Total and tropospheric ozone changes: observations and numerical modelling

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Summary. — A survey has been made of total and tropospheric ozone dynamics in the context of its impacts on climate, human health and ecosystems. Observation data on total ozone content (TOZ) in the atmosphere and relevant numerical modelling results have been discussed as well as similar information for tropospheric ozone, whose formation and changes are being determined by quite different causes. A necessity has been emphasized to get more adequate global observational data on TOZ and tropospheric ozone (this is especially important in the latter case, because information on tropospheric ozone is far from being complete). Unsolved problems relevant to both total and tropospheric ozone have been briefly considered.

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1. – Introduction

It is well known that the ozone layer in the stratosphere (about 90% of ozone resides in a layer of the stratosphere between approximately 10 and 50 km above the Earth's surface, which is called the "ozone layer") protects life on the Earth against harmful ultraviolet (UV) solar radiation [1-12]. The on-going depletion of the ozone layer due to anthropogenic impacts results in the enhancement of surface UV radiation, which may lead to dangerous consequences for man and the biosphere.

In 1970, Professor P. Crutzen has pioneered in the discovery of nitrogen oxides from fertilizers and from supersonic aircraft adverse impacts on the ozone layer. In 1974, Professors S. F. Rowland and M. J. Molina identified CFCs (chlorofluorocarbons) as ozone destroyers, which has been confirmed by subsequent studies. In recognition of their pioneering work, these scientists have been awarded the Nobel Prize for Chemistry in 1995.

Tropospheric ozone (whose amount is about 10% of the total ozone content, TOZ) is a significant greenhouse gas (GHG). Stratospheric and tropospheric ozone changes contribute differently to climate changes as well as have different effects on humans and ecosystems. An important specific phenomenon relevant to tropospheric ozone

changes is photochemical smog formation. Specific functions of stratospheric and tropospheric ozone have given certain grounds to consider stratospheric ozone as *good* ozone, while tropospheric ozone is *bad* [13].

It is thus obvious that atmospheric ozone is a component of the atmosphere, which deserves special attention. This is why the Montreal Protocol on Substances that Deplete the Ozone Layer (1987) to the Vienna Convention for the Protection of the Ozone Layer (1985) and subsequent Amendments and Adjustments to the Protocol have been signed [14, 10]. In accordance with the Helsinki Declaration on the Protection of the Ozone layer (May 2, 1989), it has been agreed to phase-out the production and consumption of CFCs controlled by the Montreal Protocol as soon as possible but not later than the year 2000.

The total phase-out has been recommended by the London Amendment to the Montreal Protocol on the basis of the 1989 assessment. The discovery of the Antarctic "ozone hole" in 1985 and conclusions of the 1991 Assessment have led to the recommendations of the Copenhagen Amendment (1992) to broaden the list of the ozone-depleting substances (ODS) by adding HCFCs (hydrochlorofluorocarbons) and methyl bromide. The subsequent 1997 adjustments and amendment marked ten years of the Protocol [10] and required the phase-out of the following categories of substances (at present there are 95 chemicals controlled by the Protocol):

Chlorofluorocarbons:

   – CFCs, Halons, Hydrobromofluorocarbons

   – HBFCs, Other fully halogenated CFCs, Carbon tetrachloride, 1,1,1 trichloroethane

   – methyl-chloroform

Hydrochlorofluorocarbons:

   – HCFCs,

Hydrobromofluorocarbons:

   – HBFCs

Methyl Bromide.

Control measures for chemicals include (in case of developed countries): phase-out of halons by 1994, phase-out of CFCs, carbon tetrachloride, methyl chloroform and HBFCs by 1996, phase-out of Methyl Bromide by 2005, phase-out of HCFCs by 2030.

It has been recommended for developing countries to phase-out HBFCs by 1996. Phase-out of CFCs, Halons and Carbon tetrachloride by 2010. Methyl Chloroform and Methyl Bromide by 2015. HCFCs by 2040.

It must be pointed out, however, that the situation with regard to methyl bromide (CH_3Br, brommethane, MeBr) is still rather controversial. Yates *et al.* [15] have shown that recently new technology has been developed, which could nearly eliminate MeBr emissions from soil fumigation, bringing into question the need for a phase-out.

It has been mentioned in [11] that the data of recent years clearly show that the growth rates of CFC-11, CFC-12, halon-1301 and halon-1211 are slowing down. Due to WMO/UNEP [16] the total combined abundance of ozone-depleting compounds in the lower atmosphere peaked in about 1994 and then started to slowly decline; the combined abundance of stratospheric chlorine and bromine is expected to peak before

the year 2000. The increase of total tropospheric organic chlorine in 1992 was only about 60ppt/year (1.6%), compared to 110 ppt/year (2.9%) in 1989. The abundance of carbon tetrachloride is also decreasing. On the other hand, the atmospheric abundance of several CFC substitutes (HCFCs, HFCs) were increasing, as anticipated.

The result of the recommendations mentioned has been a slowing-down of the growth of halocarbon concentrations in the stratosphere (the first example of an advertent positive influence of man on the atmosphere). In accordance with the observations from UARS satellite, discussed by Russel [17] global average (for the 70°N-70°S latitude band) total Cl and F ratio trends at the 55 km altitude have decreased during the time period 1991-1997 from 124 to 116 ppt/yr (Cl) and from 92 to 82 ppt/yr (F).

Bojkov [18] has emphasized that the long period of increasing total chlorine abundances in the troposphere—primarily from CFCs, carbon tetrachloride and methyl chloroform—has ended, chlorine from the major CFCs is still increasing slightly and most halons continue to increase substantially (*e.g.* halon-1211, 5% per year until now). The abundances of HCFCs and HFCs (hydrofluorocarbons) are increasing as a result of their CFC substitutes. Stratospheric halogen loading lags behind tropospheric loading by up to six years: the maximum concentrations of chlorine and bromine are expected to peak ∼ 3.7 ppb around the year 2000 and keep close to this concentration over the next one or two decades. Even a complete and immediate global elimination of all ozone depleting substance (ODS) emissions would result in the stratospheric halogen loading returning to the pre-1980 values by the year 2033. Some major scientific findings in the Ozone Assessment-1998 are as follows [128], [10], [16]:

– The rate of decline in stratospheric ozone at mid-latitudes has slowed; hence, the projections of ozone loss made in the 1994 UNEP Assessment are larger than what has actually occurred. In the northern polar latitudes, in six out of the nine last boreal winter/spring seasons, ozone has declined during some months by 25% to 30% below the 1960s average (Bojkov *et al.* [8] have shown that during the 1990s over the 35-50° middle latitude belts the ozone deficiency in the Southern Hemisphere is less than over the Northern Hemisphere by about 39%). The observed TOZ losses from 1979 in the period 1994-1997 are about 5.4% and 2.8% for northerm mid-latidudes in winter/spring and in summer/autumm, respectively; and −5.0% in southerm mid-latidudes all year round. There are no statistical TOZ trends in the equatorial region (20° S to 20° N).

– The springtime Antarctic ozone hole continues unabated. Although the extent of ozone depletion was strongest in 1998, it has, during the last 3-4 years, remained generally similar to those in the early 1990s with monthly TOZ values in September and October continuing to be 40-55% below the pre-ozone-hole values (with up to 70% decrease for periods of about one week).

– The late winter/spring ozone values in the Artic were unusually low in six out of the last nine years, those six being years that were characterised by usually cold and protracted stratospheric winters with minimum Artic circumpolar vortex (CPU) temperatures near the threshold for large chlorine activation. Ozone has declined during some spring months by 25%-35% below the pre-1976 average. Elevated stratospheric halogen abundance over the next decade or so would imply the Arctic's continuing vulnerability to large ozone losses.

– Over northern mid-latidudes, the downward TOZ trends is largest near

40–15 km ($>7\%$ per decade) and is smallest 30 km (2% per decade). The bulk of TOZ decline is between the tropopause and 5 km.

– The understanding of the reaction between increasing surface UV-B radiation and decreasing column ozone has been further strengthened by ground-based observations and new developed satellite methods show promise for establishing global trends in UV radiation.

– Stratospheric ozone losses may have caused part of the observed cooling of the lower stratosphere in the polar and upper middle latitudes and global average negative radiative forcing of the climate system. Much of the observed downward trend in lower stratospheric temperatures (about 0.6 °C per decade from 1979 to 1994) is attributed too the ozone loss in the stratosphere. The stratospheric ozone losses since 1980 may offset about 30% of the positive greenhouse gases effect over the same time period.

– Based on past emissions of ozone-depleting substances and projection of the maximum allowances under the Montreal Protocol into the future, the maximum ozone depletion is estimated to lie within the current decade or the next two decades, but its identification and the evidence for the recovery of the ozone layer lie still further ahead. It has been pointed out the WMO/UNEP Scientific Assessment of Ozone Depletion-1998 [16] that "a full recovery of the Earth's protective ozone shield could occur by the middle of the next century, but it would require that the Protocol is fully implemented".

– The increase of ozone in the troposphere since pre-industrial times is estimated to have contributed 10% to 20% of the warming due to the increase in long-lived greenhouse gases during the same period.

Sarma [10] has emphasized the role of the Montreal Protocol, as well as subsequent Amendments and Adjustments in avoiding negative environmental consequences such as: 1) at least 50% ozone depletion at mid-latitudes in the Northern Hemisphere and 70% depletion at mid-latitudes in the Southern Hemisphere, about 10 times larger than today; 2) at least doubling surface UV-B radiation at mid-latitudes in the Northern Hemisphere and quadrupling at mid-latitudes in the Southern Hemisphere compared to an unperturbed atmosphere. This compares to the current increases of 5% and 8% in the Northern and Southern Hemispheres, respectively, since 1980.

The implication of such ozone depletions would have been horrendous, including nearly 19 million cases more of non-melanoma skin cancer up to the year 2060 and 3 million more cases up to 2030. The number of eye cataracts would have increased by about 130 million cases by the year 2060, about 50% of this in developing countries. There is a number of unquantifiable effects such as loss of immunity, adverse impact on animals, lower productivity of crops, damage to aquatic ecosystems and others. It must be pointed out, however, that a number of scientists [19-21] warned against over-emphasis of such dangers, due to the ozone depletion.

Ozone problems have become essential parts of such global-scale international programmes as the World Climate Research Programme (WCRP) with its SPARC (Stratospheric Processes and their Role in Climate) Project [22] and the International Geosphere-Biosphere Programme (IGBP) including the IGAC (International Global Atmospheric Chemistry) Core Project [23], as well as many other ozone-relating projects [7].

Marked progress has been achieved in the development of satellite remote sensing aimed at obtaining information on global-scale spatio-temporal ozone and ozone-

depleting substances (ODS) variability and trends. A number of comprehensive observational programmes have been accomplished in the high latitudes of the Northern Hemisphere and in the Antarctic, to study the stratosphere and ozone dynamics. As a result, not only now well-known "ozone hole" in the Antarctic, but also ozone "mini-holes" and substantial depletion of ozone have been discovered over vast territories of Siberia [24-27]. New studies have been conducted to assess the influence of the ozone depletion on surface ultraviolet radiation (UVR) and subsequent impacts on human health and the biosphere.

Problems of tropospheric ozone changes have recently attracted much more attention than before, especially in the field of numerical modelling (observations still remain inadequate). Important success has been achieved in interactive simulation of the troposphere dynamics and ozone changes [28, 29]. Impacts of both stratospheric and tropospheric ozone on climate has been studied [30, 31]. A special attention has been paid to heterogeneous chemical reactions on surfaces of aerosol particles in the stratosphere (especially in case of polar stratospheric clouds) and troposphere [9, 32-34, 35].

As has been pointed out in the WMO/UNEP Ozone Assessment (1999):

– Enhacing anthropogenic emissions of ODS (nitrogen oxides, carbon monoxide and hydrocarbons) lead to large-scale production of ozone, which, trough long-range transport, influences the ozone concentration in large regions of the troposphere in both hemispheres. Such changes are characterised by strong spatio-temporal variability.

– The increase of ozone in the troposphere since pre-industrial times is estimated to have augmented the average radiative forcing (RF) by -0.35 ± 0.15 W/m^2, which is thought to have contributed 10%-20% of the warming owing to the increase of long-lived GHGs during the same period.

Undoubtedly, marked progress has been achieved in studying atmospheric ozone and consequences of its changes; however, quite a number of related problems remain unsolved thus far. Many aspects of ozone research have been discussed in a number of recent publications, especially in the UNEP's *Scientific Assessment of Ozone Depletion: 1994, 1998* [11, 16], as well as NATO ASI monograph *Atmospheric Ozone Dynamics* [36] and *Atmospheric Ozone* [7]. Nevertheless, there is a necessity for a more comprehensive and integrative consideration of all ozone problems in their full complexity, and this precisely is the principal purpose of this survey, which is addressed to broad circles of experts and non-experts (including students), who may be interested in the problem of atmospheric ozone changes and subsequent impacts on man and the biosphere.

2. – Stratospheric ozone

2˙1. *Observations and interpretation of observation data.* – Although total ozone content (TOZ) observations started about 150 years ago, when the existence of the ozone layer in the stratosphere was discovered, a complete enough global archive of TOZ data has been accumulated mainly during the last few decades due to satellite observations. Various remote-sensing techniques have been used for this purpose based on satellite measurements of backscattered solar UV radiation, attenuation of

UV radiation by the atmosphere under conditions of "occultation geometry", thermal emission in the 9,6îm ozone absorption band [9, 11, 16].

The most important results from the observations consist in detecting the mean global TOZ decrease and the event of "ozone hole" in the Antarctic attracting a great deal of attention, as well as, short-term but sharp TOZ decreases in the NH high latitudes [37, 2, 3, 38-40, 4-6, 41, 7, 8, 42-50, 9, 32, 51-56, 57, 58-63, 12, 64, 65].

Since the stratospheric ozone is an intensive absorber of solar radiation and the tropospheric ozone is a greenhouse gas [9, 32, 13, 66], there is no doubt that changes in the content of ozone in the atmosphere must affect the climate.

The UNEP Report on ozone [11] as well as WMO/UNEP Scientific Assessment [16] and other publications note the following most important aspects of the problem:

– Beginning from 1979, the rate of TOZ decline in the mid-latitudes of both hemispheres was about 4-5% over 10 years. On the basis of the analysis of the ozone decline in the Northern polar and middle latitudes during the winter-spring Bojkov *et al.* [8] have come to the conclusion that the ozone-mass deficiency O_3 MD (defined from the pre-1976 base average, and areal extent with negative deviations greater than ~ 2 and $\sim 3\sigma$), integrated for the first 105 days of each year, has increased dramatically from ~ 2800 Mt in the early 1980s to ~ 7800 Mt in the 1990s, exceeded 12000 Mt in the winter-springs of 1993 and 1995.

Bojkov [18] has pointed out that total ozone levels in the latidudes 60° N-60° S were at the lowest value in 1993 due to the large increase of stratospheric aerosol caused by the eruption of the Pinatubo in 1991—see Kondratyev K. Ya and Galindo I., *Volcanic Activity and Climate* (A Deepack Publ., Hampton, Virginia) 1997, p. 382, and [35]. Since 1992/1993, TOZ values over this part globe have been variable around a fairly constant level. Table I data illustrate basic features of TOZ trends [18].

The amplitude of the annual cycle of ozone at middle-to-high latidudes has decreased by 15% in the last two decades, because larger declines have occurred during the winter/spring season of maximum ozone values.

– Ozone depletion increases with latitude, particularly in the Southern Hemisphere. Little or no downward trends are observed in the tropics (20 °N-20 °S). Analysis of global TOZ data through early 1994 shows substantial decreases of ozone in all seasons at midlatitudes (30°-60°) of both hemispheres. There were downward trends in the Northern Hemisphere of about 6% per decade over 1979-1994, observed in winter and spring and about 3% per decade were observed in summer and fall. In the Southern Hemisphere the seasons difference was smaller and the midlatitude trends averaged about 4-5% per decade. Satellite and ozonesonde data show that much of the downward trend in ozone occurs below 25 km.

TABLE I. - *Total ozone trends* (*percent per decade since January* 1979) *calculated as averages of individual station trends in the indicated regions and groups of months* (*ground-based observations*). *All values are negative and statistically significant at* 2G.

Region	DJF	MAM	SSA	SON	Year
Artic	7.9	7.7	2.5	3.6	5.7
35-60N	4.1	5.7	2.9	1.6	3.7
35-60S	2.9	2.2	3.4	2.0	2.6
Antatric	6.3	2.4	6.5	20.0	8.9

– Due to WMO/UNEP Scientific Assessment [16] TOZ decreased significantly at midlatitudes (25-60°) between 1979 and 1991, with estimated linear downward trends of 4.0%, 1.8%, and 3.8% per decade, respectively, for northern midlatitudes in winter/spring; northern midlatitudes in summer/fall; and southern midlatitudes all year round. However, since 1991 the linear trend observed during the 1980s has not continued, but rather TOZ was almost constant at all midlatitudes in both hemispheres since the recovery from the 1991 Mt. Pinatubo eruption. The present-day understanding of how changes in halogen and aerosol loading affect ozone suggests some of the reasons why a linear extrapolation of the pre-1991 ozone trend to the present is not suitable [16].

– A complex 3D-spatial structure of ozone distribution has been discovered during the recent years in the form of lamination [35] and low-ozone air pockets forming during northern winter in the middle stratosphere outside the polar vortex.

– Nair *et al.* [54] have pointed out that the rapid ozone loss localized in the pockets is due to the isolation of air at high latitudes (and high solar zenith angles). Thus the low ozone levels are due to a decrease in the odd oxygen production rates and not to an increase in the loss rate by reaction with halogen species, as in the "classical" ozone hole. For the explanation of the low-ozone pockets, Morris *et al.* [67] have developed a simulation model taking account of photochemical processes and stratospheric dynamics.

– Lastovicka [17] has concluded on the basis of ozonesonde data that the number of thin ozone layers per one ozone vertical profile has decreased during the time period 1970-1993 from about 1.9 to 1.0 (with the depletion of the ozone content in such layers of about 50%).

– The lowest values of TOZ were observed in 1992-93 in the presence of the most clearly manifested "ozone hole" in the Antarctic and the lowest TOZ values in the whole observational period over the densely populated regions of the Northern Hemisphere. The conclusion that anthropogenic chlorine and bromine compounds, coupled with surface chemistry on natural polar stratospheric particles, are the cause of polar ozone depletion has been further strengthened. The links to halogen chemistry have also been established with regard to ozone losses detected in the Arctic winter stratosphere.

– According to [16], the large ozone losses during the spring in the Southern Hemisphere continued unabated with approximately the same magnitude and areal extent as in the early 1990s. In Antarctica, the monthly total ozone in September and October has continued to be 40 to 55% below the pre-ozone-hole values of approximately 320 m-atm cm (DU), with up to a 70% decrease for periods of a week or so. This depletion occurs primarily over the 12 to 20 km altitudes range, with most of the ozone in this layer disappearing during early October.

– The observations made after the eruption of Pinatubo in 1991 have resulted in the discovery of a substantial impact of such a major volcanic eruption on stratospheric ozone [68].

– Impacts of subsonic and supersonic aircraft on upper tropospheric and lower stratospheric ozone have been confirmed [69, 70, 42, 71-73].

– The earlier conclusion has been confirmed about the substantial role of methyl bromide as a ozone-destroying component, the main sources of which are the

fumigating of the crops, biomass burning and cars. The most recent data [16] indicate, however, that the role of methyl bromide as an ozone-depleting compound is now considered to be less than what was estimated in the 1994 UNEP Assessment [11], although significant uncertainties remain (the science of atmospheric methyl bromide is complex and still not well understood).

    – The planned countermeasures on the control of emissions of the ozone-depleting compounds will not greatly change the maximum level of TOZ decline to be reached during the next 10 years.

    – Due to model simulations much of the observed downward trend in lower stratospheric temperatures (about 0.6 °C per decade over 1979-1994) is attributed to the ozone loss in the lower stratosphere [16]. The decrease of the stratospheric ozone content since 1980 may have offset about 30% of the greenhouse forcing, which favored the global climate warming. However, the increase of the content of tropospheric ozone in the same period has intensified the atmospheric greenhouse effect in the Northern Hemisphere, also by $\sim 20\%$. The problem of the ozone trends with opposite signs in the stratosphere and in the troposphere claims special attention also in the context of the effect of TOZ variations on UV radiation.

    – From some published data [74], the TOZ decline in 1992-93 was not followed by any increase of UV-B radiation. Important ideas on the necessity of a thorough analysis of data on the trends of TOZ, UV-B and related biological consequences have been expressed by Ellsaesser [19]. Feister and Crewe [75] have observed, however, higher UV radiation inferred from low ozone values at northern mid-latitudes in 1992 and 1993 and pointed out that this could lead to adverse biological effects. Numerous further studies have confirmed this conclusion.

    – A general conclusion made in the WMO/UNEP Scientific Assessment [16] is that the understanding of the relation between increasing surface UV-B radiation and decreasing TOZ has been further strengthened by ground-based observations, and newly developed satellite methods show promise for establishing global trends in UV radiation. The satellite estimates for 1979-1992 indicate that the largest UV increases occur during spring at high latitudes in both hemispheres.

In spite of certain cautions against an overemphasis of ozone impacts on the environment and ecosystems, there are no doubts that this problem deserves very serious attention.

Prather *et al.* [57] have posed a number of important questions in this context. 1) What if chlorofluorocarbon (CFC) use had followed a free-market growth into all sectors and countries until the observation of stratospheric ozone depletion itself was the first warning? 2) What if the ozone hole had been discovered in 1985 (as indeed it was) but no prior suspicion had focused on chlorine from CFCs? 3) When do we now expect to see recovery of the ozone layer as provisions of the Montreal Protocol show their effects in the global atmosphere? 4) How much stratospheric chlorine and associated ozone depletion would the global atmosphere have been committed to in a likely alternative scenario?

Answering the questions mentioned, Prather *et al.* [57] have emphasized that: 1) if we had ignored the scientific evidence, or not, ozone depletion would be dramatically worse than that we are controlling today; 2) if CFCs had followed free-market growth until 2002, the Antarctic ozone hole would be a permanent fixture through the twenty-first century, instead of disappearing by 2050 as predicted in the Copenhagen

'92 scenario; 3) ozone depletion is expected to reverse and recover measurably in the first decades of the next century; unambiguous detection of the recovery will take a decade or more.

Kaye [76] and Mc Cormick [53] have summarized results of discussions of satellite TOZ observations with the use of TOMS (Total Ozone Mapping Spectrometer) and SAGE (Stratospheric Aerosol and Gas Experiment) instrumentation, respectively. By the present time a total of four TOMS instruments have flown in space—Nimbus 7 TOMS (1978-1993), Meteor-3 TOMS (1991-1994), ADEOS TOMS (1996-1997) and Earth Probe TOMS (1996-present time). The TOMS instruments have provided excellent data for TOZ, although there are some limitations that must be considered in certain applications, especially for studies of tropospheric ozone (currently, no data are released for zenith angles greater than 84°, although data are in principle available for up to 88°).

Apart from TOZ data, processing of TOMS information allows to retrieve tropospheric ozone content and surface flux of ultraviolet radiation, especially if ratios, such as that of UV-A/UV-B (UV radiation longward and shortward of 320 nm) are considered. The launches of TOMS instrumentation made it possible to accumulate a data set covering the period from late 1978 till February 1998 for zonal mean TOZ. One of the applications of the data obtained were studies of TOZ long-term trends and interannual variability in mid-latitudes (a particular emphasis has been made on dynamically driven contributions). The results suggest that changes in lower stratospheric temperature and/or tropopause height could be contributing significantly to the mid-latitude decreases observed by TOMS. It was seen that short-term meteorological events can significantly affect the zonal mean distribution of TOZ, especially in February, when there can be enormous variations from one winter to the next.

For the purposes of testing retrieval algorithms, observation data from Satellite Ozone Limb Sounding Experiment (SOLSE) and Limb Ozone Retrieval Experiment (LORE) instruments that flew on the space shuttle in the fall of 1997 are available. Measurements of a number of species with UV absorption in the ultraviolet using the Global Ozone Monitoring Experiment (GOME) instrument aboard the ERS-2 satellite have been conducted (column distributions of BrO, ClO and SO_2 have been studied).

In continuation of earlier SAGE observations three new ozone-measuring instruments for SAGE-III have been developed [53]. The first flight is scheduled for 1999 (Russian Meteor-3M satellite on sun-sychronous orbit) while the second flight will be flown on a flight of opportunity into a mid-to-high inclination orbit. The third SAGE-III instrument will be flown aboard the International Space Station (ISS), scheduled for mid-to-late 2002. Using a technique of solar occultation SAGE-III data will allow to retrieve 1 km vertically resolved middle atmosphere profiles of ozone, aerosols and a number of aerosol properties, water vapour, temperature, nitrogen dioxide and cloud presence. In addition, using lunar occulations, it will be possible to retrieve nitrogen trioxide and chlorine dioxide vertical profiles. For validation purposes, the SAGE-III Ozone Loss and Validation Experiment (SOLVE) has been planned, whose aim is a joint balloon and airborne measurement campaign in the Arctic designed to examine the processes that control polar to mid-latitude stratospheric ozone levels and aid in SAGE-III validation. An important role in solving validation problems belongs to the ozonesonde network. Guirlet *et al.* [77] described the Third European Stratospheric Experiment on Ozone (THESEO) conducted in 1998-1999 as a continuation of earlier European Arctic Stratospheric Ozone Experiment (EASOE, 1991-1992) and the Second Stratospheric Arctic and Mid-latitude Experiment

(SESAME) with principle purpose of better understanding of those processes, which determine stratospheric ozone trends in mid-latitudes on the basis of studying interactions between relevant chemical and dynamical processes. The aim is to investigate the ozone formation both within and outside of the circumpolar vortex. The observations covered a broad range of latitudes from the Tropics to the Arctic using ozonesondes, lidars, small balloons and aircraft.

Discussing ozone problems, it is proper to quote the policy Statement on Atmospheric Ozone accepted by the American Meteorological Society Council, 28 January 1996 [78]:

1. The AMS recognizes ozone as an atmospheric constituent that has a number of important beneficial as well as detrimental effects on the atmosphere, on surface ecosystems and on humankind. These include effects on both ultraviolet and long-wave radiation, resulting effects on atmospheric wind systems and direct impacts on plants and animals. Moreover, ozone is recognized as the dominant progenitor of much of the trace-gas chemistry that occurs in both the troposphere and the stratosphere. The AMS also notes that extensive couplings exist among these chemical, radiative and dynamical components of ozone's behavior and add substantial uncertainty to many of the currently available assessments of ozone's impact.

2. Despite many uncertainties, ample evidence exists to substantiate that atmospheric ozone has been affected in important and even critical ways by human activity. In case of the stratosphere, the existence of the Antarctic ozone hole is unquestionable and our evidence that it results from human-produced halocarbons is overwhelming. Ozone depletion in the midlatitude stratosphere is less dramatic; however, the general agreement of the large numbers of available column and profile measurements make it reasonable to speculate that such depletion is indeed occurring and that it is largely human-induced.

Anthropogenic activities also significantly influence tropospheric ozone. Humankind is directly responsible for the excessive ozone levels that often occur near the surface in and down-wind from populated areas. These effects are also felt throughout significant regions of the free troposphere.

The effects in both the stratosphere and troposphere are sufficiently profound to mandate substantial concern, on both a local and a global basis.

3. While the above manifestations of human impact on ozone are clear, there remain important gaps in our understanding of ozone's complex behavior. For example, currently we cannot quantitatively explain the midlatitude observations of insignificant surface UV increases. Impacts of tropospheric ozone buildup on the free troposphere's chemistry are also in a highly speculative state. These issues and others must be resolved in order to satisfactorily forecast potential future manifestations and provide a firm basis for policy analysis and associated policy actions.

4. Many of the noted uncertainties arise because of the strong couplings between chemistry, radiation and atmospheric dynamics. Because of this, their resolution will require substantial combined effort by scientists having chemical and meteorological backgrounds. The AMS intends to actively provide one component of a continuing forum for this scientific interaction and act in conjunction with other like-minded organization for this purpose.

5. Current ozone-control legislation (such as the US Clean Air Act, with 1990 amendments) and international agreement (such as the Montreal Protocol) tend to

reflect the uncertainties noted above. The State Implementation Plan approach of the current US Clean Air Act is burdened by older and largely invalid concepts of chemistry and atmospheric transport, which make ozone-standard attainment difficult if not impossible at many locations. Future amended versions of this act should incorporate more manageable and scientifically valid approaches to ozone control and substantial current meteorological and chemical research should be directed to determining effective strategies for this purpose.

With regard to the Montreal Protocol, it is encouraging to note that halocarbon limitations under this agreement appear to have resulted, recently, in decreases of some of the shorter-lived halogen-containing species. Owing to the noted uncertainties and complexities associated with stratospheric ozone depletion, however, the effects of this and other international agreements must be monitored continuously and carefully to ensure their effectiveness and to establish the basic understanding required for more effective maintenance during future years.

2˙2. *Theory of the ozone layer formation and changes.* – As has been pointed out by Crutzen [79] until about the mid-1960s, the theory suggested by Sydney Chapman in 1930 to explain the ozone layer formation was considered adequate (we shall follow Prof. Crutzen's summary of the history of ozone theory). In accordance with this theory, the formation of "odd oxygen"—O and O_3—is due to photolysis of molecular oxygen O_2 by solar radiation at wavelengths shorter than 240 nm:

$$(1) \qquad\qquad O_2 + h\nu \rightarrow 2O \quad (\lambda \leqslant 240 \text{ nm}).$$
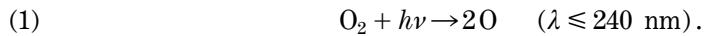
This atomic oxygen reacts quickly with molecular oxygen O_2 to form ozone O_3, which, however, will rapidly decompose again unless some energy-absorbing molecule M (N_2 and O_2) is present. Thus

$$(2) \qquad\qquad O + O_2 + M \rightarrow O_3 + M .$$

The loss of ozone is due to photolysis:

$$(3) \qquad\qquad O_3 + h\nu \rightarrow O + O_2.$$

The reactions (2) and (3) lead to the rapid establishment of a steady state for the concentration of O and O_3 without affecting the concentration of odd oxygen whose destruction (counteracting its production through photolysis (1)) occurs by reaction

$$(4) \qquad\qquad O + O_3 \rightarrow 2O_2.$$

Later on (in 1950) David Bates and Marcel Nicolet with Syndey Chapman proposed that catalytic reactions involving hydroxyl (OH) and HO_2 radicals could counterbalance the production of odd oxygen in the meso- and thermosphere which was necessary because reaction (4) was too slow. Taking this proposal into account, J. Hampson and G. Hunt suggested the reactions

$$(5) \qquad\qquad OH + O_3 \rightarrow HO_2 + O_2,$$

$$(6) \qquad\qquad HO_2 + O_3 \rightarrow OH + 2O_2,$$

$$2O_3 \rightarrow 3O_2.$$
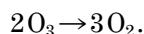
The primary source for the OH radicals was photolysis of O_3 by solar UV radiation of wavelengths shorter than about 320 nm, which leads to electronically excited $O(^1D)$ atoms. Most of $O(^1D)$ react with O_2 and N_2 to reproduce O_3, rapidly producing a null cycle with no effect on concentrations of ozone or odd oxygen. Therefore

$$(7) \qquad\qquad O_3 + h\nu \rightarrow O(^1D) + O_2,$$

$$(8) \qquad\qquad O(^1D) + H_2O \rightarrow 2OH,$$

$$(9) \qquad\qquad O(^1D) + M \rightarrow O + M.$$

P. Crutzen has demonstrated, however, that reactions (5) and (6) are too slow and therefore discarded the theory of Hampson and Hunt. The influence of nitrogen oxide compounds (a potential role of NO and NO_2 is catalysing O_3 destruction) on the photochemistry of the ozone layer has been considered instead. The presence of active nitrogen oxides $(NO_x = NO + NO_2)$ in the atmosphere results from the following reactions:

$$(10) \qquad\qquad OH + NO_2(+M) \rightarrow HNO_3(+M),$$

$$(11) \qquad\qquad HNO_3 + h\nu \rightarrow OH + NO_2.$$
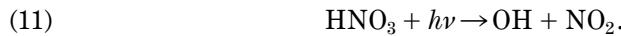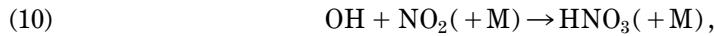
In accordance with the views mentioned above the following catalytic reactions were suggested:

$$(12) \qquad\qquad NO + O_3 \rightarrow NO_2 + O_2,$$

$$(13) \qquad\qquad O + NO_2 \rightarrow NO + O_2,$$

$$(12+13) \qquad\qquad O + O_3 \rightarrow 2O_2.$$

As can be seen, the net result of reactions (12) and (13) is equivalent to the direct reaction (4). It has later become clear that enough NO is produced in the reaction

$$(14) \qquad\qquad N_2O(^1D) \rightarrow 2NO$$

to make reactions (12) and (13) the most important ozone loss reactions in the stratosphere in the altitudes between 25 and 45 km.

Nitrous oxide is a natural product of microbial processes in soils and waters, but, on the other hand, there are various anthropogenic sources of N_2O emissions due to, for instance, applications of nitrogen fertilisers. It is known at the present time that the rate of increase in the atmospheric N_2O concentrations (0.2-0.3% per year) which was observed during the past decades was due to anthropogenic activities. The discovery of the important role of NO_x in the ozone layer formation and changes has happened to be very significant in the context of assessment of subsonic and supersonic aviation's impacts on the ozone layer [41, 42, 80, 71].

During the 1970s intensive efforts of studying the potentially large efficiency of Cl and ClO in destroying stratospheric ozone took place. In September 1974 Prof. Crutzen published a model analysis of the potential ozone depletion resulting from the continued use of CFCs, which indicated the possibility of as much as 40 per cent ozone depletion near 40 km altitude as a result of continued use of these compounds at 1974 rates [77]. Within the problem of the ozone layer changes emphasis has been made on chlorine   chemistry   to   understand   and   quantitatively   assess   anthropogenic,

chlorine-catalysed ozone destruction. Observations have confirmed that halogen chemistry plays a larger role in the chemical destruction of ozone in the midlatitude lower stratosphere than expected from gas phase chemistry. Bromine compounds require special attention, because bromine is almost 100 times more dangerous for ozone than chlorine on atom-to-atom basis [77].

An important consequence of the ozone hole discovery has been recognition of the decisive role of heterogeneous chemical reactions on aerosol particles in the atmosphere. In case of the ozone hole there are particles of polar stratospheric clouds (PSC) which form under extremely low temperatures as a result of condensation of water vapour and nitric acid. Since formation and stability of PSCs strongly depend on meteorological conditions in the stratosphere, this results in coupling between climate and ozone dynamics. Another aspect of this problem is extremely strong sensitivity to temperature of the chemical reactions responsible for stratospheric ozone depletion.

In this context Shindell et $al.$ [81] have investigated the interplay between projected future emissions of greenhouse gases (GHGs) and levels of ozone-depleting halogen species using a global climate model that incorporates simplified ozone-depletion chemistry. The numerical modelling results demonstrate that temperature and wind changes induced by the increasing GHGs concentrations alter planetary-wave propagation, reducing the frequency of sudden stratospheric warmings in the Northern Hemisphere. This results in a more stable circumpolar vortex, with significantly colder temperature in the lower stratosphere and concomitantly increased ozone depletion. Thus, GHGs concentrations increase may be a cause for the very large Arctic ozone losses to reach a maximum in the decade 2010 to 2019, roughly a decade after the maximum in stratospheric chlorine abundance, with the mean losses comparable with those in the Antarctic during the early 1990s (up to two-thirds of the Arctic ozone losses are predicted to be geographically localised). Another consequence of the "greenhouse" stratospheric cooling over the coming decades should be more severe and durable Antarctic ozone hole.

Salawitch [82] has pointed out, however, that the Arctic winter of 1997-98 has been fairly warm, with considerably less chemical loss of O_3 than in the previous five winters. This behaviour is not necessarily inconsistent with the model of Shindell et $al.$ [79], but complicates ascribing a climatic influence to the changes in temperature and O_3 that have occurred during the previous five winters. Shindell [79] has emphasised a necessity of further analysis of observation data as well as additional numerical modelling to reach more adequate understanding of the factors that regulate the temperature of the polar vortices.

Prather [83] has investigated time scales in atmospheric chemistry in connection with coupled perturbations to N_2O (which is the third most important greenhouse gas), NO_y (odd nitrogen, usually including NO, NO_2, NO_3, N_2O_5, $ClONO_2$, HNO_4, HNO_3) and O_3. This group of chemical compounds is fully coupled through stratospheric photochemistry: N_2O emitted at the surface enters the stratosphere and releases NO_y, which catalitically destroys O_3 in the mid-stratosphere; as a result, more ultraviolet sunlight is available for photolytic destruction of N_2O. Prather [81] has simulated such a coupling using a representative one-dimensional model to show how photolytic coupling leads to a more rapid (10 to 15%) decay of N_2O perturbations than anticipated from the N_2O lifetime based on steady-state budgets. This pattern will be excited by emissions of N_2O or by almost any chemical perturbation, for example, those affecting stratospheric ozone. Such coupled patterns might be discernible in the atmosphere.

Summarising achievements in the understanding of the TOZ changes, Bojkov [18]

has pointed out that contemporary simulation models, based on the observed build-up of chlorine/bromine in the stratosphere, predict an ozone depletion that is in good quantitive agreement with the altitude and latitude of the measured ozone decline during the past several decades, especially over the polar regions. This clearly confirms the predictions made by Rowland and Molina in 1974 concerning a substantial reduction of upper stratospheric ozone due to release of CFCs to the atmpsphere. Both observations and models have also confirmed a key of stratospheric sulphate aerosol (SSA) and polar stratospheric clouds (PSCs) in ozone loss chemistry through heterogeneous reactions that activate halogen species and deactivate nitrogen species. It has been recently shown that cold liquid aerosol can maintain elevated ClO in non-denitrified air. Since chlorine activation in liquid particles in the lower stratosphere (both on SSA and PSCs) decreases strongly with decrease in temperature, this process is controlled mainly by temperature and water vapour pressure and only secondarily by particle composition.

2‧3. *Biological implications of total ozone depletion.* – The biological consequences of the TOZ decreasing trend are connected mainly with the enhancement of biologically active UV solar radiation at the Earth's surface. It is proper in this context to quote the basic conclusions made in the UNEP Scientific Assessment [11]:

– Large increases in ultraviolet radiation have been observed in association with the ozone hole at high southern latitudes. The measured UV enhancements agree well with model calculations.

– Clear sky UV measurements at midlatitude locations in the Southern Hemisphere are significantly larger than at a corresponding site in the Northern Hemisphere, in agreement with expected differences due to TOZ and Sun-Earth separation.

– Local increases in UV-B were measured in 1992/93 at mid- and high latitudes in the Northern Hemisphere. The spectral signatures of the enhancement clearly implicate the anomalously low ozone observed in those years, rather than variability of cloud cover or tropospheric pollution. Such correlations add confidence to the ability to link ozone changes to UV-B changes over relatively long time scales.

– Increases in clear-sky UV over the period 1979 to 1993 due to observed ozone changes are calculated to be greatest at short wavelengths and at high latitudes. Poleward of 45°, the increases are greatest in the Southern Hemisphere.

– Uncertainties in calibration, influence of tropospheric pollution, and difficulties of interpreting data from broad-band instruments continue to preclude be unequivocal identification of long-term UV trends.

– Scattering of UV radiation by stratospheric aerosols from the Mt. Pinatubo eruption did not alter total surface-UV levels appreciably [84].

Recent information on biological implications of total ozone depletion has been discussed at the European Conference on Atmospheric UV Radiation in Helsinki [85] as well as in the monograph by Martens [86] and in a number of journal publications ([87, 88, 63] and others). As has been pointed out in the [16] increases in surface UV-R irradiance (*e.g.*, 1989-1997: 15% per decade at 300 nm, 8% per decade at 305 nm) have been detected with a few ground-based spectroradiometers at midlatitudes (near 40°) that are consistent with expected changes from the decreasing amounts of ozone. New satellite estimates of global ($\pm$ 65°) UV irradiance have been obtained from TOMS data

which made it possible to produce climatological maps of UV irradiance on a daily basis. Satellite data for the time period 1979-1992 indicate the presence of annual erythemal UV-irradiance decadal increases equal to $3.7 \pm 3\%$ at $60\,°N$ and $3 \pm 2.8\%$ at $40\,°N$ (while $3.6 \pm 2\%$ at $40\,°N$ and $\pm 6\%$ at $60\,°S$). No statistically significant trends were observed within $\pm 30°$ latitude.

As far as impacts of variable UV radiation on humans and ecosystems are concerned, the most important aspects of the problem include: human health (one of the most dangerous consequences is skin cancer [89]), health of terrestrial and marine ecosystems [90, 32].

3. – Tropospheric ozone

Increasing pollution of the troposphere has stimulated studies of anthropogenic impacts on tropospheric chemical composition [91, 92, 7, 93-100, 77, 101-109]. In this context tropospheric ozone occupies a special place in view of its importance for human health and ecosystem's functioning as well as its role as a greenhouse gas [110]. Pszenny and Brasseur [111] have pointed out that surface ozone is a human respiratory irritant. Relatively small ozone amounts can cause chest pain, coughing, nausea, throat irritation, and congestion in healthy people. It may also worsen bronchitis, heart desease, emphysema, and asthma. Surface ozone is also phytotoxic to plant species. It can produce foliar injuries, reduced crop yield and biomass production, and shifts in competitive advantages of vegetation species in mixed populations. Of great importance is photolysis of tropospheric ozone by UV radiation in the presence of water vapour which is the primary source for hydroxyl radicals (OH). Hydroxyl radicals are responsible for the removal of many trace gases (such as CH_4, HFCs, HCFCs) through oxidation process.

A number of fundamental publications [28, 29, 11, 35, 16]) contain basic information on various features of tropospheric ozone dynamics and relevant problems.

To characterise the basic achievements by the year 1994 it is enough to quote the UNEP Scientific Assessment [11]:

– Recent measurements of the NO_y/O_3 ratio have basically confirmed earlier estimates of the flux of ozone from the stratosphere to be in the range of 240–280 Tg (O_3)/y, which is in reasonable agreement with results from general circulation models.

– The observed correlation between ozone and alkyl nitrates suggests a natural concentration of 20-30 ppb in the upper planetary boundary layer (at about 1 km altitude), which agrees well with the estimate from the few reliable historic data.

– Measurements of the gross ozone production rate yielded values as high as several tens of ppb per hour in the polluted troposphere over populated regions, in good agreement with theoretical predictions. Likewise, the efficiency of NO_x in ozone formation in moderately polluted air masses was found to be in reasonable agreement with theory.

– Direct measurements of hydroxyl and peroxy radicals have become available. While they do not survey to establish a global climatology of OH, they do provide a test of our understanding of the fast photochemistry. To date, theoretical predictions of OH concentrations (from measured trace gas concentrations and photolysis rates) tend to be higher than the measurements by up to a factor of two.

– Measurements of peroxy radical concentrations in the remote free troposphere are in reasonable agreement with theory; however, significant misunderstanding exists with regard to the partitioning of odd nitrogen and the budget of formaldehyde.

– Measurements have shown that export of ozone produced from anthropogenic precursors over North America is a significant source for ozone in the tropics during the dry season. These findings show the influence of human activities on the global tropospheric ozone balance.

– Photochemical net ozone destruction in the remote atmosphere has been identified in several experiments. It is likely to occur over large parts of the troposphere with rates up to several ppb per day. Consequently, an increase in UV-B radiation (*e.g.* from stratospheric ozone loss) is expected to decrease tropospheric ozone in the remote atmosphere but in some cases will increase production of ozone in and transport from the more polluted regions. The integrated effect on hydroxyl concentrations and climate is uncertain.

It has become emphasised in the UNEP Assessment [11] that uncertainties in the global tropospheric ozone budget, particularly in the free troposphere, are mainly associated with the uncertainties in the global distribution of ozone itself and its photochemical precursors, especially CO and NO_x. The role of heterogeneous processes including multiphase chemistry in the troposphere is not well characterised, and the catalytic efficiency of NO_x in catalysing ozone formation in the free troposphere has not been confirmed by measurements.

Recent results and problems of tropospheric ozone research have been discussed by Høv *et al.* [112] in connection with the completion of the first phase of the Tropospheric Ozone Research (TOR) Project which is a part of the EUROTRAC Programme as well as by Pszenny and Brasseur [109]—in the context of the development of tropospheric ozone studies within IGAC (International Global Atmospheric Chemistry) Core Project of the IGBP [23, 32].

Pszenny and Brasseur [109] have pointed out that the most important tropospheric ozone precursors are nitrogen oxides ($NO_x = NO + NO_2$), methane and other "nonmethane" hydrocarbons (NMHCs), and carbon monoxide. All of these precursors are products of fossil fuel and biomass burning, but each also has significant sources from the biosphere. The only ozone sink are depositions to surfaces (vegetation, soil, oceans), chemical destruction *in situ*, and some export back to the stratosphere in the tropics. It is believed that the increase of ozone observed in near-surface air, which may also be occurring in the free troposphere, has been the result of increasing NO_x emissions.

According to [16], trends in tropospheric ozone since 1970 in the Northern Hemisphere show large regional differences, with increases in Europe and Japan, decreases in Canada, and only small changes in the US. The trend in Europe since the mid-1980s has reduced to virtually zero (at two recording stations). In the Southern Hemisphere, small increases have now been observed in surface ozone.

A number of field observational programmes which were accomplished during the recent years have resulted in obtaining new important information on ozone dynamics [113-118]. One of the programmes was the Pacific Exploratory Mission-West A (PEM-West A)—a major component of IGAC's East Asia/North Pacific Regional Experiment (APARE) Activity [109]. The principal aim of the PEM-West A have been investigations of the tropospheric ozone distribution over the North Pacific and of the growing emissions of the ozone precursors from eastern Asia which will be a major

contributor to the expected ozone increase on a hemispheric scale in the coming decades. Observed ozone trends were best described in terms of two geographical domains: the western North Pacific rim and the western tropical North Pacific. For both regions, ozone photochemical destruction decreased more rapidly with altitude than did photochemical formation. The ozone tendency was typically found to be negative below 6 km and positive from 6 to 8 km. On the basis of lidar sounding data from a DC-8 aircraft Newell et al. [103] studied Asian continental pollution's influence on the western Pacific in September-October 1991 and February-March 1994.

The aim of the summer 1993 intensive measurements of the North Atlantic Regional Experiment (NARE) was to investigate how major sources of gases in the surrounding industrial regions are affecting the ozone distribution over the North Atlantic Ocean [109]. The results strongly suggest that NO_x emissions from human activities have substantially increased ozone concentrations in much of the troposphere over the North Atlantic. In the boundary layer and lower free troposphere the largest increases are seen in the industrial regions of the United States and Europe.

Lee et al. [119] discussed 8 year long ozone sounding data obtained between 1989 and 1997 at Naha (Okinawa Island). These data demonstrate the continuous increase of tropospheric ozone in North-East Asia in 1990s. It has been suggested that this tropospheric ozone trend is due to the increasing emission of NO_x from North-East Asia region (China, Japan, South Korea, Taiwan) during this period with a rate of 3.9% per year.

Since the production of tropospheric ozone is due to oxidation of CO and hydrocarbons in the presence of nitrogen oxide radicals ($NO_x = NO + NO_2$) which may originate from lighting, downwelling of stratospheric air, aircraft emissions, and surface emissions (including from fossil fuel combustion) transported convectively in the upper stratosphere as well as hydrogen oxide radicals ($HO_x = OH + peroxy$ radicals), Jaeglé et al. [120] examined the origin of NO_x in the upper troposphere over the central United States using aircraft observations during the SUCCESS (SUbsonic aircraft: Cloud and Contrail Effects Special Study) campaign in April-May 1996. Simultaneous measurements of NO, NO_y, N_2O, O_3, OH, HO_2, H_2O, CO, CO_2 and CH_4 concentrations were made up to 12.5 km altitude together with aerosol, cloud and radiative observations. Observation data on correlation between NO_y (sum of NO_x and its oxidation products) and CO at 8-12 km altitude indicate that NO_x originates primarily from convective transport of polluted boundary layer air. Lighting and aircraft emissions appear to be only minor sources of NO_x. The simulation modelling has led to the conclusion that the NO_x/NO_y ratio is maintained above chemical steady state by frequent convective injections of fresh NO_x from the polluted boundary layer and by the long lifetime of NO_x in the upper troposphere (5-10 days), (see also [121]). In contrast to earlier studies Jaeglé et al. [118] found no evidence for fast heterogeneous recycling from HNO_3 to NO_x in the upper troposphere.

The sources of HO_x (OH + peroxy radicals) and the associated production of ozone at 8-12 km over the United States were examined by Jaeglé et al. [120] by modelling observations of OH, HO_2, NO and other species during the SUCCESS campaign (the O-D photochemical model was used, developed at Harvard University). The comparison with observations indicate that the HO_x concentrations measured in SUCCESS are a factor of 3 higher than what can be calculated from oxydation of water vapour photolysis of acetone. The highest discrepancy was seen in the outflow of a convective storm. Jaeglé et al. [122] have shown that convective injection of peroxides (CH_3OOH and H_2O_2) and formaldehyde (CH_2O) from the boundary layer to the upper troposphere

could resolve this discrepancy. More generally, the data collected over the central United States during SUCCESS suggest that the local convection was a major source of HO_x and NO_x to the upper troposphere. An average net ozone production of 2 ppbv/day has been found between 8 and 12 km over the continental United States in spring. Ozone production was NO_x-limited under essentially all conditions encountered in SUCCESS. The high levels of HO_x present in the upper troposphere stimulate ozone production and increase the sensitivity of ozone to NO_x emissions from aircraft and other sources.

An important component of IGAC is Biomass Burning Experiment: Impact on the Atmosphere and Biosphere (BIBEX) Activity in view of a prominent role of biomass burning as a source of atmospheric pollutants and of the important ecological functions of vegetation fires in the tropics. The Southern Africa Fire-Atmosphere Research Initiative (SAFARI-92) field experiment was conducted in the 1992 dry season in Southern Africa under the auspices of BIBEX, together with the joint Brazilian and US project Transport and Atmospheric Chemistry near the Equator-Atlantic (TRACE-A), whose field studies were also conducted in 1992 BIBEX comprised IGAC's Southern Atlantic Region Experiment (STARE) campaign.

The results of SAFARI confirmed that it is justified to consider biomass burning as a significant contributor to the overall increase in GHGs that has occurred over the last 150 years, accounting for some 10-25% of current emissions. A major finding of TRACE-A was that widespread biomass burning in both America and Southern Africa is the dominant source of precursor gases necessary for the formation of the huge amounts of ozone observed over the South Atlantic Ocean. The generation of ozone is usually enhanced in the upper troposphere where relatively high concentrations of NO_x prevail.

It has been found out that ozone in the tropical troposphere plays a key role in determining the global oxidizing power of the atmosphere. Most of the oxidation of long-lived gases by hydroxyl radical takes place in the tropics, where intense sunlight and high humidity promote the formation of OH from photolysis of ozone.

The release into the atmosphere of biogenic gases produced by the African rain forest and savanna, as well as from biomass burning, and their role in the formation of tropospheric ozone and aerosol is the focus of the IGAC Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO). Under IGAC, the Global Tropospheric Ozone Project (GTOP) is now being formulated so that all the forthcoming data can be used intelligently to provide an understanding of the global tropospheric ozone cycle [109]. A major aim of IGAC is to understand the role of biological processes in producing and consuming atmospheric trace gases.

An important contribution to studying tropospheric ozone dynamics has been made by the TOR subproject of EUROTRAC [123, 28]. As has been pointed out by Høv *et al.* [110], the main achievement in TOR was the development of suitable instrumentation for high-quality measurements of ozone precursors (NO_x, NO_y, VOC), intermediates (carbonyl compounds, RO_2) and photolysis rates and the implementation of quality assurance procedures for these measurements, the establishment of a large high-quality network and the accumulation of a significant data base. The high-quality data sets provide detailed mechanistic information on the chemical and physical processes that control the budget of ozone and its precursors in the polluted boundary layer and in the free troposphere. The vertical soundings were analysed for distribution and seasonal variation of ozone in the free troposphere over Europe and

provide insight into processes such as the exchange between the boundary layer and the free troposphere and between the troposphere and the stratosphere.

Examples of the results obtained include the concept of O_x for studying chemical ozone formation, the O_x/NO_x relation for the study of the catalytic efficiency of NO_x, the use of alkyl nitrates as a measure of peroxy radicals and the role of individual hydrocarbons in ozone formation and the use of the H_2O/O_3 correlation for the ozone budget in the upper troposphere.

A hierarchy of models was developed and/or applied in TOR for the analysis of the data. Three-dimensional transport models with coupled chemistry modules were developed in TOR and have been used to study important transport processes, such as convection, and for budget studies.

Of course, after the completion of the first phase of TOR many problems stay still unresolved because of the complexity of the processes which govern tropospheric ozone dynamics. A different aspect of the problem is the unseperable influence of transport and chemistry on the concentrations that are observed at a given location. It is also important that the net chemical balance of O_3 depends in a nonlinear fashion on the concentrations of NO_x, VOCs, H_2O and O_3 itself and on the UV radiation flux and is thus closely coupled with the atmospheric life cycles of other trace gases. At continental surface sites, dry deposition plays an important role in the net balance of ozone, in addition to advection and vertical exchange. It is quite obvious that future success may be achieved only on the basis of combined analysis of complete enough observational data and results of simulation modelling with the use of fully coupled models of chemistry and transport.

Important sources of tropospheric ozone distribution are satellite remote-sensing data [122, 123]. There are various potential techniques to retrieve tropospheric ozone from TOMS data [74]. One of them is the use of TOMS-SBUV residuals (in which tropospheric ozone is taken as the difference between TOMS total ozone and integrated stratospheric ozone from one of the Solar Backscatter Ultraviolet (SBUV) instruments) or the difference in ozone columns over mountains and nearby sea levels areas (such as have been carried out over the Andes Mountains and nearby Eastern Pacific). Another version of a residual technique suggested by S. Chandra is based on the difference between TOMS total ozone and stratospheric ozone determined from a combination of the Microwave Limb Sounder (MLS) and Halogen Occultation (HALOE) instruments aboard UARS satellite. One more similar method known as the Convective Cloud Differential (CCD) technique, derives tropospheric ozone from the average difference between TOZ over clear regions and over regions of high clouds (in the latter case reliable cloud top information becomes very important). After doing studies using TOMS data only, and TOMS/SAGE residuals, more recent work has centred on a residual approach using TOMS and SBUV data (in this case precise determination of the tropopause height is very important).

A new perspective of obtaining tropospheric ozone data is connected with the use of the Tropospheric Emission Spectrometer (TES) planned for the EOS CHEM spacecraft [124]. TES is a Fourier Transform Spectrometer, measuring in the 650 to 3000 cm^{-1} wavelength region using both nadir and limb viewing geometries; spectral resolution is 0.025 cm^{-1} in the limb mode and 0.1 cm^{-1} in the nadir mode. The primary focus of the TES instrument is the measurement of ozone and its precursors in the troposphere, although TES has excellent capability for detecting a broad range of species because of its high resolution.

Munro *et al.* [125] have discussed retrievals of ozone vertical profiles in the

troposphere from the data of the European Space Agency's Global Ozone Monitoring Experiment (GOME) on board the ESR-2 satellite launched in April 1995. GOME is an ultraviolet/visible spectrometer which measures solar radiation backscattered from the Earth's atmosphere in four contiguous wavelength bands between 137 and 790 nm at moderate resolution (0.2–0.4 nm). An important advantage of GOME in comparison with Solar Backscatter Ultra Violet (SBUV) instrument is the availability of data for the ozone Huggins bands (310–340 nm). With knowledge of the temperature profile, the temperature-dependent spectral structures in the Huggings bands yield additional ozone profile information below the ozone peak (that is, in the troposphere and lower stratosphere). The comparison between the retrieval results obtained and ozonesonde data indicates that, in cloud-free scenes and above low clouds, ozone profiles extending down through the troposphere can be retrieved from GOME measurements. A case study has been considered by Munro *et al.* [123] which demonstrates GOME's ability to detect tropospheric ozone produced by biomass burning over Africa.

From the viewpoint of future tropospheric ozone research there is quite a number of still unresolved problems, including: 1) accumulation of an adequate global information on observed variability of tropospheric ozone for long enough time periods (the lack of data is especially severe in the tropics and subtropics); equally important are observations of atmospheric ozone precursors; 2) investigations of chemistry and photochemistry of tropospheric ozone under cloudiness conditions.

As has been emphasized by Crutzen [77], the role of clouds as transporters of chemical constituents such as reactive hydrocarbons, CO and NO and their oxidation products from the boundary layer to the middle and upper troposphere (and possibly into the lower stratosphere) should be better understood and quantified, so that they can be parametrized for inclusion in large-scale photochemical models of the atmosphere. Similarly, the production of NO by lightning and its vertical redistribution by convective storms should also be much better quantified.

The interaction of chemical constituents emanating from the boundary layer with liquid and solid hydrometeors in the clouds is of special importance. The influence of clouds on the photochemically active UV radiation field is a potentially important research topic. An issue of key significance are interactions between gases and atmospheric aerosols. Since the continental biosphere is a large source of hydrocarbons, quantification of relevant sources in terms of physical (*e.g.*, temperature, humidity, light levels) and biogeochemical (solid physical and chemical properties, land use) parameters are urgently needed for inclusion in atmospheric models. The formation of ozone, carbon monoxide, partially oxydized gaseous hydrocarbons and organic aerosol may be better quantified and parametrized for inclusion in chemical transport model, if the hydrocarbon oxydation mechanisms in the atmosphere is better understood.

An important warning concerning potential surprises in photochemistry of tropospheric ozone has been made by Ravishankara *et al.* [124], who have discussed the role of hydroxyl radical OH as a nuture's atmospheric detergent responsible for cleansing the atmosphere from pollutants trough their oxydation. Ravishankara *et al.* [126] have pointed out that, in general, the reactions of electronically excited species are of negligible importance in the chemistry of the lower atmosphere, but the case of $O(^1D)$ is a notable exception: Its role is pivotal. Even though most of the $O(^1D)$ is deactivated to the ground state, $O(^3P)$, the small fraction that survives to react with H_2O and CH_4, turns out to be the major source of OH. Knowledge of how $O(^1D)$ is formed in the atmosphere is therefore critical in understanding the creation of OH.

Recent surprising findings are beginning to reveal the importance of the longer wavelength "tail" in the chemistry of $O(^1D)$ formation. The longer wavelengths are important because stratospheric ozone screens most of the short-wave ultraviolet from the lower atmosphere.

4. – Conclusions

Investigations of total ozone changes (especially in high latitudes) put the TOZ variability problem forward as a very important aim of studying global scale environmental dynamics of great significance for humans and ecosystems. The recognition of such an environmental danger led to the signing of the Montreal Protocol and further amendments to the Protocol to avoid dangerous environmental consequences of the ozone depletions. There are many lessons of the Montreal Protocol that can be applied to solving other global environmental issues [16].

The first lesson is the application of the "precautionary principle", that is taking necessary actions in time to prevent damage, rather than waiting for the damage to be proved, since by that time the damage would have been great and irreversible. Another important lesson of the Protocol is on how to act on issue when there is no scientific certainty (in 1982 when the Protocol was signed many questions stayed open). The solution has been to undertake successive steps to phase-out ozone-depleting substances and involve the scientific community to advise governments periodically on the further steps needed to protect the ozone layer and recommend alternative technologies. During the last 10 years the governments charged the Protocol four times in accordance with relevant scientific advice. One more lesson of the Protocol is in promoting universal participation, including of developing countries in the Protocol by recognizing "common and differential responsibility". Such stage resulted in almost all countries committing themselves to protection of the ozone layer. Another important lesson is the integration of science, economics and technology both in developing the control measures and in implementing them.

Sarma [10] has emphasized that one measure of success of the Montreal Protocol and its subsequent Amendments and Adjustments (according to the UNEP Assessment) is the forecast of "the world that was avoided" by the Protocol:

– The abundance of ozone-depleting substances in 2050, the approximate time in which the ozone layer is now projected to recover to pre-1980 levels, would be at least 17 ppb of equivalent effective chlorine (this is based on the conservative assumption of a 3% annual growth in ozone-depleting gases) which is about five times larger than today' s value;

– Ozone depletion would be at least 50% at mid-latitudes in the Northern Hemisphere and 70% at mid-latitudes in the Southern Hemisphere, about 10 times larger than today; and

– Surface UV-B radiation would at least double at mid-latitudes in the Northern Hemisphere and quadruple at mid-latitudes in the Southern Hemisphere compared to an unperturbed atmosphere. This compares to the current increases of 5% and 8% in the Northern and Southern Hemispheres, respectively, since 1980.

A principal cause of the attention to tropospheric ozone is its role as a greenhouse and toxic component. Reviewing the sources of changes in radiative forcing that have occurred and what is believed to be their influence on climate, J. Hansen [122] has

emphasized that key information needed includes the exact nature of changes in the vertical distribution of ozone (especially to see if increases in tropospheric ozone may have countered decreases in stratospheric ozone on their contributions to relative forcing) and the nature of aerosol particles (especially single-scattering albedo) as well as their height. In this context of urgent necessity is the further development of numerical climate modelling taking into account various minor gaseous components. G. Brasseur [122] described simulations of ozone and related chemical tracers being done with the model for Ozone and Related Chemical Tracers (MOZART) developed at the National Center for Atmospheric Research (NCAR). One of the results was the simulation of changes in surface ozone since preindustrial time, which shows that changes in ozone amounts of some 30-40 ppb in July over the US and much of Europe along with those of 20-30 ppb over most of Eurasia have occurred. The average radiative forcing coming from these increases should be approximately $0.45 \, W/m^2$ (higher in the Northern Hemisphere, smaller in the Southern Hemisphere). Predictions for the future (2050) show the largest changes of surface ozone are likely to come in the tropics.

D. Jacob described the Chemistry, Aerosols and Climate Tropospheric Unified Simulation (CACTUS) effort at Harvard University. The present targets of the effort include the climatic effects of changes in emissions of precursors to tropospheric ozone formation, the feedback of climate change on tropospheric ozone, the climate effects of changes in emissions of sulphate precursors and the response of sulphate aerosols to climate change.

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