_2O$
23.  $OH + HO_2 \rightarrow H_2O_2 + O_2$
24.  $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
25.  $N + O_2 \rightarrow NO + O$
26.  $OH + HCl \rightarrow H_2O + Cl$
27.  $Cl + H_2 \rightarrow HCl + H$
28.  $H + HCl \rightarrow Cl + H_2$
29.  $O + HCl \rightarrow OH + Cl$
30.  $Cl + O_3 \rightarrow ClO + O_2$
31.  $Cl + Cl + M \rightarrow Cl_2 + M$
32.  $ClO + NO \rightarrow Cl + NO_2$
33.  $ClO + O \rightarrow Cl + O_2$
34.  $ClO + NO_2 + M \rightarrow ClONO_2 + M$
35.  $O + ClONO_2 \rightarrow \text{products}$
36.  $OH + ClONO_2 \rightarrow \text{products}$
37.  $H + Cl_2 \rightarrow HCl + Cl$
38.  $O + Cl_2 \rightarrow ClO + Cl$
39.  $H + ClO \rightarrow OH + Cl$
40.  $Cl + H_2O_2 \rightarrow HCl + HO_2$
41.  $Cl + HO_2 \rightarrow HCl + O_2$
42.  $ClO + HO_2 \rightarrow HOCl + O_2$
43.  $OH + HOCl \rightarrow H_2O + ClO$
44.  $Cl + CH_4 \rightarrow CH_3 + HCl$
45.  $OH + CH_3Cl \rightarrow \text{products}$
46.  $OH + CH_2Cl_2 \rightarrow \text{products}$
47.  $OH + CH_3O \rightarrow HCO + H_2O$
48.  $N + NO \rightarrow N_2 + O$
49.  $O + NO_2 \rightarrow NO + O_2$
50.  $O_1 + NO \rightarrow NO_2 + O_2$
51.  $H + NO_2 \rightarrow OH + NO$
52.  $O_1 + NO_2 \rightarrow O_2 + NO$
53.  $O + NO + M \rightarrow NO_2 + M$
54.  $O + NO_2 + M \rightarrow NO_3 + M$
55.  $NO + NO_3 \rightarrow NO_2 + NO_2$
56.  $NO_2 + NO_1 \rightarrow NO + NO_2 + O_2$
57.  $NO_1 + NO_3 \rightarrow 2NO_2 + O_2$
58.  $N + NO_2 \rightarrow N_2O + O$
59.  $OH + HNO_2 \rightarrow H_2O + NO_1$
60.  $HO_2 + NO \rightarrow OH + NO_2$
61.  $N + O_3 \rightarrow NO + O_2$
62.  $OH + NO + M \rightarrow HNO_2 + M$
63.  $O + HNO_3 \rightarrow OH + NO_2$
64.  $H + HNO_3 \rightarrow H_2 + NO_2$
65.  $O + O_2 + M \rightarrow O_3 + M$
66.  $O + O_3 \rightarrow O_2 + O_2$
67.  $O + O + M \rightarrow O_2 + M$
68.  $NO + NO + O_2 \rightarrow NO_2 + NO_2$
69.  $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$
70.  $N_2O_6 + M \rightarrow NO_2 + NO_2$
71.  $N + OH \rightarrow NO + H$
72.  $N + O \rightarrow NO + hv$
73.  $H + H + M \rightarrow H_2 + M$
74.  $NO + O \rightarrow NO_2 + M$
75.  $OH + HNO_2 \rightarrow H_2O + NO_2$
76.  $HO_2 + NO_2 \rightarrow HNO_2 + O_2$
77.  $HO_2 + NO_2 \rightleftharpoons HO_2NO_2$
78.  $HO_2NO_2 \rightleftharpoons HO_2 + NO_2$
79.  $OH + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$
80.  $OH + CH_3OOH \rightarrow CH_3O_2 + H_2O$
81.  $CH_3OO + NO \rightarrow CH_3O + NO_2$
82.  $CH_3OO + HO_2 \rightarrow CH_3OOH + O_2$
83.  $CH_3OO + CH_3OO \rightarrow 2CH_3O + O_2$
84.  $OH + NO_2 + M \rightarrow HNO_3 + M$
85. soluble gas  $\rightarrow$  precipitation scavenging (units:  $s^{-1}$ ) (HCl, HNO<sub>3</sub>, HNO<sub>2</sub>, HO<sub>2</sub>NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>CO, CH<sub>3</sub>OOH)
86.  $NO + hv \rightarrow N + O$
87.  $N_2O_3 + hv \rightarrow NO_2 + NO_2$
88.  $NO_2 + hv \rightarrow NO + O$
89.  $HNO_2 + hv \rightarrow OH + NO$
90.  $HNO_3 + hv \rightarrow OH + NO_2$
91.  $N_2O + hv \rightarrow N_2 + O(^1D)$
92.  $NO_3 + hv \xrightarrow{1} NO + O_2 \xrightarrow{2} NO_2 + O$
93.  $O_3 + hv \rightarrow O_2 + O$
94.  $O_2 + hv \rightarrow O + O$
95.  $H_2O + hv \rightarrow H + OH$
96.  $CH_4 + hv \rightarrow CH_3 + H$
97.  $CO_2 + hv \rightarrow CO + O$
98.  $H_2O_2 + hv \rightarrow OH + OH$
99.  $CH_3OOH + hv \rightarrow CH_3O + OH$
100.  $HO_2 + hv \rightarrow OH + H$
101.  $H_2CO + hv \rightarrow HCO + H \rightarrow H_2 + CO$
102.  $Cl_2 + hv \rightarrow Cl + Cl$
103.  $HCl + hv \rightarrow H + Cl$
104.  $ClO + hv \rightarrow Cl + O$
105.  $ClONO_2 + hv \rightarrow ClO + NO_2$
106.  $CCl_3F_2 + hv \rightarrow CCl_2F + Cl$
107.  $CCl_3F + hv \rightarrow CCl_2F + Cl$
108.  $CCl_4 + hv \rightarrow CCl_3 + Cl$
109.  $CH_3Cl + hv \rightarrow CH_3 + Cl$
110.  $CH_2Cl_2 + hv \rightarrow CH_2Cl + Cl$
111.  $HOCl + hv \rightarrow OH + Cl$
112.  $HO_2NO_2 + hv \rightarrow OH + NO_2$
113.  $BrONO_2 + hv \rightarrow Br + NO_2$
114.  $BrO + hv \rightarrow Br + O$
115.  $HOBr + hv \rightarrow OH + Br$
116.  $Br_2 + hv \rightarrow Br + Br$
117.  $CH_3Br + hv \rightarrow CH_3 + Br$
118.  $Br + O_3 \rightarrow BrO + O_2$
119.  $Br + HO_2 \rightarrow HBr + O_2$
120.  $Br + H_2O_2 \rightarrow HBr + HO_2$
121.  $OH + HBr \rightarrow H_2O + Br$
122.  $O + HBr \rightarrow OH + Br$
123.  $BrO + NO \rightarrow Br + NO_2$
124.  $BrO + O \rightarrow Br + O_2$
125.  $BrO + BrO \rightarrow 2Br + O_2$
126.  $BrO + ClO \rightarrow Br + Cl + O_2$



# The Gas Analyser People

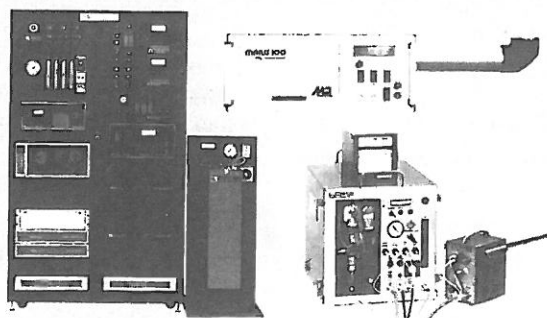
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