Atmospheric Chemistry
Chemical kinetics

FKFF05 vt-2019

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Reaction rates

Bimolecular reaction:

Reactants – A and B

Products – C and D

$$\mathrm{A + B \rightarrow C + D}$$

Reaction rate constant

Rate constant – k

Number density – $[X]$ (unit: molecules/cm^3)

$[A][B]$ proportional to the collision frequency

Chemical equilibrium

Reversible reactions $\mathrm{A + B \leftrightarrow C + D}$

$$\mathrm{A + B \rightarrow C + D} \qquad -\frac{d}{dt}[\mathrm{A}] = -\frac{d}{dt}[\mathrm{B}] = k_1[\mathrm{A}][\mathrm{B}]$$

$$\mathrm{C + D \rightarrow A + B} \qquad -\frac{d}{dt}[\mathrm{C}] = -\frac{d}{dt}[\mathrm{D}] = k_2[\mathrm{C}][\mathrm{D}]$$

Equilibrium when both reactions proceed at same rates:

$$k_1[\mathrm{A}][\mathrm{B}] = k_2[\mathrm{C}][\mathrm{D}]$$

We define an equilibrium constant *K*: $K = \frac{k_1}{k_2} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$

Three-Body reactions

- A three-body reaction involves reaction of two species A and B to yield one single product AB.
- This reaction requires a third body M to stabilize the excited product AB* by collision:

$$A + B \rightarrow AB^* \qquad (1)$$

$$AB^* \rightarrow A + B \qquad (2)$$

$$AB^* + M \rightarrow AB + M^* \qquad (3)$$

$$M^* \rightarrow M + \text{heat} \qquad (4)$$

The third body M is an inert molecule (generally N_2 and O_2)

Three-Body reactions

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}^* \qquad (1)$$

$$\mathrm{AB}^* \rightarrow A + B \qquad (2)$$

$$\mathrm{AB}^* + \mathrm{M} \rightarrow \mathrm{AB} + \mathrm{M}^* \qquad (3)$$

$$\mathrm{M}^* \rightarrow \mathrm{M} + \mathrm{heat} \qquad (4)$$

Common practice is to write the overall reaction as (heat is not counted):

Net (1,3,4):

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \rightarrow \mathrm{AB} + \mathrm{M} \qquad (5)$$

The rate of the three-body reaction is defined as the formation rate of AB by reaction (3):

$$\frac{d}{dt}[\mathrm{AB}] = k_3[\mathrm{AB}^*][\mathrm{M}]$$

Three-Body reactions

$$A + B \rightarrow AB^* \qquad (1)$$

$$AB^* \rightarrow A + B \qquad (2)$$

$$AB^* + M \rightarrow AB + M^* \qquad (3)$$

$$M^* \rightarrow M + \text{heat} \qquad (4)$$

Net: $$A + B + M \rightarrow AB + M \qquad (5)$$

$$\frac{d}{dt}[AB] = -\frac{d}{dt}[A] = -\frac{d}{dt}[B] = k_3[AB^*][M] \qquad \text{(Eq. 1)}$$

The excited complex AB* has a very short lifetime and reacts as soon as it is produced. We may therefore assume that it is in steady state at all times.

Steady state: Production = Loss i.e. $\frac{d}{dt}[AB^*]=0$

$$\frac{d}{dt}[AB^*] = k_1[A][B] - k_2[AB^*] - k_3[AB^*][M] = 0$$

$$k_1[A][B] = k_2[AB^*] + k_3[AB^*][M] \quad \Rightarrow \quad [AB^*] = \frac{k_1[A][B]}{k_2+k_3[M]}$$

Replacing into Eq. 1 gives:

$$\frac{d}{dt}[AB] = -\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{k_1k_3[A][B][M]}{k_2+k_3[M]} \qquad \text{(Eq. 2)}$$

Three-Body reactions

$$\mathrm{A + B \rightarrow AB^*} \quad (1)$$

$$\mathrm{AB^*} \rightarrow A + B \quad (2)$$

$$\mathrm{AB^{*}{+}M \rightarrow AB + M^*} \quad (3)$$

$$\mathrm{M^* \rightarrow M + heat} \quad (4)$$

Net (1,3): $\mathrm{A + B + M \rightarrow AB + M}$ (5)

$$\frac{d}{dt}[\mathrm{AB}] = -\frac{d}{dt}[\mathrm{A}] = -\frac{d}{dt}[\mathrm{B}] = \frac{k_1 k_3 [\mathrm{A}][\mathrm{B}][\mathrm{M}]}{k_2 + k_3 [\mathrm{M}]} \quad \text{(Eq. 2)}$$

Eq. 2 is the general rate expression for three-body reactions.

There are two interesting limits. In the low-pressure limit $[\mathrm{M}] << \frac{k_2}{k_3}$ Eq. 2 simplifies to:

$$\frac{d}{dt}[\mathrm{AB}] = -\frac{d}{dt}[\mathrm{A}] = -\frac{d}{dt}[\mathrm{B}] = \frac{k_1 k_3}{k_2}[\mathrm{A}][\mathrm{B}][\mathrm{M}]$$

In the high-pressure limit $[\mathrm{M}] \gg \frac{k_2}{k_3}$ Eq. 2 simplifies to:

$$\frac{d}{dt}[\mathrm{AB}] = -\frac{d}{dt}[\mathrm{A}] = -\frac{d}{dt}[\mathrm{B}] = k_1[\mathrm{A}][\mathrm{B}]$$

Photolysis -1

A photolytic reaction involves the breaking of a chemical bond by an incident photon ($h\nu$).

$$X + h\nu \rightarrow Y + Z$$

$$-\frac{d}{dt}[X] = \frac{d}{dt}[Y] = \frac{d}{dt}[Z] = k[X]$$

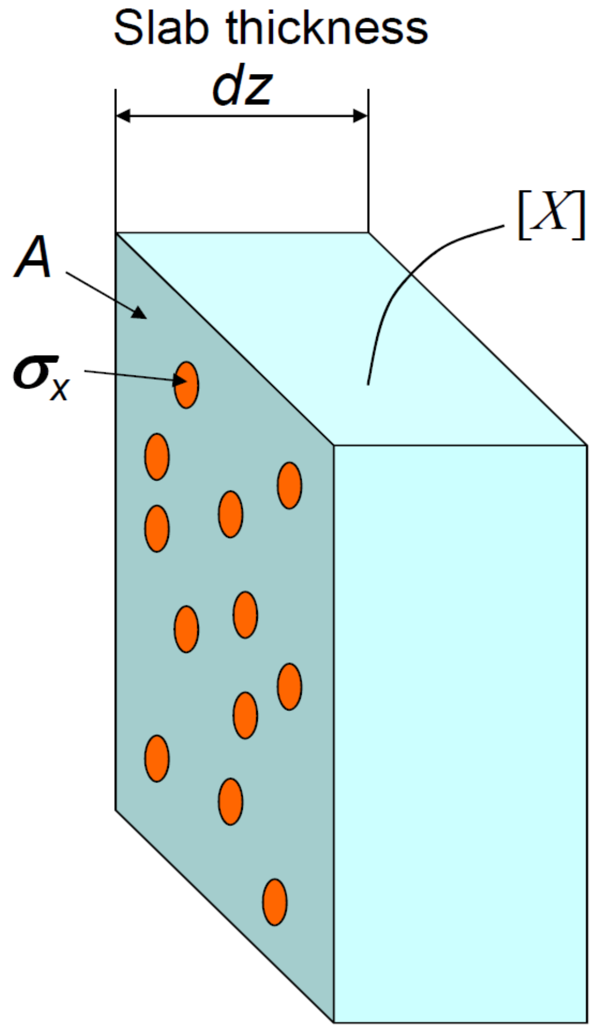
Photolysis rate constant k (s^{-1})

Absorption cross section: σ_X (m^2 molecules^{-1})

"Target area" of molecule X within which the photon is absorbed (m^2 molecules^{-1})

Probability for a photon to hit molecule X in the slap volume ($A \cdot dz$) :

$$\frac{\sigma_X}{A} \cdot [X] \cdot A \cdot dz = \sigma_X \cdot [X] \cdot dz$$



Photolysis -2

Absorption cross section: σ_x ($\mathrm{m^2\ molecules^{-1}}$)

Actinic Flux: I

Number of photons crossing the unit horizontal area per unit time (photons $\mathrm{m^{-2}\ s^{-1}}$)

Quantum Yield: q_x

Probability that absorption of a photon will cause photolysis of X (molecules $\mathrm{photon^{-1}}$)

Nr. of molecules of X that are photolyzed per unit time in the slab *dz:*

$$I \cdot q_\mathrm{x} \cdot \sigma_\mathrm{x} \cdot [\mathrm{X}] \cdot dz \cdot A$$

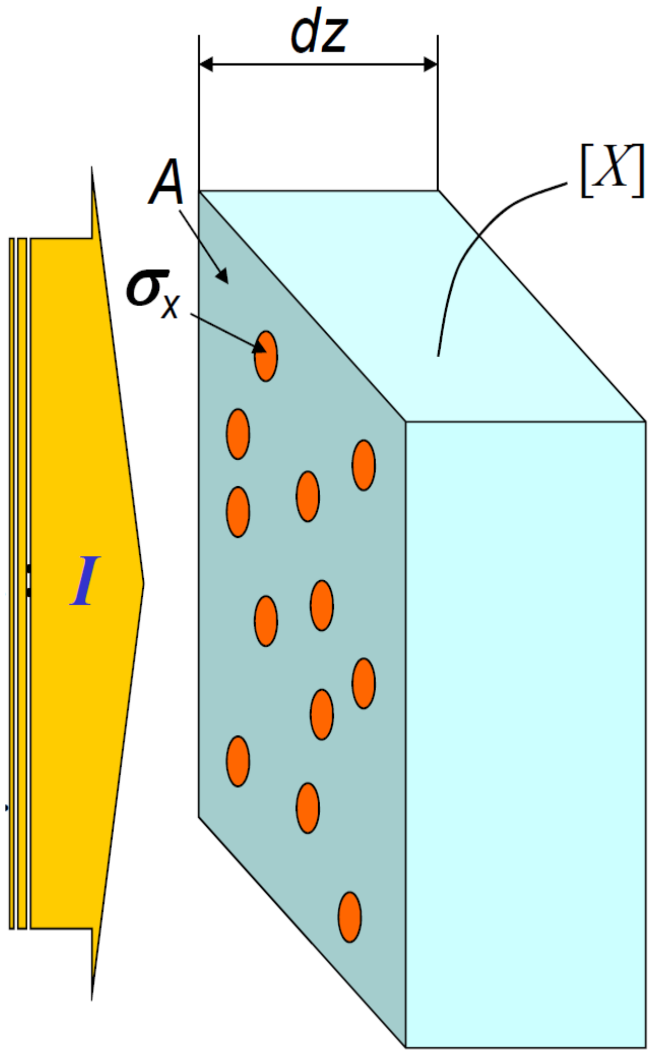
which divided by the nr. of molecules X in the slab dz:

$$([\mathrm{X}] \cdot dz \cdot A)$$

gives:

Photolysis rate constant k:

$$k = I \cdot q_\mathrm{x} \cdot \sigma_\mathrm{x} \quad (s^{-1}, \text{wavelength dependent})$$



Radical reactions

- Trace gases are found at very low concentrations in the atmosphere
- Collisions between trace gas molecules are infrequent
- Slow reaction rates unless the molecules are fairly reactive
- Chemical reactions in the atmosphere proceed almost entirely with the involvement of radicals.
- Radicals – molecules or atoms with one or more unpaired electrons (odd number of electrons)
- Hence, very reactive!
- Examples:
- NO radical (7+8=15 electrons)
- HNO_3 non-radical (1+7+(3·8)=32 electrons)

Radical reactions

Initiation of the radical chain:

non-radical + *hv* → radical + radical´ (in total two unpaired electrons)

Propagation:

radical + non-radical → radical´ + non-radical´

Termination (breaking of the radical chain):

radical + radical´ → non-radical + non-radical´

radical + radical´ + M → non-radical + M

Termination is often slower than propagation since radicals are found at extremely low concentrations (collisions very infrequent).

Initiation requires energy (endothermic process).

This energy is often provided by solar radiation (*hv*).

Radical reactions

Make a habit of identifying which molecules that are radicals. Count electrons.

Rule: An odd number of electrons reveals that the molecule has an unpaired electron and therefore is a radical.

Exceptions: **O(3P)** has two unpaired electrons and is a biradical. **O(1D)** has no unpaired electrons but is in a highly excited state, and is therefore, like a radical, very reactive.

Ozone is no radical and is thus actually fairly stable.

Learn to see which reactions that are:

- **radical initiation (most often via photolysis),**
- **radical propagation**, and
- **termination**.

Radical reactions

- In a photolysis reaction, electron pairs are split and radicals are formed (radical initiation).
- In a propagation step, the radicals on the left side in the reaction (LS) must have the same number of unpaired electrons as on the right side (RS).
- In a termination step, two radicals on the LS form two non-radicals on the RS.
- The exceptions in this course are $O(^3P)$ and $O(^1D)$.

Examples:

non-radical + *hν* → *radical* + *radical´ (photolysis initiation)*

radical + radical´ → radical´´+ radical´´´ (propagation)

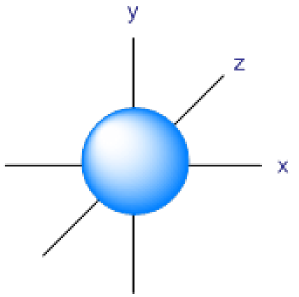
radical + non-radical → radical´ + non-radical´ (propagation)

$O(^1D)$, or $O(^3P)$ + non-radical → radical+radical´ (propagation)

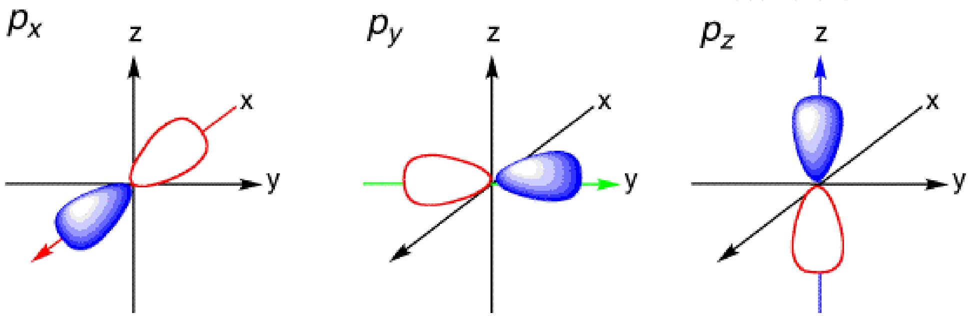
radical + radical´ + M → non-radical + M (termination)

Note on O(^{3}P) and O(^{1}D)

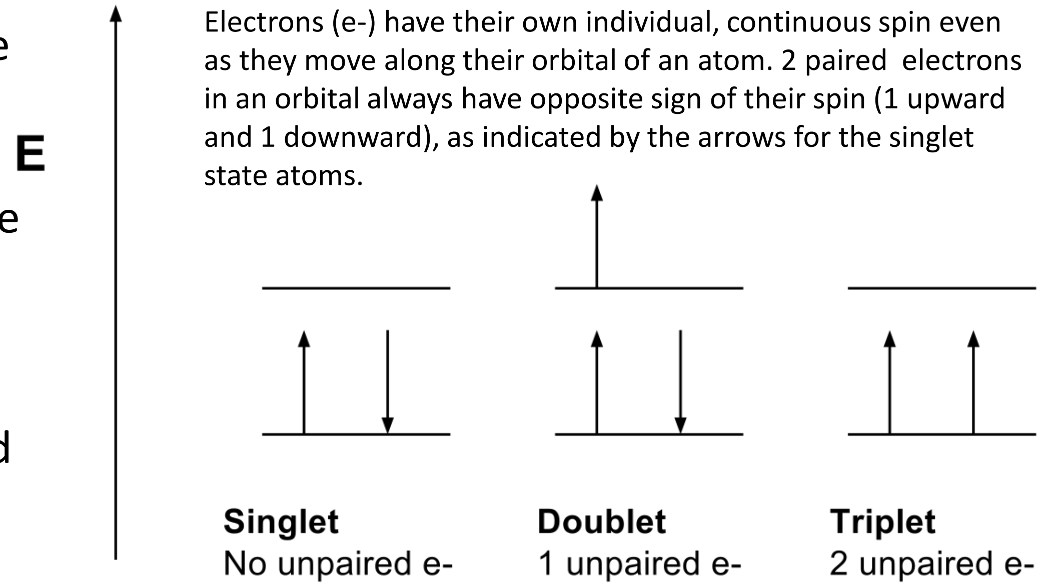
- Orbitals: A theoretical volume where each electron will be located 95 % of the time.
- Each orbital contain 0, 1 or 2 electrons
- The 2nd electron shell can contain up to 8 electrons. In the case of the oxygen atom it contains 6.
- The electrons in the s orbital have lowest energy, hence this shell is filled first (Aufbau principle) , if the atoms is in its ground state (lowest energy state).
- Hund's rule: Orbitals with the same energy (e.g. p_x p_y p_z) all receive one electron each, before any of them receives it's second electron. Also called the "bus seat rule“. This is the case for atoms in the ground state e.g. O(^{3}P): $2s^22p_x^22p_y^12p_z^1$, which is a bi-radical with 2 unpaired electrons, 1 in the p_y orbital and 1 in the p_z orbital.
- Explanation to Hund's rule: The electrons in singly occupied orbitals are less effectively screened (shielded) from the nucleus, so that such orbitals contract and electron–nucleus attraction energy becomes greater in magnitude.
- O(^{1}D) with all electrons paired $2s^22p_x^22p_y^2$ do not obey Hund's rule and is in a higher existed energy "singlet" state and more reactive than O(^{3}P). **Singlet state** refers to a system in which all electrons are paired.



2s atomic orbital
node not shown



The three p orbitals are aligned along perpendicular axes



Electrons (e-) have their own individual, continuous spin even as they move along their orbital of an atom. 2 paired electrons in an orbital always have opposite sign of their spin (1 upward and 1 downward), as indicated by the arrows for the singlet state atoms.

Oxidation State

Oxidation: Loss of one or more electrons by a substance (element, ion)

Reduction: Gain of one or more electrons by a substance (element, ion)

The **oxidation state** (number) of atoms in covalent bonds are obtained by assigning the electrons to particular atoms.

Shared electrons are assigned completely to the atom that has the stronger attraction for electrons

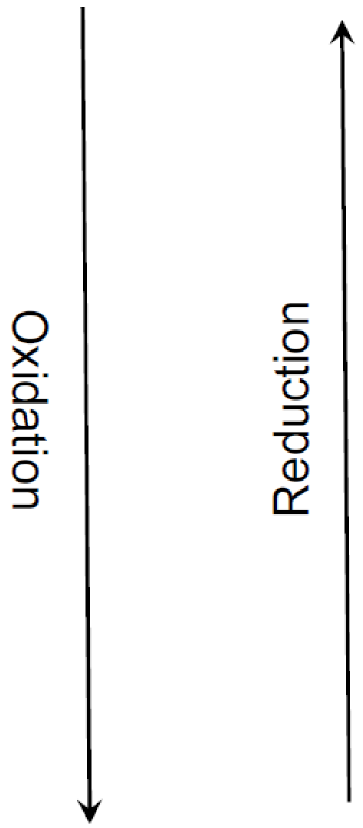
Some rules:

- Oxidation state of an atom in its elemental state is 0 (e.g. H_2).
- Oxidation state of a monatomic ion is the same as its charge.
- Oxygen is assigned an oxidation state of -2 in covalent compounds like CO, CO_2, SO_2,SO_3
- Exception O: peroxides like H_2O_2 were the O oxidation state is -1.
- In covalent compounds with non-metals, H is assigned the oxidation state +1.
- The sum of the oxidation states must be zero for a neutral compound and for an ion it is equal to its charge.

Oxidation State

Example: Oxidation states of nitrogen

NH_3, RNH_2	-3
N_2	0
N_20	+1
NO	+2
HNO_2	+3
NO_2	+4
HNO_3	+5
NO_3	+6



Draw a circle around the chemical species that are radicals:

NO CO_2 O_3 OH HNO_3 NO_3

Write down the oxidation number of the carbon atom in the species formed from the reaction sequence where methane is oxidized by OH to carbon dioxide.

CH_4 ______________________

CH_3OOH ______________________

CH_2O ______________________

CO ______________________

CO_2 ______________________

Introduction to Atmospheric Chemistry and Air Pollution

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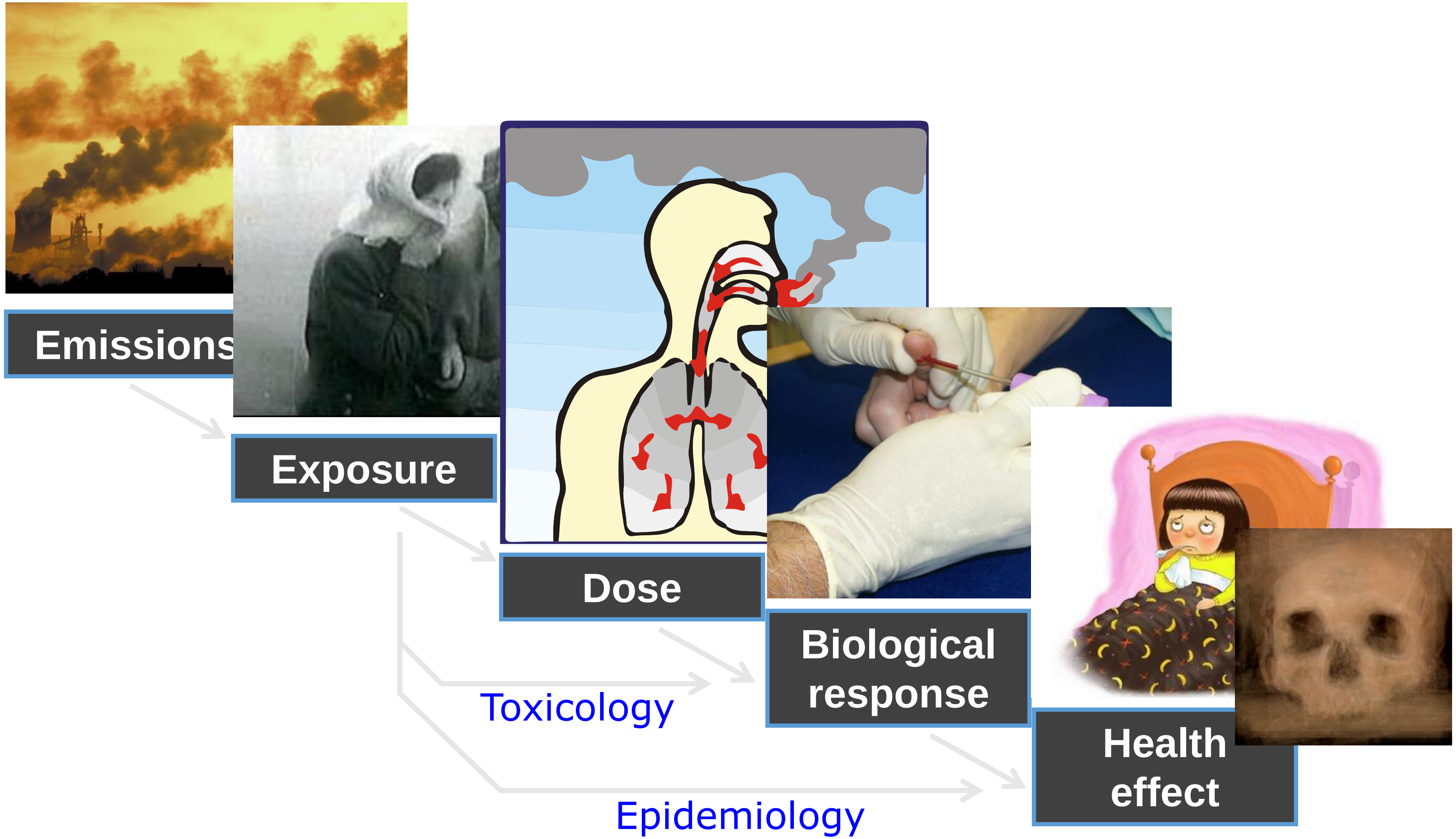
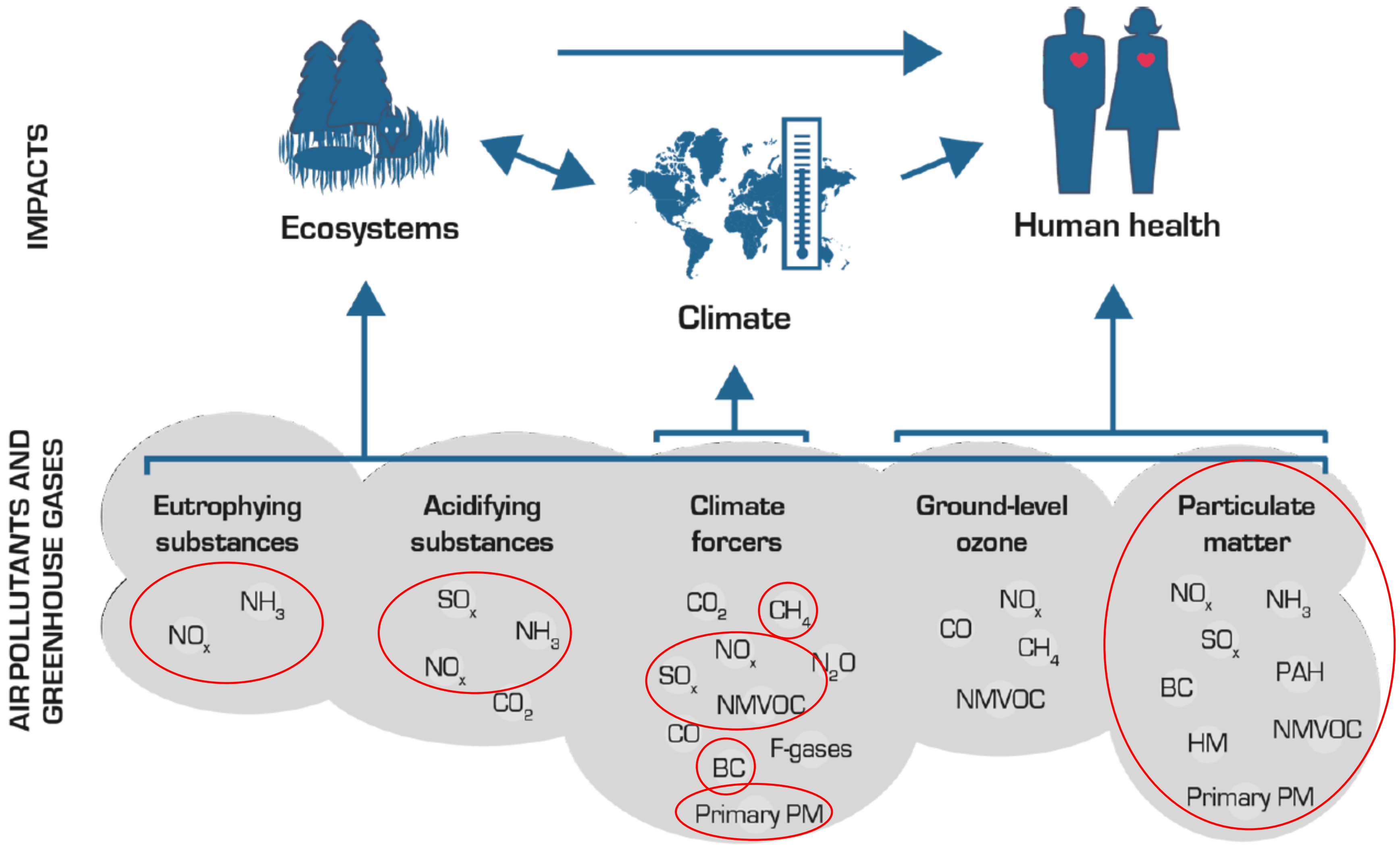
Health Effects of Air Pollution

Air Pollutant - A compound that is present at high enough concentrations in the atmosphere to cause a negative effect.



Major air pollutants in Europe, clustered according to impacts on human health, ecosystems and the climate



Short-Lived Climate Forcers / Pollutants (SLCF / SLCP)

Global estimated annual deaths (millions) by risk pollution factor – 2015

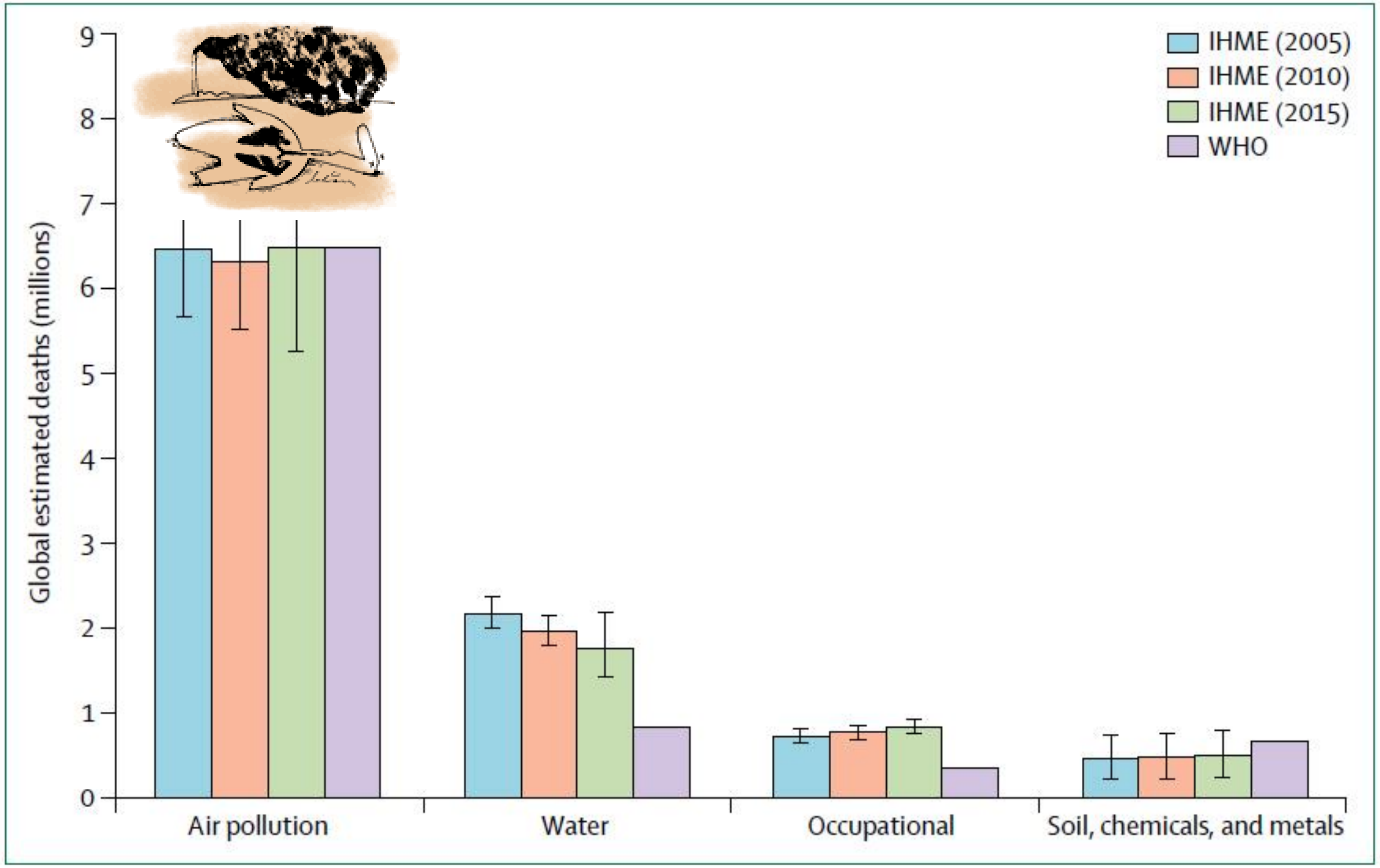
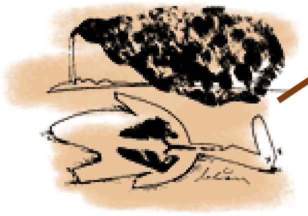


***Figure 4*: Global estimated deaths (millions) by pollution risk factor, 2005–15**
Using data from the GBD study[42] and WHO.[99] IHME=Institute for Health Metrics and Evaluation.

The Lancet 2017

Global estimated annual deaths (millions) by risk factor and cause – 2015



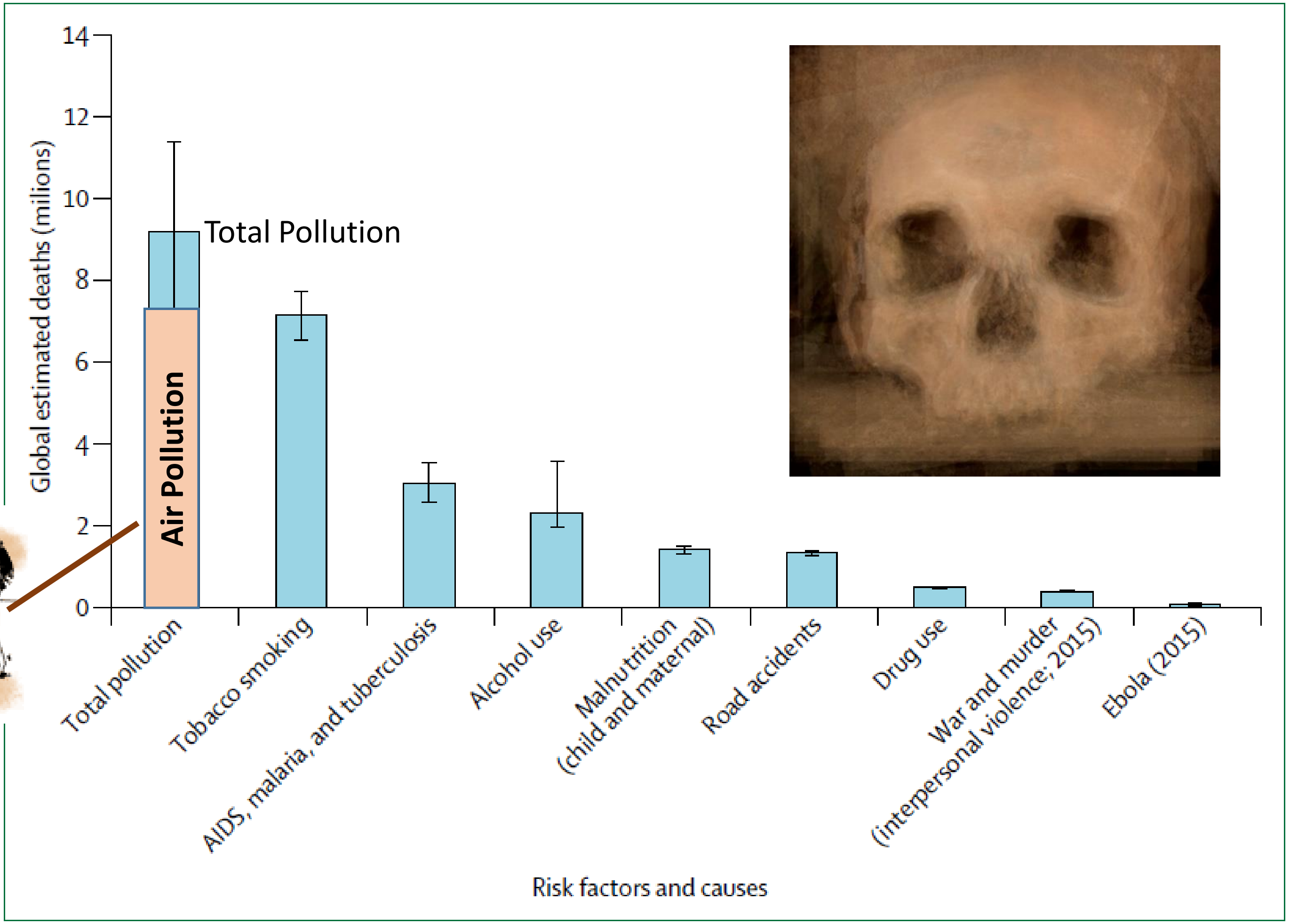


Figure 5: **Global estimated deaths by major risk factor and cause, 2015**
Using data from the GBD Study, 2016.[41]

The Lancet 2017

Health Effects of Air Pollution in Europe (EU-28)

Source: EEA, ”Air Quality in Europe - 2017 Report”

The EEA estimates (EEA, 2017) that

the health impacts attributable to exposure to fine particulate matter (PM2.5) in the EU-28 were responsible for around

PM2.5 → 399 000 premature deaths annually

Years of life lost (YLL) 4 278 800

The health impact of exposure to **NO_2** and O_3 concentrations on the EU-population was estimated to be about

NO_2 → **75 000 premature deaths per year** (YLL: 798 500)

O_3 → 13 600 premature deaths per year (YLL: 145 200)

Years of life lost (YLL) is an estimate of the average number of years that a person would have lived if he or she had not died prematurely.

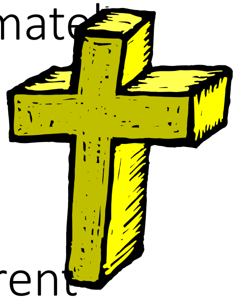
European Environment Agency

http://www.eea.europa.eu/publications/air-quality-in-europe-2017

Health Effects of Air Pollution in Sweden

Sweden:

The total number of premature deaths can be estimated to approximately



7600 per year

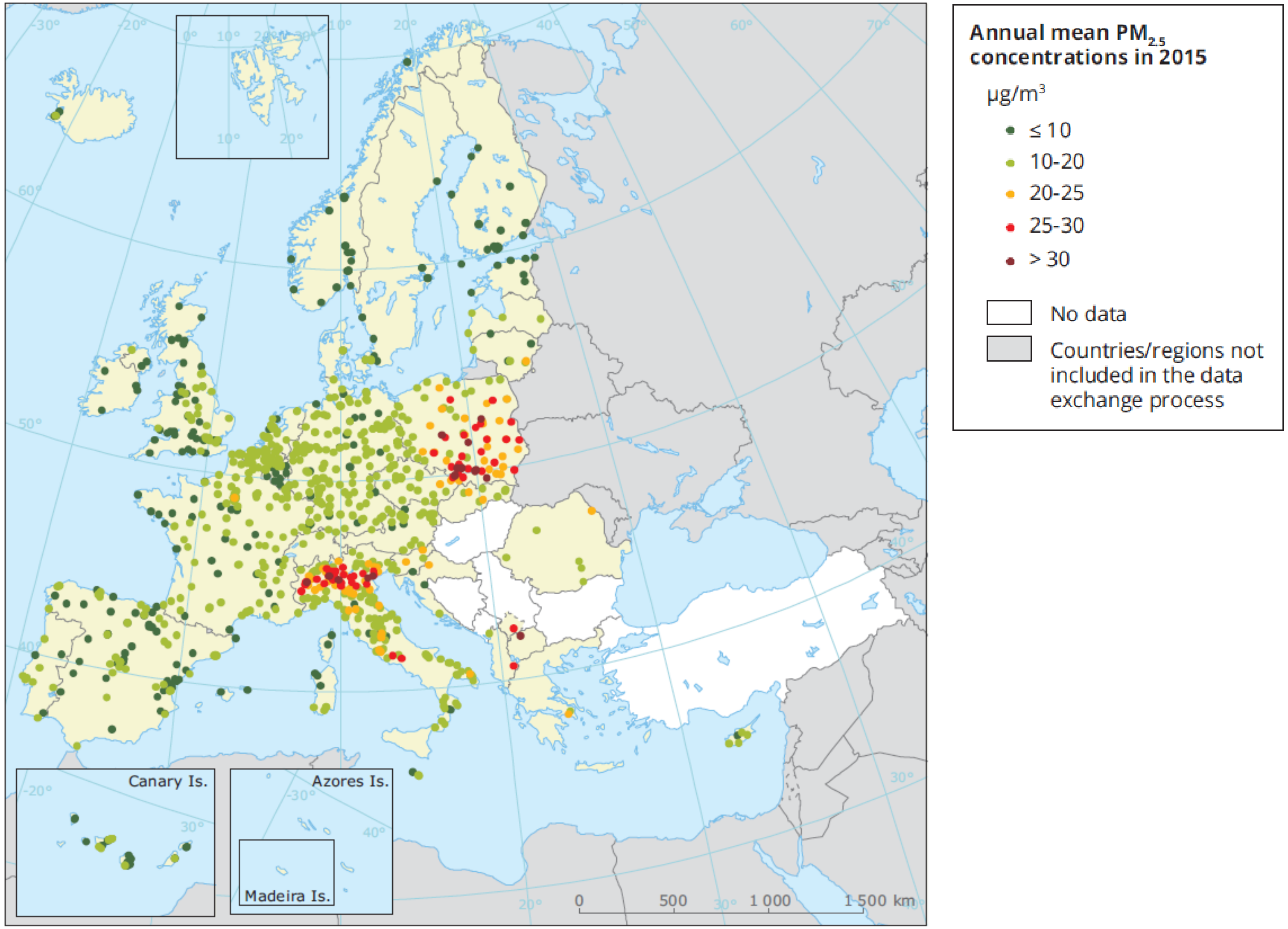
when taking into account differences in exposure-response for different PM sources.

Using the division between PM sources and NO_2 as an indicator of traffic combustion the total socio-economic cost (2015) would be

approximately 56 billion SEK

Source: Quantification of population exposure to NO2, PM2.5 and PM10 and estimated health impacts, Malin Gustafsson, Jenny Lindén, Lin Tang, Bertil Forsberg, Hans Orru, Stefan Åström, Karin Sjöberg , IVL Report C 317, 2018

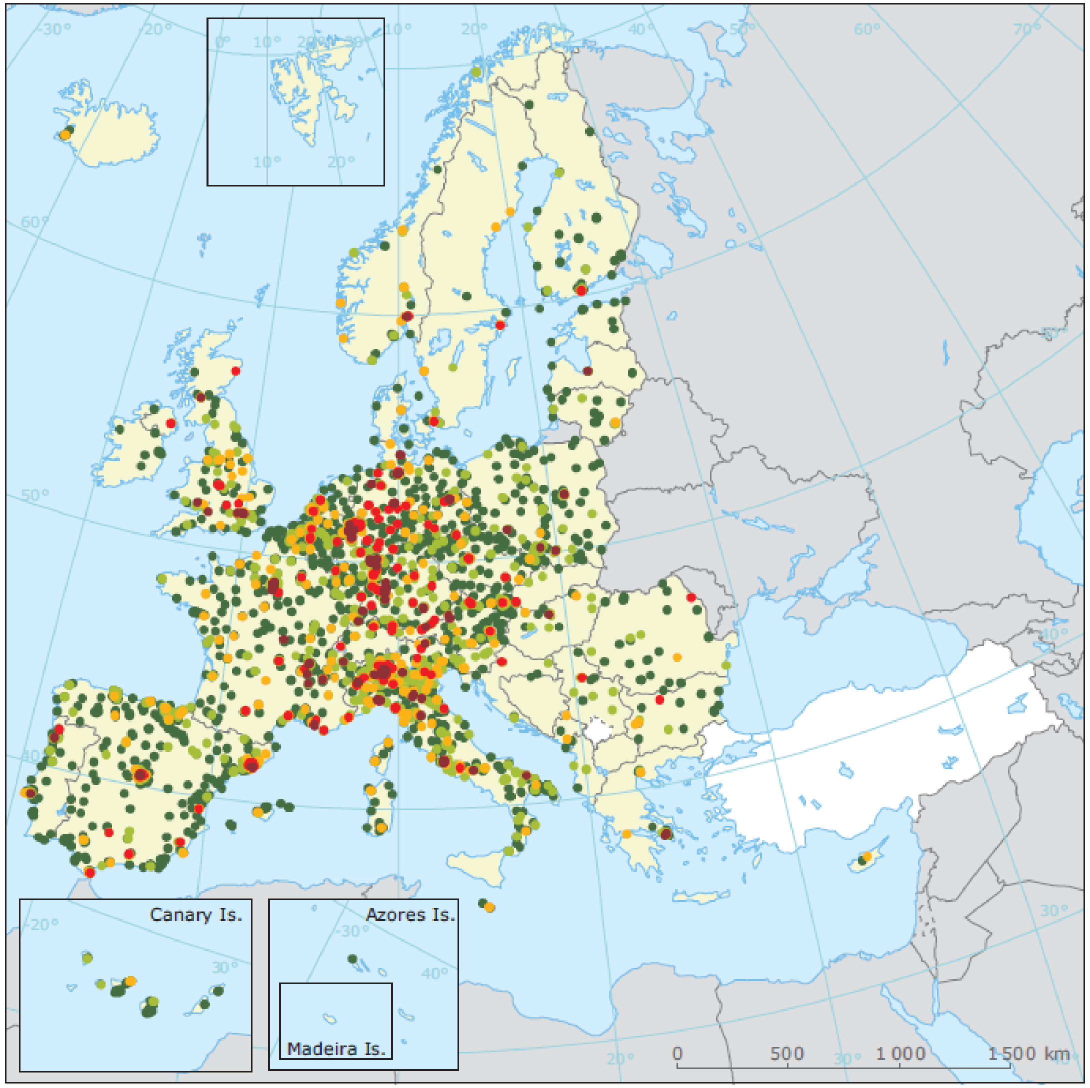
PM2.5 concentrations in Europe 2015



The dark red and red dots indicate stations reporting concentrations above the EU annual limit value (25 µg/m3).
The dark green dots indicate stations reporting values below the WHO AQG for PM2.5 (10 µg/m3).

European Environment Agency

NO_2 concentrations in Europe 2015



Annual mean NO_2 concentrations in 2015

µg/m³

- ≤ 20
- 20-30
- 30-40
- 40-50
- > 50

No data

Countries/regions not included in the data exchange process

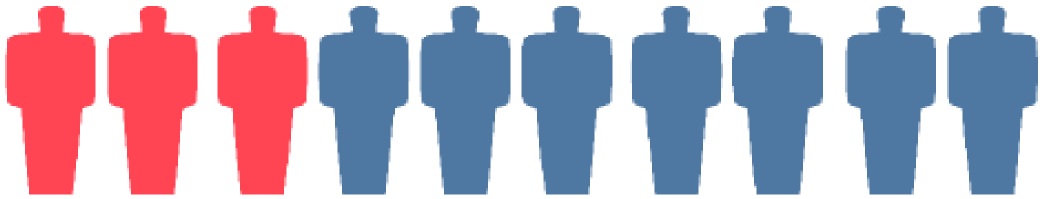
Red and dark red dots correspond to values above the EU annual limit value and the WHO AQG (40 µg/m3).

European Environment Agency

Share of urban population exposed to dangerous levels of particulate matter in Europe

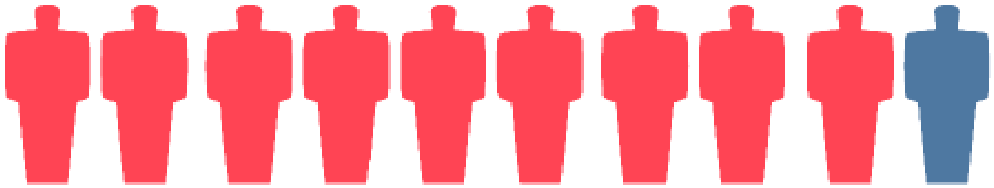
3 out of 10

exposed to exceedances of the EU daily limit value



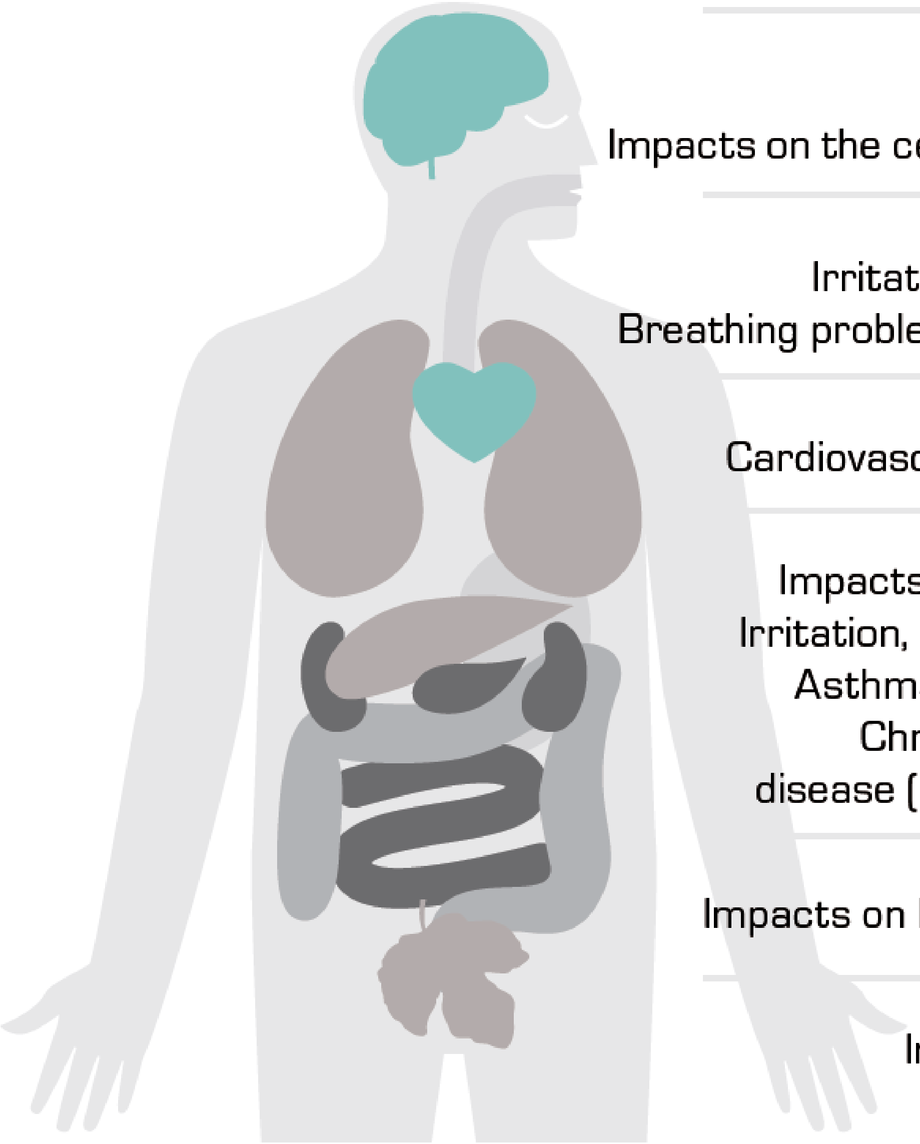
9 out of 10

exposed to exceedances of the WHO guideline value



Despite reductions in particulate matter (PM) emissions, PM concentrations have not yet declined to safe levels.

Air Pollution and Health Effects



Headache and anxiety (SO_2)
Impacts on the central nervous system (PM)

Irritation of eyes, nose and throat
Breathing problems (O_3, PM, NO_2, SO_2, BaP)

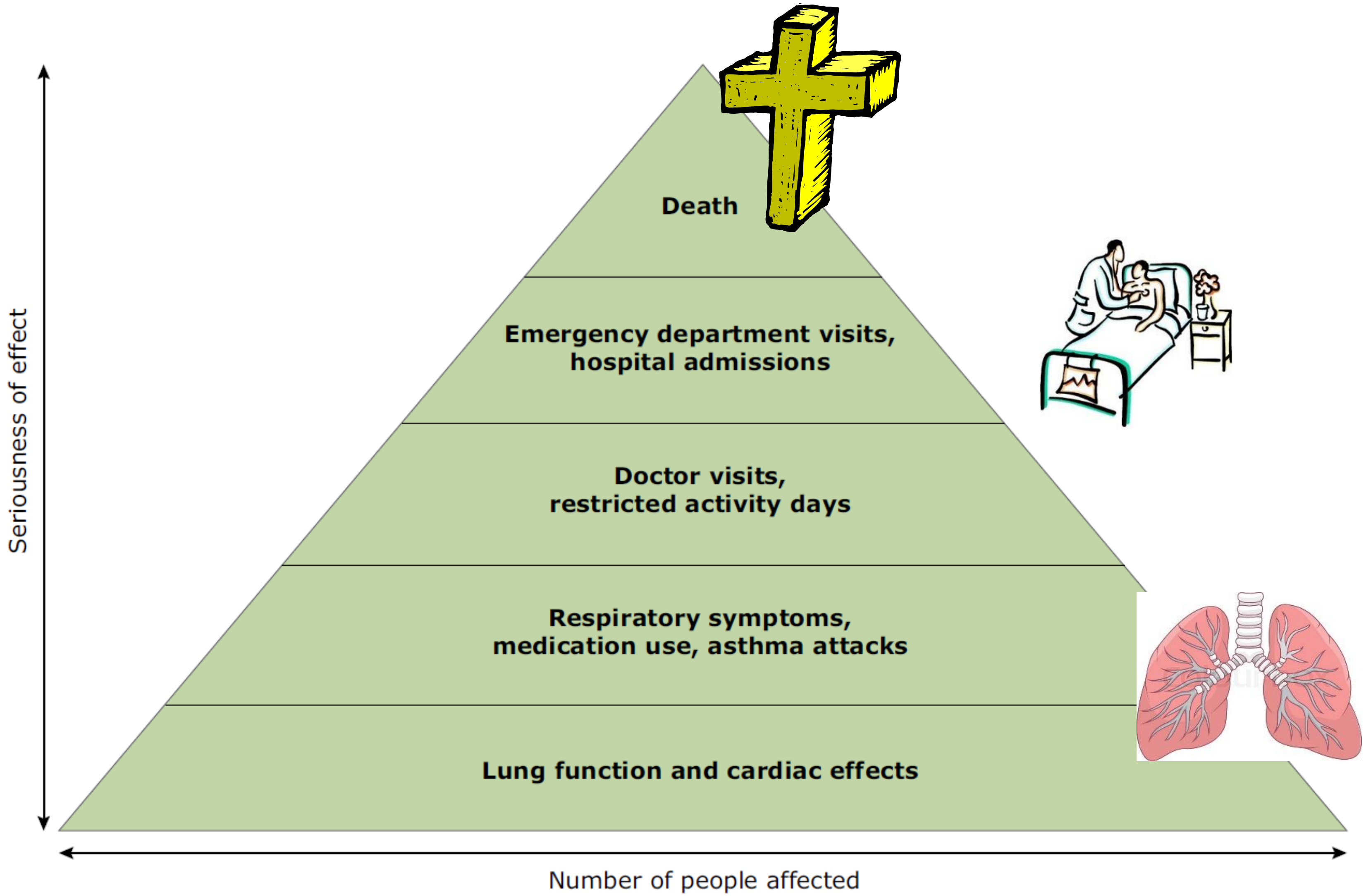
Cardiovascular diseases (PM, O_3, SO_2)

Impacts on the respiratory system:
Irritation, inflammation and infections
Asthma and reduced lung function
Chronic obstructive pulmonary disease (PM) Lung cancer (PM, BaP)

Impacts on liver, spleen and blood (NO_2)

Impacts on the reproductive system (PM)

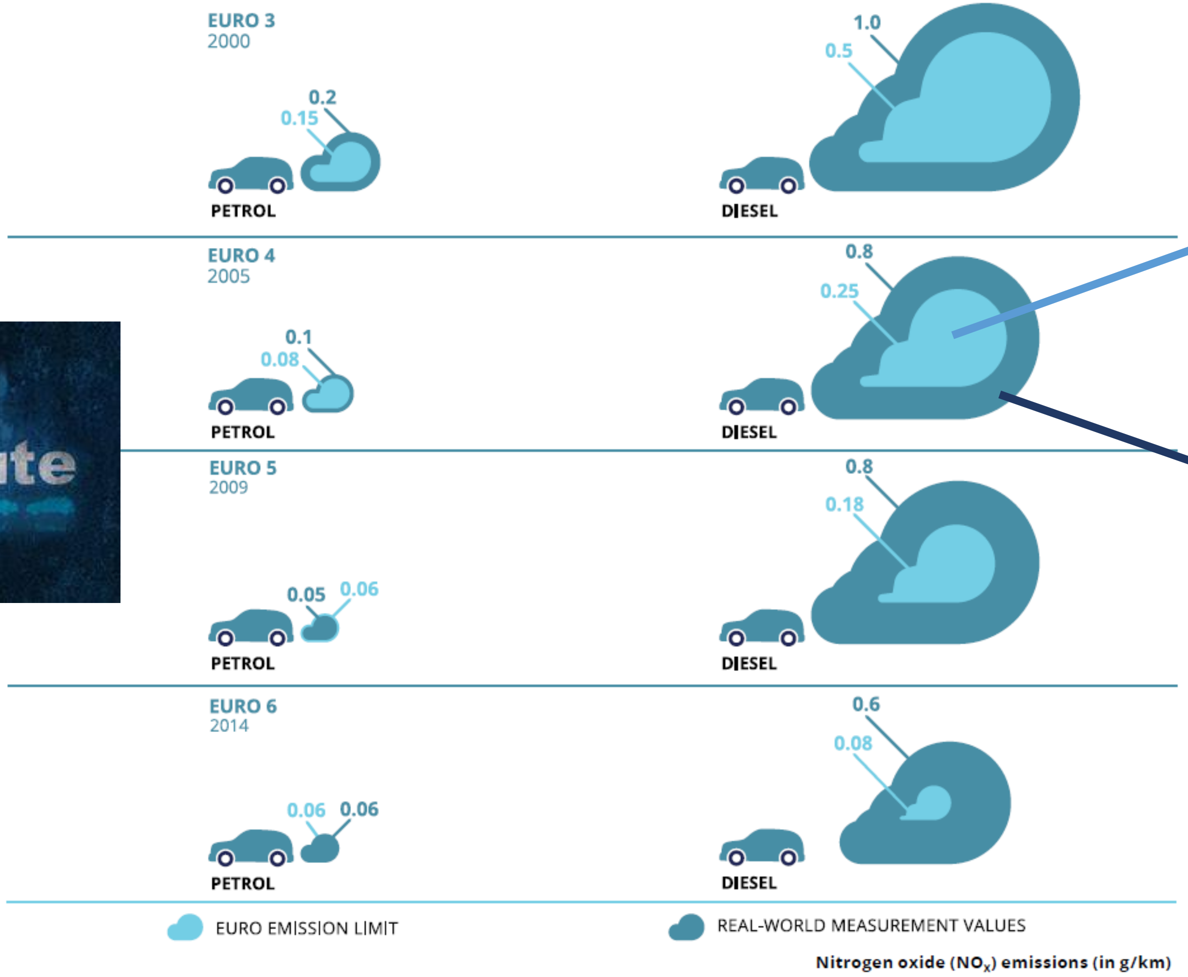
Air Pollution and Health Effects Pyramid



Vehicle emissions and Euro emission standards

Source: EEA, ”Air Quality in Europe - 2016 Report”

Comparison of NO_2 standards and emissions for different Euro classes

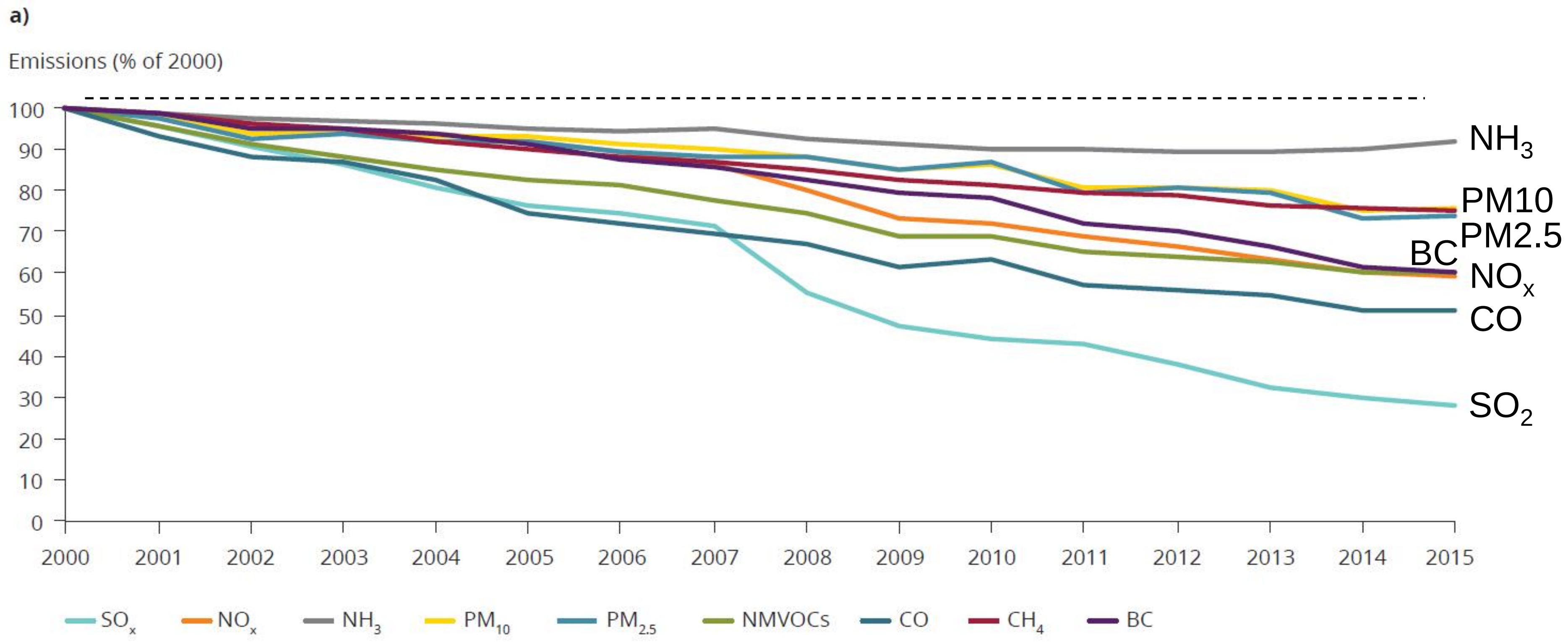


Euro emission limit

Real-world observed values

Development in EU-28 emissions (relative 2000)

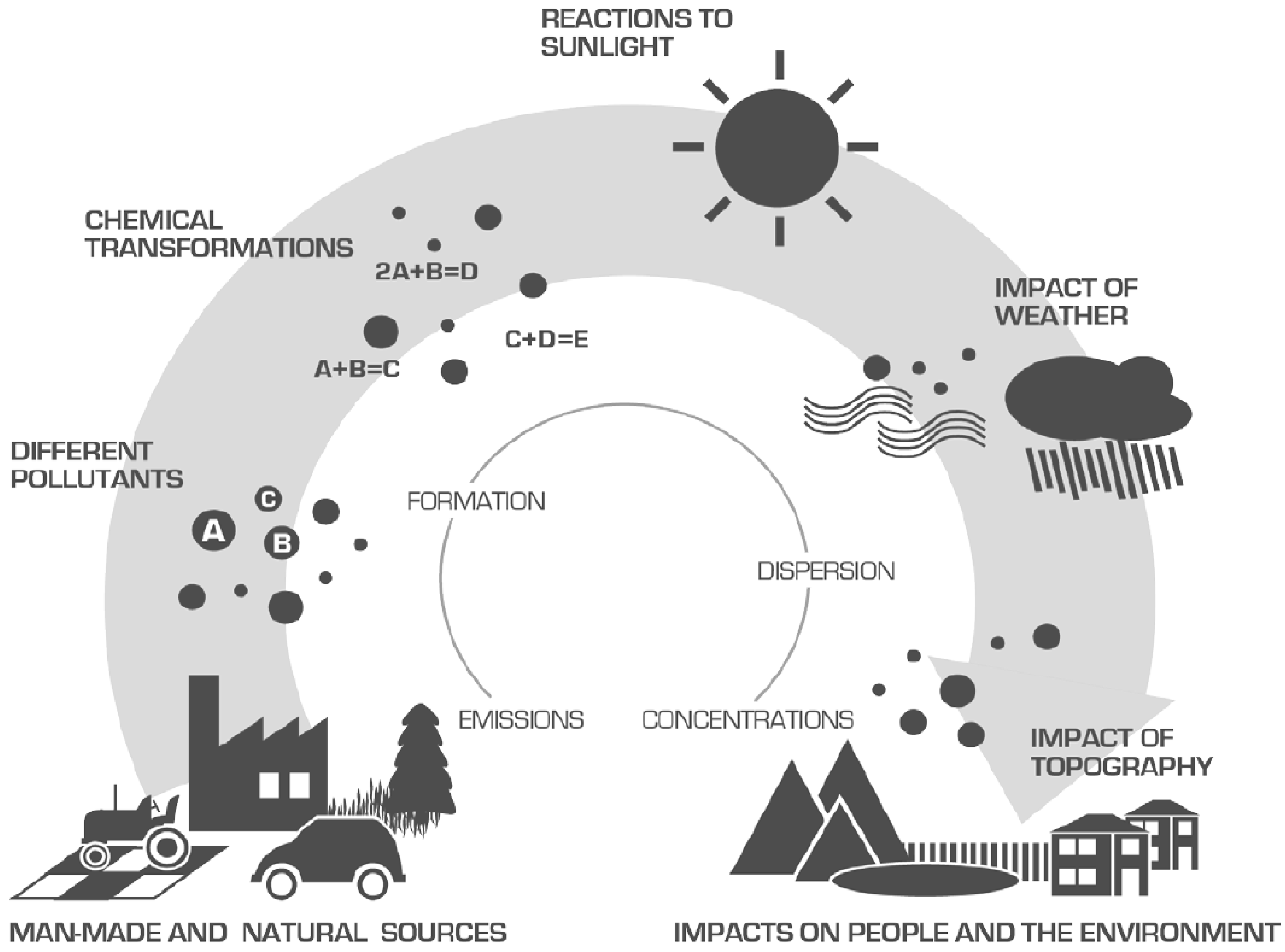
Figure 2.1 **Development in EU-28 emissions, 2000-2015 (% of 2000 levels): ([a]) SO_X, NO_X, NH_3, PM_{10}, $PM_{2.5}$, NMVOCs, CO, CH_4 and BC;**



Reducing emissions -
Reducing effects!

European Environment Agency

Reductions in emissions are not linear to reductions in concentrations, exposure and health effects!

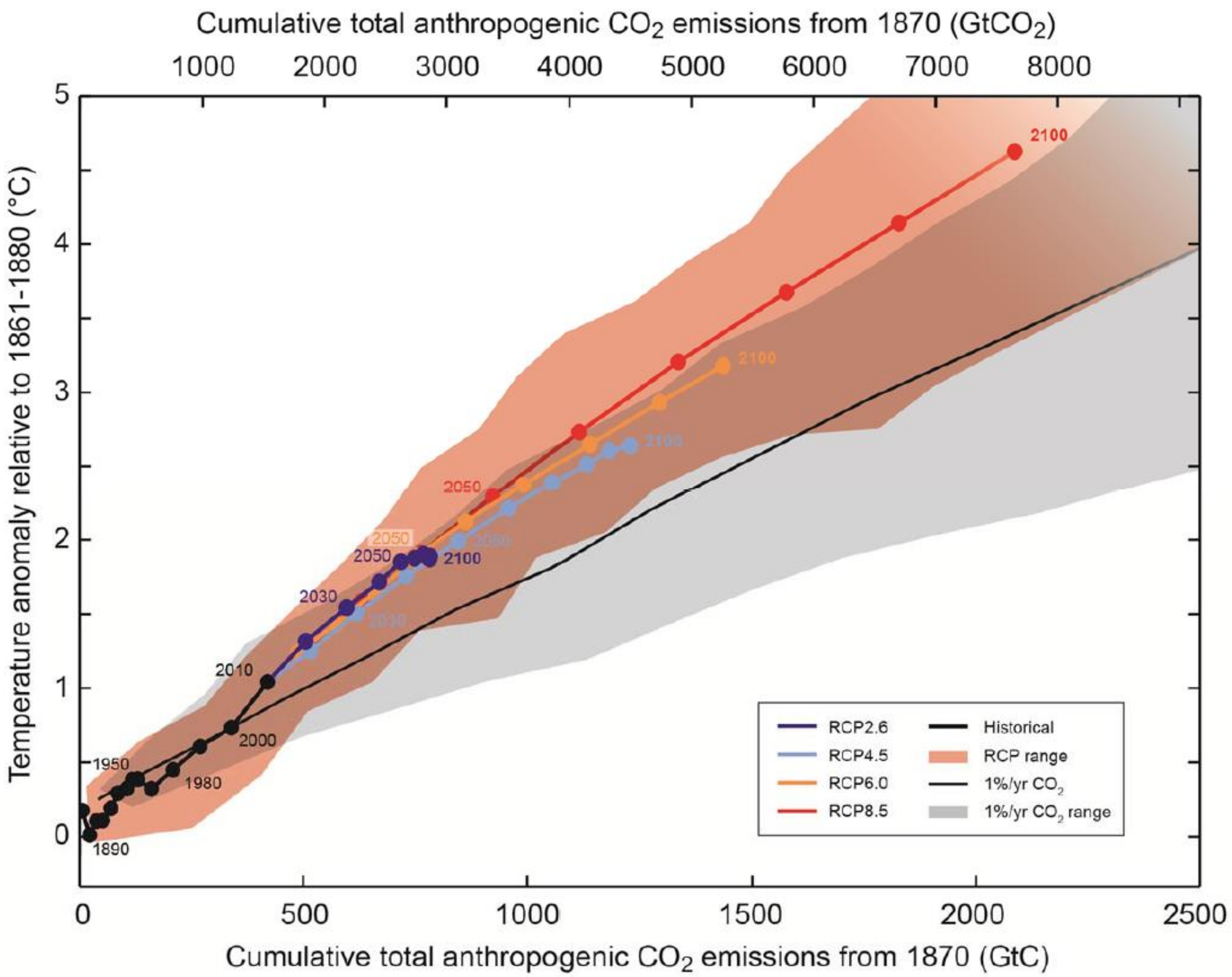


Riverside, California (1985)

Photochemical SMOG

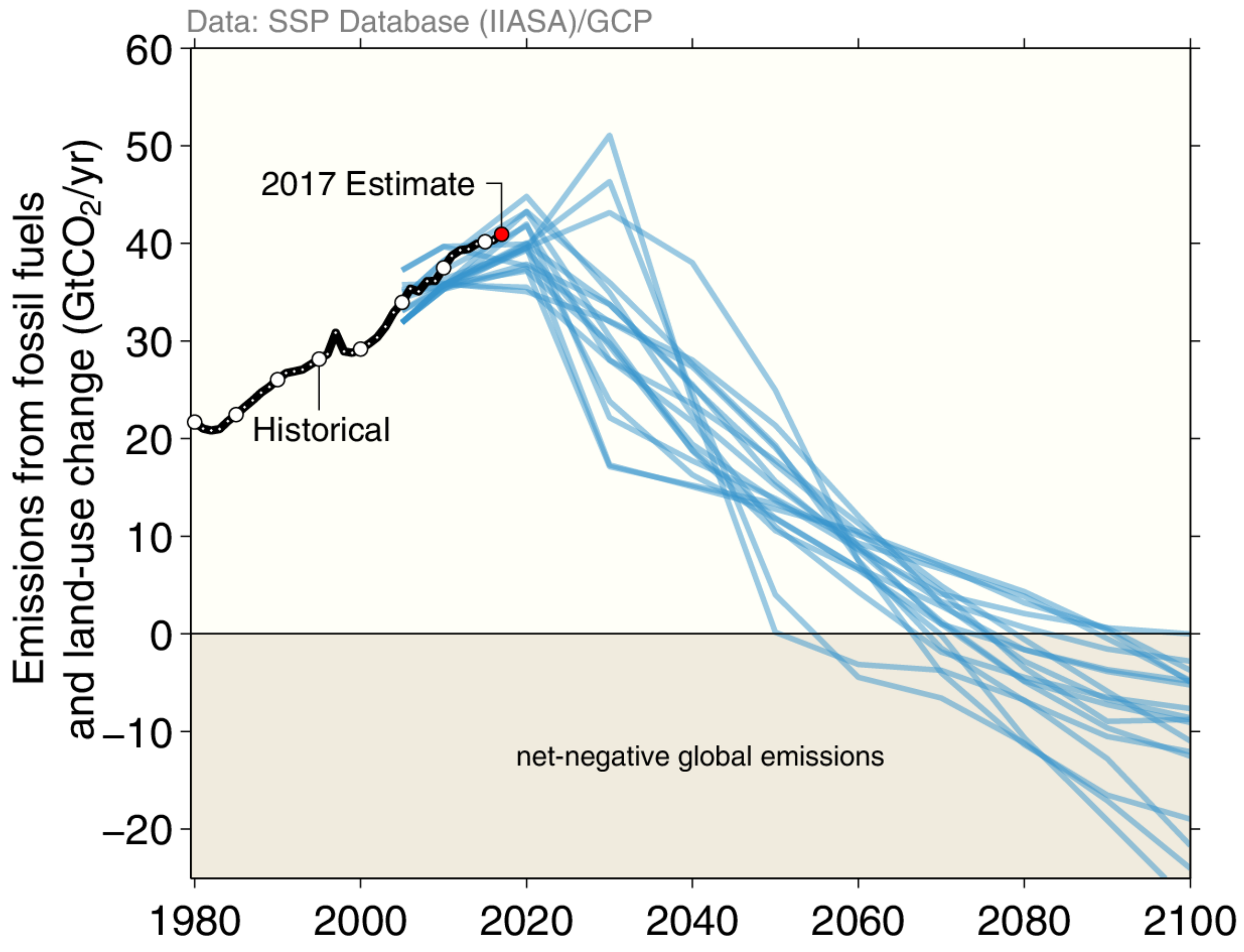

Ozone
Particles
Toxic substances e.g. PAH
PHOTOCHEMICAL SMOG
Nitrogen oxides
Hydrocarbons/organics
Sunlight

Cumulative CO_2 emissions determine global temperature change



Pathways that avoid 2°C of warming

According to the Shared Socioeconomic Pathways (SSP) that avoid 2°C of warming, global CO_2 emissions need to decline rapidly and cross zero emissions after 2050



Source: Riahi et al. 2016; IIASA SSP Database; Global Carbon Budget 2017

SUSTAINABLE DEVELOPMENT GOALS

17 GOALS TO TRANSFORM OUR WORLD

THE GLOBAL GOALS

For Sustainable Development

http://www.un.org/sustainabledevelopment/

The 16 environmental quality objectives

Reduced Climate Impact

Clean Air

Natural Acidification Only

A Non-Toxic Environment

A Protective Ozone Layer

A Safe Radiation Environment

Zero Eutrophication

Flourishing Lakes and Streams

Good-Quality Groundwater

A Balanced Marine Environment...

Thriving Wetlands

Sustainable Forests

A Varied Agricultural Landscape

A Magnificent Mountain Landscape

A Good Built Environment

A Rich Diversity of Plant and Animal Life

http://www.naturvardsverket.se/Miljoarbete-i-samhallet/Sveriges-miljomal/

Will the environmental quality objectives be achieved?

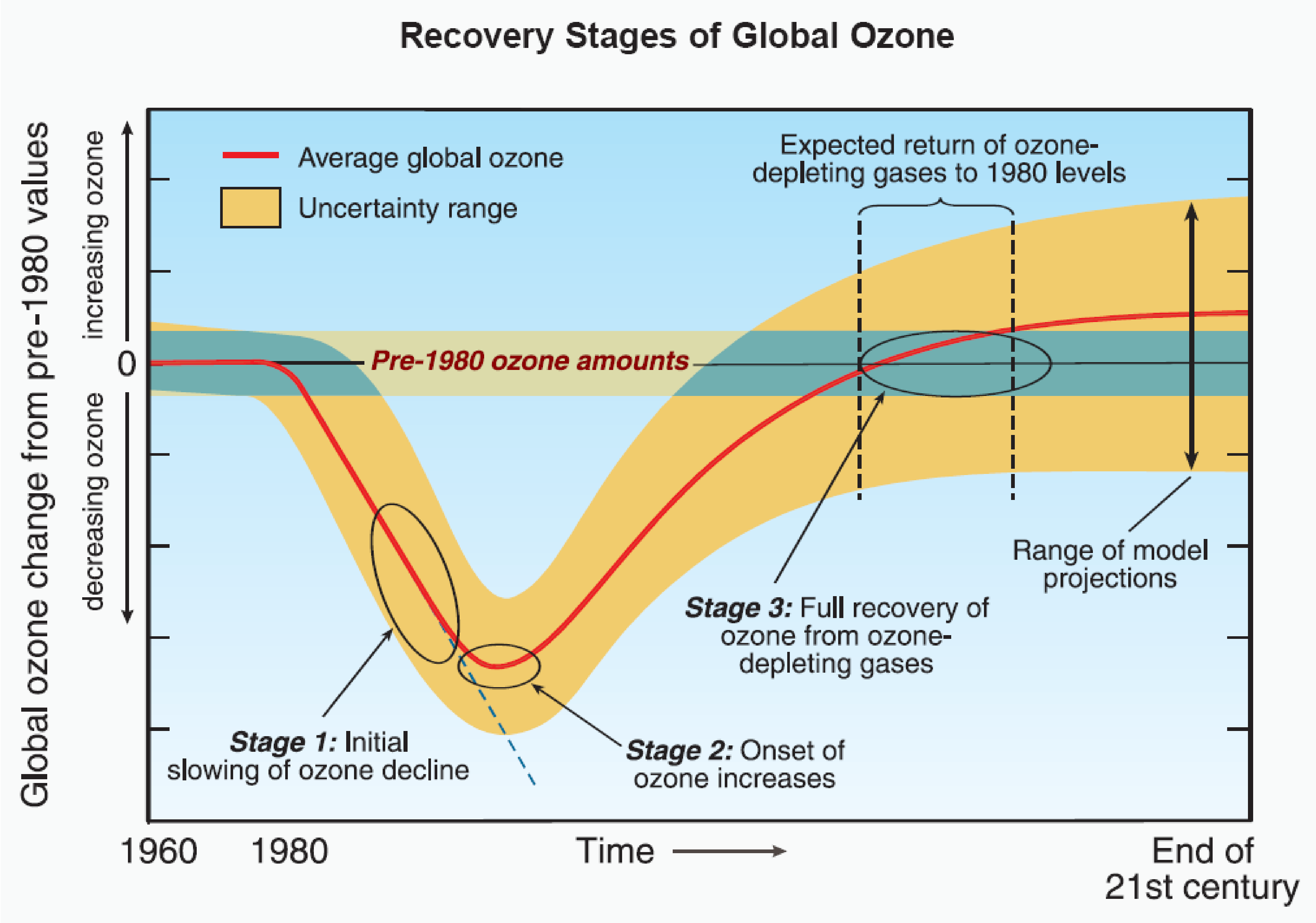
http://miljomal.nu/

OBJECTIVE	Forecast for 2020	Trend
1. Reduced Climate Impact*	☹	↘
2. Clean Air	☹	→
3. Natural Acidification Only	☹	↗
4. A Non-Toxic Environment	☹	→
5. A Protective Ozone Layer	☺	↗
6. A Safe Radiation Environment	😐	→
7. Zero Eutrophication	☹	→
8. Flourishing Lakes and Streams	😐	↗
9. Good-Quality Groundwater	😐	→
10. A Balanced Marine Environment, Flourishing Coastal Areas and Archipelagos	☹	→
11. Thriving Wetlands	😐	↗
12. Sustainable Forests	☹	→
13. A Varied Agricultural Landscape	😐	↗
14. A Magnificent Mountain Landscape	😐	↗
15. A Good Built Environment	☹	→
16. A Rich Diversity of Plant and Animal Life	☹	→

* Target year 2050, as a first step

http://www.miljomal.se/Global/24_las_mer/rapporter/malansvariga_myndigheter/2017/au2017.pdf

Stratospheric ozone - Recovery



Rådhuset Malmö

(urban background roof-top measurements in down-town Malmö)

- Gases: NO, NO_2, SO_2, CO
- PM2.5, PM10

Malmö miljöförvaltning

Montoring Trailer, *Malmö Miljöförvaltning*

ACTRIS – Sweden

Aerosols, Clouds, Trace gases
Research Infrastructure

The new Hyltemossa site
near Lund (and Vavihill)

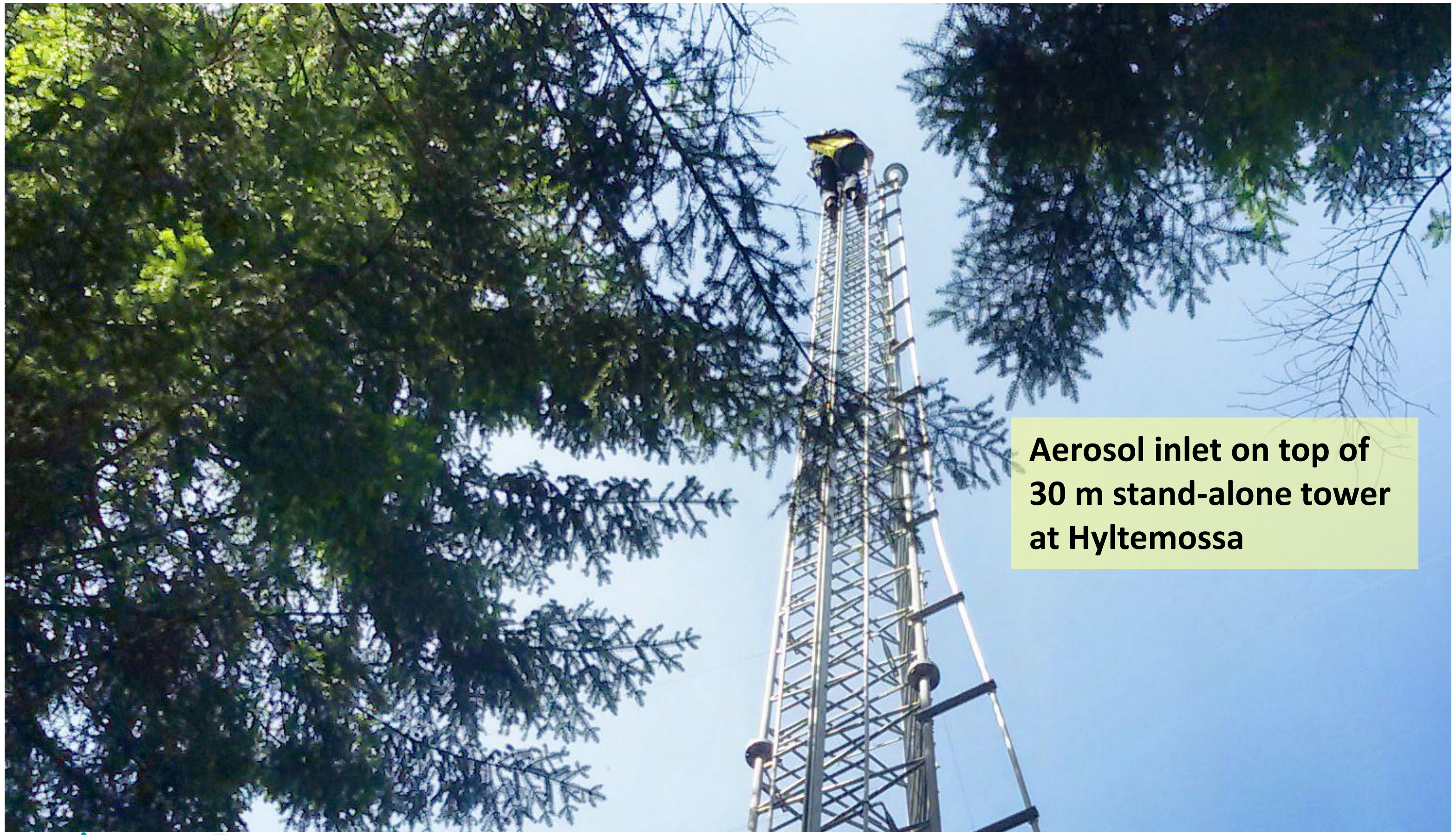

Hyltemossa 150 m high tower

icos integrated carbon observation system

A European infrastructure dedicated to high precision monitoring of greenhouse gas fluxes

ACTRIS

ACTRIS Sweden – Hyltemossa site



ACTRIS

Concentrations – Air Quality Standards

- **PM10** Big problem in many places - Unchanged
    - Long distance transport (regional pollution)
    - Locally generated wear particles from traffic (*slitagepartiklar*)
    - Local wood combustion (residential)

- **NO2** Exceedences in some locations – decreasing(?)
    - Local road traffic (exhaust)

- **Benzene** Probably no future problem(?) - decreasing
    - Road traffic
    - Local wood combustion (residential)

- **Benzo[a]pyrene** Limited problem(?) - decreasing
    - Road traffic (exhaust)
    - Wood combustion (residential)
    - Industry

- **Ozone** Potential worsening problem(?) – background increasing
    - NOx + VOC + sunshine
    - Regional problem, not local