

# ATMOSPHERIC OZONE AND CLIMATE CHANGE. SYNTHETIC OZONE AND ITS APPLICATIONS. 21TH CENTURY AND ROLE OF OZONE

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## Summary

Ozone is an interesting substance that touches on our modern society in many ways. First, it plays a significant role in stratosphere protecting the earth and all living organisms from the very dangerous UV-B (280-320 nm) radiation. In the stratosphere,

ozone is continuously created and destroyed by the sun's radiations. This results in an equilibrium concentration of ozone. The equilibrium is, however, disturbed when reactive chlorine atoms, released from photolysis of chlorofluorocarbons (CFCs), waft into the atmosphere. These atoms create an imbalance by destroying ozone molecules. The loss of ozone molecules in the upper atmosphere is termed „*depletion of stratospheric ozone*“. On another side, ozone may be formed in troposphere due to atmospheric pollution with nitrogen oxides (NO<sub>x</sub>) and hydrocarbons (C<sub>n</sub>H<sub>m</sub>) as a constituent of the photochemical smog. Tropospheric ozone is expected to continue to increase through the 21st century. In the 21st century, an increase in both temperature and water vapour in the atmosphere is anticipated. The increased water vapor would lead to a higher concentration of the OH° radical which would mute the increases in tropospheric ozone. The ability of ozone to disinfect water was recognized already in 1886. Ozone may also be used for different purposes in wastewater treatment: for disinfection, color removal, toxic and biologically resistant compounds (detergents, pesticides, nitrocompounds, oil products etc.) partial destruction before biological oxidation. Ozone in medicine is used for disinfection, wound cleansing, improved wound healing, modulation of the immune system, activation of antioxidative enzymes as radical scavengers, activation of RBC metabolism with an improvement of oxygen release etc. In the 21st century several new applications of ozone were discovered: odor control, fumigation, restoration of homes/buildings that have experienced fires, mildew control, elimination of cat urine odors in homes and cars, mold/spore control on stored foodstuffs, packaging of pharmaceuticals, treatment of plastic films prior to lamination (bonding) with aluminium, cleansing surfaces of semiconductors, etc., etc.

## 1. Introduction

Ozone is an interesting substance that touches on our modern society in many ways. First of all, ozone in stratosphere screens the surface of earth from biologically damaging ultraviolet radiation. But at the same time ozone as a strong oxidizing agent is also present in dangerous photochemical smog in troposphere. Synthesized ozone is used in many water/wastewater treatment and other industrial processes as a disinfectant and oxidant. And now, when we have entered Century 21, more and more ozone is being used around the world. It is also clear that more and more new applications for this versatile gas are being found. Potable water and wastewater treatment now can be called the “classical” applications for ozone. Ozone use for odor control, fumigation of homes and buildings, packaging of pharmaceuticals, cleansing of semiconductor chips, bleaching of pulp, kaolin and textile, regeneration of polymerization catalysts, oxidation of flue gas constituents, washing clothes, treatment, storage and processing of foods and agricultural products, medical therapy etc., etc. might be termed “non-classical”. All of these uses emerge from our basic understanding of ozone that began with the recognition by German chemist Christian Schönbein in 1840 that ozone was a unique substance produced in a variety of processes.

Like most areas of science, the discovery of ozone did not come as a bolt from the blue. In the 1770s, Priestly, in England, and Scheele, in Sweden, were studying the properties of air. They were able to separate air into two parts, one that supported combustion at an increased rate over normal air, and one that did not support combustion. They both tried to interpret their experiments in terms of the existing phlogiston theory and did not

realize that they had discovered a new element. In 1776, Lavoisier repeated many of their experiments and correctly recognized the elementary nature of the gas that he named oxygen (Stolarski, 2001).

In 1785 Van Marum passed electric sparks through oxygen and noted a peculiar smell and that the resulting gas reacted strongly with mercury. The peculiar odor in the air after a lightning strike had been known for centuries, including references in the Odyssey and Iliad. Van Marum and others attributed the odor to the electricity, calling it the „electrical odor“. It was C.Schönbein in 1840 who recognized that the odor was not due to the electricity, but was due to the properties of a substance produced during the electrical process. He named this substance ozone (from *ozein*, Greek for „to smell“) (Stolarski, 2001).

For the few decades immediately following Schönbein's discovery of ozone, many studies were carried out regarding the identity of ozone, its properties, and its possible uses. In 1845 Marignac and De la Rive interpreted their experiments as indicating that ozone was just oxygen, modified by its passage through a peculiar electrical state. But in 1848, T. Sterry Hunt put forward a hypothesis that is close to our present understanding - he described the molecule of ozone ( $O_3$ ) consisting from three oxygen atoms ( $O_3 = (OOO)$ ) (Leeds, 1880).

By the middle of the 1870s, ozone was established as a potentially important component for the normal atmosphere. Several tests had been developed to measure the amount of ozone in the air. Debates raged over the accuracy of these measurements that used litmus-type papers. Did they measure just ozone, or was there a significant contribution from hydrogen peroxide in the air ? Ozone was a very important and lively topic for research at this time. In his book „Ozone and Antizone“ Corenelius Fox (Fox, 1873) wrote:

*„To the Philosopher, the Physician, the Meteorologist, and the Chemist, there is perhaps no subject more attractive than that of ozone“.* And it has remained attractive even in the 21st century !

## 2. Stratospheric Ozone and Human-induced Trends

In 1801, Johann Ritter discovered that the intensity of the sun's radiation dropped off rapidly at wavelengths below about 300 nm. He demonstrated that the wavelength of the „cutoff“ increased as the sun set and the path through the atmosphere increased. He correctly interpreted that the cutoff was the result of an absorbing substance in the atmosphere. In 1880, W.N.Hartley (1880) suggested that the atmospheric absorber was ozone. This conclusion was based on his laboratory studies of the ultraviolet absorption by ozone. He even asked the question: *„Is ozone a constant constituent of the higher atmosphere, and, if so, in what proportion is it probably present ?“*

In 1918 R. Strutt (1918) attempted to measure the absorption by ozone from a light source located four miles across a valley. He could not detect no absorption and concluded that: *„There must be much more ozone in the upper air than in the lower.“*

By this time it was further established that ozone was not near the ground, but was in

the upper atmosphere, and a quantitative estimate of the amount of ozone had been made which was reasonably close to the amount now known to be in the atmosphere.

The next era of atmospheric ozone research started with the classic theory paper of Chapman, published in 1930 (Chapman, 1930). For several decades, laboratory measurements had been carried out to determine the mechanism responsible for ozone decomposition, but arguments persisted as to the correct mechanism. In 1930, H. Schumacher (1930) published a review of the laboratory work on ozone decomposition and concluded that the key intermediary formed in the initial absorption by ozone was atomic oxygen. Chapman (1930), in the same year, applied this knowledge to the first model of the distribution of ozone as a function of altitude in the atmosphere.

Chapman's mechanism can be described by the following equations (Sodhi, 2000). Photolysis of oxygen molecule into the reactive oxygen atoms by the ultraviolet light from the sun:



This reaction is followed by another in which a reactive oxygen atom recombines with an oxygen molecule:



The ozone formed in reaction (2) distributes itself in the stratosphere, forming a layer which is thin in some places, and thick in others. If to recalculate the amount of all ozone distributed in the stratosphere to the even gaseous homogeneous layer, it appears that the thickness of this layer around the earth will be only 3 mm (!). This layer of stratospheric ozone absorbs harmful ultraviolet radiations:



In absence of ozone these damaging solar radiations would have reached the earth, causing several ill effects: blindness of animals and humans, skin cancer etc. Thus, the ozone layer filters the incoming ultraviolet radiations and affords our natural protection. No doubt, reaction (3) destroys ozone, but it also produces reactive oxygen atoms, which combine with oxygen (reaction (2)) producing more ozone to compensate the loss.

Thus, in the stratosphere, ozone is continuously created and destroyed by the sun's radiations. This results in an equilibrium concentration of ozone. The equilibrium is, however, disturbed when reactive chlorine atoms, released from photolysis of chlorofluorocarbons (CFCs), waft into the atmosphere. These atoms create an imbalance by destroying ozone molecules. The loss of ozone molecules in the upper atmosphere is termed „*depletion of stratospheric ozone*“. When it happens, the ozone layer's capacity to filter out the harmful ultraviolet rays (< 300 nm) from the sun decreases.

The inert nature of the chlorofluorocarbons, a group of chemicals having wide industrial

applications, imparts them enormous stability. Their residence times in the atmosphere are very long. For example, two most commonly used CFCs, CFC-11 (CCl<sub>3</sub>F) and CFC-12 (CCl<sub>2</sub>F<sub>2</sub>) persist in the environment for about 75 and 110 years, respectively. Thus, even if the release of these chemicals to the atmosphere were to stop with immediate effect, they would continue depleting ozone well into the next century. In 1987 the Montreal Protocol was adopted as a completion of the Vienna Convention. Forty six countries signed an agreement aimed at a step-by-step reduction of the production and use of fully halogenized CFCs to 50% of the 1986 level by 1999.

When the CFCs are emitted and reach stratosphere, the solar radiation splits them into reactive chlorine atoms. This is followed by the next chain reactions (Sodhi, 2000):



The net reaction is:



The species M represents here another molecule (for example, N<sub>2</sub>) that absorbs the energy of reaction and remains unchanged.

As a result of this mechanism, ozone hole is formed mainly over Antarctica during spring time (September-October) and replenishes after spring (November-December). Scantly depletion, however, also occurs over Arctic and a few pockets of non-polar regions.

There is also a different, so-called dynamical theory of atmosphere according to which stratospheric air tends to circulate from higher altitudes in the tropics to lower altitudes in polar regions, carrying ozone along with it. This circulation depends on the temperature gradient between the tropics and the polar zones (Sodhi, 2000). As a result of this natural phenomenon, the concentration of ozone in non-polar regions decreases temporarily during the time following Antarctic spring. Ozone is a greenhouse gas. That is, it causes a warming of the atmosphere in its vicinity. When the concentration of ozone decreases, the temperature of the stratosphere over the non-polar regions also decreases. This means that the temperature difference between the non-polar and polar regions decreases. Due to this the circulation of stratospheric air weakens. In the years that follow, air carries lesser amounts of ozone to the Antactica after each spring. In fact, a decrease in the stratospheric air circulation activity has been recorded since 1979, and since that period the size of the ozone hole over Antarctica has consistently

increased.

Thus, according to dynamical theory of atmosphere, ozone is not depleted by a chemical process. In fact, it is not depleted at all. It is only redistributed by a geographical phenomenon. However, this theory fails to explain as to how the ozone hole, wherever it occurs, is embedded with above-normal concentrations of reactive chlorine atoms and chlorine monoxide.

Over the past few years, the atmospheric concentration of nitrous oxide has recorded a consistent increase. This has been attributed to large scale combustion of fossil fuels and enhanced use of nitrogenous fertilizers. Nitrous oxide, as well as other oxides of nitrogen, are also emitted by supersonic transport aircrafts (Sodhi, 2000). Like CFCs, nitrous oxide is quite inert, in stratosphere it may be photochemically converted into more reactive nitric oxide:



NO so formed then undergoes the following chain reactions:



Net reaction:



This mechanism has been ruled out because the oxides of nitrogen, rather than depleting ozone, act as scavengers for the ozone depleting reactive chlorine atoms.

Now let's discuss some consequences of ozone depletion. Solar ultraviolet radiations are composed of mainly UV-A (240-280 nm) and UV-B (280-320 nm) types. The UV-A radiations are absorbed both by oxygen (reaction (1)) and ozone (reaction (3)). However, the UV-B radiations are absorbed only by ozone. Exposure of the earth's environment to UV-B radiations results in more deleterious effects than exposure to UV-A radiations. The penetration of UV-B radiations through the ozone hole has the following environmental implications (Sodhi, 2000):

#### *Human health*

UV-B radiations are sufficiently energetic to break apart important biological molecules, including proteins and DNA. Exposure to UV-B radiations also causes the connective tissue of the skin to damage. As a result, the skin becomes finely wrinkled and loses its elasticity. It has been estimated that a 1% decline in ozone layer could lead to a 4-6% increase in the incidence of *malignant melanoma*, a form of skin cancer. Eyes too are vulnerable to excessive UV-B exposure. Melanoma of eyes, blindness and even

death can result. The UV-B radiations also damage the lens of the eye. A *cataract* may be formed, one of the most preventable cause of blindness.

### *Crop yields*

More than two-third of the crop species are damaged by ultraviolet rays. An increased level of UV-B radiations, therefore, adversely affects crop yield. A 1% increase in UV-B radiations is estimated to cause a 1% decline in the yield of soya beans, peas and beans.

### *Phytoplankton*

Phytoplankton, the tiny drifting plants that live near the surface of the sea, seeking light for photosynthesis, are vulnerable to UV-B damage too. These organisms are the bottom link in the marine food chain and support all other forms of life in the sea. There is thus a potential for a major upheaval in the marine ecology, which could, in turn, affect human food sources.

Are there any possibilities to abate ozone depletion? Two sets of compounds are being developed as substitutes for CFCs. These are: the *hydrochlorofluorocarbons* (HCFCs) and even better, the *hydrofluorocarbons* (HFCs) (Sodhi, 2000). These compounds have the following advantages:

- a) Their ozone depletion potential is far less than that of the cfc's.
- b) The alternative fluorocarbons carry hydrogen atoms that make them susceptible to degradation in the lower regions of atmosphere, unlike the fully halogenated cfc's, whose long lives let them survive until they reach the stratospheric ozone layer.
- c) The physical properties of alternative fluorocarbons are similar to those of cfc's, so that they could be substituted mostly without a major redesign or refitting of existing equipment.

It must be appreciated that the world moved fast to agree to phase out the CFCs once their dangers were demonstrated. This offers a hopeful precedent for international action on other threats to the global environment.

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Research interests: Ozonation of water/wastewater, advanced oxidation processes (AOPs) in water treatment, drinking water production, sustainable technology