Introduction to Ozone

Read the “Introduction to Ozone” article from the University Corporation for Atmospheric Research website and complete the assignment that accompanies it.

Introduction to Ozone

The Ozone Hole. The Ozone Hoax. Pollution. Skin Cancer. The topic of ozone makes headlines on a regular basis, but why does a single molecule merit such media coverage? How important is the ozone in our atmosphere and why are scientists so concerned about its increase near the surface of the earth and its disappearance higher up in the atmosphere?

First things first - what is ozone? Ozone is made of three oxygen atoms (\( \text{O}_3 \)). The oxygen we find in our atmosphere is made up of two oxygen atoms (\( \text{O}_2 \)). Because of its chemical formulation, a single atom of oxygen (O) is unstable. That is, it wants to combine with something else. That is why oxygen is almost always found in pairs, in its \( \text{O}_2 \) (diatomic) form, where it is more stable. \( \text{O}_3 \) is less stable than \( \text{O}_2 \), because it wants to return to the diatomic state by giving up an oxygen atom.

When enough ozone molecules are present, it forms a pale blue gas. It is an unstable molecule that readily combines with other atoms. Ozone has the same chemical structure whether it is found in the stratosphere or the troposphere. Where we find ozone in the atmosphere determines whether we consider it to be Dr. Jekyll or Mr. Hyde.
In the troposphere, the ground-level or "bad" ozone is an air pollutant that damages human health, vegetation, and many common materials. It is a key ingredient of urban smog. In the stratosphere, we find the "good" ozone that protects life on earth from the harmful effects of the sun's ultraviolet rays.

**Electromagnetic Spectrum**

To understand how ozone is generated and the functions it serves in the earth's atmosphere, it is important to know something about the electromagnetic spectrum — the energy emitted from the sun. Electromagnetic energy is sometimes described as traveling in waves and sometimes as traveling in packets of energy referred to as photons.

Progressing from short wavelengths to long wavelengths, scientists have identified gamma rays, x-rays, ultraviolet radiation, visible light (between 400 and 700 nanometers), infrared radiation (heat), microwaves, and radio waves. Short wavelengths have more energy per photon than long wavelengths.

Ozone is constantly being formed in the earth's atmosphere by the action of the sun's ultraviolet radiation on oxygen molecules. Ultraviolet light splits the molecules apart by breaking the bonds between the atoms. A highly reactive free oxygen atom then collides with another oxygen molecule to form an ozone molecule. Because ozone is unstable, ultraviolet light quickly breaks it up, and the process begins again.

**Ozone in the Stratosphere**

Ozone and oxygen molecules in the stratosphere absorb ultraviolet light from the sun, providing a shield that prevents this radiation from passing to the earth's surface. While both oxygen and ozone together absorb 95 to 99.9% of the sun's ultraviolet radiation, only ozone effectively absorbs the most energetic ultraviolet light, known as UV-C and UV-B, which causes biological damage. The protective role of the ozone layer in the upper atmosphere is so vital that scientists believe life on land probably would not have evolved - and could not exist today - without it.

The term "shield" as a description of ozone in the stratosphere is a bit misleading because the molecules do not form an impermeable sphere around the earth. Ozone continuously breaks apart into its oxygen atoms and reforms as ozone molecules, so a particular ozone molecule doesn't last very long. The "shield" changes constantly, but the atmospheric chemical processes maintain a dynamic equilibrium that keeps the overall amount of ozone constant - that is, it would if humans did not contribute to the chemical processes.
About 90% of the ozone in the earth's atmosphere lies in the region called the stratosphere between 16 and 48 kilometers (10 and 30 miles) above the earth's surface. Ozone forms a kind of layer in the stratosphere, where it is more concentrated than anywhere else, but even there it is relatively scarce. Its concentrations in the ozone layer are typically only 1 to 10 parts of ozone per 1 million parts of air, compared with about 210,000 parts of oxygen per 1 million parts of air.

**Ozone in the Troposphere**

The other 10% of the ozone in the earth's atmosphere is found in the troposphere, which is the portion of the atmosphere from the earth's surface to about 12 km or 7 miles up. In the troposphere, ozone is not wanted. Ozone is even more scarce in the troposphere than the stratosphere with concentrations of about 0.02 to 0.3 parts per million. But even in such small doses, this molecule can do a lot of damage.

And just to confuse things even further, ozone in the troposphere is one of the greenhouse gases. The naturally occurring greenhouse gases (including ozone) are what make earth habitable for life as we know it. But scientists are very concerned about the warming effects of increased greenhouse gases caused by human activity. So, in the troposphere, accelerated ozone levels deal us a double whammy - as a key ingredient in smog and as a powerful greenhouse gas.

**Concluding Thoughts**

Ozone is found in two different layers of the atmosphere - the troposphere and the stratosphere. The stratospheric ozone, or "good ozone," protects life on earth from harmful effects of the sun's UV rays. We have good reason to be concerned about the thinning of the ozone layer in the stratosphere. Tropospheric ozone, or "bad ozone," is an air pollutant that damages human health, vegetation, and many common materials. We have good reason to be concerned about the buildup of ozone in the troposphere. Although simplistic, the saying "Good up high and bad near by," sums up ozone in the atmosphere.

**Stratospheric Ozone, the Protector**

**Introduction**

The debate over the existence of an ozone problem breeds media coverage. However, the real story is not whether stratospheric ozone levels are decreasing, but what those decreases may mean for life on earth. As the percentage of ozone in the atmosphere decreases, the amount of UV-B radiation reaching the surface increases. It's the UV-B radiation, not the ozone itself that concerns scientists, because the invisible wavelengths are linked to skin cancers and other biological damage.

Measuring UV-B is tricky. Levels are affected by time of day, day of the year, latitude, weather conditions, and the amount of ozone aloft. UV is the part of the electromagnetic spectrum made up of wavelengths between 280 and 400 nanometers (billionths of a meter). Most of this is UV-A light, only mildly associated with sunburn and DNA damage and relatively benign to most plant life. But the ill effects increase more than a thousandfold in the shorter wavelengths referred to as UV-B. Below 300 nanometers, the rays are sparse but very damaging; near 315 nanometers they're more numerous but much less destructive. Close to 310 nanometers lies the middle ground, where the number and impact of rays combine to cause the greatest harm to humans and plants. Engineers face enormous challenges when designing instruments that can measure individual wavelengths, yet such precision is necessary to determine the amount of dangerous light entering the atmosphere.
The Story of the Ozone Hole

Although often referred to as the ozone 'hole', it is really not a hole but rather a thinning of the ozone layer in the stratosphere. We will use the term 'hole' in reference to the seasonal thinning of the ozone layer.

The appearance of a hole in the earth's ozone layer over Antarctica, first detected in 1976, was so unexpected that scientists didn't pay attention to what their instruments were telling them; they thought their instruments were malfunctioning. When that explanation proved to be erroneous, they decided they were simply recording natural variations in the amount of ozone. It wasn't until 1985 that scientists were certain they were seeing a major problem.

Why did it take scientists so long to solve this mystery? To begin with, observations that challenge preconceived ideas don't always get taken seriously, even in science. Two decades ago scientists did not suspect the importance of the chemical processes that rapidly destroy ozone in the Antarctic stratosphere. When they saw dramatic fluctuations in ozone levels, they assumed their instruments were in error, or that whatever was happening was due to natural processes like sunspot activity or volcanic eruptions.

They didn't realize that chlorine was the main culprit and that most of the chlorine in the stratosphere comes from human activity. The largest source is a class of chemical compounds known as chlorofluorocarbons (CFCs).

Because of their chemical stability, low toxicity, and valuable physical properties, these chemicals, versatile and stable in the lower atmosphere, at least, have been extensively used since the 1960s as refrigerants, industrial cleaning solvents, propellants in aerosol spray cans, and to make Styrofoam.

At the turn of the century, chlorine levels in the stratosphere were much lower than at present. As the use of CFCs has increased, however, so has their concentration in the atmosphere. Scientists could detect 100 parts per trillion (ppt) of CFC-12 in the atmosphere by the 1960s, 200 ppt by 1975, and more than 400 ppt by 1987. By 1990, they detected more than 750 ppt of CFC-11 and CFC-12, the two most destructive and persistent CFCs.

Once in the atmosphere, CFCs drift slowly upward to the stratosphere, where they are broken up by ultraviolet radiation, releasing the chlorine that catalytically destroys ozone. In the graphic below, the destructive cycle of a chlorine atom is shown.
1. UV radiation breaks off a chlorine atom from a CFC molecule.
2. The chlorine atom attacks an ozone molecule (\(O_3\)), breaking it apart and destroying the ozone.
3. The result is an ordinary oxygen molecule (\(O_2\)) and a chlorine monoxide molecule (ClO).
4. The chlorine monoxide molecule (ClO) is attacked by a free oxygen atom releasing the chlorine atom and forming an ordinary oxygen molecule (\(O_2\)).
5. The chlorine atom is now free to attack and destroy another ozone molecule (\(O_3\)). One chlorine atom can repeat this destructive cycle thousands of times.

Since 1974 scientists have known that chlorine can destroy ozone, but no one thought the destruction would be very rapid. Events over the Antarctic region proved them wrong. The ozone hole story began at Halley Bay in Antarctica, where British scientists had been measuring ozone in the atmosphere since 1957. In 1976 they detected a 10% drop in ozone levels during September, October, and November—the Antarctic spring. Since ozone concentrations over this region often vary from season to season, the researchers weren't concerned, even as the springtime declines occurred repeatedly. It wasn't until their instruments registered record low levels of ozone in 1983 that they realized something important was happening. By then, record springtime ozone declines had occurred during seven of the previous eight years.
Within two years, scientists determined that the ozone hole over Antarctica occurs when high levels of chlorine catalytically destroy ozone. The high levels of active chlorine are formed in the cold, dark winter stratosphere when reactions on the surface of icy cloud particles release chlorine from harmless (to ozone) chemical compounds into an active form that reacts with ozone. When the sunlight returns to the polar region in the austral spring, the active chlorine rapidly begins to destroy ozone. The extremely cold ice clouds can form over both poles during winter, but they are more common over the Antarctic region. During winter, atmospheric circulation creates a whirlpool, or vortex, of air above both poles. Very low temperatures occur inside a polar vortex, which is isolated from the rest of the atmosphere. The extreme cold fosters the formation of ice clouds during the winter and paves the way for the destruction of ozone when the light returns during spring. Scientists documented this mechanism in a series of field experiments in 1987.

The Arctic region is typically spared the worst of the ozone destruction because its vortex normally breaks down several weeks before the sun returns, dissipating the ice clouds. The larger percentage of land masses in the northern latitudes, particularly mountains, prevents an excessive build-up of ice clouds. Geography isn't always enough to dissipate the vortex, however. The North Pole's vortex was unusually strong and long-lived during the winter of 1992-1993, for example. When sunlight appeared, it drove down Arctic ozone levels well into March. Because there is more ozone over the North Pole to begin with, this decline didn't create a hole. However, it did send ozone-depleted air over populated areas of the Northern Hemisphere when the vortex broke up.

The loss of ozone over populous regions underscores the importance of following up on the 1987 Montreal Protocol. This agreement, now signed by more than 70 countries, set goals of reducing CFC production by 20% (relative to 1986 levels) by 1993 and by 50% by 1998. These targets have since been strengthened to call for the elimination of the most dangerous CFCs by 1996 and for regulation of other ozone-depleting chemicals. The United States and other nations are well on their way to meeting these goals. In 1993, global CFC production was already down 40% compared to 1986 levels. That's fortunate, since the CFCs already in circulation will continue to pose a threat to the earth's ozone layer for another hundred years. There is good news to this story. The graph below shows the skyrocketing path of CFC-11 from the 1950s until the mid-1990s. Recent measurements have shown a clear decline in CFC-11.

Concluding Thoughts

While the stratospheric ozone issue is a serious one, in many ways it can be thought of as an environmental success story. Scientists detected the developing problem, and collected the evidence that convinced governments around the world to take regulatory action. Although the global elimination of ozone-depleting chemicals from the atmosphere will take decades yet, we have made a strong and positive beginning. For the first time in our species' history, we have tackled a global environmental issue on a global scale.
Tropospheric Ozone, the Polluter

Introduction

Ozone occurs naturally at ground-level in low concentrations. The two major sources of natural ground-level ozone are hydrocarbons, which are released by plants and soil, and small amounts of stratospheric ozone, which occasionally migrate down to the earth's surface. Neither of these sources contributes enough ozone to be considered a threat to the health of humans or the environment.

But the ozone that is a byproduct of certain human activities does become a problem at ground level and this is what we think of as 'bad' ozone. With increasing populations, more automobiles, and more industry, there's more ozone in the lower atmosphere. Since 1900 the amount of ozone near the earth's surface has more than doubled. Unlike most other air pollutants, ozone is not directly emitted from any one source. Tropospheric ozone is formed by the interaction of sunlight, particularly ultraviolet light, with hydrocarbons and nitrogen oxides, which are emitted by automobiles, gasoline vapors, fossil fuel power plants, refineries, and certain other industries.

In urban areas in the Northern Hemisphere, high ozone levels usually occur during the warm, sunny summer months (from May through September). Typically, ozone levels reach their peak in mid to late afternoon, after the sun has had time to react fully with the exhaust fumes from the morning rush hours. A hot, sunny, still day is the perfect environment for ozone pollution production. In early evening, the sunlight's intensity decreases and the photochemical production process that forms ground level ozone begins to subside.

Negative Impacts of Tropospheric Ozone

While stratospheric ozone shields us from ultraviolet radiation, in the troposphere this irritating, reactive molecule damages forests and crops; destroys nylon, rubber, and other materials; and injures or destroys living tissue. It is a particular threat to people who exercise outdoors or who already have respiratory problems.
Ozone affects plants in several ways. High concentrations of ozone cause plants to close their stomata. These are the cells on the underside of the plant that allow carbon dioxide and water to diffuse into the plant tissue. This slows down photosynthesis and plant growth. Ozone may also enter the plants through the stomata and directly damage internal cells.

Rubber, textile dyes, fibers, and certain paints may be weakened or damaged by exposure to ozone. Some elastic materials can become brittle and crack, while paints and fabric dyes may fade more quickly.

When ozone pollution reaches high levels, pollution alerts are issued urging people with respiratory problems to take extra precautions or to remain indoors. Smog can damage respiratory tissues through inhalation. Ozone has been linked to tissue decay, the promotion of scar tissue formation, and cell damage by oxidation. It can impair an athlete's performance, create more frequent attacks for individuals with asthma, cause eye irritation, chest pain, coughing, nausea, headaches and chest congestion and discomfort. It can worsen heart disease, bronchitis, and emphysema.

So why can't we take all of this "bad" ozone and blast it up into the stratosphere? The answer lies in the vast quantities needed and ozone's instability in the dynamic atmosphere. Ozone molecules don't last very long, with or without human intervention. The vehicle necessary to transport such enormous amounts of ozone into the stratosphere does not exist, and, if it did, it would require so much fuel that the resulting pollution might undo any positive effect. Rather than seek such grandiose solutions, we need to decrease the production of those chemicals that break down ozone in the stratosphere and help create ozone in the troposphere.

The dual ozone problems—pollution or smog in the troposphere and depletion of the ozone layer in the stratosphere—are indeed very different. But the problems have common ties in that they both are related to air pollutants that come from industry, transportation, and other human activities.

**Concluding Thoughts**

The majority of U.S. citizens live in areas that are impacted by tropospheric ozone pollution. They are familiar with "smog-alerts," local government pleas to reduce vehicle traffic, and news reports about cities that have failed to meet EPA standards for ozone pollution levels.