

OZONE DEPLETION

3.1: Introduction:

Ozone is a gas found in the atmosphere in very trace amounts. Depending on where it is located, ozone can be beneficial (“good ozone”) or detrimental (“bad ozone”). On average, every ten million air molecules contains only about three molecules of ozone. Indeed, if all the ozone in the atmosphere were collected in a layer at Earth’s surface, that layer would only have the thickness of three dimes. But despite its scarcity, ozone plays very significant roles in the atmosphere. In fact, ozone frequently “makes headlines” in the newspapers because its roles are of importance to humans and other life on earth.

Chemically, the ozone molecule consists of three atoms of oxygen arranged in the shape of a wide V. Its formula is O_3 (the more familiar form of oxygen that one breathes has only two atoms of oxygen and a chemical formula of O_2).

Gaseous ozone is bluish in color and has a pungent, distinctive smell. In fact, the name ozone is derived from the Greek word *ozein*, meaning, “To smell or reek.” The smell of ozone can often be noticed near electrical transformers or nearby lightning strikes. It is formed in these instances when an electrical discharge breaks an oxygen molecule (O_2) into free oxygen atoms (O), which then combine with O_2 in the air to make O_3 . In addition to its roles in the atmosphere, ozone is a chemically reactive oxidizing agent that is used as an air purifier, a water sterilizer, and a bleaching agent.

3.2: Where is Ozone Found in the Atmosphere?

Ozone is mainly found in the two regions of the atmosphere that are closest to the earth’s surface. About 10 percent of the atmosphere’s ozone is in the lowest-lying atmospheric region, the troposphere. This ozone is formed in a series of chemical reactions that involve the interaction of nitrogen oxides, volatile organic compounds, and sunlight.

Most ozone (about 90%) resides in the next atmospheric layer, the stratosphere. The stratosphere begins between 8 and 18 kilometers (5 and 11 miles) above the earth's surface and extends up to about 50 kilometers (30 miles). The ozone in this region is commonly known as the *ozone layer*. Stratospheric ozone is formed when the sun's **ultraviolet (UV) radiation** breaks apart molecular oxygen (O_2) to form O atoms, which then combine with O_2 to make ozone. Note that this formation mechanism differs from the one mentioned above for ozone in the lower atmosphere.

3.3: What Roles Does Ozone Play in the Atmosphere and How are Humans Affected?

The ozone molecules in the stratosphere and the troposphere are chemically identical. However, they have very different roles in the atmosphere and very different effects on humans and other living beings, depending on their location.

A useful statement summarizing ozone's different effects is that it is "good up high, bad nearby." In the upper atmosphere, stratospheric ozone plays a beneficial role by absorbing most of the sun's biologically damaging ultraviolet sunlight (called UV-B), allowing only a small amount to reach the earth's surface.

The absorption of ultraviolet radiation by ozone creates a source of heat, which actually defines the stratosphere (a region in which the temperature rises as one goes to higher altitudes). Ozone thus plays a key role in the temperature structure of the earth's atmosphere. Without the filtering action of the ozone layer, more of the sun's UV-B radiation would penetrate the atmosphere and reach the earth's surface. Many experimental studies of plants and animals and clinical studies of humans have shown that excessive exposure to UV-B radiation has harmful effects. Serious long-term effects can include skin cancers and eye damage. The UV-absorbing role of stratospheric ozone is what lies behind the expression that ozone is "good up high". In the troposphere, ozone comes into direct contact with life-forms.

Although some amount of ozone is naturally present in the lower atmosphere, excessive amounts of this lower-atmospheric ozone are undesirable (or bad ozone). This is because ozone reacts strongly with other molecules, including molecules that make up the tissues of plants and animals. Several studies have documented the harmful effects of excessive ozone on crop production, forest growth, and human health. For example, people with asthma are particularly vulnerable to the adverse effects of ozone. Thus, ozone is “bad nearby”.

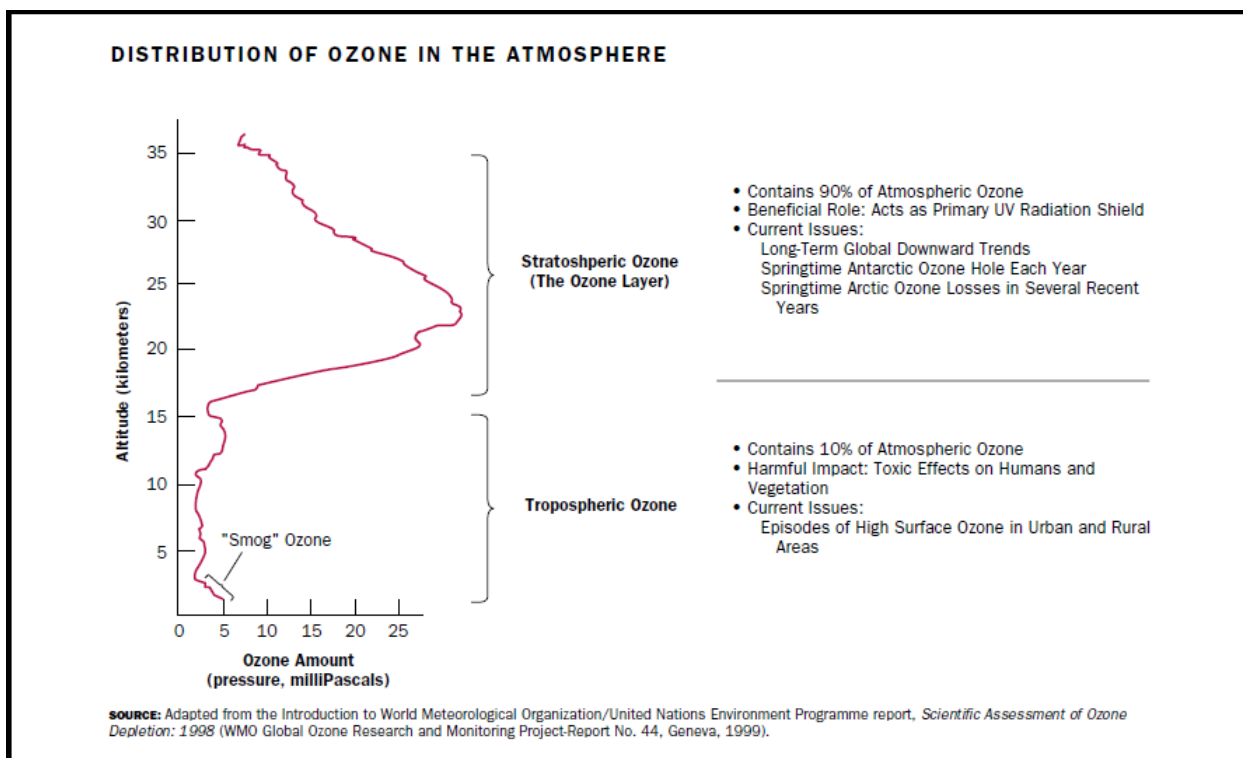
3.4: What is the Environmental Issues Associated with Ozone?

The dual role of ozone links it to two separate environmental issues often seen in the newspaper headlines. One issue relates to increases in ozone in the troposphere (the bad ozone mentioned above). Human activities that add nitrogen oxides and volatile organic compounds to that atmosphere, such as the fossil fuel burning associated with power-generating plants and vehicular exhaust, are contributing to the formation of larger amounts of ozone near the earth’s surface.

This ozone is a key component of **photochemical** smog, a familiar problem in the atmosphere of many cities around the world. Higher amounts of surface-level ozone are increasingly being observed in rural areas as well. Thus, the environmental issue is that human activities can lead to more of the bad ozone.

The second environmental issue relates to the loss of ozone in the stratosphere. Ground-based and satellite instruments have measured decreases in the amount of stratospheric ozone in our atmosphere, which is called ozone layer depletion. The most extreme case occurs over some parts of Antarctica, where up to 60 percent of the total overhead amount of ozone (known as the column ozone) disappears during some periods of the Antarctic spring (September through November). This phenomenon, which has been occurring only since the early 1980s, is known as the Antarctic ozone hole. In the arctic Polar Regions, similar processes occur that have also led to significant chemical depletion of the column ozone during late winter and spring in

many recent years. Arctic ozone loss from January through late March has been typically 20 to 25 percent, and shorter-period losses have been higher, depending on the meteorological conditions encountered in the Arctic stratosphere. Smaller, but nevertheless significant, stratospheric ozone decreases have been seen at other, more populated latitudes of the earth, away from the polar regions. Instruments on satellites and on the ground have detected higher amounts of UV-B radiation at the earth's surface below areas of depleted ozone.



Source: Adapted from the Introduction to World Meteorological Organization/ United Nations Environment Programme report, *Scientific Assessment of Ozone Depletion: 1998* (WMO Global Ozone Research and Monitoring Project-Report No. 44, Geneva, 1999).

3.5: What Human Activities Affect the Stratospheric Ozone Layer?

Initially, theories about the cause of ozone-layer depletion abounded. Many factors were suggested, from the sun to air motions to human activity. In the 1970s and 1980s, the scientific evidence showed conclusively that human produced chemicals are responsible for the observed depletions of the ozone layer. The ozone-depleting compounds contain various combinations of carbon with the chemical elements

chlorine, fluorine, bromine, and hydrogen (the halogen family in the periodic table of the elements). These are often described by the general term *halocarbons*. The compounds include chlorofluorocarbons (CFCs that are used as refrigerants, foam-blowing agents, electronics cleaners, and industrial solvents) as well as halons (which are used in fire extinguishers).

The compounds are useful and benign in the troposphere, but when they eventually reach the stratosphere, they are broken apart by the sun's ultraviolet radiation. The chlorine and bromine atoms released from these compounds are responsible for the breakdown of stratospheric ozone. The ozone destruction cycles are catalytic, meaning that the chlorine or bromine atom enters the cycle, destroys ozone, and exits the cycle unscathed and therefore able to destroy another ozone molecule. In fact, an individual chlorine atom can destroy as many as 10,000 different ozone molecules before the chlorine atom is removed from the stratosphere by other reactions.

3.6: What Actions Have Been Taken to Protect the Ozone Layer?

Research on ozone depletion advanced very rapidly in the 1970s and 1980s, leading to the identification of CFCs and other halocarbons as the cause. Governments and industry acted quickly on the scientific information. Through a 1987 international agreement known as the Montréal Protocol on Substances That Deplete the Ozone Layer, governments decided to eventually discontinue production of CFCs (known in the United States by the industry trade name "Freons"), halons, and other halocarbons (except for a few special uses). Concurrently, industry developed more ozone-friendly substitutes for the CFCs and other ozone-depleting halocarbons. If nations adhere to international agreements, the ozone layer is expected to recover by the year 2050.

The interaction of science in identifying the problem, technology in developing alternatives, and governments in devising new policies is thus an environmental "success story in the making." Indeed, the Montréal Protocol serves as a model for other environmental issues now facing the global community.

3.7: What Actions Have Been Taken to Reduce the Amount of Ozone at Ground Level?

Ozone pollution at the earth's surface is formed within the atmosphere by the interaction of sunlight with chemical precursor compounds (or starting ingredients): the nitrogen oxides (NO_x) and volatile organic compounds (VOCs).

In the United States, the efforts of the Environmental Protection Agency (EPA) to reduce ozone pollution are therefore focused on reducing the emissions of the precursor compounds. VOCs, a primary focus of many regulations, arise from the **combustion** of fossil fuel and from natural sources (emissions from forests). Increasingly, attention is turning to reducing the emissions of NO_x compounds, which also arise from the combustion of fossil fuels. The use of cleaner fuels and vehicles that are more efficient has caused a reduction in the emission of ozone precursors in urban areas.

This has led to a steady decline in the number and severity of episodes and violations of the one-hour ozone standard established by the U.S. Environmental Protection Agency (EPA) (which is 120 parts per billion or ppb, meaning that out of a billion air molecules, 120 are ozone). In 1999 there were thirty-two areas of the country that were in violation of the ozone standard, down from 101 just nine years earlier. Despite these improvements, ground-level ozone continues to be one of the most difficult pollutants to manage.

An additional, more stringent ozone standard proposed by the EPA to protect public health, eighty ppb averaged over eight hours, was cleared in early 2001 for implementation in the United States. For comparison, Canada's standard is sixty five ppb averaged over eight hours.

3.8: Ozone Depletion

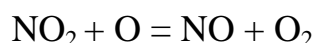
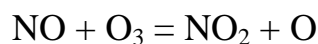
Though ozone is harmful gas near the earth surface (photo toxic), it is very useful in the upper layers (15 to 40 Km) of the atmosphere (stratosphere). 90% of the ozone is concentrated in the stratosphere and absorbs 95% of the UV radiation. It is useful gas

there, as it absorbs the ultraviolet portion of the solar radiation, which is very much harmful to human beings. It produces skin cancer and other diseases. Unfortunately, because of the air pollution, this ozone layer is depleting and wherever the concentration becomes very low it is termed as ozone hole. It came to our notice that the supersonic aircrafts release large quantities of nitric acid that reacts with the ozone and thus breaks the protective layer. It was also realized that the main culprit for ozone layer depletion are chlorofluorocarbons (CFCs). The generally used chlorofluorocarbons are CFC11 and CFC12 (Freons). As they are non-reactive, odourless, non-flammable nontoxic and non-corrosive they are extremely used in air conditioners, refrigerators and some sprays. CFCs stay for a long period in stratosphere (more than 50 years) and during this period, each chlorine atom is capable of converting up to 10⁵ molecules of ozone to O₂.

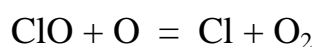
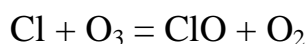
The chlorofluorocarbons release free radical of Cl that removes one 'O' from O₃. The chlorine atom and oxygen atom make chlorine monoxide ClO. Then the free oxygen 'O' pulls the other 'O' and free radical of Cl is produced. The free radical attacks another O₃ molecule and thus the chain keeps on reducing the O₃.

The following three constituents are mainly responsible for the depletion of stratospheric ozone:

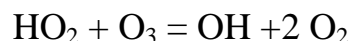
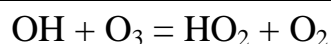
(i) Nitric oxide molecules: Nitric oxide reacts with ozone to make nitrogen dioxide, which in turn reacts with atomic oxygen to produce nitric oxide again



(ii) Chlorine atom: Chlorine atom reacts with ozone to give chlorine monoxide, which reacts with atomic oxygen to regenerate chlorine atom again



(iii) Hydroxyl ion: The photo dissociation of water molecules produces hydroxyl ion, which reacts with ozone molecule to produce HO₂, which reacts with another ozone molecule to give again the OH molecule



3.9: Causes of the Ozone Layer Depletion

(i) Use of chlorofluorocarbons: As discussed earlier mainly the CFCs are responsible for maximum damage to the ozone layer.

(ii) Nitrogenous fertilizers: Microbiological action on nitrogenous fertilizers produces nitrous oxide, which escapes into atmosphere and gets accumulated, as its decomposition is difficult.

(iii) Supersonic transport: Supersonic jetliners, rockets and space shuttles discharge various oxides of nitrogen, carbon, hydrocarbons etc. Ammonium perchlorate used in many of the rockets releases plenty of chlorides to attack the O_3 .

(iv) Nuclear tests: Huge quantity of gases is released in the nuclear explosions, which damage the ozone layer.

3.10: Effects of Ozone Layer Depletion

As the concentration of ozone reduces in the protective layer the harmful ultraviolet radiation (UV-A, UV-B and UV-C) shall reach the earth surface and shall cause many diseases like the following:

(i) Skin cancer of various types including the dangerous melanoma. About 1 people die from this disease. As an estimate, the cases of skin cancer are doubled with a 25% reduction in ozone layer.

(ii) The ultraviolet radiation directly increases the cataract (disease of eyes).

(iii) The UV radiation affects the eyes of wild life also and as they cannot protect themselves this effect is more pronounced.

(iv) The depletion of ozone leads to increased photochemical smog and degradation of outdoor paint and plastic.

3.11: Preventive Action to Ozone Depletion

In 1987 in Montreal city of Canada a convention was organized in which an international agreement was signed known as “Montreal Protocol”. It was made effective from 1st January 1989. Its goal was to cut emissions of CFCs by 35% from 1989 to 2000. After the observation of ozone hole above Antarctica in 1989, officials of more countries (93) met in London in 1990 and in Copenhagen and adopted the Copenhagen protocol that made the phasing out of ozone depleting chemicals more fast. At present 177 countries have joined their hands to protect the ozone layer and India is one out of them. The Government of India is having a time bound programme to cut the ozone depleting substances like CFCs, Halons, tetra chloromethane etc. Many alternatives for CFCs are available these days, like HCFC22, HFC 134A and hydrocarbons.

3.12: A Brief History Of Ozone Depletion

A hundred years ago, the new refrigeration industry used highly toxic gases, such as ammonia and sulfur dioxide, as coolants. Accidental leakage of such chemicals resulted in many human deaths, and in the 1920s, the US Congress attacked manufacturers for producing “killer refrigerators.” Then, in 1928, a young chemist announced the creation of a new coolant. Later he demonstrated that he could directly inhale the coolant - it had low toxicity. When exhaled, the breath could be used to blow out a candle - so it was not flammable. This impressive coolant was a chlorofluorocarbon (CFC). In 1931, it was introduced into the market as *Freon*. Its safety made it seem a godsend and Freon became widely used in refrigerators and, later, air conditioners. Other CFCs found other applications: aerosol-can propellants, industrial solvents, cleaning agents, and insulating agents (in which CFCs are blown into foam products or polystyrene cups). *Halons* are related to CFCs, but contain the element, bromine rather than chlorine. Halons became important fire-fighting chemicals.

Another property of CFCs and halons that made them so useful industrially was their lack of chemical reactivity. This stability was their Achilles' heel. By the 1970s, scientists found they were spreading around the globe. With nothing to break them down it was estimated that CFCs would survive hundreds of years. Their curiosity piqued by such information, Professors Mario Molina and F. Sherwood Rowland made calculations that led to a hypothesis that CFCs would lead to significant depletion of the stratospheric-ozone layer. Molina subsequently examined the question: Why does the greatest ozone depletion occur over Antarctica?

Laboratory work demonstrated that high-frequency UV light could break down CFCs. One of the chemicals into which CFCs were degraded was elemental chlorine; this could catalyze the breakdown of ozone (O_3). In nature, the high-intensity UV light necessary to degrade CFCs and halons is found only in the stratosphere, and CFCs were found to be making their way into the stratosphere. By 1976, scientists believed that CFCs were threatening stratospheric ozone. At that time, two-thirds of manufactured CFCs were used as aerosol propellants, and in 1979, the use of CFCs as propellants was banned by the United States and, later, by a number of other governments. Thereafter, concern about stratospheric ozone lessened. The quietude ended in the 1980s when a group of British researchers, making ground based measurements of the ozone above Antarctica, reported a 30% decline compared with its levels in earlier years. These researchers had actually observed October (spring) depletion as early as 1977, but doubted their own observations. When they reported their findings in October 1985, the US National Aeronautics and Space Administration (NASA) confirmed their observations using satellite and airborne measurements of stratospheric ozone. Since then, Antarctica's spring "ozone hole" has been actively monitored. A US National Oceanic and Atmospheric Administration (NOAA) representation of ozone disappearance over Antarctica after 1979 is seen in Figure 8.3. The region outlined at the bottom of the globe is Antarctica. By 1986, a disappearance of ozone (shaded area) is seen over this continent. This area became increasingly obvious in 1991 and 1996.

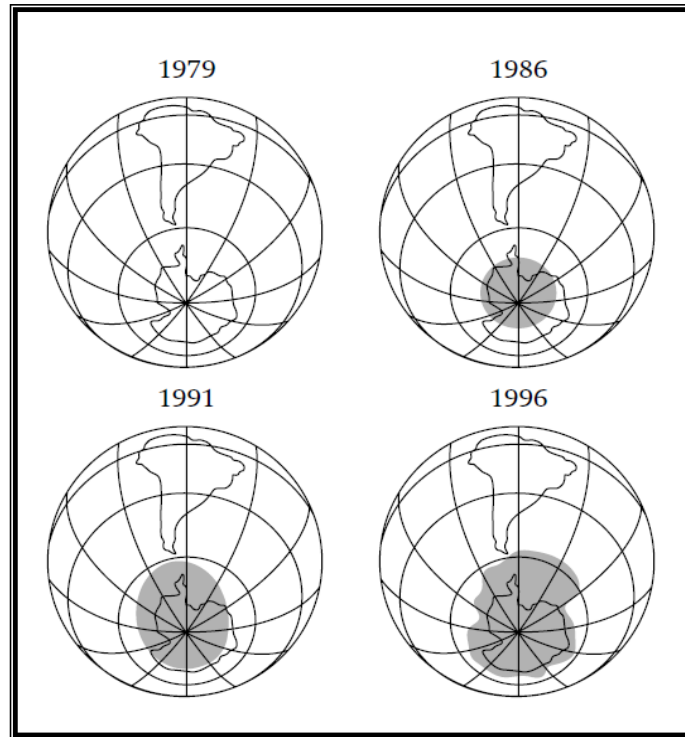


Fig 3.1: Growth of the Antarctic ozone hole. The shaded area shows the zone of ozone depletion. *Source: US National Oceanic and Atmospheric Administration*

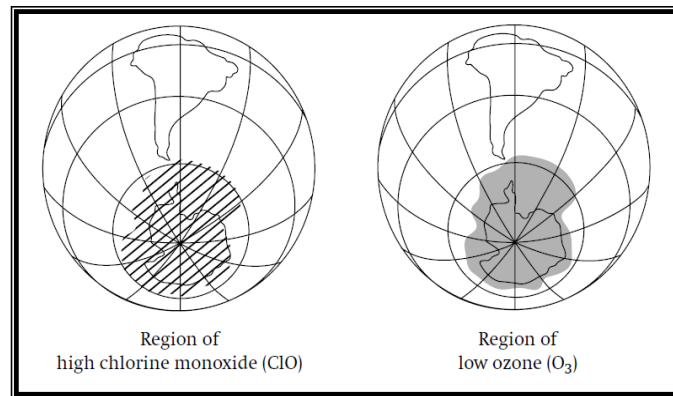


Fig 3.2: Chlorine monoxide and the Antarctic ozone hole: late August 1996. *Source: US National Oceanic and Atmospheric Administration*

General Questions about Ozone Depletion

1. Define **Ozone**?
2. What are the roles of ozone in the atmospheres and other application?
3. Where is ozone found in the atmosphere?
4. What roles do ozone play in the atmosphere and how is humans affected?
5. A useful statement for ozone's different effect is "*Good up high, Bad nearby*".
Discuss this statement.
6. What are the environmental issues associated with ozone? List it briefly.
7. What human activities affect the stratospheric ozone layer?
8. What actions have been taken to protect the ozone layer
9. What actions have been taken to reduce the amount of ozone at **Ground Level**?
10. What is the meaning of "**Ozone Depletion**"?
11. What are the causes of the ozone layer depletion?
12. List the three constituents that are mainly responsible for depletion of stratospheric ozone?
13. What are the effects of ozone's layer depletion? List it.