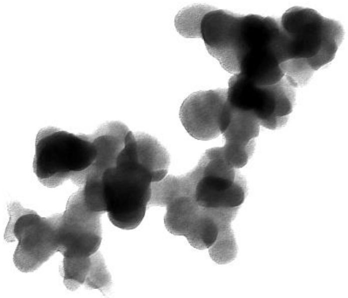
Atmospheric Chemistry
Air Pollution

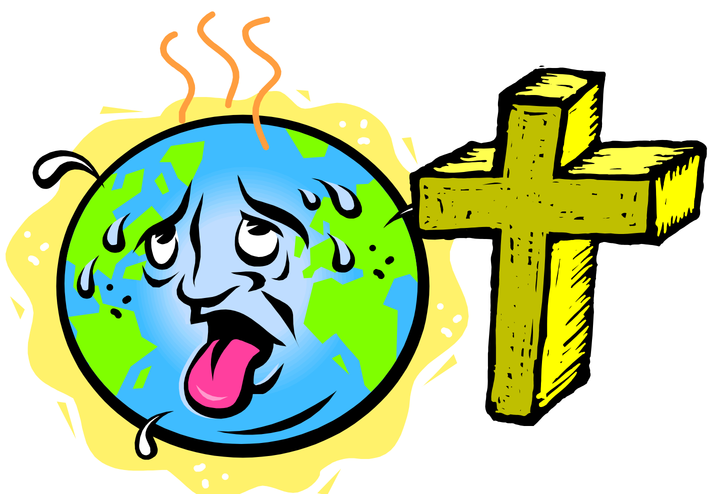
Pontus Roldin
Div. Nuclear Physics
Dep. Physics
Lund University



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?



Air Pollution

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

400 000 people die every year in Europe because of air pollutions but the 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 5500 premature deaths every year. The cost for the society is estimated to be 42 billion SEK/year.

- 7 million premature deaths due to air pollution globally each year. 400 000 premature deaths in Europe.
- 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

- Scavenging of toxic CO by the detergent of the atmosphere, the hydroxyl radical OH.
- Net production of O_3
- Needed: Emissions of CO (CH_4 or hydrocarbons), NO and sunlight ($h\nu$)

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow HO + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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

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$$HO_2 + NO \rightarrow HO + NO_2$$
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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) $NO + O_3 \rightarrow NO_2 + O_2$

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

A photostationary equilibrium exists.

More sunlight ($\lambda < 420$ nm) gives more ozone

NO consume ozone (11.14). In urban regions with strong sources of NO, the O_3 is titrated out and can be entirely depleated without sunlight (e.g. buisy street wintertime in Malmö or Copenhagen)

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Assuming "stead state" conditions for O and O_3 →

$$0 = \frac{d}{dt}[\mathrm{O}] = \mathrm{k}_{11}[\mathrm{NO}_2] - \mathrm{k}_2[\mathrm{O}][\mathrm{O}_2][\mathrm{M}] \quad \Rightarrow [\mathrm{O}] = \frac{\mathrm{k}_{11}[\mathrm{NO}_2]}{\mathrm{k}_2[\mathrm{O}_2][\mathrm{M}]}$$

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Expression for a photostationary equilibrium for ozone.

Photostationary equilibrium for ozone

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

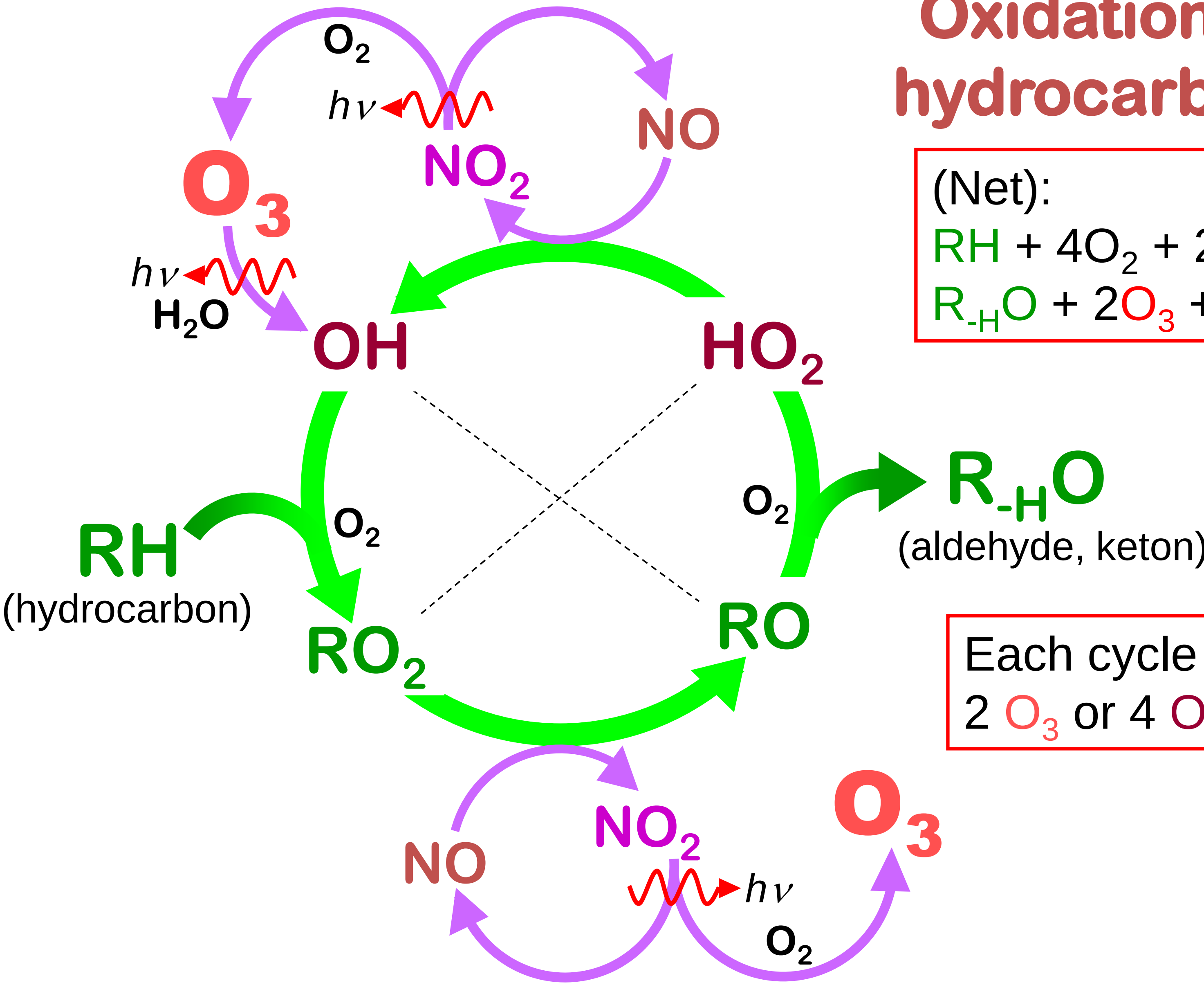
$$[O_3] = \frac{k_{11}[NO_2]}{k_{14}[NO]}$$

For initial concentrations of $[NO_2]$=[NO] = 1 ppb (nnon-time at 50˚N) the ozone levels reach a stationary state within ~100 s and with $[O_3]$ = 23 ppb.

This is less than the ozone levels that are typically observed in topospheric polluted air →

More reactions for ground-level ozone production are needed!

Oxidation av hydrocarbons



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

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 net $2O_3$ 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.
- Hydrocarbons consume NO (by producing peroxy radicals , HO_2 and RO_2 which in turn react with NO).
- More sun light gives more ozone

$$NO_2 + O_2 \overset{hv}{\leftrightarrow} NO + O_3$$

Prerequisites for high ozone levels:

- Sunlight
- Hydrocarbons and/or CO
- Nitrogen oxides (NO_x)
- Ozone production is either hydrocarbon or NO_x

Particulate matter (PM)

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

- For some of the EU air quality standards it is allowed to exceed the standards' threshold concentration during a number hours or days. This is the case for e.g. the daily PM10 limit value (LV) (35 days with concentrations above 50 mg/m3 are allowed per year.

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- 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).

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- Emissions of primary PM10 and PM2.5 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%.

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- Despite the emission reductions, 20% - 44% of the EU-27 urban population was exposed to concentrations of PM10 in excess of the EU air quality daily limit value (50 mg/m3) in the period 2002-2011.

Particulate matter (PM)

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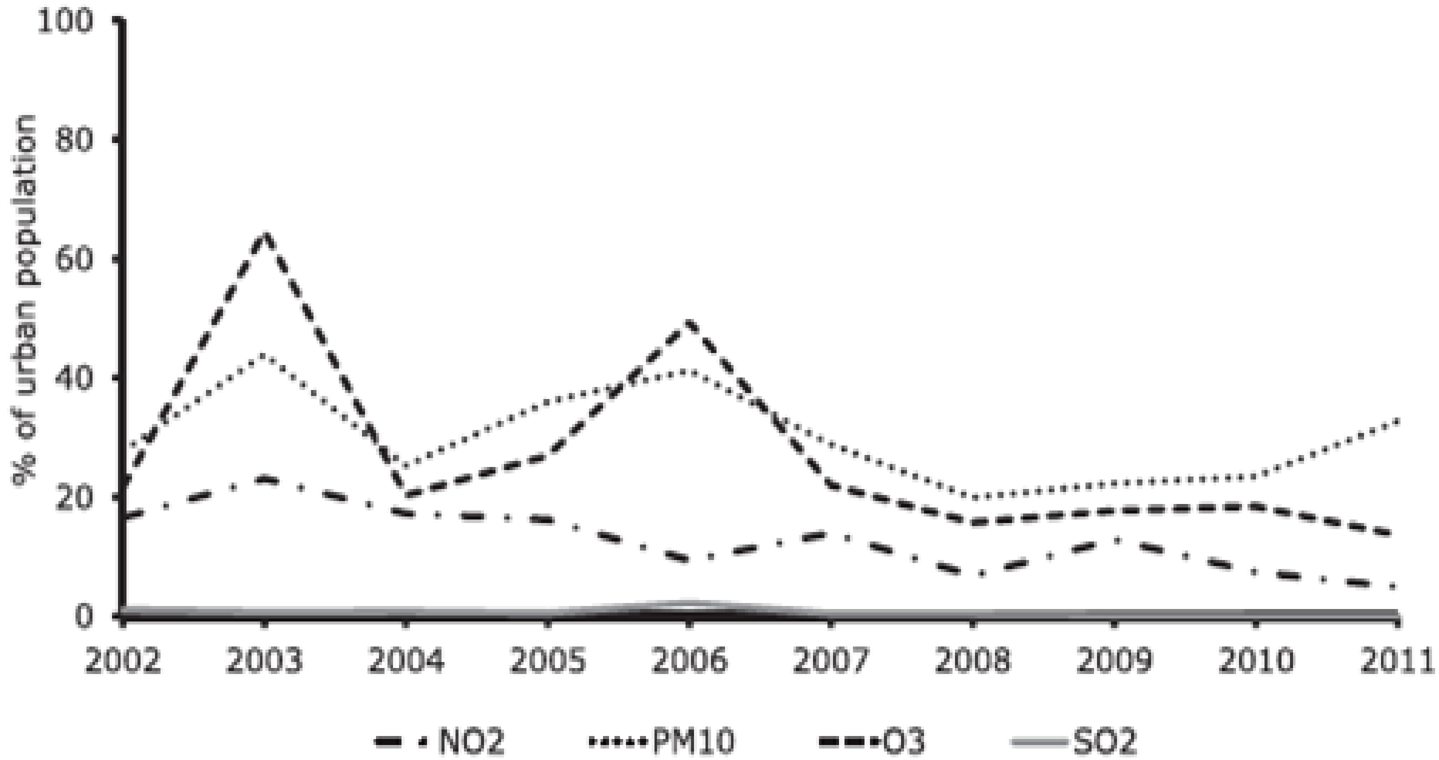

Fraction of population in EU-27 that are exposed to air pollution levels exceeding the AQ limit values in EU

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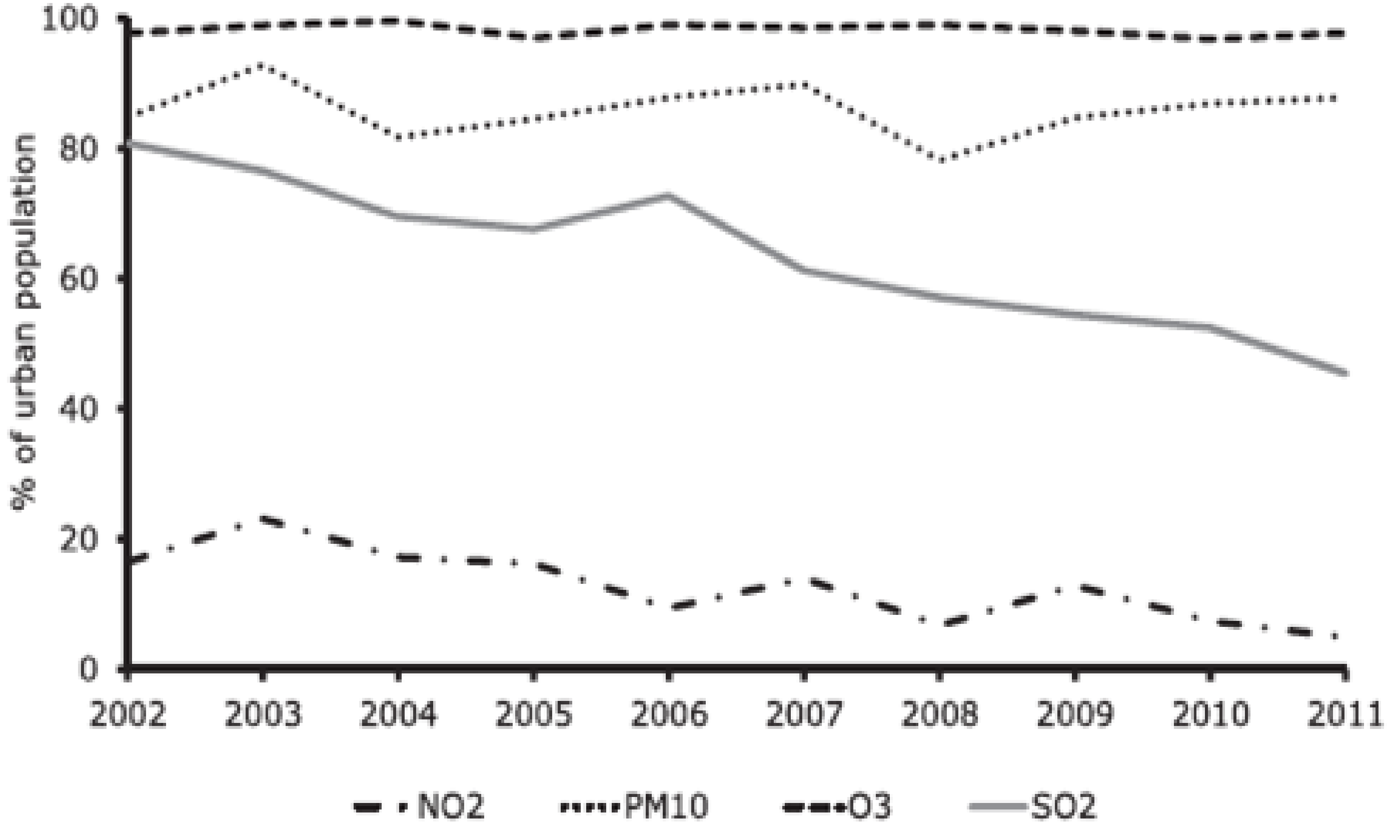

Fraction of population in EU-27 that are exposed to air pollution levels exceeding the WHO air quality guidlines

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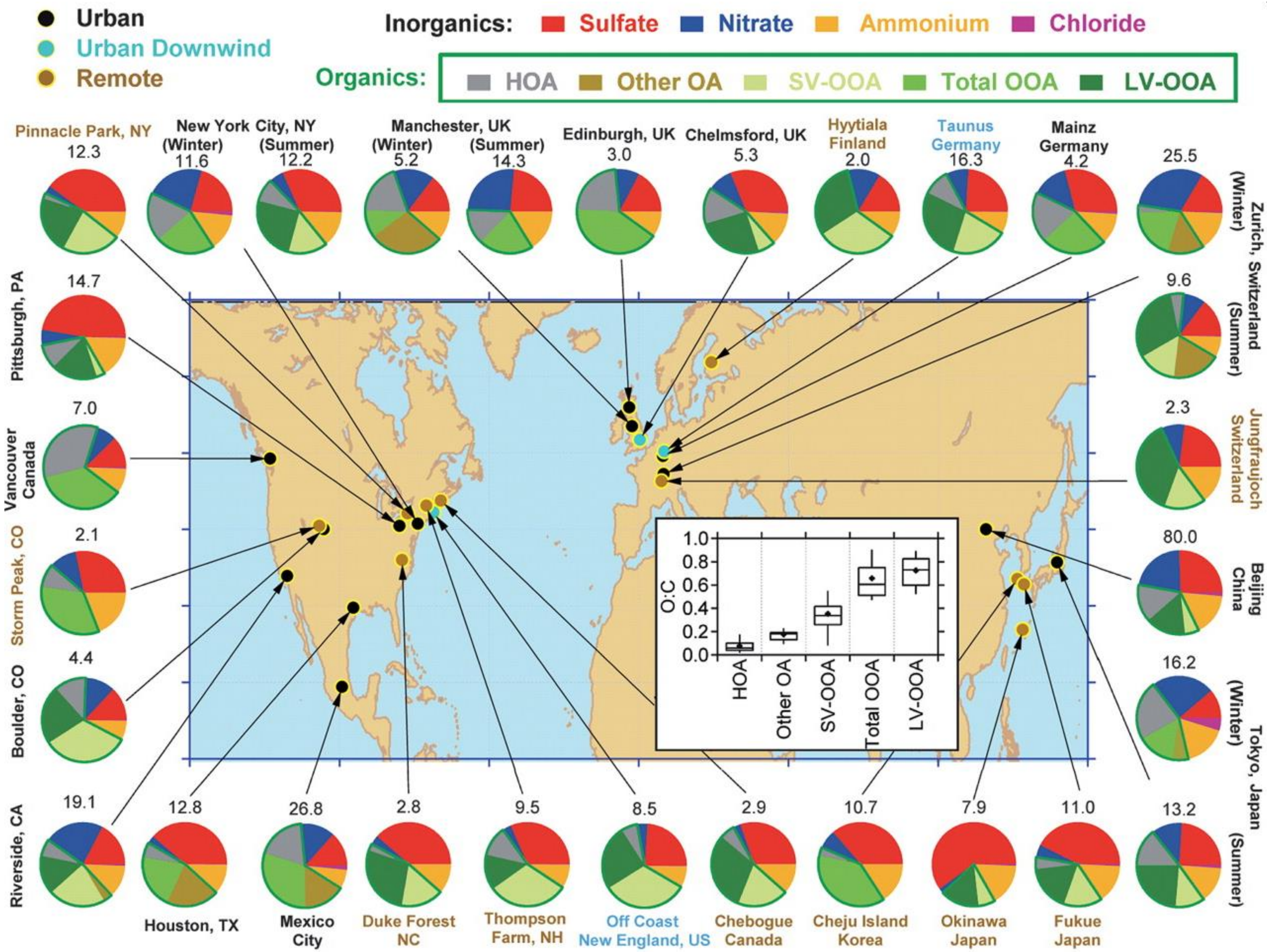
- The main sources of PM10 are emissions of mechanically generated coarse primary particles, e.g. sea spray, windblown dust, road dust.

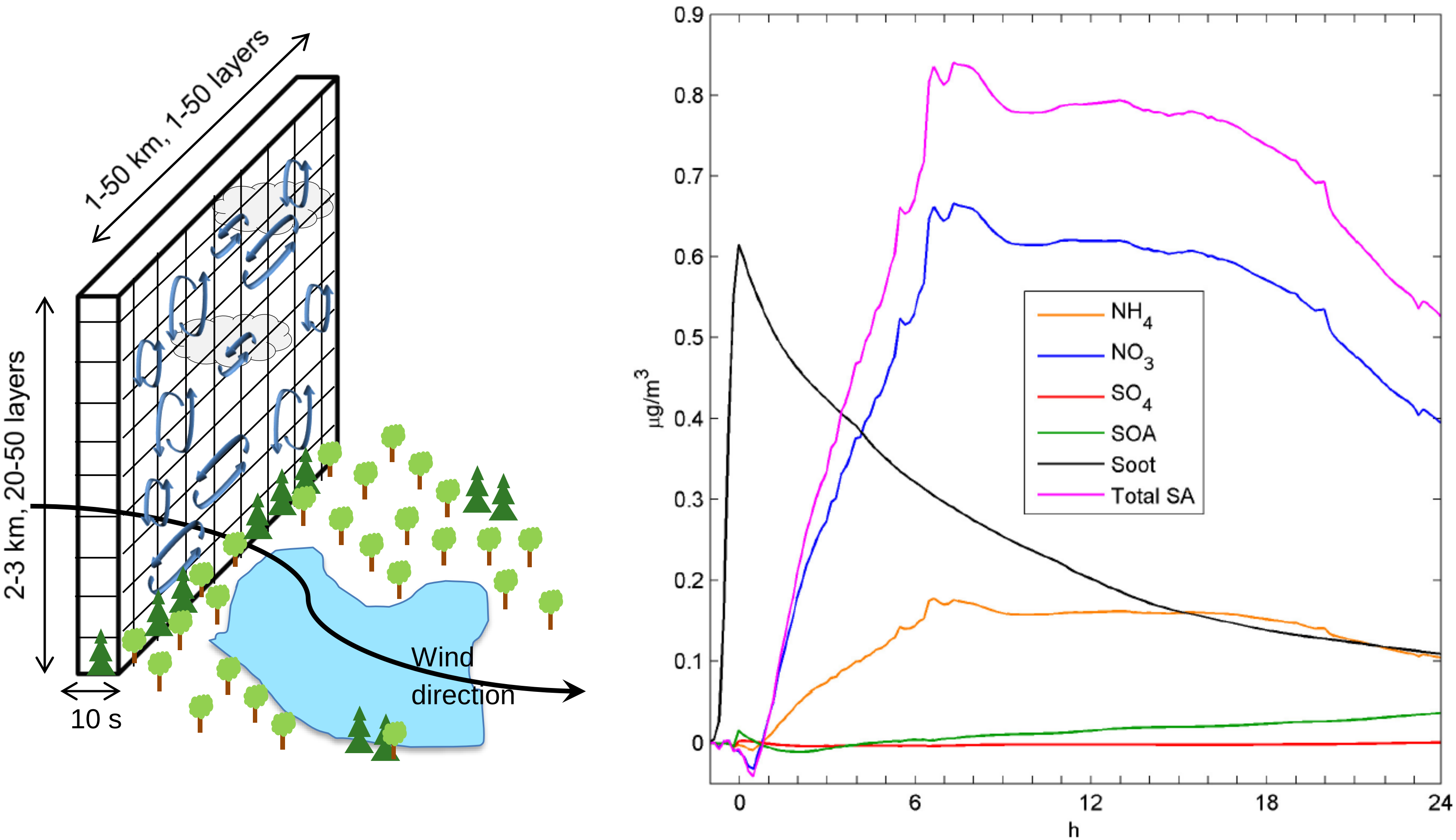
- The main source of PM2.5 can instead be secondary aerosol formation via gas-to-particle conversion (e.g. Secondary Organic Aerosol (SOA), ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$)
  Secondary aerosol precursors: NMVOCs, NO_x, SO_2 and NH_3

PM1 Aerosol Components Worldwide



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

ADCHEM model simulations of the urban plume from Malmö



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

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- Transport is the dominant sector for NOx emissions, accounting for 47% of the total in 2011, followed by the energy sector, which contributed 21% of the total.

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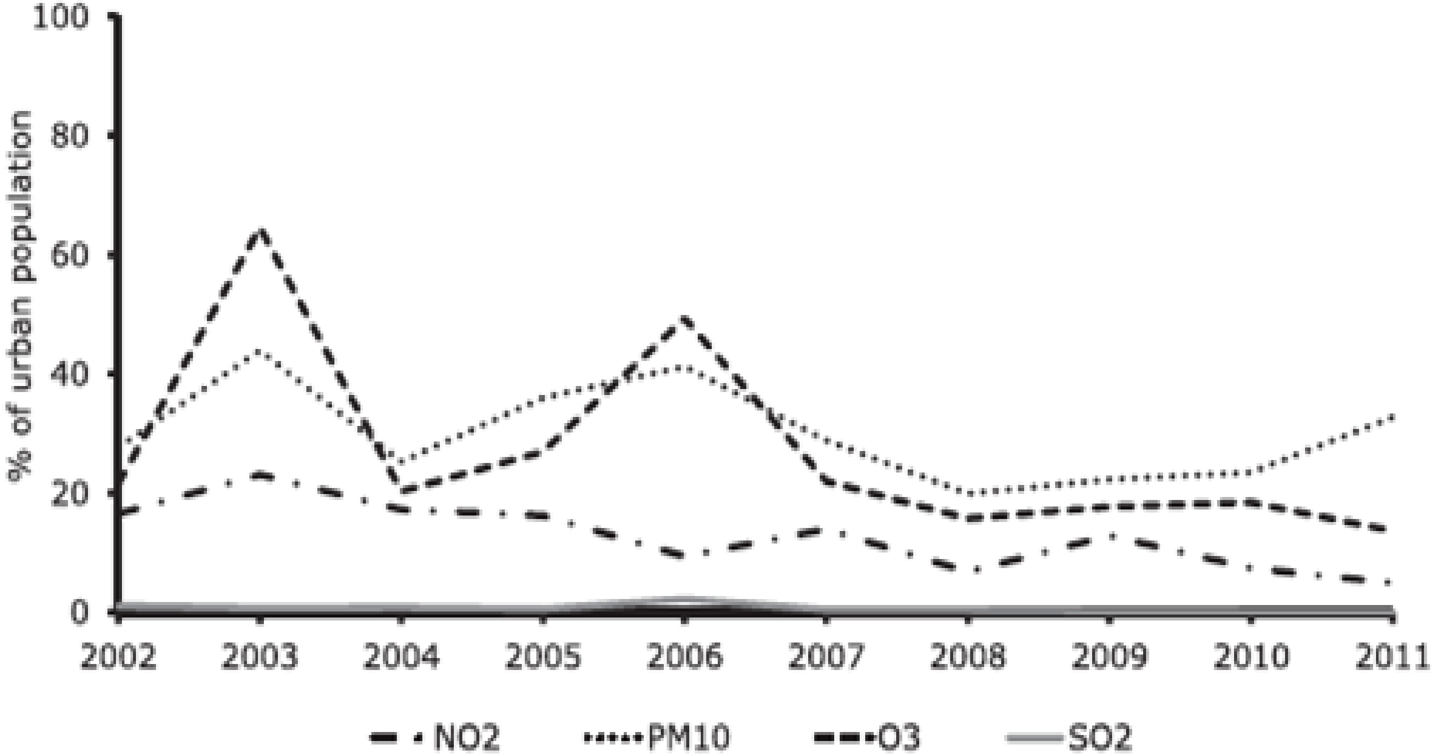

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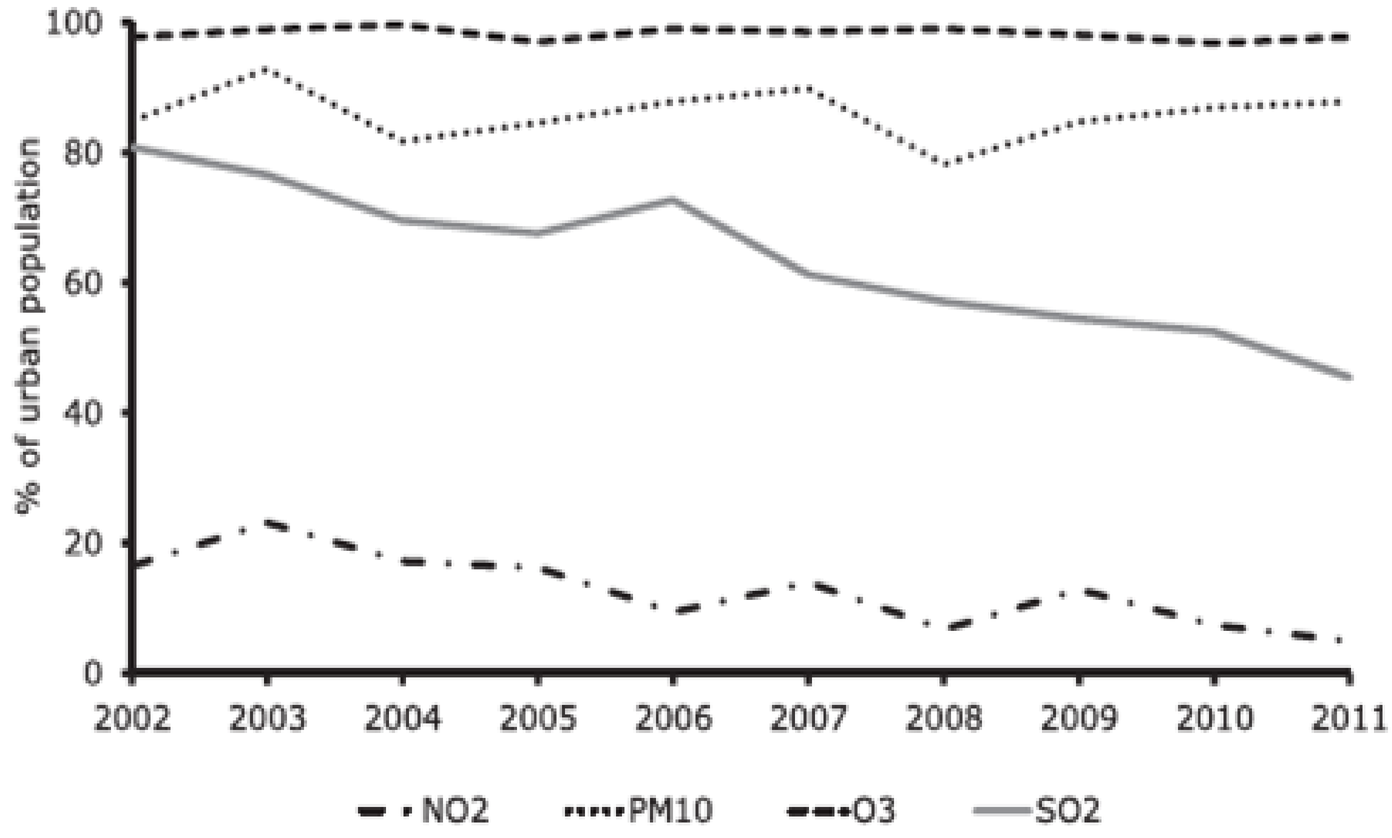

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- The area of sensitive ecosystems affected by excessive acidification from air pollution has shrunk by 92% from 1990 to 2010 mainly due to the strong reduction in SO_2 emissions (EEA, 2012).

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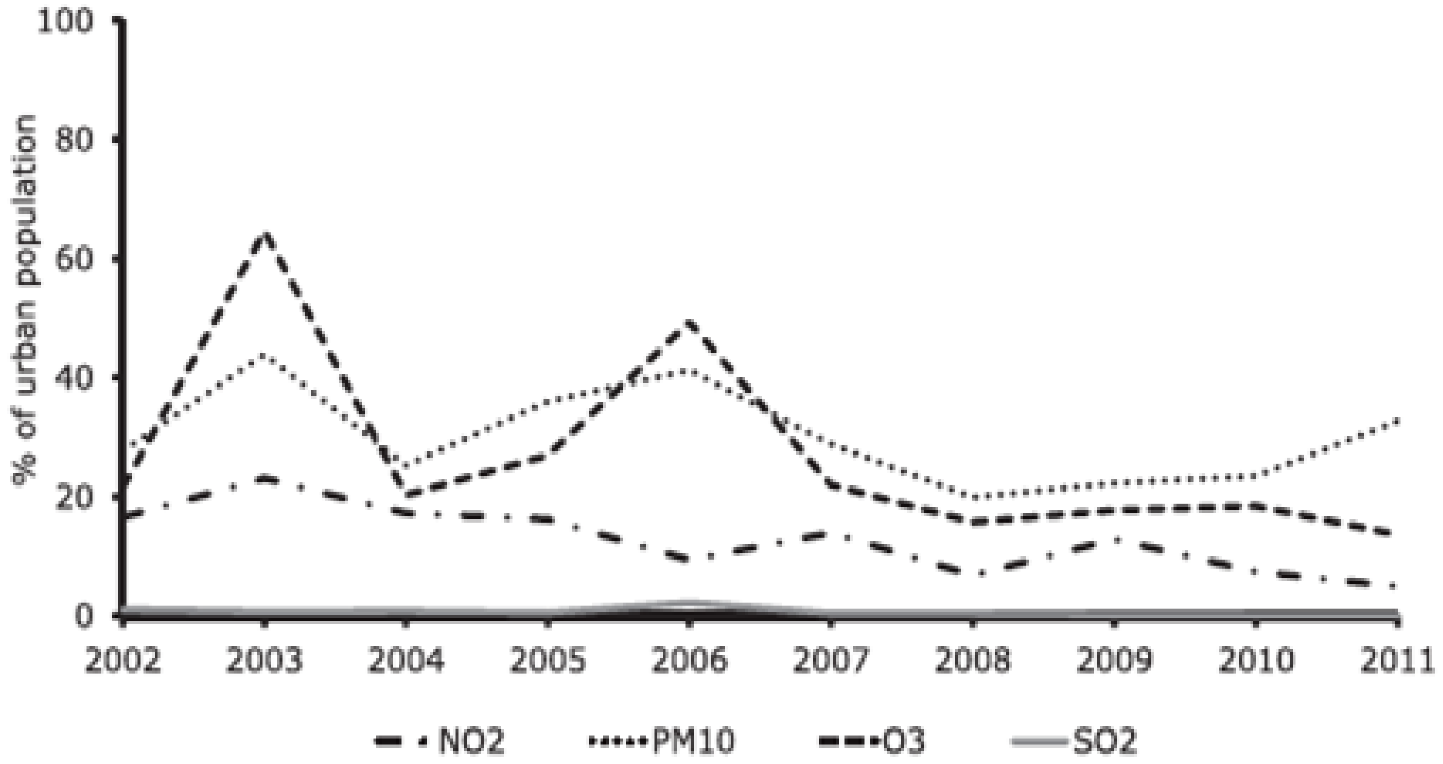

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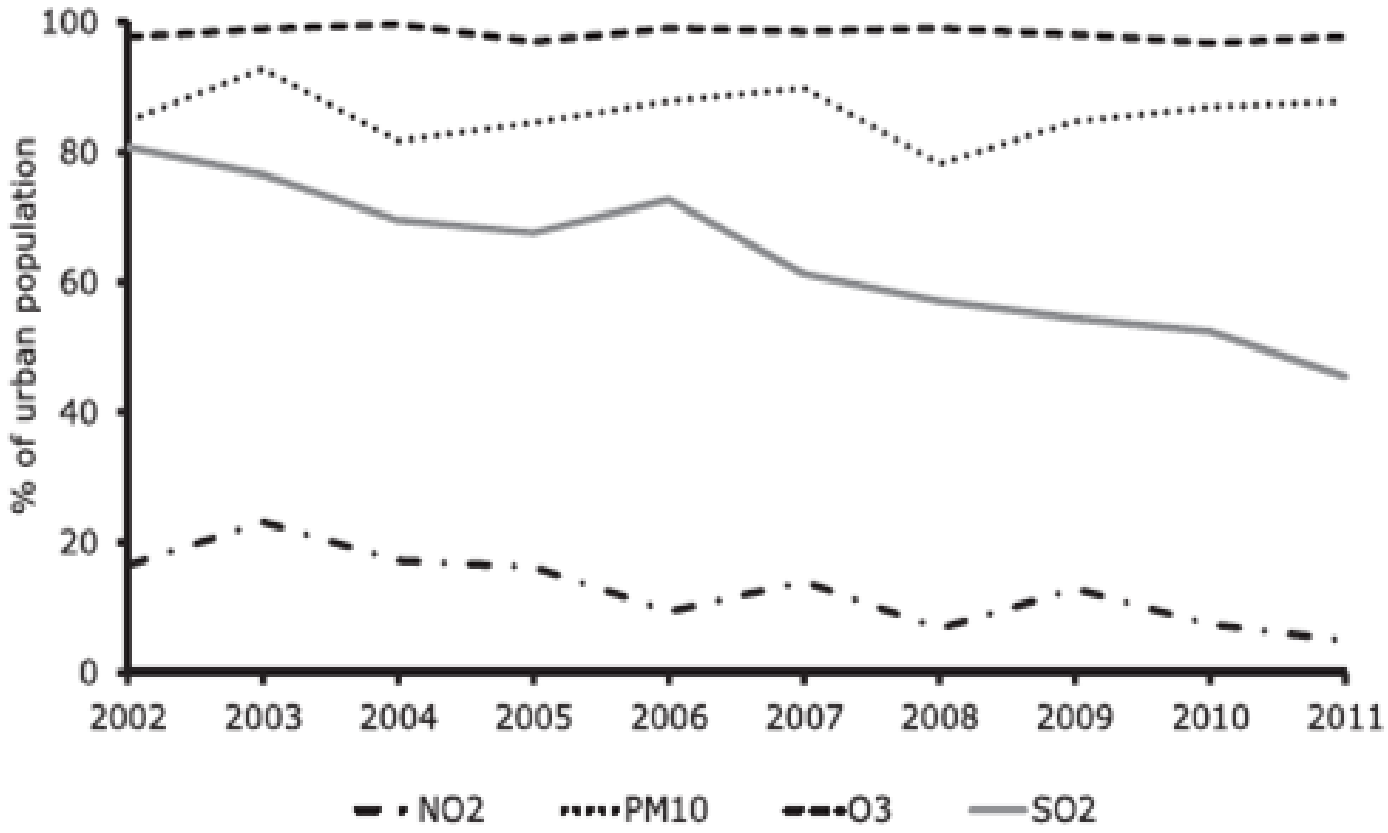

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- The observed EU-27 average reduction in CO daily 8-h maxima concentrations in the period 2002-2011 was 35%.

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- 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) $NO_2 + OH + M \rightarrow HNO_3 + M$ (daytime)

(13.10) $SO_2 + OH + M \rightarrow HSO_3 + M$ (daytime)

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

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

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- 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.