TROPOSPHERIC OZONE AND RELATED TRACE GASES

I.L. Karol and **A.A. Kiselev**
Main Geophysical Observatory, St. Petersburg, Russia

Contents

Summary

This article is devoted to the photochemistry, measurements and trends of tropospheric ozone. The ozone content depends on its precursor atmospheric concentrations. Thus, together with ozone, the behavior of active nitrogen oxides, NO and NO_2, carbon monoxide CO, non-methane hydrocarbons and hydrogen radicals, OH and HO_2, are considered. The photochemical sources and catalytic destructive cycles for ozone are described. The typical spatial and temporal tropospheric ozone content distributions are presented and discussed. The photochemistry of ozone precursors, the intensity of their sources and sinks, and measurement of their concentration are also considered. The climatic effect of ozone and its precursors is discussed. Ozone as an absorber of ultraviolet solar radiation, and its danger to humans and animals, is considered.

1. Introduction

Ozone O_3, a combination of three oxygen atoms, is a strongly odorous, explosive blue gas. Because of its strong oxidation capacity it may be used for organic compounds synthesis. Ozone kills microorganisms, and is thus used for cleaning of water and air. But ozone is a very toxic, poisonous species and only very low atmospheric concentrations are tolerable.

The proportion of ozone molecules in the atmosphere is one ozone molecule to 10^6

molecules of air gases. All ozone molecules in the atmospheric vertical column collected together at standard conditions (temperature 15 ^{o}C, pressure 1000 hPa) would be able to form a layer of about 3 mm thickness. Besides, only 10% of the total ozone mass resides in the troposphere.

Ozone forms entirely in the atmosphere and is destroyed there and on the Earth's surface. In general the ozone content depends on its atmospheric photochemical sources and sinks. Thus, the evolution of ozone volume is determined through the ozone active atmospheric species behavior. At the various altitudes the contribution of numerous species to the atmospheric ozone balance varies considerably. In the troposphere, among these species are nitrogen oxides (NO and NO_2), methane, non-Methane Hydrocarbons (NMHCs, e.g. alkanes, isoprene, terpenes, etc.), carbon monoxide CO, and hydrogen radicals, HO and HO_2. Most of them have natural as well as anthropogenic sources. Therefore, ozone depends on man-made activity also.

Owing to the world-wide efforts of the scientific community over the three last decades, there has been enormous success in the study of the atmospheric ozone layer. Our knowledge of intensity of ozone photochemical sources and sinks is based mainly on model calculations of different complexity. These model estimations are obtained with the wide use of atmospheric monitoring data and laboratory investigation results as model parameters.

2. Ozone photochemical sources and sinks

Ozone comes into the troposphere in two ways. The first is its transport down from the stratosphere. This source is most effective over oceans, i.e. for the regions distant from urban intensive pollution sources. Estimates of fluxes across the tropopause remain uncertain and have a range of 2×10^{10} to 6×10^{10} molecules cm^{-2} s^{-1} and it corresponds to the annual flux in the range of 240-820 Tg (1 Tg = 1×10^{12} g). The photochemical production is the second route of tropospheric ozone appearance. The ozone molecule in the air is generated only in a reaction between molecular and atomic oxygen with participation of a third air molecule, M.

$$O_2 + O + M \rightarrow O_3 + M.$$

Productivity of this reaction fully depends on the atomic oxygen concentration since molecular oxygen exists in the whole atmosphere in sufficient quantity (about 21% of air volume is O_2). In the stratosphere, the main source of atomic oxygen is a photolysis of O_2 by short-wave radiation with a wavelength less than 242 nm (1 nm = 1×10^{-9} m). But this source is not effective in the troposphere. There the photochemical production of oxygen atoms in general is due to the conversion of nitric oxide NO into nitrogen dioxide NO_2 and then photolysis of NO_2 by radiation with a wavelength less than 400 nm

$$NO_2 + h\nu \rightarrow NO + O.$$
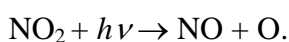
It is necessary to note that the production of both atomic oxygen and ozone occurs exclusively during the bright time of the day, and thus depends significantly on

seasonally varying daylength.

The direct ozone molecules destruction is due to their reaction with atomic oxygen

$$O_3 + O \rightarrow O_2 + O_2$$
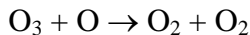
and their photolysis by solar ultraviolet (UV) and visible radiation

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$
$$\rightarrow O_2 + O.$$
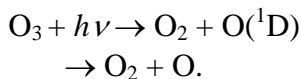
The rate of the first reaction is very slow and its contribution to ozone destruction is small. The ozone photolysis product outcome depends on the spectral wavelength: together with O_2; it is excited oxygen, $O(^1D)$, if the wavelengths are less than 310 nm and oxygen in its basic state, $O(^3P)$, for the longer wave lengths. However, the ozone photolysis products may combine together and an ozone molecule is produced again (see above). As a result, the joint action of the above reactions is very much less effective than that of ozone destructive catalytic cycles. The scheme of such cycle is simple and may be written as a pair of reactions

$$R + O_3 \rightarrow RO + O_2$$

$$RO + O \rightarrow R + O_2$$

whose sum is

$$O_3 + O \rightarrow O_2 + O_2.$$
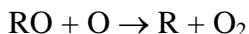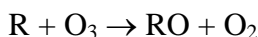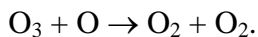
The various atmospheric radicals may be considered as "R", for example, NO, OH, Cl, Br and others. Usually, the catalytic cycles are named by relevant radical, e.g. nitrogen (if R=NO) or chlorine (if R=Cl) ones. Generally speaking, the hydrogen catalytic cycle (R = OH) makes the largest contribution to the tropospheric photochemical ozone sink. The effectiveness of this catalytic cycle depends in turn on OH abundance in the troposphere. As hydroxyl is the most reactive atmospheric radical, many air compounds, primarily, CO, NMHCs, methane, and nitrogen oxides, participate in reactions forming or destroying OH molecules. Thus, the hydroxyl concentration depends on alignment among these species. And as a result these directly nonreacting with ozone species affect significantly the tropospheric ozone balance through their control of tropospheric OH abundance.

The other route of removal ozone molecules from the troposphere is its destruction by contact with the ground surface. Interaction between ozone and the surface is most intensive over oceans but it occurs also through contact with the soil, plants, and various other materials. In particular, part of this interaction, over the oceans, is estimated to be approximately one-fourth of the net photochemical ozone sink.

In spite of obvious progress in recent studies, significant uncertainty remains in our

understanding of heterogeneous reactions (i.e. reactions on aerosols, drops and so on) forming the ozone balance. The latter due to catalytic destructive radicals depends on the season, time of the day and on latitude of location (on solar zenith angle) almost completely. So the ozone lifetime is varying significantly also in space and time. According to the calculations, ozone molecules "live" in the troposphere from several hours to few days.

3. Tropospheric ozone content measurements

Ozone monitoring in the surface air was achieved over many decades at various points of the globe and much information was accumulated. *In situ*, the ozone content mainly depends on the local climate features, in particular, on cyclone activity. It is typical for the zones of high intensity of air transport to have a rapid change of ozone concentration. As a result, ozone concentration may change sharply over a few days (or sometimes, hours). Therefore, averaged data (e.g. diurnally, monthly, seasonally or annually averaged ones) are normally used.

A typical ozone mixing ratio near the Earth's surface is 20 to 100 ppbv (parts per billion by volume) for the relatively unpolluted regions but in the urban atmosphere it may be two-three times higher. Tropospheric ozone content has significant seasonal variations: its maximum is in late spring-summer when the atmosphere is best illuminated, the ozone photochemical source is most intensive, and stratospheric ozone transport into the troposphere is at its maximum. This fact is illustrated by the data in Table 1, where seasonal variations of surface ozone mixing ratio at several points in USA are shown. As seen in Table 1, the maximum mixing ratios exceed the minimum by a factor of 1.5 to 2.5.

Site	Location	Month											
		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Harvard Forest	42°N, 70°W	22	30	38	42	42	50	48	45	35	30	23	24
Oregon	42°N, 120°W	29	31	36	38	41	42	40	45	35	30	28	26
Arizona	34°N, 110°W	30	38	47	50	50	49	50	50	45	43	40	31
Virginia	38°N, 80°W	27	30	36	52	55	60	58	56	48	40	29	20
Indiana	38°N, 85°W	22	35	36	48	50	62	58	57	46	32	20	19
Bermuda	30°N, 65°W	39	38	46	47	46	30	22	21	22	25	36	40

By data from J.L. Liang, L.W. Horowitz, D.J. Jacob, Y. Wang, A.M. Fiore, J.A. Logan G.M. Gardner, J.W. Munger (1998). Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere, *Journal of Geophysical Research*, v. 103, 13 435-13 450.

Table 1. Seasonal variations of surface ozone mixing ratio (ppbv) measured over the United States during 13:00-16:00 period except Bermuda data where diurnally averaged

data are used.

Figure 1 demonstrates the vertical distribution of ozone mixing ratio at the tropospheric altitudes for various regions of the globe. Here the means only are presented without their range of variations. These data show the increase of ozone mixing ratios with altitude. But their vertical gradient varies significantly: it is maximal for the high latitudes (Nova Scotia, Alaska) and minimal for the data over the Philippine Sea.
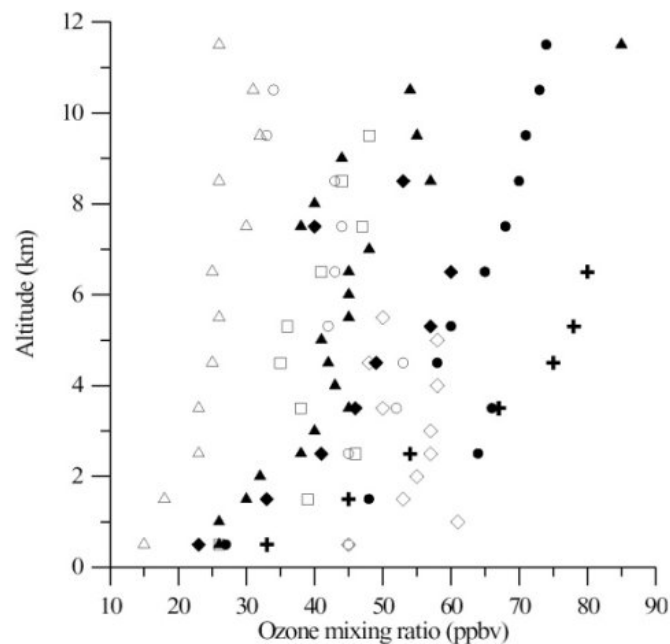

Figure 1. Vertical profiles of ozone mixing ratio (ppbv) measured in various regions of the globe: Easter Island (solid triangle), Philippine sea (open triangle), West coast of Africa (solid circle), East coast of China (open circle), Southeastern US (open diamond), Nova Scotia, Canada (solid diamond), Eastern coast of Brazil (open square), Alaska (plus). Data are from Emmons L.K. (National Center for Atmospheric Research, archive (http://aoss.engin.umich.edu/SASSarchive/) and B.A. Ridley, J.G. Walega, J.-F. Lamarque, F.E. Grahek, M. Trainer, G. Hübler, X. Lin, F.C. Fehsenfeld (1998) Measurements of reactive nitrogen and ozone to 5-km altitude in June 1990 over the southeastern United States, *Journal of Geophysical Research* **103**, 8369-8388.

Long term measurements of surface ozone content indicate some growth of its annually averaged mixing ratio in the northern hemisphere but its decrease in the Antarctic. For example, trends of surface ozone mixing ratio at the Mauna Loa observatory (19°N) and at Cape Barrow (71°N) are about 0.30-0.36% yr^{-1} against -0.72% yr^{-1} at the South Pole lasting recent years. At the same time, there are significant differences in surface ozone content: 25-28 ppbv near the poles against 40 ppbv at Mauna Loa (data averaged during the 1974-1997 period). The recent measurements by the dense ozonemetric net of western Europe has shown some decrease of surface ozone growth rate in many industrial European regions. But high levels of ozone mixing ratio (50-70 ppbv) remained there. Such levels are of anthropogenic origin.

-
-
-

TO ACCESS ALL THE **17 PAGES** OF THIS CHAPTER,
Visit: http://www.eolss.net/Eolss-sampleAllChapter.aspx

Bibliography

Brasseur G.P., Solomon S. *Chemistry and Physics of the Stratosphere and Mesosphere* (1984). D. Reidel Publishing Company. [This monograph is devoted to the various aspects of stratospheric and mesospheric processes.]

Brunner D., J Staeheln, D. Jeker (1998). Large-Scale Nitrogen Oxide Plumes in the Tropopause Region and Implications for Ozone. *Science* **282**, 1305-1309. [This contains the aircraft measurements of NO_X over the US and North Atlantic.]

Climate change 1992. The supplementary report to the Intergovernmental Panel on Climate Change scientific assessment (1992) /Eds. Houghton J.T., Callander B.A., Varney S.K. - Cambridge University Press, UK, 200p. [This contains the improved scenarios of probable emissions of greenhouse gases during first half of 21st century and estimates of their effect on climate.]

Climate Monitoring and Diagnostics Laboratory (1998). No. 24, Summary Report 1996-1997. /Eds. Hofmann D.J., Peterson J.T., Boulder, Colorado, USA, 166 p. [This contains atmospheric species measurement results during the last decade.]

Emmonds L.K., M.A. Carroll, D.A. Hauglustaine, G.P. Brasseur, C. Atherton, J. Penner, S. Silman, H. Levy II, F. Rohrer, W.M.F. Wauben, P.F.J. van Velthoven, Y. Wang, D. Jacob, P. Bakwin, R. Dickerson, B. Doddridge, C. Gerbig, R, Honrath, G. Hübler, D. Jaffe, Y. Kondo, J.W. Munger, A. Torres, A. Volz-Thomas (1997). Climatologies of NO_X and NO_Y: A comparison of data and models. *Atmospheric environment* **31** (12), 1851-1904. [This work is devoted to the inventory and analysis of the NO_X data obtained in various regional measurement projects.]

Haan D., D. Raynaud (1998). Ice core record of CO variations during the last two millenia: atmospheric implications and chemical interactions within the Greenland ice. *Tellus* **50B**, 253-262. [This contains the ice core data of carbon monoxide content in Antarctica and Greenland.]

Liang J.L., L.W. Horowitz, D.J. Jacob, Y. Wang, A.M. Fiore, J.A. Logan G.M. Gardner, J.W. Munger (1998). Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere, *Journal of Geophysical Research* **103**, 13 435-13 450. [This contains the seasonal variations of surface ozone concentration in various points of the US.]

Ridley B.A., J.G. Walega, J.-F. Lamarque, F.E. Grahek, M. Trainer, G. Hübler, X. Lin, F.C. Fehsenfeld (1998). Measurements of reactive nitrogen and ozone to 5-km altitude in June 1990 over the southeastern United States, *Journal of Geophysical Research* **103**, 8369-8388. [This presents the ozone and NO_X data in the lower troposphere over the US.]

Scientific Assessment of Ozone Depletion: 1994 (1994). WMO Global Ozone Research and Monitoring Project, Report No. 37, Geneva, Switzerland, 542p. [This presents the inventory and expert estimates of nitrous oxide sources.]

Wuebbles D.J., Edmonds J. (1991). *Primer of greenhouse gases*. Chelsea, Michigan, Lewis Publishers, 160p. [This book is devoted to review of the major greenhouse gases: their sources, sinks, evolution in the atmosphere.]

Biographical Sketches

I.L. Karol was born on 27 July 1927 in Leningrad, USSR. In 1944 he entered the Hydrodynamics Dept. of Leningrad State University, Mathematics and Mechanics Faculty, graduating in 1949. He passed postgraduate studies from 1949 to 1952, when he received a scientific degree of Candidate in Maths & Physics. After three years of lecturing in mathematics at the Ural University in Sverdlovsk, in 1956 he entered the Institute of applied Geophysics USSR Academy of Sciences in Moscow as a senior scientist. In 1959 he was transferred to Institute of Experimental Meteorology of USSR Hydrometeorological Service in Obninsk, near Moscow, where he was nominated as chief of laboratory in 1970. Since 1972 he has been with Main Geophysical Observatory of USSR Hydrometeorological Service in Leningrad (now St. Petersburg) after receiving the USSR scientific degree of Doctor of Math & Physics, presenting in 1970 his theses, which was published in 1972 as a book by Gidrometeoizdat Publishing House "Radioactive isotopes and global transport in the atmosphere". This book was translated into English and published in 1974. Since 1953 I.L. Karol has published 10 scientific monographs and more than 140 papers individually or with co-authors. The original papers are dealing with modeling of global atmospheric composition and climate changes due to natural and anthropogenic causes. During several periods he served as a member of various international commissions and committees of the International Association of Meteorology and Atmospheric Physics, of the World Meteorological Organization, of the World Climate Research Program Joint Scientific Committee. Since 1974 he has been the USSR (now Russian) co-leader of the joint project: "Composition of the atmosphere and climate changes" of the US-Russian Cooperation in Environmental Protection. He was the author or co-author of numerous scientific reports, which he presented at international and national scientific meetings throughout his scientific career.

A.A. Kiselev was born on 26 April 1953 in Leningrad, USSR. In 1970 he entered and in 1975 he graduated from the Hydrodynamics Dept. of Leningrad State University. From 1977 to 1981 he passed postgraduate studies at the Mathematics and Mechanics Faculty. In 1986 he received scientific degree of Candidate in Maths & Physics after presenting the candidate theses in geophysics. In 1975 he entered in the Main Geophysical Observatory of USSR Hydrometeorological Service in Leningrad as a junior scientist. Since 1990 he took position of senior research scientist in Main Geophysical Observatory. Since 1975 A.A. Kiselev has published about 30 papers individually and with coauthors. He is a contributor to the Intergovernmental Panel on Climate Change Reports of 1990 and 1999. The original papers are dealing with modeling of photochemical processes in the atmosphere, of global atmospheric composition change due to natural and anthropogenic causes.