Atmospheric Chemistry
Chemical kinetics

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Reaction rates

Bimolecular reaction

Reactants – A **and** B
Products – C **and** D

$$A + B \rightarrow C + D$$

$$-\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{d}{dt}[C] = \frac{d}{dt}[D] = k[A][B]$$

Reaction rate constant

Rate constant – k
Number density – $[X]$ **(unit: molecules/cm^3)**
$[A][B]$ **proportional to the collision frequency**

Chemical equlibrium

Reversible reactions $A + B \Leftrightarrow C + D$

$A + B \rightarrow C + D$ $\quad -\frac{d}{dt}[A] = -\frac{d}{dt}[B] = k_8[A][B]$

$C + D \rightarrow A + B$ $\quad -\frac{d}{dt}[C] = -\frac{d}{dt}[D] = k_9[C][D]$

Equlibrium when both reactions proceed at same rate:

$$k_8[A][B] = k_9[C][D]$$

We define an equlibrium constant K**:** $\quad K = \frac{k_8}{k_9} = \frac{[C][D]}{[A][B]}$

Photolysis –1

A photolytic reaction involves the breaking of a chemical bond by an incident photon.

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

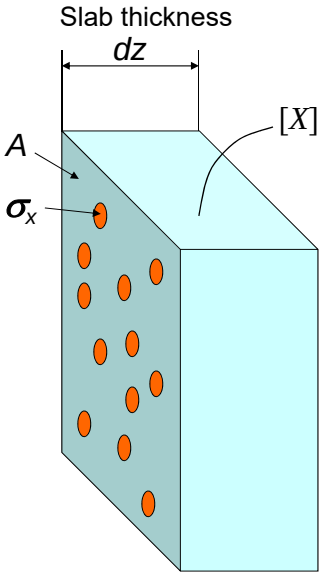
$$-\frac{d}{dt}[X] = \frac{d}{dt}[Y] = \frac{d}{dt}[Z] = k[X]$$

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

Concentration: $[X]$ **molecules/m³**
Volume dV = A · dz

Absorption cross section: σ_x
"Target area" of molecule X within which the photon is absorbed ($m^2 \cdot$ molecule $^{-1}$)

Probability for a photon to hit X**:**
(σ_x**/A)** · $[X]$ · **A · dz =** σ_x · $[X]$ · **dz**



Photolysis - 2

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

Actinic Flux (Ljusflöde) : I
Number of photons crossing the unit horizontal area per unit time (photons · m^{-2} · s^{-1})

Quantum Yield (Kvantutbyte) : q_x
Probability that absorption of a photon will cause photolysis of X (molecules · photon $^{-1}$)

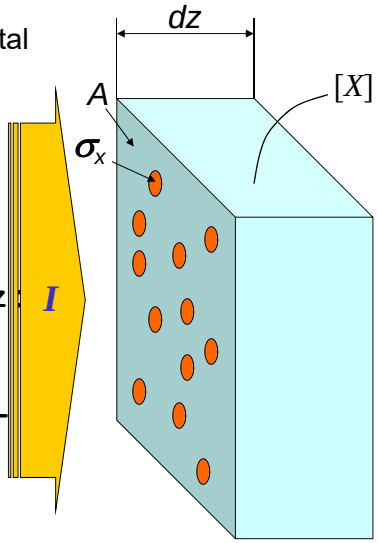
Number of molecules of X that are photolyzed per unit time in the slab dz :

$$I \cdot q_x \cdot \sigma_x \cdot [X] \cdot dz$$

which divided by the number of molecules X in the slab dz ($[X] \cdot dz$) gives :

Photolysis rate constant k :

$$k = q_x \cdot \sigma_x \cdot I$$ (s^{-1}, 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) →
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 + $h\nu$ → 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 ($h\nu$).

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 + *hv*	**→ *radical + radical´***	***(photolysis initiation)***
radical + radical´	**→ radical´´+ radical´´´**	**(propagation)**
radical + non-radical	**→ radical´ + non-radical´**	**(propagation)**
O1D, or O(3P) + non-radical	**→ radical+radical´**	**(propagation)**
radical + radical´ + M	**→ non-radical + M**	**(termination)**

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.

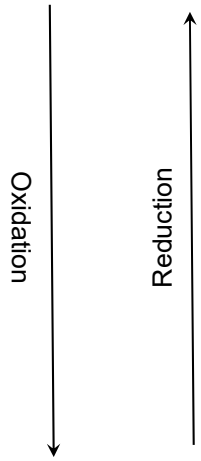
Shared electrons are assigned completely to the atom that has the stronger attraction for electrons

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.

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



Introduction to Atmospheric Chemistry and Air Pollution

FKFF01 vt-2017

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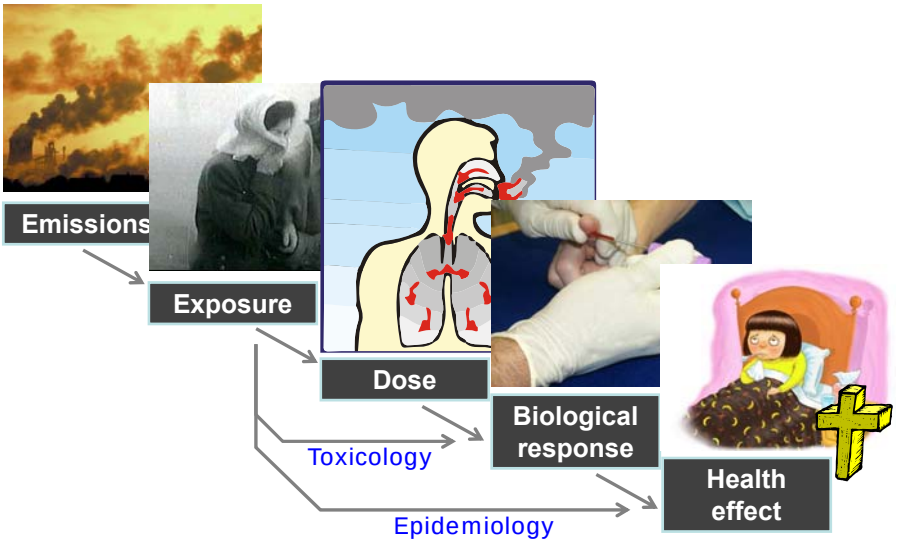
Health Effects of Air Pollution

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



Recent EEA reports on Air Quality

European Environment Agency
(http://www.eea.europa.eu/)

http://www.eea.europa.eu/publications/air-quality-in-europe-2016

European Environment Agency

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

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

The EEA recently estimated (EEA, 2016) that

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

PM2.5 → **436 000 premature deaths annually**

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

NO_2 → **68 000 premature deaths per year**
O_3 → **16 000 premature deaths per year**

European Environment Agency

http://www.eea.europa.eu/publications/air-quality-in-europe-2016

Health Effects of Air Pollution in Sweden

Sweden:

The total number of premature deaths can be estimated to approximately

5 500 per year **(EEA: 3 180)**

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

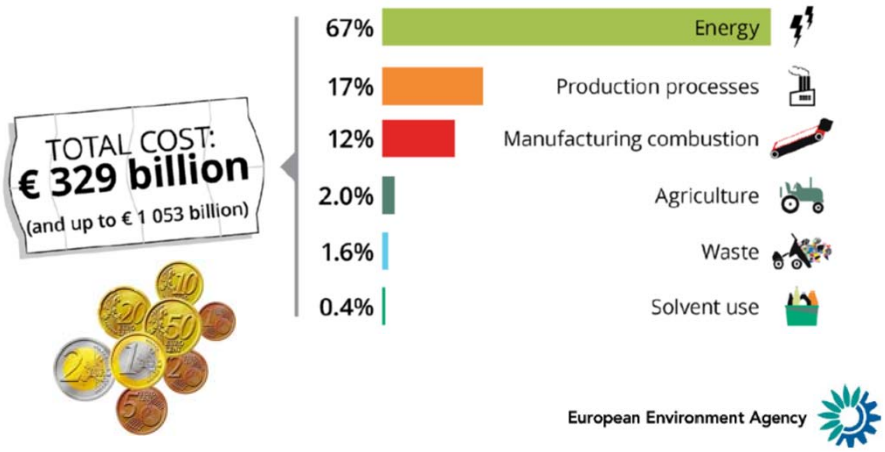
Using the division between PM sources and NO_2 as an indicator of traffic combustion the total socio-economic cost (2010) would be

approximately 42 billion SEK

Source: Quantification of population exposure to NO2, PM2.5 and PM10 and estimated health impacts in Sweden 2010, Gustafsson, mfl, IVL Report B 2197, Dec 2014

Health Damage Costs by the Industrial Sector in Europe 2008-2012

Source: "Costs of air pollution from European industrial facilities 2008–2012 — An updated assessment", EEA Technical report No 20/2014



http://www.eea.europa.eu/publications/costs-of-air-pollution-2008-2012

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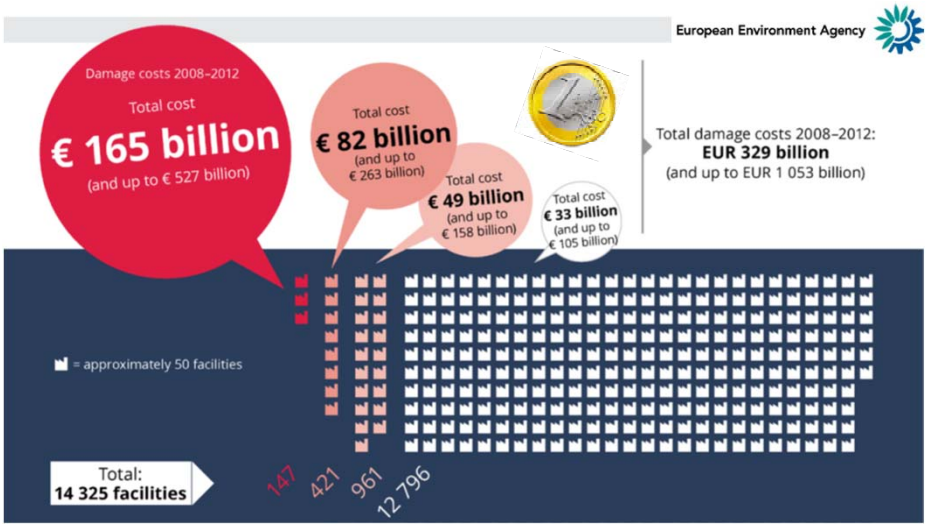
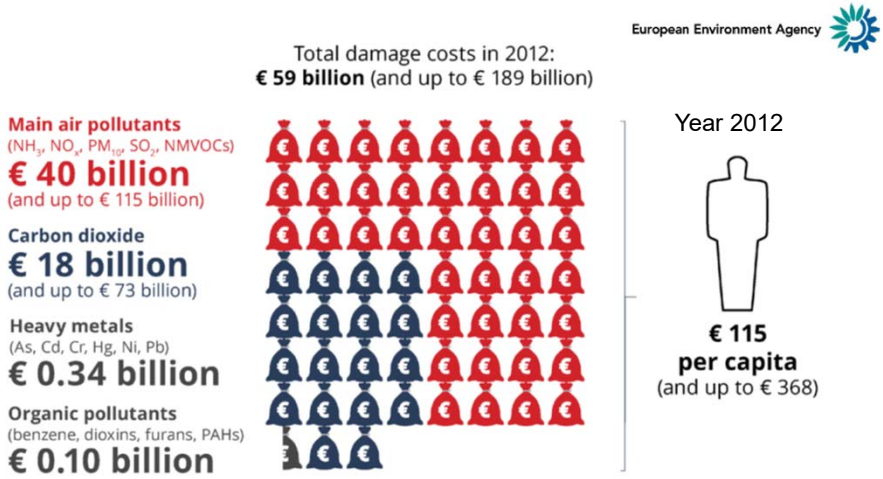


http://www.eea.europa.eu/publications/costs-of-air-pollution-2008-2012

Health Damage Costs by the Industrial Sector in Europe – Year 2012

"Costs of air pollution from European industrial facilities 2008–2012 — An updated assessment", EEA Technical report No 20/2014



http://www.eea.europa.eu/publications/costs-of-air-pollution-2008-2012

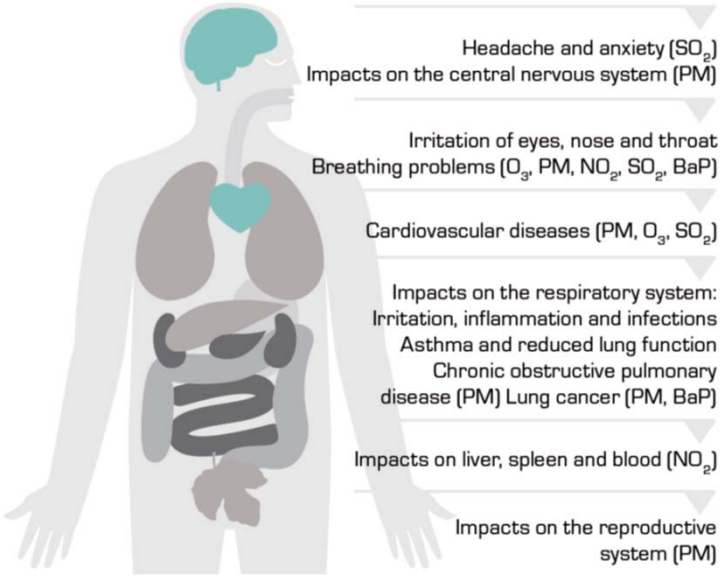
Damage cost of air pollution in Europe (2010) and policy response

Source: " EC, 2013: Impact assessment for new policy package to clean up Europe's air"

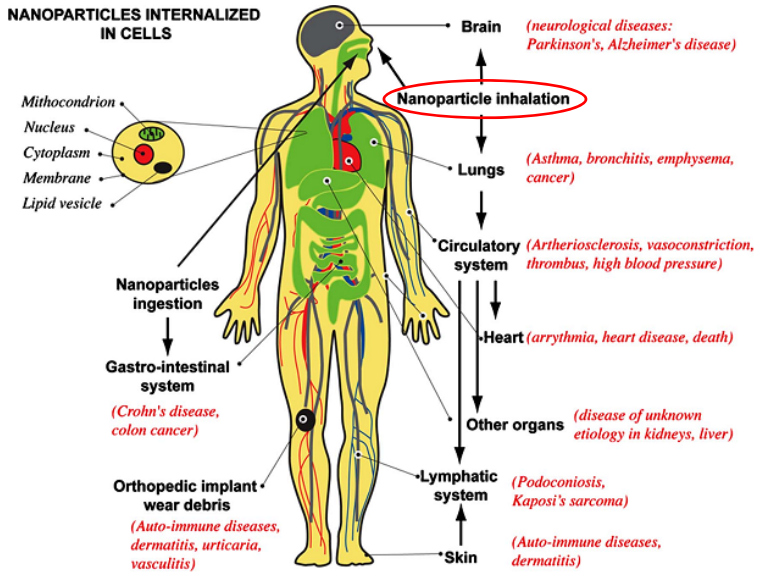
- Damage cost of mortality – at least EUR 330 billion
- Direct economic damage - EUR 15 billion from workdays lost
- Direct economic damage - EUR 4 billion in healthcare cost
- Direct economic damage - EUR 3 billion crop yield loss

European Environment Agency

Air Pollution and Health Effects

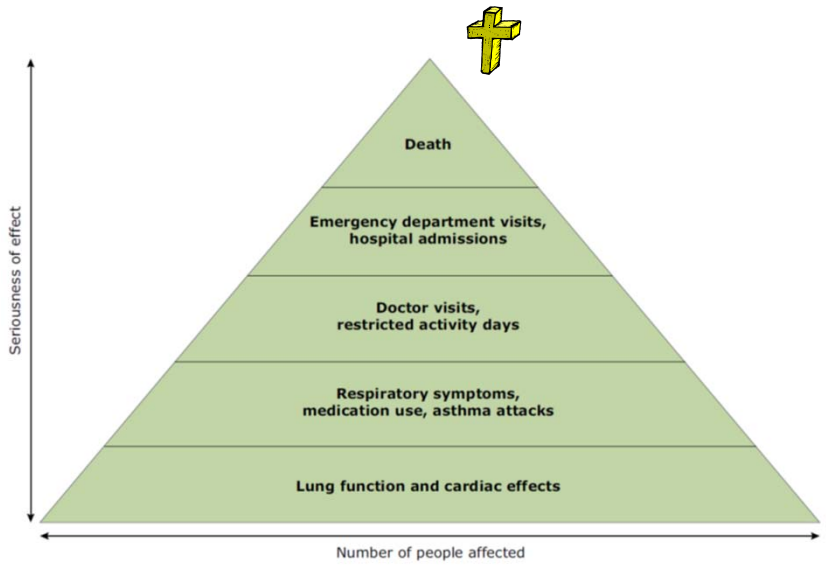


Pathways of exposure to nanoparticles, affected organs, and associated diseases from epidemiological, in vivo and in vitro studies.



Buzea, Pacheco, and Robbie: Nanomaterials and nanoparticles: Sources and toxicity, Biointerphases (2007)

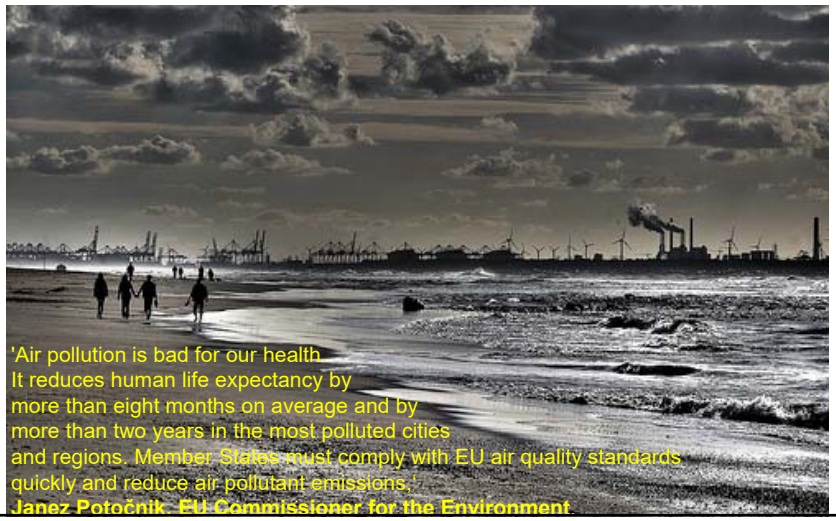
Air Pollution and Health Effects Pyramid



http://www.eea.europa.eu/highlights/2013-kicking-off-the-2018year

2013: The 'Year of Air' in the EU

Clean air was the focus of EU environmental policy discussions throughout 2013, the Year of Air.



Air Pollution and EU Policy Response

Legislation in Europe regulating emissions and ambient concentrations of air pollutants

Policies \ Pollutants		PM	O_3	NO_2 NO_x NH_3	SO_2 SO_x	CO	Heavy metals	BaP PAHs	VOC
Directives regulating ambient air quality	2008/50/EC	PM	O_3	NO_2	SO_2	CO	Pb		Benzene
	2004/107/EC						As, Cd, Hg, Ni	BaP	
Directives regulating emissions of air pollutants	2001/81/EC	(a)	(b)	NO_x, NH_3	SO_2				NMVOC
	2010/75/EU	PM	(b)	NO_x, NH_3	SO_2	CO	Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V		VOC
	Euro standards on road vehicle emissions	PM	(b)	NO_x		CO			VOC, NMVOC
	94/63/EC	(a)	(b)						VOC
	2009/126/EC	(a)	(b)						VOC
	1999/13/EC	(a)	(b)						VOC
	91/676/EEC			NH_3					
Directives regulating fuel quality	1999/32/EC	(a)			S				
	2003/17/EC	(a)	(b)		S		Pb	PAHs	Benzene, VOC
International conventions	MARPOL 73/78	PM	(b)	NO_x	SO_x				VOC
	LRTAP	PM (a)	(b)	NO_x, NH_3	SO_2	CO	Cd, Hg, Pb	BaP	NMVOC

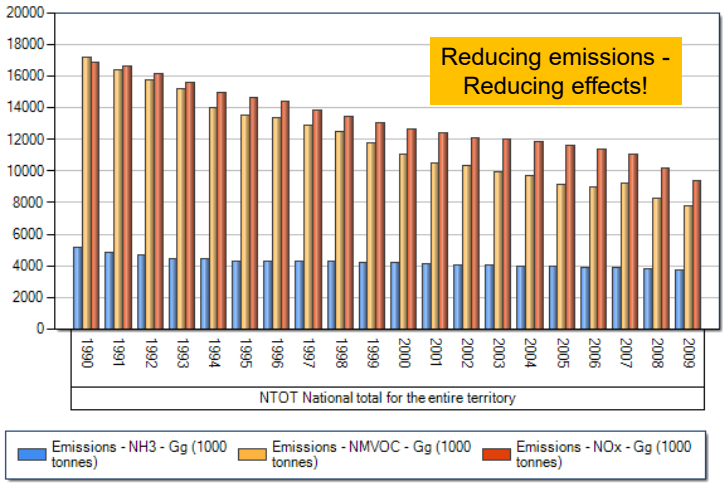
Note: (a) Directives and conventions limiting emissions of PM precursors, such as SO_2, NO_x, NH_3 and VOC, indirectly aim to reduce particulate matter ambient air concentrations.

(b) Directives and conventions limiting emissions of O_3 precursors, such as NO_x, VOC and CO, indirectly aim to reduce troposphere O_3 concentrations.

European Environment Agency

Total Emissions in EU Countries 1990-2009

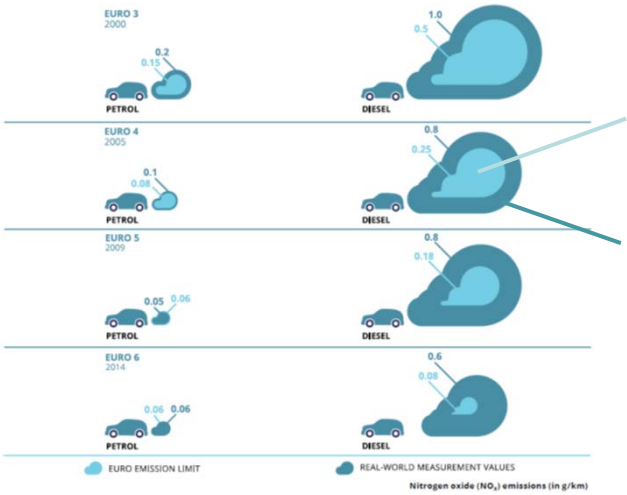
Air pollutant emissions data viewer (LRTAP Convention)



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

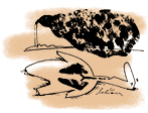
Real-world observed values

More information from an NGO

AirClim
Air Pollution & Climate Secretariat

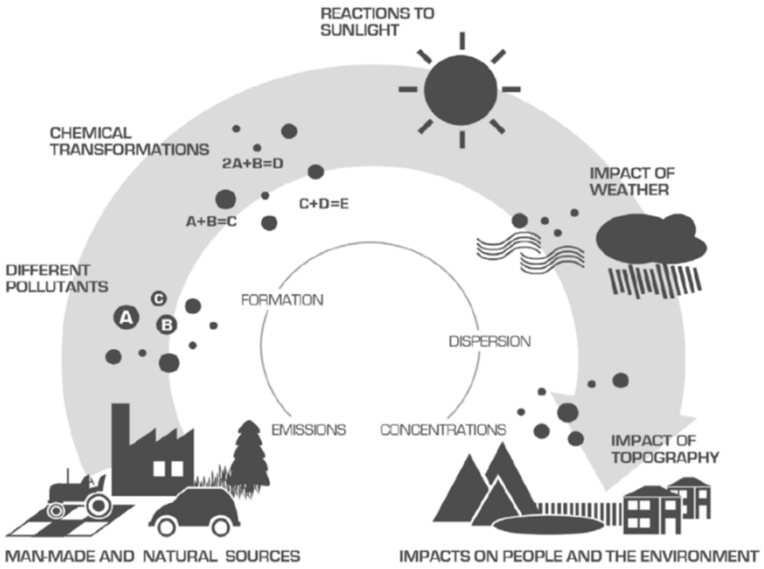
http://www.airclim.org/

Air pollution **Climate Change** **Policy initiatives**

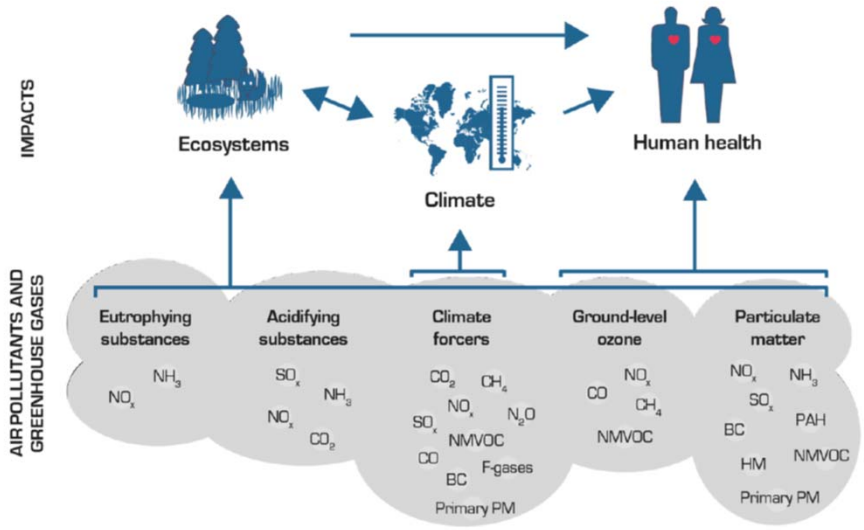


http://www.airclim.org/subscribe-acid-news

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



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



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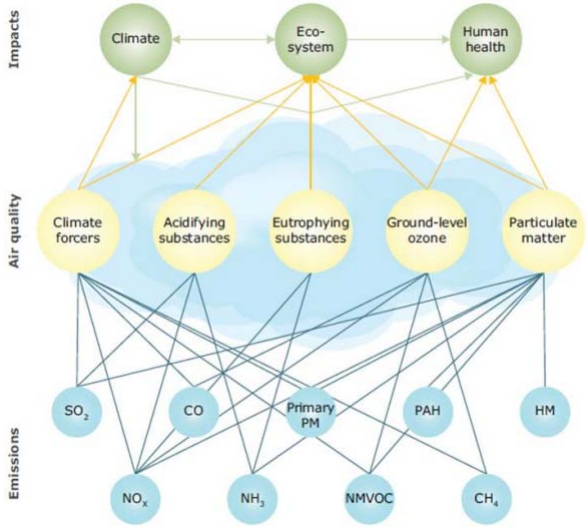


Air quality in Europe — 2011 report, European Environmental Agency
http://www.eea.europa.eu/publications/air-quality-in-europe-2011

Riverside, California (1985)

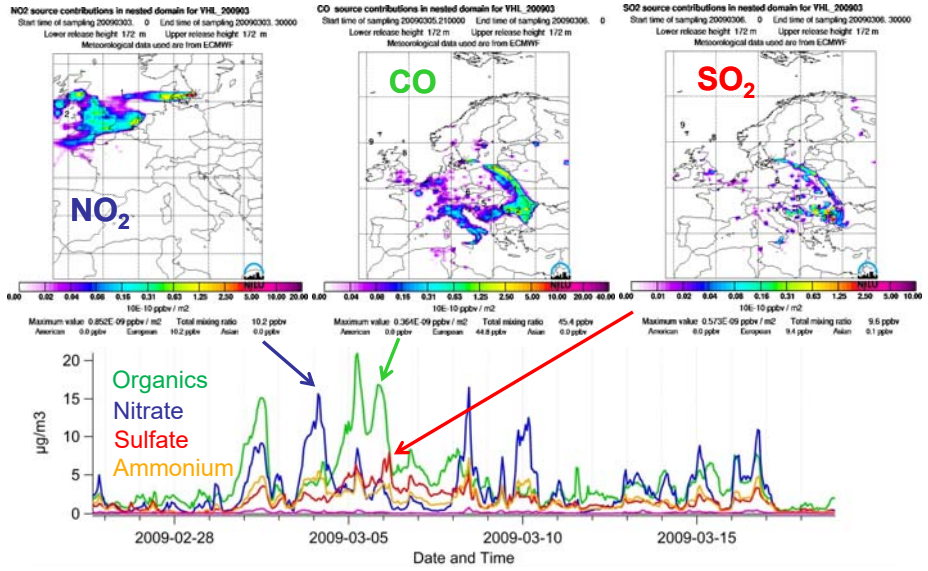
Photochemical SMOG

Nitrogen oxides
Hydrocarbons/organics
Sunlight

PHOTOCHEMICAL SMOG

Ozone
Particles
Toxic substances e.g. PAN

Aerosol measurements at Vavihill – Source regions

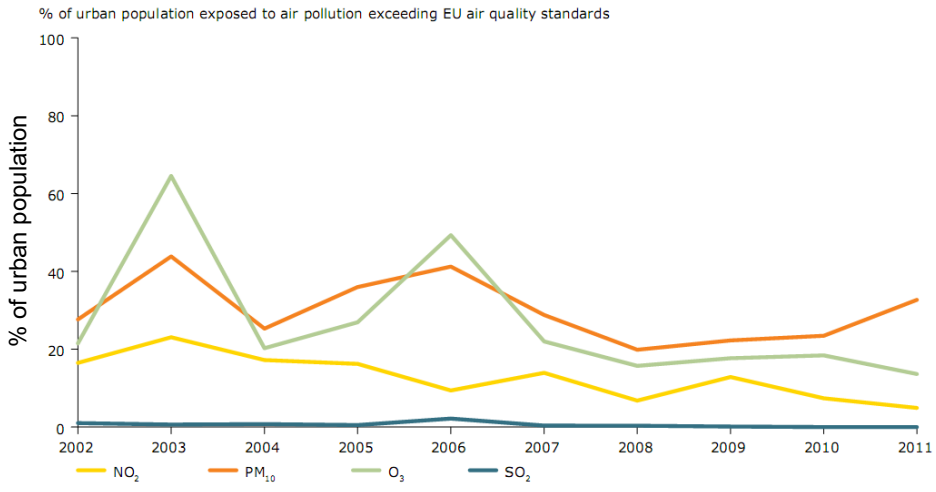


Measured with an Aerosol Mass Spectrometer

FLEXPART source region calculations: http://transport.nilu.no/flexpart-projects?stn=VHL

Percentage of the EU urban population exposed to air pollution exceeding **EU air quality standards**

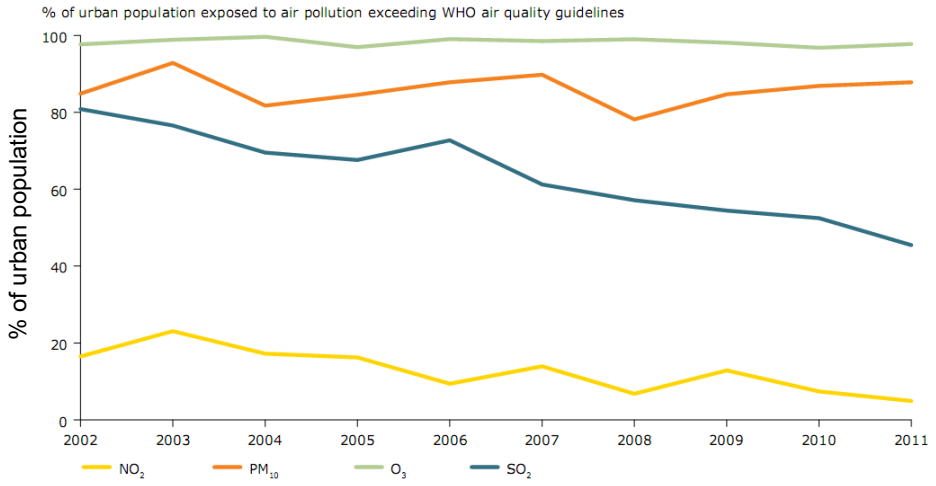
Source: EEA, "Air Quality in Europe 2013"



www.eea.europa.eu/publications/air-quality-in-europe-2013

Percentage of the EU urban population exposed to air pollution exceeding **WHO air quality guidelines**

Source: EEA, "Air Quality in Europe 2013"



www.eea.europa.eu/publications/air-quality-in-europe-2013

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

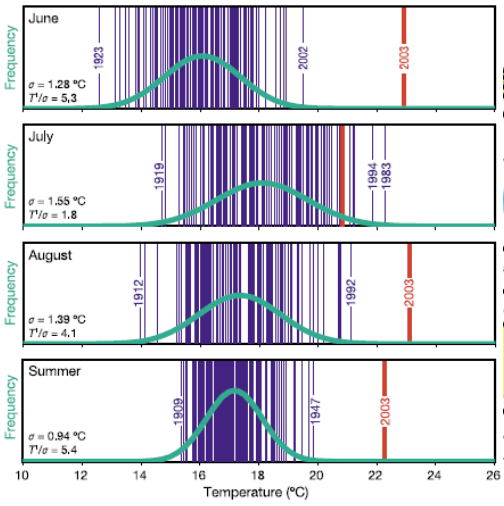
9 out of 10
exposed to exceedances of the WHO guideline value

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

Heat wave in Central Europe summer 2003

Switzerland

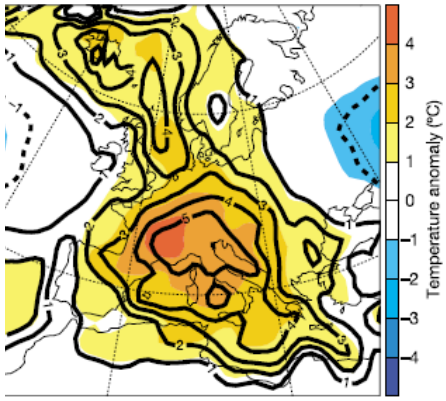
Summer temperatures (monthly averages) 1864–2003



Deviations from average temperatures 1961-90 (June, July, August)

Colour scale: Temperature dev. in oC.

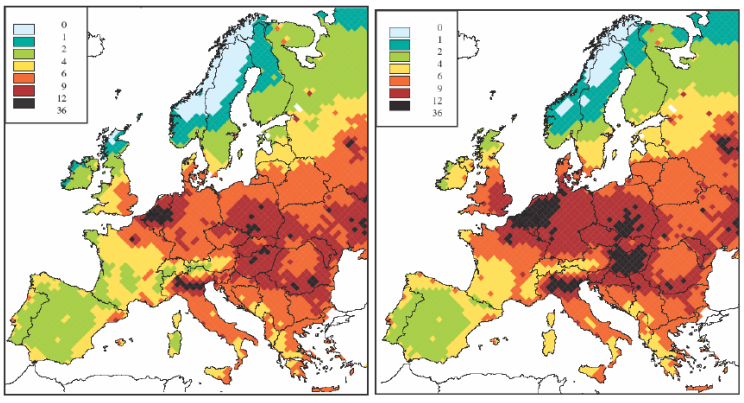
Contoures: Standard deviaitons



Baseline Scenarios for the CAFE Programme

Final Report, February 2005

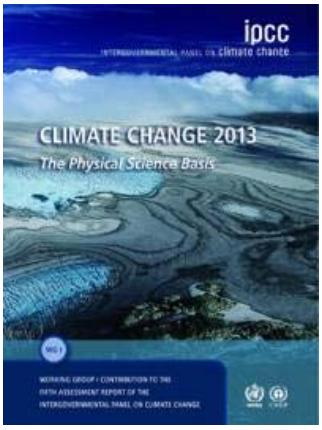
Meteorology 2000 Meteorology 2003



Loss in statistical life expectancy that can be attributed to the identified anthropogenic contributions to PM2.5 (in months), for the emissions of the year 2000.

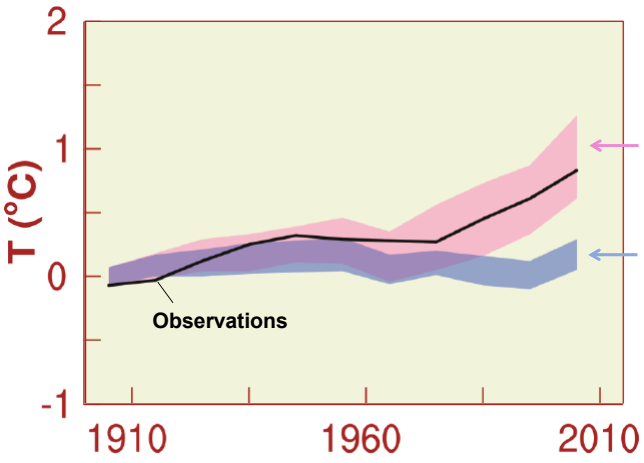
Main Messages
IPCC AR5 WG1 - 27 Sept 2013

- Climate (continues) to change
- It is our fault
- To mitigate climate change, we need forceful actions – and fast!



http://www.naturvardsverket.se/Om-Naturvardsverket/Publikationer/ISBN/6500/978-91-620-6592-8/

Humans are the cause of climate change



After IPCC 2013, SPM. Approved 27 Sep 2013.

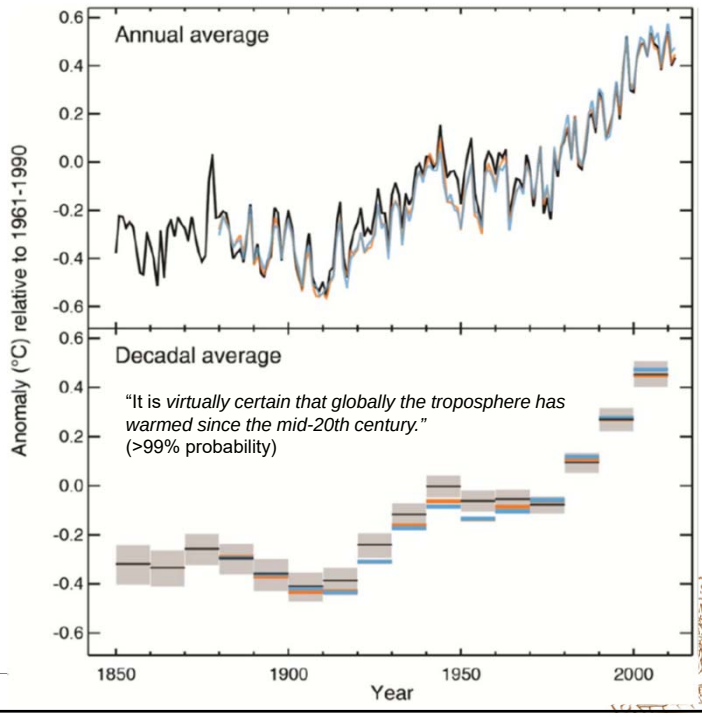
Planet Earth is warming

Global average

Surface temperature land and sea

Period: 1880–2012

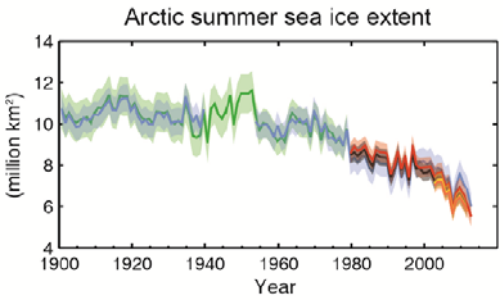
+0.85 ºC

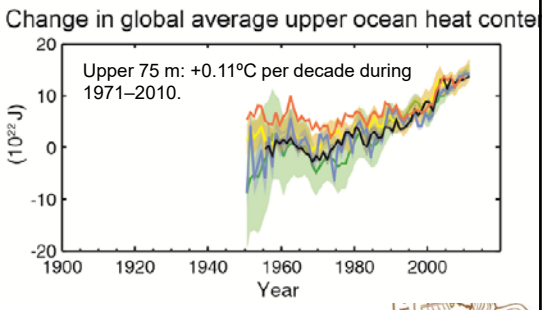


"It is *virtually certain that globally the troposphere has warmed since the mid-20th century.*" (>99% probability)

IPCC 2013, SPM

- …
- Decreasing Arctic sea ice
- Increasing ocean heat content
- Rising sea level
- Oceans acidify
- Shrinking land ices
- More weather extremes
- …





A constant supply of heat through the ocean surface at the rate of 1 W m^{-2} for 1 year would increase the ocean heat content by 1.1 x 10^{22} J.

- …
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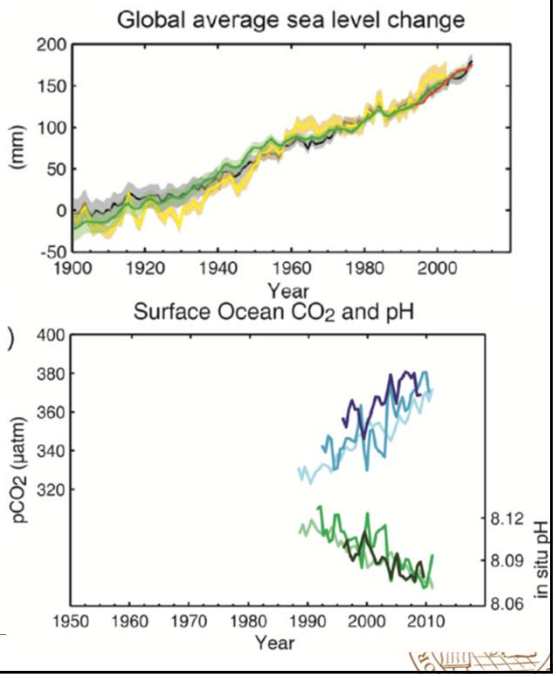

IPCC 2013, SPM

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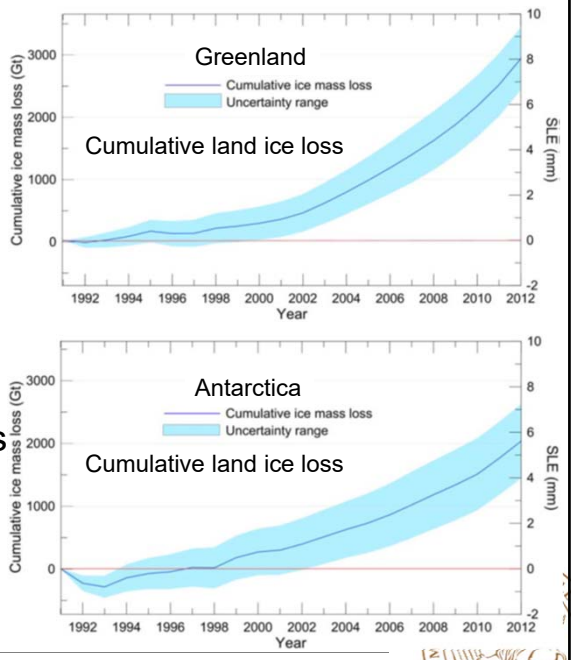
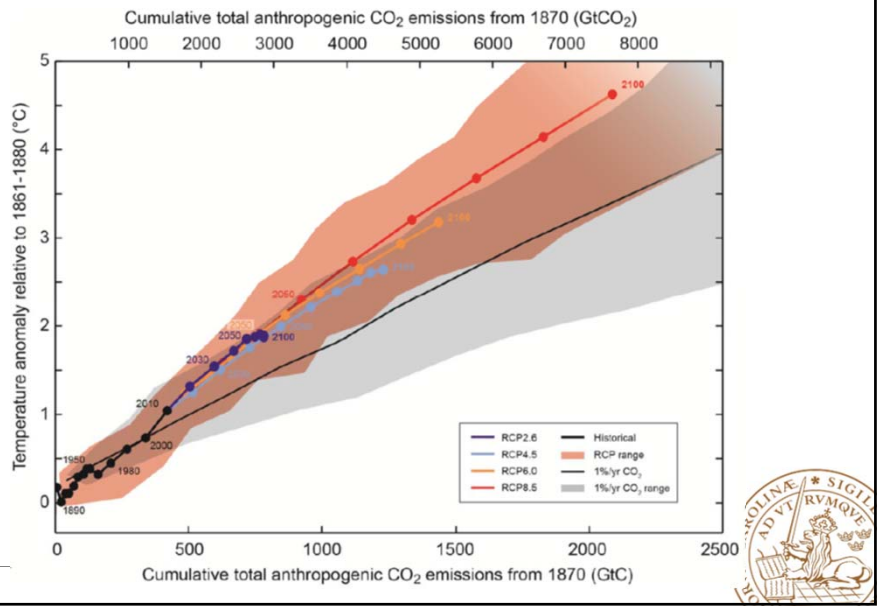
- …



IPCC 2013, SPM

Cumulative CO_2 emissions determine global temperature change



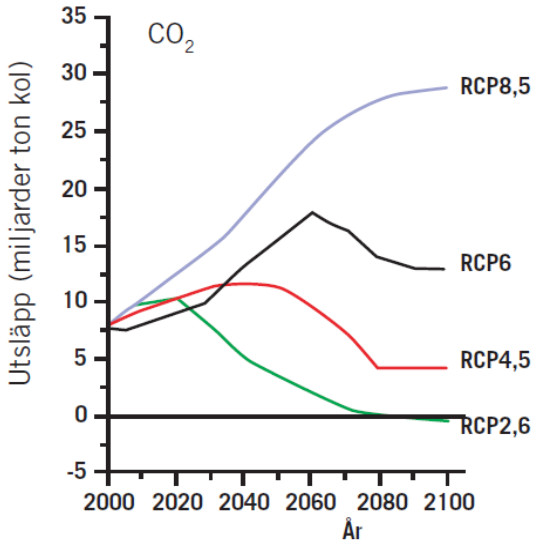
What matters are near the future CO_2 emissions

RCP2,6

RCP4,5

RCP6,0

RCP8,5



A Sustainable Society - Sweden 2020

Sweden's 16 environmental quality objectives describe a state of the environment that is sustainable in the long term.

The environmental quality objectives are intended to:

- promote human health
- safeguard biodiversity and the natural environment
- preserve the cultural environment and cultural heritage
- maintain long-term ecosystem productivity and
- ensure wise management of natural resources

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

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/

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

Will the environmental quality objectives be achieved?

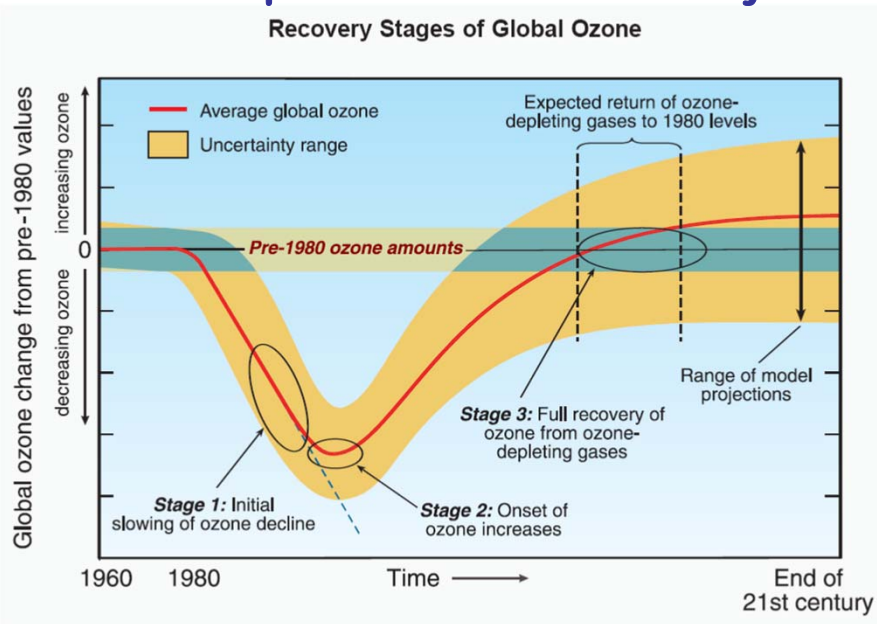
http://miljomal.nu/

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



Swedish Environmental Protection Agency on Environmental Quality Standards ***Miljökvalitetsnormer (MKN)***

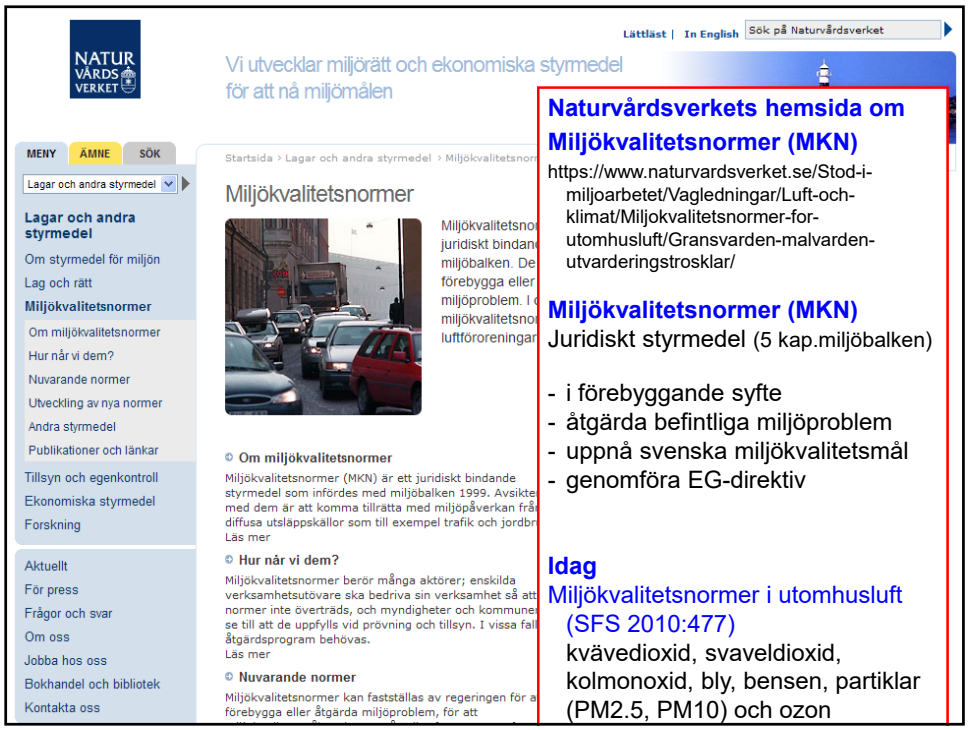
https://www.naturvardsverket.se/Stod-i-miljoarbetet/Vagledningar/Luft-och-klimat/Miljokvalitetsnormer-for-utomhusluft/Gransvarden-malvarden-utvarderingstrosklar/

Legally binding limits for an environmental status which may not be infringed, or is to be attained where possible, after a specified date. (Environ. Code, 1999)

Currently

Standards in outdoor air (SFS 2010:477)

NO_2, SO_2, CO, Pb, benzene, particles (PM2.5, PM10) and ozone



Naturvårdsverkets hemsida om Miljökvalitetsnormer (MKN)

https://www.naturvardsverket.se/Stod-i-miljoarbetet/Vagledningar/Luft-och-klimat/Miljokvalitetsnormer-for-utomhusluft/Gransvarden-malvarden-utvarderingstrosklar/

Miljökvalitetsnormer (MKN)

Juridiskt styrmedel (5 kap.miljöbalken)

- i förebyggande syfte
- åtgärda befintliga miljöproblem
- uppnå svenska miljökvalitetsmål
- genomföra EG-direktiv

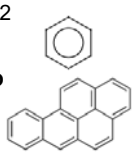
Idag

Miljökvalitetsnormer i utomhusluft (SFS 2010:477)

kvävedioxid, svaveldioxid, kolmonoxid, bly, bensen, partiklar (PM2.5, PM10) och ozon

Most important air pollutants from a health perspective

• Particles, PM_{10}	Standard since 2005
• Particles, $PM_{2.5}$	New standard 2015
• Ozone, O_3	New standard 2010
• Nitrogen dioxide, NO_2	Standard since 2006
• Benzene, C_6H_6	Standard since 2010
• Benzo[a]pyrene, BaP	New standard 2010
• PAH	New standard 2010
• Heavy metals (Cd, Pb, Cu, Hg, As, Cr)	2010 (Pb 2001)
• Voltile Organic Compounds, VOC	Emission ceiling objective
• Carbon monoxide, CO	Standard
• Sulphur dioxide, SO_2	Standard



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*

Substance	Concentration not to be exceeded (year of compliance)
Nitrogen oxides (NO2 and NOX)	
Hour (NO2) 1)	90 µg/m3 (2006)
24 h (NO2) 2)	60 µg/m3 (2006)
Year (NO2)	40 µg/m3 (2006)
Year (NOX, ecosystems)	30 µg/m3 (2001)
Sulphur dioxide (SO2)	
Hour 1)	200 µg/m3 (2001)
24 h 2)	100 µg/m3 (2001)
Year (ecosystems)	20 µg/m3 (2001)
Winter half-year (ecosystems)	20 µg/m3 (2001)
Carbon monoxide (CO)	
24 h 3)	10 mg/m3 (2005)
Lead	
Year	0,5 µg/m3 (2001)
Benzene	
Year	5 µg/m3 (2010)
Particulate matter (PM10)	
24 h 4)	50 µg/m3 (2005)
Year	40 µg/m3 (2005)
Ozone	
8 h mean 3)	120 µg/m3 (2010)
Summer half-year (Apr–Sep) 5)	18 000 AOT40 (2010), 6 000 AOT40 (2020)

PM2.5 (2015)
Year: 25 µg/m^3

Sweden

Air Quality Standards in force

1) To be exceeded not more than 175 times per year (98 percentile, hour)
2) To be exceeded not more than 7 times per year (98 percentile, 24-h)

3) Rolling 8 hour mean value

4) To be exceeded not more than 35 times per year (90 percentile, 24-h)

5) AOT 40 (expressed as µg/m3 x h) calculated as the sum of differences of hour-mean concentrations over 80 µg/m3 (=40 ppb) and 80 µg/m3 for values measured between 08–20 mean European time every day during the season 1 May to 31 July each year.

EU **Air pollution limit values and target values established for the protection of human health**

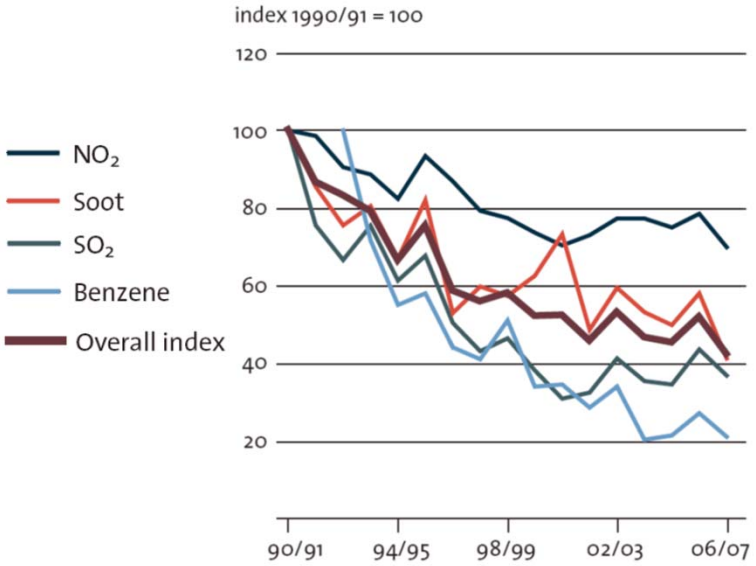
Compound	Limit value	Target value	Value		Entry into force
Particulate matter (PM_{10})	Annual average		40 µg/m³	PM2.5 (2015) Year: 25 µg/m^3	2005
	Daily average		50 µg/m³		
				May be exceeded up to 35 days a year	2005
Nitrogen dioxide (NO_2)	Annual average		40 µg/m³		2010
	Hourly average		200 µg/m³	May be exceeded up to 18 hours a year	2010
Ozone (O_3)		Eight-hour average	120 µg/m³	May be exceeded up to 25 days a year (1)	2010
Sulphur dioxide (SO_2)	Daily average		125 µg/m³	May be exceeded up to three days a year	2005
	Hourly average		350 µg/m³	May be exceeded up to 24 hours a year	2005
Carbon monoxide (CO)	Eight-hour average		10 mg/m³		2005
Lead (Pb)	Annual average		0.5 µg/m³		2005 (2)
Benzene (C_6H_6)	Annual average		5 µg/m³		2010
Arsenic (As)		Annual average	6 ng/m³		2013
Cadmium (Cd)		Annual average	5 ng/m³		2013
Nickel (Ni)		Annual average	20 ng/m³		2013
Benzo[a]pyrene		Annual average	1 ng/m³		2013

Note: (1) As an average over the three preceding years.
(2) 2010 in the immediate vicinity of specific industrial sources, notified to EC before 19 July 2001.

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 (climate-related)
  - Regional problem, not local

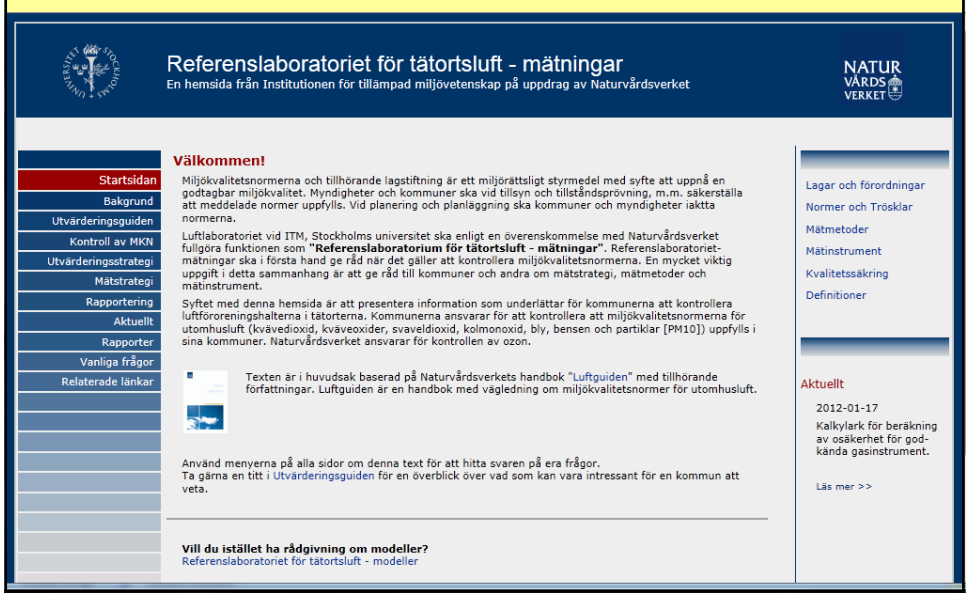
Air quality trend in Swedish towns and cities during the winter period (1990/1991–2006/2007)



http://www.naturvardsverket.se/Documents/publikationer/978-91-620-1273-1.pdf

Vägledning om mätmetoder för tätortluft

http://www.aces.su.se/reflab/



Introduction to Atmospheric Chemistry and Air Pollution

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