Our Shrinking Ozone Layer

Global Perspectives and Remedial Measures

Shashi K Pathak and Nigel J Mason

Depletion of the Earth's ozone layer is one of the major environmental concerns for the new millennium having serious implications on human health, agriculture and climate. In the past decades, research by the international scientific community has been directed towards understanding the impact of human interference on the Earth's atmosphere. The importance of ozone radiation absorption in the atmosphere and the general kinetics of the stratospheric ozone depletion mechanisms have motivated many theoretical and experimental studies on various chemical species. The distribution of ozone and other trace gases in the atmosphere is governed by the complex interaction of dynamical, chemical and radiative processes. This article concentrates on the basic concepts underlying the problems that may be faced by humankind due to reduction in the ozone layer in coming decades, and the ways in which the scientific community can contribute to predicting and remediating these effects through design of international treaties, regulations and amendments.

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Introduction

Our planet is surrounded by a thin layer of bluish gas called 'ozone layer' between 20 to 50 kms above the Earth's surface. Ozone (O_3) is the triatomic allotrope of oxygen. The maximum concentration of ozone in this layer is only 300 ppb (parts per billion) hence if all the ozone was brought down to the Earth's surface it would only form a thin ring 3 mm thick around the Earth. Ozone layer in the stratosphere is popularly known as the 'ozone shield', because this layer shields the Earth's surface from ultraviolet (UV) radiation generated by the Sun (*Figure* 1). The

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Ozone layer, stratosphere, ozone hole, ozone shield, atmosphere.

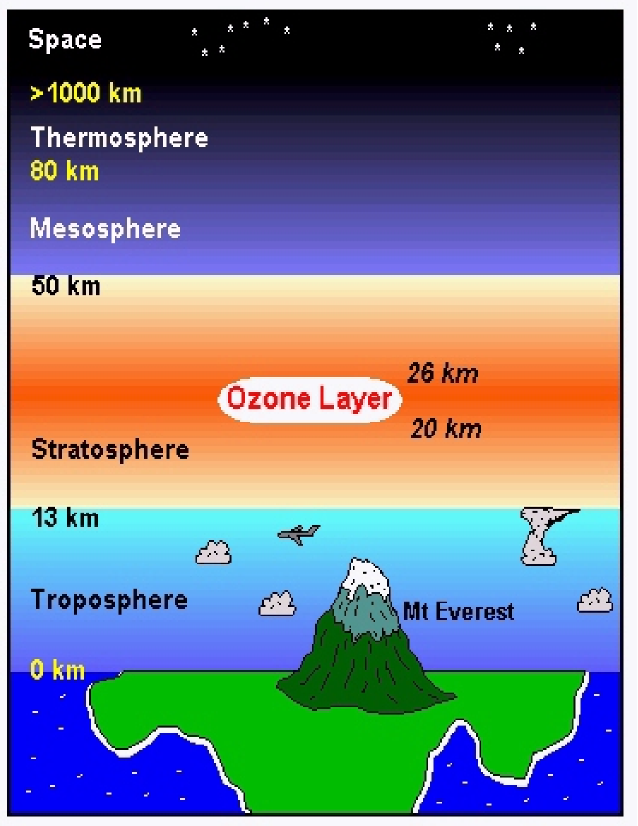

Figure 1. ***The ozone layer in relation to the rest of the Earth's atmosphere.***

ozone shield has safeguarded life on planet Earth for nearly a billion years. As we know, life is only possible because of the protection afforded by an ozone layer from harmful stellar ultraviolet radiation. However in recent decades, this ozone shield has been severely damaged by polluting the air with chemicals [1] arising from industrial processing. Depletion of the ozone layer is therefore having significant effects on life on Earth, for example – there is now a significant danger to the ecosystem in Antarctica, which may in turn affect the lives of millions of people living in the Southern Hemisphere.

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In this article we review how the ozone layer was formed and how it is being damaged by industrial pollution, and how the international community incorporating remedial measures has taken up this issue understanding the grave consequences of global ozone loss.

Ozone as a UV Shield

Ozone in the stratosphere absorbs most of the Sun's emitted ultraviolet radiation. Ultraviolet radiation consists of wavelengths between 100 nm and 400 nm and may be conveniently divided into UV-A, UV-B and UV-C. UV-C has the shortest wavelength and is the most energetic part of ultraviolet radiation spectrum. It has sufficient energy to break down diatomic oxygen (O_2) into two individual oxygen atoms. Each of these oxygen atoms may combine with an O_2 molecule to create ozone. UV-C is completely absorbed in the stratosphere, and none reaches the surface of the Earth. UV-A has the longest wavelength and is only partially absorbed in the stratosphere. Some may therefore reach the Earth's surface and is the main solar radiation that causes the sunburn. UV-B radiation is absorbed by stratospheric ozone but any reduction in ozone levels will allow the radiation to reach the Earth's surface. Biological molecules have been evolved under conditions of such filtering that they do not absorb visible light but can absorb ultraviolet radiation. *Figure* 2, shows the solar emission spectrum reaching the Earth's surface for wavelengths below 340 nm together with the absorption spectra of two important biomolecules, DNA, the carrier of the genetic code, and α-crystallin, the major protein of

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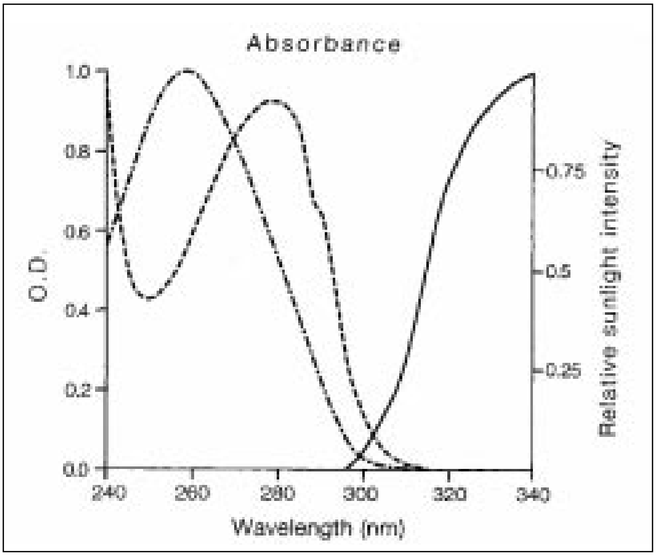

Figure 2. UV absorption spectra of DNA (·—·—) and α-crystallin (– – –), a mammalian eye protein. The strength of absorption cross-section is measured as optical density (OD). The solid line (——) indicates the solar spectrum reaching the ground after transmission through the Earth's ozone layer.

the mammalian eye lens [2]. The absorption of light by both these biological molecules is essentially zero in the region $320 < \lambda < 400$ nm, the near-UV or UV-A region, but it is intense in the region $200 < \lambda < 290$ nm, the far UV or UV-C region. The presence of ozone in the terrestrial atmosphere ensures that the absorption spectrum of these biological molecules only overlaps the solar spectrum at the Earth's surface in the wavelength region $290 < \lambda < 320$ nm, the mid-UV or UV-B region.

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It is interesting to note that ozone is the only known significant atmospheric gas that absorbs UV-B. The statistical data indicates that approximately 99% of all UV radiation, which consists of all UV-C, and most UV-B is absorbed and filtered out in the ozone layer. Hence, one can easily understand that increasing ozone depletion in the stratosphere will automatically result in more UV-B reaching the Earth and will cause damage to human, plant and animal life by breaking down the biomolecules.

Ozone Depletion and Chlorofluorocarbons

Ozone is naturally formed in the stratosphere when solar UV radiation dissociates O_2 into two free oxygen atoms. One of the liberated oxygen atoms then combines with O_2 to form O_3 a process that may be summarized as;

$$O + O_2 + M \longrightarrow O_3 + M \qquad (1)$$

where M is any atom or molecule (e.g. O_2, N_2) capable of absorbing excess energy liberated in the exothermic chemical reaction. Ozone itself is then naturally broken down by ultraviolet radiation or in collisions i.e.,

$$O_3 + h\nu \longrightarrow O_2 + O \qquad (2)$$

$$O + O_3 \longrightarrow O_2 + O_2 \qquad (3)$$

but there is always a net balance between the rate of formation and destruction producing a slight excess of ozone formation, and hence allowing the formation of the thin ozone layer in the Earth's stratosphere.

This balance has lasted for thousands of millions of years until, in the second half of the 20th century chemical industry manufactured chlorofluorocarbons (CFCs) [3]. The most widely used CFCs have been CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2). These chemicals were commonly used as propellants in spray cans, shaving foams, hair spray, deodorants, paints, insecticides, etc. Originally chosen by industry due to their stability they are highly unreactive and have a very long residence time – about 50 to 100 years in the lower atmosphere. However, the lower atmosphere is very fluid and allows abundant mixing: CFCs eventually move upward and enter the stratosphere. In the stratosphere, they are broken down by UV radiation releasing chlorine, which destroys ozone in a fast and efficient chemical reaction.

$$CFCl_3 + \text{UV light} \longrightarrow CFCl_2 + Cl \qquad (4)$$

The basic mechanisms may be summarized in the following way.

$$\begin{array}{llr} Cl + O_3 & \longrightarrow ClO + O_2 & (5) \\ O_3 + \text{UV light} & \longrightarrow O_2 + O & (6) \\ ClO + O & \longrightarrow Cl + O_2 & (7) \\ \hline \text{Net:} \quad 2O_3 & \longrightarrow 3O_2 & \end{array}$$

Hence Cl or ClO is recycled such that once released, one Cl or ClO molecule may destroy thousands of O_3 molecules.

Even if the emissions of all ozone depleting substances were halted today, ozone depletion will continue for more than 50 years because there are millions of metric tons of these chemicals already in the lower atmosphere moving towards the stratosphere, a process that may take 50 years.

Thus despite their usefulness to industry, we have to decide whether it is possible to continue to use chemicals which are so damaging to our planet. Indeed, even if the emissions of all ozone depleting substances were halted today, ozone depletion will continue for more than 50 years because there are millions of metric tons of these chemicals already in the lower atmosphere moving towards the stratosphere, a process that may take 50 years. Also, there are considerable amounts of CFCs manufactured in recent years which have not been admitted to the atmosphere because they are inside airconditioners, refrigerators, foam insulators, etc. and won't be released until these goods are disposed off. Hence there needs to be a careful disposal policy of existing stocks of CFCs as well as prevention of further emissions [4].

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The Vortex

The most dramatic evidence for the effect of CFCs on the Earth's ozone shield has been observed in the spring over the Antarctica with smaller depletions over the Arctic in the late winter and early spring. This is due to the special climate in these regions in the winter. During the Antarctic winter air temperatures above the continent fall below –80 °C forming a large weather system called 'vortex' which isolates the Antarctic continent from the rest of the world and form a giant containment vessel for pollutants. These conditions produce very low stratospheric temperatures below –80° C, which in turn lead to the formation of high altitude clouds commonly known as polar stratospheric clouds (PSCs). The polar stratospheric clouds are formed due to condensation of nitric acid (HNO_3), sulphuric acid (H_2SO_4), and water (H_2O) in the stratospheric region. When freezing, the hydrates of HNO_3 become stable and are commonly known as nitric acid dihydrate (NAD = $HNO_3.2H_2O$) and nitric acid trihydrate (NAT = $HNO_3.3H_2O$). The particles that contain appreciable HNO_3 are termed as Type I PSCs. Alternatively, the liquid aerosol can freeze to form sulphuric acid tetrahydrate (SAT) or other sulphate hydrates especially in the absence of HNO_3, these are known as Type II PSCs. Thus, the basic difference between the two types of PSC is that the condensation of HNO_3 plays a dominant role in the Type I, whereas in Type II, H_2SO_4 condensation predominates. These clouds are responsible for chemical changes and promote rapid ozone loss during the winter cycle in September and October each year resulting in the so-called 'ozone hole'.

In the spring, sunlight penetrates the vortex (during winter it is nearly always night) and triggers chemistry on the surface of the ice in the PSCs, breaking down the CFC's and releasing Cl

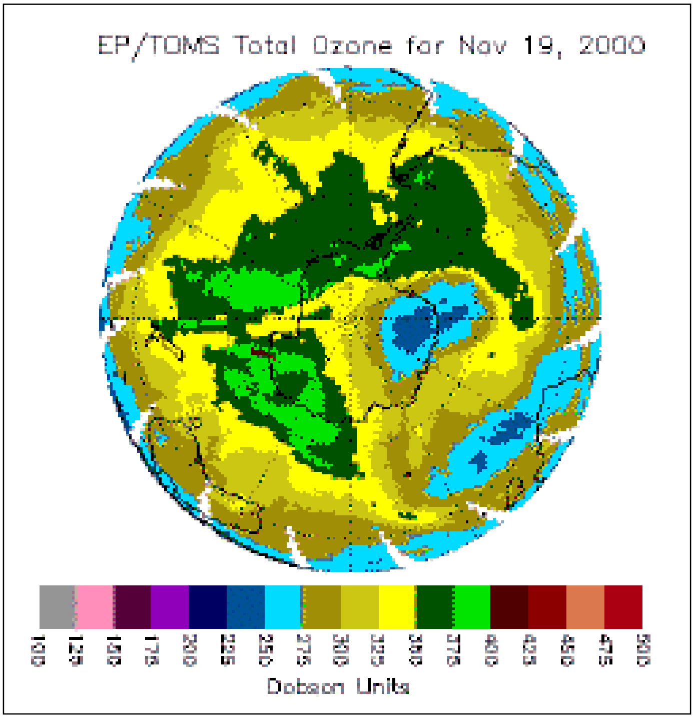

Figure 3. Picture of ozone hole.

which rapidly destroys the ozone and leads to a dramatic decline in local ozone concentrations (up to 80%) producing what is known as the ‘ozone hole’ (*Figure* 3). According to research studies, area of the ozone hole was largest in graphic size in 1998 but was deepest (i.e. the largest decline in ozone levels) in the year 2000. Total column ozone over the South Pole reached a minimum reading of 100 Dobson units in 2001, compared to a minimum of 98 Dobson units in 2000.

In the Northern Hemisphere, the Arctic vortex is smaller and does not get as cold as the Antarctic due to major differences in the meteorology of the two polar regions. The South Pole is a part of a very large landmass that is completely surrounded by the ocean whereas the northern polar region lacks the land-ocean symmetry characteristic of the southern polar region area. Therefore, as a consequence, Arctic stratosphere air is generally much warmer than in the Antarctic and gives rise to fewer PSC clouds. Hence there is much less ozone depletion in the Arctic than in the Antarctic.

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The Effects of Ozone Hole on Life

Some of the serious environmental effects of ozone depletion include the damages to Earth's food chains both on land and in the oceans, to human health including increases in all types of skin cancers, cataracts and also the suppression of immune systems.

The observed increase in the size of ozone hole clearly indicates that more UV-B radiation is able to reach the Earth's surface. Increased UV-B levels may affect the life on this planet in many ways [5]. Some of the serious environmental effects of ozone depletion include the damages to Earth's food chains both on land and in the oceans, to human health including increases in all types of skin cancers, cataracts and also the suppression of immune systems. UV-B radiation may damage eyes, causing cataracts, an eye disease characterized by the lens becoming opaque and impairing vision. People are therefore now more often choosing glasses that block the ultraviolet radiation. An increase in the exposure to ultraviolet radiation may also reduce the efficiency of the human immune system. Indeed it has been suggested that ozone depletion may weaken the immune system of people exposed to AIDS.

However, while humans may take precautions against exposure to UV-B (e.g. wearing sunglasses and sun cream), animals and plants cannot. Increased levels of UV-B may lead to skin cancers and cataracts in livestock (e.g. cows and pigs), the latter having a surprisingly similar physiology to humans, while increased UV irradiation is believed to have led to a dramatic fall in the number of photoplankton in the southern oceans, plankton that are the main food for many larger organisms.

The most dramatic effect of increased solar UV-B levels has been found in plants. Exposure of new seedlings to UV radiation leads to dramatic fall in the growth rate and hence in the productivity of the field. In New Zealand, it has recently been shown that even a day's exposure to higher UV-B levels may lead to a fall in the crop yield to ¾ th its original value.

International Responses with the Discovery of Ozone Hole and its Implications

With the discovery of increasing detrimental consequences of increased ozone loss, international action was necessary to limit (and ultimately remove) those compounds that cause ozone depletion. The nations of the world have taken effective measures to stop the production and use of ozone destroying chemicals by signing an accord in 1987 called the Montreal Protocol on Substances that Deplete the Ozone Layer. As a consequence, a series of intergovernmental agreements have been formulated, beginning in 1985 with the Vienna Convention on the Protection of the Ozone Layer. These were followed by the London, Copenhagen, Vienna, Montreal and Beijing Adjustments of 1990, 1992, 1995, 1997 and 1999. First, the halogen containing chemicals were banned, then the chlorofluorocarbons (CFCs), and now there is a push to ban the hydrochlorofluorocarbons (HCFCs) on a time scale which becomes shorter with each new adjustment to the protocol. These actions are however, interpreted differently in various parts of the world, and there are different requirements for the developing and the industrialized countries. The production of these chemicals is to be ceased by the year 2006 in developed countries, however developing nations (including India) have been given an extension until 2010, for the phase out. For HCFCs, the official phase-out dates are 2030 for the industrialized countries and 2040 for the developing countries. Thus it is hoped that by 2040 there will be no emissions of ozone depleting compounds and that the 'ozone hole' will gradually repair itself until it is 'sealed' at the end of this century [6]. However there are still many gaps in our knowledge of the mechanisms of ozone loss and there may be other compounds being produced today that may, in the future, result in ozone depletion.

Concluding Remarks

From the human point of view, ozone depletion is regarded as a significant global environmental problem, unequivocally shown to result from human activity. It is beyond any doubt that the destruction of our 'ozone UV shield' will, if not checked at an early stage, result in grave consequences for our living environment. The destruction of ozone shield will result in more ultraviolet radiation reaching the Earth's surface in the next few

Suggested Reading

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[6] World Meteorological Organization, Report No 37, 1998.

decades causing potential environmental disruption and human health problems. The troubling aspect is that if we stop manufacturing, using and even emitting all ozone depleting chemicals today, the problem will not go away immediately. Since what we have already emitted will be in the atmosphere for another 50 or more years. Theoretically, the 'ozone hole' should gradually heal as international regulations cease the flow of ozone destroying chemical substances in the atmosphere but it is an open question whether complete repair is possible. Model predictions and computer simulation studies will have to be modified in order to assess the exact remedies of this global phenomenon. However, we should take notice of how by our own actions we have initiated a major atmospheric climate change to the Earth in just 50 years. As we seek further industrial growth and increase the number of chemicals released in the atmosphere we must be careful that we do not trigger catastrophic changes to our world. The 'ozone hole' is a warning that we cannot 'play god' without taking risks.

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K S Krishnan's photo in his old house.

K S Krishnan's house.