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Ozone in the Atmosphere

Basic Principles, Natural and Human Impacts

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Note from the Author

Because of severe health problems which even deteriorated by mid-2013, I had to stop working for this book with two subchapters still missing. Thus, its publication in 2014, 30 years after the discovery of the Antarctic Ozone Hole, was at risk.

Sections 5.1 and 5.4 had not been written, and therefore I asked Prof. Dr. Martin Dameris of DLR Oberpfaffenhofen to step in and write these two sections. Martin, a world-renowned atmospheric modeller and member of the WMO Ozone assessment team, just the right person for this job, readily agreed. That way the manuscript was completed, and the book can appear.

I am very grateful to Martin whose excellent articles fit very well. The authorships are stated under the respective chapter titles.

Preface

In spring 2013, when Prof. Dr. Peter Fabian asked me to assist him during the final phase of writing this book about atmospheric ozone, only two sections were not finished at that time. Being asked by Peter Fabian has been a privilege for me. It was a real pleasure to work with him and to discuss the content of this book. We had several meetings in my office, and Peter Fabian, despite being seriously ill, was always full of energy and optimistic. We finished writing the manuscript for the book in December 2013. We received the galley proofs in mid-February 2014. Immediately, Peter and I started to check the proof. On 2 March I visited him for the last time in the hospital. We discussed the final changes of the manuscript, and we finally agreed on the subtitle of the book: “Basic principles, natural and human impacts”. The final wish of Peter Fabian was to hold the printed book in his hands. Sadly enough, this wish was not fulfilled—Peter Fabian deceased on 11 March 2014, at the age of 76 years.

Peter Fabian studied Physics, Geophysics and Meteorology in Göttingen (Germany) and Innsbruck (Austria). For his thesis on atmospheric ozone, he was awarded the doctor’s degree in 1966. As a postdoctoral research associate he worked at the University of California (UCLA), USA. From 1968 to 1988 he chaired the department “Trace substances in the atmosphere” at the Max-Planck-Institute in Katlenburg-Lindau (Germany). He received his habilitation in 1981 and became professor at the University of Göttingen. In 1988, Peter Fabian was appointed a full professor in München (chair of Bioclimatology and Immission Research). In 2003 he was conferred the emeritus status.

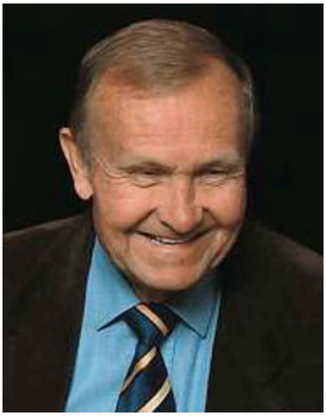
His numerous research papers were particularly devoted to the chemistry of the air and the transport of trace gases in the atmosphere. Peter Fabian was a pioneering scientist for investigations of aircraft emissions on the composition of the atmosphere. Among others, he studied the impact of nitrogen oxide emissions on the stratospheric ozone layer. Beyond that, his measurements of the vertical distribution of important halogen hydrocarbons were essential for the understanding of ozone depletion in the stratosphere. He was acknowledged as a worldwide recognised expert in ozone research. Therefore, in 1988 Peter Fabian received the honorary doctor (doctor honoris causa) of the Universidad de Mendoza (Argentina).

During his time in Munich, Peter Fabian was focusing on tropospheric photochemistry in congested urban areas. For example, he investigated the changes of ozone and related precursors in connection with aviation in the area of the Munich airport.

His enormous knowledge is documented in several books, for example in “Atmosphere and Environment” or “Living in a Greenhouse”. He had the extraordinary competence to write complex scientific findings in a manner which is also understandable for non-experts. He inspired students in his lectures, seminars and scientific talks on conferences about atmospheric science. He mentored many diploma and PhD students, who successfully passed their exams and to whom Peter Fabian became a decisive supporter for their career. Peter Fabian’s ideas and hints were always taken with pleasure.

Many of us have known and appreciated Peter Fabian as a leading scientist, colleague, advisor and friend. We will always remember his friendly and authentic manner.

Munich, Germany Martin Dameris



Prof. Dr. Peter Fabian

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Chapter 1
Introduction

Ozone (O_3), formed from three oxygen atoms, is a pungent smelling poisonous gas. Although it is a rare component of the Earth's atmosphere—in every ten million molecules of air, only about three are ozone—it is of fundamental importance for life on Earth.

Most of ozone, about 90 % of its total atmospheric abundance, is found in the stratosphere, between about 10 and 50 km altitude. In this higher part of the atmosphere, solar ultraviolet (UV) radiation can split (photolyze) oxygen (O_2) molecules, thereby producing oxygen atoms (O). These can react with O_2 molecules forming O_3. The stratospheric ozone belt, usually called the ozone layer, is maintained by a complex interplay of photochemistry and atmospheric dynamics.

In addition, the decomposition of long-lived trace gases mixed up from the surface provides a source of reactive substances which interfere with the ozone photochemistry. The most important of such natural "source gases" is nitrous oxide (N_2O) produced by soil bacteria. Its continuous flux into the atmosphere causes stratospheric ozone levels to be about 25 % lower than pure-oxygen photochemistry would predict. Man, by applying huge and increasing amounts of nitrogen fertilisers, has been increasing the flux of this natural "ozone depleter" N_2O. Moreover, the emission of halogenated hydrocarbons from spray cans, leaking refrigeration and air conditioning devices as well as solvents has lead to a significant global depletion of the ozone layer and severe seasonal ozone losses observed at high latitudes (polar ozone hole).

As most of these ozone depleting substances have atmospheric life times of hundreds of years, ozone losses still largely prevail, although production and thus further emission of such halogen compounds have been terminated by legislative measures.

The stratospheric ozone layer absorbs all but a small fraction of the solar ultraviolet (UV) radiation and thus prevents it from reaching the Earth's surface. High doses of UV radiation have potentially harmful effects on human health, animals, plants, microorganisms and materials. Thus, any reduction of the ozone layer thickness causing an increase of the UV flux bears important consequences for life. Further, the very existence of the stratosphere, an atmospheric layer with a

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positive temperature gradient that plays an important role in the atmospheric general circulation, depends on the ozone residing in this altitude region. It would not be an exaggeration to emphasise that life on the Earth's surface in its present form would not have evolved in the absence of the ozone layer. Thus, the ozone residing in the upper atmosphere is often called the "good ozone".

The remaining about 10 % of the atmospheric ozone is found in our direct environment, the lowest 10 km of the atmosphere called troposphere. In the natural troposphere free from anthropogenic influences, about 10–20 ozone molecules are found in every thousand million (one billion) molecules of air. At sea level these 10–20 parts per billion (ppb) correspond to about 20–40 micrograms per cubic metre ($\mu g/m^3$). These are mainly the result of downward transport from the stratosphere where ozone is produced photochemically. Human emissions from fires, automobile exhaust, and industry, however, provide substances from which ozone is produced in the troposphere as well. Such photosmog reactions can increase ozone levels up to several hundred ppb and more in polluted regions and, as a result of global mixing, to significantly elevated global ozone levels.

When ozone was discovered in the atmospheric environment, it was considered beneficial for human health. The good smell of forest air was thought to be due to ozone (it is rather hydrocarbons emitted by trees that cause that smell). City developers have often tried to lure settlers to ugly areas by creating street names such as "Ozone Avenue". On the contrary, ozone is poisonous and detrimental to human health at levels which are often exceeded in many areas of the world. Thus tropospheric ozone, the ozone in the air we breathe, is now often called the "bad ozone".

This is even more true since ozone is an efficient greenhouse gas as it absorbs thermal radiation around 9.6 μm wavelength. Thus, the increase of ozone in the troposphere directly enhances the Earth's greenhouse effect and contributes to global climate warming caused by CO_2 ond other man-made greenhouse gases.

The very existence of the ozone layer is due to the fact that the Earth's atmosphere contains oxygen. Unlike the other planets in the solar system whose atmospheres hold, if at all, traces of oxygen only, almost 21 % of the air we breathe is oxygen. This large fraction of oxygen is the result of life on Earth which evolved about 4 billion years ago under favourable conditions unique in the solar system: Earth orbits the Sun at a distance of about 150 million km where an average surface temperature of about 15 °C enables the existence of liquid water and thus oceans. It is well established that life evolved and flourished, before the atmosphere contained oxygen and thus an ozone shield against UV radiation, in the oceans. Myriads of microorganisms produced oxygen via photosynthesis, most of which was used up in the oxidation of iron and sulphur compounds. The remaining free oxgen gradually accumulated, and about 2 billion years ago atmospheric oxygen and the corresponding ozone layer were probably sufficient for the first organisms for settling on land. The biological activity and evolution of species accelerated leading to biodiversity and atmospheric conditions of the pre-industrial world.

The privileged conditions on Earth towards life can be realised by comparison with our neighbours in the solar system: Mars, orbiting the Sun further away than

Earth, at about 228 million km distance, has an average surface temperature of −50 °C, whereas Venus, with 108 million km distance closer to the Sun than Earth, exhibits deadly 460 °C.

Oxygen is not the only product of biological activity. The metabolism of microorganisms in the ocean and the continental soils liberates huge amounts of gaseous substances emitted into the atmosphere, such as nitrous oxide (N_2O), methane (CH_4) or methyl chloride (CH_3Cl). On the other hand, the biosphere takes up substances from the atmosphere, such as carbon dioxide (CO_2), water (H_2O) and nitrogen compounds. Actually, all atmospheric constituents, except the noble gases, circulate through the biosphere. Thus, our atmosphere largely is a product of biological activity and hence a consequence of life.

On the other hand, the atmosphere provides ideal climatic conditions for the biosphere. It constitutes a huge greenhouse which protects against harmful UV radiation but lets the visible radiation necessary for photosynthesis penetrate to the surface almost unattenuated. It also reduces the thermal emission from the surface: greenhouse gases such as H_2O, CO_2, O_3, N_2O and CH_4 (in the order of their importance) absorb and re-emit parts of the Earth's thermal radiation, thus reducing the energy loss to space. Because of this (natural) greenhouse effect, the average surface temperature is 15 °C, about 33° higher compared to an Earth without such atmosphere. This natural greenhouse effect has continuously been increasing by anthropogenic emissions of greenhouse gases from burning of fossil fuels, destroying forests and various agricultural and industrial practices. Over the past 100 years, global average temperatures have risen by about 0.7°, and they are likely to increase further, by up to 5° until 2100, if greenhouse gas emissions continue to grow unabated. Global warming and related consequences are among the most severe problems for the well-being of our planet. This book dealing with the ozone layer will not explicitely address the issue of climate change. It will, however, touch upon it in as much as ozone is involved.

The Earth's atmosphere has evolved over more than 4 billion years, in close interaction with the biological evolution. Man, supposed to be the highest form of this evolution, is about to massively alter this greenhouse, by misusing the atmosphere as a waste dump. Severe ozone losses in the stratosphere, large ozone increases in the troposphere and climate changes are manifestations of human impact.

Chapter 2
Discovery of Ozone in the Atmosphere

The 1770s stand out as an epoch making period in the research of the atmospheric composition. During this decade, several of the most important constituents were identified and named. In 1774, J. Priestley and C.W. Scheele independently discovered oxygen. In the same year, Scheele identified chlorine and in 1777 nitrogen. Priestley discovered nitrous oxide (N_2O) in 1773, hydrogen chloride (HCl) and ammonia (NH_3) in 1774, sulphur dioxide (SO_2) in 1775 and carbon monoxide (CO) in 1779.

Although in 1785 van Marum noticed the characteristic smell of ozone in a gas discharge, and a little later J.W. Ritter observed its solar absorption, its discovery is credited to C.F. Schönbein (Fig. 2.1).

In 1839, while working in the laboratory, he detected a gas with a characteristic pungent smell which he called ozone (a greek word for smell) [1]. Schönbein was also the first to develop its monitoring technique, which later was adopted for ozone measurements at many meteorological observatories in the world. In 1858 Houzou and Levy initiated its first absolute measurements by a chemical method [2].

Paris was one of the first cities in the world to have initiated air quality monitoring in general and ozone measurements in particular, as early as 1865, with a network of 20 stations. Daily observations were coordinated by A. Levy, a chemist at the Montsouris observatory, and published in the Bulletin de la Statistique Municipale de la ville de Paris. The network was operated for 10 years and provided valuable information of ground level ozone levels at a time when air pollution was almost negligible, even in Paris. A modern evaluation of the Montsouris series of ozone measurements by Volz and Kley [3] indicates ozone levels of about 10 ppb, with spring values slightly higher than autumn values.

It is interesting to note that ozone was first discovered in the troposphere where ozone mixing ratios are very low compared to the stratosphere where the bulk of ozone resides. It was in 1878 that Cornu discovered, when he performed spectroscopic studies in the visible and UV regions, a sudden break off in the solar spectrum at wavelengths shorter than 300 nm. He also observed this to shift towards longer wavelengths when the solar elevation decreased and concluded this absorption to have been caused by atmospheric constituents [4]. Two years later,

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