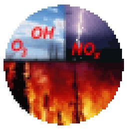

Lower Atmosphere

Basics

Unit 3

Ozone and nitrogen oxides as key compounds

Most chemical processes which occur in the atmosphere are oxidation processes. The key chemical compounds involved are the hydroxyl radical (OH), ozone (O_3) and the nitrogen oxides ($NO + NO_2 = NOx$).

In this unit we look at the formation and main characteristics of these compounds. We look particularly at the role of ozone which is essential in the stratosphere but harmful in the troposphere.

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Part 1: Ozone

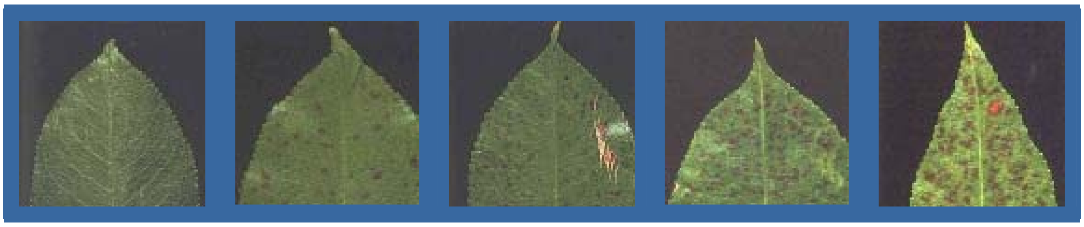
Tropospheric Ozone

Ozone is probably the most famous gas in climate science. Why is this the case?

Ozone is a very contradictory gas. It is essential in the stratosphere where it protects us from damaging ultra-violet radiation from the Sun, but it is harmful in the troposphere with high levels causing health problems. In some large cities, car traffic is banned on particular days to prevent ozone smog events from occurring.

As well as causing health problems, tropospheric ozone acts as a strong greenhouse gas and contributes to global warming.

In this unit we look at how tropospheric ozone is harmful to plants and humans and how it acts as a greenhouse gas. In the topic on the Upper Atmosphere, we look at how stratospheric ozone protects us from harmful ultra-violet radiation.

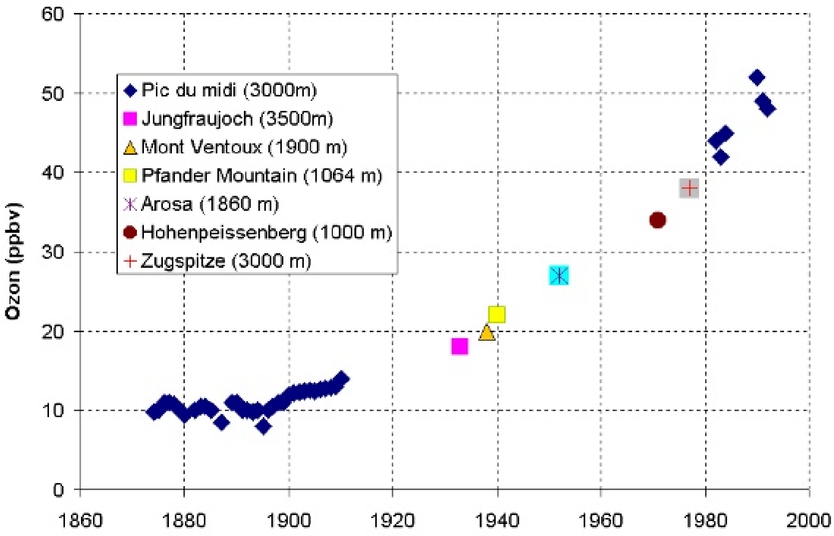


1. a-e) Chronic plant damage is one of the negative impacts of ozone. These photographs show leaves from prunus serotina (the autumn cherry) 0%, 4.4%, 7.8%, 12.3% and 24.5% damage. Source: Innes, Skelly, Schaub - Ozon, Laubholz- und Krautpflanzen, ISBN 3-258-06384-2, Copyright by Haupt Verlag AG / Switzerland.

Ozone is a gas with many different properties. Some of them are helpful, some of them are not. Ozone is found in different layers of the atmosphere:

The ozone layer in the stratosphere occurs at altitudes of greater than 10 km. This ozone is essential since it prevents harmful ultra-violet radiation from the Sun reaching the Earth and prevents us from getting skin cancer.

We need a small amount of ozone in the troposphere since it helps clear the air of harmful chemicals. However over the past few decades, ozone levels have risen continuously. During ozone smog events, levels can be so high that they are dangerous to our health.



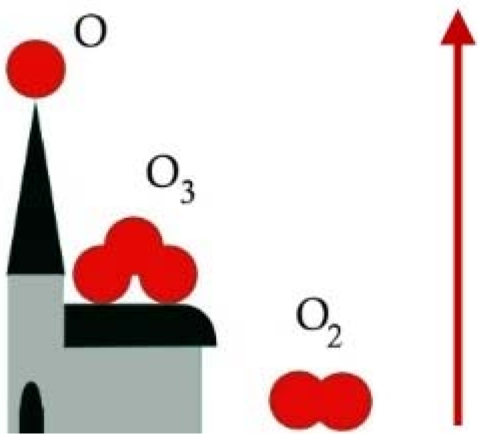
2. Tropospheric ozone levels have continuously increased since the first measurements were made in 1870. The diagram shows the fraction of ozone in every billion volume fraction of air = ppbv. Composed by Valérie Gros, MPI Mainz, adapted from: Marenco et al., 1992 (Long term evolution of ozone at the mid-latitudes of the Northern Hemisphere, European Geophysical Society, XVII General Assembly, 6-10 April 1992, Edinburgh).

Danger to the respiratory system

Ozone is a reactive and irritant gas and, in high concentrations, leads to respiratory problems. It causes inflammation in the lungs and bronchia. Our bodies try their best to protect our lungs from the ozone. However, preventing ozone from entering the lungs also reduces the amount of oxygen we can take up and this makes our hearts work harder. People with respiratory problems such as asthma are particularly at risk of health problems. In the worst case, high ozone levels can cause death.

Ozone - a special form of oxygen

Ozone is a special form of oxygen. Normal oxygen molecules (O_2) consists of two oxygen atoms whereas ozone consists of three (O_3). It is less stable, more reactive and is able to destroy organic material. This is how it damages plants and causes human health problems. We look at how this happens in more detail in the *'read more'* section of this Unit.



3. The three forms of oxygen, all with very different stabilities. The arrow shows increasing reactivity. Image by Elmar Uherek.

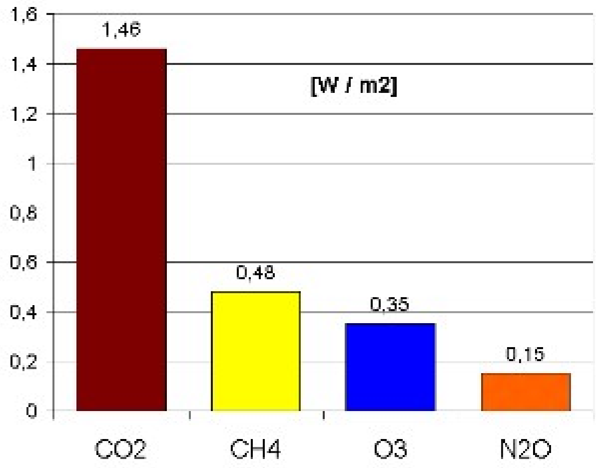
Forms of oxygen in the air

form of oxygen	number of atoms	chemical stability	appearance in air
atomic oxygen	1 atom	unstable / very reactive	slightest traces
'normal' oxygen	2 atoms	stable	21% of the air
ozone	3 atoms	fairly stable / reactive	10 - 100 ppb

ppb = parts per billion

Ozone as a greenhouse gas

After carbon dioxide (CO_2) and methane (CH_4), tropospheric ozone is the third most important greenhouse gas, able to absorb heat radiation coming from the surface of the Earth and trap this heat in the troposphere. The additional radiative forcing (ΔF) since the Industrial Revolution (about 1750) gives us a measure of the contribution of human activity to the warming of the Earth. The graph shows the impact of tropospheric ozone compared to other greenhouse gases.



4. The contribution of different greenhouse gases to radiative forcing (ΔF).

Tropospheric ozone causes health problems for animals and damage to plants and acts as a strong greenhouse gas contributing to global warming. So we need to look for ways to reduce ozone concentrations in the troposphere.

Calculate how much each greenhouse gas contributes to global warming!

The diagram above shows the contribution of several greenhouse gases to the positive change in radiative forcing ΔF at the tropopause (given in W m^{-2}). The equation below shows how the average temperature at the Earth's surface (ΔT_S) changes in response to changes in this radiative forcing.

ΔT_S / ΔF = 0.5 °C / W m^{-2}

Can you calculate the temperature change (ΔT_S) caused by cabon dioxide, methane, ozone and nitrous oxide?

Part 2: Nitrogen oxides

Nitrogen oxides - formation and relevance

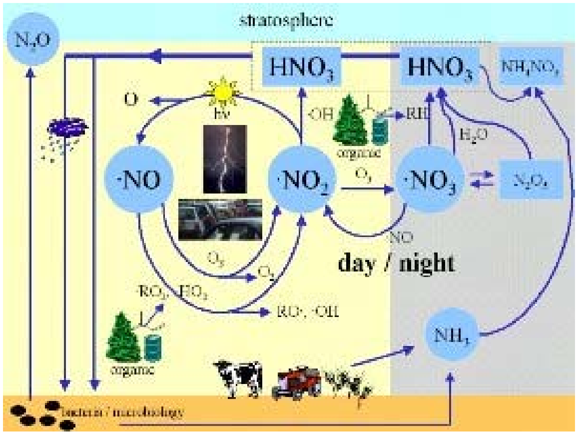
Nitrogen oxides play an important role in the chemistry of our atmosphere. In this section we look at how they are formed and why they are so important.

1. Traffic, an important source of nitrogen oxides. (c) FreeFoto.com

Where do nitrogen oxides come from?

The most important forms of reactive nitrogen in the air are nitrogen monoxide (NO) and nitrogen dioxide (NO_2) and together we call them NOx. Nitrogen oxides are formed in the atmosphere mainly from the breakdown of nitrogen gas (N_2). Because the two nitrogen atoms in N_2 are bound very strongly together (with a nitrogen to nitrogen triple bond), it isn't easy to break N_2 down into its atoms. A few bacteria have developed special mechanisms to do this and very high temperatures can also break the molecule down. Vehicle engines operate at high enough temperatures and nitrogen oxides are emitted in the exhaust fumes. Catalytic converters fitted to cars decrease the production of these harmful compounds. Nitrogen oxides can also be formed when biomass is burnt and during lightning.

2. right: Lightning is another important source of nitrogen oxides. Picture by Bernhard Mühr / Karlsruher Wolkenatlas.



3. This figure gives an overview of the role of nitrogen oxides in some of the most important processes in atmospheric chemistry. By Elmar Uherek.

Where are they involved?

NOx (= NO + NO_2) and other nitrogen oxides are important in almost all atmospheric reactions. Another form of nitrogen oxide, the very reactive nitrate radical (NO_3) is formed in the dark and this controls the chemistry of the night time atmosphere. Nitrogen oxides react with water to form nitric acid (HNO_3). Nitric acid is not only a major contributor to acid rain but is also the main way in which nitrogen oxides are removed from the air, either by dry deposition of the acid directly or by removal in rain. Nitric acid is also important in polar stratospheric cloud chemistry. Here it occurs as nitric acid trihydrate and this species plays a part in the formation of the ozone hole.

Names of nitrogen compounds:

Formula	**Systematic Name**	**Common Name**
NO	nitrogen monoxide	nitric oxide
N_2O	dinitrogen monoxide	nitrous oxide
NO_2	nitrogen dioxide	nitrogen peroxide
N_2O_5	dinitrogen pentoxide	nitric anhydride
N_2O_3	dinitrogen trioxide	nitrous anhydride
HNO_3	-	nitric acid
NH_3	-	ammonia

Nitrogen oxides are very important in the formation and loss of tropospheric ozone. They are involved in catalytic cycles and continuously react and reform. Nitrogen dioxide (NO_2) is broken down by sunlight to form nitrogen monoxide (NO). This NO then re-reacts to form more NO_2. Ozone and unstable oxygen compounds known as peroxy-radicals can also be involved in this cycle. We will look at these reactions in more detail later.

We emit far too much of these nitrogen oxides during combustion proceses, particularly from vehicles. The main aim of fitting catalytic converters to cars is to reduce the emission of these compounds into the air.

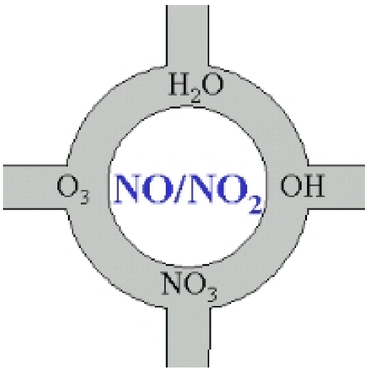
Other important nitrogen gases in the atmosphere include:

Nitrous oxide (N_2O) which is formed during microbiological degradation processes. It is an important greenhouse gas but does not react in the troposphere. In the stratosphere it destroys ozone.

Ammonia (NH_3) is the most important basic gas in the atmosphere. It comes mainly from agriculture, both from the storage of animal wastes and from fertiliser use. It reacts in the atmosphere with acid species like nitric acid to form aerosol particles.

Nitrogen oxides - at the centre of atmospheric chemistry

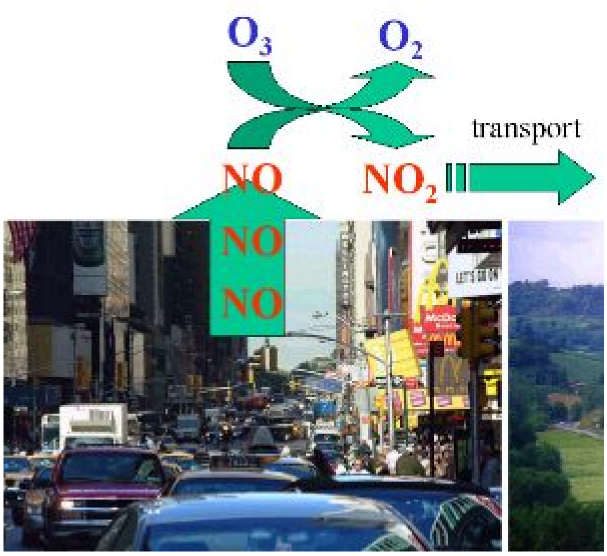
Nitrogen oxides are really at the centre of atmospheric chemistry. Most chemical compounds which are oxidised and removed from the air or are transformed into other chemical species come into touch directly or indirectly with NO or NO_2.



4. Nitrogen oxides - at the centre of atmospheric chemistry. Image Elmar Uherek.

Part 3: Ozone smog

Ozone smog is a significant problem in big cities. Ozone is formed as part of a complicated process involving nitrogen oxides, ozone formation and ozone loss. Ozone smog formation shows just how interconnected processes in the atmosphere really are.



1. NOx emissions in the city. Image: Elmar Uherek, photograph © FreeFoto.com.

What happens in the city?

Lets make the example simple and assume almost all nitrogen oxides come from combustion processes happening in car engines. Nitrogen monoxide (NO) rich air rises from the roads. This NO reacts with ozone (O_3) already in the air to form nitrogen dioxide (NO_2). So the first part of the reaction cycle actually causes a loss of ozone from the atmosphere. Indeed, directly over roads, ozone concentrations are often very low. During ozone smog periods, ozone concentrations in cities can be lower than in the rural areas around. The plumes of NOx rich air are then transported by the wind to the countryside.

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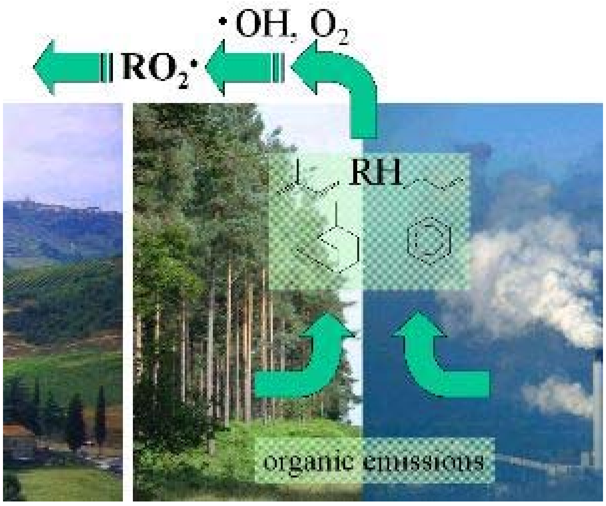
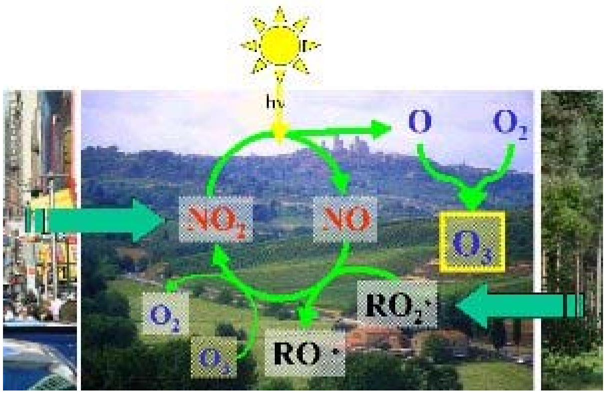


2. Organic emissions from forests and industry.
Image: Elmar Uherek, Photograph © FreeFoto.com.

Where do organic compounds come from?

The second partner needed in the reaction cycle are organic peroxides. What are these and where do they come from? Organic molecules are emitted from forests and other plants but also from human sources (e.g. solvents or fuel at filling stations). The structure of a few organic compounds, which are abbreviated as RH, are shown here. These compounds are chemically attacked in the air. The typical reaction favoured during the day is the reaction with the hydroxyl radical (OH) followed by addition of an oxygen molecule (O_2). The result is a peroxy-radical (RO_2), with R representing the unreactive organic part of the molecule. Radical species have a spare electron which makes them very reactive.



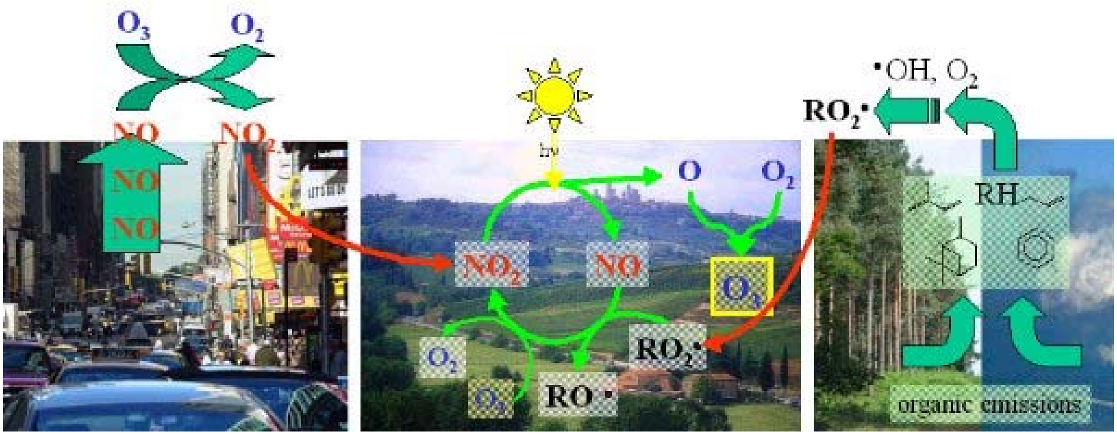
3. Formation of ozone smog. Image: Elmar Uherek, photgraph © FreeFoto.com.

When are the best conditions for ozone smog?

Over rural areas, downwind of cities, the ozone formation cycle starts:
1) Nitrogen dioxide (NO_2) is broken down by the Sun to form oxygen atoms (O) and nitrogen monoxide (NO).
2) The O atoms react with oxygen gas (O_2) to form ozone (O_3).
3) The NO reacts with peroxy radicals RO_2 forming NO_2 again.
4) Some O_3 is removed by reaction with NO. The amount lost depends on the concentration of the competing RO_2 radicals.

In the end the peroxy radicals are lost and ozone is formed while the nitrogen oxides are always recycled. This cycle only happens if:

a) There is enough sunlight to breakdown NO_2 into NO and O (the reaction happens on hot sunny days).
b) If the mixture of peroxy-radicals and nitrogen oxides favours the reaction.



4. The complete ozone oxidation cycle, 960 px width. Image: Elmar Uherek.

If no nitrogen oxides are available, the reaction cycle can't take place.
If nitrogen oxide concentrations are very high, NO reacts not only with peroxy radicals but also with ozone and this removes ozone from the system.
If sunlight is not available, NO can't be recycled again and not enough peroxy radicals are formed to keep the cycle going.

Nitrogen oxide concentrations are usually low enough to prevent severe ozone smog events occurring but if we continue to emit them during combustion processes, ozone smog events are likely to increase. A comparable situation is seen in the smoke plume of a vegetation fire as the temperatures generated in these fires are hot enough to allow nitrogen oxide to form.