

03.06 Near Ground Ozone (Edition 1996)

Overview

What is ozone? Where does it occur?

Ozone is a natural trace gas in the atmosphere. In contrast to diatomic oxygen (O_2), ozone consists of oxygen with three atoms (O_3). Whereas the air contains about 20 % O_2 , ozone occurs in very much smaller concentrations.

In comparison to atmospheric oxygen, the ozone content is subject to very large temporal and spatial fluctuations caused by the generation and decomposition of ozone. Ozone formation depends on the splitting of one oxygen atom from either atmospheric oxygen or other oxygenous molecules. The chemical stability of these molecules means that this usually requires a considerable energy expenditure. Therefore natural ozone only occurs where electrical discharges (e.g. lightning) or high energy (solar) radiation (UV light) is available, such as in the upper layer of the atmosphere, the so-called **stratosphere** at 12-40 km altitude.

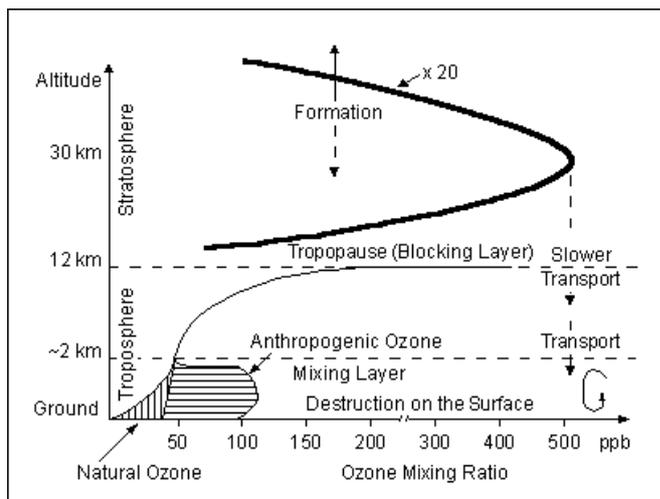


Fig. 1: Schematic Vertical Profile of the Ozone Mixture in the Atmosphere (according to Schurath 1984)

A part of the hazardous UV radiation is consumed there in the formation of ozone from O_2 . A further part is absorbed by the ozone itself (c.f. Fig. 1). The existence of the ozone layer is therefore an absolute requirement for life on our planet. Its existence is endangered through the anthropogenic emission of materials, elements of which cause a shift in the sensitive chemical balance between ozone formation and decomposition in favor of ozone destruction in the stratosphere.

In the **troposphere**, the ground floor of the atmosphere, ozone formation from O_2 is no longer possible because of the lack of high energy radiation. The weaker part of UV light, which manages to penetrate the ozone layer is indeed in the position to form ozone from nitrogen oxides and hydrocarbons. Without human influence, these materials are found only in relatively slight concentrations in the atmosphere. This ozone decomposes upon contact with materials on the ground. Normally, also because of the only slowly decreasing vertical transport from the stratosphere, only relatively slight ozone concentrations are generated in the troposphere (c.f. Fig. 1).

Here ozone functions due to its avidity as a cleaner of the atmosphere. It oxidizes other trace substances, such as sulfur dioxide and nitrogen oxides. At the end of these chemical processes

reaction products are created, so-called aerosols, which lead to the haze in the atmosphere and are washed out with the rain.

Tropospheric ozone plays a further role as a greenhouse gas. It absorbs, just like carbon dioxide, a part of the thermal radiation emitted from the ground and contributes with it to the warming of the atmosphere. The effect of each ozone molecule as greenhouse gas is thereby slighter the further it is from the ground which emits the warmth in the atmosphere. Thus the relatively high amount of ozone in the stratosphere contributes only slightly to the greenhouse effect, while the tropospheric ozone can be held responsible, despite its relatively low concentration, for about 8 % of the anthropogenic greenhouse effect (c.f. German Bundestag 1992).

Possible Damage Due to Ozone at Ground Level

However, the avidity of ozone has adverse effects on nature if additional ozone is produced from the anthropogenic precursors through photochemical processes causing higher concentrations to appear in ground proximity. Because of its highly oxidizing quality, damaging effects appear on surfaces which come in contact with higher ozone concentrations. These are

- at buildings, the surface of metal parts on which ozone exercises a corroding effect,
- on plants, the leaf and needle surfaces. O₃ can damage the corresponding protective layer and/or the leaf tissue itself. Increased parasite attack and a decrease in plant growth can be the consequence. Various plant kinds react very differently to ozone. The increased ozone values in the summer are considered to be a forest-damaging element,
- on persons and animals, above all, the respiratory tract. Since ozone is hardly water-soluble, it gets into the lung and has a destructive effect on lung tissue in higher concentrations.

Motor vehicle traffic counts as the first **cause** of the primary emissions responsible **for ozone formation**. Nitrogen oxides are produced in fuel combustion in the motor, likewise as a part of the hydrocarbons through incomplete or failed combustion of the gasoline. Further nitrogen oxides emitters are the power plants, industrial furnaces and the domestic heating sector (c.f. SenStadtUm 1995b).

An essential part of the hydrocarbons enters the atmosphere through evaporation of gasoline from the motor vehicle tanks or from the transfer of fuel in tank farms. It reaches nearly half of the hydrocarbon quantity emitted directly from motor vehicle exhausts (c.f. Obermeier 1995 and Map 03.09 SenStadtUm 1997). Further sources for hydrocarbons are the evaporation of solvents from paints and varnishes, different processes in the industry and small business, and also the discharges from vegetation and the oceans. Of course, the quantities of volatile hydrocarbons emitted from natural sources clearly exceed, on a worldwide scale, the anthropogenic emissions (c.f. German Bundestag 1990). Ozone formation also plays an important role in industrial regions. Thus the ozone formation affects of hydrocarbon emissions in Baden-Württemberg, which arise primarily from deciduous and coniferous forests, nearly the same levels as that of the other anthropogenic hydrocarbon sources (c.f. Obermeier 1995).

In Table 1 **threshold values for ozone concentration** are listed among others which have been taken from the EC Guideline for ozone, valid throughout Europe since September 1992. These threshold values were taken in the Regulation 22 for the implementation of the Federal Pollution Control Law (BImSchV) in 1994. The so-called threshold value for (human) health protection indicates the concentration, which should not be overstepped in case of long continuing loads. The same applies for the threshold values for the protection of the vegetation in excess of which damage to plants can occur. The threshold value for notifying the public, 180 µg/m³ ozone as median value over an hour, is to be seen as the threshold at which persons who react especially sensitively to ozone can be effected. The responsible authorities then recommend that particularly unusual and strenuous exertion outdoors in the afternoon be avoided. At 360 µg/m³, an identical warning is directed to the entire population. At these and higher concentrations the mentioned irreversible damage of the lung can occur. The irritation of the pharynx and the tears in the eyes, often to be observed, are not however due to ozone, but to other, simultaneously occurring substances (z. B. PAN).

Tab. 1: Indicators and Guide Values for Ozone Concentration		
EC Guideline 92/72/EWG/22. BImSchV Threshold values: for health safety	110 µg/m ³	as average over 8 hours
for the protection of vegetation	200 µg/m ³ 65 µg/m ³	as average over an hour as average over 24 hours
for the notification of the public	180 µg/m ³	as average over an hour
for activation of warning systems	360 µg/m ³	as average over an hour
Ozone alarm accord. § 40a BImSchG	240 µg/m ³	as average over an hour at three stations in intervals of 50 - 250 km each
Maximum Pollution Limit VDI ¹⁾ (for health safety) – Guideline 2310, Bl. 15	120 µg/m ³	as average over an half-hour
Maximum Pollution Limit VDI ¹⁾ (for the protection of vegetation) – Guideline 2310, Bl. 6	150 µg/m ³ 300 µg/m ³ 350 µg/m ³ 500 µg/m ³ 500 µg/m ³ 1,000 µg/m ³	for very sensitive plants: as average over an hour as average over an half-hour for sensitive plants: as average over an hour as average over an half-hour for less sensitive plants: as average over an hour as average over an half-hour
WHO Guideline Values ²⁾ (for health safety)	150 to 200 µg/m ³ 100 to 120 µg/m ³	as average over an hour as average over 8 hours
WHO Guideline Values ²⁾ (for the protection of terrestrial vegetation)	60 µg/m ³ 65 µg/m ³	as average over the vegetation period as average over 24 hours
Critical Level UN ECE ³⁾ (1988)	150 µg/m ³ 60 µg/m ³	as average over an hour as average over 8 hours
Critical Level UN ECE ³⁾ Recommendations of 1992	3,000 ppb × h 10,000 ppb × h	AOT 40 ⁴⁾ for agricultural plants AOT 40 ⁴⁾ for forests
<p>¹⁾ "Maximum pollution values" are used for defining the pollution limits. These aim to prevent health damage to humans, esp. children, elderly and infirm even under conditions of long-term exposure as well as to protect animals, plants and property. The "maximum pollution values" are purely effect-related, scientifically-based and derived from practical experience with medical and scientific indicators. They take no account of technical feasibility.</p> <p>²⁾ The WHO Air Quality Guidelines were developed on the basis of toxicological and ecological findings. They are recommendations for the establishment of statutory standards.</p> <p>³⁾ These values are based on the measures adopted in resolutions by the UN-ECE member-states under the 1979 Geneva Air Purity Convention for the reduction of transborder pollution in Europe (SO₂ and NO_x Protocols of 1985 and 1988) (c.f. Köble et al. 1992).</p> <p>⁴⁾ AOT 40 (Accumulated Ozone above Threshold 40 ppb): cumulative dose as sum of the differences between the hourly average concentration and 40 ppb (0.80 µg/m³), if the concentration exceeds 40 ppb (only by daylight).</p>		

Tab. 1: Indicators and Guide Values for Ozone Concentration

A further value often used for assessment is the so-called MIK value (VDI 2310) (c.f. Tab. 1), which with 120 µg/m³ (at the half hour average) represents the lower limit for the appearance of health effects caused by ozone and possibly further accompanying photochemical substances.

A new threshold hourly average for the ozone alarm has been introduced as of 28 July 1995. §40a of the Federal Pollution Control Law (BImSchG) now prescribes a limit of 240 µg/m³. If this level is exceeded at at least three measuring stations lying between 50 and 250 km apart, then a driving prohibition for motor vehicles which are not rated as low pollution takes effect as of 6 a.m. the following day, should similar levels be expected. Driving prohibitions apply to those states where the limit has been exceeded at at least two stations. In the case of city-states, such as Berlin, it is sufficient if one measuring station there or in a neighboring county exceeds the limit.

Statistical Base

Measuring Units

Ozone is measured primarily in ppm ("parts per million" = 10⁻⁶) or ppb = 1/1,000 ppm. Ppm means that among a million air particles only few ozone particles are found. In ground proximity, the ozone

concentration is also often indicated in $\mu\text{g ozone}/\text{m}^3$ air instead of this ratio. In the formula for converting mixture composition (X) in concentration units (ρ) of ozone

$$\rho [\mu\text{g}/\text{m}^3] = 0.5773 \times P/T \times (X) [\text{ppb}]$$

the air pressure (P) [hPa] and the temperature (T) [K] are also counted. As a rule of thumb for mid-range pressure (1,013 hPa) and temperature conditions (20 °C = 293 K) the following formula applies for near ground values:

$$[\mu\text{g}/\text{m}^3] = 2 \times [\text{ppb}].$$

A further unit which is used particularly for describing the vertical distribution of ozone is the so-called ozone partial pressure [Pa], expressed in nbar [nanobar] = 0.1 mPa. This means the portion of air pressure due to the small amount of ozone. In other words, the product of X [ppb = 10^{-9}] and air pressure.

Vertical Distribution

Already before discovery of the deterioration of the ozone layer in the stratosphere, the vertical distribution of ozone was measured at many places in the world with the help of balloons. This method is still routinely applied today to carry a wet chemical ozone probe. The sensor is attached to the ascending helium-filled balloon which rises to the stratosphere. On its way, the probe continuously records the ozone concentration. In Germany, such daily measurements have been undertaken in Hohenpeissenberg (Bavaria) and in Berlin since 1966 and 1967 respectively. The Berlin measurement was discontinued in 1973 and continued shortly afterwards in Lindenberg, 50 km away.

Information from altitudes of over 35 km was collected in the past with the help of rocket probes. Recently, use has been made of the increasingly precise spectral measuring methods of satellites. The advantage of the satellite measurements consists in the availability of wide-area pictures of the ozone distribution with the help of which the geographical extent of ozone decomposition in the Antarctic (ozone hole) became clear for the first time.

With the help of the spectral fingerprint of ozone, its concentration can be determined by examining the reflective dispersion of artificially-radiated laser beams. These so-called LIDAR instruments can be used both for the measurement of more vertical as well as more horizontal ozone profiles. Such a device belonging to the FU Berlin has been installed on the roof of the Charité hospital in Berlin Mitte since June 1996.

Thickness of the Ozone Layer

In order to assess the possible consequences of a change in the ozone level on the solar radiation reaching the ground, it is normally enough to know the total ozone content in the atmosphere. It is measured in DOBSON units. These correspond to an 1:100 mm indicated thickness of the pure ozone layer, if it were determined under ground level pressure and temperature conditions.

The most frequently used process, already developed in the 20s, applies the UV filter effect of ozone described above to determine the layer's thickness. Meanwhile, it is used at about 85 measuring stations throughout the whole world. The results obtained by the *Deutsche Wetterdienst* (German weather service) operated station at the Meteorological Observatory Potsdam shows that the ground air pressure compressed ozone available in the atmosphere is only between 2.5 and 4 mm thick layer (c.f. Fig. 2). The wide area measurement of the total ozone was taken in the previous years largely from satellites whose measurements were calibrated with the help of the above-mentioned ground measurements.

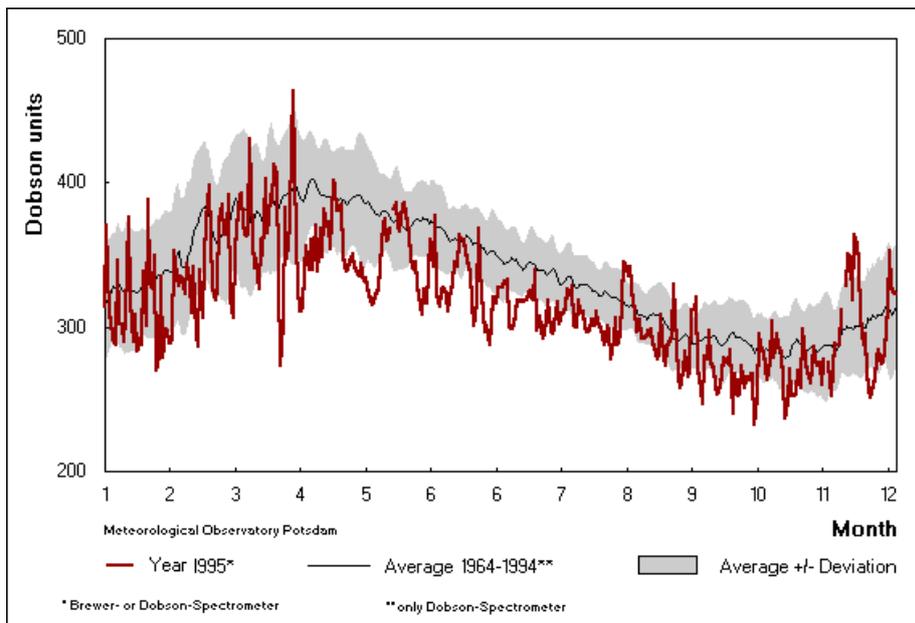


Fig. 2: Thickness of the Total Ozone Layer, Measured at the Meteorological Observatory Potsdam (Feister 1995)

Near Ground Ozone and Other Parameters

Already in 1840, the first measurements of near ground ozone were taken with the help of the Schönbein paper named after its discoverer. The potassium iodide soaked paper becomes colored through the formation of iodine blue caused by ozone. Today much more accurate measuring instruments are used. These utilize the UV absorption properties of ozone and thereby a purely physical measuring technique (UV-photometry). Until recently, these instruments had been calibrated using the wet chemical potassium iodide process (VDI-Guideline 2468, Page 1). Since the EC ozone Guideline took effect in 1992, the direct UV-photometric process has been prescribed throughout Europe. This is substantially more precise however, its yields results which are systematically 10 % lower than those from the wet chemical process. This accounts for the fact that the measurements for Berlin are 10 % higher than those taken since 1 January 1995. This also applies to the comparability of data between federal states which in some cases applied a reference temperature of 0°C instead of the currently prescribed 20°C in converting from ppb to $\mu\text{g}/\text{m}^3$. The EC Guidelines will avoid the systematic variances of up to 16 % by measurement and calculation of ozone concentrations in future.

A further method for measuring ozone, often used to make comparisons, is based on the emission of light during the reaction of ozone and ethylene (chemical luminescence).

Induced by the growing public interest in increased ozone concentrations during summer, the number of the ozone measuring stations was enlarged considerably in the last years. A dense network of continuous measuring stations has been in operation in California (USA) since the 1970s. This is due to the extremely high concentrations, between 400 and more than 800 $\mu\text{g}/\text{m}^3$ (c.f. NRC 1991). In recent years, Germany has also been equipped with 365 continuously operating measuring stations belonging to the states and the Federal Environmental Agency (UBA), thus enabling a virtually total measurement of the entire territory (c.f. UBA 1996). In Berlin ozone has been measured continuously since 1984 at a station in Wedding and since 1987 at several stations of the Berlin Air Quality Monitoring Network (BLUME). The since 1994 reached final extension of the monitoring network includes altogether ten stations for ozone at which other pollutants like sulfur dioxide and nitrogen oxides are also registered (c.f. SenStadtUm 1995a). Of these five measuring stations are found on the outskirts of town and three in inner city residential areas. Per a measuring station has been installed at the city expressway and in 324 m height on the radio tower in Frohnau. The measuring station in Grunewald determines, alternately each half hour, the pollutant concentrations at approximately 4.5 m height as well as at 24 m height above the ground and 10 m over the treetops.

Methodology

The somewhat complicated connections between generation and decomposition of ozone in the different layers of the atmosphere as well as its effect on living and inanimate environment are elucidated in the schematic depiction of Map 03.06.1.

Map 03.06.2 contains a wide-area depiction of 1995 maximum ozone levels interpolated to show the distribution through Germany.

In Map 03.06.3 the frequency with which the guide values was exceeded at Berlin measuring stations in 1995 is depicted. This provides a characterization of the ozone load in Berlin.

High ozone concentrations in the near ground atmosphere are a national problem as can be seen in Map 03.06.2. Nevertheless, it remains an issue whether and to what extent conurbations like Berlin cause additional ozone formation in the city and vicinity. The aim of the Berlin - Brandenburg state joint measuring project "FluMOB" (airborne and surface measurement of ozone and precursors to estimate the effectiveness of emission reduction measures in Greater Berlin-Brandenburg) was to answer the question whether and what contribution can be made by short-term measures to reduce emissions of ozone producing substances toward the reduction of ozone loads.

The main constituent was the measurement of ozone and other significant pollutants during a typical ozone weather condition between 23 and 27 July 1994 both near the ground and in the atmosphere, as measured from airplanes. The results of such measurement flights have been prepared in Maps 03.06.5 and 03.06.6. The development of the wide area ozone loads is shown in Map 03.06.4. Map 03.06.7 illustrates the temporal progression of some parameters as measured in Berlin.

It is only possible to answer the question regarding potential effects of emission reduction measures by using a simulation calculation of ozone concentration (for 25 July 1994, 4:00 p.m., in Map 03.06.8). If all other conditions remain unchanged, it is possible to reduce the emissions in the test area by any amount (here 30 % for nitrogen oxide and hydrocarbons). The effect of such reduction scenarios on the ozone distribution is shown in Map 03.06.9.

Map Description

Map 03.06.1: Generation - Decomposition

The natural balance in the stratosphere

As presented schematically in Figure 1, the ozone concentration greatly increases above 12 km altitude in the stratosphere and reaches 20 to 30-fold the values in ground proximity. The reason for this is the generation of ozone induced by the effects of energy-rich solar radiation from space (wavelengths < 240 nm) on the uppermost layers of the atmosphere. The plentiful molecular oxygen O₂ available there is split into both its atoms which join subsequently with a still intact O₂ molecule to form ozone (O₃) (c.f. Fig. 3).

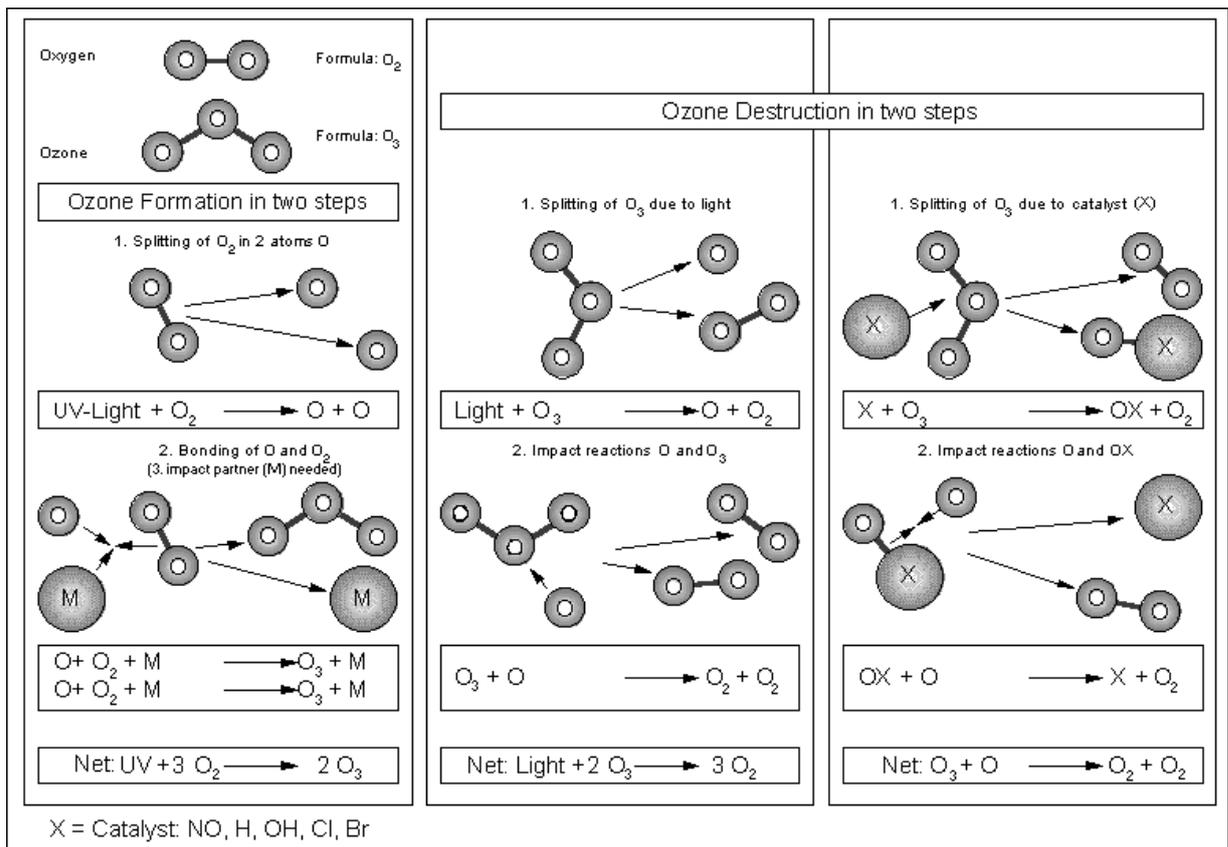


Fig. 3 : Schematic Display of Ozone Formation and Decomposition in a Pure Oxygen Atmosphere and of Catalytic Ozone Destruction (from left after to right; source: German Bundestag 1990)

This ozone production stands in balance with the natural ozone decomposition which depends on the absorption of less energy-rich radiation (wavelengths by 200 to about 300 nm and weaker). Since ozone has a slighter bonding energy than oxygen, O₂ and a single oxygen atom are created when these molecules decompose (c.f. Fig. 3). This atom can bond itself again with an oxygen molecule to form O₃, so that in the balance the ozone loss remains first of all slight. If one calculates the **global ozone distribution** alone under consideration these reactions discovered by Chapman in 1930, the actually observed density of the ozone layer in the stratosphere must have about 50 % more ozone and an incorrect vertical distribution. Thus there must still be other ozone destroying reactions about which more will be said below.

At altitudes over 30 km, photochemical balance prevails and the atmospheric transport plays hardly a role for the ozone distribution. The highest ozone values are found in the area with the highest amount of radiation. That means at the equatorial regions and decreasing toward the poles.

In layers between 15 and 30 km high the ozone distribution is clearly influenced by the horizontal and vertical transport processes. The average global distribution of the total ozone, which is determined to over 70 % by the stratospheric ozone in this layer, shows a minimum of around 250 Dobson units (DU) in the equator region and an increase toward the poles.

Since in the tropics through the heavy weather activity an ascending air movement prevails, there low-ozone air climbs from below into the stratosphere. There it is transported in a meridional direction to the poles and there it sinks again. Because of the high UV-radiation the largest ozone production occurs in the tropical and subtropical stratosphere, so that polewards because of the transport process the ozone values rise to over 400 DU. Since the meridional air movement is most predominant in the late winter and spring of the respective hemisphere, the ozone maximums are to be observed in the higher latitudes of both hemispheres respectively around this season. In the respective summer, the total ozone values sink and reach their minimum in the late fall. As an example for the annual cycle in our latitudes the average course of the total ozone values (and their standard deviation) over many years at the observatory in Potsdam is presented in Figure 2.

For several years, the spring ozone maximum in the **Antarctic**, with on average over 340 DU has exhibited a dramatic **decline** to less than half. In the Antarctic spring 1993 (September/October), the

total ozone quantity sank there over a wide area to even under 100 DU, an effect which occurred again in 1994 and 1995. In Figure 4, the penetration of the ozone layer at the end of September can be seen from the seasonal variations in the vertical ozone distribution. The ozone concentrations found in the ozone layer, as measured by the ozone sensors of the German Antarctic station, located at 70° S, vary from 140 nbar in winter to a drastic reduction sometimes lower than 10 nbar at the end of October. At the beginning of the summer the ozone layer thickness rose again nearly to normal values. This can be traced back to the movement of ozone-rich air from lower latitudes. This is practically suppressed in the winter and up to the beginning of the spring because of the stable wintry polar vortex over the Antarctica. The cause of the rapid ozone decomposition is still to be discussed.

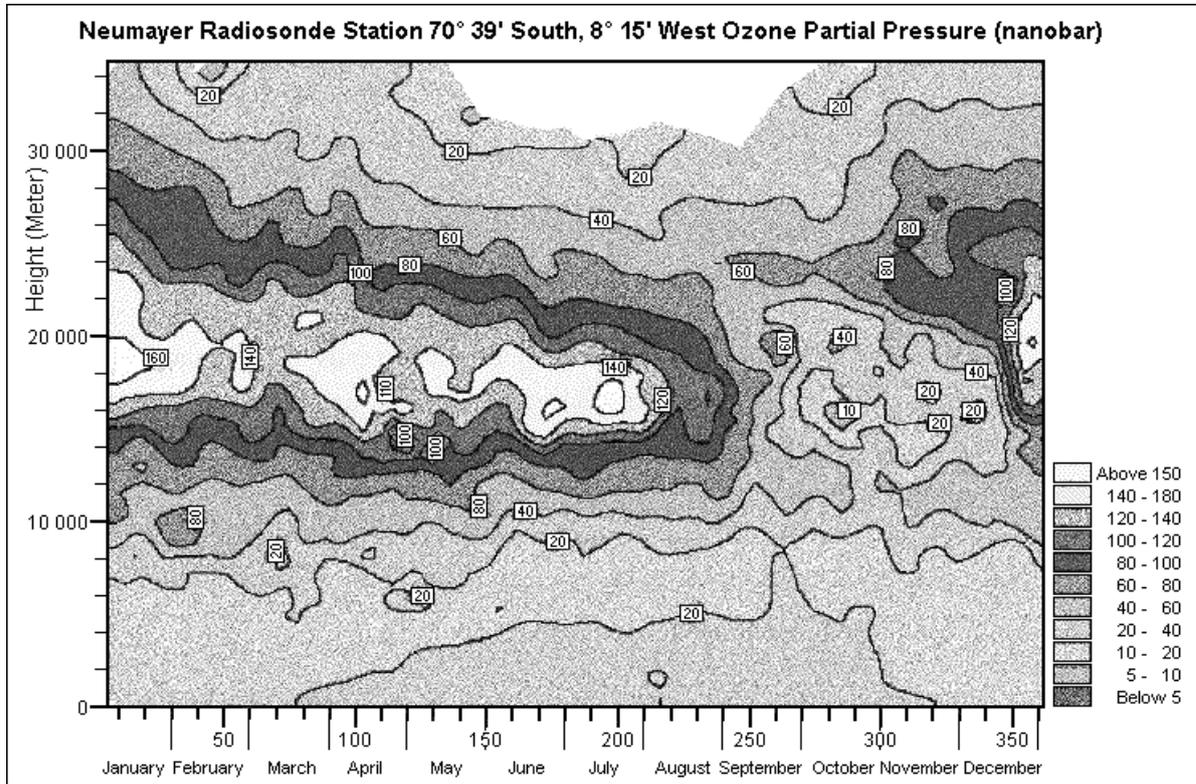


Fig. 4: Ozone Vertical Distribution in 1995 at the Georg von Neumayer Station (from Alfred Wegener Institute for Polar and Marine Research; from the Internet)

The phenomenon known as the "ozone hole" has no counterpart in the **northern hemisphere**. There the meridional transport processes start earlier because the wintry polar vortex over the north pole disappears sooner. Indeed a gradual **decomposition of the ozone layer thickness** is also to be observed in the northern hemisphere. With 7 to 9 % in the winters 1992 and 1993, it had increased - with reference to the value 10 years before, end of the 80s in winter over North America and Europe about 3 % (c.f. German Bundestag 1990). In the summer, the decline is significantly lower here as well as in the equatorial regions. Nonetheless, the 1995 ozone layer thickness (c.f. Fig. 2), as measured at the Meteorological Observatory in Potsdam, has declined in the summer even compared with the 30 year average. The deviation was approximately minus 8 % as in summer 1994 and 1996. On account of the higher solar position and subsequently higher UV-B background this is of greater significance than the occasionally heavier variation in winter.

The anthropogenic destruction of the ozone in the stratosphere

Since 1974 when the two American scientists Molina and Rowland alarmed the world public with their thesis of the destruction of the ozone layer by human-induced trace gas emissions, it has become even more clear that the complex aerochemical balance in the atmosphere can be easily disturbed through anthropogenic activities. Also trace materials, which due to their chemical inertia endure the long transport from the ground to the stratosphere or are introduced there directly by airplanes and volcanic eruptions, contribute to this effect. Like the atmospheric oxygen, they are also broken down by the energy-rich solar radiation into their elements of which some massively react on the chemical balance at the expense of the ozone.

The best known human-induced trace gases are the chlorofluorocarbons (CFC) and the related halons. These are hydrocarbon compounds in which one or several hydrogen atoms have been replaced by fluorine and chlorine and/or bromine. On account of their chemical inertia, these are industrially versatile materials (coolant, solvent, propellant etc.) Their worldwide output has reached the considerable quantity of 1 mil. t/a. The only known compound from this class of materials with a natural source is methyl chloride, which is emitted by the oceans into the atmosphere. It contributes however only 10 to 20 % of the chlorine content of the stratosphere, which is responsible for the ozone decomposition located there.

A further important material class with both natural as well as anthropogenic sources are the nitrogen oxides. They play a role in form of laughing gas (N_2O), which is introduced both as consequence of bacteriological processes in the ground as well as through the increased discharge of nitrogen fertilizer in the atmosphere. Also NO as an element of airplane exhaust fumes counts as an ozone-decomposing element.

Water plays likewise a role in the stratosphere as an ozone-decomposing substance. Due to the extremely low temperatures at the lower edge of the stratosphere considerable water quantities arrive however only through the air traffic and volcanic eruptions in the higher atmosphere layer.

Catalytic ozone decomposition

The significant ozone-decomposing effect of these trace materials is without the influence energy-rich solar radiation independent of the time of day. They stand in contrast to the incredibly low concentrations in which these materials occur in the atmosphere. The catalytic decomposition reactions sketched in Figure 3 can mean, for instance, that one CFC molecule in a billion other air particles is responsible for the destruction of several thousand ozone molecules. The ozone-decomposing elements of the trace materials in Figure 3 substitute for the different substances marked X and lie again in their original form namely at the end of a reaction chain. They can perform their destructive work repeatedly before they are removed from circulation in part only after several years by other chemical reactions.

The catalyst thereby attacks two-fold at the expense of the ozone in the chemical balance: On one hand it transforms an ozone molecule into oxygen O_2 and bonds with the remaining oxygen atom. On the other hand, individual free oxygen atoms are consumed at this degeneration of ozone in oxygen, which are no longer available for ozone formation (c.f. Fig. 3).

Chlorine and bromine which originate predominantly from CFC and/or the halons, as well as NO and OH radicals, work as catalysts. The latter come from steam, methane and hydrogen and originate from predominantly natural sources.

The simplicity of the current depiction belies the intense complexity and non-linearity of the aerochemical processes in the stratosphere. The different reaction cycles are coupled with each other strongly and in different ways. For instance, BrO, NO or OH can be involved in the reverse process of ClO to Cl instead of an O atom as partner. A further important role is played by heterogeneous reactions in which the ozone-decomposing materials are conveyed in harmless substances or conversely from ozone-neutral reservoir compounds and are activated as catalytic substances again. This explains the sudden significant decomposition of the ozone layer in the spring over the Antarctica.

Heterogeneous reactions

The reasons are chemical reactions in the stratospheric clouds. They are composed of ice and nitric acid particles, on which the chlorine from compounds forms residues which are stored before and withdrawn from the ozone decomposition cycle. The clouds emerge only at temperatures under minus $80^\circ C$ and are observed predominantly in the area of the stable wintry polar vortex over Antarctica. Energy-rich solar radiation is also necessary for the reactivation of the chlorine, which is available first at the end the polar night, therefore at the beginning of the Antarctic spring. In this period the chlorine is released in large quantities from the reservoir of substances formed in the winter. Since the supply of ozone-rich air transmitted from the lower latitudes through the polar vortex is suppressed until the spring, the massive ozone loss over the Antarctica takes its course. Through the transport processes which begin again in the summer, the ozone deficit is again largely equalized (c.f. Fig. 4).

In the northern hemisphere, a comparably large and long existing polar vortex does not exist, so that the low temperatures necessary are reached only rarely or short-term and meridional air currents occur more frequently. Nonetheless the question must be raised whether the increase in the

greenhouse effect leads to a cooling off of the stratosphere and thereby increased stratospheric cloud formation in the northern hemisphere as well. This would lead to an increased ozone decomposition caused by heterogeneous reactions. In February and March 1996, it was possible to detect for the first time in central European latitudes such stratospheric clouds at altitudes of between 20 and 24 km using the LIDAR device operated by the FU Berlin. At the same time, the Potsdam measurements of the ozone layer decreased to about 250 DU - the long time average lies at about 370 DU. However, the drop lasted only a few days.

Further influential factors

As mentioned at the outset, volcanic eruptions also influence the thermal structure and the chemistry in the upper atmosphere. Due to the high intensity of the energy released at an outbreak, material and gases are shot into the stratosphere, whose chemical composition draws from that of the early earth's crust and differ therefore very greatly from the present composition of the atmosphere. It is suspected that they directly or indirectly favor the origin of the above described polar stratospheric clouds. Besides the ozone-decomposing chlorine is brought directly in the stratosphere in the form of hydrochloric acid. As measurement results from a large laid out research program 1993 showed, over the northern polar region, an increasing amount of dust particles was found which had originated from the Pinatubo eruption in 1991 and spread out over wide parts of the hemisphere. Indeed there was no spatial coincidence between the incidence of volcano dusts and the stratospheric clouds which appeared in the area of the northern polar vortex in the winter 1992/93. The thinning of the ozone layer at this time can not be explained directly as a result of volcanic eruption. In contrast to the relatively rare emissions through volcanic eruptions, the ozone layer is not in the position from which to recover from the decimation of continuous CFC emissions.

This also applies to the possible increase in the supersonic air traffic in the stratosphere, through which nitrogen oxides and water vapor, which contribute directly and indirectly to ozone decomposition, are directly emitted.

Future development

Which consequences a further increase of the trace gas emissions on the ozone layer will have in future, can only be estimated with the help of mathematical model calculations because of the numerous influence factors.

If unhindered CFC emissions are considered in the long-term consequence assessment along with the most important heterogeneous reactions which lead to creation of the Antarctic ozone hole, then the increase of the UV radiation at the ground in the global average can reach 20 to 25 % (c.f. German Bundestag 1992).

Damage to the ecosystem

Since the area marked as UV-B short-wave radiation (290 to 330 nm) has a cell damaging effect, a significant increase in intensity has direct negative effects on the animals and flora and also on humans.

Indirectly humans are affected as the last link in a long food chain by a possible **decline of plant growth**. Under these circumstances an important reciprocally strengthening connection rests also itself between ozone decomposition and global temperature increase. The photosynthesis performance of plants is damaged by a higher UV dose, particularly that of the phytoplanktons in the ocean. It draws as much carbon dioxide from the atmosphere through its metabolism as do all terrestrial plants together. If the increasing UV B radiation would deaden for instance 10 % of the plankton, almost so much less carbon would be removed from the atmosphere annually, as the entire mankind discharges through the fossil fuel combustion. The result would be a further **reinforcement of the greenhouse effect** and with it a further warming of the earth's atmosphere.

An increasing UV B radiation intensity can become a direct danger since larger radiation quantities, when hitting the skin, induce a **carcinogenic effect** and can cause over and above this **damage to the eye lens** (gray star). Since the damage gains with the reduction of the wavelength and with a weakening of the ozone layer the short-wave spectrum of the UV light becomes stronger, a thinning of the ozone layer by 1 % can lead to an increase in skin damage of around 1.7 %. Due to the strong seasonal fluctuations in UV intensity, in the summer four to five-fold the usual winter values with a cloudless sky, the ozone layer thickness in the summer half-year plays a role in the assessment of a possible additional health threat.

Also there is a fair-sized variation of the UV radiation with the geographical latitude because of the different distances for the radiation through the atmosphere. The solar radiation is during summer with cloudless skies around 40 to 100 % more intense in the Tropics than in our latitudes. Therefore the clear rise in skin cancer illnesses can also be traced to the travel fever of an increasing number of persons whose skin is only genetically adjusted to the slighter radiation intensity in higher latitudes and is exposed to the more intense solar radiation in the equatorial vacation areas.

High resolution spectral measurements of UV-B radiation, as needed for assessing pollutant effects, have only been available for a few years due to the recent development of the corresponding measuring technology. For instance, it has only been since July 1993 that all seven measuring stations in Federal Environmental Agency and German Weather Service have been able to generate UV-B spectral measurements of sufficiently high resolution so as to allow the calculation of the "so-called biologically weighted UV-B radiation" on the basis of the frequency of heavily varying pollutant effects.

Comparisons between such new measurement between Germany and a location at a similar latitude in the southern hemisphere in New Zealand showed a 1.4 to 1.8 times greater UV-B radiation level. Here a factor between 1.3 and 1.6 is solely due to the decomposition of the ozone layer in the southern hemisphere (c.f. Seckmeyer and McKenzie 1992). Measurements in Canada between 1989 and 1993 showed an increase in the sunburn-inducing UV-B radiation of five percent in winter and two percent in summer (c.f. Kerr and McElroy 1993). An increase in the DNA-damaging radiation of seven percent per decade for the regions between 45 and 55 °N could be determined based on satellite data from the past fifteen years (c.f. Herman et al. 1996). The increase in the ozone and dust concentrations in the lower atmospheric layers in Europe and the USA could have had an inhibiting effect on the increase in UV-B radiation.

Ozone production and destruction in the troposphere

The up to 100 times higher ozone concentrations in the stratosphere (c.f. Fig. 1), in comparison with the near ground values, contribute because of the vertical exchange to the fact that ozone occurs naturally also in the near ground air layers. Indeed this contribution is limited, since according to geographical latitude in 8-15 km altitude between both stories of the atmosphere there is a blocking layer. This so-called Tropopause forms the lower edge of one globe encompassing temperature inversion, i.e. the temperature does not drop with altitude but increases. This increase is caused by the warming of the air through the above described filter effect of the ozone layer. It prevents the mixing of the larger mass of warmer and relatively seen, lighter ozone-rich stratospheric air with the colder tropospheric air lying below. The anvil form of high-reaching thunderclouds, which appear to expand at the Tropopause like at an invisible room ceiling, comes about in this way.

The **vertical transport** of ozone from the stratospheric ozone layer downward is thus only relatively weak. It occurs predominantly in the area of low pressure areas. Its contribution to the increased ozone concentrations, which occur at high pressure weather conditions with high solar radiation, is accordingly very slight. It is at the beginning of the spring the strongest because at this time both the ozone layer in the stratosphere as well as the low pressure activity have reached their average maximum.

As expected, the **average year course** of the ozone concentration in the southern hemisphere in Figure 5 shows the maximum to be in the spring. Historic ozone measurements from the previous century, taken near Paris, show a qualitatively equal course (c.f. Volz-Thomas et al. 1988). The vertical transport of ozone from the stratosphere is in the southern hemisphere, resp. was in the pre-industrial era also in Europe, the main influential factor for the ozone level in ground proximity. The year course registered today in the northern hemisphere, with a maximum in the midsummer, shows that a further very weighty element for the formation is the near ground of ozone has been added. It is caused predominantly by emissions of pollutants originating from anthropogenic combustion processes which are relatively low in the southern hemisphere.

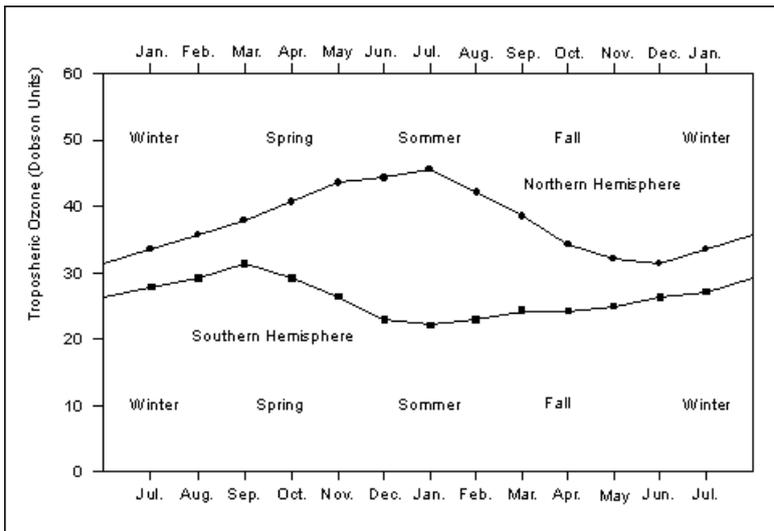


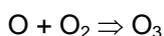
Fig. 5: Year Course of the Tropospheric Ozone Concentration of both Hemispheres (35 - 45 °C) (source: German Bundestag 1992)

How high the ozone level caused through natural processes in our latitudes is can only be estimated imprecisely since there is hardly a test series which remains unaffected by the anthropogenically formed ozone. On the basis of measurements on mountain stations (c.f. Schurath 1984), with aerial ozone sensing and test series from unindustrialized areas, this share lies (c.f. Logan 1985) between 50 and 90 $\mu\text{g}/\text{m}^3$. Similar values have been obtained on the radio tower in Frohnau in 324 m elevation if fresh, clean polar air masses has reached the Berlin region from the North Sea.

Figure 1 shows a schematic ozone profile with a continual decline in the ozone at decreasing elevation is conditioned by the **natural decomposition of the ozone** on its way to the earth's surface and at the ground through contact with materials. This effect can be seen in the difference between the ozone values taken at the measuring station Grunewald at 4.5 meters and again at 10 meters above the forest stock (c.f. Fig. 7).

In addition, there are also predominantly **anthropogenically induced decomposition processes**. Ozone reacts as strong oxidant with other substances characterized as pollutants and assumes thereby an important cleaning function in the atmosphere. Sulfur dioxide, for instance, is transformed by ozone into sulfate and into a fine dust which precipitates either on the ground or is washed out as acid rain. Still important in this connection is the reaction of ozone with nitrogen oxides. They are discharged as a final product from nearly all combustion processes as nitrogen monoxide which reacts immediately with ozone. Therefore a lower ozone concentration is to be found in most cases within conurbations and industry regions, in other words where pollutants and particularly NO are emitted. The number of the infringements of the EC notification level of 180 $\mu\text{g}/\text{m}^3$ is in many so-called pure air areas and at the edge of the cities similarly high or even higher than in the centers of conurbations (c.f. UBA 1996).

To reach these frequent infringements of the threshold values, there needs to be an additional **formation process for ozone on the ground**. The requirement for it is, like for the described generation in the stratosphere, the availability of free oxygen atoms. Indeed the splitting of oxygen molecules in the lower atmosphere layer is not possible for want of energy rich radiation. Instead the nitrogen dioxide (NO₂) functions as supplier of the oxygen atoms. It is the only material, which can become photolyzed already at the lower energy rich radiation in ground proximity and deliver individual oxygen atoms:



Globally considered, 60 % of the nitrogen oxides discharged into the atmosphere originate from anthropogenic sources. The remaining part is predominantly the result microbacterial processes in the ground (c.f. German Bundestag 1990). In highly industrialized Central Europe this part is insignificant in contrast to the nitrogen oxide quantities originating from the numerous combustion processes. Thereby 90 % of nitrogen oxides are emitted however as nitrogen monoxide (NO) which must be

transformed first through oxidizing processes into nitrogen dioxide. As mentioned ozone itself also plays an important role since it changes the NO into NO₂ and is thereby decomposed:



The most important decomposition reaction for ozone is near nitrogen oxide sources. The decomposition runs within seconds and minutes because of the fast reaction time.

The ozone formation from the photolysis of NO₂, occurring in the vicinity of conurbations, is partially compensated through the reaction with nitrogen monoxide. Since however high ozone values sometimes also appear, there have to be additional processes, which convert freshly emitted NO into ozone-forming NO₂, without allowing ozone to function as an oxidant and thereby decompose.

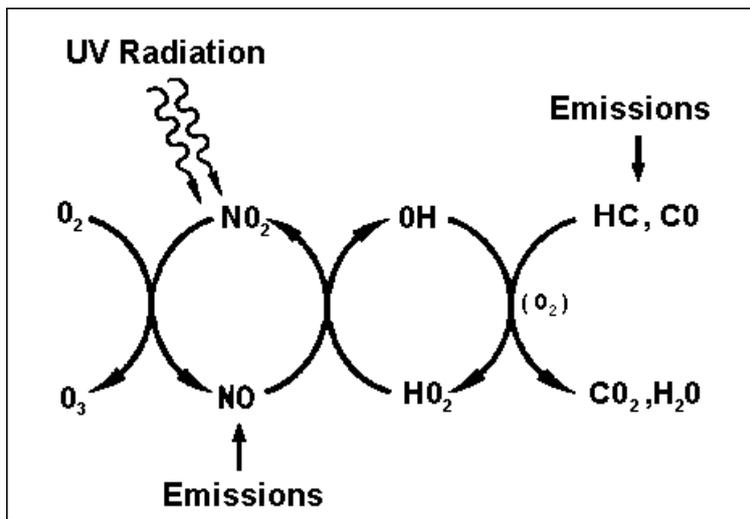


Fig. 6: Schematic Display of Photochemical Ozone Formation in the Troposphere (Volz-Thomas et al. 1990)

The requirement for it is the availability of carbon monoxide (CO) and different reactive hydrocarbon compounds (HCs), which with OH and peroxyradicals (HO₂) within more multiple and complicated reaction schemes cause the oxidation of NO to NO₂ without ozone consumption and so shift the chemical balance in the direction of ozone formation. Thereby it is just the simultaneous emission of hydrocarbons and nitrogen oxides, which at accordingly high solar radiation and air temperature make possible the formation of high ozone concentrations. CO and hydrocarbons work as fuel for photochemical ozone formation. Radical (OH and HO₂) and nitrogen oxides (NO and NO₂) play the role of catalysts, without which no ozone is formed (c.f. Fig. 6). The necessary spur is provided by the UV radiation up to 400 nm.

The speed with which these formation reactions proceed is very different and is intensely non-linear with respect to meteorological conditions and the concentration and composition of the predecessors involved. A cause analysis of high ozone concentrations alone from the measuring courses is therefore quite difficult. Therefore to illuminate the connection between emission, meteorological conditions and ozone concentration model calculations are used in which the chemical processes and atmospheric transport processes are simulated (c.f. Map 03.06.8). Using the measuring courses of ozone it can still be ascertained that the formation of ozone proceeds relatively slowly compared with its destruction through NO, with a time scale from several hours up to days.

Despite its avidity, numerous measurements with airplanes, on mountain stations and finally at the Frohnau tower measuring point show (c.f. Fig. 7) that ozone remains in the free atmosphere over several days. In the course of midsummer weather conditions with strong solar radiation and photochemical ozone formation high ozone concentrations can develop in the near ground air layers. Besides for dynamic reasons the vertical mixing remains in the lower 2,000 m limits in the area of high-pressure areas even in the afternoon. This favors the enrichment of ozone.

At night a temperature inversion develops under clear skies by cooling of the ground which almost completely paralyzes the vertical air exchange. The decline of the ozone values thus occurs only in the lower 100 m to ground proximity. In the layer above it the higher ozone level of the past day almost completely remains. It reacts on the next morning when the sun has warmed the cold air at the ground

and the vertical air exchange starts, as ozone reservoir, so that the ozone concentration also rises quickly at the ground.

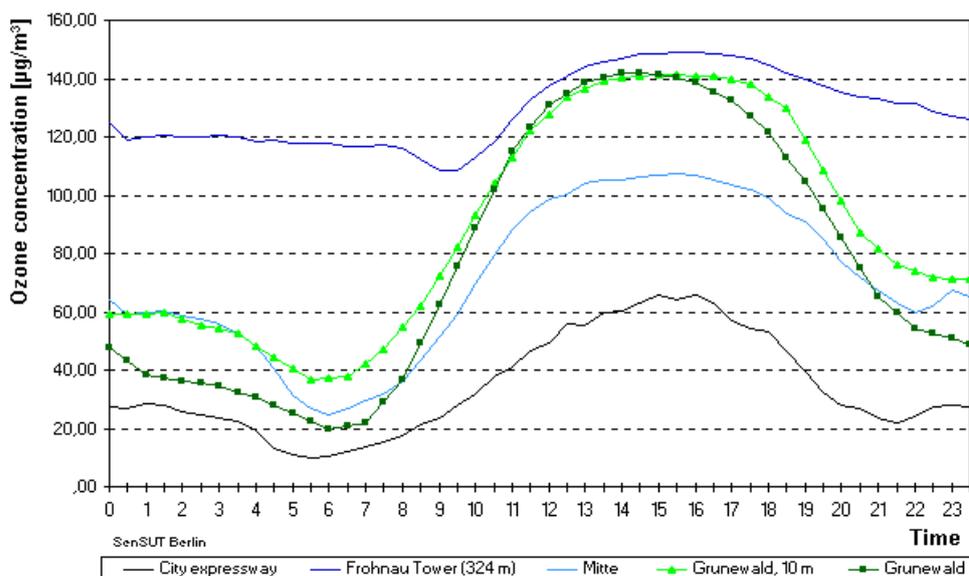


Fig. 7: Average Ozone Daily Course at BLUME-Stations on Summer Days (days with temperatures above 25 °C) in 1994 and 1995

Using the typical day courses for high ozone days at various BLUME measuring stations (c.f. Fig. 7) enables a clear description of these events.

The form of the day course curves at the three ground stations Grunewald, Mitte and the freeway are to be explained in first approximation by the superimposition of the course of nitrogen oxide emissions through the motor vehicle traffic and the exchange conditions of the atmosphere. The ozone minimum is to be found between 5:00 and 7:00 o'clock in the morning hours. At this time the motor vehicle traffic is already quite heavy, the nightly ground inversion however still pronounced. Hence it is virtually impossible for the ozone-decomposing nitrogen oxides to move upward and/or the ozone-rich air from the top to move downward. The ozone decomposition takes effect on the city's edges because that is where the pollutants are transported- for example from the AVUS to the measuring station in Grunewald 1.5 km away. This results in a heavier ozone decomposition on the ground and therefore lower values than obtained above the tree crowns. Nonetheless this difference is also a result of the constant decay reactions of ozone with the materials on the ground and with reactive hydrocarbon compounds which the trees discharge especially in the afternoons. The latter could be a reason why this vertical ozone differential can be seen even in the afternoon after 4:00 p.m., a time of good vertical exchange.

The conditions at 324 m elevation, recorded by the gauge at the radio tower in Frohnau, are completely different. There the ozone level remains at the value of about $120 \mu\text{g}/\text{m}^3$, because this air layer is isolated at night by ozone-decomposing processes on the ground. This changes in the morning when the sun has warmed the blocking layer on the ground so far that the vertical air exchange starts. Then the tower measuring point is temporarily affected by the polluted air ascending from the ground, in which slighter ozone concentration is present. The minimum at the tower normally appears between 9:00 and 10:00 o'clock in the morning.

At this time the ozone concentration at the other stations has already risen noticeably because ozone from the superimposed storage layer is transported to the ground. The further thinning by the ozone-decomposing pollutants and the photochemical processes, urged on through the intense solar radiation, have caused the ozone concentration in the entire lower atmosphere to rise further.

Near nitrogen oxide sources, particularly at the city expressway and somewhat more weakly at the station Mitte (Parochialstrasse), the ozone-decomposing effect of the freshly issued pollutants also remains clearly perceptible in the afternoon. Indeed the increase in traffic during the late afternoon rush-hour hardly has any impact at all. The horizontal and vertical air exchange assure a relatively fast thinning of the ozone-decomposing pollutants. First in the evening, when the wind and also the vertical transport become weaker, the ozone concentration decreases greatly, accelerated by the nitrogen

oxide emission of the persistent motor vehicle traffic in the evening. The ozone concentration above the near ground cold air layer has remained unaffected. The negligibly decreasing ozone level yields a reservoir at height of the tower for a further rise at the next day.

Since even under fair-weather situations considerable winds can be found at elevations over 300 m because of the lack of ground friction, a **transport of ozone** also over larger areas is to be expected. This is also the reason that increased ozone concentrations are not spatially narrowly limited phenomena, but usually occur, like high air temperatures, over wide areas (c.f. Map 03.06.4).

In this connection **long-term trends of the ozone concentration** will be discussed briefly. From Figure 8 it is obvious that in Berlin the average maximum value on summer days indicates no significant trend.

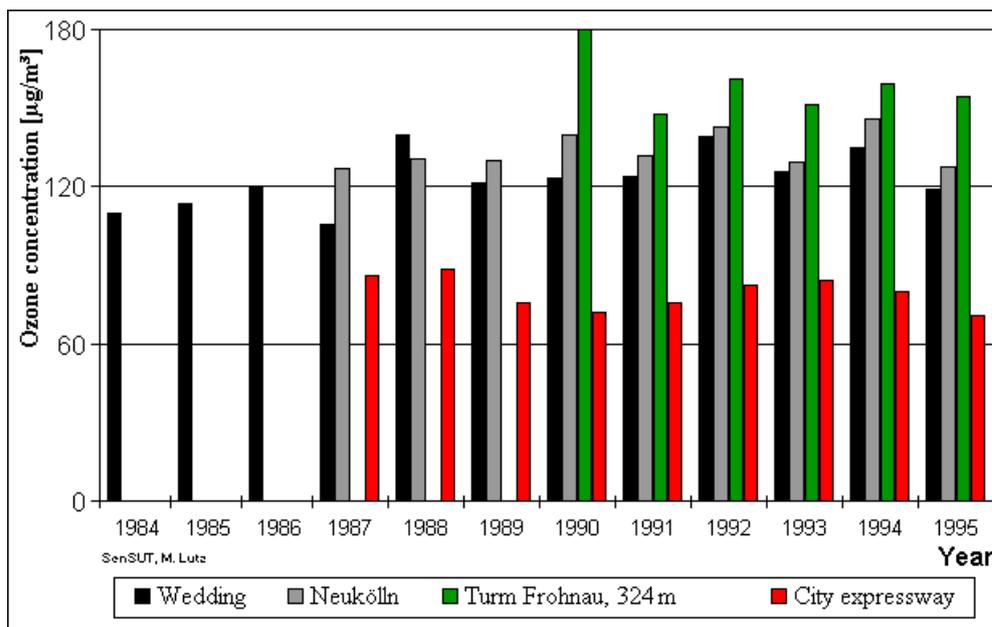


Fig. 8: Median Value of the Daily Ozone Maximums on Summer Days (days with maximum temperatures above 25 °C)

Indeed a 1 to 2 % increase in the ozone concentration per year since the mid-70s is to be assumed for other stations, particularly far away from conurbations, e.g. on the Zugspitze (c.f. German Bundestag 1990). This increase of the wide area background concentration is probably due particularly to the rise in traffic emissions in the 70s and 80s. An increase can also be found at the rural stations in Baden-Württemberg although this would appear not to have continued over the last three years (c.f. UBA 1996).

Map 03.06.2: Distribution of Ozone Maximum 1995

The map shows the distribution of the highest one-hour-maximum 1995 at all state measuring stations and those of the Federal Environmental Agency. In order to obtain an all-inclusive representation, the values between individual stations were spatially interpolated.

Values over 180 µg/m³ were recorded everywhere with the exception of some areas in South Bavaria and in Eastern Germany. There are regions where measurements in excess of 240 µg/m³ have been taken particularly in the West and Southwest. These areas are primarily located near heavily industrialized and densely populated conurbations such as the Ruhr region, the Rhine-Main region around Frankfurt, the regions Mannheim and Karlsruhe as well as greater Stuttgart where the maximum measurement of 297 µg/m³ was taken (c.f. UBA 1996).

There is accordingly a significant gap in the pollution load from the West to the Southwest in the direction of the eastern part of the country. Nonetheless, this situation corresponded to a similar one in the past summer where a similar distribution of sunshine and temperature so that there would seem to be a purely climatological explanation. In Summer 1995, the distribution of the daily temperature high in Germany was very even (c.f. Bruckmann et al. 1994 and FU Berlin 1995). In some regions of the Northeast there were even more hours of sunshine measured. However, in some regions the

Northeast, there has occasionally been more hours of sunshine than in the West. However the high air pressure center often lay in the northwest and north of Germany during the summer months thus accompanying otherwise high summer conditions often in the range of a northeast to easterly airstream. This brought with it the advantage of an inflow of air for the Northeast, which benefited the areas already with relatively low ozone forming substance emission levels (e.g. the Baltic and northern Poland). In the past, this had already led to relatively low ozone levels in the Berlin region (c.f. Lutz 1994), although weather conditions favorable to ozone formation had predominated. The West and Southwest are at a disadvantage in such cases since the air has already been heavily filled with ozone forming substances by the time it has reached these areas. Together with the locally induced contribution due to orography (e.g. Oberrheingraben), this leads to higher ozone levels. The question whether the influence of local pollution emissions can have on ozone formation will be described in the results of the FluMOB measurement campaign.

Map 03.06.3: Infringement of Ozone Threshold Values 1995

In this map the average spatial distribution of ozone in Berlin is presented based upon the frequency with which the threshold values are exceeded at individual stations of the Berlin Air Quality Monitoring Network. The number of half hour averages above the "Maximum Pollution Concentration Level" (MIK) according to VDI 2310 of $120 \mu\text{g}/\text{m}^3$. In addition, the days in which the EC Threshold Values for Information of the Population and Protection of Vegetation were exceeded is also presented (c.f. Tab. 1).

To make clear the dependence of the ozone burden on the local nitrogen oxide emission, the frequency with which the values were exceeded was collated with the distribution of nitrogen oxide emission from traffic. In the comparison of both statements it becomes clear that high nitrogen oxide emissions lead to clearly fewer infringements of the ozone threshold values in the vicinity of a measuring station. Thus the MIK is 20 to 40 times more seldom exceeded than at stations on the edge of the city where in summer the level of $120 \mu\text{g}/\text{m}^3$ ozone was recorded more than 300 hours. The load at the other measuring stations, those not directly near the main traffic arteries in the city center, lie in between with durations between 70 and 200 hours in which the MIK was exceeded. The respective surpassing of the MIK at each measuring station are at first glance also applicable to other parts of the city with comparable nitrogen oxide emissions.

The $180 \mu\text{g}/\text{m}^3$ excess of the EC threshold value shows a similar pattern. At the inner city residential measuring stations there was no incidence of surpassing these levels, resp. in Neukölln this occurred only three times while at the edge of the city there was an incidence of up to nine times.

At the city's edge and thereby in the effected areas where, as a rule, Berlin's forests are to be found, the pollution at the forest measuring station Grunewald exceeds numerous guide values (as shown in Table 1) for the protection of vegetation. Daily average values (EC Guideline) of $65 \mu\text{g}/\text{m}^3$ were exceeded on 75 days in sampling at 10 m above the trees and 57 days at 4.5 m in the forest where ozone can decompose on plant parts. This brings with it damaging effects to the plants which is furthermore a substantial element of damage to the entire forest ecological system (c.f. results of the Monitoring Program and the Long-term Observation of the Forest Eco-System).

Maps 03.06.4, 03.06.5, 03.06.6 and 03.06.7: Results of the FluMOB-Measuring Campaign in Berlin and Brandenburg from 23 July to 27 July 1994

The most frequent exceeding of the threshold values for ozone and the discussion arising from it, whether and in what manner the regional measures to reduce the ozone precursor substances can contribute was the reason for a measuring project jointly financed by the states of Berlin and Brandenburg. Along with the states commissioning the study, a further seven research institutes from Berlin, Brandenburg, Bavaria and Switzerland participated.

From 23 to 27 July 1994, two motor gliders measured the morning and afternoon ozone, nitrogen oxide and hydrocarbon concentrations (VOC) at altitudes between 300 and 3,000 m both within the city and the outlying regions.

These measurements were also taken at the broadcast tower in Frohnau and at 3 Air Quality Measuring vehicles. These were positioned in addition to the fixed ground stations of the Berlin and Brandenburg Monitoring Network in order to measure the pollution load in front of and behind the city.

By means of an additional vertical measurement at several locations, the air currents and other meteorological phenomena were recorded (c.f. Stark et al. 1995).

Weather conditions and wide area ozone load

The measuring campaign of 23 to 27 July 1994 took place at the beginning of a long high summer period in which Berlin experienced an unprecedented series of 11 "hot days" with maximum temperatures of over 30 °C. The wide area air pressure distribution was characterized by a low pressure zone from the eastern Atlantic and high pressure zone from the Baltic Sea, southern Scandinavia, and the Baltic states.

Exemplary for the Berlin region are the wind direction and speeds at the BLUME measuring station 314, Charlottenburg City Hall tower, shown in **Map 03.06.7 (Correlations of Different Parameters from 23 July to 27 July 1994)**. In comparison with these measuring points 60 m above ground, the measurements for the wind velocity at the Grunewald station (10 m above the stands) have been given.

From 23 to 25 July, an east to southeasterly air current with low humidity prevailed in Berlin and until noon on the 25 July a very continental air mass too. On the morning of 26 July, the wind turned toward the Northwest, combined with the injection of more humid, intensely subtropical air mass with a high dust concentration.

In order to assess this episode's **contribution to transregional transport**, a reverse trajectory was calculated from a three-dimensionally analyzed field of meteorological measurements (c.f. Reimer and Scherer 1991). In the **Map 03.06.4 (Ozone Concentration from 23 July to 27 July 1994 at 4:00 p.m. CET)** are the reverse trajectories with travel time data until arrival in Berlin on each afternoon on four different days of the campaign are presented. According to the trajectory of 24 July, which closely resembled that of 23 July, the air originated until 25 July from the Baltic sea region and central and northern Poland, a region with relatively low emissions of ozone precursor substances. Therefore it contained only a relatively low ozone load of between 120 and 150 $\mu\text{g}/\text{m}^3$.

Map 03.06.4 also shows the spatially interpolated ozone concentration each day at 4:00 p.m. CET on the five days of the measurement campaign. Thus the largest wide-area ozone distribution at the time of the daily maximum is presented. Until 25 July, only values under 180 $\mu\text{g}/\text{m}^3$ were recorded in the Northeast.

On 26 July, the reverse trajectories come out of the Czech Republic, Austria, Saxony, and on 27 July, from Switzerland and southern Germany. If one determines the ozone concentration of the air mass under way 48 hours before, using the figure in Map 03.06.4, then one comes to an ozone level already at 180 to 200 $\mu\text{g}/\text{m}^3$ at the beginning of each trip. Also the high level of solar radiation on the way to Berlin means a significantly increased initial load of a similar magnitude to the second phase of the campaign could be expected.

This conforms with the development of ozone and NO_2 concentrations at the Frohnau broadcast tower documented in Map 03.06.7. Especially during the last two measuring days, a 40 $\mu\text{g}/\text{m}^3$ higher ozone level and even higher nitrogen oxide levels could be observed at the tower whose measurement series represents more the transregional pollution influences because it lay windward to Berlin.

Results of the Airborne Measurements

In the course of the measuring campaign between 23 - 27 July, an average of one morning and one afternoon flight per day was undertaken by each aircraft.

The **horizontal distribution** of the minute average for the ozone concentration on the flight path at about 500 m altitude has been shown using the example in **Map 03.06.5 (Spatial Distribution of Ozone Concentration)** for the afternoon of 25 July.

The circle's diameter is the measure for the recorded concentration in ppb (comprises somewhat less than 2 $\mu\text{g}/\text{m}^3$) interpolated between the smallest and largest level measured. **Map 03.06.6 (Spatial Distribution of NO_2 Concentration)** yields the same picture for the nitrogen dioxide levels.

Leeward to the main wind direction, there is a significant rise in the ozone concentration. This area lay northeast of the city on 25 July (and the previous days), while on 27 July, the areas south of Berlin were effected by the ozone increase due to the change in the wind to NW-N. This is the explanation for the heavy increase in the ozone values at the Müggelsee station on the 26th and 27th July as can be seen in Map 03.06.7. On these days, the maximum values exceeded the windward levels of over 50 $\mu\text{g}/\text{m}^3$ recorded at the broadcast tower in Frohnau.

In both maps, the airborne measurements depicted show a good correspondence between the ozone and NO₂ maximum and the spatial extension of Berlin as emission source for ozone-forming substances. The measured NO₂ concentrations serve as an excellent index- the windward levels were only 2 - 4 ppb, while the peak concentration in the air layer above the city lay at over 20 ppb. As Map 03.06.6 shows, the leeward side of the city exhibited increased NO₂ levels even as far as 30 - 40 km from the city.

In contrast to the source proximate areas, where maximums for nitrogen oxide concentrations, as a result of their ozone-decomposing effect, correspond to the ozone minimums (c.f. Map 03.06.3), shows a simultaneous increase in both types at the outgoing air vane. The highest ozone levels appeared leeward. In comparison to the windward levels, they were usually combined with higher NO₂ concentrations. This applies also to the majority of the recorded hydrocarbon compounds and indicates a significantly increased ozone formation potential leeward.

A comparison of the leeward and windward ozone levels measured on all afternoon flights is shown in Figure 9. From 23 - 25 July, the lee effect decreased due to the mixing layer and the higher wind velocity on 24 July. It was much less on both of the last days on which an increase in the ozone concentration up to 44 % of the windward level occurred.

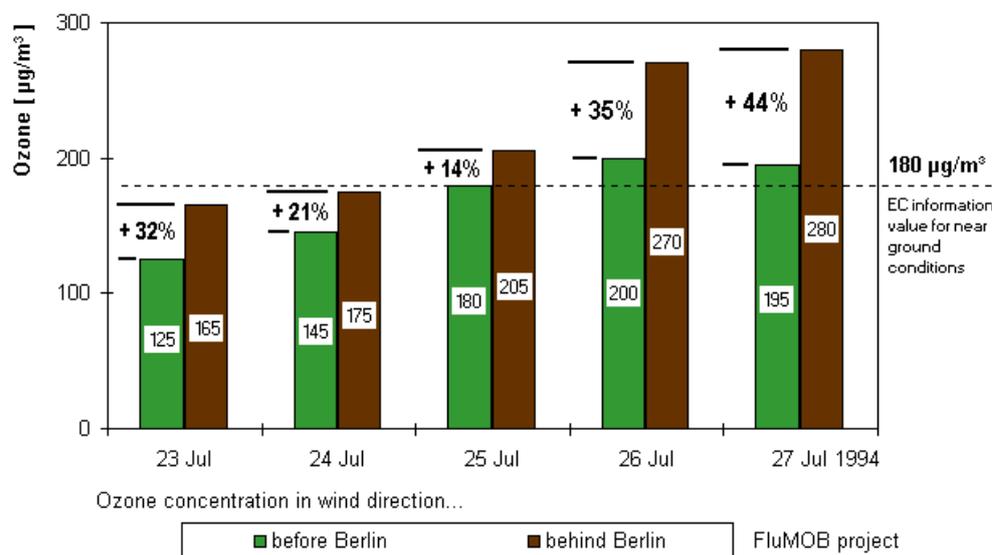


Fig. 9: Ozone Concentration During the Airborne Measurements at approx. 500 m Altitude from 23 to 27 July 1994, Afternoons

Table 2 shows a compilation of the **near ground ozone concentration** windward and leeward levels measured in the afternoon in the Berlin municipal area. Just as in the aircraft data measured afternoons, there is a continuous increase in the windward prior pollution load on the outskirts amounting to approximately 20 µg/m³ per day. On 26 and 27 July, it exceeds the information value of 180 µg/m³ prescribed by the EC Guidelines. Within the urban residential areas of Berlin, a slightly lower level prevails due to the ozone destruction by freshly emitted nitrogen oxides.

The proportional growth in ozone pollution leeward lay at the same level as had been calculated by the aircraft measurements and was the lowest on 25 July. It increased significantly on the days following, 26 and 27 July.

Maps 03.06.8 and 03.06.9: Results of the Photochemical Simulation Calculation

In **Map 03.06.8 (Calculated Near Ground Ozone Concentration)**, a simulation of the ozone distribution in Berlin and greater parts of Brandenburg using the photochemical dispersion model REGOZON is shown for 25 July 1994, 4:00 p.m. CET (c.f. Mieth and Unger 1993). All available meteorological data and emission information about as many relevant pollutants as possible was taken from the Berlin and Brandenburg emission cadastre to try to generate a computer model of the complicated chemical and meteorological processes. This has the advantage, providing that the

simulation is sufficiently correspondent with reality, that different emission scenarios can be simulated under exactly the same conditions to test their effects on ozone reduction.

Date	23 July	24 July	25 July	26 July	27 July
Windward	120 - 135	130 - 150 (1:00 p.m.) 130 - 140 (4:00 p.m.)	160 - 180	180 - 205	150 - 180 (outskirts) 200 - 210 (city)
City (Residential Areas)	140 - 150	140 - 150	140 - 170	170 - 195	180 - 210
LEE	180	170	200	230 - 255	230 - 250
Growth (rel. to windward)	42%	21% (1:00 p.m.) 26% (4:00 p.m.)	18%	26%	37% (outskirts) 17% (city)

Tab. 2: Level of Measured Near Ground Ozone Concentration from 23 to 27 July 1994 given in $\mu\text{g}/\text{m}^3$

As Map 03.06.8 shows, the highest afternoon ozone values in Brandenburg have been calculated for Northwest of Berlin. In Berlin only the northwestern boroughs of Spandau, Heiligensee and Frohnau are effected by increased ozone concentrations. In contrast, areas with significantly higher emissions (esp. the city center) exhibit significantly lower ozone levels during the entire simulation. Altogether, the 25 July also shows a visible ozone producing potential caused by emissions in the area under investigation. The calculated background concentrations lie between 160 and 180 $\mu\text{g}/\text{m}^3$. The position of the calculated ozone vane as well as the calculated levels in the vane in the afternoon coincide well with observations. The breadth of the vane is somewhat underestimated (c.f. Map 03.06.5 with 03.06.8).

Scenarios

The emission reduction for the scenario calculation was oriented on measures and effect prognoses which, according to then current planning, could have been implemented for acute measures in the context of a summer smog ordinance.

The reductions which could have been obtained for the various polluter groups are shown in Table 3.

	VOC	NO _x
Power stations and industrial plants	10%	10%
Small business and small industrial plants	15%	15%
Households	5%	5%
Motor vehicles - moving traffic	47%	40%
Motor vehicles - stationary traffic	26%	-
All polluter groups	27%	32%

Tab. 3: Emission Reductions for Individual Polluter Groups in Percent

The effect of an emissions reduction by approx. 30 %, as difference between the calculated concentrations in the scenario and real case, is shown in **Map 03.06.9 (Difference in the OX Concentration $\text{OX} = \text{O}_3 + \text{NO}_2$)**. The result is a significant decrease in ozone load in the conurbation's outgoing air vane of up to 15 $\mu\text{g}/\text{m}^3$, resp. of about 7 %. In the Berlin city center, the ozone concentration increases a little bit above the background load level. Since the city center is subject to heavy NO emissions from motor vehicle traffic, which in turn reacts with the ozone to form NO₂, the ozone concentration drops relative to the background load in the reference run. Nonetheless, the sum of oxidants OX ($\text{OX} = \text{O}_3 + \text{NO}_2$) generally increases. To assess the effect of the measures, the difference between the OX concentrations in the scenario and reference run are shown in Map 03.06.9. This makes it possible to recognize an improvement in the air by means of a reduced oxidant load in the especially polluted Berlin city center.

The same simulation of conditions on the last day of the campaign (27 July 94) yields a somewhat greater reduction in the ozone maximums by 10 % in the leeward area of the city. If one calculated the size of the area with the concentrations above 180 $\mu\text{g}/\text{m}^3$ ozone for reference and scenario cases, then there is a quite respectable reduction of 60 % on 25 July. Since there was a high pollution level of nearly 180 $\mu\text{g}/\text{m}^3$ on 27 July (c.f. Fig. 9 and Tab. 2) which could not have been effected by the measures in the region, the reduction in the area with ozone levels exceeding 180 $\mu\text{g}/\text{m}^3$ was only marginal.

Measures to Protect the Stratospheric Ozone Layer and to Reduction of the Near Ground Ozone Load

High near ground concentrations are a great wide-area problem in central Europe. The measurements and simulations from the FluMOB project and similar activities in other federal states (c.f. LAI 1996) show that high ozone peaks have been reached on a few days of the year leeward of the larger conurbations. These lie between 15 and 40 % above the wide-area ozone load. Temporary regional measures during an ozone alarm can help to reduce the regional extra production if a drop in the emissions of ozone precursor substances (nitrogen oxide and hydrocarbons) has reached at least 20 %. However, the area in a larger conurbation subject to such measures must include all the areas of neighboring conurbations in order to take into account regional transport. This makes the approach realized in the Ozone Law (§ 40a BImSchG) really sensible: namely, to declare ozone alarm normally for a larger region. An ozone reduction, which should avoid exceeding the EC-wide valid threshold values, requires nonetheless a combination of wide-area and regional measures which include at least a one third reduction in the emission of ozone precursor substances. This requires a concept which agreed at national and European levels.

To prevent the **thinning out of the ozone layer in the stratosphere** globally or to limit it, reduction of the CFC emissions and the decrease in air traffic in the stratosphere must be striven for as fast as possible. A first attempt, as part of the Montreal conference of 1987, proved unsuitable because of its excessively long time limits for ending emissions and its abundant exceptions. At the follow-up conferences in 1990 and 1992 in London and Copenhagen, a production stop could be agreed for most CFC compounds by the turn of the millennium. Within the European framework, this has already taken place. Until 2015, there are exceptions for partially-halogenated substances which have a reduced ozone-destroying potential. It is decisive for the global reduction of chlorine and bromine emissions that the developing and newly industrialized countries can be convinced to quickly discontinue their not insignificant CFC and halon production capacity and that they receive the financial aid and support for the production of substitutes.

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