WHAT'S HAPPENING WITH THE OZONE HOLE?

- A REVIEW

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Introduction

Discovered by Schonbein in 1839, ozone (O_3) is a highly reactive and toxic form of oxygen with a pungent smell. It occurs both naturally and as an atmospheric pollutant at ground level. Ozone is found in low concentrations in the stratospheric layer of the earth’s atmosphere, 10 to 50 km above the surface, where it acts to shield the earth from solar UV radiation, between 220 and 320nm (Christie, 2000).

Measurements of stratospheric ozone began at Oxford in 1924 where Dobson and Harrison found seasonal variations in ozone levels. They also found significant variability in short term ozone levels, later recognised as being associated with weather patterns and changes in surface air pressure. The units used for measuring ozone concentrations are known as Dobson units (DU) and represent the amount of ozone in a square centimetre column through the atmosphere. A typical measurement is about 300 DU, which means that if you took all the ozone in a vertical column above the instrument down to sea level, it would form a 3mm thick layer.

The need for a global network of ozone monitoring stations was soon recognised and with the International Geophysical Year of 1957 - 58 the network expanded to include the first measurements of ozone in Antarctica, from the British Station at Halley Bay on the coast of the Weddell Sea. It was from here that regular ozone monitoring, from the 1960s to the mid 1980s, led to the 1985 report in “Nature” of a 50% spring-time depletion of the ozone layer above Antarctica. In this paper, Farman, Gardiner and Shanklin (1985) linked the reduction in ozone levels to increases in inorganic chlorine and the very low temperatures of the Antarctic stratosphere. The ozone hole had been discovered.

The Chemistry of Stratospheric Ozone

Ozone (O_3) is created in the stratosphere, predominantly near the equator, by the action of photons of ultraviolet light (UV) on diatomic oxygen (O_2). A third molecule (M), which may be an oxygen or nitrogen molecule, acts as a catalyst (Equations 1.1 and 1.2):

\[ O_2 + UV \rightarrow O + O \]  \hspace{1cm} (1.1)
\[ O_2 + O + M \rightarrow O_3 + M \]  \hspace{1cm} (1.2)

The UV light which enables ozone to form can also break it apart (Equation 1.3):

\[ O_3 + UV \rightarrow O_2 + O \]  \hspace{1cm} (1.3)

In addition, other chemical reactions occur including those involving nitrogen and hydrogen oxides which participate in the reaction to convert ozone (O_3) back to (O_2), without being affected themselves (Equation 1.4):

\[ O + O_3 + M \rightarrow O_2 + O_2 + M \]  \hspace{1cm} (1.4)

In 1928 the first chlorofluorocarbons (CFCs) were invented by Thomas Midgely, when he was asked to create a safe refrigerant for General Motors. They proved ideal
for the purpose and were subsequently developed and used in cooling systems and as aerosol propellants, foam blowing agents and solvents for the electronic industry (Reid, 2000). These inert compounds are capable of surviving 50 - 100 years in the atmosphere (Toon and Turco, 1996).

Although very stable at lower altitudes, CFCs are broken up by sunlight in the stratosphere. The resulting atomic chlorine (Cl) can act as a catalyst to destroy ozone, at least five times more efficiently than nitrogen oxide (Equations 1.5 and 1.6):

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  
(1.5)

\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]  
(1.6)

Bromine (Br), a gas similar to chlorine, can also take part in the catalytic reactions and destroy ozone. Anthropogenic sources of bromine include fire fighting chemicals and methyl bromide, used primarily as a soil fumigant and also occurring as a combustion by product (Makhijani and Gurney, 1995).

**The Role of the Antarctic Climate in Forming the Ozone Hole**

Although ozone is formed mainly over the equator it is distributed via a global circulation system to the whole of the stratosphere. This system is driven by the temperature differences between the equator and the poles. Prior to the 1970s there was far more ozone over Antarctica, typically 450 DU in winter, than over the tropics, typically 200 - 250 DU (Reid, 2000). Similarly CFCs, which are produced primarily in the northern hemisphere are slowly distributed throughout the whole of the stratosphere. Although it takes many months for one cycle, this system is powerful enough to prevent the large CFC molecules, which are heavier than air, from settling out and accumulating at the earth’s surface.

During early winter a jet stream develops in the high-latitude stratosphere over the poles, about 15 - 50 km above the earth. This forms a spinning, cone-shaped vortex (wider at the top) which only breaks down as the sun rises in spring. The polar vortex acts like a semi-porous container, inside which ozone depleting chemistry occurs very efficiently. As winter proceeds, more air arrives at the top of the cone, via the equator to pole circulation system, and sinks down bringing more ozone as well as the chemicals that destroy it. Although some air escapes from the bottom and sides of the vortex and streams off towards mid-latitudes, the proportion is only small. However, Tuck (1989) suggests that the Antarctic vortex still plays a significant role in processing ozone rich air, which is later released as ozone poor air and transported back to mid-latitudes. A similar polar vortex sets up in the Arctic but it is not as stable due to mountainous terrain and surrounding landforms disrupting the flow and making conditions less efficient for ozone destruction.

**Polar Stratospheric Clouds**

Temperatures within the Antarctic polar vortex often fall below -80°C creating conditions suitable for the formation of Polar Stratospheric Clouds (PSCs). These beautifully coloured “mother-of-pearl” clouds consist mainly of nitric acid and water
in the form of nitric acid trihydrate crystals (HN\textsubscript{3}0\textsubscript{3}(\textsubscript{2}H\textsubscript{2}0)). Because the stratosphere is extremely dry, very low temperatures are necessary for these clouds to condense. Under normal conditions, most of the chlorine released by CFCs into the stratosphere forms harmless compounds such as chlorine nitrate (ClO\textsubscript{2}N\textsubscript{2}) and hydrogen chloride (HCl), however PSCs perform a special role by providing surfaces from which active chlorine is released.

As the sun rises in early spring, ozone destruction begins in earnest (Equations 1.5 and 1.6). Although there is no more chlorine over Antarctica than anywhere else in the world it is the physical conditions provided by the PSCs which result in such efficient ozone destruction. At low temperatures the reactions are very fast and a single chlorine atom can destroy tens of thousands of ozone molecules before being removed to a stable compound. Bromine, which has no such stable species, persists much longer. Fortunately it is about 100 times less abundant (Reid, 2000) although, whereas chlorine is declining, the total amount of bromine in the atmosphere is still increasing (WMO, 1999). As spring progresses, the sunlight which allowed these reactions to occur, gains strength and reduces the strength of the polar vortex. By November the polar vortex breaks up and the ozone hole is filled by mid-latitude air with higher ozone concentrations.

Due to the more irregular circulation of the Arctic polar vortex, temperatures do not drop as low as PSCs are less common, thus preventing ozone depletion to the same degree as in the Antarctic.

**Methods Used to Measure Ozone**

Traditionally ozone has been measured using a Dobson spectrophotometer, an instrument which compares the intensities of two different wavelengths of UV light either from the sun or, during the polar winter, indirectly from sunlight reflected off the moon. One of these wavelengths is strongly absorbed by ozone while the other is not. Once calibrated, the instrument can be used to determine the ratio of intensities and hence, the amount of ozone in the atmosphere (Shanklin, 1998).

Other methods must be used to determine the vertical distribution of ozone through the atmosphere. Balloons carrying a chemical sensor, known as an ozone sonde, can be used. This relies on the reaction between ozone and a potassium iodine solution to create an electrical current which is amplified and used to transmit a signal back to earth. Ozone concentration is proportional to the strength of the signal (Shanklin, 1998).

Measurement from Halley Station show that ozone concentrations normally peak at an altitude of 17 km above the earth although during spring most of the ozone between 14 and 20 km is destroyed. Temperature readings from meteorological balloons can also be used, as there is a strong link between temperature and ozone concentration at certain altitudes.

In September 1987, an international study using a spy plane, converted by NASA for high-altitude research, measured the chemical composition of the atmosphere across the Antarctic polar vortex. Combined with the results of Lidar (laser radar) and
microwave experiments from McMurdo and the South Pole, it was shown conclusively that chlorine plays a major role in forming the ozone hole.

With more recent technology, further information can be obtained from satellite instruments capable of measuring atmospheric ozone and other trace gases around the globe. Maps from these measurements show how the ozone hole forms in early spring and subsequently recovers in summer (Fig. 1).

**Figure 1** The ozone hole over Antarctica on 7 October 2000 (from Berkman 2002, p129)

**Changes in the Size of the Ozone Hole**

Throughout the 1980s the ozone hole grew rapidly, although the rate of growth generally slowed in the 1990s (Fig. 2). Spring ozone levels in Antarctica are now about 40 to 55% below the pre-ozone hole levels, peaking at up to a 70% decrease for periods of a week or so. In 1998 the largest and longest lasting ozone hole up until that time was recorded, this was followed in 1999 by a hole that was only slightly smaller (Waterhouse, 2001).

In year 2000, the ozone hole broke all records for size but came and went with unusual speed. It had disappeared by the end of November whereas it usually persists to mid-December or later. On 30 September 2000, the National Institute of Water and Atmospheric Science (NIWA) measured a new minimum total ozone value of 126 DU at Arrival Heights, in the Ross Sea Region of Antarctica. At its maximum, the size of the ozone hole (defined as the area containing ozone concentrations of less than 220 DU) was approximately thirty million square kilometres. In 2001 the ozone was smaller than for the two previous years (NIWA, 2002).
Figure 2   Growth of the Antarctic Ozone Hole since 1979 (from WMO, 1999, p.xxxiv)

In the lower stratosphere, between 12 and 20 km, the monthly mean ozone levels in recent years have been on average between 60 and 90% below the pre-ozone hole values and at times ozone is nearly totally destroyed. In contrast, changes in ozone levels in equatorial regions (20°S to 20°N) have not been statistically significant (Fig. 3). This shows the critical importance of conditions within the polar vortex.

Figure 3.   Diagram of the North to South Ozone Depletion: 1979 - 1997 (from WMO, 1999, pxxxviii)
Montreal Protocol

As the role of CFCs in ozone depletion become clear and other potential causes, such as supersonic aircraft and volcanic gases, were ruled out as less significant it became obvious that action was required. This created considerable opposition from industries which stood to lose financially. Nevertheless, the evidence had grown to support the theory, first published in “Nature” by Molina and Rowland (1974), that CFCs could be broken apart by UV radiation. The liberated chlorine was then free to react with other atoms in the atmosphere, including ozone which it would break apart into its oxygen components. Their results convinced them to publish a warning that CFCs might pose a greater threat to stratospheric ozone than supersonic aircraft (Christie, 2000).

In 1987, the governments of many nations agreed to limit, and eventually phase out the industrial and domestic use of CFCs. The Montreal Protocol, on substances that deplete the ozone layer, was drawn up and has since been strengthened by a number of amendments. Of these, one of the more significant was the London 1990 amendment which called for a ban on the production of the most damaging ozone-depleting substances by 2000 in developed countries and by 2010 in developing countries. The subsequent 1992 Copenhagen amendment further strengthened the Protocol by changing the date of this ban to 1996 in developed countries.

The past and projected stratospheric abundances of chlorine and bromine without the protocol, under the protocol’s original provisions, and under its subsequent amendments assuming full compliance are shown in Figure 4.

![Figure 4](image.png)

**Figure 4** Effect of the International Agreements on Ozone Depleting Stratospheric Chlorine and Bromine (from WMO, 1999 p.xxxix)

The relative speed with which the Montreal Protocol was agreed to was due to a combination of factors. Environmental awareness was becoming an important issue internationally, while at the same time the discovery and subsequent investigation of
the Antarctic ozone hole helped lead to scientific consensus. Politics also played an important role: "The framing of the ozone problem as a human health issue rather than an ecological one conditioned the political context of the entire debate" (Litfin, 1994, p52). Perhaps one of the most notable achievements of the negotiations was the "dissolving of boundaries" both between academic disciplines and to some extent, between nations (Rowlands, 1995).

The challenge now is to gain full compliance with the Protocol and its amendments. While significant progress has been made (Fig 5), there are still ozone depleting chemicals in use, even though manufacturing has ceased for many. The financial implications of compliance for Third World Nations is also a difficult issue. Finding suitable cost-effective substitutes for ozone depleting chemicals must be a priority.

**Figure 5** Timeline showing the interaction between scientific discoveries and policy decisions during the ozone crisis (from Reid, 2000, p105)
Effects of Ozone Depletion

Antarctica

Associated with ozone depletion is an increase in the levels of biologically harmful UV light reaching the earth’s surface, in particular UV-B which has a wavelength between 280 - 320mm (Karentz, 1991). Small changes in ozone concentration can cause disproportionate changes in the harmfulness of UV-B including potential damage to DNA resulting in genetic mutations. UV-B can also cause changes to the membrane structure and chemical environment of cells, thus interfering with normal metabolic processes. These effects can be particularly significant for short lived single-celled organisms where the entire individual may be radiated and also where more generations are affected in a shorter timeframe (Berkman, 2002).

Many Antarctic plants and animals have developed pigments to help protect them from UV-B for example some bright orange lichens contain flavonoid and carotenoid pigments. Other lichens and some microbes live inside translucent rock to shelter from high radiation levels and from the desiccating winds (Shanklin, 1998). In addition to these protective strategies, some Antarctic species also have repair mechanisms that can correct UV-B induced damage (Karentz, 1994).

Antarctic waters are extremely transparent allowing UV light to penetrate up to 20 metres (Karentz, 1991). This has particular implications for phytoplankton as their photosynthesis is sensitive to UV radiation, particularly within the UV-B range (Nilsson, 1996). These microscopic plants form the base of the Antarctic food chain and are fed on by krill which in turn are a major food source for sea birds and whales in the Southern Ocean. Phytoplankton also play an important role in the global circulation of carbon, affecting the concentrations of carbon dioxide, a major greenhouse gas, in the atmosphere. In the State of the Environment Report for the Ross Sea Region (Waterhouse, 2001) it is noted that there is potential for UV radiation to change the species composition of the phytoplankton community. This could potentially change the overall productivity of the marine environment. There is evidence that some changes may have already occurred.

The outlook for terrestrial biota appears a lot brighter as snow and ice cover during spring, along with the protective pigments of these plants and animals, appears to provide effective protection. However, research in this area is limited and long term effects may not yet be apparent.

New Zealand

UV-B radiation has adverse effects on human health including skin damage (sunburn and skin cancers), eye abnormalities (snow blindness and cataracts) and changes in the immune system, which may alter the course of cancer or infectious disease (Kondratyev and Varotsos, 2000).

A recent study shows that UV radiation over New Zealand increased by 12% between 1989 and 1999 making our population more exposed to these adverse health effects (MIE, 2001a). In particular, skin cancer rates in New Zealand are amongst the
highest in the world, with over 250 deaths each year and an annual treatment cost estimated at $33M/year (MfE, 2001b).

While the causes of skin cancer are not fully understood, solar UV radiation is accepted as an important factor. A pale skin is an additional risk factor, and is not helped by the outdoor lifestyle of New Zealanders with plentiful sunshine and relatively low air pollution. High skin cancer rates, however, cannot be entirely contributed to enhanced UV-B levels as there is a long delay in the onset of melanoma. With high UV rates expected for some years yet, public awareness and precautions to limit exposure must remain a priority, especially as other forms of skin such as basal cell carcinoma rates appear to be more directly linked to UV exposure (UNEP, 1998).

While the ozone hole itself never reaches as far north as New Zealand, it does influence ozone levels over the country. In early summer the polar vortex begins to break apart, spreading ozone depleted air over the mid-latitudes of the southern hemisphere. The resulting low ozone levels in combination with the high summer sun has led to increased UV levels. In addition to the release of packages of low ozone air as the vortex breaks up, the Antarctic ozone hole has a general diluting effect on New Zealand ozone levels. It is estimated that levels are about 8% lower than they would be with no ozone depletion. NIWA (2002) is currently developing a model which will follow the movement of air parcels in the stratosphere to help improve our understanding of the impact of the Antarctic ozone hole on New Zealand. This may also assist in predicting "at risk" periods.

In addition to effects on people, high UV levels can also affect stock, wildlife and plants. Experiments have shown that crops can be affected. In Portugal, maize yield was reduced by 20% under 10 - 15% increased UV radiation, and in the Philippines and Japan rice yields were reduced by 25% (Tevini, 1998). One of the difficulties with such experiments is determining and quantifying other environmental factors which may be stressing plants and affecting yields. Effects from increased UV levels also have the potential to accumulate from year to year in long-lived plant species such as forest trees (UNEP, 1998).

More research in this area is required before any effects of increased UV levels on New Zealand crop production could be quantified. The effect on native flora and fauna is also unclear.

The Future of the Ozone Hole

On their website, NIWA state that “the ozone holes are probably now as bad as they will ever be. Measures to reduce the levels of chlorine pollutants are starting to take effect, but it could be 50 years before ozone levels are restored” (NIWA, 2002). This optimism is also shown in the WMO report, although they add the warning that full compliance with the Montreal Protocol and its amendments will be required to achieve this expected recovery (WMO, 1999).

Net tropospheric concentrations of chlorine and bromine containing compounds have been decreasing since 1995, however the effect will not be noticeable for at least
another three to six years, the time it takes for these chemicals to reach the stratosphere. WMO (1999) state that, all other things being constant, the ozone layer is expected to return to a normal state during the middle of this century. The slow recovery is due to the time it takes for natural processes to eliminate CFCs and halons from the atmosphere. Most CFCs and halons have atmospheric residence times of between about 50 to several hundred years.

While there is agreement that chlorine and bromine levels are almost under control, there is now a suggestion that recovery will be delayed by 15 - 20 years, and that the most severe ozone losses will occur during the decade 2010 - 2019. (Schindell et al, 1998). Under this scenario the earliest recovery to 1980 levels would not be before 2060. These forecasts are based on a model with parameters set on the climatic conditions expected with future global warming. Recovery of the ozone layer may be delayed due to the cooling of the stratosphere, which is expected to occur with climate change. A colder stratosphere promotes more efficient ozone-destroying chemistry.

This effect is due to a positive feedback system where, although absorption of solar UV by ozone is responsible for warming the stratosphere, with less ozone there to cause this warming, the stratosphere cools even further. This enhances ozone-destroying chemistry. The effect is further compounded if greenhouse gases trap infrared radiation near the earth’s surface, preventing it from reflecting back through the stratosphere and warming it. Schindell (1998) suggests that global ozone depletion can also adversely influence the chemistry in the troposphere by allowing more UV light into this layer of the atmosphere.

When recovery does occur, it is unlikely that the ozone layer will ever be the same as it was prior to the 1980s as it will be affected, to some degree, by changes in climate and by the addition of anthropogenic compounds such as methane, nitrous oxide and sulphate particles. However, as long as there is compliance with the Montreal Protocol, we can be hopeful that a major deterioration in the earth’s protective ultraviolet shield has been prevented.

Conclusions

The role of Antarctic science in discovering the ozone hole and subsequent monitoring of ozone levels has played a significant part in averting an environmental disaster of global proportions.

Although it may be some time before the ozone hole recovers, the Montreal Protocol has ensured that further damage to the ozone layer is minimised. In the meantime, UV levels will remain high and there is much still to be learnt about the effects this will have on people, plants and animals. The resources, so far, have concentrated on understanding the dynamics of the ozone phenomena, it may now be time to learn more about the impacts it will have in the future.
References


**Figures**

**Figure 1** The ozone hole over Antarctica on 7 October 2000 (from Berkman 2002, p129)

**Figure 2** Growth of the Antarctic Ozone Hole since 1979 (from WMO, 1999, p.xxxiv)

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