



Tananyag fejlesztés idegen nyelven

Prevention of the atmosphere

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Pollutants in the air (gases II. and particulates)

Lecture 6
Lessons 16-18)



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Lesson 16

Gas pollutants in the air: - carbon-oxides,
VOC and methane



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c) Carbon oxides

Carbon monoxide (CO) is a colorless, odorless toxic gas, undetectable to human senses. In indoor pollution gas toxicity may be fatal (number of death resulted from CO presence is constant from year to year)

The complete combustion of fossil fuels generates global pollutant carbon dioxide (CO₂). It does not harm human health (until today's concentrations). We do not consider CO₂ as a local pollutant. (We discuss CO₂ on global level later)

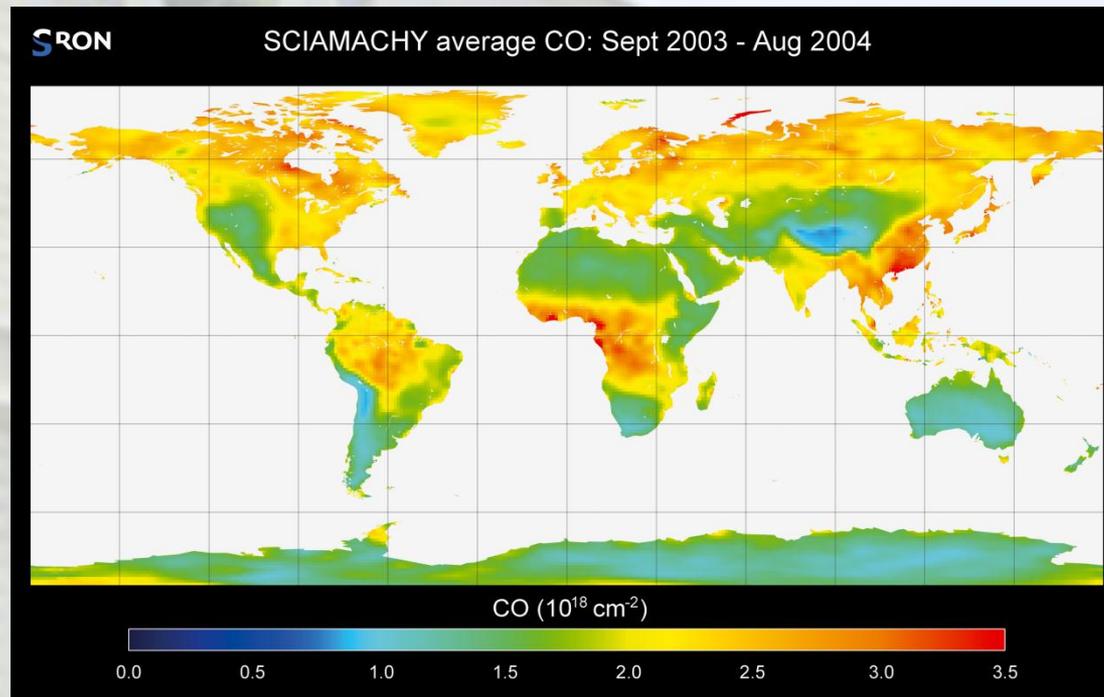
Incomplete combustion of carbonaceous materials induces carbon monoxide (CO) production



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Fig. 52 The global distribution of carbon monoxide



http://atmos.caf.dlr.de/projects/scops/sciamachy_book/sciamachy_book_figures/chapter_10/fig_10_12.jpg



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- Investigated period contains one year (between 2003 and 2004) – see Fig. 52!
- Elevated CO is present in regions due to biomass burning. See red colored data of Africa!
- The emission of vehicles is the second main reason of increased CO emission – yellow spots
- The published measured data is largely consistent with model results

(Image was taken by H. Schrijver, SRON)



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Antropogenic sources of CO

- Transportation is the major source of CO (vehicles)
- cigarette smoke
- industry (metal processing, refineries etc.)

The congested urban areas, large cities (high population and vehicle density, low ventilation) and neighborhood of highways are the mostly exposed areas.

CO is a stable gas. It leaves the air in an oxidized form as

CO₂. The main sinks are:

- oceans
- soils (micro organisms)
- vegetation





d) Volatile Organic Compounds (VOCs); non-methane VOC

Easily evaporative (volatile) compounds in the atmosphere

A very populous family including a wide range of organic matters (hydrocarbons, other organic compounds containing chlorine, sulfur, or nitrogen etc.).

The methane is excluded from this category due to historical reasons (we did not consider its impact) earlier.

This is not acceptable nowadays. The reason is the high level agricultural contamination of methane coming from

- rice production and
- ruminant breeding



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Emissions are high in India and parts of China due to very intense agricultural activities but also over tropical rainforests. In case of China it is due to high population density. The reason of tropical rain forest increment is still unknown. Until know this phenomenon is obvious in measurements compared with model calculations.

In the bottom panel the difference between retrieved and modeled densities is shown with discrepancy 'hot spots' in Indonesia, Central Africa and South America.

(Images were taken by Frankenberg et al. 2005- see Fig. 53.)





Antropogenic sources of VOC

- Combustion of fuels (gasoline evaporation)
- Dry cleaning, solvent application (including paints, adhesives, aerosols, metal cleaning, printing)
 - Transport processes
- Oil production and refining
- Extraction and distribution of fossil fuels

Agriculture alone responsible for VOC emission in:

- Production of alcoholic drinks (breweries and distilleries)
- crop growing, silage manufacture
- sludge spreading





Natural Sources of Volatile Organic Compounds

The most important natural sources are the rainforests because of organic decomposition of vegetation.

They release about the half of the total natural emission.

Plants synthesize and emit a huge amount of organic compounds of different matters (do not forget, that they are out of pollutants due to their natural feature)





- The antropogenic release in case of VOCs is relatively small. Some of them has of primary importance due their:
 - possible leisure relating toxic effect on human beings and crops; and
 - they are very reactive gases (see also photochemical smog formation)

The highest harm is waited close to traffic roads and overpopulated large cities





d/1) Methane excluded of VOC

Methane is a colorless and odorless gas in the air. As a gas it is flammable in a narrow range of concentrations (5–15%) of the air. Methane may form explosive mixtures with air that makes it a potential source of harm. It does not danger our health directly.

The relative abundance of methane in nature makes it an attractive fuel; however, it is a gas (normal air temperature and air pressure), and as a gas is difficult to transport from for long distance its source.

The major source of methane is extraction from geological deposits from natural gas fields.



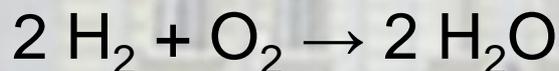


- Combustion of methane

The process is known as pyrolysis. During its burning methane forms formaldehyde (HCHO or H₂CO). Later on the formaldehyde transforms formyl radical (HCO), which then transforms further into CO. This is the oxidative pyrolysis:



In the next step H₂ oxidizes, forming H₂O, and releases heat quickly



In the last step the CO also oxidizes forming CO₂ and producing more heat.



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Lesson 17

Methane II. Secondary pollutant in the air - PAN



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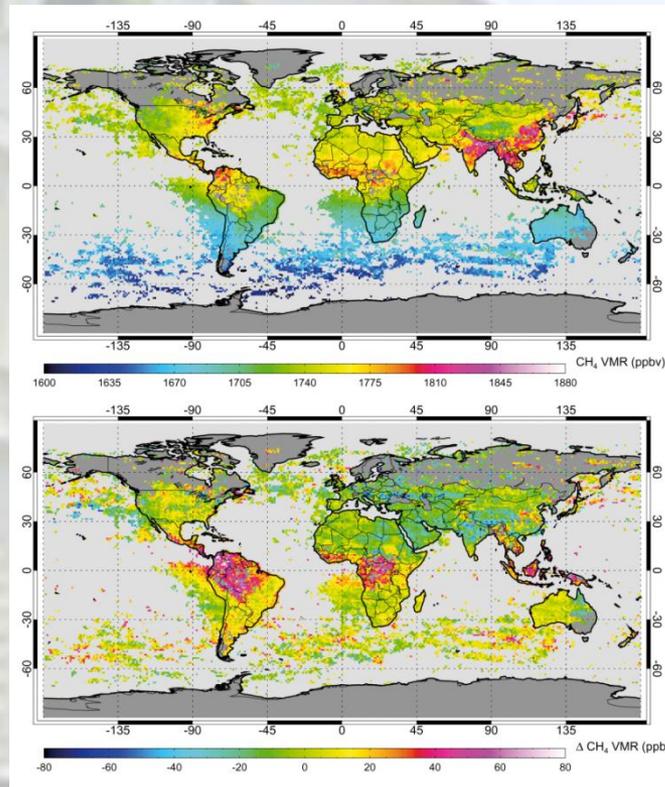


- The abundance of methane in the Earth's atmosphere in 1998 was 1745 parts per billion (ppb), up from 700 ppb in 1750.
- By 2008, however, global methane levels, which had stayed mostly flat since 1998, had risen to 1,800 ppb.
- By 2010, methane levels, at least in the arctic, were measured at 1850 ppb, a level scientists described as being higher than at any time in the previous 400,000 years.
- Sources and sinks see later in the chapter of discussing global warming





Fig. 53 Distribution of methane concentrations for Aug-Nov 2003



http://atmos.caf.dlr.de/projects/scops/sciamachy_book/sciamachy_book_figures/chapter_10/fig_10_14.jpg



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e) Secondary pollutants in the air

- In the atmosphere, inside an oxidizing medium, a few transformation happen; with two or more pollutants, or pollutants and components of the air are reacting continuously. In most cases photochemical reactions used to be.
- One of the most important result of the above photochemical reactions is the tropospheric ozone formation. Ozone is one of the most important pollutant of the troposphere. We discuss it in the frame of Los Angeles (oxidizing) smog.

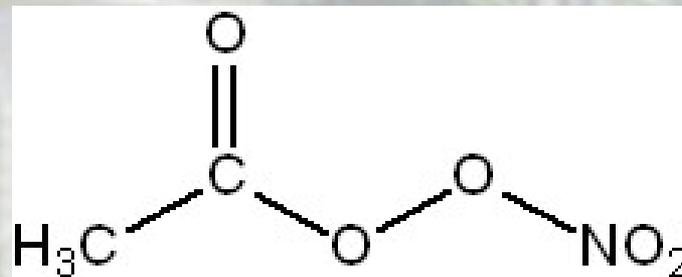




PAN

The other notable products of the oxidizing smog are the PAN (peroxiacetil nitrat) and the aldehydes.

The building block of aromatic hydrocarbons is the benzene ring. There are three double bonds that are not restricted to the positions shown and are free to pass around the ring. PAN structure is:



http://jila.colorado.edu/research/images/chem_PAN.jpg



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They are formed from reactions that involve hydrocarbons and nitrogen oxides including ozone.

The PAN is a naturally occurring chemical in the air existing in low quantities (of a few parts per billion in polluted areas down to about one part per trillion or less over oceanic areas). It was identified in the 1950s, as a compound of smog, when ground-level ozone episodes were observed. It can irritate the eyes and throat, as well as damage plants.





- PAN is a very stable molecule at low air temperatures, and may travel for thousands of kilometers high in the atmosphere before descending, breaking apart, and releasing nitrogen oxide.
- PAN acts as a transport agent of atmospheric pollution. It is also responsible for increase of ground-level ozone concentration.



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Japanese researchers measured the altered sensitivities of different crop species to PAN. This pollutant is a phytotoxicant, can be a restraint of plant growth in closed ecosystems as well as in the field. There has been much difficulty to investigate the effects of PAN on plants due to the presence of other pollutant at the same time, and the low gas concentration. Finally they solved this problem by using a special way of analysis using special instrument.



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They observed that the susceptibilities of species to PAN are not well correlated with the foliar uptake rates of PAN among tested species, suggesting that differences in susceptibility to this pollutant among species are dependent on differences in the competence of the metabolic processes to detoxicate this pollutant.

The PAN is very dangerous for humans also as its derivatives are mutagenic. In most cases they are responsible for skin cancer.

Finally the PAN decomposes into peroxyethanoyl radical and nitrogen dioxide gas.





Fig. 54 Injury typical of Peroxyacetyl Nitrate (PAN) creates a glazy bronzing on the underside of newly expanded potato leaves



<http://www.omafra.gov.on.ca/english/crops/facts/91-01514.jpg>



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Fig. 55 PAN injury of different levels



www.tutorvista.com/.../air-pollution.php



Lesson 18

Aerosols in the atmosphere. Their size and distribution. Sources of particulates



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2. Aerosols (particulates)

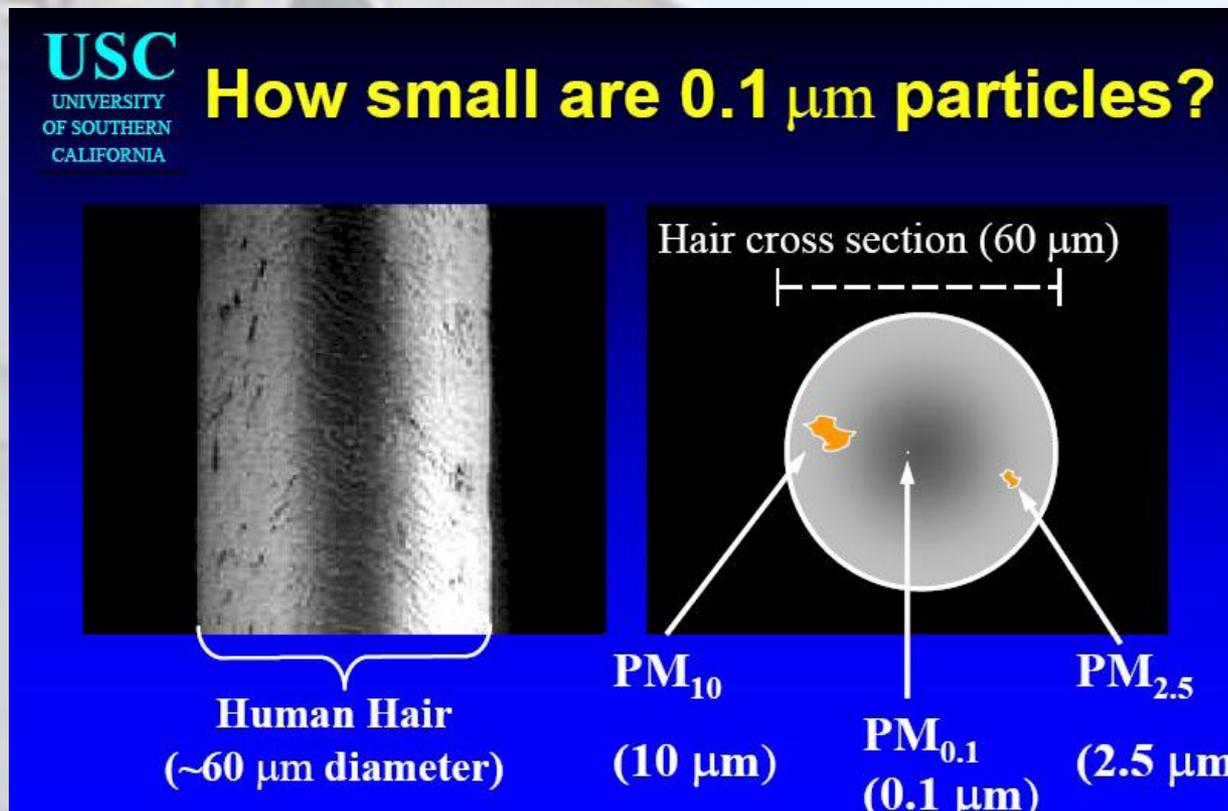
Small sized fragments of solid or liquid nature suspended in the atmosphere are the particulates. The meaning is the same as the aerosols.

Size of particulates covers a wide range from tens of micron up to $10\ \mu\text{m}$. The smaller particles remain in the atmosphere for a longer time period; the role of atmosphere is more important than at larger particles.

Residence time of particulates less than $1\ \mu\text{m}$ is several days. In case of particles above $10\ \mu\text{m}$ diameter the residence time is only a few hours.



Fig. 56 Size of particles in the air



http://www.charlestoncleanair.com/images/point1micron_particles.jpg



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PM₁₀; PM_{2.5} and PM_{0.1}

We use the notation PM_x for aerosols whose aerodynamic diameters are less than or equal to a given value (in μm). In practice there are two groups of particulates: PM₁₀ and PM_{2.5}.

The aerodynamic diameter is defined as the diameter of a sphere with a density (mass per volume) of 1 gcm⁻³ and with a settling velocity equal to that of the particle.

The aerodynamic diameter is very close to the diameter for small aerosols.

Distribution function is applied to write down the different groups of particulates





Distribution curve contains separate nodes fitted to log-normal function of the diameter using the below formula:

$$n(d_p) = \sum_{l=1}^{N_m} \frac{N_l}{\sqrt{2\pi} \ln(\sigma_l)} \exp \left[-\frac{1}{2} \left(\frac{\ln^2(d_p/D_l)}{\ln^2(\sigma_l)} \right) \right]$$

where for the given mode l ,

N_l is the number concentration

D_l is the median diameter

and σ_l is the variance of the mode



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The number of modes is typically 3 or 4

- The nucleation mode (D1 size-diameter [1, 10]nm)
- the accumulation mode (D2 size-diameter [10, 100]nm)
- the Aitken mode (D3 size-diameter [100, 1000]nm)
- the coarse mode (D4 size-diameter [1, 10] μm)

Physical processes such as

- condensation (evaporation)
- coagulation
- depositions (dry and wet) and also reactions

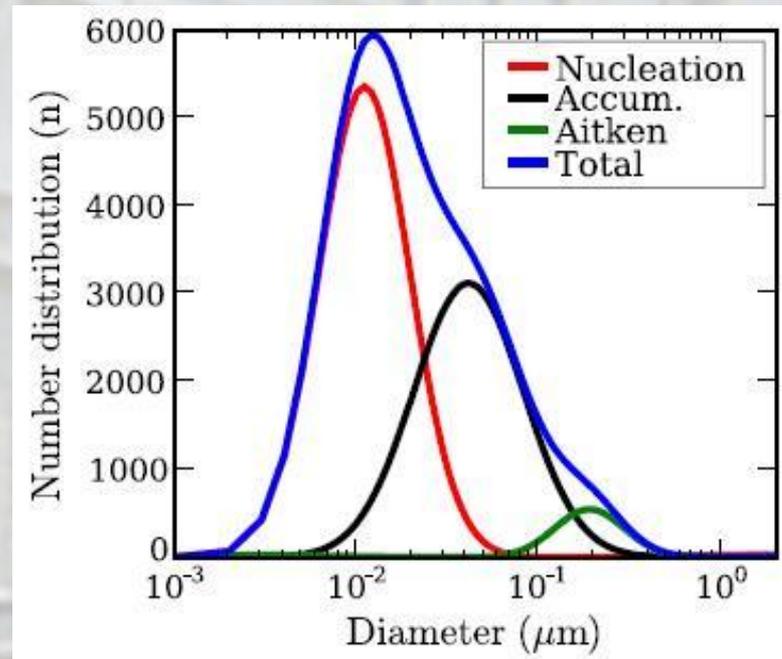
governed by the above modes vary depending on the diameter of the particulates



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Fig. 57 The distribution of particulates depending on their nuclei diameter; the four modes



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Particulates –similarly to gases- are *primary* or *secondary* ones. The pollutants emitted directly into the atmosphere without any chemical or physical change form the so called primary pollutant group. They can be found close to the sources. The *secondary* pollutant are transformed in the atmosphere by reactions of the primary contaminants.

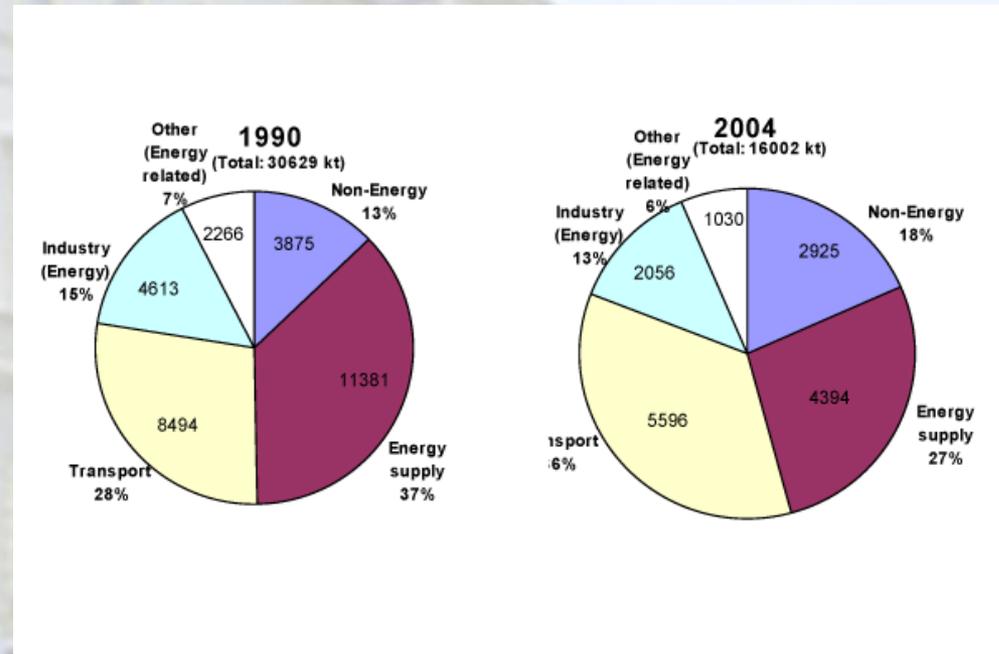
Solid particles between 1 and 100 μm in diameter are called dust particles. Solid particles less than 1 μm in diameter are called fumes, or smoke.

Natural sources are dominant in particulate emission producing more than 90% of the total one.



Fig. 58 Sectoral shares of primary particulate matter and secondary PM10 formation pollutants (energy and non-energy components) in total emissions, EU-25.

Values within the segments indicate the level of particulate emissions (kt) arising from each sector. - Secondary particulate matter



http://themes.eea.europa.eu/Sectors_and_activities/energy/indicators/EN07,2007.04/Fig2b.gif



- Main natural sources are
 - deflation of soil by wind. These particles are the so called dust, and they may reach even far places of the world. Most commonly they contain carbon and silica, but all the element of the soil crust can be appeared in the atmosphere too (iron, magnesium, lead, calcium, cadmium, copper, nickel, beryllium, asbestos, chromium)
 - evaporation of sea water. They result in sea salt crystals suspended in the air
 - volcanoes
 - forest fires
 - vegetation



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- The antropogen sources release the remaining one tenth:
 - combustion
 - power station burnings (coal and oil)
 - domestic burnings
 - transport and refuse incineration
 - industrial processing
 - cement and brick factories
 - metal processing
 - human surface activities as building etc.





Types and sources of atmospheric pollutants (modified after Varney and McCormac, 1971).

Type	Source	
	Natural	Anthropogenic
Particulates	Volcanoes Wind action Meteors Sea spray Forest fires	Combustion Industrial processing
Sulphur compounds	Bacteria Volcanoes Sea spray	Burning fossil fuels Industrial processing
Carbon monoxide	Volcanoes Forest fires	Combustion engines Burning fossil fuels
Carbon dioxide	Volcanoes Animals Plants	Burning fossil fuels
Hydrocarbons	Bacteria Plants	Combustion engines
Nitrogen compounds	Bacteria	Combustion

Table 6 There is a summary of the most important pollutant groups with their sources after Oke



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Debrecen Egyetem
Mezőgazdaság- Élelmiszertudományi és
Környezetgazdálkodási Kar



Pannon Egyetem
Georgikon Kar



Thank you for attention!



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