

Ozone, sources of emission, destiny in the environment, future scenarios

This essay is an exercise for the course "Biomonitoraggio degli ambienti terrestri". It mostly aims to summarise the lecture about ozone in case it might help other students to study for the course. Since the time reserved for the course is limited, the text is based mostly on the lectures and lecture slides of prof. Mauro Tretiach. When additional sources are used (mostly secondary sources), they are referred to in the text.

Introduction

Ozone (O₃) is a gaseous chemical compound formed by three oxygen atoms. It is found mostly in the stratosphere and in the troposphere (Staehelin et al. 2001). In stratosphere, it forms the ozone layer protecting from the harmful UV radiation. In the troposphere, instead, it causes great damage to human and nature. The concentration of tropospheric ozone has increased due to human activity. Direct ozone emissions are negligible, but it is formed as a secondary pollutant in response to emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs). In addition, intense formation of ozone requires light and high temperatures. Thus, the highest concentrations are reached during hot bright days in areas with much NO_x and VOC pollution, especially in the lack of wind that would disperse the ozone in a larger area. In this kind of situations, the mixture of pollutants turns into extremely harmful photochemical smog, or Los Angeles smog. The term "photochemical smog" refers to the formation of ozone in light. Ozone concentrations are expected to rise in the future due to increasing emissions of NO_x and to climate change, which will lead to higher temperatures and more favourable conditions for the formation of ozone.

The formation of ozone

Ozone can be formed in many processes. The stratospheric ozone layer is formed in the following reaction with UV-light of suitable wavelength:

- 1) $O_2 + h\nu \rightarrow O + O$ ($\lambda < 242 \text{ nm}$)
- 2) $O_2 + O \rightarrow O_3$

The wavelengths of UV below 242 nm are thus consumed already in the stratosphere by the reaction breaking down oxygen. Thus, this reaction ceases lower down in the atmosphere. (Staehelin et al. 2001)

In the troposphere, there are three main processes increasing the concentration of ozone. Firstly, it can descend from the stratosphere with air currents under some special conditions. Secondly, it is created in chemical reactions triggered by lightning strikes. Thirdly, and most importantly, it is formed in a complicated series of chemical reactions that depend on NO_x and VOCs, as well as on environmental conditions, especially light and temperature. To understand the NO_x- and VOC-dependent process of ozone formation, let's have a look at what NO_x and VOCs are.

NO_x

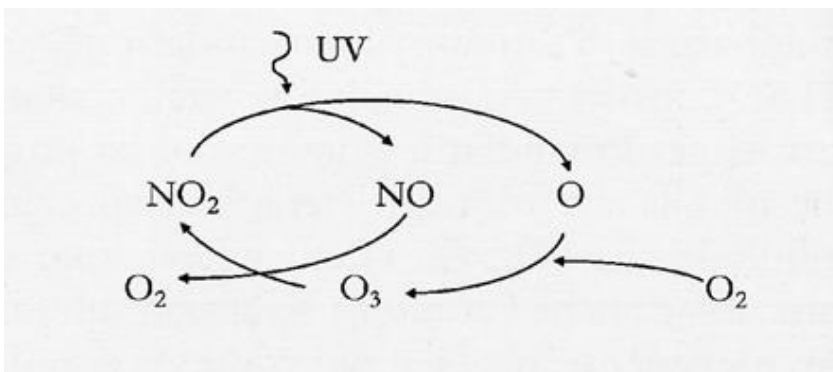
The term NO_x is used to refer to oxides of nitrogen, most importantly nitrogen monoxide (NO) and nitrogen dioxide (NO₂), but also for example nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃) and dinitrogen pentoxide (N₂O₅). NO_x are released in the atmosphere both in natural and anthropogenic processes, anthropogenic emissions being much higher. Most of NO_x are released by combustion processes, in which they can be formed in two different ways. Firstly, the nitrogen already present in the fuel / burning material can be released in the form of NO_x. Secondly, combustion in high temperatures leads to a reaction between nitrogen (N₂) and oxygen (O₂) present in the air, forming NO_x. The main anthropogenic sources of NO_x emissions are the combustion processes involved in traffic, industry and power plants. The most important natural sources of NO_x are fires, such as forest fires, but NO_x are also created during lightning strikes and by microbial activity.

VOC

Volatile organic compounds (VOCs) are organic compounds that readily diffuse in the air. They are released in the air by natural and anthropogenic sources. The relative importance of anthropogenic and natural VOC emissions for the formation of ozone depends on the area, and either of them can be the major source regionally (Jenkin and Clemitshaw 2000). Vegetation is the main natural source of VOCs. Plants produce important quantities of VOCs, such as terpenoids, phenylpropanoids and fatty acid derivatives. Their functions in plants include attracting pollinators, protecting from herbivores and pathogens, signalling, and protecting from abiotic stresses, such as high temperatures and drought. The production of VOCs in plants is affected by many factors, such as species, growth stage, part of the plant, mechanical damage, light intensity and temperature (Dudareva et al. 2013). For example, the production of isoprene is at its highest in bright light during hot days. By affecting factors, such as temperature, rainfall and the type of vegetation, the climate change could lead to an increase in the release of VOCs from plants (Fuentes et al. 2000). Anthropogenic VOC sources include, for example, solvents and incomplete combustion of fossil fuels (Borbon et al. 2013). Compounds, such as hydrocarbons, trichloroethane, benzene and ethanol are released in the air.

The reactions of ozone and its precursors:

The atmospheric NO_x follow the following cycle (from Tretiach's slides):



The cycle consists of the following reactions:

- 1) Nitrogen dioxide (NO_2) breaks down in nitrogen monoxide (NO) and an oxygen atom (O), in the presence of light.
- 2) The oxygen atom (O) reacts with a molecule of oxygen (O_2) to form ozone (O_3).
- 3) The ozone (O_3) reacts with nitrogen monoxide (NO) to form nitrogen dioxide (NO_2) and oxygen (O_2).

This cycle is altered in the presence of VOCs. The break-down of VOCs in the air produces radicals, such as hydroxyperoxy (HO_2) and organic peroxyradicals (RO_2), that oxidise NO into NO_2 . Thus, NO is oxidised into NO_2 without consuming ozone, whereas the following break-down of NO_2 in light leads to the production of ozone. Consequently, the balance of the abovementioned cycle is altered in favour of the production of ozone. Ozone also reacts with VOCs, seemingly consuming ozone. However, these reactions produce radicals that lead to the regeneration of ozone, and, under some conditions, possibly even to a net increase in its concentration (Jenkin and Clemitshaw 2000). In the absence of light, the breakdown of NO_2 slows down and the concentration of ozone collapses. Some reactions produce ozone without light, but they are not nearly as intense as those occurring in light. (Jenkin and Clemitshaw 2000)

The break-down of VOCs is a complex set of reactions, and a wide variety of organic compounds are produced, for example, organic nitrates (RONO_2) and organic peroxy nitrates (RO_2NO_2), such as peroxy acetyl nitrate (PAN). (Jenkin and Clemitshaw 2000)

Ozone is quickly removed from the air since it reacts quickly with other compounds. This is seen at night, when the ozone-producing reactions slow-down and its concentrations collapse. However, it is reproduced for as long as there are enough NO_x and VOCs in the atmosphere and the environmental conditions are suitable. NO_x and VOCs are removed from the air, for example, by deposition as nitrous acid (HNO_3) and by the break-down of the carbon skeleton of VOCs. Nevertheless, they are continuously released in the air by man and nature. Thus, they maintain the production of ozone. (Jenkin and Clemitshaw 2000)

The dependence of ozone on NO_x and VOCs (from Jenkin and Clemitshaw 2000):

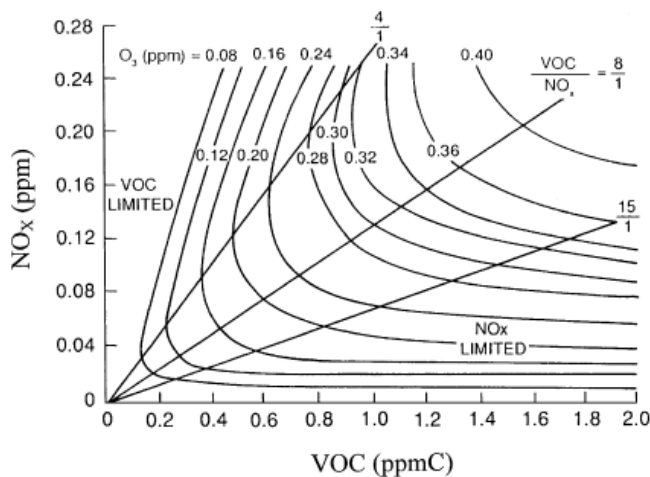
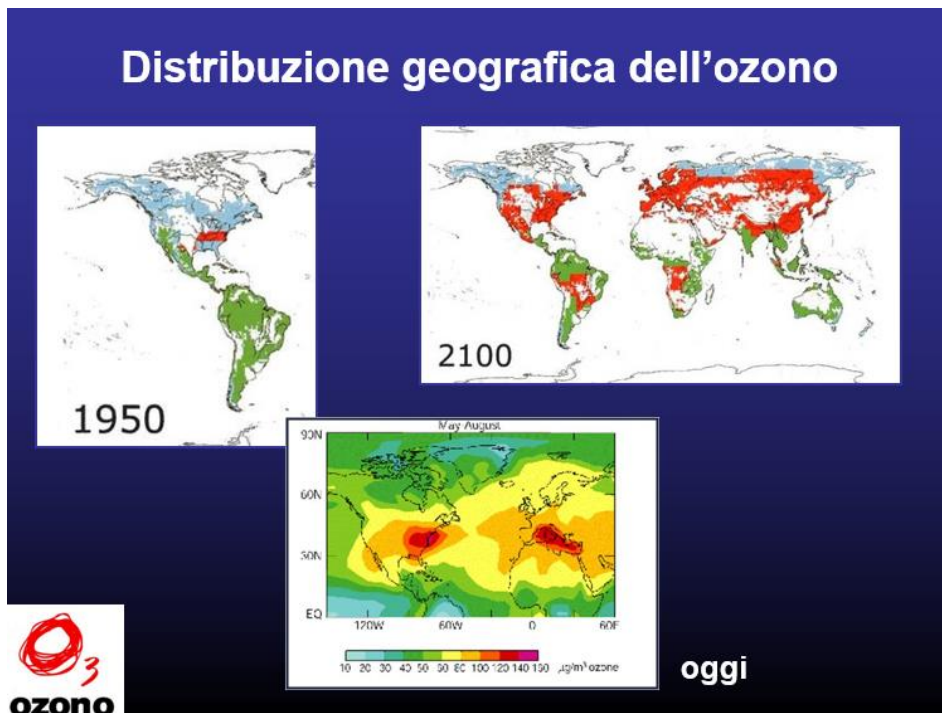


Fig. 3. Example of an isopleth diagram illustrating calculated peak O₃ concentrations generated from various initial concentrations of NO_x and a specified VOC mixture using the US EPA empirical kinetic modelling approach (diagram adapted from Dodge, 1977). Although the methodology was originally developed for highly polluted scenarios, and the reagent concentrations on the axes are thus significantly greater than typically observed in the boundary layer, the characteristic shape of the O₃ isopleths as a function of VOC/NO_x ratio also applies to lower reagent concentrations (detailed discussion is given in the text).

The spatio-temporal pattern in ozone concentrations

As mentioned, the main factors affecting the concentration of ozone are: the concentrations of NO_x and VOCs, together with temperature and light. Thus, logically, the highest concentrations of ozone are found in areas with high concentrations of NO_x and VOCs, with high temperatures and with intense radiation. In Europe, for example, the increasing temperatures and radiation from north to south makes it increasingly easier to reach high concentrations of ozone in the south. Due to favourable environmental conditions and high-enough emissions, the Mediterranean region shows the highest levels of ozone at the European level, and the limits set for the ozone are frequently exceeded in this area. High concentrations of ozone can also be found in Eastern North America and some parts of Asia.

Capture from Tretiach's slides:



In addition to a large-scale spatial pattern of ozone, dependent mostly on emissions and temperatures, there are temporal patterns in the concentrations (small-scale spatial patterns can be complicated and variable). A daily cycle is observed, since the reactions leading to the most intense formation of ozone require light. Thus, ozone levels generally collapse in night, start rising in the morning, reach the top during the hot hours of the afternoon and start decreasing towards the evening. The yearly ozone cycle depends much on temperatures and radiation. Thus, the hot summer months generally show the highest levels of ozone, and cold winter months the lowest levels. However, the situation is not that simple and contrasting patterns have been observed. For example, many remote areas show a summer minimum and a winter maximum (Monks 2000).

Globally, the concentrations of ozone are expected to increase due to increasing emissions of ozone precursors and due to climate change leading to higher temperatures. Due to climate change, ozone concentrations are expected to increase even in Europe and North America where NO_x emissions have been levelling up or even decreasing. Even higher increases in tropospheric ozone are probable to be found in Asia where the emissions of ozone precursors are expected to increase. The concentrations already frequently exceed the levels set as the limit for the protection of human health and vegetation, and these levels will be broken more drastically and in wider areas.

Why is ozone harmful?

Ozone is a highly reactive compound and an excellent oxidiser. It diffuses quickly and dissolves easily in water. Thus, it enters easily in living cells, for example through the stomata of plants and the lungs of animals. Ozone reacts easily with organic compounds, such as lipids and proteins, for example, by breaking carbon-carbon double bonds ($\text{C}=\text{C}$). When the organic molecules in the cells break down, the functioning of the cells is disrupted, and repairing the oxidative damage consumes energy. Under increasing ozone stress, organisms start suffering and eventually die.

In cells, ozone reacts quickly to form reactive oxygen species (ROS). Reactive oxygen species, similarly to ozone, cause oxidative damage in the cell leading to the destruction of lipids, proteins, carbohydrates, DNA and many other organic compounds. Plants also encounter ozone and ROS naturally. ROS are even produced by many normal processes in plant cells, for example, in the photosystems and the electron transfer chain in the mitochondria (Gill and Tuteja 2010). In addition, they are produced under many stressful conditions, such as pathogen attack, the response to which shares many similarities with the response to ozone stress. The ROS produced under stress act as signals that launch processes (such as changes in gene expression) aiming to protect the plant from the stress. Plants have adapted to ROS by developing systems that scavenge them. These systems, such as Halliwell-Asada cycle, involve, for example, small-molecular weight antioxidants. The antioxidants are oxidised by ROS, which in turn become harmless. The antioxidants are reduced back in their functional form with the reductive power of NADPH (Langebartels et al. 2002).

Ozone damages human health mainly by lungs. It causes, for example, worsening of respiratory diseases, such as asthma, lowered lung functioning, increased visits to hospitals and increased mortality (Thurston and Ito 1999). Old people, children and people with weaker health are particularly vulnerable.

Ozone symptoms in plants include cell death, chlorosis, necrosis, accelerated senescence, changes in root-shoot ratio and lowered chlorophyll fluorescence. Plants can tolerate low levels of ozone, but under more intense exposure, they start dying and withering, and eventually die. Along with other plants, crops are damaged. Ozone can lead to losses of tens of percents in the production and to lower-quality products. Differences in species' capacity to tolerate ozone could lead to changes in the composition of ecosystems and to losses in biodiversity.

Stable low levels of ozone are not so harmful as acute high levels of ozone. This is taken in account, for example, by the AOT40 index, which measures the cumulative sum of hourly ozone concentrations exceeding the concentration of 40 ppb in a certain period. The limit of 40 ppb has been estimated as the level above which plants start suffering from ozone. The index has been criticised, but can be used as an estimate of the ozone damage that plants suffer. (Paoletti and Manning 2007)

Limits set for ozone in EU

Since ozone is extremely harmful, limits for its concentration have been set. The EU directives 2002/3/CE and 2008/50/CE set several limits differing, for example, in the object to be protected and the way of measuring. The directives set target values to be reached by the 1st January 2010, as well as long term objectives. These values were set separately for the protection of human health and vegetation. The values for health are measured as the maximum daily eight-hour mean. As the long-term objective, the limit of 120 $\mu\text{g}/\text{m}^3$ should not be exceeded at all, even though after the beginning of 2010, it can still be exceeded on 25 days per calendar year averaged over three years. The information limit (180 $\mu\text{g}/\text{m}^3$) and the alert limit (240 $\mu\text{g}/\text{m}^3$) are for measurements made as one-hour average. To launch an alert, the alert limit should be reached or predicted to be reached in three consecutive hours.

The target values for vegetation (for 2010 and for long terms) are set as the hour-based AOT40 measured in May-July. The target value for 2010 is 18 000 $\mu\text{g}/\text{m}^3\text{h}$ as a five-year average, and the long-term objective is below 6000 $\mu\text{g}/\text{m}^3\text{h}$, which should not be exceeded at all. In addition, the Commission is to be informed of the values regarding the limits set for the protection of forests and material goods. These limits are to be adjusted along with new scientific information. For the protection of forests, the AOT40 measured in April-September should not exceed 20 000 $\mu\text{g}/\text{m}^3\text{h}$. For the protection of material goods, the one-year average should not exceed 40 $\mu\text{g}/\text{m}^3$. All the AOT40 measurements are taken between 8:00 and 20:00 of the Central European time.

Capture from Tretiach's slides:

18 - Valori di concentrazione per l'Ozono previsti dalla Direttiva 2002/3/CE e 2008/50/CE

Tipo	Scopo	Parametro	Soglia	Note	Dal
Valore bersaglio	Protezione salute	Media massima di 8 ore nell'arco delle 24 ore fra le medie mobili trascinate delle 8 ore precedenti rilevate a decorrere da ogni ora	120 $\mu\text{g}/\text{m}^3$	Max 25 giorni di superamento per anno solare come media su 3 anni (o se impossibile 1 anno)	2010
	Protezione vegetazione	AOT40, calcolata sulla base dei valori di 1 ora fra maggio e luglio (*)	18.000 $\mu\text{g}/\text{m}^3\text{h}$	Media su 5 anni (o se impossibile 3 anni)	2010
Valore obiettivo a lungo termine	Protezione salute	Media massima di 8 ore nell'arco delle 24 ore fra le medie mobili trascinate delle 8 ore precedenti rilevate a decorrere da ogni ora	120 $\mu\text{g}/\text{m}^3$		
	Protezione vegetazione	AOT40, calcolato sulla base dei valori di 1 ora fra maggio e luglio (*)	6.000 $\mu\text{g}/\text{m}^3\text{h}$		
Soglia di informazione	Protezione salute	Media di 1 ora	180 $\mu\text{g}/\text{m}^3$		
Soglia di allerta	Protezione salute	Media di 1 ora	240 $\mu\text{g}/\text{m}^3$		
Informazioni da trasmettere alla Commissione	Protezione beni materiali	Media di 1 anno	40 $\mu\text{g}/\text{m}^3$	Valore da rivedere alla luce degli sviluppi delle conoscenze scientifiche	
	Protezione delle foreste	AOT40: Aprile-settembre (*)	20.000 $\mu\text{g}/\text{m}^3\text{h}$		

(*) Per AOT40 s'intende la somma della differenza tra le concentrazioni orarie superiori a 80 $\mu\text{g}/\text{m}^3$ (= 40 parti per miliardo) ed il valore 80 $\mu\text{g}/\text{m}^3$ in un dato periodo di tempo, utilizzando solo i valori di un'ora rilevati ogni giorno tra le 8:00 e le 20:00, ora dell'Europa centrale.

People, plants and material goods respond differently to ozone. Thus, different kinds of indices are used to estimate the damage suffered. For human health, for example, using the maximum daily eight-hour mean takes in account that maximum concentrations are more harmful than low concentrations. On the other hand, averaging over several hours and years, as well as allowing the limits to be exceeded a limited number of times per year, balances the extreme variation in the ozone concentrations. In addition, the information and alert limits are set to inform people not to go outdoors during the worst ozone peaks.

According to the EU directives, AOT40 is measured during the period estimated as the most intense growth period when the effects of ozone are supposed to be the highest. On the other hand, the growth period varies between regions. In addition, most of the year is left out of the reach of the index. AOT40 has indeed been criticised for several reasons. For example, it cannot estimate the actual flux of ozone into the leaves through stomata. In addition, it cannot take in account the processes detoxifying the ozone. Furthermore, the index is still based on little data. In addition, the same index is used for all plants in all situations, even though natural variation could

lead to very different responses even under the same AOT40. For example, the natural tolerance of vegetation could be higher in the South of Europe than in the North, due to adaptation to the natural higher levels of ozone in the South. Regardless of the critique on the use of AOT40, other models used for the same purpose also have their problems. There is still work to do to define the best way of estimating the ozone damage suffered by vegetation. (Paoletti and Manning 2007)

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