Environmental Studies
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Ozone Update

This Factsheet provides an update on the success of the Montreal Protocol and summarises the type of exam questions which appear on stratospheric ozone and its depletion.

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.

Stratospheric ozone

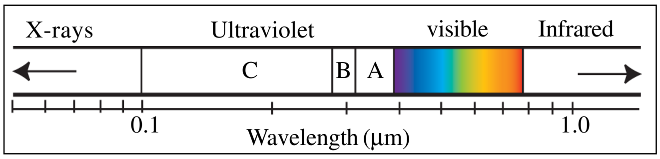
Straospheric ozone is produced because oxygen, rising up from the top of the troposphere, reacts under the influence of sunlight to form ozone. Most of this is created over the Equator and the Tropics since this is where solar radiation is strongest. However, winds within the stratosphere transport the ozone towards the polar regions where it tends to concentrate.

The ozone layer occurs between 15 and 35 km (in particular between 16 and 25 km) above the earth's surface and shields the earth from the harmful UVB radiation that would otherwise destroy most life on the planet.

Ozone and UV radiation

The sun emits UV radiation across a broad spectrum (Fig 1).

Fig 1



UV A (320-400nm) is used by the skin to synthesise Vitamin A but it also causes sunburn and can damage our eyes. Higher energy UV B (290-320nm) damages organic molecules such as DNA. Even higher energy UV C would be rapidly fatal –but. fortunately it gets filtered out before it reaches the ground.

Because organic molecules absorb and are severely damaged by UV B and C, life could only evolve in places shielded from this UV radiation - in oceans and beneath organic material.

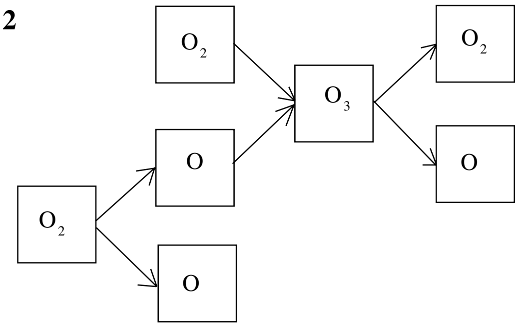
Then, around 2 billion years ago, plant-like organisms started photosynthesizing and released oxygen. In the outer reaches of the atmosphere molecular oxygen (O_2) absorbed short-wave UVC radiation and, in the process, decomposed into oxygen atoms (O). Then these atoms could recombine with oxygen molecules to form tri-atomic oxygen – ozone (O_3).

Ozone absorbs wavelengths up to about 310 nm. Thus, all of the harmful UVC and most of the UVB radiation was absorbed in the 'ozone layer' and this allowed evolution to accelerate.

Typical Exam Questions

Fig 2 shows some of the reactions which occur in the ozone layer in the stratosphere.

Fig 2



(a) Describe the role of UV radiation in the processes shown in Fig 2 (3)

(b) What is the significance of the ozone layer for life on Earth? (3)

(c) Explain how man-made gases have damaged the stratospheric ozone layer. (3)

Answers

(a) UV absorbed;
energy converted to chemical energy;
breaks up/splits diatomic oxygen/ oxygen molecules/ photodissociation;
splitting/destruction of ozone;
reversible reaction/dynamic equilibrium/cycle repeated;

So the key point is that there is a constant formation and destruction of ozone. Humans have upset that equilibrium (and lots of others!).

(b) Less/no UV reaches Earth's surface/ ozone absorbs UV/ UV is filtered out;
prevents all/tissue damage/example of effect;
DNA damage/(skin) cancer/cataracts/damage to phytoplankton;

(c) CFCs absorb UV radiation/short wavelength radiation;
chlorine is released. Free radicals released;
chlorine reacts with monatomic oxygen;
chlorine released again;
reduced levels of O/increased levels of O2;
ozone level reduced/less ozone formed/ozone hole/thinner ozone layer;

NOTE: Many candidates lost marks because they made vague references to "radiation", instead of specifying UV radiation. The examiners did not credit "CFCs break down ozone" – they wanted precise details.

Does everywhere on Earth receive the same dose of UV radiation?

No.

The quantity of UV striking the earth's surface depends on:

- ***Cloud cover and atmospheric pollutants***- these can absorb or reflect the UV
- ***Time of day*****:** UV levels are usually greatest around noon because the sun is at its highest point in the sky, thus the sun's rays have the least distance to travel through the atmosphere before striking the earth's surface.
- ***Altitude:*** UV intensity increases with altitude because there is less atmosphere to absorb the radiation.
- ***Season:*** The angle of the sun in relation to the earth surface varies with the seasons. In the Northern hemisphere, UV intensity is highest during the summer months when the incident angle is close to 90 degrees.
- ***Latitude:*** The sun's rays are strongest at the equator,where the sun is most directly overhead and the UV radiation travels the least distance through the atmosphere. Ozone is also naturally thinner near the equator, so there is less ozone to absorb the UV radiation as it passes through the atmosphere.

Stratospheric Ozone Depletion

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 concentrations 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

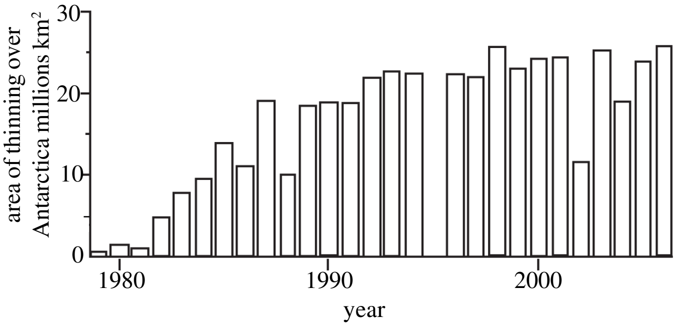
The ozone 'hole' is an area of reduced concentration of ozone in the stratosphere, which varies from place to place and over the course of a year.

Definition : The ozone hole is defined as the area having less than 220 Dobson units (DU) of ozone in the overhead column (i.e., between the ground and space).

The hole in the ozone layer over Antarctica was first discovered in 1982. It follows a very clear seasonal pattern. 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 released by human activities.

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 gone and the chlorine is converted to other compounds such as chlorine nitrate until the following winter. The ozone hole thus fills in. As early as 1987 the ozone hole covered an area the size of continental USA and was as deep as Mount Everest (Fig 3) In addition to human activities, volcanic eruptions can also have an impact on the ozone layer.

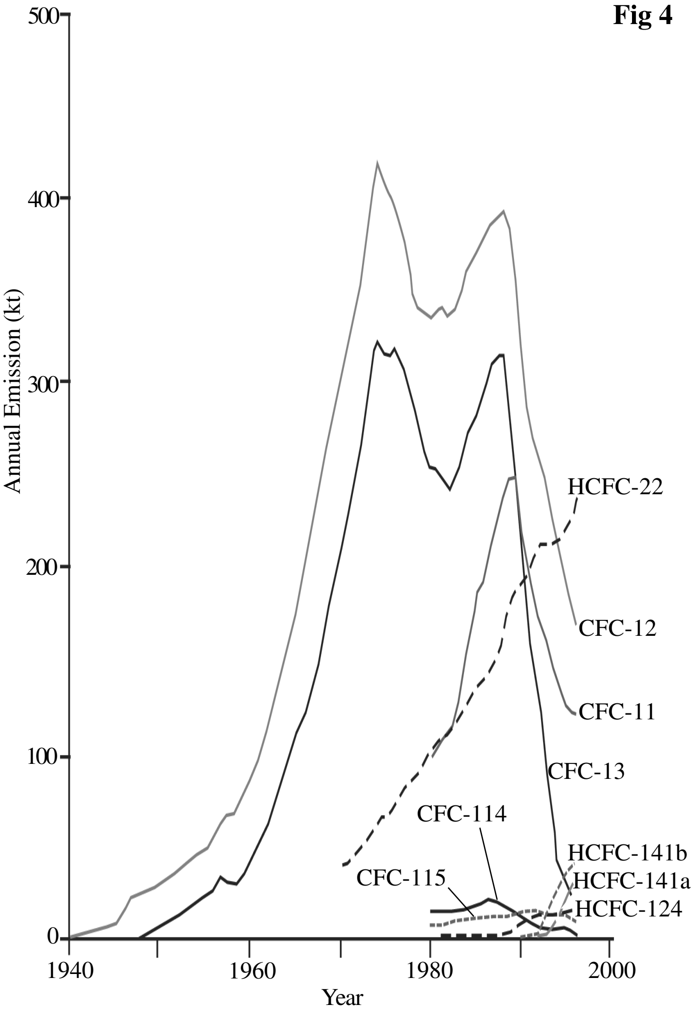
Fig 3. Ozone thinnning over Antarctica



Note: No data was acquired during 1995 season

The stratospheric ozone layer has been depleted by chlorofluorocarbons (CFCs) and other man - made chemicals.

However international cooperation between governments has been successful. The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer has reduced the consumption of ozone-depleting substances (ODS) by more than 90%. By the end of 2002, industrialized countries had reduced their ODS consumption by more than 99% and developing countries had reduced their consumption of ODS by slightly more than 50% (Fig 4)



Production and consumption of chlorofluorocarbons (CFCs), halons and other ozone depleting chemicals have been almost completely phased out in industrialized countries and the timetable for banning the use of methyl bromide, a pesticide and agricultural fumigant, has been agreed.

Developing countries have been given a longer time period over which to phase out their release of ODS. The most widely used ozone-depleting substances (CFC-11 and CFC-12) have often been replaced with HCFCs. Although these are greenhouse gases, their global warming potential (GWP) is less than CFCs.

However, even greater GWP reductions can be achieved by replacing CFCs with substances such as hydrocarbons (e.g. n-pentane, cyclopentane and isobutane), ammonia, carbon dioxide, water and air. These substances contribute only minimally (or not at all) to GWP (Table 1).

Table 1. CFCs, HCFC's and their replacements

Compound	Use	Atmospheric lifetime yrs	ODP relative to CFC-11	GWP relative to CO_2 at 100 yrs	Current main substitute
Compounds already phased out in developed countries					
CFC-11	Foam expander	50	1	4000	HCFC-141
CFC-12	Refrigerant	102	1	8500	HCFC-134a
CFC-113	Solvent	85	0.8	5000	Other technology
CFC-114	Propellant	300	1.0	9300	Hydrocarbon
Halon-1211	Fire extinguishant	20	3.0	No data	Dry powder
Carbon tetrachloride	Raw material	42	1.1	1400	None
Compounds due to be phased out by the Montreal Protocol					
HCFC- 22	Refrigerant	13.3	0.06	1700	HFC blends
HCFC-123	Refrigerant	1.5	0.02	93	HFC blends
HCFC-124	Refrigerant	5.9	0.02	480	HFC-134a
Potential replacements, emissions controlled under Kyoto Protocol					
HFC-32	Refrigerant	5.6	0	650	
HFC-125	Refrigerant	32.6	0	2800	
HFC-134a	Refrigerant	14.6	0	1300	
HFC-152a	Propellant	1.5	0	140	
HFC-236	Foam expander	209	0	6300	

The Montreal Protocol now covers all CFCs, most halons, carbon tetrachloride and methyl chloroform. Consumption of these compounds is prohibited in the developed world, although their use in existing equipment, and limited manufacture for essential uses and for use by the developing world, is still permitted.

It is clear from Table 1 that a combination of replacements and technologies will be required - there is no single replacement for each CFC.

In the past, huge quantities of CFCs were used as propellants in aerosol sprays but most of this demand is now met by hydrocarbons and other technologies. After aerosols, refrigeration was the next most important use for CFCs and it seems likely that a combination of HFCs, ammonia, carbon dioxide and hydrocarbon refrigerants will replace them.

Besides these replacement compounds, a whole raft of alternative procedures have been implemented - e.g. trigger sprays have replaced aerosol propellants, leaking CFCs have been collected, some CFC waste has been incinerated and old fridges have been locally or centrally collected.

Ground Level Ozone

At ground level ozone is considered a pollutant. Ground level ozone forms when VOCs (volatile organic compounds) react with nitrogen oxides and sunlight. Volatile organic compounds (VOCs) 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. 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.

Air pollution is associated with high pressure. This is because winds in a high pressure system are usually weak. Hence, pollutants remain in the area and are not dispersed. Poor air quality often persists for many days.

In some climates, notably Mediterranean climates, stable high pressure conditions persist all season, hence poor air quality can remain for months. 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.

Practice Questions

1. Fig 1 shows projected changes in the atmospheric concentration of CFC-11. Fig 2 shows the levels of ozone above the Antarctic between 1960 and 1990.

Fig 1

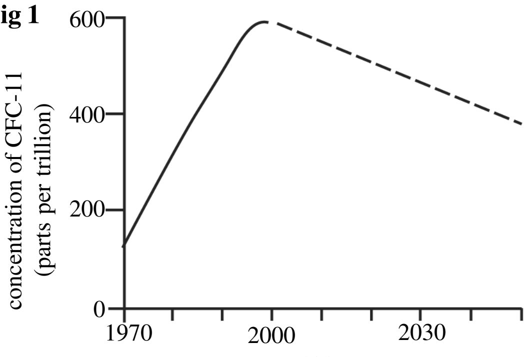
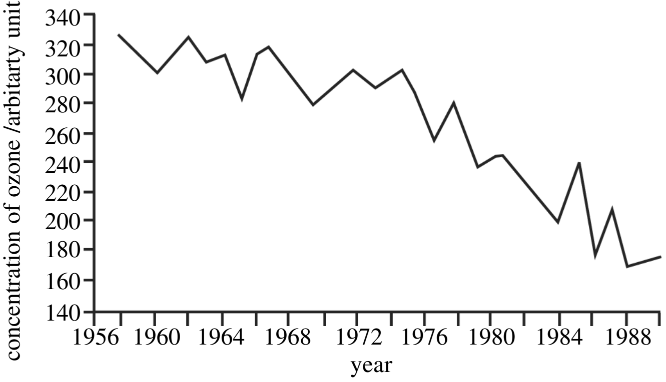


Fig 2



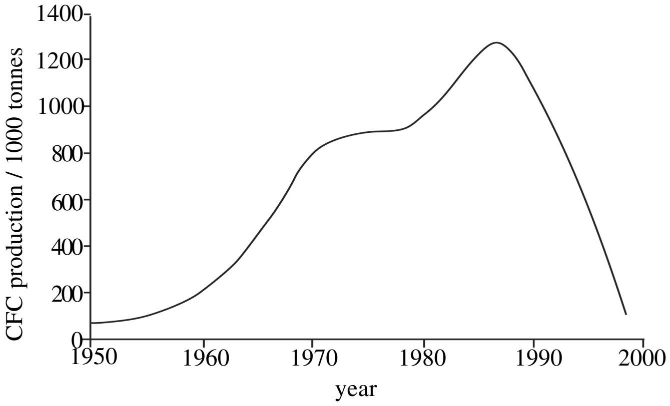
(a) Suggest reasons for the increase in the concentration of CFC-11 between 1970 and 1990.(2)

(b) Explain how this increase may be responsible for the trend shown in Fig 2

(c) Using information in Figure 1 and 2, and your own knowledge, evaluate the success of international agreements to reduce stratospheric ozone depletion. (4)

NOTE: From 2008, this type of question –evaluate/discuss/ comment - is going to become more important and will always appear in the A level papers.

2. The graph shows the global annual production of CFCs between 1950 and 1998.



(a) Name the international agreement that led to the decline in production of CFCs. (1)

(b) Explain why the international community believed that it had to act to stop CFC production. (4)

Answers

1. (a) aerosol propellants ;
coolants in refrigeration systems ;
air conditioning systems ;
polystyrene/expanded foam manufacture/ fast-food packaging;
cleaning agents;

(b) sunlight breaks down CFCs / release of chlorine free radicals ;
chlorine reacts with ozone ;
producing chlorine monoxide ;
which reacts with an oxygen atom ;
to produce free radicals of chlorine again ;
this can be repeated hundreds of times ;
increase in concentration of CFC-11 after 1970;
coincides with accelerated loss of ozone;

(c) Use of CFCs being phased out;;
development of alternatives ;
Montreal Protocol (1987) ;
ozone layer protection treaty (1989) ;
large volumes of CFCs were released in the 1970s and 1980s
CFCs are, persistent / long-lasting ;
some industrial opposition to phasing them out caused a delay ;
not all countries are prepared to reduce CFC production ;
developing countries given longer to phase out ODS;

2. (a) Montreal protocol;
(b) ozone layer blocks UV light from the sun ; increased levels of UV light reaching the earth ; problems if these are over inhabited areas ; increased level of, mutation / damage to DNA ; increase in skin cancers ;
damage to eyes / cataracts ;
damage to (human) immune systems ;
reduced crop yields ;
damage to marine food chain/phytoplankton;

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.

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