Geo Factsheet

September 2005 Number 188

THE OZONE PROBLEM

TOO LITTLE UP THERE, TOO MUCH DOWN HERE

Setting the scene

Ozone is a highly reactive and unstable triatomic form of molecular oxygen (O_3) formed through the action of the sun's energy on the diatomic form of molecular oxygen (O_2).

- In the lower atmosphere, ozone is considered an atmospheric pollutant, whereas in the upper atmosphere it is an essential constituent.
- In the lower atmosphere, ozone harms human health and vegetation, while in the upper atmosphere it shields the earth from harmful UV rays.

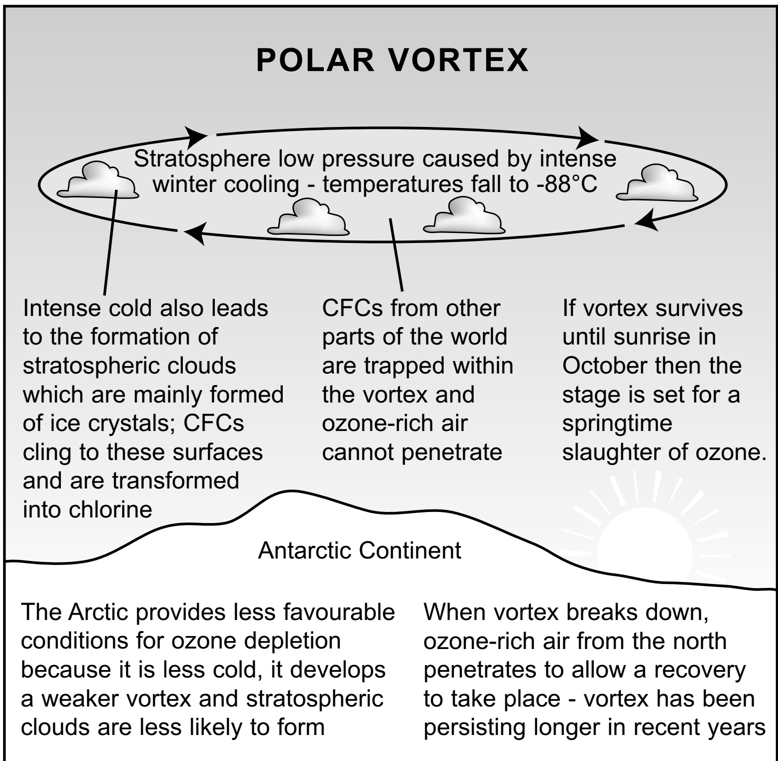
A. STRATOSPHERIC OZONE

The earth's atmosphere consists of about 78% nitrogen, 21% oxygen, 0.04% carbon dioxide and small amounts of other gases including argon. The amount of ozone in the atmosphere is a small but vital component of the atmospheric composition. Ozone occurs because oxygen rising up from the top of the troposphere reacts under the influence of sunlight to form ozone. Most of this is created over the Equator and the Tropics since this is where solar radiation is strongest. However, winds within the stratosphere transport the ozone towards the polar regions where it tends to concentrate.

Ozone is essential for sustaining life. The highest concentration of ozone occurs in the upper part of the atmosphere, the stratosphere, where it is formed through the action of ultraviolet (UV) radiation on oxygen. The ozone layer - which occurs between 15 and 35 km (in particular between 16 and 25 km) above the earth's surface shields the earth from harmful radiation that would otherwise destroy most life on the planet.

Ozone has the vital role of absorbing UV (0.25 – 0.8µm) radiation. It absorbs some outgoing terrestrial radiation (10-12µm) - so it is also a greenhouse gas. Ozone is constantly being produced and destroyed in the stratosphere in a natural dynamic balance i.e. as well as being produced by sunlight it is also being destroyed by nitrogen oxides. Short-wave (UV) radiation breaks down O_2 into two single oxygen molecules. The free oxygen atoms (O) combines with oxygen (O_2) to form ozone (O_3). However, the ozone that is formed is not stable and there are processes that destroy ozone. These include photochemical (involving solar radiation) interactions with molecular oxygen and oxides of nitrogen. Other important mechanisms in the break up of ozone involve chlorine and bromine.

Fig. 1 How ozone is destroyed.



A June through November cycle in Antarctica:	
June	Southern Hemisphere winter begins. As temperatures fall, stratospheric winds - the polar vortex - roar around Antarctica blocking outside air.
July/August	As stratospheric temperatures fall below around minus 88°C clouds form from water vapour and nitric acid. Snow falling from the clouds carries nitrogen from the air which helps form chlorine reservoirs. Chemical reactions taking place on the clouds' ice crystals, which wouldn't take place in the air. Free chlorine atoms form.
September	Sunlight returns to Antarctica, temperatures begin rising and clouds evaporate. Chlorine begins destroying ozone.
October	Lowest levels of ozone are detected as temperatures continue rising.
November	Polar vortex weakens and breaks down, allowing ozone-poor air to spread over the Southern Hemisphere.

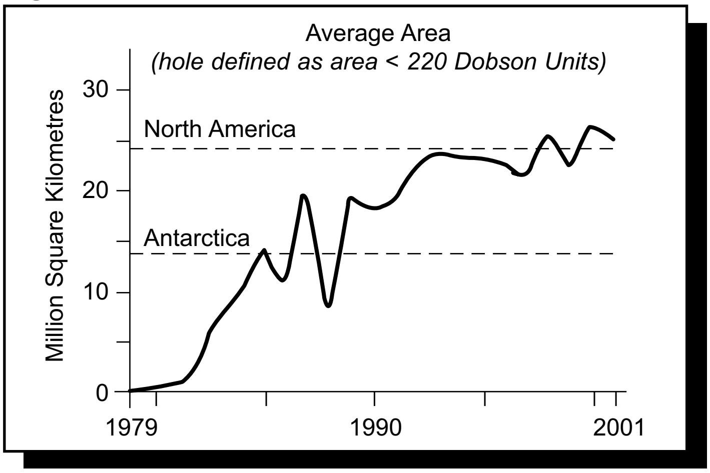
Although ozone is constantly produced and destroyed, human activities may tilt the balance one way or the other. There is now clear evidence that human activities have led to the creation of a hole in the ozone layer over Antarctica *(see Fig. 1, page 1)*.

Monitoring of ozone concentrations suggests an annual loss of 1% p.a. As a result of this there is an estimated rise in the rate of skin cancers of 4%. Increasing measurements of CFCs correlate with declining ozone levels. There are important natural sources of chlorine such as volcanoes and forest fires, but the increases are probably too large to be purely natural. There are now 'ozone holes' at both poles, the one over Antarctica stretching as far as to Argentina.

The ozone hole

The ozone 'hole' is an area of reduced concentration of ozone in the stratosphere, which varies from place to place and over the course of a year. The hole in the ozone layer over Antarctica was first discovered in 1982. It follows a very clear seasonal pattern - each springtime in Antarctica (between September and October) there is a huge reduction in the amount of ozone from the stratosphere *(see Fig. 1)*. At the end of the long polar night ozone is present in roughly the same quantities that were there in the 1960s and 1970s; as the summer develops the concentration of ozone recover - so what causes the depletion in ozone during the spring time? During winter in the Southern Hemisphere the air over Antarctica is cut off from the rest of the atmosphere by circumpolar winds - these winds block warm air from entering into Antarctica. Therefore the temperature over Antarctica becomes very cold, often down as far as –90°C in the stratosphere. This allows the formation of clouds formed of ice particles. Chemical reactions take place on this ice which include chlorine compounds resulting from pollution by human activities. These reactions release chlorine atoms. Once the sun returns during the summer the chlorine releases atomic chlorine which destroys ozone in a series of chemical reactions. Hence the hole in the ozone layer occurs very rapidly in the spring. By summer however, the ice clouds have evaporated and the chlorine converted to other compounds such as chlorine nitrate until the following winter. The ozone hole fills in, although it returns each spring. The size of the hole is also impressive as well as variable *(Fig. 2)*. As early as 1987 it covered an area the size of continental USA and was as deep as Mount Everest. In addition to human activities, volcanic eruptions can also have an impact on the ozone layer.

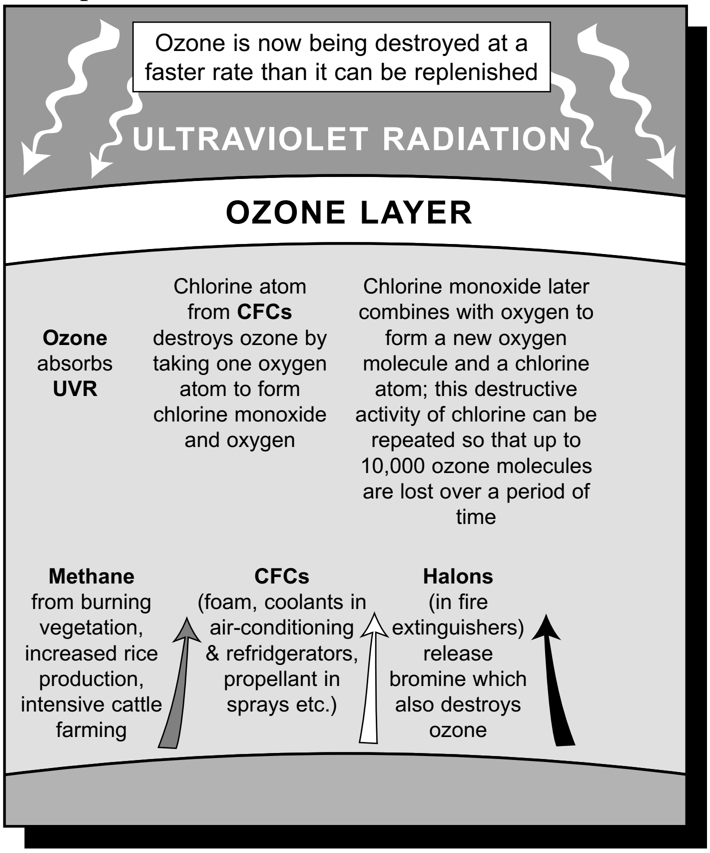
Fig. 2 The Antarctic Ozone hole.



Ozone destroyers

Nitrogen oxides produced by human activities can also destroy the ozone layer just as chlorine atoms can *(see Fig. 3)*. The sources of chlorine atoms are known as Chlorofluorocarbons (CFCs) and include materials used in fridges (for the working fluid in the pipes and fridge), air cooling systems, foamed plastic and aerosols. CFCs are particularly dangerous because they can be very long lived - over a hundred years - and they spread throughout the atmosphere. In the case of Antarctica the build up of chlorine appears to have had very little impact until it reached a critical threshold. Once that was reached only a small increase in chlorine led to a huge change in the ozone layer.

Fig. 3 How human activity destroys ozone in the atmosphere.



There are major implications of an increase in the hole in the ozone layer. This is because ultraviolet radiation would reach the ground in increased quantities. Some ultraviolet reaches the ground already - it is in the 290-320 wave band. This is known as UV-B, and can cause cell mutations, sunburn, skin cancer and eye problems such as cataracts.

CFCs last a long time – up to 100 years, so banning their use will not have any impact for a long time. Consumer demand has not decreased although many CFCs have been replaced by other substances such as HCFCs (hydrochlorofluorocarbons). However, HCFCs are problematic since they contain chlorine. Another recently highlighted problem is the role of aircraft in the stratosphere as they are flying even higher.

B. GROUND LEVEL OZONE

At ground level ozone is considered a pollutant. In the lower atmosphere ozone is formed by sunlight splitting oxygen molecules into atoms which regroup to form ozone. Unlike other pollutants, ozone is not directly emitted from man-made sources in large quantities. Ozone occurs naturally in the atmosphere, but the chemical reaction between VOCs (volatile organic compounds), nitrogen oxides and sunlight can produce ground level ozone.

Volatile organic compounds (VOCs) include a large number of chemical compounds which are able to evaporate into a gas and take part in chemical reactions. They include methane, ethane and alcohol. The main sources of VOCs and nitrogen dioxides are road transport, solvent release (e.g. as paints, glues or inks dry) and petrol handling and distribution. These reactions may take hours or days to produce ozone. Photochemical reactions between nitrogen oxides and VOCs in sunlight create ozone. Due to the role of photochemical reactions in the formation of ozone, ozone concentrations are greatest during the day, especially during warm, sunny, stable conditions. Above 20°C reactions are accelerated. Therefore low-level ozone is a hazard of summer heatwaves.

Ozone measured at a particular location may have arisen from VOC and nitrogen oxides emissions many hundreds or even thousands of kilometres away. Maximum concentrations, therefore, generally occur downwind of source emissions. Background concentrations of ozone are highest in the rural areas of Great Britain.

Ozone pollution

Air pollution is associated with high pressure. This is because winds in a high pressure system winds are usually weak. Hence pollutants remain in the area and are not dispersed. Poor air quality often persists for many days. This is because it is associated with stable high-pressure conditions which generally last for a few days. In some climates, notably Mediterranean climates, stable high pressure conditions persist all season, hence poor air quality can remain for months. In monsoonal areas smogs occur in the dry season. Although smogs occur under certain atmospheric conditions (namely high pressure), human activity (the emission of pollutants) is responsible for the environmental hazard.

Summer smog occurs on calm sunny days when photochemical (solar) activity leads to ozone formation. Ozone is formed when nitrogen oxides and VOCs react in the sunlight. Other compounds are formed including acid aerosols (sulphates, sulphuric acid, nitrates and nitric acid), aldehydes, hydrogen peroxide and PAN (peroxacetyl nitrate). This process may take a number of hours to occur - by which time the air has drifted into surrounding suburban and rural areas. Hence ozone pollution may be greater outside the city centre. The effect of ozone pollution is to cause stinging eyes, coughing, headaches, chest pains, nausea and shortness of breath, even in fit people. Asthmatics may experience severe breathing problems.

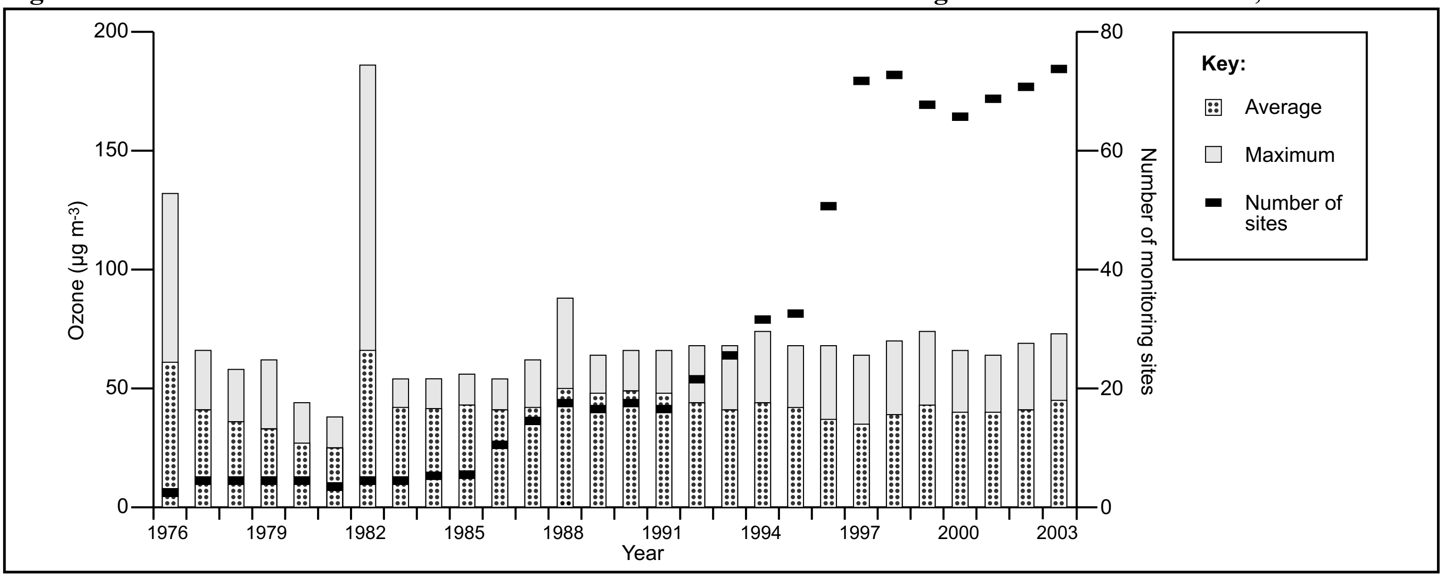
Trends in low-level ozone

Tropospheric ozone is normally measured using diffusion tubes. These are inexpensive and easy to use equipment which work through exposing absorbent materials to ambient air for a period of time. The material is then analysed to assess the concentration of ozone.

Annual average concentrations of ground level ozone have fluctuated between 25 and 66μg/m^3 *(Fig. 4)*. Remember, ozone tends to reach its highest concentrations in rural areas. The highest annual average of any individual site over the 20 year period was measured in 1982 in rural Harwell, Oxfordshire. The short term objective of 100 ug/m^3 (measured as a running 8 hour mean not to be exceeded more than 10 times a year) has been exceeded at many monitoring sites over the last 20 years.

Background levels of ground-level ozone have risen substantially over the last century. There is evidence that the preindustrial near ground-level concentrations of ozone were typically 10-15 ppb. The past 100 years so that current annual mean concentrations are approximately 30 ppb over the UK. The number of hours of 'poor' ozone concentrations tends to increase from the north to the south of the country. Concentrations can rise substantially above background levels in summer heat waves when there are continuous periods of bright sunlight with temperatures above 20°C, and light winds. Once formed, ozone can persist for several days and can be transported long distances. Thus pollution transported with tropical continental air masses plays a significant role in UK ozone episodes.

Fig. 4 Annual ozone concentrations measured at the continuous monitoring network sites in the UK, 1976 to 2003.



In Oxford, in 2001 for example, the air quality objective level for ozone (50ppb daily maximum 8-hour running mean) was exceeded at East Oxford on 15 days and at St Ebbes (city centre) on 15 days (10 days are permitted under the Air Quality Strategy). All of these incidences took place between May and August. At Harwell in rural Oxfordshire, there were 42 days when the objective was exceeded. These were believed to be related, in part, to large stable air masses that originated in Central Europe and produced high pressure conditions in the region.

Impacts of increasing ground-level ozone

Ground level ozone affects plant photosynthesis and growth and so may significantly reduce crop yields. Crop exposure to levels above a 40ppb threshold (used by the UNECE to measure crop damage) tends to be higher in the southern UK and affect extensive areas of arable farming.

Ozone can harm lung tissues, impair the body's defence mechanism, increase respiratory tract infections, and aggravate asthma, bronchitis and pneumonia. Even at relatively low levels, coughing, choking and sickness increase. The long-term effects include the premature ageing of the lung. Children born and raised in areas where there are high levels of ozone can experience up to a 15% reduction in their lung capacity.

A new study in the USA has found that exposure to ground-level ozone is associated with an increased risk of death in the US. Increases in the ozone contribute to thousands of deaths every year.

The risk of death is similar for adults of all ages but slightly higher for people with lung or heart problems. The increase in deaths occurs at ozone levels below the clean air standards of the Environmental Protection Agency (EPA). National air quality and mortality data from 95 large urban areas in the USA for the years 1987-2000 were used to investigate whether daily and weekly exposure to ground-level ozone was associated with mortality. The researchers adjusted for particulate matter, weather, seasonality, and long-term trends. An increase of 10-ppb (10 parts per billion) in the daily ozone levels for the previous week was associated with a 0.52% increase in daily mortality. This corresponds to 3,767 additional deaths annually in the 95 urban areas studied. According to the study, if ozone in the USA levels were reduced by about a one-third, about 4,000 lives each year would be saved.

Conclusion

There are two main forms of ozone – stratospheric and ground level. Both are important for different reasons. Stratospheric ozone protects us from harmful ultraviolet waves whereas ground level ozone is an important source of pollution. The trend in stratospheric ozone is one of decline, whereas ground level ozone is increasing in places, especially near large urban areas where there is a high density of vehicles. Both trends are worrying for the health implications.

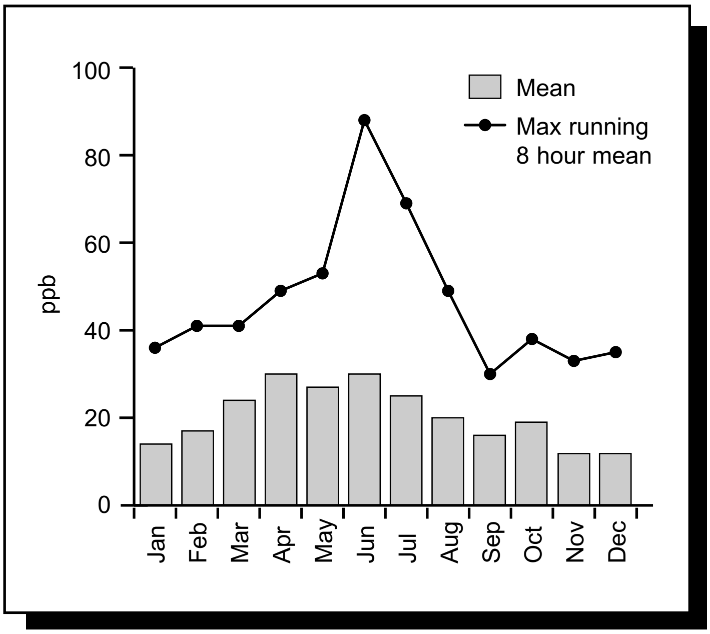
Question

Study *Fig. 5* which shows trends in the mean and maximum running 8-hour mean for low-level ozone in central Oxford in 2001.

Describe the trends in:
- mean, and
- maximum running 8 hour mean.

Suggest reasons for these trends.

Fig. 5 Ozone levels in central Oxford.



Exam Hint: Remember the importance of summer anticyclonic conditions.

Further Research

The ascent of the atmospheric sciences, Crutzen, P and Ramanathan, V. Science, 290, 299-304 (2000).

Useful websites

- *www.grid.unep.chh/datasets/gnv-data.html* for Global ozone measures 1978-91.
- *www.environment-agency.gov.uk* for the Environment Agency. Follow the links to *Your Environment, Environmental Facts and Figures, Air, Air quality* and *Ground level* ozone to get data on ground level ozone for the UK.

Acknowledgements
This Factsheet was researched by Garrett Nagle of St. Edwards School, Oxford.
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