The story of Ozone: Why it matters

The compound ozone plays a crucial role in the natural atmosphere and the protection of organisms from harmful UV radiation. However, with increasing industrialisation and chemical production, scientists have observed depletions in the layer; the layer absorbs UVB and UVC radiation and thus prevents many health issues for organisms. As the layer was depleting at an alarming rate, it was obvious that action must be taken to restore ozone to its natural levels in the atmosphere and prevent further damage: for this to occur, the role of ozone must be understood. Scientists continue to research ways in which to restore the ozone layer, as its importance is obvious in regards to the health of organisms and the natural balance of the earth.

Ozone formation and its effects

The earth's atmosphere consists of multiple spheres; when considering ozone, the stratosphere and troposphere are most important. The troposphere is the closest layer to the earth's surface, and as a result of gravitational pull contains the most mass, around 75-80%; it extends upwards to approximately ten kilometres above sea level. The stratosphere is the next layer in the atmosphere, extending from ten kilometres to fifty kilometres above sea level; it is in the troposphere that the ozone layer is contained. The ozone layer is generally contained in the lower levels of the stratosphere, near to the tropopause- the intersection between the troposphere and stratosphere- between fifteen to thirty kilometres above sea level (Department of the Environment and Energy, n.d).

It is in the stratosphere that most natural formation of ozone occurs. Ozone is formed through coordination covalent bonding between oxygen atoms that occurs when shared electrons come from one atom; this process is modelled in Figure 1. UV radiation is required for natural ozone formation, as the energy leads to the photodissociation of a diatomic oxygen molecule, and from this, two oxygen radicals are formed (Thickett, 2006). The process of solar formation continues as these energised molecules collide with another O_2 molecule, and consequently an ozone molecule is formed. This is shown by the formula:

$$O_2(g) + UV \rightarrow 2O\cdot(g)$$

$$2O\cdot(g) + 2O_2(g) \rightarrow 2O_3(g)$$

$$\text{Therefore } 3O_2(g) \rightarrow 2O_3(g)$$

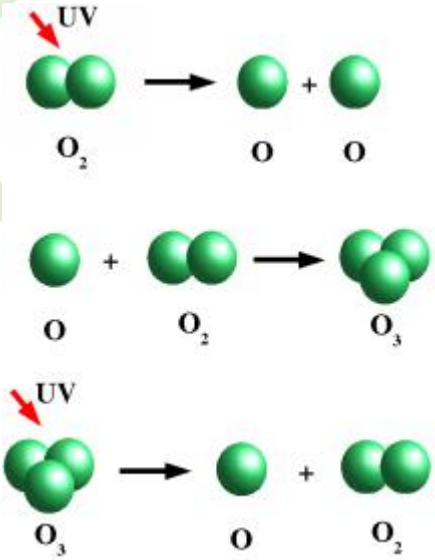

Figure 1: Ozone formation (Source: De Backer and Delcloo, n.d.)

Ozone is formed through the striking of O_2 with UV radiation, which catalyses an oxygen radical to produce O_3.

Thus, the ozone layer forms in the stratosphere because of the relatively high concentration of atmospheric oxygen, due to the earth's gravity and thus the density of gaseous molecules

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altitude. These ozone molecules are useful in the stratosphere, as UV radiation that strikes the molecule is absorbed, and the weak coordinate covalent bond is broken. Within the process of ozone depletion, the UV that strikes the ozone is absorbed, preventing the radiation from reaching the lower levels of the atmosphere and the earth's surface. This is shown by:

$$2O_3(g) + UV \rightarrow 2O\cdot(g) + 2O_2(g)$$

This is an advantage to humans as the process absorbs most harmful radiation that falls within the wavelength range of 200-310nm, UVB and UVC (Thickett, 2006). Gleason (2008) says, "Stratospheric ozone…plays a beneficial role by absorbing most of the biologically damaging ultraviolet sunlight," and hence the presence of the ozone layer is crucial to both the stratosphere and the health of organisms; UV radiation causes skin and eye problems, and affects natural ecosystems. However, in the troposphere ozone acts as a pollutant, producing photochemical smog, and causing issues such as respiratory problems (UCAR, 2011). Consequently, the presence of ozone provides benefits for the management of natural earth processes, and aids organisms in the sense of the removal of harmful ultraviolet radiation; but its balance is delicate in both the atmosphere and troposphere, and thus must be managed accordingly.

Ozone depletion and environmental impacts

With the industrialisation of the earth, pollutants began to be produced without the scientific knowledge or evidence to demonstrate their potential environmental effects. Chlorofluorocarbons (CFCs) were produced on an industrial scale in the past for use in aerosols and refrigerants as they are nontoxic, non-flammable, and stable (Elkins, 1999). However, it is only with research in the late 20th century that the impact of CFCs and other substances such as bromine-containing compounds and halons on the environment was recognised; they reduce levels of ozone present in the stratosphere, and hence the amount of UV radiation that is absorbed.

CFCs can reach the atmosphere since they are insoluble in water, and mostly unreactive in the atmosphere; due to their long lifespan they cause monumental damage. The process of ozone depletion through CFC is shown below and in Figure 2:

1. Ultraviolet radiation strikes a CFC molecule and causes a chlorine radical to split.

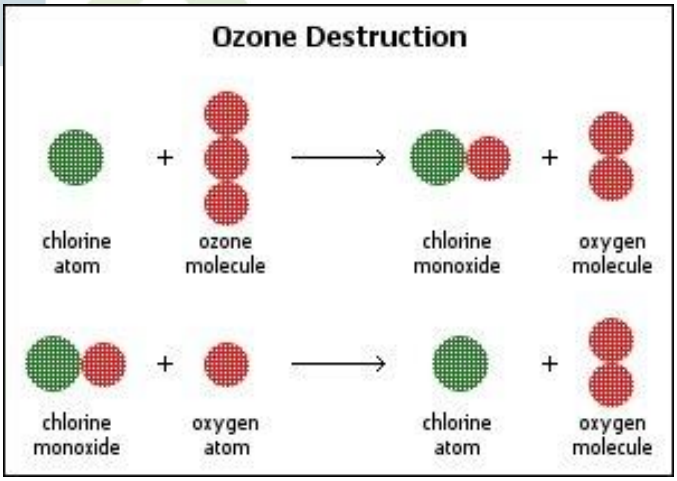

Figure 2: Ozone Destruction

(Source: Fisher, n.d)

Ozone destruction occurs when CFCs are split through the energy from UV radiation. This has led to ozone depletion, and negatively effects human health and the environment.

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2. This chlorine radical collides with an ozone molecule, forming chlorine monoxide and an oxygen molecule.
   $Cl\cdot(g) + O_3(g) \rightarrow ClO\cdot(g) + O_2(g)$
3. An oxygen radical collides with this chlorine monoxide, causing the oxygens to covalently bond, and freeing the chlorine.
   $ClO\cdot(g) + O\cdot(g) \rightarrow Cl\cdot(g) + O_2(g)$
4. This chlorine radical continues destroying ozone molecules.

Due to this process, one chlorine radical has the potential to deplete the atmosphere of many ozone molecules. This leads to a reduction in the ozone layer, and has caused 'holes', particularly above Antarctica. The thinning of the layer is also influenced by seasons, when sunlight levels differ: "In the southern spring and summer, when the sun shines for long periods of the day, chlorine reacts with ultraviolet rays, destroying ozone on a massive scale, up to 65 percent," (National Geographic, n.d). The thinning of the ozone layer has drastic effects on the earth, as a reduction in ozone means that harmful UVB and UVC are not absorbed to the extent that they are in a healthy atmosphere. These effects include:

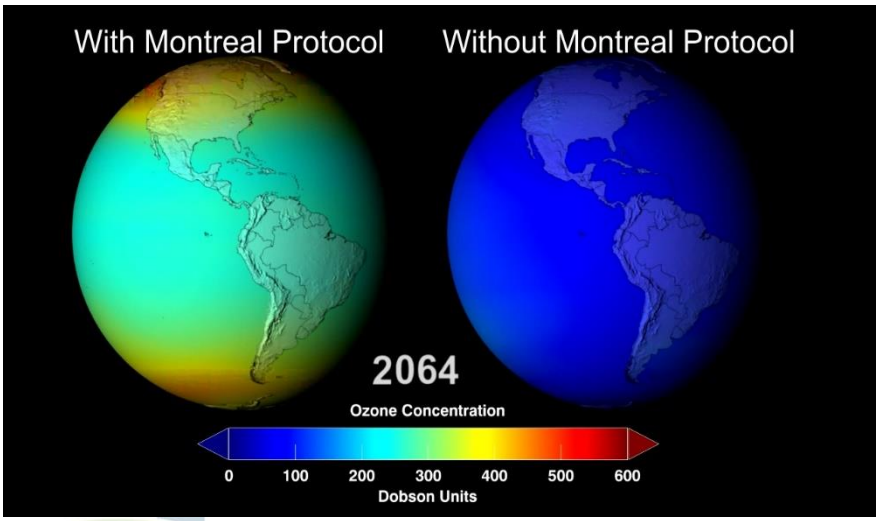

Figure 3: Montreal Protocol Before vs After

(Source: Schindler, 2009)

The above computer simulation from NASA demonstrates the effect of continued use of harmful substances on the ozone layer. Ozone is measured in Dobson Units, and above, a low count corresponds to a low level of atmospheric ozone, and consequently harmful effects. The Montreal Protocol is discussed later in the report.

- Increased levels of skin cancers, sunburn and eye conditions such as cataracts in humans, which leads to health issues because of mutations caused by radiation. These effects are more common in areas with high sun exposure, such as Australia, where there has been a 5-9% reduction in the ozone layer over the last 50 years (Department of Environment and Energy, n.d).
- Plants can be effected by UVB radiation, causing "changes in plant form, how nutrients are distributed within the plant, timing of developmental phases and secondary metabolism," (Department of Environment and Energy, n.d). Due to this, agriculture is impacted, as are worldwide ecosystems.
- UVB radiation especially has been proven to affect the growth rates of fish and crustaceans, and reducing phytoplankton survival rates (Department of Environment and Energy, n.d). Due to this, the entire marine ecosystem can be negatively affected, as reductions in small organisms can influence larger marine creatures.

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- Some materials are at risk of faster degradation when exposed to UV light, such as certain paints, fabrics, polymers etc.

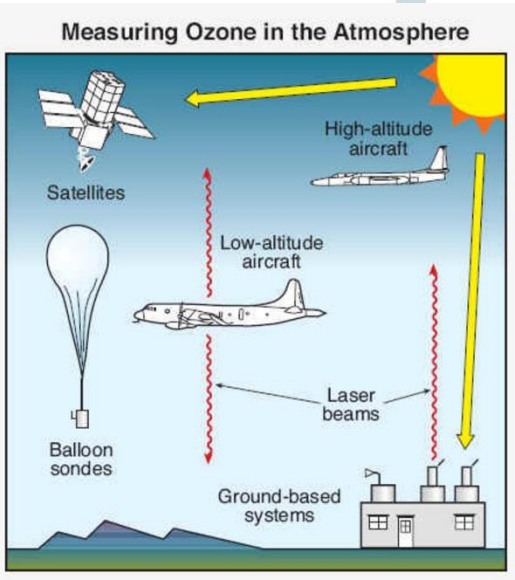
Thus, as a result of these negative effects of ozone depletion, research was conducted in order to analyse long-term impacts of some chemical emissions, and discover strategies to repair the ozone layer to its natural levels.

Measuring Ozone levels

Measurements of ozone levels have led to the discovery of the effect of chemicals on ozone depletion, and thus have played a crucial role in solving the problems that come with this depletion.

Local measurements

Local measurements of ozone require air to be drawn into the equipment. They measure UV radiation intensity through the absorption, or through the levels of electrical current or light produced from reactions with ozone. These instruments are often utilised through ozonesondes, which are balloons that are released into the atmosphere to measure ozone concentrations inside an attached monitor and transmit results; rockets and aircraft also measure ozone levels at differing altitudes (Fahey, D. and Higglin, M, 2010). Thus, data concerning ozone concentrations in differing geographical areas is available and is useful in determining levels in certain areas and hence management plans that can be developed.



Remote measurements

Remote measures of ozone levels are those that are detected at long distances and without contact with the molecules. Most ozone measures of this kind rely on analysing UV radiation absorption, as areas with depleted ozone absorb less UV than areas that are unaffected. Other methods include comparing the absorption of laser light, infrared radiation or microwaves; some are listed below:

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Figure 4: Measuring Ozone in the Atmosphere

(Source: Fahey, D. and Higglin, M, 2010).

Local measurements of ozone include balloon sondes and aircraft. Remote measurements measure large areas, and include satellites and some ground-based systems. Local measurements give a snapshot of a local area, while remote areas map large areas of ozone.

- Dobson spectrometer: "precisely measures the intensity of sunlight at two ultraviolet wavelengths: one that is strongly absorbed by ozone and one that is weakly absorbed. The difference in light intensity at the two wavelengths provides a measure of total ozone above the instrument location," (Fahey, D. and Higglin, M, 2010).
- LIDAR: Compares the amount of scattered laser light; one wavelength is absorbed by ozone, and one is not, giving profiles of concentration over altitude (NASA, 2016).
- Satellite measurements (e.g TOMS): Satellites can now carry instruments that measure global ozone levels, through IR, UV scattering, and scattering of sunlight.

<u>Case study: Antarctic Ozone hole, 1986</u>

In 1986, NASA scientists used a Total Ozone Mapping Spectrometer (TOMS) and the Solar Backscatter Ultraviolet (SBUV) to demostrate spring-time ozone losses in Antarctica and link this to the use of certain chemicals. It is through this initial work that continued research into ozone depletion began, and hence the effect of chemicals on ozone was discovered.

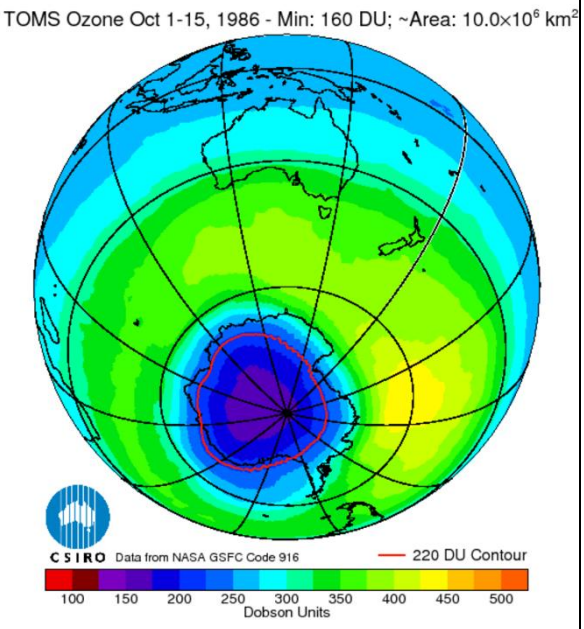

Figure 5: Antarctic Ozone Hole 1986

(Source: Department of the Environment and Energy, 1986)

This image was generated from a TOMS system, and provided some of the first evidence of seasonal ozone depletion in Antarctica.

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Solutions to Ozone depletion

The Montreal Protocol

In the late 1980s, the Montreal Project was enacted to reduce the number of CFCs and ozone-harming products that are emitted. The protocol binds countries to a schedule of chemical reduction, thus reducing overall emissions of harmful products and aiming to restore them to natural atmospheric levels (Department of Environment and Energy). There is evidence that ceased use of certain products has meant levels in the atmosphere have not increased, however "only after mid-century will the effective abundance of ODSs fall to values that were present before the Antarctic ozone hole was observed in the early 1980s," (Fahey & Heglin, 2010). However, the Montreal Protocol has not considered the effects of the introduction of Hydrochorofluorocarbons, which have replaced CFCs, and are now causing problems as they act as insulators and contribute to global warming; hence, more research must be undertaken into the effect of the protocol and long-term effects. Thus, while the protocol has advantages, it must be continually revised against current research for the best solution to be found.

Summary of Montreal Protocol control measures

Ozone depleting substances	Developed countries	Developing countries
Chlorofluorocarbons (CFCs)	Phased out end of 1995[a]	Total phase out by 2010
Halons	Phased out end of 1993	Total phase out by 2010
CCl_4(Carbon tetrachloride)	Phased out end of 1995[a]	Total phase out by 2010
CH_3CCl_3 (Methyl chloroform)	Phased out end of 1995[a]	Total phase out by 2015
Hydrochlorofluorocarbons (HCFCs)	Freeze from beginning of 1996[b] 35% reduction by 2004 75% reduction by 2010 90% reduction by 2015 Total phase out by 2020[c]	Freeze in 2013 at a base level calculated as the average of 2009 and 2010 consumption levels 10% reduction by 2015 35% reduction by 2020 67.5% reduction by 2025 Total phase out by 2030[d]
Hydrobromofluorocarbons (HBFCs)	Phased out end of 1995	Phased out end of 1995
Methyl bromide (CH_3Br) (horticultural uses)	Freeze in 1995 at 1991 base level[e] 25% reduction by 1999 50% reduction by 2001 70% reduction by 2003 Total phase out by 2005	Freeze in 2002 at average 1995-1998 base level[e] 20% reduction by 2005 Total phase out by 2015
Bromochloromethane (CH_2BrCl)	Phase out by 2002	Phase out by 2002

Figure 6: Summary of Montreal Protocol Control Measures

(Source: Environment.gov.au, n.d)

The Montreal Protocol provides strict dates for chemical phase-outs, in the hope of causing direct action based on a worldwide effort.

Other methods for ODS reduction

Whilst the Montreal Protocol has advantages, other methods to reduce ozone depletion must be considered. These include:

- The Kyoto Protocol: A legislation between nations to reduce greenhouse emissions, which failed due to a lack of implications for countries that did not comply after they signed. Thus, higher penalties are required, and more incentive is needed, as Henson (n.d) says, "the two biggest emitters of all – the United States and China – churned out more than enough extra greenhouse gas to erase all the reductions made by other countries during the Kyoto period."

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- Discouraging the use of some vehicles and the use of nitrous oxides and HCFCs. HCFCs act as an insulator, and when NO_x compounds migrate to the ozone layer, they react with ozone to form oxygen, and then with oxygen radicals to form NO (Kemsley, 2009). Thus, they also contribute to the reduction of the ozone layer and hence action must be taken.

$$NO_2(g) + UV \rightarrow NO(g) + O\cdot(g)$$

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

$$NO_2(g) + O\cdot(g) \rightarrow NO(g) + O_2(g)$$

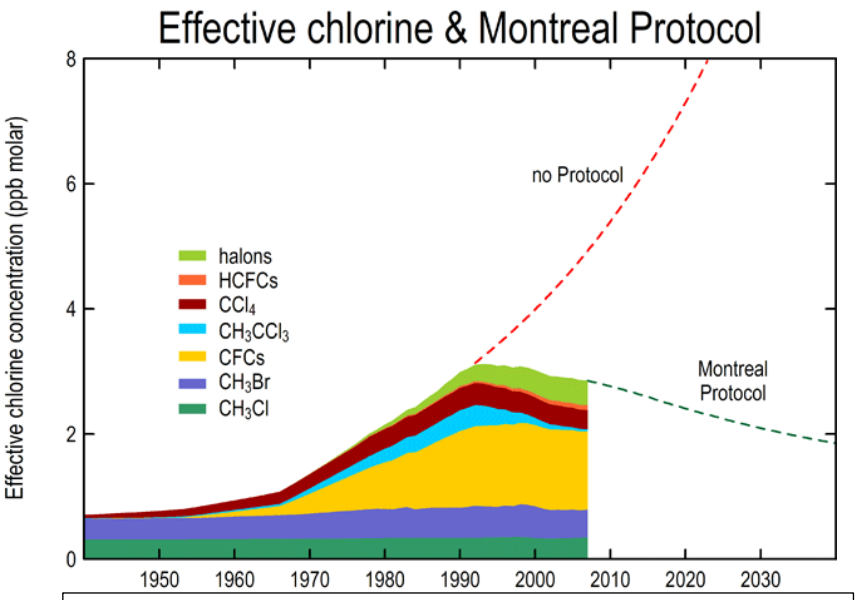

Figure 7: Chlorine and the Montreal Protocol

(Source: Sibila, n.d)

The ultimate effects of the Montreal Protocol have not been recognised yet because of the long lifespan of ODSs in the atmosphere. However, the effect of HCFCs and other harmful gases such as nitrous oxides must be accounted when considering ozone and overall planet health.

Overall, efforts to combat ozone depletion have been effective. However, more research must be completed to analyse impacts of all products on the environment, as, currently, solutions do not consider the long-term effect of all chemicals on the depletion of ozone.

Conclusion

Ozone is a crucial compound in the earth's atmosphere, as it prevents environmental damage and risks to human health. Thus, it is important that it is protected, and it is hoped that with more time and research the ozone layer will be restored as the full impact of human activity is realised.

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