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The phenomenon

Press reports and publications about ozone address two distinct phenomena. "Not enough up top, too much down below" is one succinct formula frequently used to describe the problem. At altitudes between 25 and 35 kilometres the ozone layer is being depleted, especially in the southern hemisphere, while near the ground high ozone concentrations are measured in the summer months, not only in densely populated areas. What are the reasons for this phenomenon, and what effects can it have on man and his environment?

The purpose of this article is to take a closer look at the subject of ozone, even though some incongruities remain and not all questions can be definitively answered.

The concept

Ozone is the triatomic form of oxygen (O_3) and for this reason is also known as trioxygen. Unlike diatomic oxygen (O_2), which is vital to the majority of living organisms, ozone is a highly toxic gas. It is heavier than air and takes the form of a dark-blue liquid at temperatures below −111.9 °C and blackish-blue crystals below −192.5 °C.

The name is derived from the Greek "ozein", meaning "to smell of something". It is perceptible as of concentrations as low as 0.01 ppm (parts per million). The smell is described as being reminiscent of cloves, hay or chlorine, depending on the concentration. At one time, the smell of ozone was thought to be the same as the smell of fresh forest air, giving rise to the myth that ozone is good for the health. Nowadays we know not only that ozone is a health hazard but also that the high ozone content of forest air is due to the inflow of nitrogen oxides from built-up areas and to hydrocarbons (terpenes) released from plants and trees.

Occurrence in nature

Ozone accounts for about 10^{-5} to 10^{-6} % by volume (≈ 0.1–0.01 ppm) of the Earth's atmosphere. Around 90 % is present at altitudes between approximately 11 and 50 km (the stratosphere), reaching a broad maximum of about 10 ppm at an altitude of 30 km (equivalent at this altitude to roughly 600 micrograms/m^3). The remaining 10 % of the ozone is to be found in the region between ground level and an altitude of about 10 km (the troposphere).

Formation and interaction with the environment

There are various reaction paths leading to the formation of ozone. The actual mechanism in any particular case will depend on the ambient conditions at the place of origin.

Ozone in the stratosphere

According to a theory by Chapman (1930), ozone is created by photodissociation of oxygen modules under the influence of short-wave ultra violet radiation (wavelengths < 242 nanometres; UV–C*):

I O_2 + UV radiation —> O + O

II O + O_2 —> O_3 + energy

* UV-A: 400–320 nanometres – radiation browns the skin
UV-B: 320–280 nanometres – radiation damages the skin (skin cancer possible)
UV-C: 280–200 nanometres – radiation negligible at ground level, as virtually com-

Under longer-wave UV radiation (242–360 nanometres), the generation of ozone is compensated by ozone disintegration:

III O_3 + UV radiation —> $O + O_2$

IV $O_3 + O$ —> $2\,O_2$

This dynamic equilibrium between the reactions I – IV (known as the Chapman equilibrium) explains why ozone has the effect of absorbing the short-wave UV radiation that is particularly harmful to the skin. Stratospheric ozone thus serves as a screen protecting life on earth.

The disintegration of ozone due to UV radiation can be accelerated by the decay products of trace gases released into the troposphere by human activity, in particular by industry and combustion plants. These decay products act as catalysts promoting the depletion of the ozone. The associated reactions can be represented as follows:

V $O_3 + X$ —> $O_2 + XO$

VI $XO + O$ —> $O_2 + X$

in which X may be: oxides of nitrogen, sulphur dioxide, chlorine or bromine atoms released by the breakdown of chlorinated, fluorinated or brominated hydrocarbons. An X may be involved in several reactions of type V or VI, as it is not itself consumed in the process.

Natural phenomena such as volcanic eruptions which discharge large quantities of ash and sulphur dioxide reaching into the stratosphere may also influence reactions involving ozone. The size of the hole in the ozone layer and accelerated ozone depletion show correlations with violent volcanic activity.

The distribution of the ozone in the stratosphere is extremely heterogeneous, varying according to altitude, latitude, weather conditions and time of year. The main reason for these differences is the horizontal stratospheric currents, which follow a seasonal pattern. The vertical distribution of the ozone concentration results from the balance between the ozone generation and ozone depletion reactions (Chapman equilibrium) and also depends on the trace gases that are present at any place and time and the reactions that these induce.

The global reduction in the ozone concentration in the stratosphere over the past ten years is estimated at about 2 % overall. The hole in the ozone layer is particularly noticeable over the Antarctic. The reason for this is thought to be that the air masses experience very little mixing in this region. The countries of the southern hemisphere – especially Australia and New Zealand – are most severely affected by these conditions. Ozone depletion over the Arctic is not so pronounced, because there is a constant inflow of ozone-bearing air currents.

Since the stratospheric ozone layer constitutes a natural filter for the UV-B radiation that causes biological damage, thinning of the ozone layer can cause an increase in the UV-B radiation reaching the surface of the Earth. The following biological effects are the subject of media and scientific discussion:

- rising incidence of skin cancer among humans;
- increasing frequency of eye complaints (cataracts) among humans;
- debilitation of the human immune system;
- disturbances in the metabolic systems of plants and microorganisms, reducing the yield of cultivated plants;
- reductions in phytoplankton populations.

Other publications, by contrast, maintain that the ozone depletion to be observed world-wide has not produced any verifiable change in the UV-B radiation at surface level up to now. Those who subscribe to this opinion point to the dispersal effects of aerosols in the troposphere and to the build-up of ozone near ground level.

Ozone in the troposphere

The sources of ozone in the troposphere are downmixing from the stratosphere and the photochemical reactions producing ozone in the troposphere itself. The mean ozone concentration in the troposphere in the northern hemisphere has doubled over the past hundred years.

Ozone is formed mainly by photochemical reaction from oxides of nitrogen and hydrocarbons or other volatile organic substances:

I NO_2 + light —> NO + O

II $O + O_2 \longrightarrow O_3$

However, the nitrogen oxide thus formed can immediately break down ozone again in the reaction described by III, releasing free oxygen:

III $O_3 + NO \longrightarrow NO_2 + O_2$

This reaction is dependent on the concentration present and can take place only if NO is not captured by other substances, for instance hydrocarbons. Depending on the concentration of NO and NO_2, either ozone formation or ozone breakdown will predominate. If high-NO combustion exhaust gases* are present, the probability of the ozone disintegration reaction is just as high as that of the ozone generation reaction, so that no ozone build-up is to be expected overall. This is why the air in rural regions with very low NO concentrations may have a higher ozone content even than that in major conurbations.

Since both reaction I and the reaction in which NO is captured by hydrocarbons require an energy input, they can only take place in the presence of UV radiation and therefore cease after sunset.

The ozone concentration at near-ground level is normally 0.02–0.03 ppm (= 40–60 micrograms/m^3). Emissions with a high hydrocarbon content from combustion plants can significantly increase these concentrations and may, in combination with warm spells or other weather conditions involving a low air exchange rate, give rise to smog with ozone burdens up to 0.5 ppm (1,000 micrograms/m^3).

In humans, elevated ozone concentrations can upset the central nervous system and irritate the respiratory tissues. Damage has also been observed in plants and micro-organisms. It has now been established that ozone is one of the factors responsible for forest impairment, especially for damage to leaves and needles.

Ozone in the troposphere also contributes to the anthropogenic greenhouse effect, accounting for 0.8 % of the unwanted, man-made climate change due to global warming.

Properties and fields of application

Ozone is the strongest oxidising agent after fluorine, able to convert all metals – with the exception of gold, platinum and iridium – into their oxide forms and to bleach many organic compounds.

This high reactivity makes ozone suitable for use as a disinfectant, particularly so since it leaves no residues. This field of application makes cleaning by means of ozone a major factor in the context of environmental conservation.

Typical applications are:
- o sterilisation and breakdown of organic impurities in drinking water without detriment to taste;
- o sterilisation of swimming pool water;
- o disinfection in breweries, cold storage areas, etc.;
- o eliminating odours, e. g. in effluent treatment;
- o bleaching of oils, greases, waxes, fibres, textiles, paper, cellulose;
- o accelerated ageing of brandies.

Toxicity and effects

Ozone is toxic and has an irritant effect on the eyes and mucous membranes. Its toxic impact takes the form of impaired pulmonary functions, respiratory difficulties, nosebleeds and bronchitis, possibly culminating even in pulmonary oedema. The physiological effects are attributable in part to the oxidation of fatty acids in the organism and may be intensified by vitamin E deficiency. Administering vitamin E can ease the symptoms.

Ozone has toxic effects on plants, too: in this context a threshold of 80 ppb (parts per billion) equivalent to 160 micrograms/m³ is cited. The toxic impact is reflected in damage to the leaves and stunted growth.

Limits and analysis

MAK value (Germany)*	200 micrograms/m³
MIK value (Germany)**	120 micrograms/m³
Public alert threshold (Germany)***	180 micrograms/m³
WHO (1-hour exposure)****	150–200 micrograms/m³
WHO (8-hour exposure)****	100–120 micrograms/m³

100 micrograms/m³ = 0.1 mg/m³ = 0.05 ppm

In 1995 a Summer Smog Ordinance was introduced in Germany in an attempt to respond rapidly to reduce critical ozone levels. This legislation provides for short-term bans on driving or the imposition of speed limits for vehicles with or without catalytic converters, depending on the ozone concentration at any time.

There are various methods for measuring ozone, including:
- electrochemical probes for measuring the ozone content in the air (operating principle: electrochemical oxidation of potassium iodide to iodine);
- UV spectroscopy;
- direct photometric procedures.

The thickness of the ozone layer can be determined with the aid of spectrometers either from the Earth's surface or from satellites. The vertical ozone distribution is measured locally by means of balloon- or rocket-borne probes or by means of high-sensitivity measuring equipment from the ground or from satellites.

Unresolved issues

The MAK limits currently in force relate only to the irritant effects of ozone on the mucous membranes. It is not yet clear whether ozone also has a carcinogenic effect. Experiments on mice and rats have up to now shown no such effect at concentrations of 240 micrograms/m³; carcinogenic effects on the lungs have, however, been identified at concentrations of 1,000 to 2,000 micrograms/m³. Experiments on humans, on the other hand, indicate that the body's own defence mechanisms may enable the individual to adapt to elevated ozone levels.

* MAK = maximum workplace concentration
** MIK = maximum exposure concentration
*** In some states of Germany, an alert is issued with recommendations of measures to be taken

Controversial opinions abound about the repercussions of the rising UV-B burden at ground level and as to the extent to which the depletion of the ozone filter in the stratosphere and an increase in tropospheric ozone and dispersal effects could tend to compensate each other.

What is certain is that we do not yet know all the factors influencing the depletion of the ozone layer in the stratosphere. And even the measures being taken now to combat the parameters known to be causing the build-up in tropospheric ozone, for instance the trace gases, will in many cases not take effect for a very long time, as these gases have retention times of up to 170 years.

Conversely, we have certainly not identified all the factors exercising a positive influence, either.

Tips for the underwriter
Ozone-forming and ozone-depleting emissions

In the light of the complexity of the chemical reactions and the climatic influences involved, there appears little likelihood at the moment of any particular emitter being identified and called upon to pay damages that could give rise to an insurance claim. Nevertheless, attention should be paid in general to the topic of climate change with a view to the possibility of future cumulative damage.

In this context a number of lines of business may be directly or indirectly affected via scenarios should as flooding, forest fires, windstorms, etc., but also through more widespread skin damage and a higher incidence of skin cancer (life and health insurance).

A potential demand for special insurance products is conceivable, for instance:

- no-snow covers (for ski resort operators);
- covers for ozone-induced loss of harvest;
- business interruption/loss of profit due to ozone;
- business interruption due to bans on driving;
- contingency covers for special events – e.g. the Olympic Games.

The subject of exposure to ozone in the office environment due to electrical equipment (e.g. photocopiers), much discussed in recent years, has now been recognised as a valid problem. It is caused by energy released by office equipment splitting oxygen modules, the atoms of which then recombine to form ozone. The remedy is to remove the energy at source.

Technical applications of ozone

The repercussions of the use of ozone in technical applications could affect liability insurers in particular. Claims could conceivably arise from applications such as:

- disinfection/sterilisation in the foodstuffs industry;
- construction of industrial facilities (e.g. sterilisation plants);
- disinfection of swimming baths.

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