Ozone in the Earth's Atmosphere

March 18, 2003

By: Wendy M. Thompson

First of all: What is Ozone? Ozone is a molecule formed when three oxygen atoms are combined to into one molecule; it has the chemical formula of O_3. Ozone is found in only two layers of the Earth's atmosphere, the troposphere (the layer in which we live and all weather occurs) and the stratosphere (the layer right above the troposphere), and is relatively rare when compared to other molecules in the Earth's atmosphere. Ozone is also very reactive since it is not a stable form of oxygen like O_2. The reactivity causes ozone it to be classified as bad or good depending on its location in the atmosphere. In the troposphere ozone is classified as bad and in the stratosphere it is good, this duel role of ozone creates two very different environmental issues. In the instance of tropospheric ozone it needs to be eliminated, but in the other instance stratospheric ozone needs to be protected and even increased.

Bad ozone found in the troposphere makes up approximately ten percent of the atmospheric ozone. Here ozone is not naturally occurring but is created mainly by manmade substances such as cleaning solvents, industrial emissions, vehicle exhaust, and many others products that release nitrogen oxides and volatile organic compounds into the air, these substances can be seen as smog in large cities around the world but the levels in smaller cities and rural areas are on the rise. Once any of these products is released into the air and exposed to intense sunlight they undergo the process to create ozone. Ozone in this level of the atmosphere is bad because it reacts with human tissue causing many health problems such as lung damage, chest pain, coughing, throat irritation, and asthma. It also has harmful effects on crop production, forest growth and wildlife. Due to these life damaging effects there have been regulations put into place such as The Clean Air Act and its Amendments. Acts such as this require manufacturers to either create systems to clean up the harmful products they have already released and/or eliminate the use of these products all together both of these help in the effort to clean up and hopefully eliminate ozone production were we live.

The other ninety percent of the ozone is found in the stratosphere and is known as good ozone. It is formed naturally in the stratosphere and is produced and destroyed at a constant pace when outside influences are not taken into account. In this layer ozone is formed when an O_2 molecule is split apart due to the vibrations caused by ultraviolet radiation coming into the atmosphere from the sun. The individual oxygen atoms then combine with other O_2 molecules to form O_3. The destruction of ozone happens when an individual atom of oxygen then combines with the unstable O_3 molecule which is then split into two separate O_2 molecules and the process starts over. This layer of ozone helps protect the earth in two ways. First it creates a very thin protective layer around the Earth that absorbs harmful ultraviolet radiation and prevents it from reaching the Earth's surface. The ozone layer plays a vital role in our lives. Without ozone in this layer of the atmosphere life on Earth would not be possible. The second role ozone plays is the creation of the stratosphere in which the temperature rises as you increase in height. This process also regulates the weather patters in the troposphere. Unfortunately the rate of destruction has been increased by the presence of harmful ozone destroying products like fire extinguishers, coolants, foaming agents, solvents, and aerosol propellants created from produces like chlorofluorocarbons (CFC), carbon tetrachloride, bromides, methalchloroform, and halons. With the increasing destruction of the ozone layer more and more harmful ultraviolet light will be allowed down to the Earth's surface. The increasing levels of harmful ultraviolet light at the surface can cause more sun burns, eye problems like cataracts, decreased immune systems, impacts on the growth of both land and water plants.

CFC's and other products like them were invented in 1920's. With the invention of these products a new wave of technology began. These products allowed the invention of refrigerants used refrigerators, car and home air conditioner, aerosols, cleaners, and even electrical and buildings parts and solvents. Unlike previous products CFC's were found to be extremely stable, nontoxic, and non flammable which made them perfect products to be used where large populations of people were constantly exposed to them. In 1974 two chemists from the University of California, Irvine, F. Sherwood Roland and Mario Molina, discovered that these types of products over a long period of time were rising from the troposphere where they were stable and into the stratosphere where they were destroying the ozone layer.

The research done by these two chemists showed that once the CFC's rise to stratospheres ozone layer they are hit by ultraviolet radiation from the sun. The ultraviolet radiation breaks up the molecule leaving a very unstable, extremely reactive chlorine atom. This extremely reactive form of chlorine then reacts with the already unstable ozone molecules. This reaction results in one atom of oxygen being taken away from the ozone molecule with the end result being one oxygen molecule (O_2) and a molecule of chorine and oxygen (ClO). The ClO molecule then reacts one of two ways. First it can react with another ozone molecule stealing yet another oxygen atom, which in turn takes the existing oxygen away from the ClO leaving two ozone molecules destroyed, two new oxygen molecules (O_2) created, and the unstable chlorine atom in the ozone layer to start the process over and continue destroying more ozone. Second the ClO molecule can react with another ClO molecule. In this process two ozone molecules are also destroyed when making the two ClO molecules, once the two ClO molecules combined the oxygen atoms will come off and combine to form a molecule of oxygen (O_2) leaving the two unstable chlorine atoms to restart this process over continue destroying ozone. The unstable and extremely reactive forms of chlorine stay in the stratosphere destroying ozone until something like a nitrogen oxide is able to combine with it and form a more stable compound that stays in the stratosphere or allows the molecule to fall back to the Earth's surface. During his research Molina also discovered that it takes years for the different CFC's and related products to circulate through the continual motion of the atmosphere and end up in the stratosphere. Because of the delay in these products entering the stratosphere the effects on the ozone layer were not immediately apparent at the time which caused the scientific community and the world to doubt his and Roland's research. Roland and Molina took a lot of criticism from both colleges and industries such as Du Pont for their announcement that the ozone layer was being destroyed before they had tangible evidence that it was being caused by the CFC's and similar products.

For the next decade the debate over the Roland-Molina ozone depletion hypothesis/theory and the impending depletion of the ozone layer continued but started to fall through the crakes due the continual involvement of the multi million dollar CFC industry. These industries used arguments such as nature has been taking care of its self for years and will there is no proof that it will not continue to do so. A second argument was made that volcanoes where partly responsible for the problem. Another argument used was that the ozone layer has always naturally fluctuated on an eleven year sun spot cycle and what Roland and Molina were seeing was just the low point in that cycle.

In the early 1980's a small group of scientists call the British Antarctic Survey, based in the Antarctic found a trend starting in the measurements they were taking. These measurements showed a continuing depletion of the ozone layer above the Antarctic in the early spring (from September to November). The ozone depletion was first noticed in the data collected in the spring of 1982 and continued in 1983. At first the data was thought to be flawed so in 1994 the scientist decided to take the measurements from two different location in the Antarctic and compare the results. When the data had been collected and analyzed the results showed a forty percent drop in the ozone layer over both location for the same thirty day time period from

September to October. In the mid 1990's these figures would rise to sixty percent. Once this trend from 1982 thru 1984 was located an inspection of the earlier data showed a slow but still increasing depletion during since 1977. The ozone hole phenomenon is thought to be associated with the formation of a polar vortex, a swirling mass of cold air over the Antarctic, that forms every winter. This vortex is an extreme weather phenomenon that forms due to the geological uniqueness of the Antarctic. This unique geology is found in the Antarctic because there are no mountains, very little other geological land masses and it is surrounded by water. This means that the vortex has nothing that would disrupt its circulation patters. The extremely cold temperatures caused by the formation of the vortex and the lack of sunlight in the winter months causes polar stratospheric clouds to form. These clouds promote the formation of stable chlorine and bromine molecules and hold them in the clouds. Once the Antarctic spring starts in September and the sunlight starts to increase and intensify there is a chain reaction in the clouds that turns the stable chlorine and bromine into their active forms. Once the stable forms of these molecules are activated the ozone layer is set for rapid depletion. This process is also accelerated by the fact that a reaction at the edges of the clouds prevents nitrogen oxides from entering the cloud and capturing the active forms of chlorine and bromine and changing them into more stable compounds. As a result the chlorine and bromine molecules are longer lived than normal causing increases in the ozone depletion. Once the polar vortex breaks apart the end of November there is an in rush of ozone from surrounding areas of the atmosphere. This in rush causes the ozone hole to be filled explaining why the ozone hole is only viable during the spring months from September to November.

The ozone layer above the Antarctic may have the greatest percentage of ozone depletion during the year, but it is not the only area that depletion is taking place. The natural expectation is that an ozone hole would also form from the same conditions in the Arctic. Although there is ozone depletion in the Arctic the expectation that it would be like the depletion seen over the Antarctic is wrong. This difference is due to the changes in weather patterns seen in the Arctic. The Arctic still has a polar vortex that forms in much the same way as in the Antarctic but there are other weather systems that cause the vortex to be more unstable over the Arctic. There is o still the formation of polar stratospheric clouds they are just not as thick and due to the lack of cold weather in March when there is finally enough sunlight to start the ozone depletion reaction the ozone depletion amounts tend to be far less than in the Antarctic.

In recent years the ozone depletion in the Arctic has increased. In fact research from the 1989 Airborne Arctic Stratospheric Expedition uncovered an intense mini-hole in the ozone layer above the Arctic. Although mini-holes are found in the peninsula of the Antarctic and in the Arctic at times, this particular mini-hole revealed measurements that rivaled the worst recorded in the Antarctic. It was thought that the Arctic was lucky to have escaped without a full ozone hole forming that year. Because of the extremely low temperatures and the increasing chlorine levels found that year there was the perfect setup for a ozone hole to appear. The formation of the hole was stopped by anticyclones over the Pacific and Atlantic that disturbed the vortex and made temperatures increase which limited the ozone depletion that year.

There have also been more recent detections of ozone depletion over the mid-latitude region. In December of 1987 depletions up to ten percent were recorded over Australia and New Zealand. Ozone reductions has now been measured to be year round in both the northern and southern hemispheres nearer to the equator. In the mid-latitudes of the northern hemisphere there are ozone depletion amounts seen in the winter months up to ten percent an the summer months up to six percent and the amounts seem to be increasing. Since the research suggests the ozone depletion is mainly due to chlorine and bromine that comes from CFC's and related products this increasing will continue until the use and production of these products is limited and finally eliminated. In the lower latitudes the ozone depletion could have some other causes helping. First this help comes from the breakup of the polar vortex which sends out reactive chlorine and bromine as it moves away from the Antarctic. Sulfuric acid particles may also play a part in triggering these ozone depletion.

Fortunately the conformation of the Antarctic ozone hole in 1986 made people start taking notice of the ozone depletion problem again. Discussion by policy and law makers resumed the debate over the cause of the ozone depletion and how it was going to be stopped. After several failed attempts and many revisions the Montreal Protocol as signed into affect in 1987 by many developed and developing countries and was to become affective in 1989. The initial compromises of the protocol called for developed countries to put a freeze on their CFC's and similar product levels at the 1986 levels by 1990; a reduction of fifty percent by the middle 1990's, the protocol also gave a ten year extension on these times for developing countries. It also contained a clause that the countries would ultimately eliminate CFC's and similar products by having follow-up meetings to tighten the protocols based on continuing scientific research.

Several amendments have already been made since the initial signing of the protocol. The 1990 London Amendment went as far as to ban the most damaging ozone depleting substances by 2010 in developing countries and by 2000 in developed countries, but that date for developed countries was changed to 1996 by the 1992 Copenhagen Amendment. Further amendments include the 1995 Vienna and the 1997 Montreal Amendments have further restricted the use and development of ozone depleting substances.

The good news about the ozone depletion is that starting in 1997 these has been clear signs that the 1987 Montreal Protocol with its Amendments is working. Research shows the tropospheric measurements of chlorine levels peaked in the early 1990's and are slowly starting to decrease, but measurements during the same time period shows the stratospheric levels were still increasing due to the time it takes the products to move from the troposphere into the stratosphere. Further studies have shown that by 1997 chlorine levels in the stratosphere peaked and will hopefully slowly start to decrease. The measurement results of the studies may take a while to be confirmed due to the concentration changes that naturally happen in the atmosphere and scientists wanting to wait and make sure the ozone depleting levels continue to drop. There are even reports starting to come out stating the atmosphere has already seen the worst and that the ozone layer should start to recover. Of course these results rely on the fact that the 1987 Montreal Protocol with its Amendments will continue to be followed and enforced in both the developed and developing countries.

Although the elimination of ozone depleting products is going to be a slow process since these products survive for years in the troposphere before they are moved into the stratosphere where they also stay for a long time destroying ozone. Due to this the ozone will not be able to return to its normal state until hopefully the middle of the 21st century. Even then the ozone layer will more than likely never return to its state prior to creation of the ozone depleting products due to the human factor.

Even though the ozone layer is now starting to recover there are still thing that everyone can do to help. An article by the EPA "Ozone, Good up High, Bad Nearby" give a list of things individuals can do to help decrease ozone formation in the troposphere and decrease the ozone depletion in the stratosphere. Following are the lists:

Ground-level "Bad" Ozone:

- Keep your automobile well tuned and maintained

- Carpool, use mass transit, walk, bicycle, and/or reduce driving, especially on hot summer days.
- Be careful not to spill gasoline when filling up your car or gasoline-powered lawn and garden equipment. During the summer, fill your gas tank during the cooler evening hours.
- Make sure your car's tires are properly inflated and your wheels are aligned.
- Seal containers of household cleaners, workshop chemicals and solvents, and garden chemicals to prevent volatile organic chemicals from evaporating into the air. Dispose of them properly.

High-Altitude "Good" Ozone:

- Make sure that technicians working on your car air conditioner, home air conditioner, or refrigerator are certified by an EPA approved program to recover the refrigerant (this is required by law).
- Have your car and home air conditioner units and refrigerator checked for leaks. When possible, repair leaky air conditioning units before refilling them.
- Contact local authorities to properly dispose of refrigeration or air conditioning equipment.
- Protect yourself against sunburn. Minimize sun exposure during midday hours (10 a.m. to 4 p.m.). Wear sunglasses, a hat with a wide brim, and protective clothing with a tight weave. Use a broad spectrum sunscreen with a sun protection factor (SPF) of at least 15 and 30 is better.

For more information on what individuals can do to help lower levels of ozone in the troposphere and prevent ozone depletion in the stratosphere please contact the local Environmental Protection Agency.

References

Arny, Thomas T. *Explorations an Introduction to Astronomy* 3rd Ed. New York:McGraw-Hill Company, 2002.

Kerr, Richard A. "A Brighter Outlook for Good Ozone." *Science v* 297 (September 6, 2002): 1623-1625

Masood, Ehsan. "Ozone Recovery will be Long-Term Affair." *Nature v* 393 (June 25, 1998): 723

Monastersky, Richard. "A Sign of Healing Appears in Stratosphere." *Science News v* 156 (December 18-25):391

Multiple International Authors. *Scientific Assessment of Ozone Depletion: 1998, Volume 1*. World Meteorological Organization Global Ozone Research and Monitoring Project – Report #44, 1998.

Nemecek, Sasha. "Rescuing the Ozone Layer." *Scientific America* v 277 (November 1997): 40+

Roan, Sharon. *Ozone Crisis, The 15-Year Evolution of a Sudden Global Emergency.* Wiley Science Editions, John Wiley & Sons, Inc., 1989.

United Nations Environment Programme (UNEP/GEMS Environment Library #7). *The impact of Ozone Depletion*. Nairobi:UNEP, 1992.

United States, Environmental Protection Agency, Office of Air Quality Planning & Standards. "Ozone, Good Up High, Bad Nearby." Research Triangle Park, NC:US EPA, Office of Air Quality Planning & Standards, 1997. (microfiche)