

10.2.3: Stratospheric Ozone and Ozone Depletion

Learning Objectives

- Explain where the ozone layer is located in the atmosphere (stratosphere).
- Describe the natural formation of ozone through UV radiation interaction with oxygen molecules.
- Describe the depletion of the ozone layer.
- Explain how chlorine and bromine atoms react with ozone that leads to the depletion of the ozone layer.
- Identify chlorofluorocarbons (CFCs) as the primary ozone-depleting substance.
- Policies to Reduce Ozone Destruction

The earth's stratospheric ozone layer plays a critical role in absorbing ultraviolet radiation emitted by the sun. In the last thirty years, it has been discovered that stratospheric ozone is depleting as a result of anthropogenic pollutants. There are a number of chemical reactions that can deplete stratospheric ozone; however, some of the most significant of these involves the catalytic destruction of ozone by halogen radicals such as chlorine and bromine.

Introduction

The atmosphere of the Earth is divided into five layers. In order of closest and thickest to farthest and thinnest the layers are listed as follows: troposphere, stratosphere, mesosphere, thermosphere and exosphere. The majority of the ozone in the atmosphere resides in the stratosphere, which extends from six miles above the Earth's surface to 31 miles. Humans rely heavily on the absorption of ultraviolet B rays by the ozone layer because UV-B radiation causes skin cancer and can lead to genetic damage. The ozone layer has historically protected the Earth from the harmful UV rays, although in recent decades this protection has diminished due to stratospheric ozone depletion.

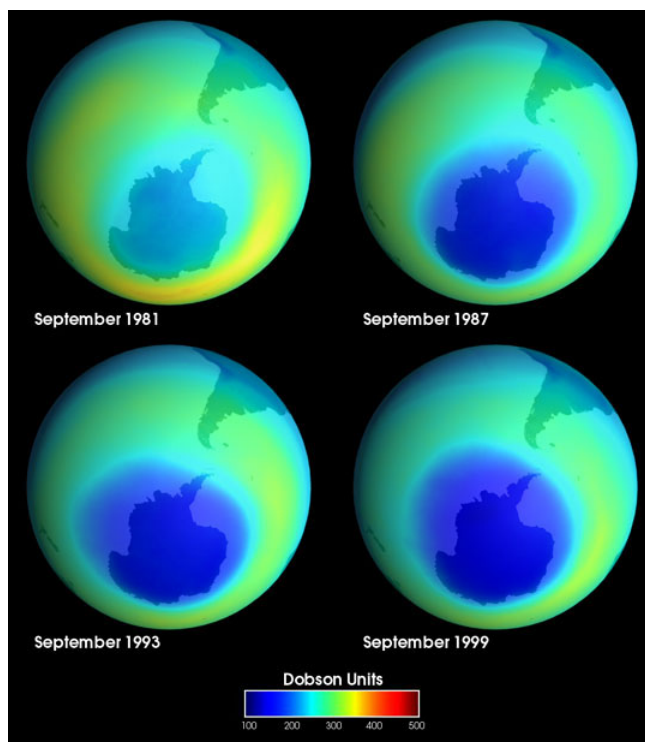


Figure courtesy of NASA.

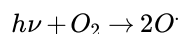
Ozone depletion is largely a result of man-made substances. Humans have introduced gases and chemicals into the atmosphere that have rapidly depleted the ozone layer in the last century. This depletion makes humans more vulnerable to the UV-B rays which are known to cause skin cancer as well as other genetic deformities. The possibility of ozone depletion was first introduced by scientists in the late 1960's as dreams of super sonic transport began to become a reality. Scientists had long been aware that nitric oxide (NO) can catalytically react with ozone (O_3) to produce O_2 molecules; however, NO molecules produced at ground level

have a half life far too short to make it into the stratosphere. It was not until the advent of commercial super sonic jets (which fly in the stratosphere and at an altitude much higher than conventional jets) that the potential for NO to react with stratospheric ozone became a possibility. The threat of ozone depletion from commercial super sonic transport was so great that it is often cited as the main reason why the US federal government pulled support for its development in 1971. Fear of ozone depletion was abated until 1974 when Sherwood Rowland and Mario Molina discovered that chlorofluorocarbons could be photolyzed by high energy photons in the stratosphere. They discovered that this process could release chlorine radicals that would catalytically react with O_3 and destroy the molecule. This process is called the Rowland-Molina theory of O_3 depletion.

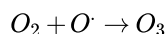
The Chapman Cycle

The stratosphere is in a constant cycle with oxygen molecules and their interaction with ultraviolet rays. This process is considered a cycle because of its constant conversion between different molecules of oxygen. The ozone layer is created when ultraviolet rays react with oxygen molecules (O_2) to create ozone (O_3) and atomic oxygen (O). This process is called the *Chapman cycle*.

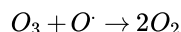
Step 1: An oxygen molecule is photolyzed by solar radiation, creating two oxygen radicals:



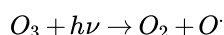
Step 2: Oxygen radicals then react with molecular oxygen to produce ozone:



Step 3: Ozone then reacts with an additional oxygen radical to form molecular oxygen:



Step 4: Ozone can also be recycled into molecular oxygen by reacting with a photon:



It is important to keep in mind that ozone is constantly being created and destroyed by the Chapman cycle and that these reactions are natural processes, which have been taking place for millions of years. Because of this, the thickness of the ozone layer at any particular time can vary greatly. It is also important to know that O_2 is constantly being introduced into the atmosphere through photosynthesis, so the ozone layer has the capability of regenerating itself.

Chemistry of Ozone Depletion

CFC molecules are made up of chlorine, fluorine and carbon atoms and are extremely stable. This extreme stability allows CFC's to slowly make their way into the stratosphere (most molecules decompose before they can cross into the stratosphere from the troposphere). This prolonged life in the atmosphere allows them to reach great altitudes where photons are more energetic. When the CFC's come into contact with these high energy photons, their individual components are freed from the whole. The following reaction displays how Cl atoms have an ozone destroying cycle:



Chlorine is able to destroy so much of the ozone because it acts as a catalyst. Chlorine initiates the breakdown of ozone and combines with a freed oxygen to create two oxygen molecules. After each reaction, chlorine begins the destructive cycle again with another ozone molecule. One chlorine atom can thereby destroy thousands of ozone molecules. Because ozone molecules are being broken down they are unable to absorb any ultraviolet light so we experience more intense UV radiation at the earth's surface.

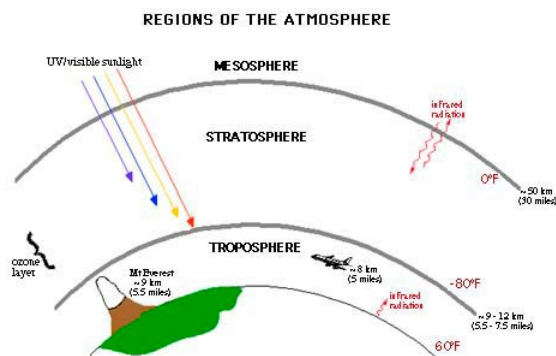


Figure courtesy of NOAA.

From 1985 to 1988, researchers studying atmospheric properties over the south pole continually noticed significantly reduced concentrations of ozone directly over the continent of Antarctica. For three years it was assumed that the ozone data was incorrect and was due to some type of instrument malfunction. In 1988, researchers finally realized their error and concluded that an enormous hole in the ozone layer had indeed developed over Antarctica. Examination of NASA satellite data later showed that the hole had begun to develop in the mid 1970's.

The ozone hole over Antarctica is formed by a slew of unique atmospheric conditions over the continent that combine to create an ideal environment for ozone destruction.

- Because Antarctica is surrounded by water, winds over the continent blow in a unique clockwise direction creating a so called "polar vortex" that effectively contains a single static air mass over the continent. As a result, air over Antarctica does not mix with air in the rest of the earth's atmosphere.
- Antarctica has the coldest winter temperatures on earth, often reaching -110 F. These chilling temperatures result in the formation of polar stratospheric clouds (PSC's) which are a conglomeration of frozen H_2O and HNO_3 . Due to their extremely cold temperatures, PSC's form an electrostatic attraction with CFC molecules as well as other halogenated compounds

As spring comes to Antarctica, the PSC's melt in the stratosphere and release all of the halogenated compounds that were previously absorbed to the cloud. In the antarctic summer, high energy photons are able to photolyze the halogenated compounds, freeing halogen radicals that then catalytically destroy O_3 . Because Antarctica is constantly surrounded by a polar vortex, radical halogens are not able to be diluted over the entire globe. The ozone hole develops as result of this process.

Recent research suggests that the strength of the polar vortex from any given year is directly correlated to the size of the ozone hole. In years with a strong polar vortex, the ozone hole is seen to expand in diameter, whereas in years with a weaker polar vortex, the ozone hole is noted to shrink

Policies to Reduce Ozone Destruction

One success story in reducing pollutants that harm the atmosphere concerns ozone-destroying chemicals. In 1973, scientists calculated that CFCs could reach the stratosphere and break apart. This would release chlorine atoms, which would then destroy ozone. Based only on their calculations, the United States and most Scandinavian countries banned CFCs in spray cans in 1978. More confirmation that CFCs break down ozone was needed before more was done to reduce production of ozone-destroying chemicals. In 1985, members of the British Antarctic Survey reported that a 50% reduction in the ozone layer had been found over Antarctica in the previous three springs.

Two years after the British Antarctic Survey report, the "Montreal Protocol on Substances that Deplete the Ozone Layer" was ratified by nations all over the world. The **Montreal Protocol** controls the production and consumption of 96 chemicals that damage the ozone layer (Figure 10.2.310.2.3). CFCs have been mostly phased out since 1995, although they were used in developing nations until 2010. Some of the less hazardous substances will not be phased out until 2030. The Protocol also requires that wealthier nations donate money to develop technologies that will replace these chemicals.

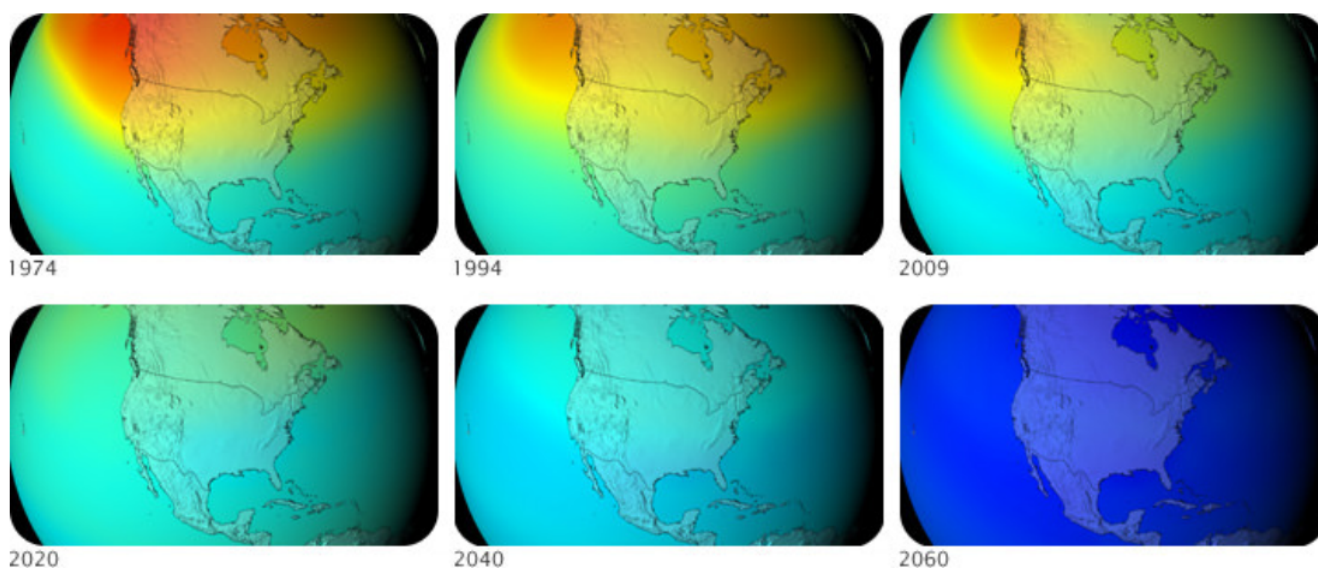


Figure 10.2.310.2.3. Ozone levels over North America decreased between 1974 and 2009. Models of the future predict what ozone levels would have been if CFCs were not being phased out. Warmer colors indicate more ozone.

Because CFCs take many years to reach the stratosphere and can survive there a long time before they break down, the ozone hole will probably continue to grow for some time before it begins to shrink. The ozone layer will reach the same levels it had before 1980 around 2068 and 1950 levels in one or two centuries.

Ozone Depleting Substances

The following substances are listed as ozone depleting substances under Title VI of the United State Clean Air Act:

Table 10.2.3.1: Ozone Depleting Substances And Their Ozone-Depletion Potential. Taken directly from the Clean Air Act, as of June 2010.

Substance	Ozone- depletion potential
chlorofluorocarbon-11 (CFC-11)	1.0
chlorofluorocarbon-12 (CFC-12)	1.0
chlorofluorocarbon-13 (CFC-13)	1.0
chlorofluorocarbon-111 (CFC-111)	1.0
chlorofluorocarbon-112 (CFC-112)	1.0
chlorofluorocarbon-113 (CFC-113)	0.8
chlorofluorocarbon-114 (CFC-114)	1.0
chlorofluorocarbon-115 (CFC-115)	0.6
chlorofluorocarbon-211 (CFC-211)	1.0
chlorofluorocarbon-212 (CFC-212)	1.0
chlorofluorocarbon-213 (CFC-213)	1.0
chlorofluorocarbon-214 (CFC-214)	1.0
chlorofluorocarbon-215 (CFC-215)	1.0
chlorofluorocarbon-216 (CFC-216)	1.0
chlorofluorocarbon-217 (CFC-217)	1.0
halon-1211	3.0

Substance	Ozone- depletion potential
halon-1301	10.0
halon-2402	6.0
carbon tetrachloride	1.1
methyl chloroform	0.1
hydrochlorofluorocarbon-22 (HCFC-22)	0.05
hydrochlorofluorocarbon-123 (HCFC-123)	0.02
hydrochlorofluorocarbon-124 (HCFC-124)	0.02
hydrochlorofluorocarbon-141(b) (HCFC-141(b))	0.1
hydrochlorofluorocarbon-142(b) (HCFC-142(b))	0.06

Summary

- Any disruption of the balance that results in a higher rate of ozone destruction than ozone creation would result in depletion of ozone.
- Some compounds that release chlorine or bromine when they are exposed to intense UV light in the stratosphere contribute to ozone depletion, and are called ozone-depleting substances (ODS)
- The Montreal Protocol is an international agreement that committed all parties (signatory nations) to a schedule for phasing out the production and use of CFCs and other substances known to be harmful to the ozone layer.

Contributors and Attributions

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