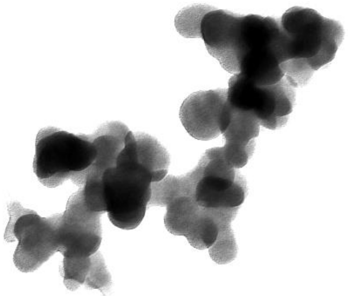
Atmospheric Chemistry
Air Pollution

Pontus Roldin
Div. Nuclear Physics
Dep. Physics
Lund University



Conflict between ”positive” climate cooling effects and negative human health effects

Are there “good” aerosol particles that cool but do not kill?

Or ----- is the cooling also negative since it delays the recognition of climate change?

Without present anthropogenic aerosol cooling effects we may already have + 2 °C global temperature change compared to preindustrial conditions!

Is it possible to fulfil the 2016 Paris agreement?

What is sustainable development?

On Swedish television (SVT 2017-10-12):

https://www.svt.se/nyheter/vetenskap/miljorapport-luftkvaliten-pa-battringsvag

/ VETENSKAP

Vägtrafiken bidrar till stora utsläpp av föroreningar i Europa. Arkivbild.
FOTO: TT

Miljörapport: Luftkvalitén på bättringsväg

Varje år dör hundratusentals européer i förtid på grund av luftföroreningar. Men en ny rapport från Europeiska miljöbyrån EEA visar att luftkvalitén långsamt förbättras – och därmed människors hälsa.

~500 000 people die every year in Europe because of air pollutions but a new report from the European Environmetal Agency (EEA) show that the air quality slowly is getting better.

On Swedish television (SVT 2017-01-26):
http://www.svt.se/nyheter/inrikes/risker-med-oren-luft-underskattas

According to the Swedish Environmental Research Institute IVL air pollutions in Sweden casus 7600 premature deaths every year. The cost for the society is estimated to be 56 billion SEK/year.

- ~7 million premature deaths due to air pollution globally each year, ~500 000 in Europe, ~7600 in Sweden, ~870 in Scania.
- Particulate matter (PM) is a major fraction in the term ”air pollution”.
- Common disorders includes chronic obstructive pulmonary disease (COPD), cardiovascular diseases and cancer.
- Carbonaceous compounds such as poly aromatic hydrocarbons (PAH) and Black Carbon (soot) are considered carcinogenic and hazardous.

Health Effects of Air Pollution in EU-28

Source: EEA, ”Air Quality in Eureope -216 Report”

PM2.5 → 436 000 premature deaths annually

PM2.5 (Mass of particles less than 2.5 µm in diameter)

NO_2 → 68 000 premature deaths annually

O_3 → 16 000 premature deaths annnally

Repetition of tropospheric chemistry

Toxic CO and hydrocarbons are scavenged by the detergent of the atmosphere, the hydroxyl radical OH

OH is produced from:

$O_3 + h\nu \rightarrow O_2 + O(^1D)$

$O(^1D) + H_2O \rightarrow 2OH$

Tropospheric O_3 production requires:

1. CO, CH_4 and hydrocarbons

2. NO_x

3. Sunlight ($h\nu$)

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + NO \rightarrow OH + NO_2$

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

$O + O_2 + M \rightarrow O_3 + M$

(Net): $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$

Ground-level ozone

- Tropospheric ozone is both good and bad.

- O_3 needed to produce OH radicals via:

  $O_3 + h\nu \rightarrow O_2 + O(^1D)$ and $O(^1D) + H_2O \rightarrow 2OH$

- But high levels of ozone are dangerous to humans, plants and materials. Tropospheric ozone is also a greenhouse gas.

- Preindustrial $[O_3]$~10-15 ppb. Today $[O_3]$~30 ppb

Photostationary equilibrium for ozone

- In a sunlit atmosphere with NO and NO_2 ,but without hydrocarbons and CO:

(11.11) $NO_2 + h\nu \rightarrow NO + O$ ($\lambda < 420$ nm)

(10.2) $O + O_2 + M \rightarrow O_3 + M$

11.14) $NO + O_3 \rightarrow NO_2 + O_2$

A photostationary equilibrium exists: $NO_2 + O_2 \overset{hv}{\leftrightarrow} NO + O_3$

- More sunlight ($\lambda < 420$ nm) gives more ozone
- NO consumes ozone (11.14).
- In urban regions with strong sources of NO, the O_3 is titrated out and can be entirely depleated if their is no sunlight (e.g. buisy street wintertime in Malmö or Copenhagen)

Photostationary equilibrium for ozone

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Assuming "stead state" conditions for O and O_3 →

$$0 = \frac{d}{dt}[O] = k_{11}[NO_2] - k_2[O][O_2][M] \quad \Rightarrow [O] = \frac{k_{11}[NO_2]}{k_2[O_2][M]}$$

$$0 = \frac{d}{dt}[O_3] = k_2[O][O_2][M] - k_{14}[NO][O_3] \Rightarrow [O_3] = \frac{k_{11}[NO_2]}{k_{14}[NO]}$$

Expression for a photostationary equilibrium for ozone.

Photostationary equilibrium for ozone

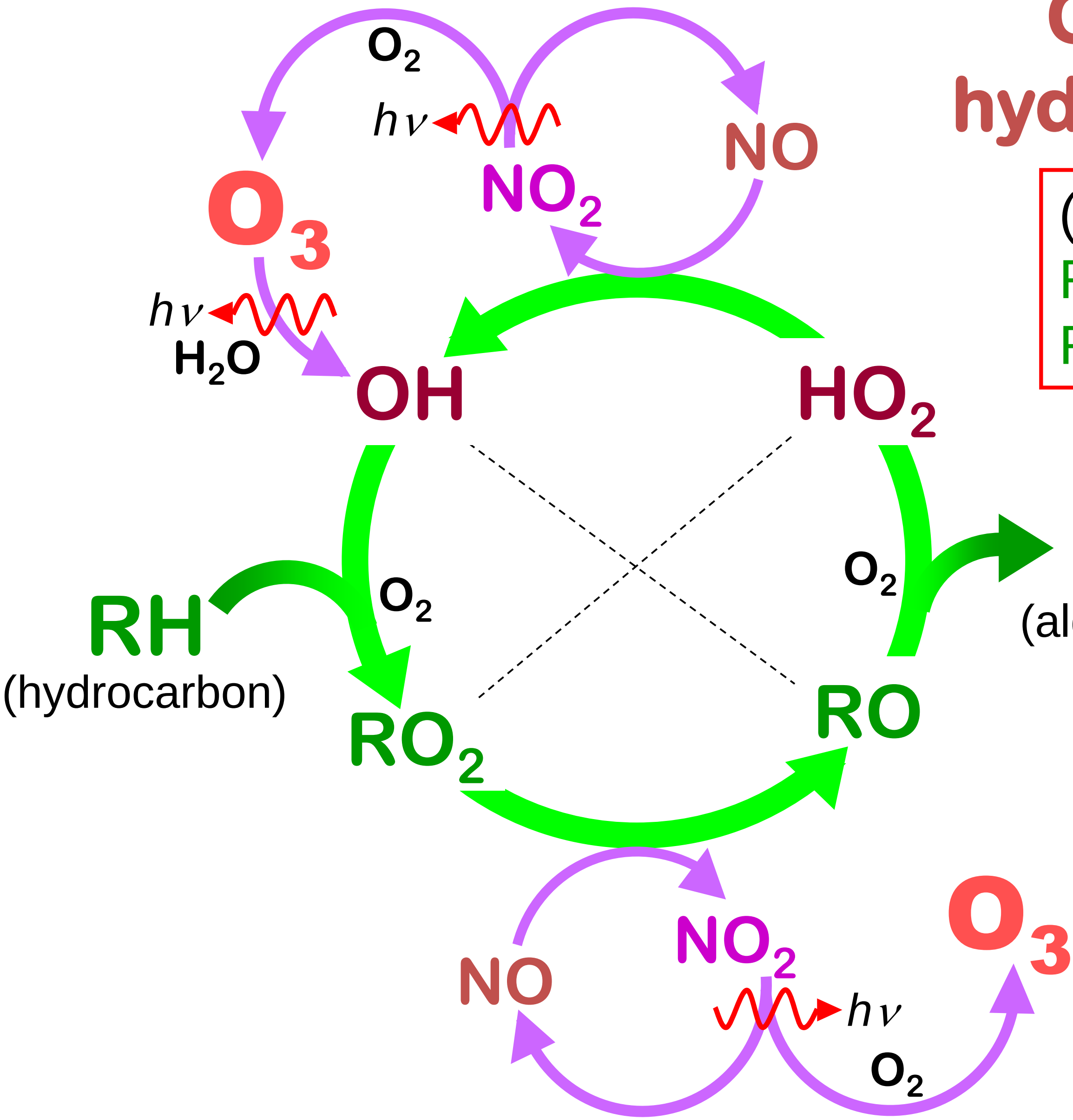
We can use the photostationary equilibrium for ozone in a sunlit atmosphere with NO and NO_2 but without hydrocarbons to calculate $[O_3]$:

$$[O_3] = \frac{k_{11}[NO_2]}{k_{14}[NO]}$$

- For initial concentrations of $[NO_2]$=[NO] = 1 ppb (non-time at 50˚N) the ozone levels reach a stationary state within ~100 s and gives $[O_3]$ = 23 ppb.
- This is less than the ozone levels that are typically observed in tropospheric polluted air.
- More reactions for ground-level ozone production are needed!

Oxidation of hydrocarbons RH

(Net):
RH + $4O_2$ + 2hv → $R_{-H}O$ + $2O_3$ + H_2O



Each cycle gives net 2 O_3 or 4 OH.

Oxidation of hydrocarbons RH

Examples: Alkanes RH

$RH + OH \rightarrow R + H_2O$

$R + O_2 + M \rightarrow RO_2 + M$

$RO_2 + NO \rightarrow RO + NO_2$

$RO + O_2 \rightarrow R_{-H}O + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

(Net) $RH + 2O_2 + 2NO \rightarrow R_{-H}O + 2NO_2 + H_2O$

(2x) $NO_2 + h\nu \rightarrow NO + O$ $O + O_2 \rightarrow O_3$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2OH$

Each cycle produces $2O_3$ or $4OH$!

Shifting the equilibrium towards more ozone

- Hydrocarbons are needed to shift the equilibrium to the right, that is towards a higher ozone production.

$$NO_2 + O_2 \overset{h\nu}{\leftrightarrow} NO + O_3$$

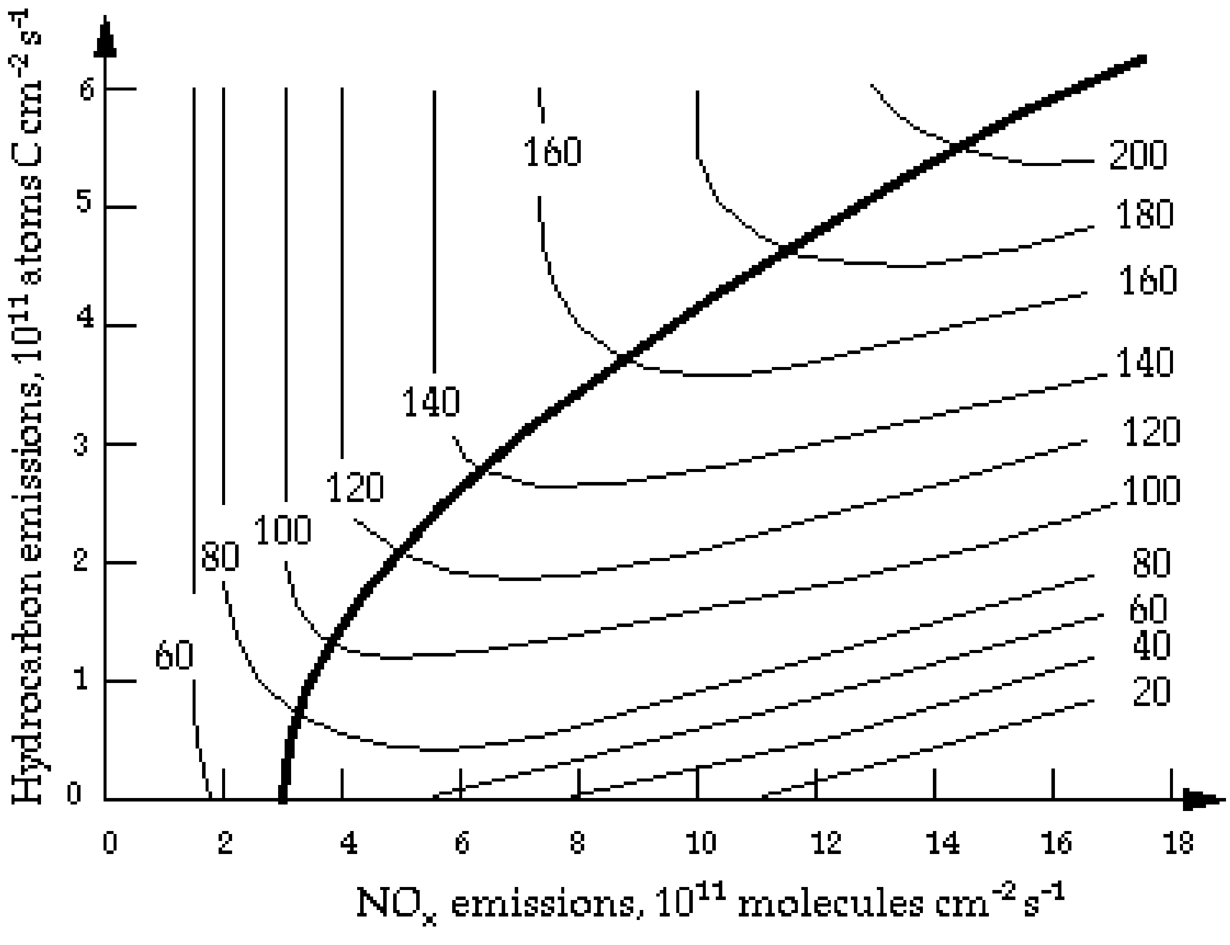
- Hydrocarbons consume NO (by producing peroxy radicals, HO_2 and RO_2 which in turn react with NO).

3 prerequisites for high ozone levels:

1. Intense sunlight
2. High concentrations of hydrocarbons and/or CO
3. High concentrations of nitrogen oxides (NO_x)

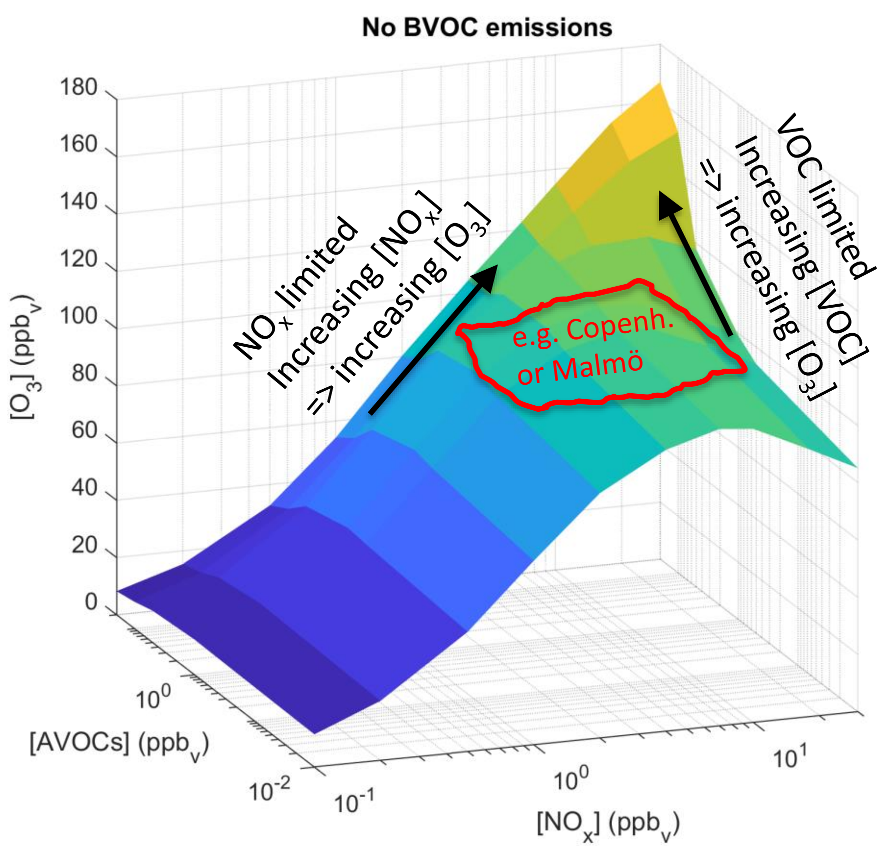
Ozone production can be either hydrocarbon or NO_x limited

Ozone production can be either hydrocarbon or NO_x limited



Modelled ozone concentration (ppbv) (Fig. 12-4 in Jacob, 1999)

Ozone production can be either hydrocarbon or NO_x limited

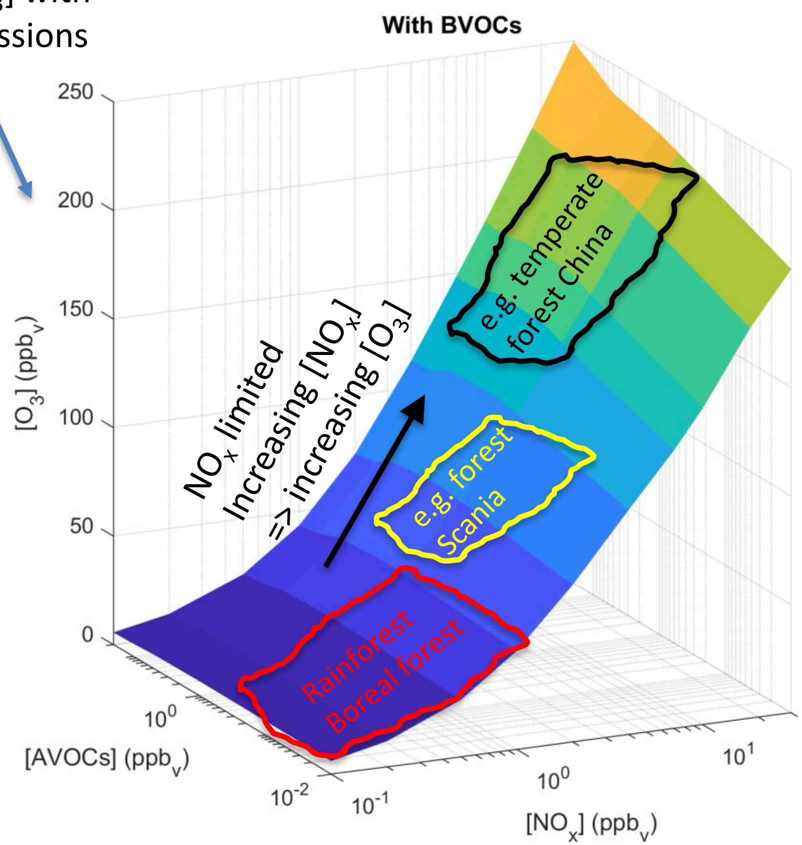


Without substantial VOC emissions from the vegetation, the O_3 production can be either NO_x or VOC limited.

Example of modelled $[O_3]$ (ppbv) using the Master Chemical Mechanism (MCMv3.3.1) http://mcm.leeds.ac.uk/MCM/, assuming: Summer, $[BVOC]=0.0\ ppb_v$, $[CO]=150\ ppb_v$, $[CH_4]=1900\ ppb_v$ and variable Anthropogenic VOC (AVOC) concentrations

Ozone production can be either hydrocarbon or NO_x limited

Higher $[O_3]$ with BVOC emissions



Atmospheric models need to take into account emissions from the vegetation! Otherwise they will underestimate $[O_3]$ and may falsely predict that the O_3 production is VOC limited, when it in fact is NO_x limited.

Other tropical rainforest and in the summer over boreal and temperate forests the BVOC concentrations can reach several ppb_v. BVOCs are generally more reactive than AVOCs because they are alkenes (R-C=C-R).

Example of modelled $[O_3]$ (ppbv) using the Master Chemical Mechanism (MCMv3.3.1) http://mcm.leeds.ac.uk/MCM/, assuming: Summer, [BVOC]=2.0 ppb_v, [CO]=150 ppb_v, $[CH_4]$=1900 ppb_v and variable Anthropogenic VOC (AVOC) concentrations.

Particulate matter (PM)

Source: Guerreiro et al. (2014), the additional material at course homepage

- In terms of potential to harm human health, PM poses the greatest risk, as it penetrates into sensitive regions of the respiratory system and can lead to health problems and premature mortality.
- PM in the atmosphere originates from primary particles emitted directly and secondary particles produced as a result of chemical reactions involving PM forming (precursor) gases: SO_2, NO_x, NH_3 and non-methane volatile organic compounds (NMVOC) (i.e. Hydrocarbons).

Particulate matter (PM)

Source: Guerreiro et al. (2014), the additional material at course homepage

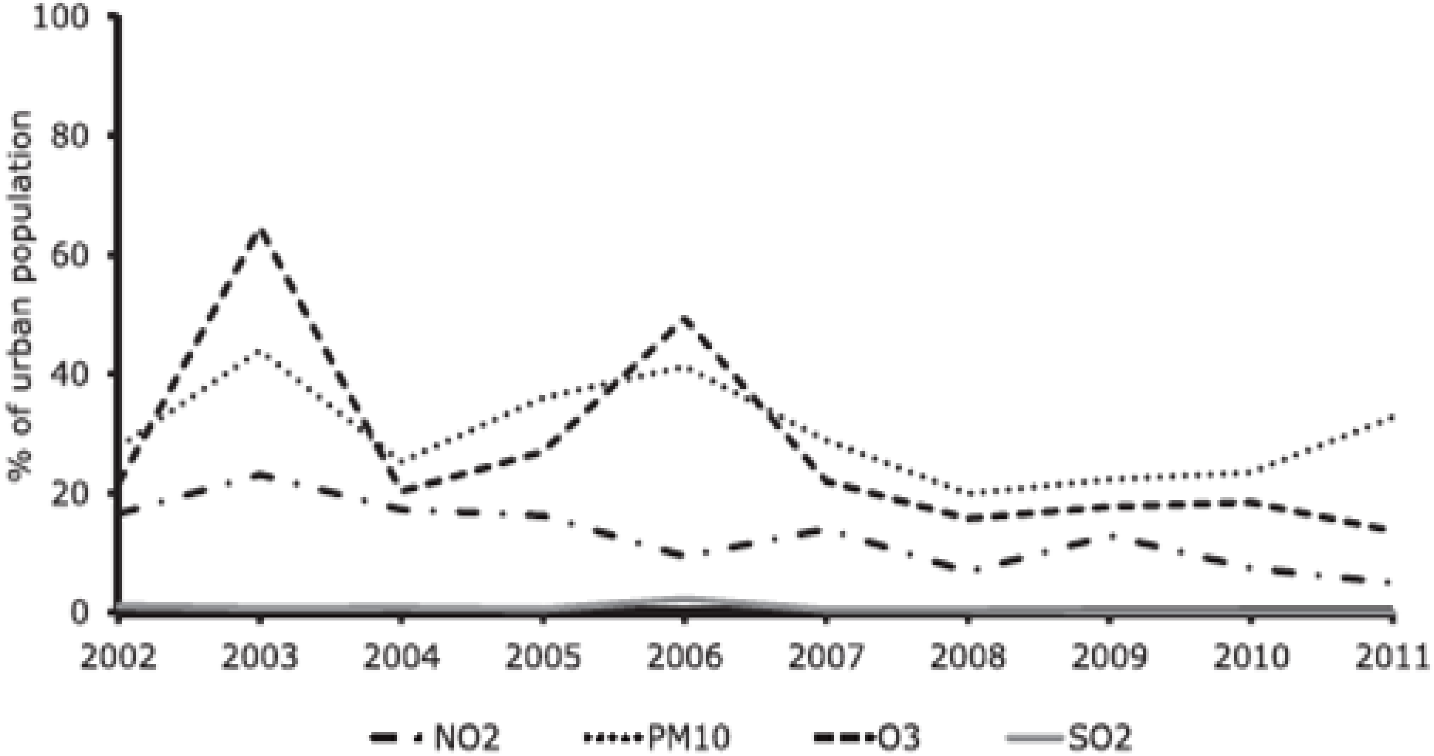
- Emissions of primary PM_{10} and $PM_{2.5}$ decreased by 14% and 16% respectively in the EU-27 between 2002 and 2011.

- PM precursor emissions continued to decrease between 2002 and 2011. In the EU-27 Sulphur oxides (SO_X) emissions fell by 50%; NO_X emissions fell by 27%; NH3 emissions fell by 7%; NMVOCs emissions fell by 28%.

- Despite the emission reductions the EU-27 urban population was exposed to concentrations of PM_{10} in excess of the EU air quality daily limit value (50 $\mu g/m^3$) in the period 2002-2011.

Particulate matter (PM)

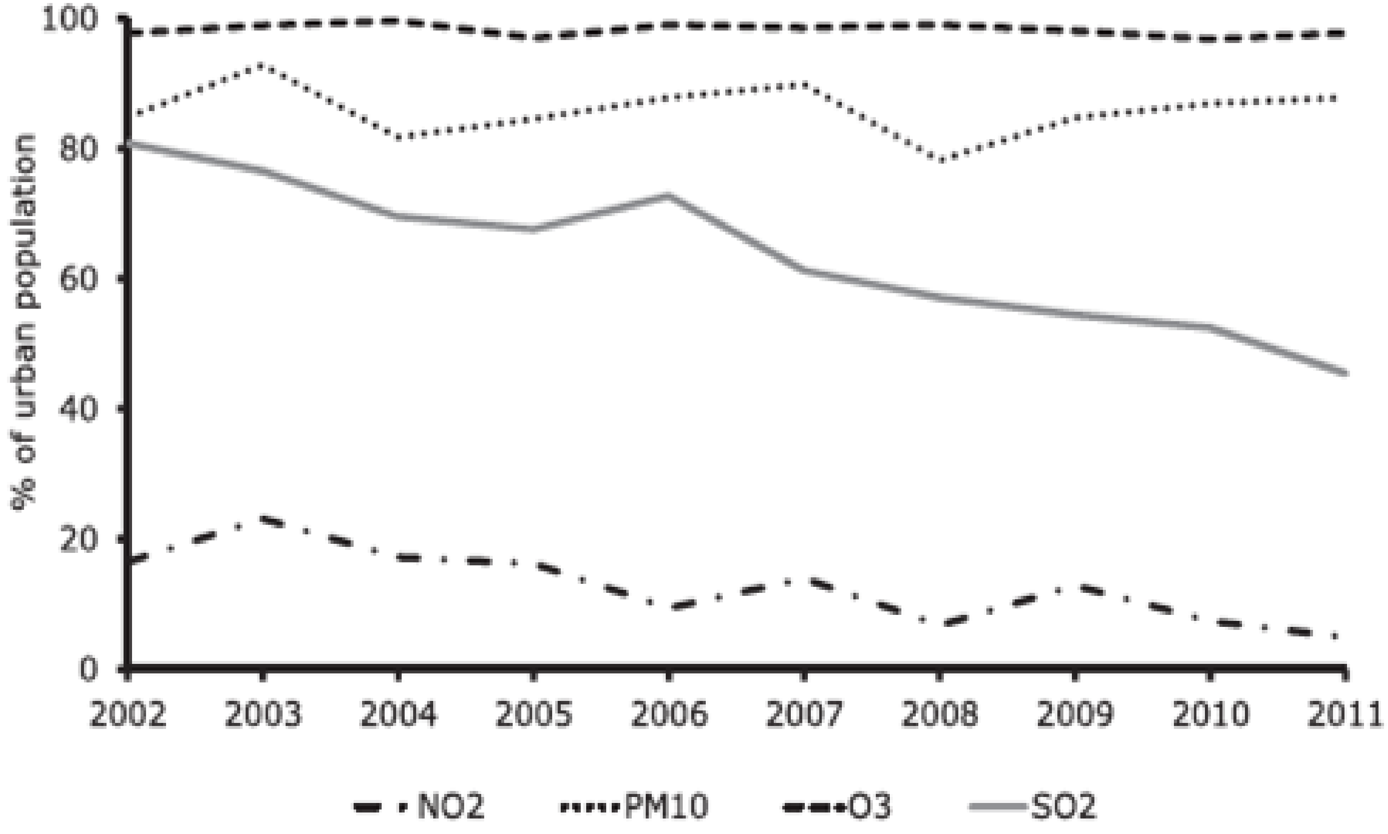
Source: Guerreiro et al. (2014), the additional material at course homepage



Fraction of population in EU-27 that are exposed to air pollution levels exceeding the AQ limit values in EU

Particulate matter (PM)

Source: Guerreiro et al. (2014), the additional material at course homepage



Fraction of population in EU-27 that are exposed to air pollution levels exceeding the WHO air quality guidelines

Particulate matter (PM)

Source: Guerreiro et al. (2014), the additional material at course homepage

- While the trends of PM_{10} are in average decreasing across Europe, the same is not registered for $PM_{2.5}$ concentrations.

Why?

- Due to the complex links between emissions and air quality, emission reductions do not always produce a corresponding drop in atmospheric concentrations, especially for secondary pollutants like PM and ozone.

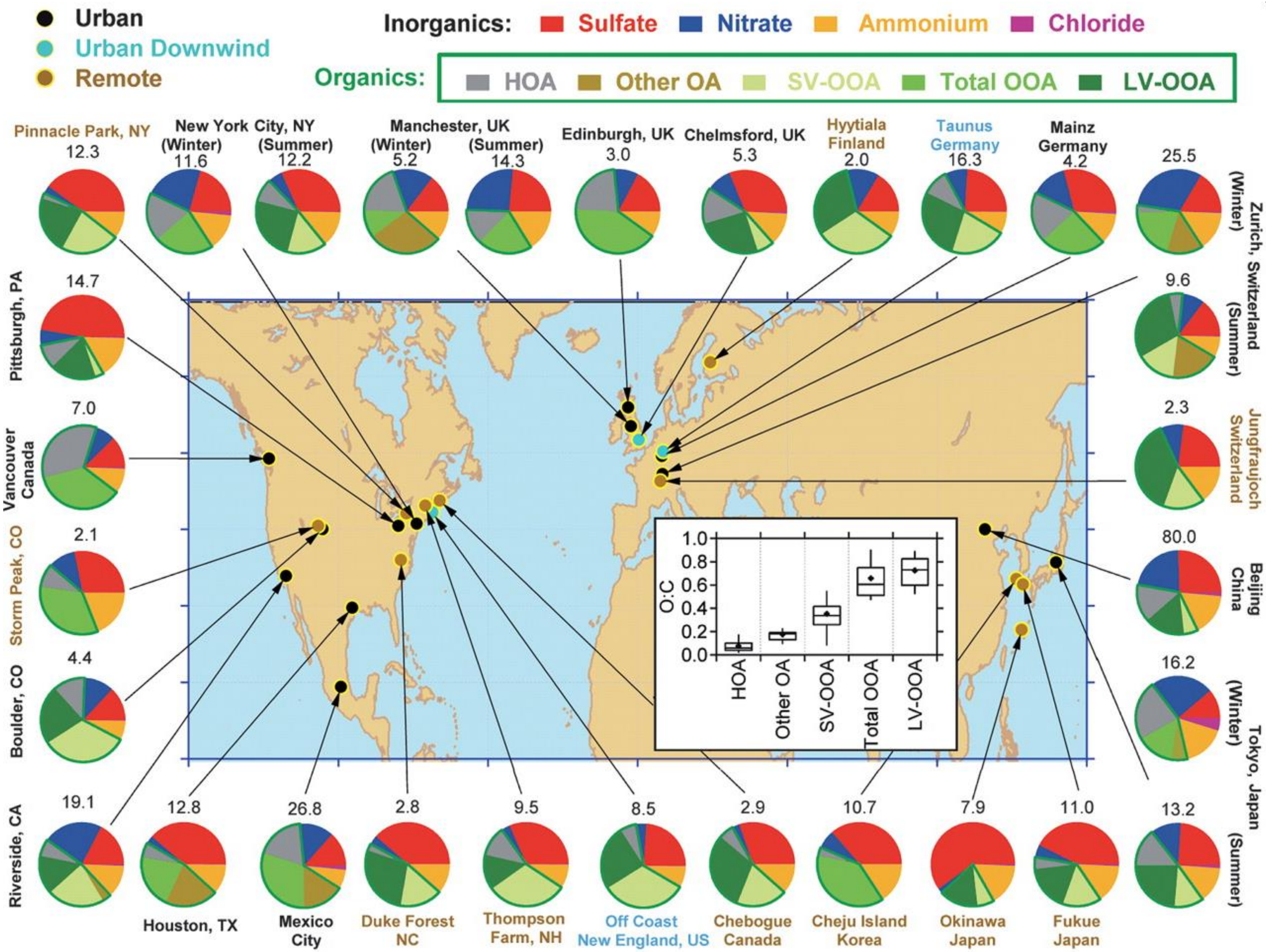
- The main sources of PM_{10} are emissions of mechanically generated coarse primary particles, e.g. sea spray, windblown dust, road dust.

- The main source of PM2.5 can instead be secondary aerosol formation via gas-to-particle conversion (e.g. Secondary Organic Aerosol (SOA), ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$)

  Secondary aerosol precursors: hydrocarbons (i.e. NMVOCs*), NO_x, SO_2 and NH_3

**NMVOC (Non-Methane Volatile Organic Compounds)*

PM1 Aerosol Components Worldwide



Jimenez, Canagaratna, Donahue, et al., Science 326, 1525 (2009)

Measured PM_1 chemical composition at the field station Hyltemossa in Scania

Sources of PM_1 at Hyltemossa:

- >95 % long-distance transport from outside Scania

<u>BC (Black Carbon)</u>: Cars, coal burning, wood burning, ships

<u>Nitrate (NO_3)</u>: NO_x(g) emissions from cars

$NO_2 + OH \rightarrow HNO_3$

<u>Ammonium (NH_4)</u>: Ammonia (NH_3(g)) emissions from agriculture

$HNO_3(g) + NH_3(g) \leftrightarrow NO_3^-(aq) + NH_4^+(aq)$

$HNO_3(g) + NH_3(g) \leftrightarrow NO_3NH_4\ (s)$

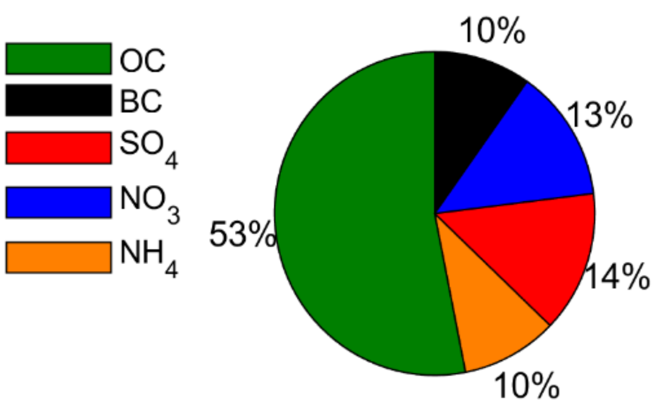
<u>Sulfate (SO_4)</u>: SO_2(g) from fossil fuels e.g. coal burning

$SO_2 + OH + M \rightarrow HSO_3 + M$,

$HSO_3 + O_2 \rightarrow SO_3 + HO_2$ (fast)

$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$ (fast)

$H_2SO_4(g) \rightarrow H_2SO_4(aq)$ (Condensation)



<u>OC (Organic Carbon)</u>: Mainly Secondary Organic Aerosols (SOA)

$RH + OH \rightarrow RO_2$ RH: Hydrocarbons

$RO_2 + HO_2 \rightarrow RCO_x$

$RO_2 + NO \rightarrow RCO_x + NO_2$

(Oxidized organic compounds (RCO_x) which can condensate onto existing aerosol particles and form SOA.

Measured PM_1 chemical composition at the field station Hyltemossa in Scania

Sources of PM_1 at Hyltemossa:

- >95 % long-distance transport from outside Scania

BC (Black Carbon): Cars, coal burning, wood burning, ships

Nitrate (NO_3): NO_x(g) emissions from cars

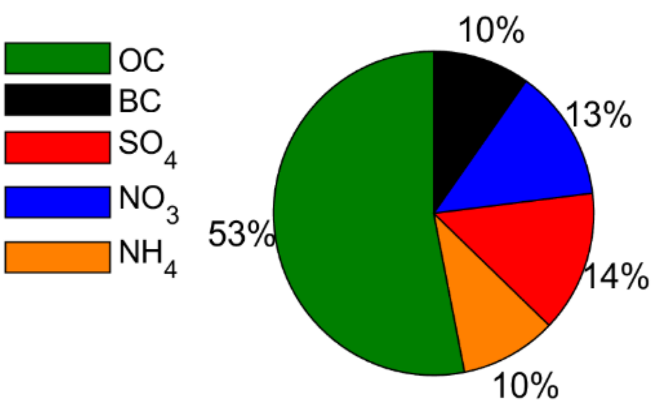
Most PM_1 and $PM_{2.5}$ are secondary aerosols produced in the atmosphere by chemical reactions followed by condensation

Atmospheric Chemistry and Physics is Important!

$HSO_3 + O_2 \rightarrow SO_3 + HO_2$ (fast)

$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$ (fast)

$H_2SO_4(g) \rightarrow H_2SO_4(aq)$ (Condensation)



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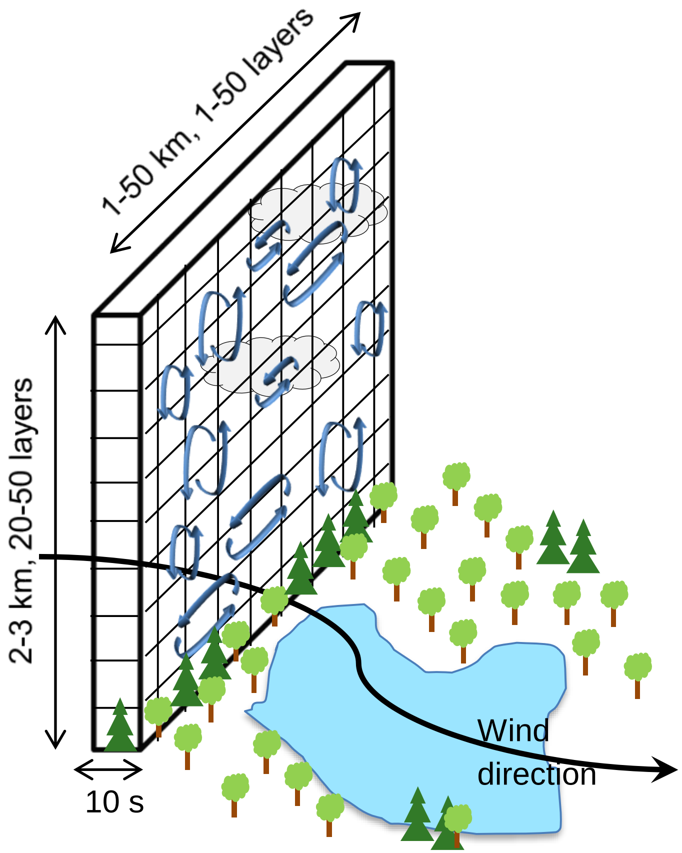
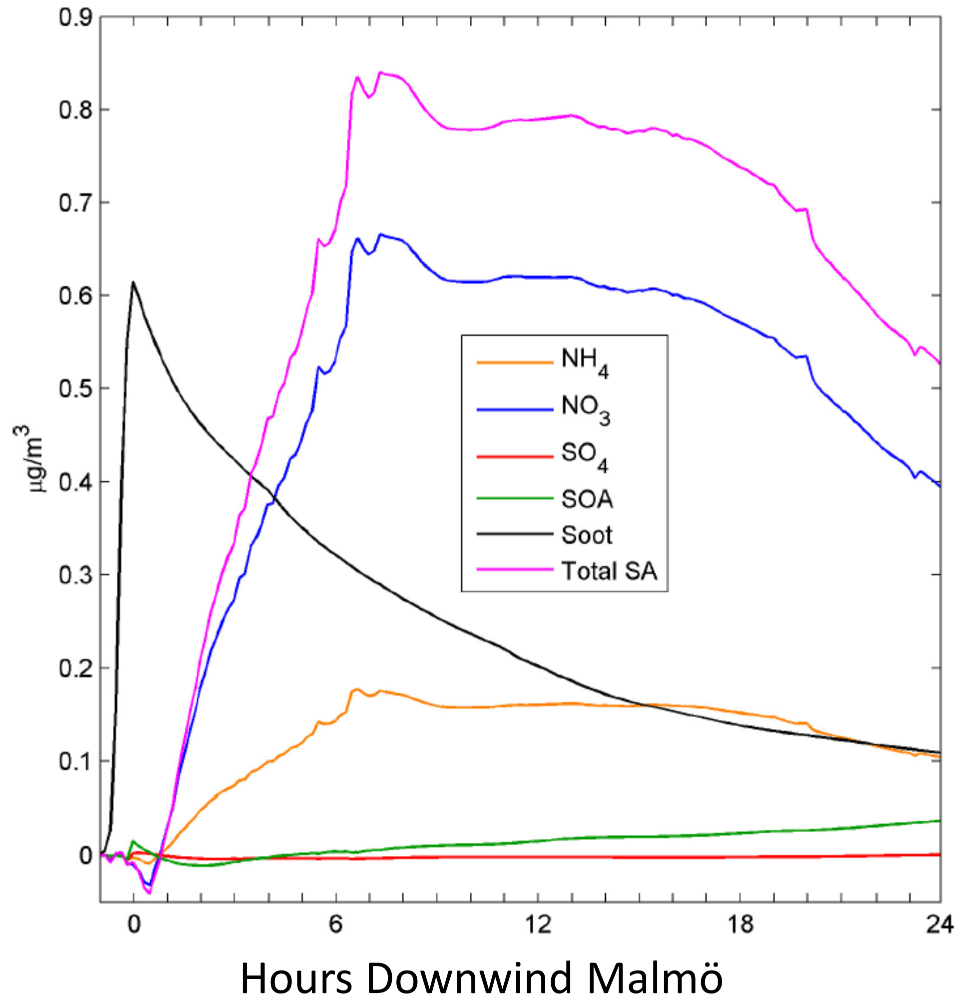
Model simulations of the urban plume from Malmö





Roldin et al., Atmos. Chem. Phys., 11, 5897–5915, 2011

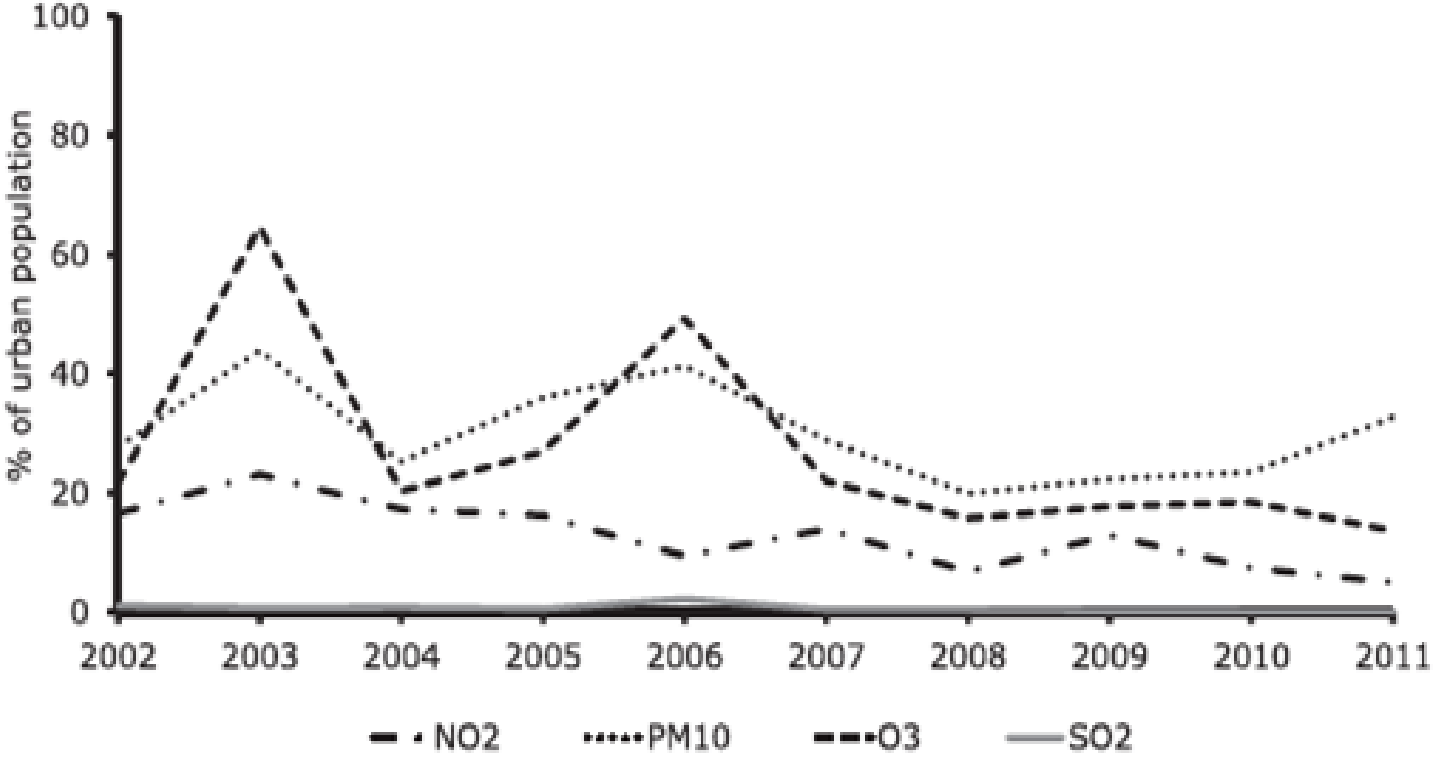
Nitrogen Oxides (NO_x)

Source: Guerreiro et al. (2014), the additional material at course homepage

- NO_x is emitted during fuel combustion, such as by vehicle engines, industrial facilities and domestic heating.
- NO_2 is associated with adverse effects on health, as high concentrations cause inflammation of the airways and reduced lung function.
- NO_x may also cause adverse effects on vegetation and contributes to the formation of secondary inorganic PM and O_3 with associated effects on health, ecosystems and climate.
- EU emissions of NO_x fell by 27% in the period 2002-2011. Nevertheless, total NO_x emissions in 2011 were about 5% higher than the emissions ceiling for the EU as a whole.
- Transport is the dominant sector for NO_x emissions, accounting for 47% of the total in 2011, followed by the energy sector, which contributed 21% of the total.

Nitrogen Oxides (NO_x)

Source: Guerreiro et al. (2014), the additional material at course homepage



Fraction of population in EU-27 that are exposed to air pollution levels exceeding the AQ limit values in EU

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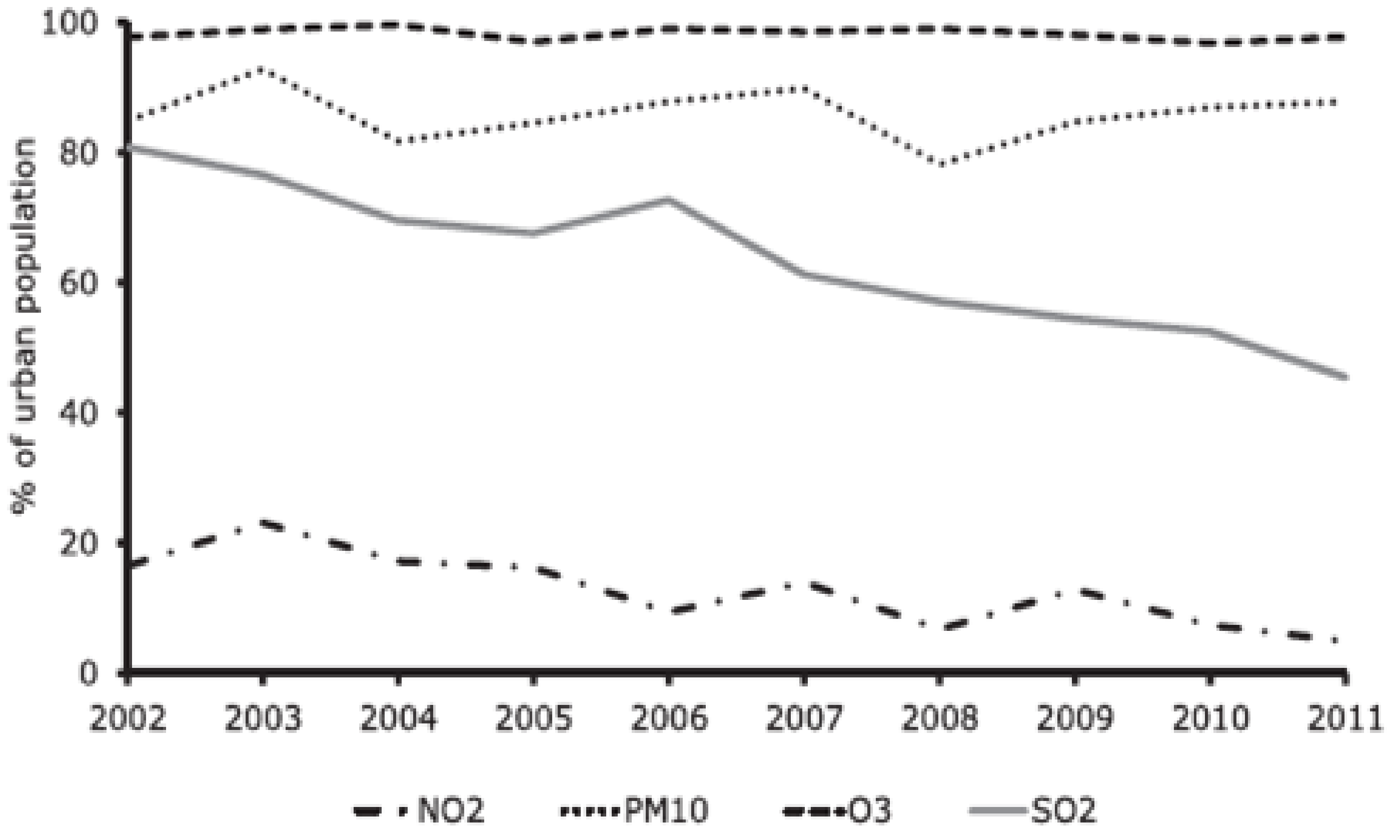


Fraction of population in EU-27 that are exposed to air pollution levels exceeding the WHO air quality guidlines

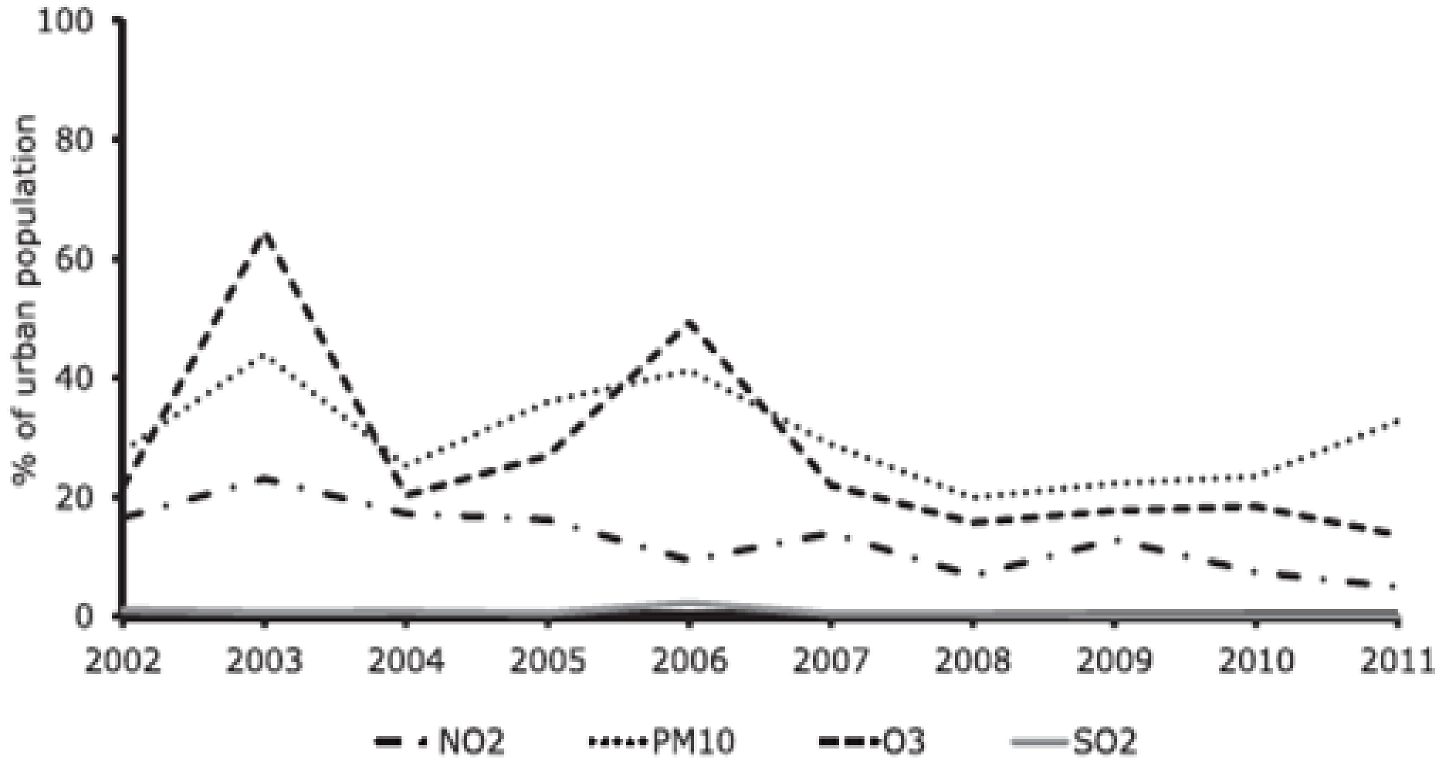
Sulfur dioxide (SO_2)

Source: Guerreiro et al. (2014), the additional material at course homepage

- Sulphur dioxide is emitted when fuels containing sulfur are burned or from high temperature industrial processes involving raw materials high in sulfur content (such as smelters).
- It contributes to acidification, the impacts of which can be significant, including adverse effects on aquatic ecosystems in rivers and lakes; damage to forests and terrestrial ecosystems; as well as reduced biodiversity.
- SO_2 can affect the respiratory system and reduce lung function.
- It is also a major precursor to PM, which is associated with significant health effects.
- In the period 2002-2011, EU-27 Member States cut their SO_x emissions by 50%, leading to a fall in SO_2 concentrations of about one third.
- The area of sensitive ecosystems affected by excessive acidification from air pollution has shrunk by 92% from 1990 to 2010 mainly due to the strong reduction in SO_2 emissions (EEA, 2012).

Sulfur dioxide (SO_2)

Source: Guerreiro et al. (2014), the additional material at course homepage



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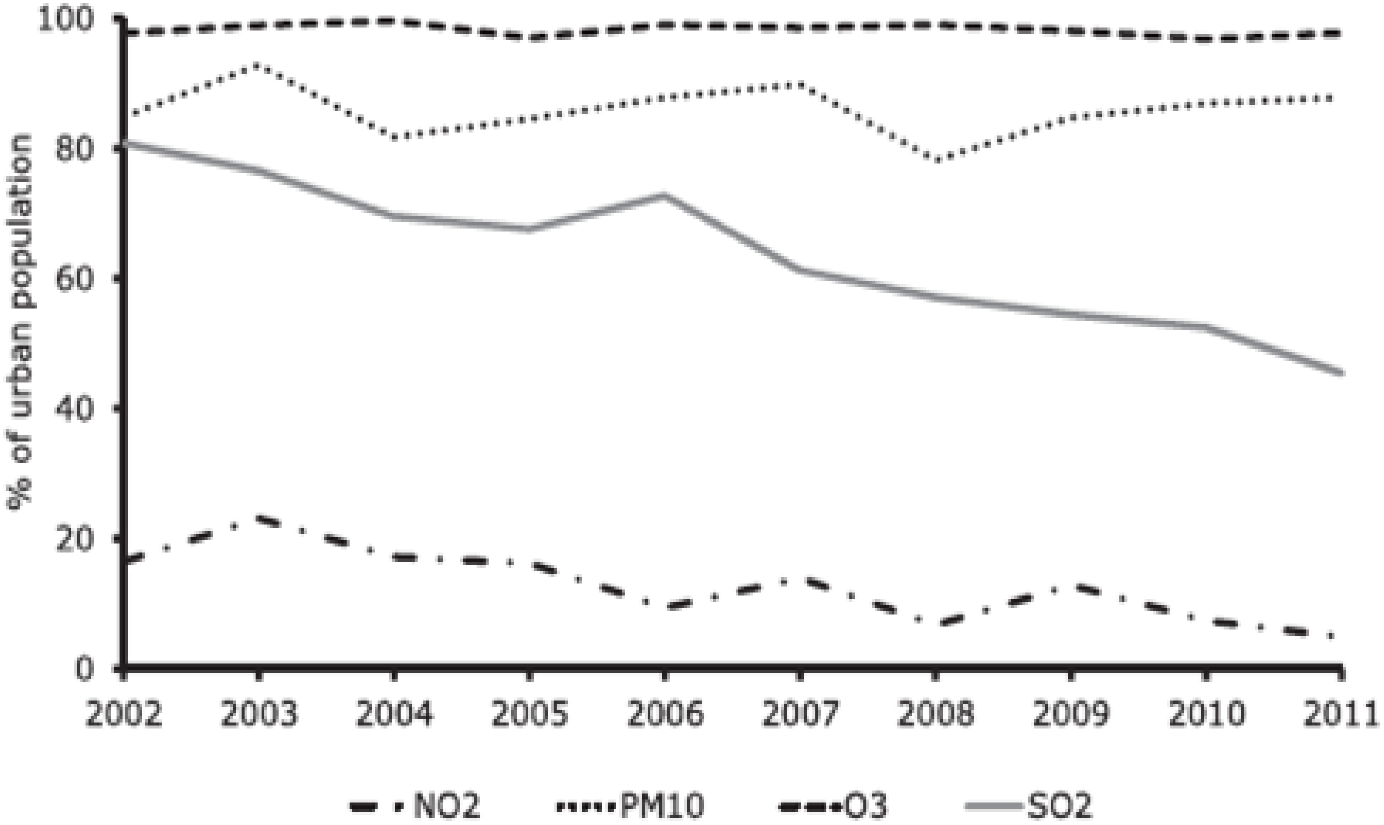

Fraction of population in EU-27 that are exposed to air pollution levels exceeding the WHO air quality guidelines

Carbon monoxide (CO)

Source: Guerreiro et al. (2014), the additional material at course homepage

- Carbon monoxide is emitted due to incomplete combustion of fossil fuels and biofuels, and enters the body through the lungs.
- Exposure to CO can reduce the oxygen-carrying capacity of blood, thereby reducing oxygen delivery to the body's organs and tissues.
- The atmospheric lifetime of CO is about three months. This relatively long lifetime allows CO to slowly oxidize into carbon dioxide (CO_2), also forming O_3 during this process.
- CO therefore contributes to the atmospheric background concentration of O_3, with associated effects on the health of humans and ecosystems.
- The observed EU-27 average reduction in CO daily 8-h maxima concentrations in the period 2002-2011 was 35%.

Air quality improvements and challenges in EU

- Emission reductions have resulted in a notable reductions of ambient concentrations of SO_2 and CO.
- However, due to the complex links between emissions and air quality, emission reductions do not always produce a corresponding drop in atmospheric concentrations, especially for secondary pollutants like PM and O_3.
- Agriculture is responsible for 93% of ammonia emissions, which exert pressure on both human health and the ecosystems. Ammonia together with NO_x and SO_2 emissions contributes to secondary ammonium nitrate aerosol formation:

(11.30)	$NO_2 + OH + M$	→	$HNO_3 + M$	(daytime)
(13.10)	$SO_2 + OH + M$	→	$HSO_3 + M$	(daytime)
(13.11)	$HSO_3 + O_2$	→	$SO_3 + HO_2$	(fast)
(13.12)	$SO_3 + H_2O + M$	→	$H_2SO_4 + M$	(fast)

- HNO_3, H_2SO_4 and NH_3 are condensing onto existing particles (e.g. primary particles from road traffic, e.g. soot) and form ammonium sulfate $(NH_4)_2SO_4$ and ammonium nitrate (NH_4NO_3). One of the main PM1 constituents in Southern Sweden and Denmark.

What is a secondary pollutant?

- A secondary pollutant is formed in the atmosphere by chemical and physics process (i.e. Atmospheric Chemistry and Physics).

Important examples:

1. SOA (Secondary Organic Aerosols)
2. Ammonium sulfate aerosols
3. Ammonium nitrate aerosols
4. Ozone

Name 3 prerequisites for high tropospheric ozone concentrations

1. High levels of solar radiation

2. High concentrations of CO and/or hydrocarbons

3. High concentrations of NO_x