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Ground-level ozone

An important group of pollutants are the photochemical oxidants. Common to these is that they are formed by other pollutants in the air through the action of sunlight, and they are highly reactive.

Ozone (O_3) usually makes up more than 90 per cent of the oxidants in the air. This chapter looks at how ozone is formed, its current levels and trends, and touches briefly on the reductions in emissions of ozone-forming substances that are needed in order to avoid harm to people and plants.

OZONE AT HIGH AND LOW ALTITUDES

The ozone layer in the stratosphere, at an altitude of 10–40 kilometres, protects us from ultraviolet radiation from the sun and is an essential requirement for all higher life on the Earth.

When ozone is present at ground level it may be harmful to people, animals, plants and materials. The first effects of ozone and other photochemical smogs on our health are irritation of the eyes and mucous membranes. At higher levels the irritation becomes more troublesome, and additional effects such as headaches and breathing difficulties can occur.

In plants, it has been found that damage can occur at concentrations only slightly higher than current background levels. This has a significance on yields from agriculture and forestry, as well as affecting natural ecosystems.

The effects on nature and people are described in more detail in chapters 2 and 3. The rising background level of ozone also helps to reinforce the greenhouse effect.

SUMMER AND SUN

Oxidants are reactive substances, and the term photochemical indicates that they are formed in reactions that are driven by the energy in sunlight.

The way that ozone is formed is described on opposite page. In addition to sunlight there must also be nitrogen oxides and volatile organic compounds in the air. Volatile organic compounds are a large group of diverse hydrocarbons with differing propensities to take part in ozone formation. The most effective contributors are alkenes, aldehydes and aromatic compounds. Methanol and ethanol react slowly and only make a small contribution.

The concentration of ozone is generally highest on sunny days in late spring and summer, during periods of high pressure. Sunshine accelerates ozone formation, and the high pressure means that air masses move slowly, resulting in little mixing of the air. The overall effect is that high concentrations can build up.

HOW OZONE IS FORMED

Ozone is formed by various chemical processes whose sequence is complicated but relatively well known. A simplified description might look as follows:

It is a prerequisite for ozone formation in the troposphere that sunlight breaks down nitrogen dioxide. This results in the formation of nitrogen monoxide and a highly reactive oxygen atom:

(A) NO_2 + sunlight $\rightarrow$ NO + O•

The free oxygen atom can then react with oxygen gas to form ozone:

(B) O• + $O_2 \rightarrow O_3$

If there are no volatile organic compounds in the air, the ozone reacts again with the nitrogen monoxide to reform nitrogen dioxide:

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

This process does not lead to the formation of high levels of ozone. It is formed and used up at roughly the same rates.

In order for larger quantities of ozone to be formed, other substances must intervene and convert nitrogen monoxide into nitrogen dioxide, so that breakdown of the ozone molecules in reaction (C) is reduced or ceases altogether. This process is fuelled by certain so-called radicals, which are formed when volatile organic compounds are broken down by sunlight.

The nitrogen dioxide that is formed when volatile organic compounds are involved in the reaction process can be reused for further ozone formation in accordance with reactions (A) and (B). High levels of ozone can therefore build up when volatile organic compounds, nitrogen dioxide and sunlight are all present at the same time.

It may seem surprising that the level of ozone is often lower in an urban environment and close to major roads than in the background air. The explanation for this is that car exhaust fumes, when they are released, contain a large amount of nitrogen monoxide and only a small amount of nitrogen dioxide. As shown by reaction (C), nitrogen monoxide is able to “soak up” ozone, and can therefore reduce the ozone levels locally.

When the ozone is used up, nitrogen dioxide is formed instead, and this can then take part in reactions that form many new ozone molecules. High ozone levels can therefore build up at several tens of kilometres distance from the source of the emissions.

Travelling long distances

Although ozone is highly reactive and breaks down relatively quickly, once it has formed it can be carried considerable distances in the air. Periods when levels rise temporarily due to movement of this type are generally referred to as episodes. Ozone is very much a transboundary air pollution problem. But in locations that are downwind of areas with high emissions of ozone-forming substances (large cities or densely populated areas with heavy traffic) the local contribution can still be significant.

In addition to the ozone that is formed close to ground level, ozone is also formed at slightly higher altitudes, where it contributes to the background level. The gases that are active in forming this ozone are primarily nitrogen oxides, carbon monoxide and methane. The background level is contributed to by emissions not only from Europe but from the whole of the northern hemisphere.

CRITICAL LEVELS

As with acidification and eutrophication, attempts have been made to estimate nature's "tolerance level" to ozone exposure. In the case of gaseous substances these tolerance limits are expressed as critical levels (see factfile, next page). Attempts have also been made to establish a critical level below which there is no harm to people's health.

In the case of the effects of ozone on plants it is the total (accumulated) dose that is of most interest. The critical level is calculated from the length of the time and the amount by which the ozone level exceeds a given threshold value. The threshold has been set at 40 parts per billion (ppb). For sensitive crops the critical level is set at 3000 ppb hours daytime during a three-month growing season (May–July). This exposure is believed to result in crop losses of less than 5 per cent. (To find out how ppb hours are calculated, see factfile.)

For trees in a forest the critical level has been set as 10,000 ppb hours, calculated in daytime over a six-month growing period. One element of uncertainty in this respect is that, for practical reasons, almost all trials have been carried out on young trees. It is not clear whether older trees are more or less

CRITICAL LEVELS

Critical levels are usually defined as "the concentration of pollutants in the air above which directly harmful effects can occur in plants, ecosystems and materials, according to the current state of knowledge".

Critical levels are generally given for one pollutant at a time. However, polluted air almost always consists of a mixture of substances, which in many cases can aggravate each other's effects (synergism). If the effects of this interaction are to be taken into account in calculations then the critical levels should as a rule be set at lower values in order to avoid harm.

The exposure index that is used for ozone, AOT40, requires some further explanation. Taking a threshold value of 40 ppb of ozone, we then count how many ppb hours this level is exceeded (AOT stands for Accumulated Exposure over a Concentration Threshold). If the level is 50 ppb for one hour this counts as 10 ppb hours, while a level of 39 ppb for one hour is not counted at all (the threshold of 40 must be exceeded by at least one ppb).

Critical levels for harmful effects on vegetation have been determined for sulphur dioxide, nitrogen oxides and ammonia, as well as ozone.

sensitive than younger ones – the studies carried out point both ways.

There have been insufficient studies on natural vegetation, but it is believed that the critical level for crops can also be applied to wild flora. Researchers have not found any indications that show they have greater sensitivity, in fact the opposite seems likely. Variations in sensitivity between different species could however lead to changes in ecosystems.

The AOT40 measurement is actually a rather blunt instrument, since a given ozone level in the air can give rise to very different effects. The uptake by plants varies with air and soil humidity. In dry weather the stomata of plants are mostly closed, so the ozone uptake is low compared to when the humidity is high. Figure 7.1 therefore overestimates the effects in dry, warm areas, and underestimates them in cool, moist areas, such as Scandinavia.

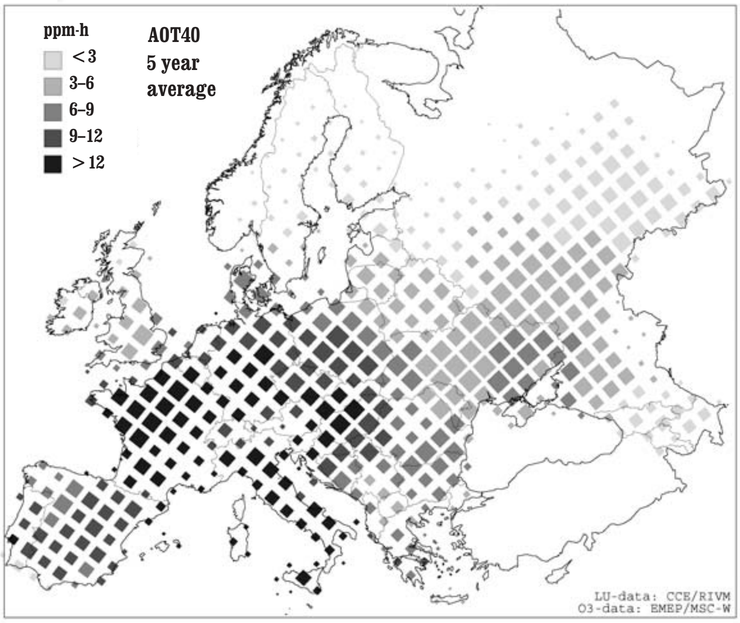

FIGURE 7.1. Exposure of agricultural crops to ground-level ozone. The map shows a five-year average of estimated AOT40 values, i.e. the number of ppm hours that the ozone level exceeds the threshold value of 40 ppb. The critical level is 3 ppm hours (1 ppm hour = 1000 ppb hours). The darker the shade, the greater the exposure. The size of the squares is proportional to the area of agricultural land in each 150 × 150 km square. (Max Posch, CCE/RIVM, the Netherlands, 2000.)

CONTINUING HIGH LEVELS

Measurements that have been in progress since the 1950s show that the levels of ozone in the air over Europe have risen by an average of 2 per cent a year, and that the background level today is two to four times as high as it was in the 1950s. The critical levels, which were presumably only exceeded occasionally at the start of the last century, are now exceeded regularly over almost all of Europe. Figure 7.1 shows where and by how much the critical level for ozone damage to crops is exceeded. The critical level for forest trees is not exceeded as often or as much as that for crops.

The limits that have been set to protect people's health are also regularly exceeded by a significant degree. The situation is worst in the Mediterranean countries of Italy, France, Greece and Spain, and in parts of Germany.

It has been possible to detect two different trends in ozone levels over the past decade, which to some extent cancel each other out:

- There seem to be fewer occasions when levels are really high. It is believed that this is because emissions of ozone-forming substances in Europe have decreased markedly.
- The background level is rising throughout the northern hemisphere because emissions of ozone-forming substances – nitrogen oxides, carbon monoxide and various hydrocarbons, including methane – are still rising, especially in Asia.

The latter trend is worrying since the harmful effects of ozone are largely due to cumulative exposure over a long time – short periods when levels are high are not as important in this respect.

EMISSIONS OF OZONE-FORMING SUBSTANCES

Ozone is formed, as mentioned above, by nitrogen oxides and volatile organic compounds. Emissions of **nitrogen oxides** are described on page 96.

Emissions of **volatile organic compounds** are still relatively poorly mapped out, but the major sources are exhaust fumes from motor vehicles, evaporation of solvents from paints and varnishes, and small-scale combustion. The petrochemical industry can also produce high emissions locally.

It may be worth pointing out in this context that volatile organic compounds cause other problems in addition to contributing to ozone formation. Many of them are highly toxic to people. Some also contribute to the breakdown of the atmospheric ozone layer and/or act as greenhouse gases.

Emissions of VOCs in Europe

According to the emissions data that is reported to the Convention on Long-range Transboundary Air Pollution the manmade emissions of VOCs in Europe totalled just under 16 million tonnes (excluding methane) in the year 2000, which represents a reduction of 35 per cent since 1990, when around 24 million tonnes were emitted. Emissions from each country are shown in table 7.1.

The downward trend is due in part to active measures in many countries, including the introduction of catalytic converters on petrol-driven cars, and partly to economic recession and changes in production in the eastern European economies in the early 1990s. The international undertakings of countries for the year 2010 are shown in table 9.2.

Natural emissions of VOCs

Plants give off considerable amounts of volatile organic compounds that can also affect ozone formation. These emissions are certainly less than manmade emissions, but they are of the same order of magnitude. The most important in this context is probably isoprene, which is primarily given off by broadleaf trees.

However, computer modelling indicates that the role of this substance in ozone formation in Europe is fairly small. This is because the highest emissions into the air occur in southern Europe, where ozone formation is limited by the availability of nitrogen oxides. In those parts of Europe where volatile organic compounds are the limiting factor in ozone production, isoprene emissions from forests are relatively low in comparison with anthropogenic emissions. It is however possible that periods of high ozone levels in Spain, for instance, are aggravated by the isoprene given off by broadleaf trees.

A group of substances that are chemically related to isoprene are terpenes. Some of these, especially monoterpenes, are also volatile. These are mainly given off by coniferous trees. Emissions are high, almost as high as those of isoprene, but their role in ozone formation is probably fairly minor.

TABLE 7.1. European emissions of non-methane volatile organic compounds, 1990 and 2000. Unit: 1000 tonnes a year. (EMEP 2002)

	1990	2000
Austria	345	232
Belgium	274	233
Denmark	162	129
Finland	224	161
France	2473	1726
Germany	3220	1605
Greece	255	305
Ireland	111	90
Italy	2041	1557
Luxembourg	19	15
Netherlands	492	278
Portugal	371	463
Spain	1555	1453
Sweden	498	304
United Kingdom	2425	1418
Sum European Union	**14465**	**9969**
Albania	31	34
Bosnia & Herzegovina	51	42
Belarus	533	225
Bulgaria	217	120
Croatia	105	80
Cyprus	14	14
Czech Republic	441	227
Estonia	88	34
Hungary	205	173
Iceland	13	10
Latvia	143	69
Lithuania	108	61
Norway	294	367
Poland	831	599
Macedonia	19	17
Moldova	157	22
Romania	772	638
Russia	3668	2450
Serbia & Montenegro	142	129
Slovakia	262	89
Slovenia	44	40
Switzerland	279	159
Ukraine	1369	271
Sum non-EU	**9786**	**5870**
Sum Europe	**24251**	**15839**
Sum Int. shipping	84	84
Sum Europe + ships	**24335**	**15923**
Turkey	463	726

HOW MUCH MUST EMISSIONS BE REDUCED?

In order to bring down ozone levels far enough to prevent EU target values from being exceeded, emissions of both nitrogen oxides and VOCs must be reduced. However, in some areas it is more important to reduce emissions of nitrogen oxides, while in others volatile organic compounds are the priority. The deciding factor is how many times each molecule of nitrogen oxide takes part in the ozone-forming reaction before it is converted into nitric acid.

In areas with a high pollutant load, as in central Europe, this transformation is relatively quick. So in this case it is emissions of volatile organic compounds that set the limit for how much ozone is formed. But the cleaner the air, the more ozone molecules can be formed by each molecule of nitrogen oxide. In Scandinavia, for example, nitrogen oxides are therefore the limiting factor in ozone formation.

Emissions of ozone-forming substances in Europe are expected to fall quite sharply over the coming decade. The way this could affect ecosystems and people's health can be seen in table 9.3. There is some uncertainty about development in other regions however – the ozone levels in Europe are to some extent affected by emissions in the whole of the northern hemisphere. Another element of uncertainty is the feared rise in temperature, which could lead to increased formation of ground-level ozone.