

## Review

# THE TROPOSPHERIC OZONE PROBLEM

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Derived from measurements it has been concluded that in the last hundred years the ground-based ozone concentration has risen by about a factor of two. Models also show a doubling of the tropospheric ozone content due to human activities. It is very likely that mean ozone concentration will further increase. In contrast, episodes with excess ozone levels ("summer smog") have become rare in Central Europe during the last five years. This controversial finding is explained by the reduction of  $\text{NO}_x$  (being the "catalyst" in ozone formation) as well as of reactive ozone precursors like non-methane volatile organic compounds (NMVOC) due to catalytic converters in motor cars. On the other hand, a further increase of methane emissions and probably carbon monoxide is responsible for regional and even global background increase of ozone. The principal formation mechanisms are well understood, despite some open questions concerning the contribution of specified organic substances, especially from biogenic sources. Less known, however, are chemical sinks, especially heterogeneous processes. A better knowledge of these processes may influence the global ozone budget by up to 30 % and the regional/local even more. The key question considering ozone abatement is that for determining precursors in time and space. Air quality control has also to consider the question of ozone impact on vegetation, animals and man. Moreover, ozone also contributes to the greenhouse effect. Air pollution control, based on ecological and economic principles, needs a complex understanding of the atmosphere and its interaction with the biosphere. Measures should not be focused on single pollutants, but on impacts, which always have complex causes. Only quantified impacts with consequences unaccepted by society may be a problem.

**KEY WORDS:** *air pollution, atmospheric chemistry, concentration variation, emission abatement, human health, summer smog, vegetation injures*

Ozone was first found in 1840 by the German chemist *Schönbein* (1), but was first identified as  $\text{O}_3$  (by *Olding*) in 1861. However, the characteristic odour combined with lightning has already been known since antiquity and had been named "sulphuric odour". In 1786 *Marum* was the first who identified this "odour" (the later derived name ozone is based on Greek  $\text{o}\xi\epsilon\text{i}\nu$  = smell). *Linus Pauling* was the first to suspect the triangular structure in 1932. In 1933 *Hetter* suggested an angular structure. Only in 1948 was the bonding structure explained by quantum chemistry by *Dewar*.

As early as over 130 years ago scientists expressed from teleological point of view - despite any knowledge of other chemical trace species in the atmosphere

- that ozone may have an important function in maintaining nature, regardless of its small concentration (2). In the early 19<sup>th</sup> century, apart from oxygen and nitrogen as main constituents of air,  $\text{CO}_2$  (carbonic acid), ammonia and  $\text{NO}_x$  (nitrous acid) were considered as permanent minor species. *Schönbein* introduced a detection method, based on paper penetrated by KI solution and dried afterwards, which, however, showed a number of interferences with water vapour and other oxidising species. *Schöne* had already shown this in 1880. *Fonrobert* (3) made millions of ozone "measurements" in the 19<sup>th</sup> century, which only had qualitative characteristics. However, even the very early "measurements" make it possible to draw plausible conclusions on diurnal and seasonal cycles.

Ozone has been measured for more than 100 years, based on physical (in the 1870s spectrometric by *Day*, *Chappuis*, *Hartley* and *Schöne*) and later physico-chemical methods (fluorescence measurement was first introduced by *Konstantinova-Schlesinger* (4) in Russia at the end of the 1920s). We now believe that its concentration has risen by a factor of around 2.5 in the lower troposphere of the northern hemisphere and by a factor of 2 since 1950 (5).

Germicidal and bleaching properties of ozone have been found in the 1880s. In 1898 Siemens and Halsky Co. near Berlin established the first water plant, where ozone was used for sterilisation. At the beginning of the 20<sup>th</sup> century ozone was also proposed for application in the improvement of air quality (!). By that time however, its negative impact on domestic animals had already been described (lethal dose 15-20 ppm). *Sigmund* found that ozone damages plants in 1905. From the 1920s onwards, numerous investigations have been conducted on the ozone impact on humans [cf. (6)]. It follows that, pure ozone can have a harmful effect on humans in concentrations >20 ppm (in case of pollution with NO<sub>x</sub> the threshold is decreasing to 1 ppm), whereas the lethal dose was determined at the concentration of 1000 ppm (about 0.1 %); a permanent stay in Röntgen (X-ray) laboratories, where up to 1.25 ppm O<sub>3</sub> have been measured, did not show any effects. Modern clinical studies over the past 20 years have shown [cf. (7)] that reversible effects (irritations) can be detected only at levels >200 ppb.

In 1944, plant injuries were reported in the Los Angeles area, which for the first time were not related to "classical" pollutants (like SO<sub>2</sub> or fluorine compounds). Only a few years later, *Haagen-Smit* and *Fox* (8) made automobile exhaust gases responsible for ozone formation, which were then considered as the impact species. Since that time, ozone has been regarded as the key species for the oxidation capacity of the atmosphere, and ozone episodes and summer smog became highly relevant environmental issues. In the 1970s, unexplained (and therefore later called "new-type") forest damages were observed in Germany (9), which were mainly attributed to ozone [e.g. (10)]. Many facts, however, suggest that other factors and species (e.g. hydrogen peroxide) could have had a predominant role (11). However, the present large-scale annual mean ozone concentration of 35 ppb already lies within the range of suggested threshold for conifers.

Ozone has also been identified as a greenhouse gas. The Intergovernmental Panel on Climate Change (IPCC) (12) assessed the increase of total tropospheric ozone since 1950 to 36 %, resulting in positive climate forcing of + 0.35 W m<sup>-2</sup>.

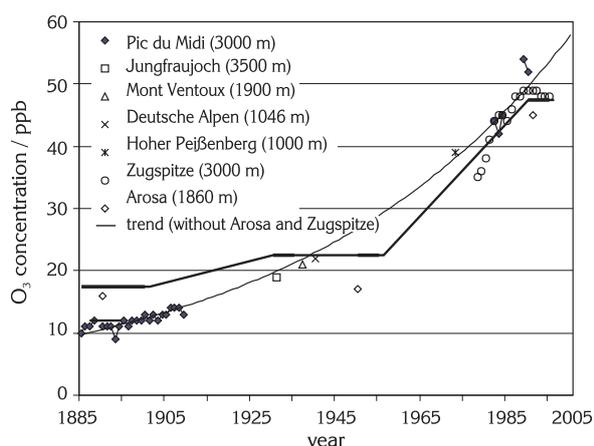
There is no doubt that the increase in tropospheric ozone concentration is the result of human activity. Observations in the last 20 years show that ozone has increased about 1 % per annum in the northern hemisphere (13). In the German Democratic Republic, ground-based ozone increased by 2 % per annum between 1955 and 1985 (14). With the beginning of the 1990s, different ozone trends were observed at different German stations. Some stations (e.g. Mt. Zugspitze) showed stagnating ozone concentrations whereas other stations (e.g. Bayreuth forest, Mt. Brocken) showed further increase in the annual mean ozone concentration. It is obvious that the number of episodes with excess ozone (>90 ppb) decreased significantly. Since 1998 no ozone values over 100 ppb have been measured at any German station (15). On the other hand, all measures to reduce precursors (CO and NMVOC, NO), especially by the application of catalytic converters for automobiles, have not reduced the average ozone concentration.

Ozone impact on man has also been assessed to be inconsistent. Present knowledge suggests that ozone concentrations much higher than 100 ppb show negative influences on individuals. Despite large differences in the ozone threshold for different plants, vegetation seems to be much more sensitive, but the effects cannot yet be quantified. Apart from ozone, there are other photo-oxidants with potentially much stronger toxic effects to be considered. These substances (e.g., aldehydes, organic N compounds, peroxides), however, show complex relationships to ozone, and have different formation pathways. It is therefore a mistake to attribute oxidative stress effects to ozone alone.

This paper seeks to present a critical assessment of the ozone issue, based on the current state of knowledge. We present a new budget estimation of sources and sinks, whereas chemical and transport processes have been taken into account only phenomenologically.

#### *The historical increase of ozone*

The curve given by *Marenco et al.* (16) is well known (Figure 1). Its exponential increase is very significant ( $r^2=0.97$ ), showing annual increase of 1.54



**Figure 1** Historical trend of ozone. Trend line from (16), thick line based on additional data from Arosa (5) and Mt Zugspitze (39)

%. However, there have been some critical discussions due to the fact that data from different sites and various altitudes have been included in this diagram. Some additional values are now introduced in this diagram from Arosa and Zugspitze, suggesting that there is no continuous exponential slope over the entire period. There is also some belief that the old data from Pic du Midi are too low. Values around 10 ppb and less were typical for urban areas at the sea level (known from Paris and Moscow around 1900). Generally, strong vertical dependence of ozone concentration has to be taken into account (see next section). It can be seen from Swiss data (5) that ozone concentrations may have risen by a factor of 2.5 in the last century (Table 1), which is also supported by global models (Table 2). Other, widely known ozone data from the

Soviet Union (4, 17), measured in Moscow and in the Caucasus Mountains, support ozone figures in the lower mountain region between 20 and 30 ppb for the 1930s (also see Figure 4). We therefore assume that there has been a stepwise increase shown by the thick line in Figure 1 with periods of increase (1905-1930, 1950-1990) and periods of stagnation in between. The first period of increase, however, was probably very short. Thus, similar to other "classical" air pollutants SO<sub>2</sub> and NO<sub>x</sub>, ozone significantly rose after 1950. The following values can be taken as typical for the altitudes of 2000±1000 m a.s.l.:

- 1885-1900 15-20 ppb
- 1930-1935 20-25 ppb
- 1950-1955 20-25 ppb
- 1990-1995 45-50 ppb

The first European ozone long-term measurements started in Wahnsdorf near Dresden (former observatory of the Weather Service) in 1952 (Figure 2). The measurement method was based on iodometry with strong interference due to SO<sub>2</sub>. Thus between 1952 and 1971 a "constant" O<sub>3</sub> concentration of 8±2 ppb was registered due to increasing SO<sub>2</sub> concentrations. Only the data of 1967, when SO<sub>2</sub> remained constant, and data since 1972, when a pre-filter was introduced, may be considered representative. The following regression is valid for the mean summer season figure (in µg m<sup>-3</sup>):

$$[O_3] = 38.9 \mu\text{g m}^{-3} + 1.4 \mu\text{g m}^{-3} \text{ a}^{-1} (a - 1974) \quad (1)$$

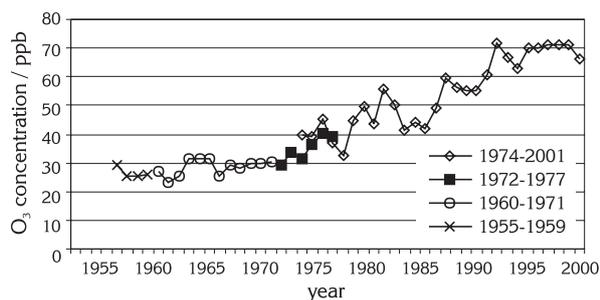
(r<sup>2</sup> = 0.80; a = 1974...2001)

**Table 1** Ozone concentration in different periods and seasons in the surroundings of Arose (Switzerland), (5)

Period	Winter (ppb)	Summer (ppb)	Increase (ppb)	Increase factor	Summer/winter ratio
1889-1891	~15	15-20	-	-	1.2
1950-1951 and 1954-1958	10-12	20-25	5	1.3	~2
1989-1991	35-40	45-50	25	2.2	1.3

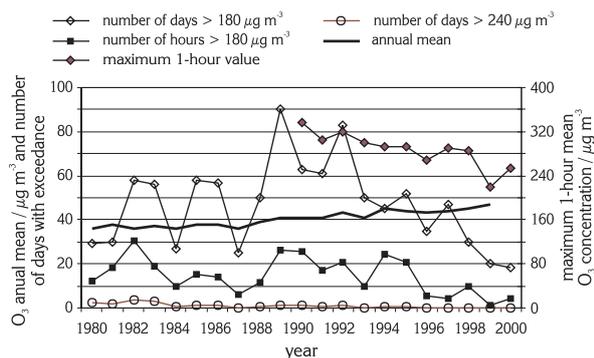
**Table 2** Global tropospheric ozone sources and sinks (Tg a<sup>-1</sup>)

Process	Sources		Sinks			
	(31)		(23)	(31)		(23)
	Present	Pre-industrial	Present	Present	Pre-industrial	Present
Photochemistry	3940	1780	4100	3120	1630	3700
Stratosphere	480	480	400	-	-	-
Dry deposition	-	-	-	1300	670	800
Total	4420	2260	4500	4420	2300	4500



**Figure 2** Trend of ozone at Radebeul-Wahnsdorf (near Dresden); iodometric method according to Cauer without filter (1956-1959 corrected by factor 4.1 and 1960-1971 by factor 1.74), modified method with SO<sub>2</sub> filter 1972-1977, iodometric method according to Herrmann 1978-1990, fluorescence method since 1991 [Küchler W. Personal communication. Wahnsdorf, Saxonia: Landesamt für Umwelt und Geologie (State Agency for Environment and Geology);2001]

With the beginning of the 1990s, some stations showed no further O<sub>3</sub> increases (for example Wahnsdorf in Figure 2). The number of days with high ozone concentrations (exceeding thresholds of 180 and 240 μg m<sup>-3</sup>) significantly decreased (Figure 3) in Germany. This coincides with the reduction of some precursor emissions (NMVOC and NO). However, it seems that there are differences between seasons and site locations (background, rural, urban). In the Netherlands between 1992 and 2000, the 90th percentile decreased in summer by 1.1 ppb per annum and increased in winter by 0.26 ppb per annum (18). We found similar evidence on Mt Brocken (19) (Figure 6).



**Figure 3** Number of days and sums of hours with excess ozone (>180 and 240 μg m<sup>-3</sup>, resp.) for at least one station in Germany; annual mean of all stations and maximum 1-hour value (number of stations in 1990: 201, in 1999: 368), from (39, 40, 24)

In assessing ozone levels between different sites and different periods, it is essential to take into consideration the “typical” variation of ozone with altitude, season and daytime, which is discussed in the following sections.

### Ozone dependence on altitude

In general, ozone concentrations increase with altitude. In the first few hundred meters (within the mixing height), strong diurnal variation (see next section) may lower the mean figure (daily average). Thus, Kley *et al.* (20) suggested to select the ozone concentrations averaged around noon for the comparison of summer data from different stations. These authors found a linear regression between altitude  $z$  (0.9 - 2.4 km) and ozone concentration (in ppb):

$$[\text{O}_3] = 44.0 \text{ ppb} + 3.8 \text{ ppb km}^{-1} \cdot z \quad (2)$$

( $r$  = unknown;  $z$  = altitude in km)

An increase in concentration with altitude has been known for many years. From Swiss data (5) it follows

$$[\text{O}_3] = 41.7 \text{ ppb} + 5.0 \text{ ppb km}^{-1} \cdot z \quad (3)$$

( $r^2 = 0.99$ ;  $z$  = altitude in km)

that between 0.8 and 3.5 km there is a somewhat stronger increase with height. Historical data show a much stronger gradient  $d[\text{O}_3]/dz \approx 11 \text{ ppb km}^{-1}$ . This is because of missing anthropogenic ozone production in the lower troposphere, i.e. the Earth's surface acts as a sink (via dry deposition) and the upper troposphere as a source (O<sub>3</sub> downward transport from the stratosphere). Data from the former Soviet Union (Figure 4) for the mid-1930s result in the equation ( $z = 0.1 - 14 \text{ km}$ ):

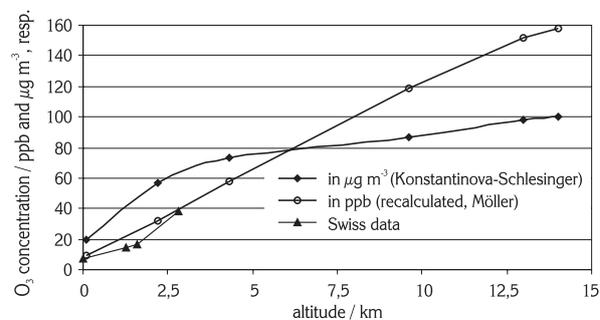
$$[\text{O}_3] = 9.5 \text{ ppb} + 10.9 \text{ ppb km}^{-1} \cdot z \quad (4)$$

( $r^2 = 0.99$ ;  $z$  = altitude in km)

Remarkable is the same gradient in the Swiss data from the 1920s (see also Figure 4):

$$[\text{O}_3] = 3.5 \text{ ppb} + 11.0 \text{ ppb km}^{-1} \cdot z \quad (5)$$

( $r^2 = 0.90$ ;  $z$  = altitude in km)



**Figure 4** Ozone in dependence of altitude (historical data). Former Soviet Union: Moscow (100 m), Elbrus 2200 m and 4300 m and aircraft above Elbrus at 9620, 13000 and 14000 m (3, 17); Swiss data: Geneve 200 m, Zermatt 1650 m, Rochers de Naye 2045 m and Gornergrat 3200 m (6)

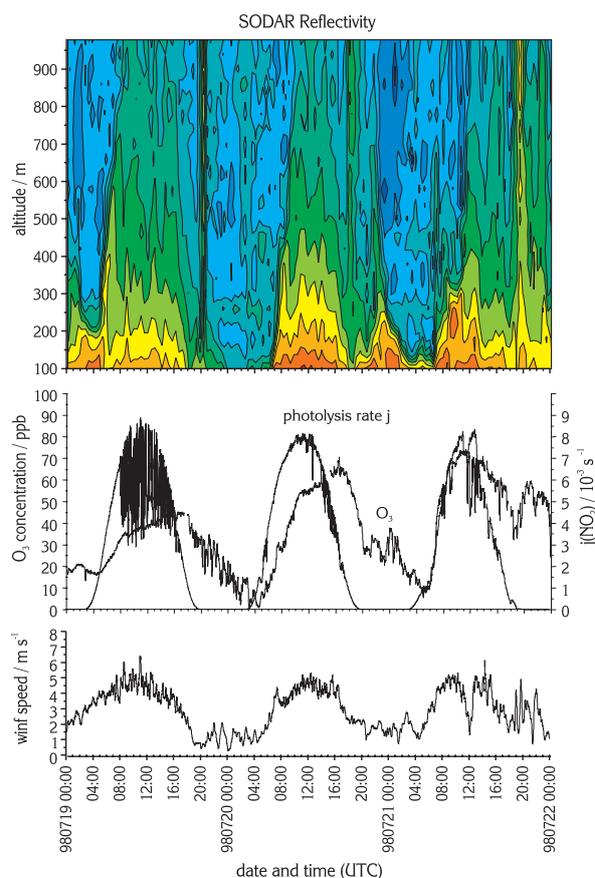
It does not seem reasonable to derive an ozone concentration value for  $z=0$  from these equations, which would be too high for the present time (Eqs. 2 and 3) and too low for the period before World War II (Eqs. 4 and 5). Such relationships are valid only within the given range of altitudes. The equations clearly show how the anthropogenic ozone formation in the lower troposphere, reduces the vertical concentration gradient but increases the concentration.

### Ozone time dependencies

Any ozone variation in recurring time periods (day, year) is caused by secondary interrelations between the source, as well as transport processes and time. It is important to study these time dependencies when evaluating trends and comparing different geographic sites. As ozone does not have direct sources from the Earth's surface one has to take into consideration the variations of so-called  $O_3$  precursors, the rate of photolysis (mainly solar flux), meteorological elements and other atmospheric properties influencing horizontal and vertical air mass transport.

### Diurnal ozone variation

A "typical" diurnal ozone variation coincides with the intensity of solar radiation whereas the maximum is shifted towards afternoon (Figure 5). However, daily photochemical local ozone production amounts to only a small percentage of the daytime maximum concentration. We found that vertical transport processes determine the diurnal variation, which is significant only on sunny and slightly overcast days. The daytime maximum  $O_3$  concentration is the result of a well-mixed boundary layer. In summer, the maximum net photochemical  $O_3$  production is around 15 ppb per day; the ozone formation rate is proportional to the photolysis rate, assuming that there is no variation in precursors (NMVOC). Thus,  $O_3$  photochemical production shows a maximum at noon. The diurnal variation, however, represents the budget (sources-sinks). At night (no photochemical production),  $O_3$  is removed by dry deposition and chemical reaction with  $NO_x$ . In case of nocturnal inversion layer, no ozone transport from the residual layer (above the mixing height) occurs and, consequently,  $O_3$  concentration is decreasing (even to zero in urban areas). After the sunrise, the inversion layer breaks up and  $O_3$  is transported down by vertical mixing. Figure 5 clearly shows the correlation between the fine structure of  $O_3$  concentration and SODAR (Sonic Detection and



**Figure 5** Diurnal variation of ozone (ppb), photolysis rate of  $NO_2$  ( $10^{-3} s^{-1}$ ), wind speed ( $m s^{-1}$ ) and SODAR back scattering signal (in dependence of height above ground) during the BERLIOZ measurement campaign at Eichstadt near Berlin (19-22 July 1998)

Ranging) reflectivity, representing the atmospheric stability. Additional, photochemical production is increasing. After reaching the maximum (which represents the state when sources equal sinks) in the late afternoon, the inversion layer builds up again (no more vertical  $O_3$  mixing in) and finally dry deposition and surface-based chemical reactions reduce the ozone concentration. Thus, vertical transport is dominant in determining the diurnal variation and, consequently, wind speed and temperature (again linked with radiation) are key meteorological parameters showing a correlation with  $O_3$ .

### Seasonal ozone variation

Similar to diurnal variation, seasonal variation is driven by photochemical ozone production with a maximum in summer. The winter minimum represents reduced photochemical activity (Figure 6), but also possible chemical ozone depletion (see chapter Ozone depletion). As seen in Figure 6, daily variation may

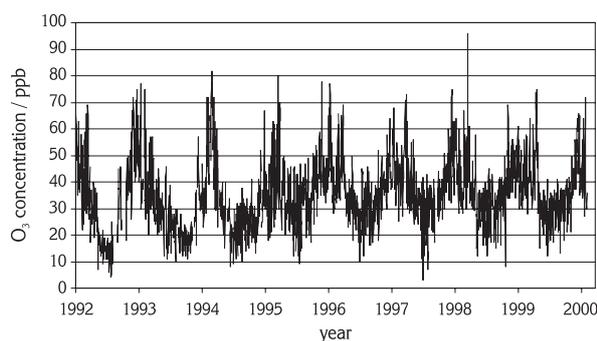


Figure 6 Ozone variation at Mt Brocken (Harz, 1142 m a.s.l.) between 1992 and 2000 based on daily means

even be larger due to changes of air masses with different characteristics in ozone production and depletion. Differences from year to year depend on a large-scale weather situation as well as on varying stratosphere-troposphere exchange processes (STE), the main source of tropospheric ozone.

In spring 1993 an ozone maximum concentration was observed on Mt Brocken (Figure 6) due to enhanced stratospheric  $O_3$  intrusion. This stratospheric ozone often reaches a maximum in spring and has been made responsible for the maximum in annual ozone variation found in the northern hemisphere (21, 22). Modelling has also shown (23) that this maximum, also found in remote areas outside the tropics, is a result of stratospheric  $O_3$  (which is transported in late winter into the troposphere) and photochemical  $O_3$  production in the free troposphere (with a maximum in spring).

This may also be explained by seasonal variation of the tropopause height (Fiedler F. Personal communication. Karlsruhe: Institute for Meteorology and Climatology; 2002) with its minimum in January. With increasing tropopause height after January, vertical mixing gives rise to ozone transport downwards (surface ozone maximum originated), and finally the same amount of (column) ozone is distributed within a higher troposphere resulting in lower near-to-surface concentrations (seasonal minimum).

The summer of 1994 (and likely 2003) was showing the highest  $O_3$  concentrations all over Europe due to several "summer smog" episodes. Again, mean  $O_3$  concentration correlates well with mean temperature (25). From the air pollution point of view only tropospheric ozone production is of interest; transport processes may not be influenced by humans. The seasonal amplitude being the ratio of summer to winter concentrations represents a measure for annual photochemical ozone production (neglecting possible seasonal ozone sink variation). In the past (i.e.

before 1950s), seasonal ozone variation was small. Considering the  $O_3$  concentration as an expression of the source-sink budget, even the summer-winter ratio must be a sensitive parameter. It also depends on altitude, showing a characteristic increase with height (Figure 7). It is remarkable that annual variation - with the exception of Mt Brocken - is negligible (at lower altitudes, however, it increases). It suggests that the amplitude represents a (chemical) climatic element. The exceeding of the ozone seasonal amplitude at Mt Brocken before 1995, and the continuous decrease since the beginning of observation in 1992, has been explained by atypical low winter values due to heterogeneous ozone destruction (26, 19). Thus, the changed emission scenario which in the 1990s in Central Europe changed the "chemical climate" reflected here in a decreased ozone depletion potential. Figure 6 clearly shows the increase in ozone winter minimum after 1994.

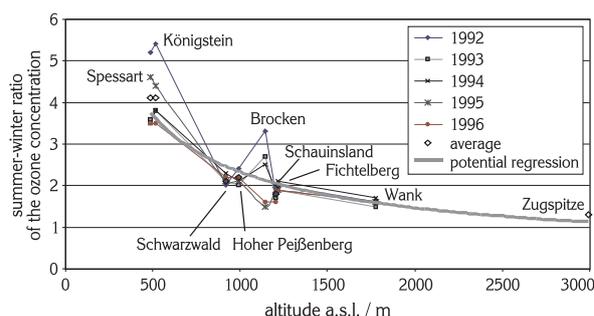


Figure 7 Dependence of ozone summer-winter ratio (seasonal amplitude) on altitude for German mountain stations and different years. Thick line shows mean regression  $y=227.3 \cdot x^{-0.66}$  ( $r^2=0.92$ )

#### Sources and sinks of ozone: budget discussion

Basically, at a given site the ozone concentration may have two different sources. The first is the local *in-situ* photochemical formation and the second is the *on-site* transportation (vertical and horizontal) of ozone. Local sinks of ozone are dry deposition (irreversible flux to the ground) and chemical reactions in the gas phase, on aerosol particles and in droplets. Air masses have different formation and destruction potentials of ozone. Depending on the type of air mass, the past and the fate of ozone (in relation to the site) may be characterised by production and/or destruction (positive or negative budget). With changing air masses, the ozone level may also drastically change.

The atmospheric ozone residence time which depends on sink processes alone is extremely

variable. It amounts from a few days near ground to several months in the upper troposphere. Thus, ozone may be transported over long distances in the free troposphere. The advective transport to a receptor site is therefore an important source of local ozone. Breaking down of the morning mixing layer may increase ozone by 20-30 ppb within 2-3 hours, which is much more than *in-situ* chemistry may produce. Short-time ozone peaks might be related to vertical transport from upper layers (27). Ozone is stored within the residual layer, mostly between 1 and 2 km altitude levels. The vertical ozone profile is very non-homogeneous and is changing at short time intervals, as we observed using lidar sounding (28). In sum, the major source of local ozone is the photochemical production at other places, i.e. during transportation of air masses with ozone formation potential. The area needed for this process may have a horizontal extension between several hundred and a few thousand kilometres.

#### Photochemical formation

Chemical formation principally occurs via reaction between  $O(^3P)$  radicals and  $O_2$  molecules. The only known sources of  $O(^3P)$  in the troposphere are the photolysis of  $NO_2$  and  $O_3$  itself. Due to fast photolysis of  $O_3$ , photostationary equilibrium is reached without net production of  $O_3$ . Only the presence of components which are able to transform OH into  $HO_2$  [e.g. volatile organic compounds (VOC), CO, but also  $SO_2$ ] may lead to a net production of  $O_3$ , where one molecule of CO produces one  $O_3$  whereas one VOC produces two molecules of  $O_3$  within an ideal cycle (Figure 8).

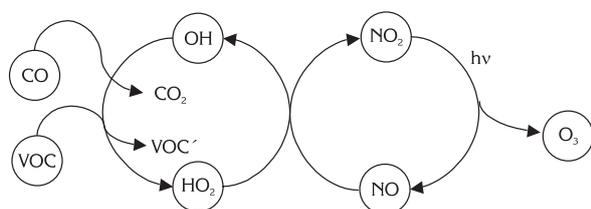


Figure 8 Photochemical ozone cycle:  $NO_x$  being "catalyst", and VOC and CO being precursors ("fuels")

With or without the presence of very little NO (< 10 ppt), ozone will be destroyed via reactions between  $O_3$  and OH as well as  $HO_2$ . This destruction process is relatively slow (residence time about one month).

From the point of view of air pollution control, it is necessary to consider the ozone formation potential (production rate)  $P(O_3)$ . As in each chemical reaction system, it depends on the rate-limiting step in the

overall system. Thus, it does not make any sense to define the  $NO_2$  formation and subsequent (fast)  $NO_2$  photolysis as  $P(O_3)$ ; Volz-Thomas *et al.* (29) define this rate as *in-situ* ozone production:  $P(O_3) = k[NO][HO_2]$ . Hough and Derwent (30) define the attack of precursors (VOC, CO) by OH as rate limiting. Due to the extremely low reaction rates between  $CH_4$  and OH (residence time 7.9 years),  $CH_4$  is separated from VOC. NMVOC have a significantly shorter residence time ( $\tau = 1/k_{OH}$ ): alkanes about 1 week, alkenes and substituted aromatics a few hours. It follows that

$$\Delta(O_3) = (k_1[CO] + k_2[CH] + \sum k_4^i [NMVOC]) [OH] \quad (6)$$

where  $k_1 = 2.4 \cdot 10^{-13}$ ,  $k_2 = 6.86 \cdot 10^{-15}$ , and  $k_4$  is varying with a maximum about  $10^{-11}$  (all in  $cm^3 \text{ molecule}^{-1} s^{-1}$ ). Thus, taking mean concentrations into account, contributions to  $P(O_3)$  are 0.5-2.0 ppb  $d^{-1}$  due to CO and 0.5 ppb  $d^{-1}$  due to  $CH_4$ . Consequently, these rates are too small to be responsible for excessive ozone concentrations during "summer smog" episodes which show an ozone increase of up to 15 ppb  $d^{-1}$ . Global models (23) show an ozone production between 1-5 ppb  $d^{-1}$ , depending on season and location.

This photochemically produced ozone - we call it *hot ozone* - is a result of much faster NMVOC oxidation. Figure 9 shows a typical "summer smog" episode. Despite the diurnal variation at the lowland station near Berlin, the Mt Brocken station (1142 m a.s.l.), which is situated about 300 km to the southwest, shows the same slope, suggesting that such episodes occur on mesoscales. The daily increase between 10 and 15 ppb has been observed at many other sites in Europe [e.g. (31)]. Local accumulation is only possible

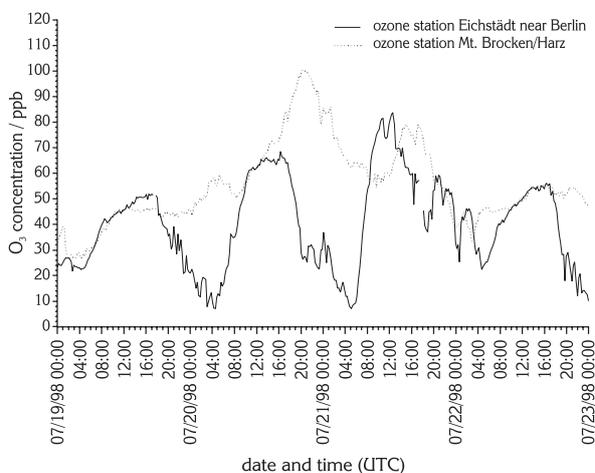


Figure 9 Diurnal variation of ozone at Eichstadt near Berlin and at Mt Brocken (Harz) during the BERLIOZ measurement campaign (19-23 July 1998)

when sources dominate over sinks of ozone, which needs a homogeneous air mass with characteristic time >24 h, i.e. about 300 to 500 km when wind speed is between 3 and 6 m s<sup>-1</sup>. That is the reason why local measures (e.g., traffic lights, and speed limits) can never influence the local O<sub>3</sub> concentration.

Methane is the main source of tropospheric ozone (23, 30). We call that *base ozone* or background (residual) ozone. Thus, it is clear that *base ozone* (a) increases with the CH<sub>4</sub> emission rate increase of about 1 % per annum (32) and (b) that it is relatively constant in space and time.

It should be noted that biogenic NMVOC - which are probably underestimated in their source strength - play an important role in photochemical O<sub>3</sub> formation, especially in the Mediterranean area. Possible contribution of isoprene and terpenes to the photochemical ozone formation is still unclear. Locally, it has been shown in the USA, during several measurement campaigns, that biogenic emission can control ozone formation even in urban areas [cf (33)].

Ideally, each C atom in NMVOCs is capable of producing two molecules of O<sub>3</sub>. However, many intermediates and reaction products will not be totally oxidised or deposited or oxidized within a NO-poor atmosphere (which means ozone decay). It has been estimated that 40-50 % of all carbon atoms will not produce O<sub>3</sub>. Very probably, CO and CH<sub>4</sub> will totally oxidise into CO<sub>2</sub>. Within the first oxidation step, CH<sub>4</sub> forms formaldehyde (HCHO) which may soon be photolysed (an important source of HO<sub>2</sub> and subsequent OH) and/or oxidised by OH into CO (845 Tg CO or 35 % of the total CO emission) (32). HCHO reacts with OH several orders of magnitude faster than CH<sub>4</sub>. About 50 % of the global photochemical ozone production is related to anthropogenic precursor substances (31), i.e. about 2000 Tg per annum. NMVOC may contribute to this figure by only 10-15 % (200-300 Tg per annum, based on 50 % of 50 % of 800-1200). Model results [23] suggest that ozone concentration in the free troposphere will decline only by 15 % when the model runs without NMVOC. Thus, CO and CH<sub>4</sub> contribute dominantly (80-90 %) to the global ozone tropospheric budget. Already in 1981, it was stated (34) that CO and CH<sub>4</sub> are the "fuels" of ozone formation in the troposphere.

The budget of ozone is given by the difference between sources and sinks

$$\Delta(O_3) = P(O_3) - S(O_3) \text{ transport.} \quad (7)$$

S(O<sub>3</sub>) represents dry deposition and chemical destruction: the transport term may be positive or negative in the sense of incoming (importation) and outgoing (exportation) ozone.  $\Delta(O_3)$  is also called net ozone production, which however, may be negative. We refer to NO<sub>x</sub>-limiting ozone production, when [NO] is <1 ppb. In this situation, P(O<sub>3</sub>) depends linearly on [NO], and not all HO<sub>2</sub> (as well RO<sub>2</sub>) radicals will transform NO into NO<sub>2</sub>. In other words, the stoichiometry (or yield), i.e. ratio between oxidised precursors and O<sub>3</sub>, becomes smaller. For [NO]>1 ppb, the ozone formation is VOC-limiting, i.e. the atmospheric amount of VOC (and CO) determines the number of ozone molecules produced in time.

From modelling and field site measurements it has been estimated that 4-6 molecules of O<sub>3</sub> are produced for each NO (29, 35). For [NO]<1 ppb, the number of produced O<sub>3</sub> increases up to 20 molecules because NO<sub>x</sub> also consumes O<sub>3</sub> via NO<sub>y</sub> formation.

#### Ozone depletion

Beside dry deposition, most models, including global ones, (Table 2) take into account only ozone photolysis and subsequent reactions between HO<sub>x</sub> and O<sub>3</sub>. Photochemical destruction of ozone is very important in the free troposphere, as a global ozone sink of stratospheric origin ([NO] < 10 ppt is the precondition). It is a catalytic process according to the net reaction 2O<sub>3</sub>→3O<sub>2</sub>.

The troposphere also produces O<sub>3</sub> photochemically under natural conditions, since the biosphere (at least the terrestrial) emits NO and NMVOC. This naturally emitted NO is, however, small compared with natural emission of VOCs. Thus, wide areas of the Earth are assumed to have been ozone sinks in the pre-industrial times. Due to a long-range transport of NO<sub>x</sub> and NO<sub>y</sub>, these areas may have now be transformed into ozone source areas. This fact has hardly been considered in models. Moreover, aircraft emission of NO may be rather significant, should it exceed the threshold of NO~10 ppt, and may transform tropospheric areas from those consuming ozone into those producing it. The situation gets more complicated when it is lightning because this emission rate has been but vaguely assessed (5-15 Tg of N per annum). Thus, in the natural atmosphere we observe ozone formation or consumption in dependence of time and space. Other ozone removal pathways are less well described in budget estimates:

- reaction of O<sub>3</sub> with olefins in the gas phase,

- S(IV) oxidation in the liquid phase,
- O<sub>3</sub> decay by radicals in the aqueous phase,
- catalytic O<sub>3</sub> decay on surfaces, especially on aerosol particles

These pathways have been discussed elsewhere (7, 36, 37). The percentage of these removal pathways in the global budget remains speculative. We believe that up to 30 % of the budget (as given in Table 2) may be changed by these processes. Ozone budget on regional and local scales, may even be more influenced. Figure 10 shows all possible chemical reactions in the atmospheric multiphase system consuming O<sub>3</sub>.

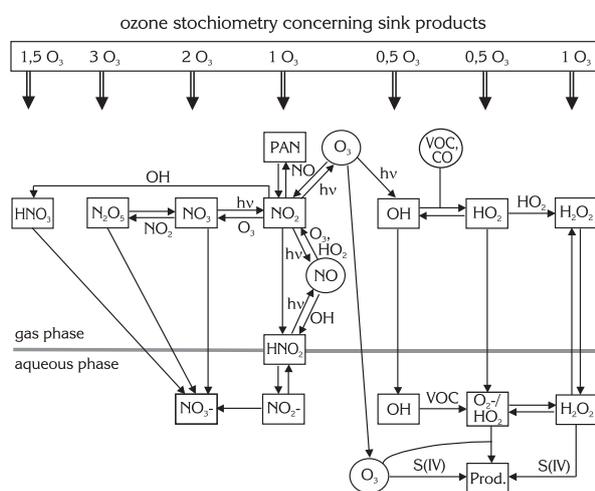


Figure 10 Scheme of chemical ozone removal pathways in the gas and aqueous phase

Clouds may have the most important influence on ozone in the boundary layer. They lead to the following effects:

- reduction of available radiation; i.e. reducing the rate of photolysis below clouds (above clouds

photolytic reactions may be enhanced due to scattering of solar radiation),

- reduction of gas-phase O<sub>3</sub> formation due to scavenging of HO<sub>2</sub> and disturbance of the ozone formation cycle (Figure 7),
- destruction of O<sub>3</sub> in the aqueous phase by different chemical reactions (including dissolved SO<sub>2</sub> and radicals).

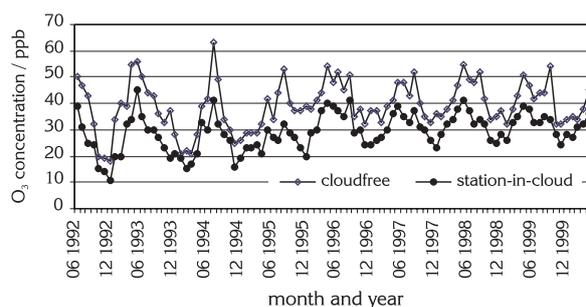


Figure 11 Ozone variations at Mt Brocken (based on monthly means) for periods with clouds and without clouds

On average, clouds reduce ozone by about 30 % (Figure 11). Table 3 summarizes the O<sub>3</sub> statistics at our cloud chemistry monitoring site at Mt Brocken. The reduction of ozone concentration under cloud conditions versus cloud-free conditions is significant (10 ppb in winter and 14 ppb in summer), and corresponds to one third of O<sub>3</sub> concentration under non-cloudy conditions (that does not mean sunny days, but only that the measurements were not taken in a cloud). We call this an O<sub>3</sub> depletion potential of clouds. The summer-winter ratio is constant at about 1.6, suggesting that O<sub>3</sub> destruction is not caused by photochemical processes, but heterogeneous chemical processes. The winter value under non-cloudy conditions represents minimum photochemical production and minimum chemical destruction. In

Table 3 Statistical parameters for summer (15 April – 15 October), winter (16 October - 14 April) and annual mean of O<sub>3</sub>, based on monthly means (1992-1997) at Mt Brocken for "cloud-free" and "cloudy" episodes (ppb), frequency of "station-in-cloud" (%) and liquid water content LWC (mg m<sup>-3</sup>)

	Winter	Summer	Annual mean	Summer/winter ratio
[O <sub>3</sub> ] all events (ppb)	26.3±4	44.0±3	34.2±3	1.7
[O <sub>3</sub> ] cloudfree (ppb)	31.1±5	47.1±2	37.4±4	1.5
[O <sub>3</sub> ] „station-in-cloud” (ppb)	21.1±4	33.5±3	26.8±4	1.6
„station-in-cloud” (%)	59±16	28±10	45±2	0.5
LWC (mg m <sup>-3</sup> )	272±22	272±27	263±63	1.0
Δ[O <sub>3</sub> ] „station-in-cloud” - cloudfree (ppb)	10.0	13.6	10.6	1.4
[O <sub>3</sub> ] „station-in-cloud” / [O <sub>3</sub> ] cloudfree	0.68	0.71	0.72	1.0

other words  $31 \pm 5$  ppb could serve as a reference for the European background ozone concentration, where *hot* ozone (from NMVOC) plays a minor or even negligible role. In other words, this value represents the hemispheric ozone from stratospheric input and methane oxidation. Compared to the winter ozone concentration of 100 years ago (Table 1), the increase factor of 2 is established again. It is very remarkable that winter values of 10-12 ppb from around 1950 (Table 1) were smaller than those in 1900 (15 ppb). It seems reasonable to assume that the NMVOC increase (as well  $\text{CH}_4$ ) was not significant before 1950, in contrast to "classical" pollutants such as  $\text{SO}_2$  and NO. These pollutants, however, essentially show an ozone depletion potential in winter (Figure 10).

#### Mean ozone concentration: contributors

The budget of ozone at a given site (mathematically a point or the smallest grid element of a chemistry transport model) strongly depends on the position on the vertical axis. Meanwhile, it is widely accepted that the free troposphere is the main producer of ozone. In the upper troposphere, mixing occurs between photochemically produced ozone in the lower troposphere with the stratospheric ozone. The boundary layer is the area of effective ozone destruction by dry deposition and heterogeneous processes.

Mt Brocken data indicate that 31 ppb may represent the background ozone value. This idea has been supported by Beck and Grennfeldt (38) who measured an average of  $32 \pm 2.8$  ppb in summer and  $31 \pm 2$  ppb in winter at four European "background" stations (Mace Head, Svanvik, Jergul, Strath Vaich), which all have a small diurnal variation (less than 1.4) and practically no seasonal variation. All these stations are on the most western European edge, which means they are mostly influenced by the sea and little by the continental *hot* ozone. On the other hand, the difference of 18 ppb between summer and winter under cloud-free conditions (Mt Brocken) refers mostly to *hot* ozone (some contribution from  $\text{CH}_4$  and CO can not be excluded). Thus, for long-term investigations and trend analysis it is recommended to take into account winter mountain values concerning background situation as well as summer values concerning NMVOC abatement effect on ozone levels.

It has been discussed in sections above that any ozone concentration represent the budget, that is, the difference between sources and sinks. Measurements

at various stations in Central Europe (38) indicate that the summer ozone production from NMVOC is 10-15  $\text{ppb d}^{-1}$  [ $\Delta(\text{O}_3)$  in Eq. 7], which corresponds to our own estimation of about 15  $\text{ppb d}^{-1}$  (under chemically "ideal" conditions), and that, in winter these values are  $-5$ - $10$   $\text{ppb d}^{-1}$  (depletion). This difference (15-25  $\text{ppb d}^{-1}$ ) directly corresponds to the concentration difference we found at Mt Brocken (18 ppb) between summer production and winter depletion (non-production and destruction).

Summarising figures presented in this paper, we are able to assess different ozone contributors (sources). The mean (annual) background  $\text{O}_3$  concentration for Central Europe (between 1990-2000) is  $32 \pm 3$  ppb, with the following contributions from potential "sources":

- $10 \pm 2$  ppb of stratospheric ozone with small seasonal variation (spring peak),
- $6 \pm 2$  ppb of natural biogenic ozone from natural VOC with seasonal variation (0-12 ppb),
- $16 \pm 2$  ppb of anthropogenic ozone from  $\text{CH}_4$  and CO.

This *base* ozone of 32 ppb shows a seasonal variation between 26 ppb in winter and 38 ppb in summer, where about 50 % is anthropogenic. Additional to the *base* ozone is the contribution of:

- 5 ppb of anthropogenic *hot* ozone from NMVOC with seasonal variation (0-15 ppb) and strong short-term variation (0-70 ppb).

In total, the "typical" European annual mean amounts to 37 ppb (25 in winter and 47 in summer). It is clearly shown that the "acute" problem is *hot* ozone (from NMVOC) which contributed to the long-term averages in the 1990s with only 5 ppb (25 % of anthropogenic contribution and 14 % of total ozone). The "chronic" problem is represented by methane oxidation (and partly by CO) contributing to *base* ozone (50 %). In Germany, and stepwise in all other European countries, the *hot* ozone problem will be solved. The problem of background ozone connected with  $\text{CH}_4$ , will not be solved. The reduction of *hot* ozone has led to constant ozone levels or only minor ozone increases in the 1990s, but in future ozone levels will again rise with the increase in  $\text{CH}_4$  emission.

## CONCLUSION

Ozone as a secondary trace species exists in a non-linear relationship with its processors. Ozone concentration is a result of sources and sinks. The stratospheric  $\text{O}_3$  input into the troposphere is much

smaller (10-20 %) than believed in the earlier decades, and the photochemical tropospheric production is the main ozone source (80-90 %). An indirect and most important locally related source is advective ozone transport. Sinks include dry depositions (1/3) and radical photochemical ozone destruction processes (2/3). Ozonolysis and heterogeneous processes, mainly in clouds, are until now not considered in global budgets. It is likely that cloud processes may modify global ozone budget up to one third. Reactive NMVOC in industrial and urban areas are responsible for ozone peak levels and excess concentrations. In addition, anthropogenic emissions of SO<sub>2</sub> and NO in industrial areas may largely contribute to ozone formation and destruction. Methane and CO may exclusively be responsible for a long-term increase in tropospheric ozone levels. Ozone formation from these precursors is a very slow process and cannot explain high ozone levels and growing rates of up to 15 ppb d<sup>-1</sup> found during "summer smog" episodes. This increase, however, is not based on net production but mainly on lower ozone sink capacity in special weather conditions. There is no doubt that limitations imposed on NMVOC emission will lead to a decrease in the number of days with excess ozone levels (> 90 ppb). Because the emission of less reactive ozone precursors (mainly CH<sub>4</sub>) has been and will further be increasing, the mean ozone level will not be going down (as may have been expected as a result of the introduction of catalytic converters in the "western world"). Moreover, without global CO and CH<sub>4</sub> emission abatement the mean ozone concentration will rise even more. Not even a drastic reduction of NMVOC will particularly affect the mean ozone level. The only "positive" effect, however, can be seen in reducing fast ozone production and in lowering the frequency of summer smog episodes. From an impact point of view it is however questionable, whether this effect is sufficient, even "positively" taking into account the economic expenses.

Judging from the present knowledge, ozone in the troposphere may be harmless to humans. Its impact on vegetation requires further research. It is likely that ozone-related impact (oxidative stress) is mainly caused by peroxides. When it comes to a comprehensive impact assessment, it is still open which ozone level or concentration-time behaviour may be tolerated. Scenarios for ozone control can be developed only if an impact-related approach is adopted (as opposed to the approach focused on concentration alone).

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## Sažetak

### TROPOSFERSKI OZON

Mjerenja su pokazala udvostručenje koncentracije prizemnog ozona tijekom posljednjih stotinu godina. Primjena modela pokazala je udvostručenje koncentracija ozona u troposferi kao posljedice ljudskih aktivnosti. Srednja vrijednost koncentracije će vjerojatno i nadalje rasti. Nasuprot tomu, epizode povišenih koncentracija (ljetni smog) u Srednjoj Europi postale su rijetke tijekom posljednjega petogodišnjeg razdoblja. Objašnjenje te pojave pronađeno je u sniženju koncentracije NO (koji je katalizator pri stvaranju ozona), kao i sniženju koncentracija prekursora ozona poput NMVOC (nemetanskih hlapivih organskih spojeva), što je posljedica uporabe katalitičkih konvertera motornih vozila. Porast pozadinskih koncentracija (background concentrations) na regionalnoj i globalnoj razini posljedica je daljnjeg povećanja emisija metana i vjerojatno ugljikova II oksida. Osnovni mehanizmi stvaranja ozona su dobro poznati, no još nije dovoljno razjašnjena uloga nekih specifičnih organskih spojeva podrijetlom iz biogenih izvora. Manje su međutim poznati mehanizmi nestajanja/razgradnje ozona, osobito u obliku heterogenih procesa. Bolje poznavanje navedenih procesa moglo bi pridonijeti do približno 30% sniženja sadržaja ozona u zraku na lokalnoj ili regionalnoj razini. Ključ za rješavanje problema ozona je poznavanje vremenskog i prostornog ponašanja njegovih prekursora. Kontrola kakvoće zraka treba polaziti kako od rezultata mjerenja tako i od poznavanja štetnih utjecaja ozona na biljni i životinjski svijet, a i na ljude. Štoviše, ozon pridonosi učinku staklenika. Kontrola onečišćenja zraka temeljena na ekološkim i ekonomskim principima zahtijeva dubinsko razumijevanje atmosfere i njezine reakcije s biosferom. Mjere se ne trebaju oslanjati samo na izučavanje pojedinačnih onečišćenja, već i na učinke, koji su redovito rezultat složenih uzroka. Problem su mjerljivi učinci kojih su posljedice neprihvatljive za zajednicu.

**KLJUČNE RIJEČI:** kemija atmosfere, mjere smanjivanja emisija, onečišćenje zraka, oštećenje vegetacije, smog, variranja koncentracija, zdravlje ljudi

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