

## TROPOSPHERIC OZONE POLLUTION

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**Keywords:** Aldehydes, alkanes, alkenes, air pollution, carbon dioxide, carbon monoxide, computer models, emissions, fossil fuels, global scale, hydrocarbons, hydrogen peroxide, hydroxyl radical, methane, nitrogen oxides, nitric acid, nitrous acid, ozone, photochemistry, photooxidants, photosmog, troposphere, ultraviolet radiation, urban scale, regional scale, smog, traffic

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### Summary

The earth's atmosphere is an oxidizing environment. The principal oxidants in the lower atmosphere apart from molecular oxygen ( $O_2$ ) are ozone ( $O_3$ ), the hydroxyl (OH) and nitrate ( $NO_3$ ) radicals and hydrogen peroxide ( $H_2O_2$ ). The concentration of ozone is often used to assess regional air quality. Ozone concentrations can range from a few parts per billion by volume (ppbv) in less polluted areas to more than 100 ppbv in areas polluted by human activities.

The reasons for surface ozone formation are in principle understood: volatile organic compounds (VOC), carbon monoxide (CO) and nitrogen oxides ( $NO_x$ ) act as photochemical precursors for ozone generation during daylight. The key chemical reaction steps have also been identified, at least for carbon monoxide and alkanes, in the presence of nitrogen oxides. Hydroxyl radicals attack carbon monoxide and VOCs forming peroxy radicals which oxidize nitrogen monoxide (NO) to nitrogen dioxide ( $NO_2$ ). The photolysis of nitrogen dioxide immediately leads to ozone formation. Nitrogen monoxide is also oxidized by ozone itself. In the presence of a well balanced  $[VOC]/[NO_x]$  concentration ratio the consumed radicals are efficiently regenerated within a chain.

It is now well established that the burning of fossil fuels has led to a marked increase in nitrogen oxides and subsequently to higher concentrations of ozone particularly in the northern troposphere. Measurements of data in regions where fossil fuel emissions of

nitrogen oxides dominate over other sources, such as the eastern U.S. and western Europe, show a marked increase in tropospheric ozone in the northern hemisphere.

Numerical modeling of the ozone formation is quite advanced, however, important details on the formation of ozone and in particular of other photooxidants such as PANs, organic nitrates, aldehydes and hydroperoxides are less reliable. Several major gaps are still evident which require a better quantitative understanding for the development of effective abatement strategies.

## 1. Introduction

The history of atmospheric ozone began approximately 2 billion years ago. At the beginning of the development of our Earth before 4.6 billion years the air mantle contained virtually no oxygen. Initially an atmospheric layer evolved with chemically reducing properties. It was only as the photosynthesis of green algae began that the atmosphere slowly became enriched with oxygen. From the present-day state-of-knowledge, we now know that ozone ( $O_3$ ) must also have been formed along with the increase in molecular oxygen ( $O_2$ ), since the short wavelength portion of sunlight can split molecular oxygen into two oxygen atoms which can add to oxygen molecules to form ozone. This ozone progressively shielded the Earth's surface more and more from life destroying short wavelength radiation thus enabling the development of green vegetation, which via photosynthesis removed carbon from the atmosphere and released oxygen. Through the evolution of other life forms and the deposition of a portion of the carbon in the form of fossils the atmosphere attained about 400 million years ago its present-day composition with approximately 21 volume percent molecular oxygen ( $O_2$ ) and strong oxidizing characteristics. The vegetation during this development had to learn how to protect itself with antioxidants against cell oxidizing agents. An equilibrium between the emissions from the biosphere and the photochemical processes in the atmosphere resulted in the formation of a protective ozone layer at a height of 10-50 km above ground level which shields life on Earth from harmful UV radiation; this layer contains approximately 90 percent of the total atmospheric ozone. This also resulted in a pronounced temperature profile in the atmosphere, which slowed down the exchange processes between the lower and higher layers. Based on the temperature at the different heights the atmosphere is divided into the following major partitions:

The lowest partition is the mixing layer or planetary boundary layer (PBL), which is often visible through the cloud cover. Directly over this layer is the free troposphere, in which the temperature decreases with increasing height. Above the tropopause, the area with the lowest temperature begins the stratosphere, which contains the protective ozone layer.

The discovery of ozone in the atmosphere can be traced back to Ch. F. Schönbein in the year 1839. Schönbein was Professor for physics and chemistry at the University of Basel and experimented with oxidizing chemical substances. In electrical discharges and in the air above electrolysis processes he found a pungent smelling substance, which he named ozone (*das Riechende*). Reports on this stinging smell close to electrified machinery had already been published in Holland in 1785 by M. van Marum

and somewhat later W. Cruickshanks reported the same smell during the electrolysis of water. Schönbein discovered that ozone colored iodized starch paper blue and observed that this process occurred in the atmosphere too. Schönbein did not know the chemical nature of ozone and how this strongly oxidizing substance was formed in the atmosphere, but his ozone detection method found general acceptance and resulted in nearly world-wide measurements of ozone at ground level. These measurements showed a maximum for ground-level ozone in spring. Today we know that although ozone is the main substance which colors iodized starch paper blue there are also contributions from different other oxidants. In the year 1864 it was postulated that ozone was an  $O_3$  molecule, however, it was not until 1898 that the structure was finally validated.

Atmosphere  
Earths Surface/Troposphere/Stratosphere

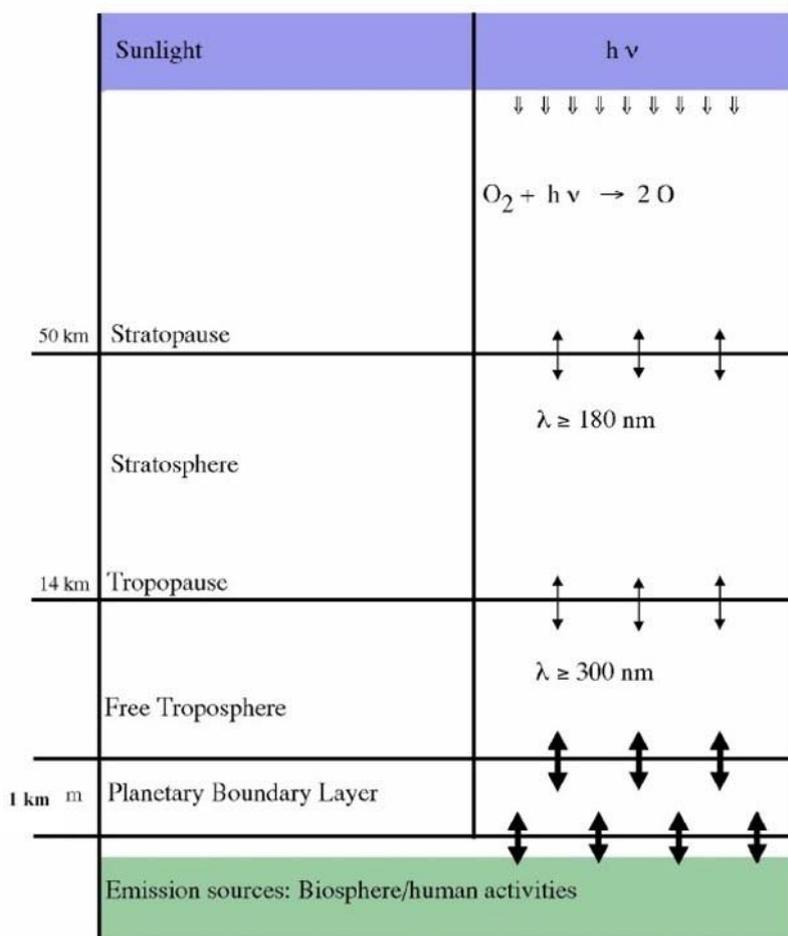


Figure 1. Structure of the atmosphere: tropospheric/stratospheric, mixing layer

With new spectroscopic methods geophysicists and geochemists uncovered further details about ozone in the atmosphere. A major contribution came from the work of W.N. Hartley in 1881, which explained the short wavelength limit of sunlight at the

Earth's surface through the presence of ozone in the stratosphere. From the work of Chapman on the formation of ozone and observations from a world-wide measurement network, built up by G.M.B. Dobson in the 1920s for the determination of the total column height of ozone, the theory developed that ozone was formed exclusively in the stratosphere but a portion was transported to ground level and destroyed at the surface.

Through debates on subjects such as weather sensitivity, “bio-climate” and “medicinal meteorology” many ideas developed about the importance of ozone, which had their basis in subjective impressions and general meteorological influences. Ozone was attributed to healing and generally good health properties, in particular by infections, and was often employed as a “remedy” for many illnesses. This was a notion which endured until the 1970s at least in Europe.

The influence of electrical discharges in air and also changes in the ozone concentration on human health could never be objectively confirmed. With hindsight one can see, that a natural background concentration is very important for “cleaning” the air through oxidation and that ozone in regional air persists longer as in city air. A relatively high background concentration is also a sign for pristine air; this aspect will be dealt with in detail below. In general, one can say that until the 1970s it was widely accepted that ground-level ozone originated in the stratosphere. It was also recognized that ozone was formed by lightning and in silent discharges between high-voltage cables.

After the discovery of summer smog in Los Angeles during the 1940s more and more evidence was gradually found showing that ozone can be damaging for humans, plants and materials (see *Formation and Effects of Smog and Air Pollution Damage to Vegetation*). The particular symptoms of this new type of air pollution in Los Angeles were, in the first instance, eye irritation, respiratory difficulties and damage to sensitive plant types. It was not until several years later that ozone was identified as the main culprit for these effects. Today it is beyond doubt that above certain threshold values ozone is detrimental for human health and damages plants. However, ozone does kill bacteria and is applied, for example, in the purification treatment of drinking water.

In closing this introduction it should be again emphasized that there is a natural background ozone concentration, which contributes to the natural cleansing of the atmosphere and which cannot be influenced by environmental control measures. Summer smog can only be controlled by manipulation of the anthropogenic emissions. It is, however, possible, that the background ozone concentration has significantly increased during the last hundred years in the northern hemisphere. Evidence for such an increase comes from measurements performed by Levy on the Montsouris Observatory in Paris in the 1880s, which have recently been corrected and re-interpreted. Further, the present-day yearly ozone maximum does not occur any more in spring as in the past, it now appears in the summer. The reason for both changes probably lies in the elevated nitrogen oxide emissions in the highly developed industrial states in the northern hemisphere and in the increased photochemical activity during the summers.

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### Useful web links dealing with different aspects of tropospheric ozone:

<http://www.epa.gov/airlinks>

<http://www.cgenv.com/Narsto/>

[http://clinton3.nara.gov/WH/EOP/OSTP/Environment/html/fac\\_trop\\_oz.html](http://clinton3.nara.gov/WH/EOP/OSTP/Environment/html/fac_trop_oz.html)

<http://code916.gsfc.nasa.gov/Public/Analysis/trop/trop.html>

[http://code916.gsfc.nasa.gov/Data\\_services/cloud\\_slice/](http://code916.gsfc.nasa.gov/Data_services/cloud_slice/)

<http://www.asahi-net.or.jp/~wt2y-ttm/what.htm>

[http://earthobservatory.nasa.gov:81/Library/glossary.php3?xref=tropospheric%20ozone%20\(O3\)](http://earthobservatory.nasa.gov:81/Library/glossary.php3?xref=tropospheric%20ozone%20(O3))

<http://www.al.noaa.gov/WWWH/Doc/TropoRural.html>

<http://reports.eea.eu.int/TOPO8-98/en>

<http://www.al.noaa.gov/WWWH/Doc/GlobalTropo.html>

<http://homepage.boku.ac.at/krueger/ozontrop.htm> (site with many links)

<http://www.co2science.org/journal/2001/v4n27c1.htm>

### Biographical Sketches

**Karl Heinz Becker**, born 1935 in Leverkusen-Opladen, studied physics and chemistry at the Universities of Tübingen and Bonn. In 1964 he received his PhD from the University of Bonn on a physical chemistry topic over the photochemistry of simple atmospheric gases. In the period 1965/66 he worked as a guest scientist in the Chemistry Department of the University of California in Los Angeles on elementary chemical reactions in combustion systems. In 1970 he qualified as a university lecturer (Habilitation) at the University Bonn in the Faculty of Physical Chemistry and one year later was appointed to “Wissenschaftlichen Rat and Professor”. Since 1974 he is head of the Physical Chemistry at the Bergische University – Gesamthochschule Wuppertal. As University Professor he serves the Land of Nordrhein-Westfalen. His major interests concern the chemical processes, which take place in the various compartments of the atmosphere, and possible perturbations to these processes through anthropogenic influences. The results of his research are documented in over 200 articles in scientific journals and several books. Prof. Becker participates in different national and international committees that are concerned with the preservation of the atmosphere and the conception of appropriate research programs. He has coordinated many EU research projects and, in particular, he has constructed, in collaboration with Spanish colleagues, a large outdoor simulation chamber in Valencia for the investigation of tropospheric reactions. He recently coordinated a large BMBF co-operative research project in Germany (TFS/LT3) in which 36 groups were working to understand the atmospheric chemical processes which lead to the formation of photo-oxidants.

**Ian Barnes**, born 1951 in Carrickfergus, Northern Ireland, studied chemistry at the University of Salford and the Queen’s University of Belfast. In 1977 he received his PhD from the Queen’s University of Belfast on a physical chemistry topic over the atmospheric chemistry of ozone. Since 1979 he has worked in the Physical Chemistry Department at the Bergische University - Gesamthochschule Wuppertal. He has been a member of the department virtually from its concept and is currently one of two senior scientists in charge of running research in the department. Dr. Barnes has over 20 years of experience in the investigation of the kinetics and mechanisms of atmospheric oxidation processes using different state-of-the-art-techniques, in particular large volume photoreactors, which within the last few years have been adapted to measure particle formation. His major interests concern the chemical processes, which take place in the various compartments of the atmosphere, and possible perturbations to these processes through anthropogenic influences. The results of his research are documented in over 80 articles in scientific journals and several books. At present he is vice coordinator of the steering committee for the EUROTRAC-2 subproject CMD-GPP. He also actively assists the Steering Committee of the European Photoreactor EUPHORE at CEAM, Valencia, Spain in the organization of the research work at the facility and in writing and editing of annual reports.