Lower Atmosphere

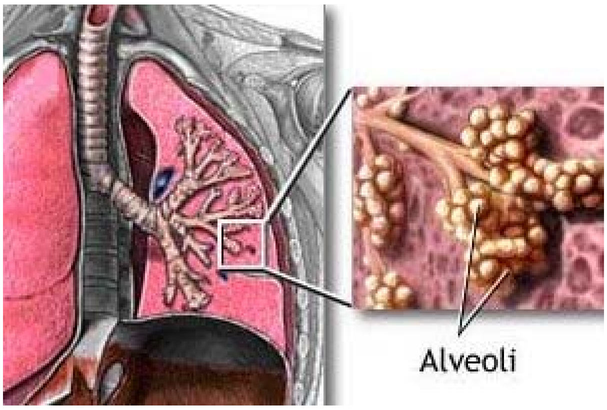
Read more

Unit 3
More on ozone and fire

Ozone is a rather aggressive gas. In this unit we look at how it attacks other molecules and what impact it has on human health.

Atmospheric concentrations of ozone are difficult to predict because they depend strongly on the local conditions at a particular time and on the chemical composition of the air. We look at the factors which control the atmospheric concentration of ozone here.

Fires are an important source of carbon dioxide, nitrogen oxides and ozone. In the final text of this unit, we look at the chemistry of fires and fire events worldwide.



High ozone concentrations affect the alveoli in our lungs. Do you know why? © US national library of medicine.

Part 1: Ozone reactions

Why is ozone dangerous?

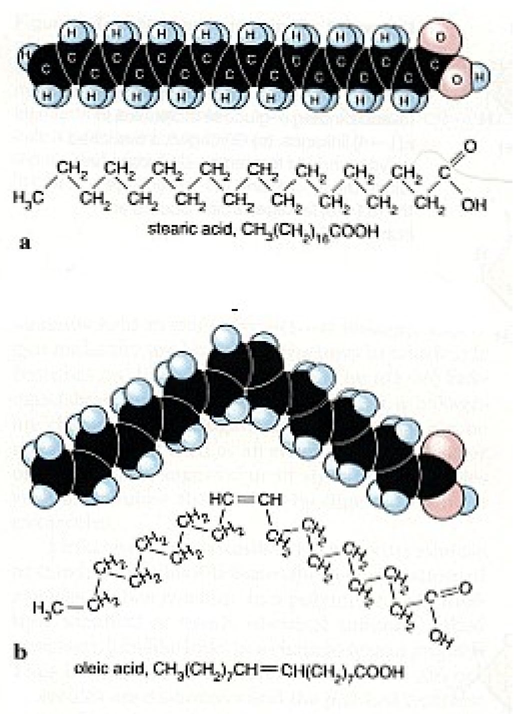
Stratospheric ozone protects us from harmful ultra-violet radiation from the Sun. However, in the troposphere, ozone is dangerous to our health and in this section we look at the damage ozone does.

A little bit of ozone is needed

Its not true that we don't want any ozone in the troposphere. We need low levels in the air to form hydroxyl radicals (OH) to clean the air of harmful chemicals. However, high concentrations of ozone are harmful to our health and damage plants. In swimming pools ozone is sometimes even used to kill bacteria. So what makes ozone so aggressive?

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (\lambda < 310\ \text{nm})$$
$$O(^1D) + M \rightarrow O - M \quad 97\%$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$O(^1D) + H_2O \rightarrow 2OH \quad 3\%$$

1. OH formation can only take place if there is a small amount of ozone in the air. scheme: Elmar Uherek.



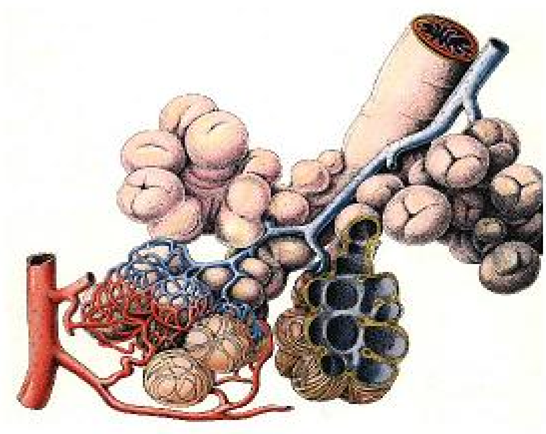
2. Not all fatty acids have double bonds. Some are (a) saturated and so just have C-C single bonds. Many of them are, however, (b) unsaturated and have C=C double bonds. Source: NTRC, Univ. of Texas Kingsville.

Ozone attacks our respiratory system

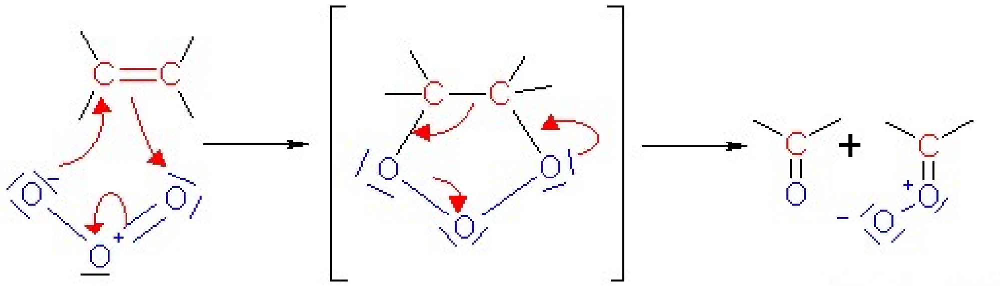
We know that organic compounds made up of carbon (C) and hydrogen (H) are present in all living organisms, in plants, in animals and in our bodies. As well as C and H, these compounds may also contain oxygen (O), nitrogen (N), sulphur (S) and phosphorous (P). The main structures of organic compounds are made of carbon, and generally include C-C single bonds and C=C double bonds. C=C double bonds are found everywhere; in unsaturated fatty acids, haemoglobin, proteins, on the surface of the pulmonary alveoli in our lungs and its mucus membrane and in many other bio-molecules.
Ozone attacks these C=C double bonds.
The other two main oxidants, OH and NO_3, have extremely short lifetimes and react immediately they are formed. Ozone, however, can enter the lungs. Every day we breathe 20,000 liters of air into our lungs. This air carries many chemicals and particles, including ozone.

Ozone breaks down double bonds.

Ozone reacts with fatty acids in the lungs in the same way that it does in the air. Ozone reacts with the C=C double bonds and breaks down the molecule into very reactive radicals. These radicals then react further. The end result is inflammation of the lungs. This causes breathing problems in previously healthy people and is particularly dangerous for people with asthma. If ozone levels are high it can be dangerous to do sports or hard physical activity.



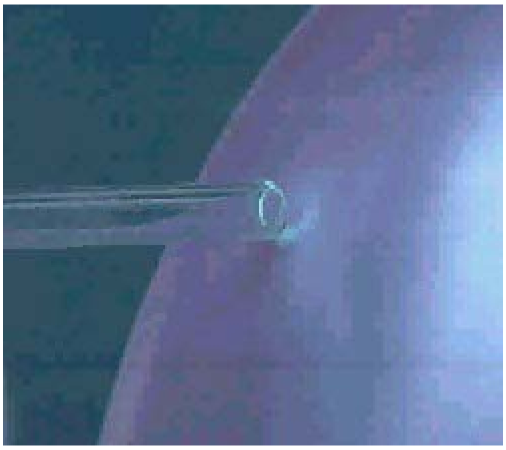
3. Our lungs have a surface area of 80 - 100 m^2 and we breathe in 20,000 litres of air each day. This air contains many chemicals and particles, including ozone and this ozone attacks the alveoli and mucus membranes of our lungs. © emphysem-info.



4. The reaction of ozone with double bonds (ozonolysis) breaks down (cracks) the C=C bond. scheme: Institute for chemical education - Univ. of Duisburg, Germany.

Ozone not only breaks down the C=C double bonds in our lungs, it also attacks the double bonds of terpenes from plants, many other molecules in the air and causes damage to plant leaves. At very high concentrations ozone can even destroy the double bonds in the rubber of an air balloon and make it burst.

5. a + b) Rubber contains C=C double bonds. If you expose a balloon to a stream of ozone rich air ...



... it becomes thinner and thinner and finally the balloon bursts. Experiment: Institute for chemical education - University of Duisburg, Germany.

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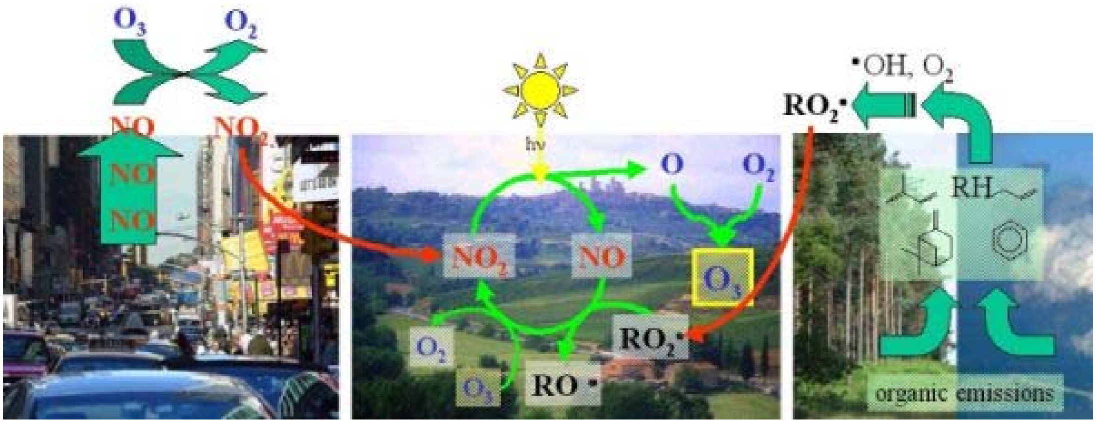
Part 2: Ozone abundance

Understanding tropospheric ozone abundance

In this section we look at where ozone comes from and how is removed from the air.

Ozone control by nitrogen oxides and organic compounds

In Unit 3 of the basics section of the Lower Atmosphere topic we learnt about the diverse characteristics of ozone and how ozone smog forms. Have a look at the chapter on 'ozone smog' again and at the scheme below.



1. How ozone smog is formed. - Scheme: Elmar Uherek.

High ozone concentrations are formed in and around urban areas on hot sunny days when volatile organic compounds (VOC's) and nitrogen oxides from traffic react together.

The presence of nitrogen oxides and sunlight (hv) alone does not necessarily lead to ozone formation. This is because the ozone which forms simply reacts again with nitrogen oxide (NO) and is destroyed. So this reaction cycle (a so called null cycle) results in no net production or depletion of ozone in the air.

$$NO_2 + h\nu \longrightarrow NO + O$$

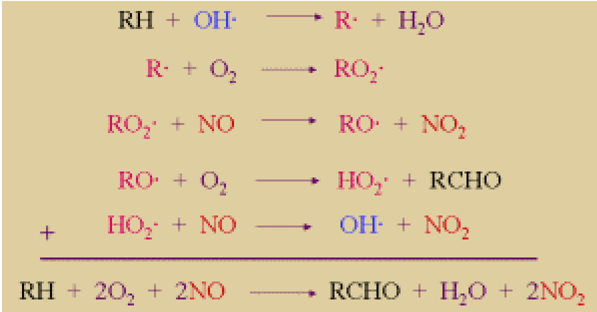
$$O + O_2 \longrightarrow O_3$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

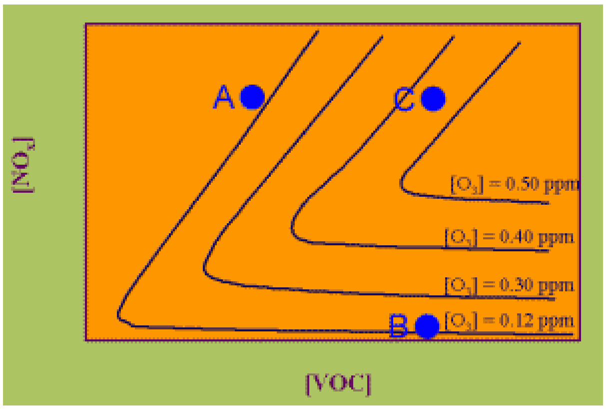
2. a) Cycle of ozone formation and consumption. Although there is high conversion of nitrogen dioxide (NO_2) into ozone, there is no net production or depletion of ozone overall.

However the air also contains volatile (gaseous) organic compounds (VOC's). In chemical reactions these are often abbreviated to RH. They react with OH radicals to form peroxy radicals RO_2 and these radicals oxidise NO. This prevents the NO from reacting with ozone and levels of ozone rise.

hv stands for sunlight, since light energy is given by the quantum mechanical expression E = hv



2. b) The peroxy chemistry of organic compounds RH competes with ozone for the NO.



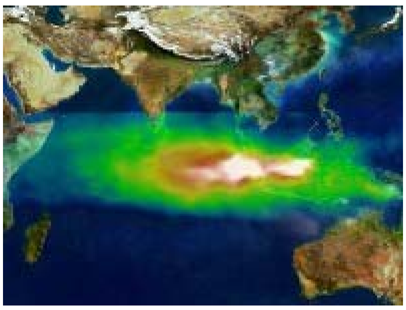
3. Ozone isoplethes - The graph shows the dependence of the formation of high ozone concentrations on the mixture of volatile organic compounds (VOC) and nitrogen oxides (NOx). Images 2+3 are adapted from a lecture given by Mike Hannigan, Univ. of Colorado, Boulder, U.S.A.

In a diagram of so called isopleths you see black lines representing the same ozone concentrations. Production of more or less ozone strongly depends on the mixture of nitrogen oxides (NOx) and VOC's (RH) in the air. If levels of NOx are high but VOC levels are low, ozone will not be formed (blue point A) and may even be consumed in the city centre. If levels of VOC's are high but NOx levels are low, ozone concentrations are also low (point B). It is only when both NOx and VOC levels are high that ozone levels increase (point C).

Since ozone levels respond quickly to the local conditions, ozone concentrations vary depending on the time of day, on how much sunshine there is and on NOx and VOC concentrations. This makes it difficult to calculate a global average ozone concentration.

Other sources

Urban traffic is not the only source of nitrogen oxides and is, therefore, not the only source of ozone. Nitrogen oxides are emitted during other combustion processes such as vegetation fires. The image on the right shows smog in white and increasing ozone concentrations from green to yellow to red in the plume of the big fires in Indonesia in 1997.



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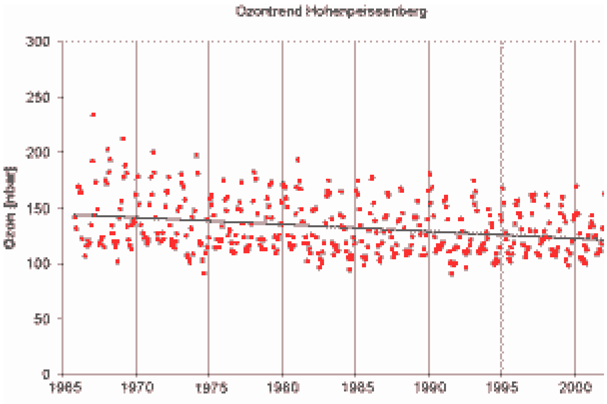
Lightning is another source of nitrogen oxides. Some high ozone concentration events in Australia are actually the result of nitrogen oxides formed during thunderstorms and heavy lightning over South Africa.

4. Smog plume from vegetation fires in Indonesia. Image courtesy NASA GSFC Scientific Visualization Studio, based on data from TOMS.



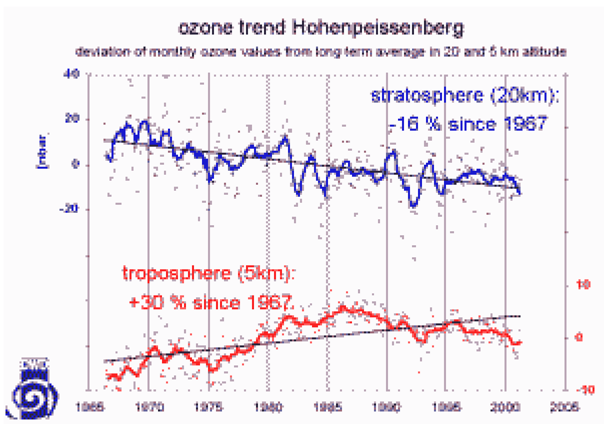
5. Trend in the monthly ozone abundance measured at the Hohenpeissenberg Observatory. Image: courtesy of the German Weather Service.

Measuring ozone

There are only a few surface ozone measurement stations in Indonesia and none over the ocean so how did we get the information about ozone concentrations during the fires? Ozone is observed from space by instruments installed on satellites. When we use satellite data we have to take into account that the instruments measure the concentration in the whole atmosphere and not just in the surface layer. Look at the ozone trend measured at the German Hohenpeissenberg Observatory. Does this mean that ozone in Germany is decreasing? Previously we learnt that tropospheric ozone levels have increased almost everywhere.

Although the data suggests it, tropospheric ozone levels are not falling.

Ozone trends depend on the location and there are large variations in levels over the Earth. We cannot estimate ozone trends either from the global view of satellites or from the local view of a single ground station. The figure on the right gives ozone data at two different heights in the atmosphere and shows that ozone distributions have different trends depending on the altitude. The data shows that ozone levels are decreasing in the stratospheric ozone layer (have a look in the 'Higher Atmosphere' topic for more information on this) and increasing in the troposphere.



6. Ozone data from Hohenpeissenberg separated for two altitudes, 5 km in the troposphere and 20 km in the stratosphere.
Image: courtesy of the German Weather Service

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Satellites see both the troposphere and the stratosphere at the same time. The data obtained, therefore, needs to be carefully interpreted to enable accurate representations of ozone trends at different altitudes in the atmosphere.

Part 3: Fire

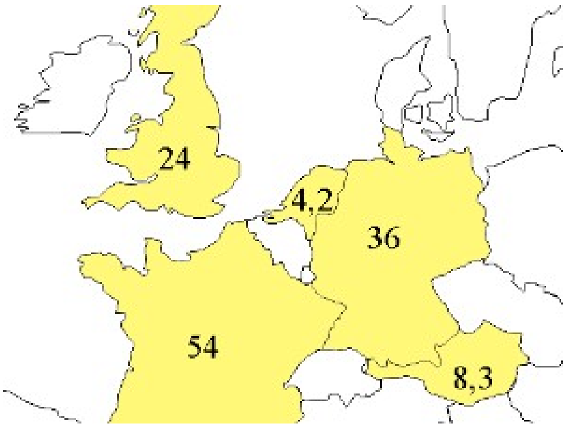
Fire chemistry and its global importance

Every year, large areas of our planet burn:

10 million hectares of boreal forest in the northern latitudes
40 million hectares of tropical and sub-tropical forest
500 - 1000 million hectares of open forest and savannah

where 1 million hectares = 10,000 km^2

Imagine the area:



1. Area of European countries in millions of hectares. The Netherlands, for example, covers an area of 41,500 km^2. image: Elmar Uherek.

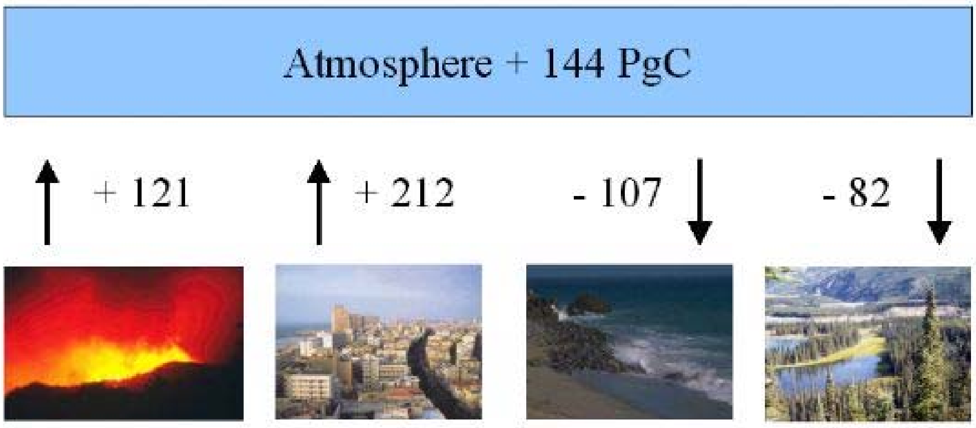
2. Smoke over Siberia. Image courtesy of the SeaWiFS Project

Because most of the focus is on the destruction of the rainforests by fire, its easy to forget that large areas of the boreal forests in, for example, Siberia and Canada also burn each year. These boreal forests cover an area of 920 million hectares, make up 73% of the global coniferous forest area and 29% of the total world forest. Nowadays, boreal forest fires are not only caused by nature but also by humans.

The global carbon budget of CO2 exchange for the period 1850 - 1990.

Values in Pg Carbon (Pg C) 1 Pg = 1015 g = 1 billion tons.

Emissions from man-made fires are an important source of carbon to the atmosphere.



3. Carbon dioxide - sources and sinks - image: Elmar Uherek

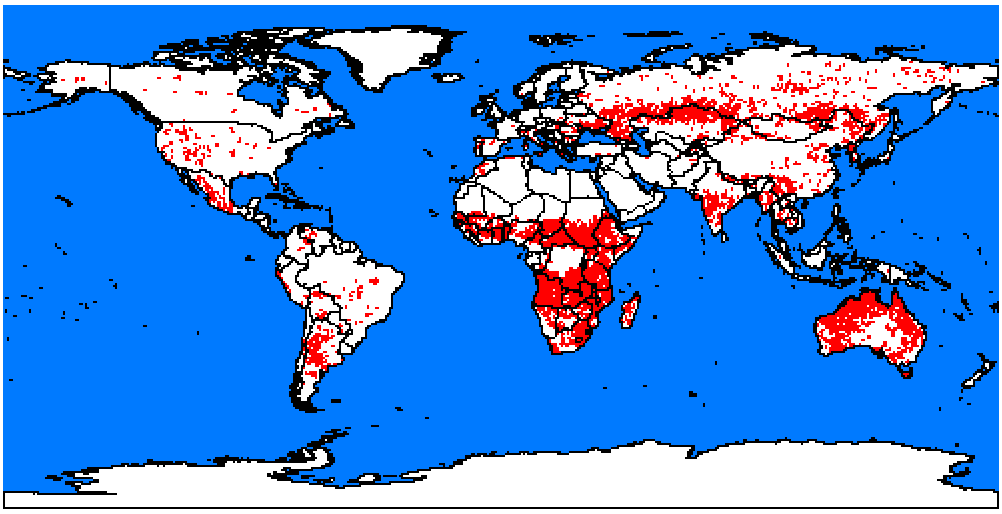
The main sources are:
1) landuse change (+ 121 Pg C)
2) fossil fuel burning (+ 212 Pg C)

The main sinks are:
3) CO_2 uptake by the oceans (- 107 Pg C)
4) CO_2 uptake by continents (- 82 Pg C)

The uptake of carbon dioxide by the continents is poorly understood but is thought to be primarily the result of increasing plant growth in places other than the typical burning regions.

90% of the CO_2 emissions from landuse change are from deforestation. A major problem in the rainforests is that once the forest has burnt, secondary vegetation grows. This secondary vegetation burns yearly. This stops new trees establishing themselves and prevents reforestation.

Natural vegetation fires can be short term CO_2 sources to the atmosphere. Over the long term, however, natural fires have either very little influence on CO_2 levels or may actually represent a very small carbon sink (< 0.1 pG C y^{-1}) since carbon containing sediments are stored in the ground. Open forest and savannah fires occur in cycles of 1-3 years over much larger areas than rainforest fires and have little influence on the climate system.



4. Fires spots around the word. Map: from Global fire monitoring centre.

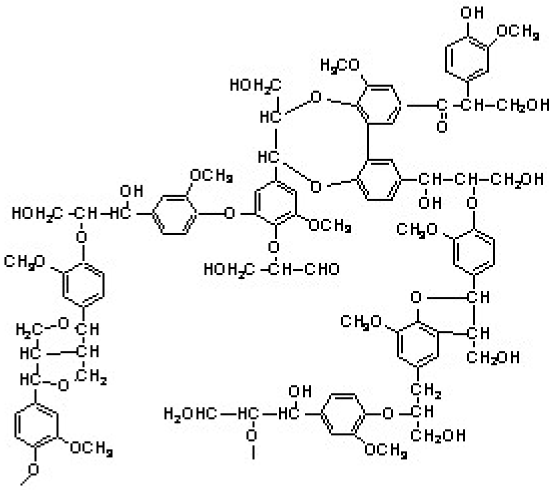
What is formed during the combustion process?

This depends on;
a) what the plants consist of
b) the temperature of the flames
c) how much oxygen is available
d) whether it is an open fire or a smouldering fire

What do plants consist of?

Plants contain up to 60% water although their water content is generally lower than this before the fire season as the vegetation looses a lot of water during drought times.
The typical elemental composition of the dry organic matter in plants is;
carbon (C) 45%
oxygen (O) 42%
hydrogen (H) 6%
others (N, S, P) 7% (S 0.1 - 0.5%)
Plants typically have the following components:
cellulose and hemicellulose [carbohydrates $(C_6H_{10}O_5)_n$] 50-70%
lignin 15-35%
smaller amounts of: proteins, amino acids, other metabolites
minerals up to 10%

5. The picture shows a forest area during fire and two years later after reseeding and rehabilitation efforts. photo: Dylan Rader. Wildland fire pictures.



6. Lignin gives the wood its structure. It is formed when water is irreversibly lost from sugars to form aromatic (ring) containing polymers.

The burning process

After ignition, oxygen levels are sufficiently high to allow a period of open fire to occur. As oxygen levels fall, the fire begins to smoulder. During the period of open fire, a simple mixture of fully oxidised compounds, including CO_2, are formed. Incomplete oxidation occurs during the smouldering fire stage and a complex mixture of compounds are formed which may even include methane (CH_4).

7. a) open fire; photo by Dylan Rader

7. b) smouldering fire; photo by Meredith Rader.

After ignition (> 180°C / 450 K) flaming combustion (> 580°C / 850 K) starts. Simple molecules such as CO_2, H_2O, NO, N_2O, N_2 and SO_2 are released as oxidation products. As oxygen levels fall, the flames cease ....

... and smouldering (< 580°C / 850 K) begins. Due to a lack of oxygen, CO and many partially oxygenated organic compounds (including formaldehyde, acetaldehyde, methanol, acetone and methane) are released.