«Air Quality Alteration»

Environmental Engineering
Academic year:
2020-2021

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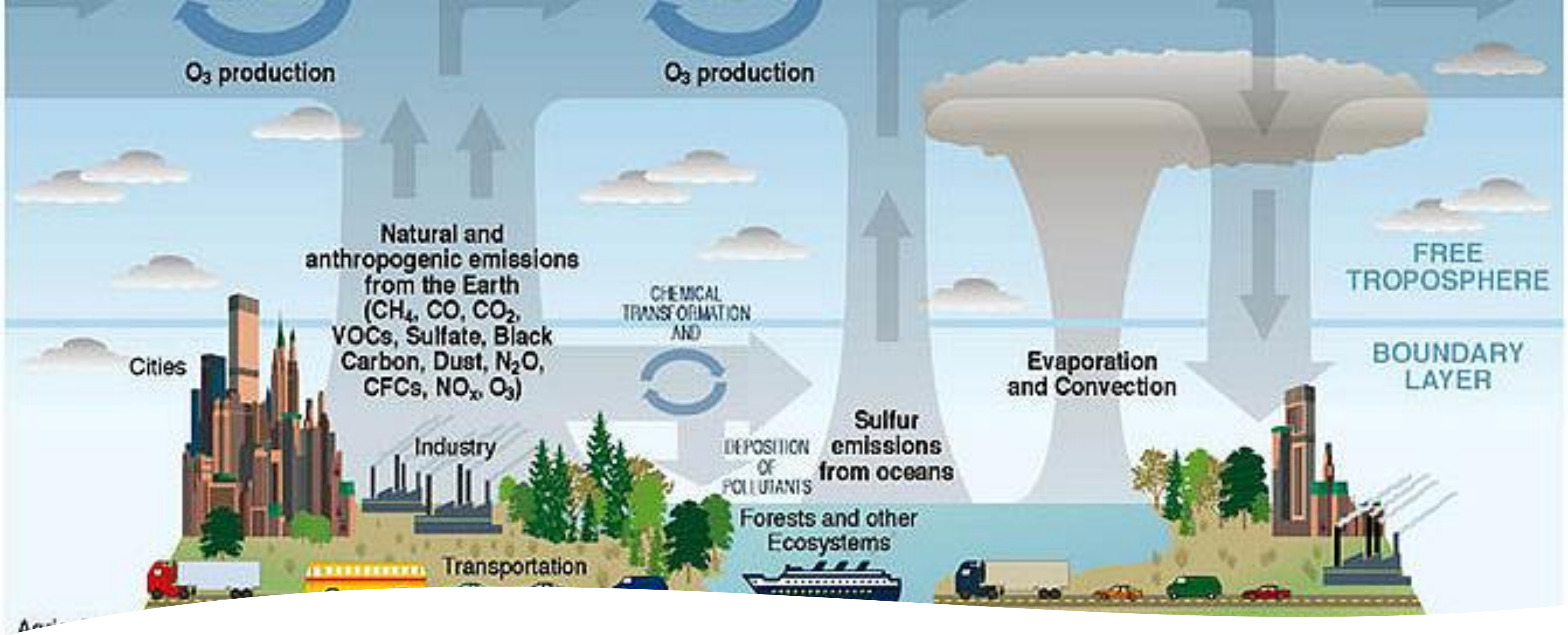


AIR QUALITY ALTERATIONS - Scale

- QUESTION:
- At what distance from the emission point a specific pollutant exerts its adverse affect?

AIR QUALITY ALTERATIONS - Scale

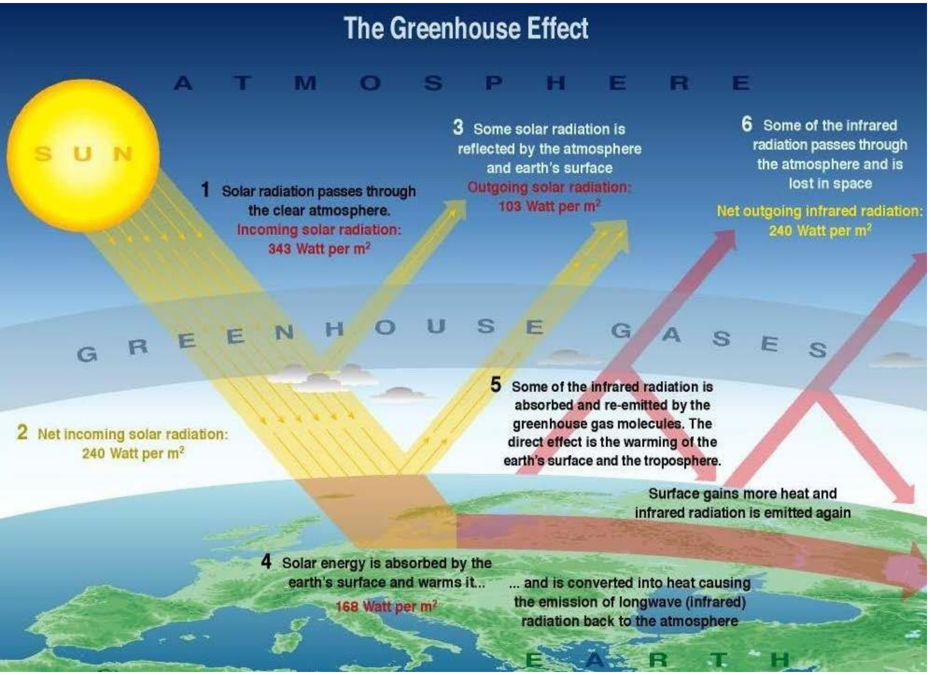
- **MICROSCALE - LOCAL SCALE** < 1 km, minutes
  - ground based sources, terrain effects (buildings, surface roughness)
  - urban vehicular traffic, lower height stationary emissions
- **LOCAL SCALE** < 10 km, hours
  - highest impact of primary pollutants
  - stack point sources, chemical/nuclear accidental releases
- **LOCAL - REGIONAL SCALE** 10-100 km, days
  - photochemical production of secondary pollutants (seasonal smog, fine particles)
  - extended residential and/or industrial areas, large stationary sources
- **REGIONAL - CONTINENTAL SCALE** ≥ 100 - 1000s km
  - non stationary, non homogeneous long range atmospheric transport, conversion and deposition
  - acid deposition, stratospheric ozone depletion, transboundary pollution clouds, trace toxic persistent pollutants
- **GLOBAL SCALE** whole atmosphere, years-centuries
  - global alterations in atmospheric composition
  - climate change

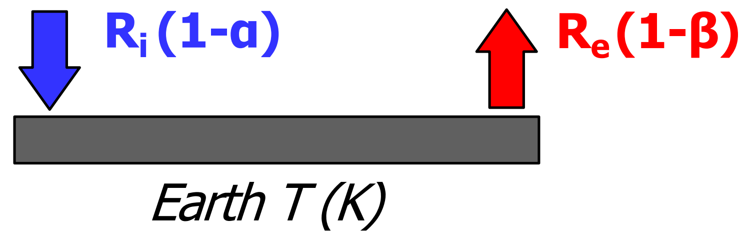
AIR QUALITY ALTERATIONS - Scale

Issue	Spatial scale			
	Global	Regional-continental	Local-regional	Local
Climate change	X			
Stratospheric O_3 depletion	X	X		
Tropospheric O_3		X		
Acid deposition		X		
Photochemical smog		X	X	
Primary smog		X	X	
Urban air quality			X	
Industrial pollution		X	X	X
Chemical and industrial accidental releases		X	X	X
Vehicular traffic pollution				X

CLIMATE CHANGE

Climate change





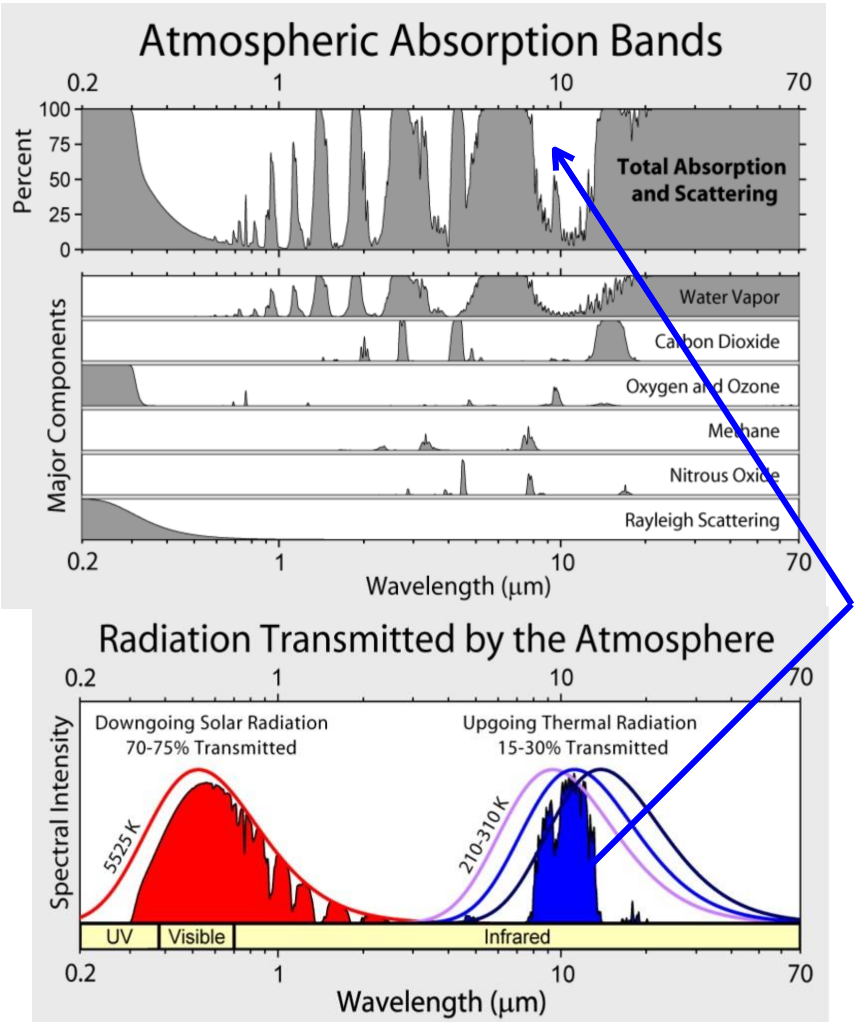
R_i: solar constant = 343 W/m²
α: albedo
(mean reflectance) ≈ 0,34

R_e: Stefan-Boltzmann
= $\sigma \cdot T^4$ [W/m²]
β = mean
absorption ≈ 0,4

unaltered atmosphere: T≈288 K = 15°C

- β increase from increasing presence of normal absorbing constituents or immissions of new absorbing species: "greenhouse" effect
  - increase in <u>temperatures</u> → climate change

Climate change

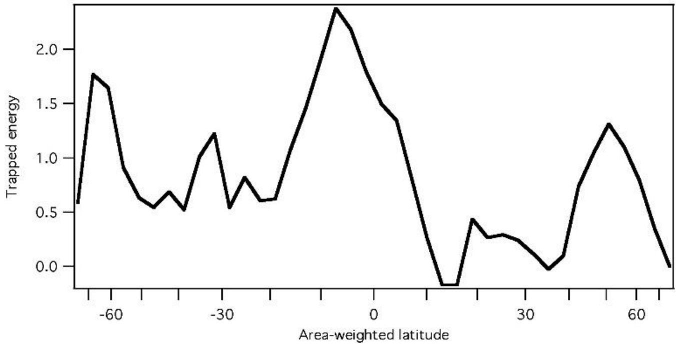


Atmospheric "window" ~ 7 – 12 µm (long wave IR)

- Greenhouse gases: potential contribution dependent on
  - absorption intensity within atmospheric window (long wave IR)
  - mean global atmospheric lifetime: sources/sinks
  - major contributors of man made origin
    - carbon dioxide
    - methane
    - nitrous oxide
    - halocarbons (CFCs, HCFCs)

What about water vapor?

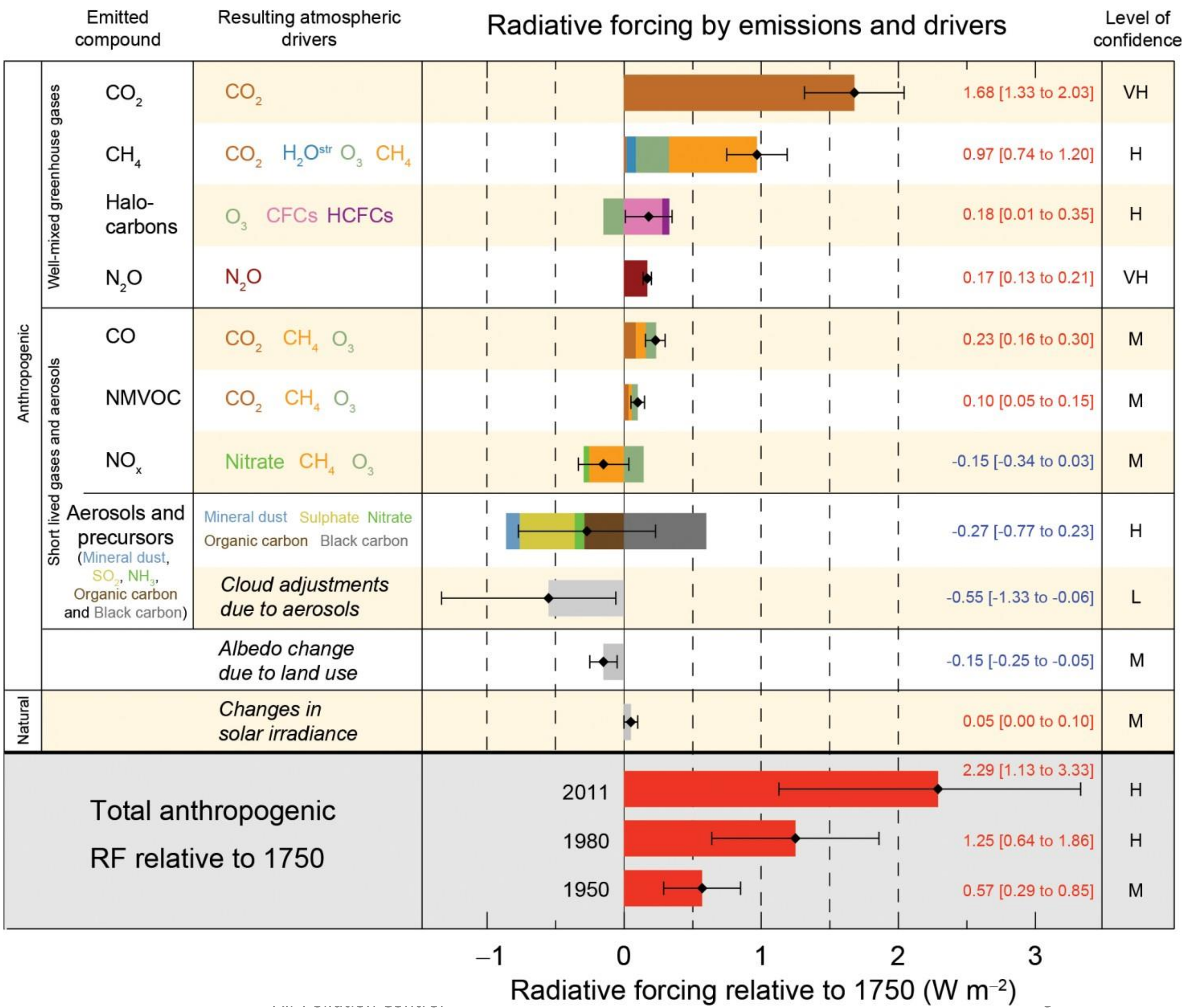
- "Everyone agrees that if you add carbon dioxide to the atmosphere, then warming will result," Dessler said. "So the real question is, how much warming?"
- The answer can be found by estimating the magnitude of water vapor feedback. Increasing water vapor leads to warmer temperatures, which causes more water vapor to be absorbed into the air. Warming and water absorption increase in a spiraling cycle.
- Water vapor feedback can also amplify the warming effect of other greenhouse gases, such that the warming brought about by increased carbon dioxide allows more water vapor to enter the atmosphere.
- "The difference in an atmosphere with a strong water vapor feedback and one with a weak feedback is enormous," Dessler said.
- Climate models have estimated the strength of water vapor feedback, but until now the record of water vapor data was not sophisticated enough to provide a comprehensive view of at how water vapor responds to changes in Earth's surface temperature.



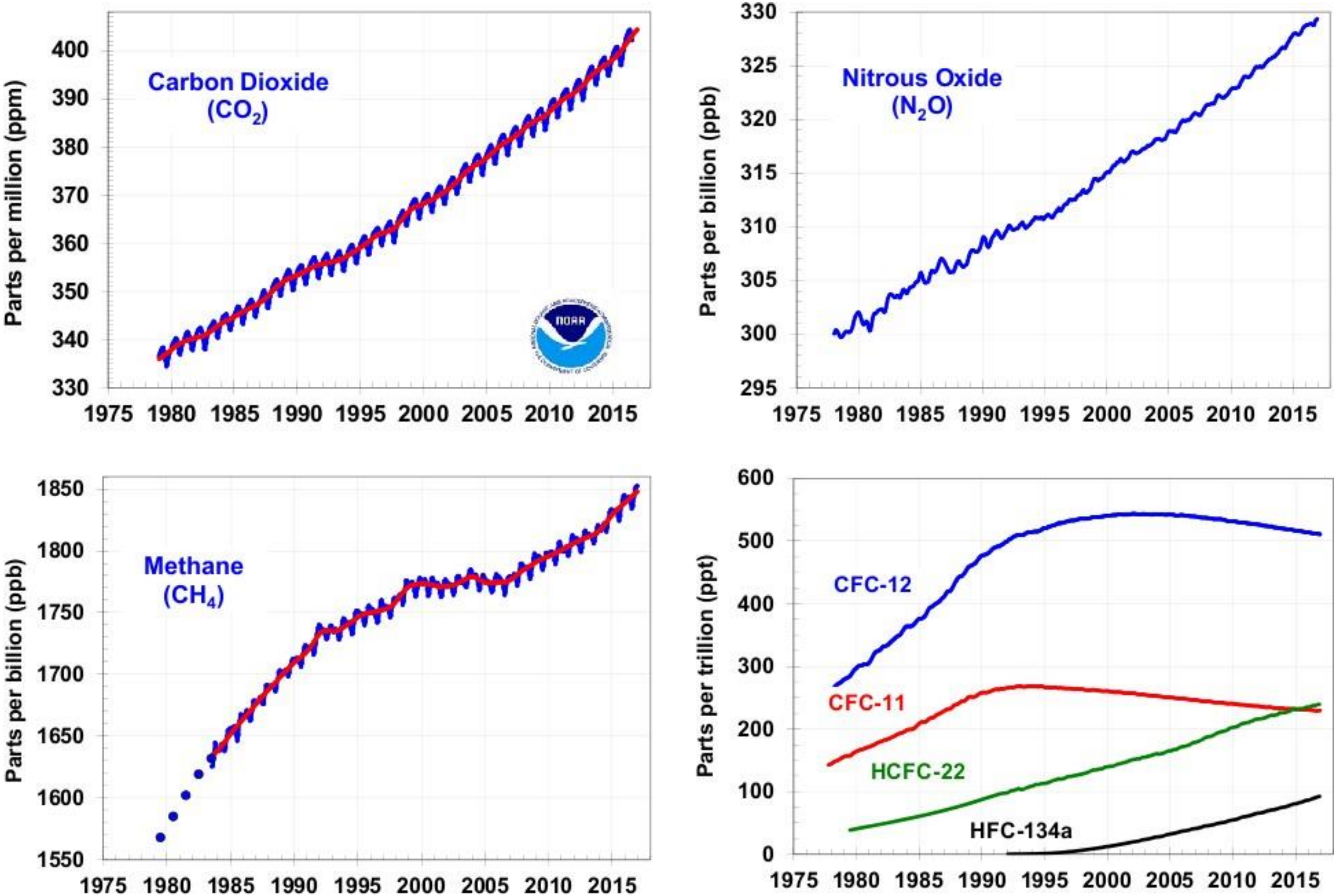
https://www.nasa.gov/topics/earth/features/vapor_warming.html#:~:text=Water%20vapor%20feedback%20can%20also,vapor%20to%20enter%20the%20atmosphere.&text=And%20since%20water%20vapor%20is,the%20warming%20from%20carbon%20dioxide.%22

Climate change

Radiative forcing measure of how the Earth's energy balance is being shifted away from its normal state when factors that affect climate are altered



Climate change



Climate change

Human sources of main greenhouse gases

- CO_2: combustion, cement production (direct), deforestation (indirect)
- CH_4: combustion, pipelines leakage, waste disposal, extensive cattle breeding and agriculture
- N_2O: combustion, industrial processes, soil fertilization, extensive cattle breeding
- halocarbons: HVAC equipment, plastic foams manufacturing, industrial solvent, aerosol propellants (phasing out)
- tropospheric O_3: combustion, industrial processes (atmospheric photochemical production from NMVOC and NO_x)

Climate change

Comparative evaluation index: GWP (Global Warming Potential)

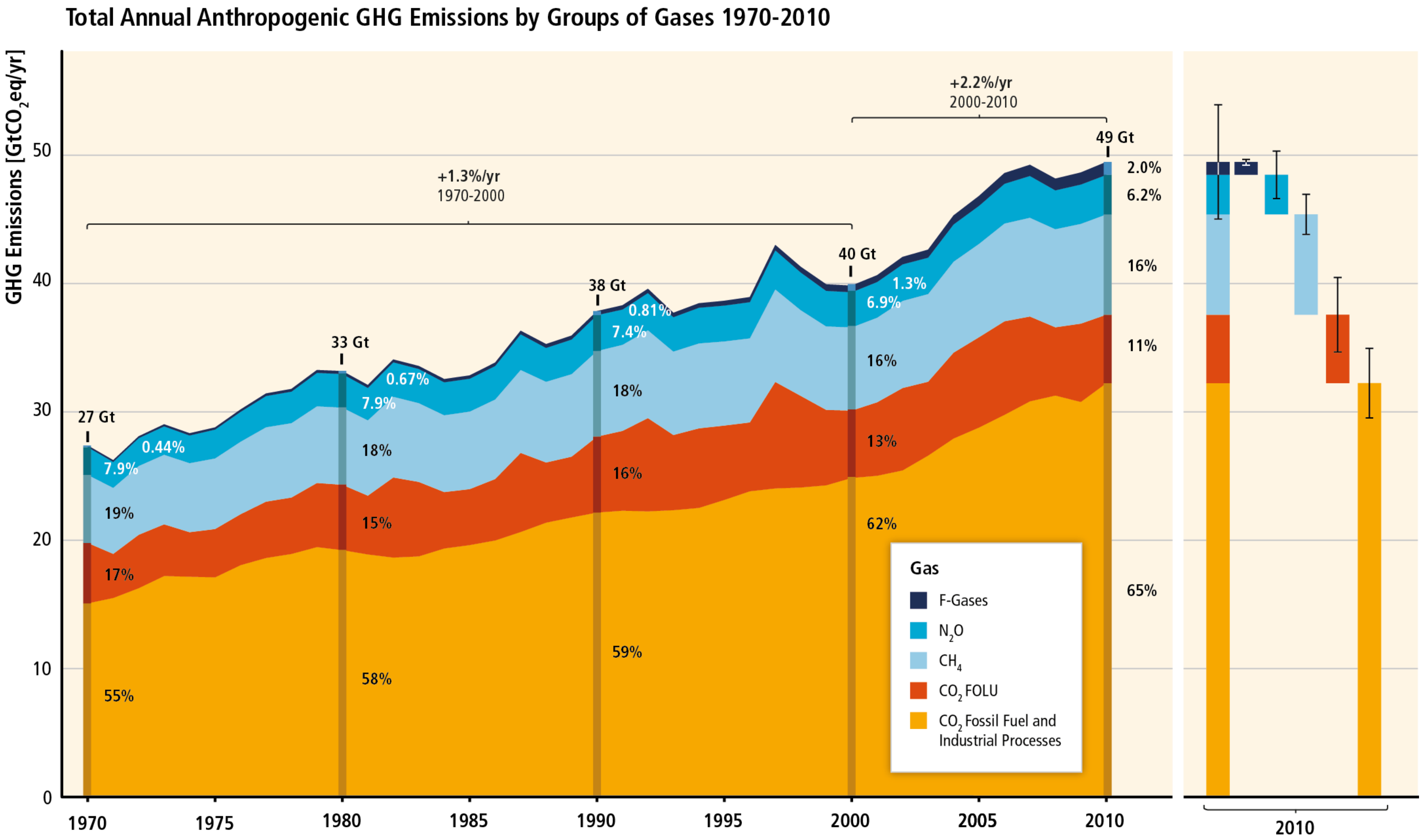
- radiative forcing of a unit mass of a gas relative to that of carbon dioxide over a defined time period

- mass of CO_2 equivalent to a unit mass of the gas in terms of potential climate effects

Chemical specie	Lifetime (years)	GWP	
		20 years	100 years
CO_2	~ 150	1	1
CH_4	~ 10	56	21
N_2O	~ 120	280	310
CFC-11	~ 50	5000	4000
CFC-12	~ 100	7900	8500
CFC-114	~ 300	6900	9300
HCFC-22	~ 10	4300	1700
HCFC-141B	~ 10	1800	630
HCFC-142B	~ 20	4200	2000
HFC-134A	~ 14	3400	1300

Climate change

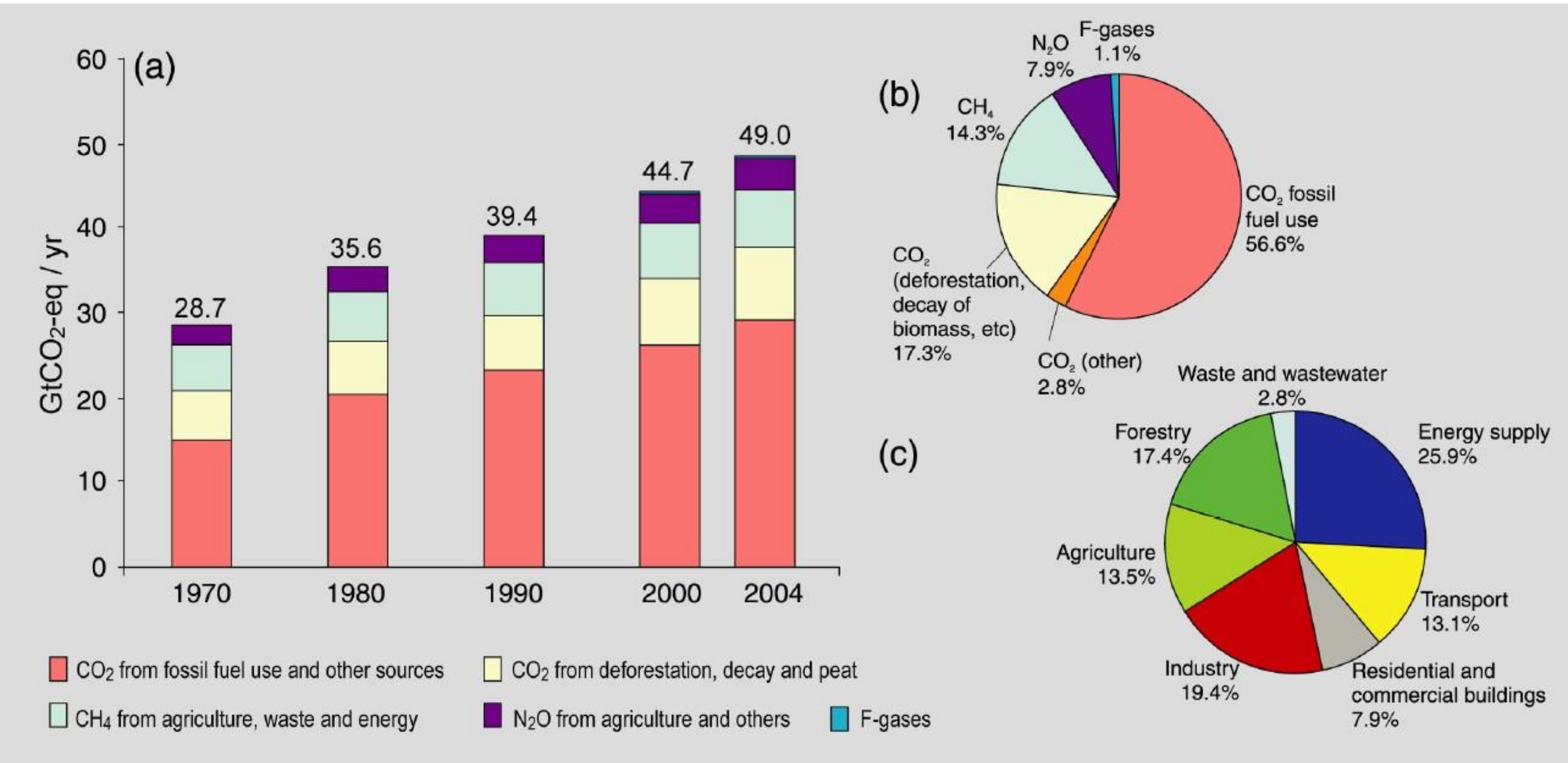
key source categories and GHG inventory



Climate change

key source categories and GHG inventory

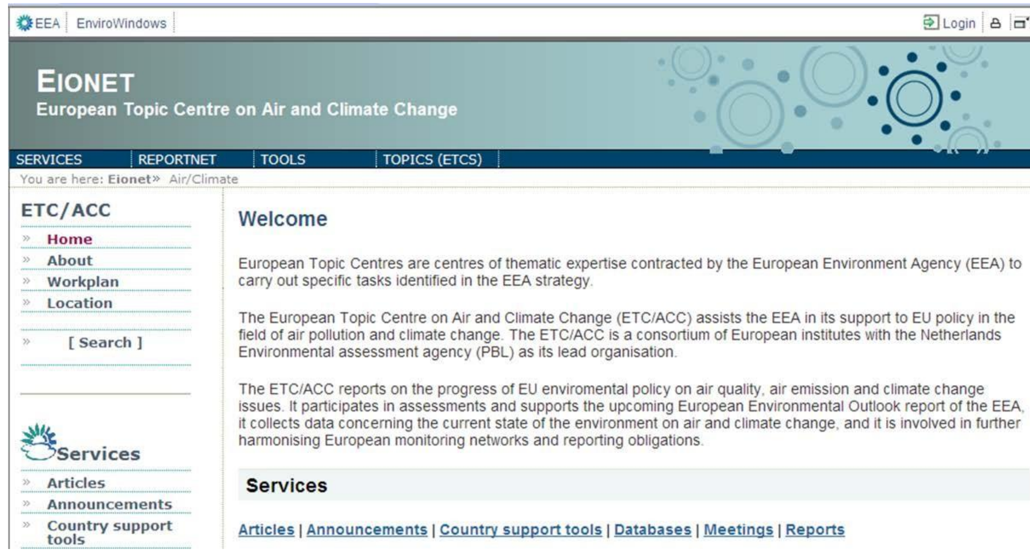
Global anthropogenic GHG emissions



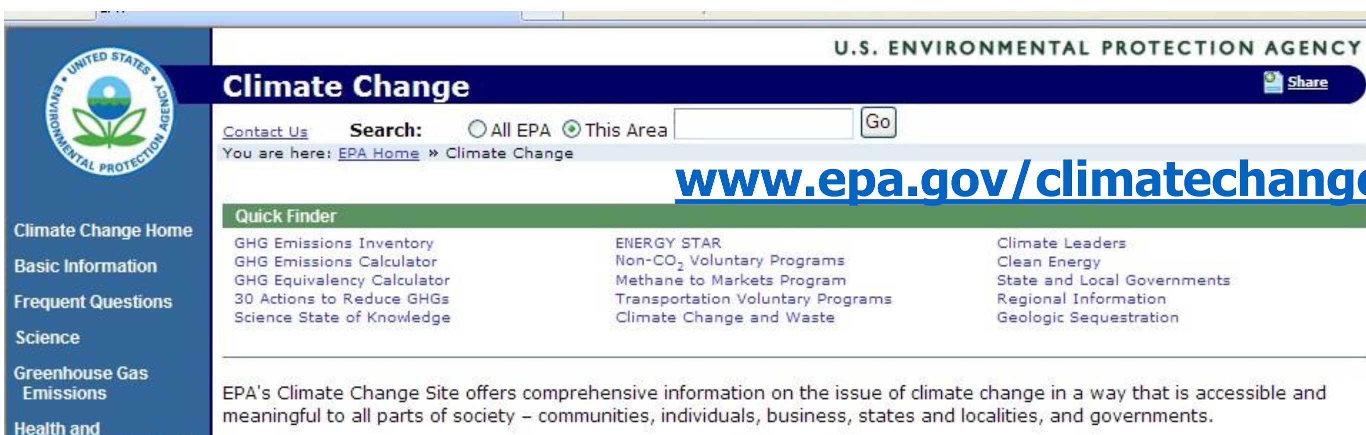
Climate change

More WWW infos/reviews/updates

http://www.ipcc.ch/



http://air-climate.eionet.europa.eu



www.epa.gov/climatechange

ACID DEPOSITION

Acid Deposition

- alteration of precipitation acidity with respect to natural expected values
- precipitations acidity in remote areas essentially arising from CO_2 dissolution and dissociation

  CO_2 dissolution from gas phase: $CO_{2\,(g)} \leftrightarrows CO_{2\,(l)}$ ↔ $H_L = 3.4 \cdot 10^{-2}$ mol/(l·atm)

  dissociation of dissolved CO_2: $CO_{2\,(l)} + H_2O \leftrightarrows HCO_3^- + H^+$ ↔ $K_a = 4.5 \cdot 10^{-7}$

  - for average remote concentrations: $CO_{2\,(g)} \approx 380$ ppm
    $CO_{2\,(l)} = 12.9 \cdot 10^{-6}$ mol/l = 0.57 mg/l → $H^+ = 10^{-5.6}$ mol/l
  - natural background precipitations mildly acidic: pH ≈ 5.6

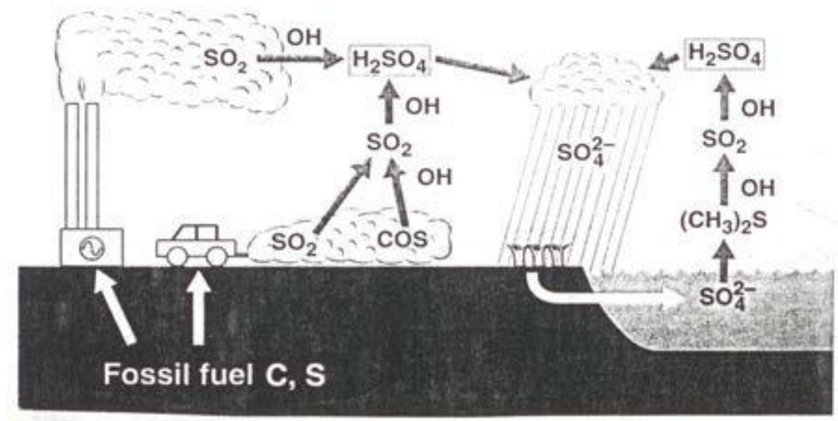
acid deposition: any precipitation with pH lower than 5.6

- main pH alterations from strong acids
  - sulphuric acid, nitric acid

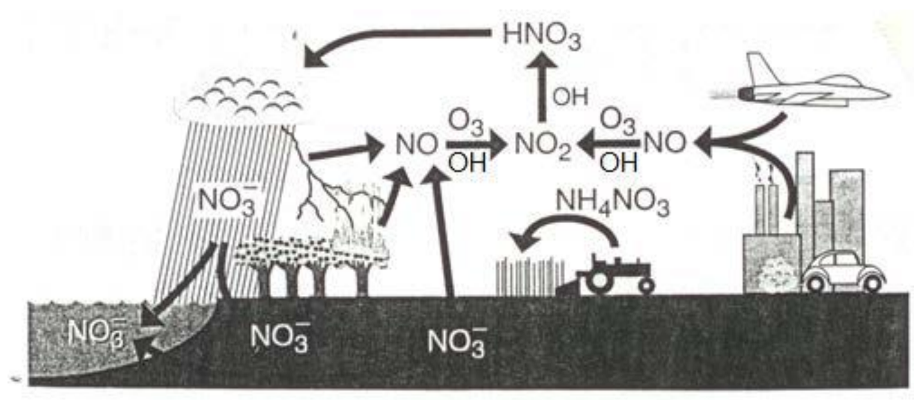
  and neutralization capacities of bases
  - ammonia, particulate matter

Acid Deposition

- SO_2 → H_2SO_4



- NO_x → HNO_3

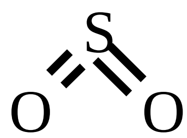


time required for transformations □ alterations at regional/continental scale

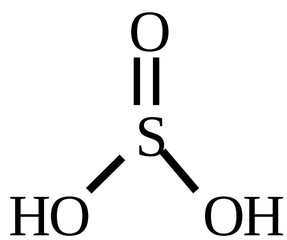
S(IV) and S(VI) Families

S(IV) Family

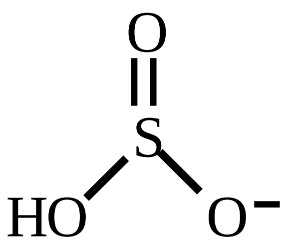
Sulfur dioxide
SO_2(g,aq)



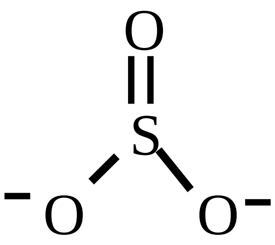
Sulfurous acid
H_2SO_3(aq)



Bisulfite ion
HSO_3^-

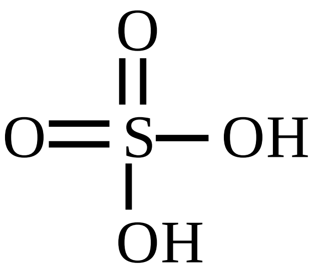


Sulfite ion
SO_3^{2-}

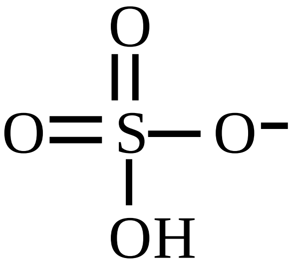


S(VI) Family

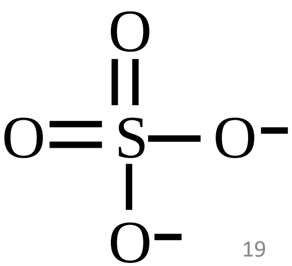
Sulfuric acid
H_2SO_4(g,aq)



Bisulfate ion
HSO_4^-



Sulfate ion
SO_4^{2-}



Mechanisms of Converting S(IV) to S(VI)

Why is converting to S(VI) important?

It allows sulfuric acid to enter or form within cloud drops and aerosol particles, increasing their acidity

Mechanisms

1. Gas-phase oxidation of SO_2(g) to H_2SO_4(g) followed by condensation of H_2SO_4(g)

2. Dissolution of SO_2(g) into liquid water to form H_2SO_3(aq) followed by aqueous chemical conversion of H_2SO_3(aq) and its dissociation products to H_2SO_4(aq) and its dissociation products.

Acid Deposition

Acidification processes

Sulphur oxides

- SO_2 poorly water soluble
- emissions: $SO_2 >> SO_3$

$SO_2 \rightarrow H_2SO_4$ conversion

Gas phase

$SO_2 + OH\cdot + O_2 \rightarrow SO_3 + HO_2\cdot$

$SO_3 + H_2O \rightarrow H_2SO_{4\,(aq)}$

$O_3 + H_2O \xrightarrow{\text{solar radiation}} O_2 + 2OH\cdot$

Liquid phase (clouds → prevailing)

$SO_2 + H_2O \rightarrow H_2SO_{3\,(aq)}$

$H_2SO_{3\,(aq)} + H_2O_2 \rightarrow H_2SO_{4\,(aq)} + H_2O$

(H_2O_2: hydrogen peroxide)

Production of H_2O_2 from $OH\cdot$ (hydroxyl) and $HO_2\cdot$ (hydroperoxide) radicals

$OH\cdot + O_3 \rightarrow O_2 + HO_2\cdot$ ⟶ $2HO_2\cdot \rightarrow H_2O_2 + O_2$

⟶ $2OH\cdot \rightarrow H_2O_2$

Acid Deposition

Acidification processes

Nitrogen oxides (NO + NO_2)

- NO poorly water soluble
- emissions: NO >> NO_2

$NO \rightarrow HNO_3$ conversion

NO_2 formation (photochemical smog)

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

$$NO + HO_2\cdot \rightarrow NO_2 + OH\cdot$$

(hydroperoxide radical)

$$NO + RO_2\cdot \rightarrow NO_2 + RO\cdot$$

(organic reactive radical)

Nitric acid formation (HNO_3)

$$NO_2 + OH\cdot \rightarrow HNO_3$$

Acid Deposition

- Surface waters
  - alcalinity reductions

$$\text{Alcalinity} = [HCO_3^-] + 2[CO_3^=] + [OH^-] - [H^+]$$

  Buffer of excess acidity (H^+):

$$[H^+] + [CO_3^=] \rightarrow [HCO_3^-] + [H^+] \rightarrow H_2CO_3$$

  → buffer capacity reductions, with loss of water quality from *pH reductions*

  → water mobilization of metal cations from bottom sediments

  - eutrophication from excess N loadings
- Soils
  - mobilization of nutrient metal cations (Ca^{++}, Mg^{++}, Na^+, K^+) in low pH conditions with soil productivity losses
  - mobilization/leaching of toxic metals (Al^{+++}, Mn^{++}, Fe^{++}, Cd^{++}) in surface and groundwaters with loss of water quality
  - eutrophication from excess N loadings
- Direct effects
  - buildings/materials disruption from acid attack

  F.ex.: limestone

$$H_2SO_4 + \underset{\text{Marble}}{CaCO_3} \rightarrow H_2CO_3 + \underset{\textit{Gypsum}}{CaSO_4}$$

  - enhanced vulnerability and loss of vegetation and forests for low pH deposition

Neutralizing Acids

Add ammonium hydroxide to a lake

$$NH_4OH(aq) + H^+ \rightleftharpoons NH_4^+ + H_2O(aq)$$

Ammonium hydroxide | Hydrogen ion | Ammonium ion | Liquid water

Add slaked lime to a lake

$$Ca(OH)_2(aq) + 2H^+ \rightleftharpoons Ca^{2+} + 2H_2O(aq)$$

Calcium hydroxide | Hydrogen ion | Calcium ion | Liquid water

Calcium carbonate is a natural neutralizing agent in soil

$$CaCO_3(s) + 2H^+ \rightleftharpoons Ca^{2+} + CO_2(g) + H_2O(aq)$$

Calcium carbonate | Hydrogen ion | Calcium ion | Carbon dioxide gas | Liquid water

Liming of a Lake in Sweden

Tero Niemi / Naturbild

Neutralizing Acids

Sea salt is a natural neutralizing agent near the coast

$$NaCl(s) + H^+ \rightleftharpoons Na^+ + HCl(g)$$

Sodium chloride	Hydrogen ion		Sodium ion	Hydrochloric acid

Ammonia is a neutralizing agent

$$NH_3(aq) + H^+ \rightleftharpoons NH_4^+$$

Dissolved ammonia	Hydrogen ion		Ammonium ion

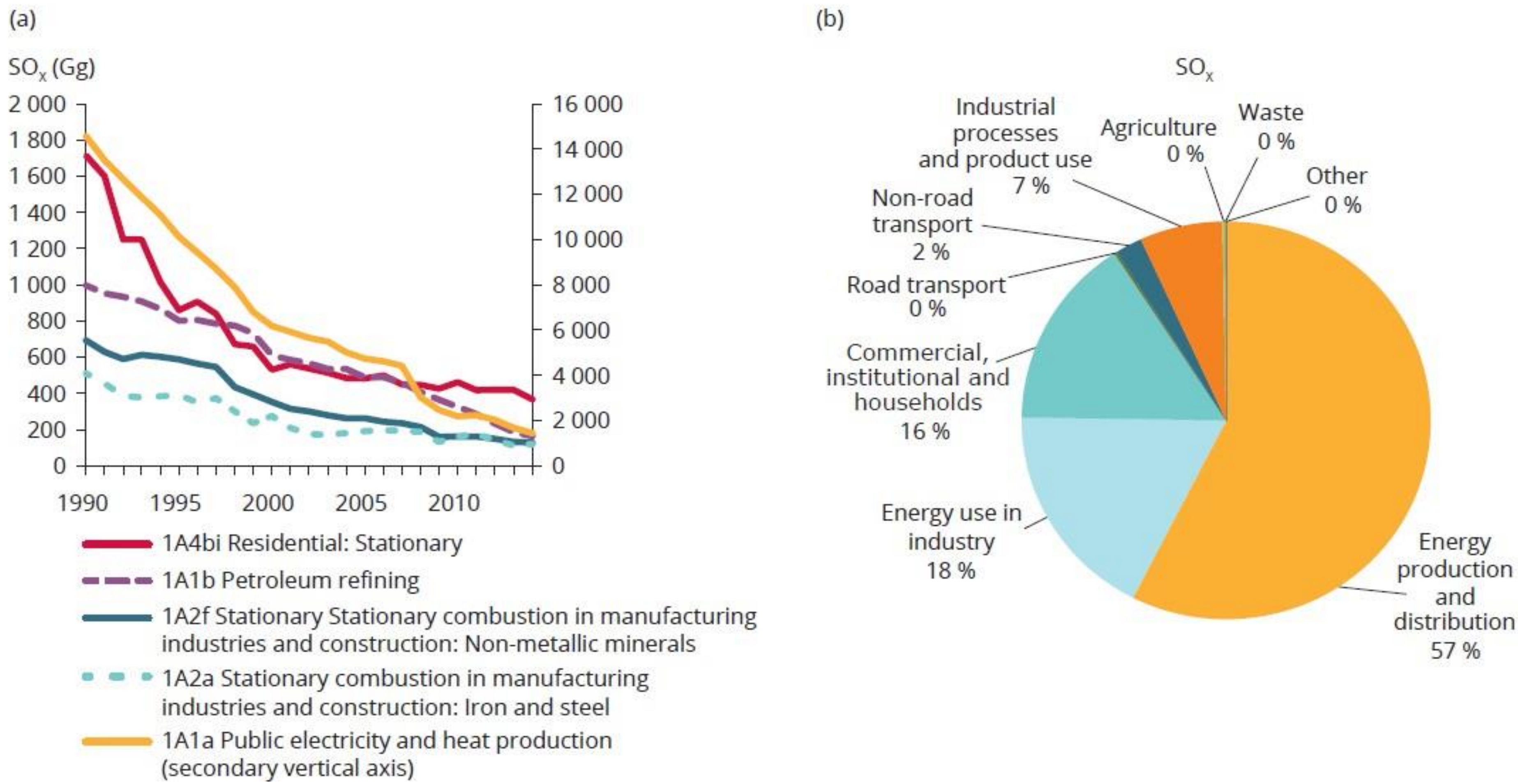
Acidified forest near Most, Czechoslovakia (1987)

Owen Bricker, United States Geological Survey

Acid Deposition

Source categories inventory

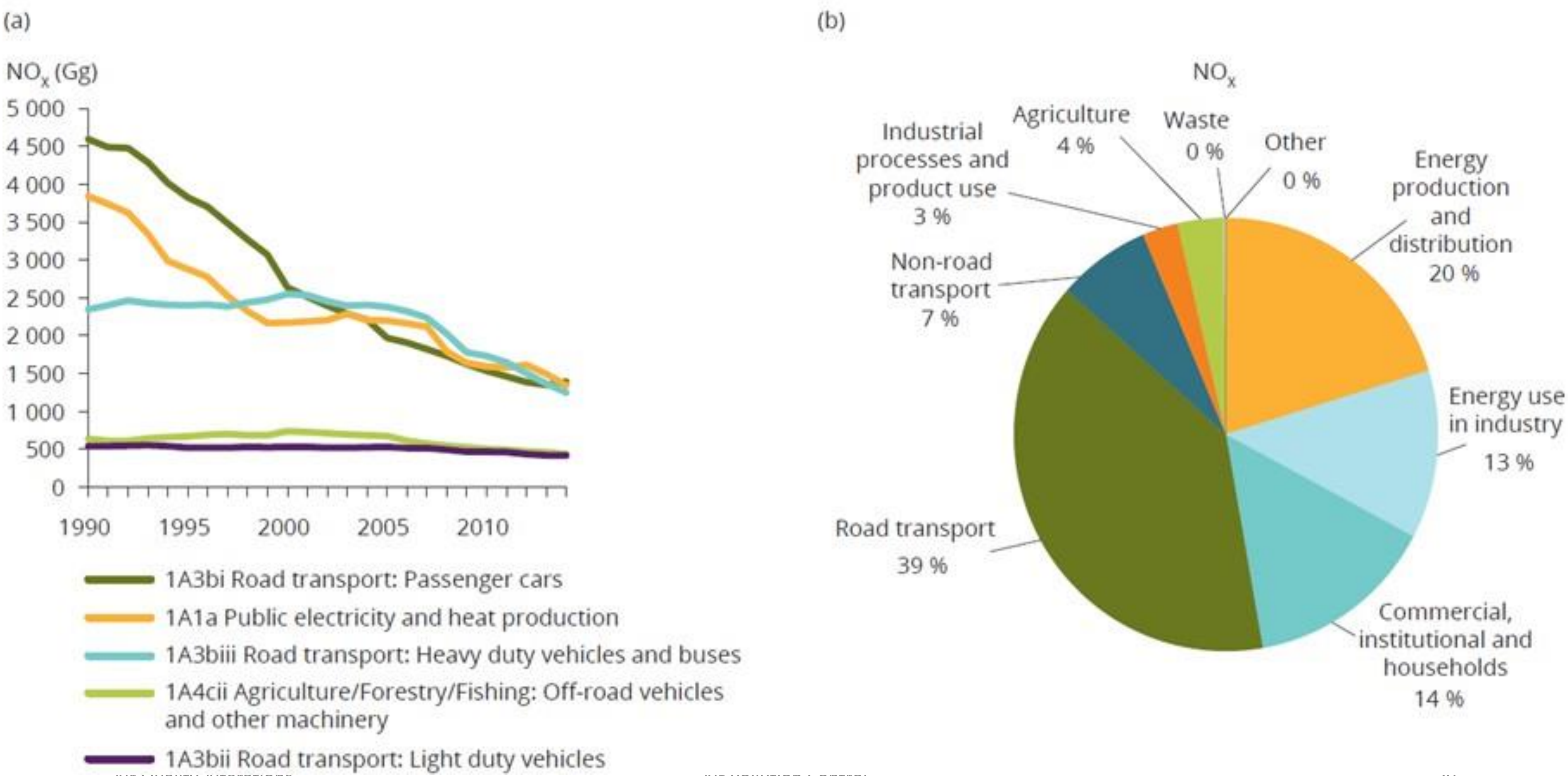
Figure 3.7 SO_x emissions in the EU-28: (a) trend in emissions from the five most important key categories, 1990–2014; (b) share by sector group, 2014; (c) sectoral trends in emissions



Acid Deposition

Source categories inventory

Figure 3.5 NO_x emissions in the EU-28: (a) trend in emissions from the five most important key categories, 1990–2014; (b) share by sector group, 2014; (c) sectoral trends in emissions



PHOTOCHEMICAL SMOG

Photochemical smog

Photochemical smog: local → regional scale

- Secondary origin: complex photochemical chain of reactions dependent on
  - primary emissions of NO_x and NMVOC
  - meteorology (wind, atmospheric dispersion, solar radiation)
- Main components
  - **Primary pollutants** → directly emitted from sources

→ SO_2
→ CO
→ NMCOV (hydrocarbons)
→ "coarse" particulates (TSP, PM_{10})
→ NO_x (mainly NO)

} Primary smog ("London" type)

  - **Secondary pollutants** → photochemical conversion of primary species in the atmosphere

→ O_3
→ NO_2, HNO_3, organic nitrates
→ reactive organic gases (ROG)
→ fine and ultrafine particulates ($PM_{2.5}$, PM_1, nanoparticles)

} Photochemical smog

Photochemical smog

Photochemical smog – origin

"Natural" atmosphere

$$NO_2 + UV \rightarrow NO + O\bullet$$
$$O\bullet + O_2 \rightarrow O_3$$
$$NO + O_3 \rightarrow NO_2 + O_2$$

} photostationary cycle ➡ NO-NO_2-O_3 equilibrium

$$[O_3] \propto ([NO_2]/[NO])$$

Polluted atmosphere ⇒ NMVOC emissions (Non Methane VOC)

- competitive oxidative reactions of NO to NO_2 *without O_3 consumption*

O_3 build-up, reactive organics (ROGs) production

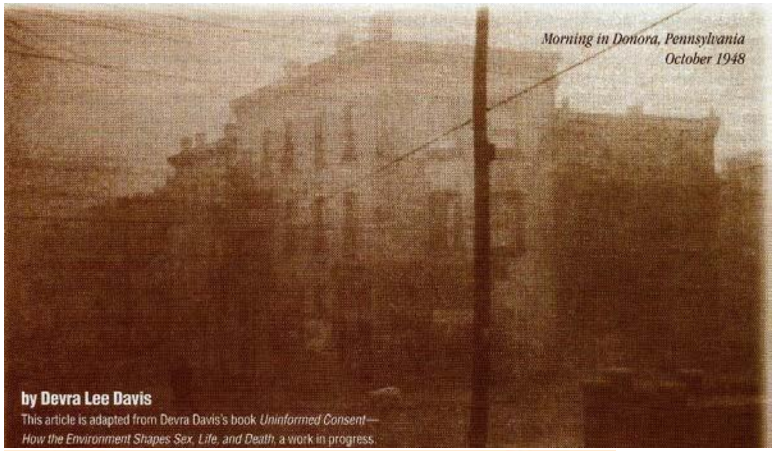
$$NO_2 + UV \rightarrow NO + O\bullet$$
$$O\bullet + O_2 \rightarrow O_3$$
$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO + NMVOC \rightarrow NO_2 + \text{reactive organics (ROGS)}$$

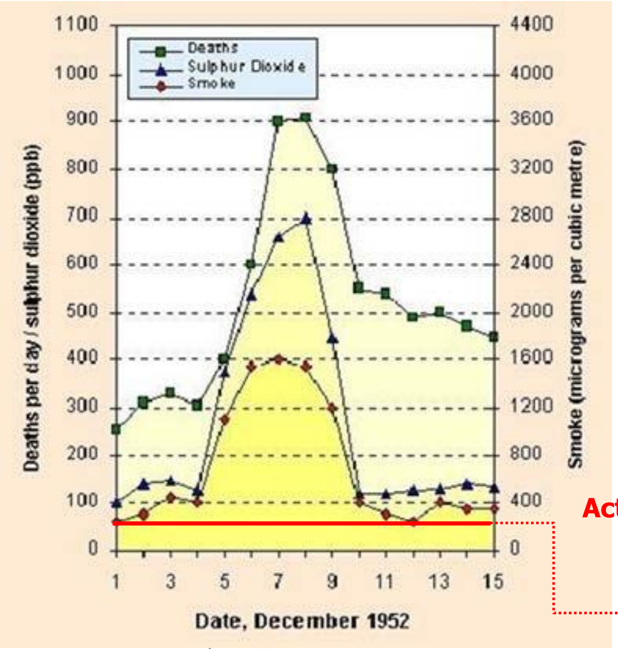
$$NO + NMVOC \xrightarrow{☺} NO_2 + O_3 + ROGs$$

Primary — **Secondary (photochemical smog)**

Photochemical smog

Primary smog





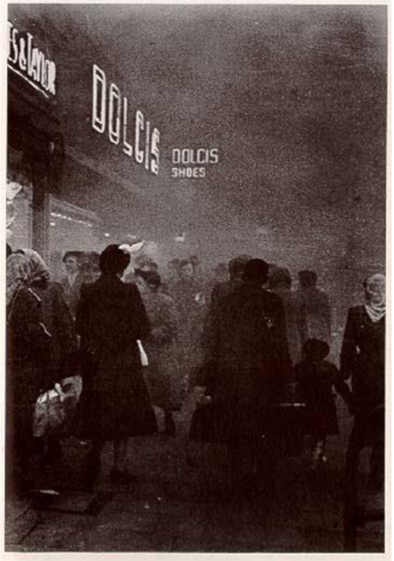
Actual SO_2 limit: 40 ppb

Donora, Pennsylvania - October 1948

- Pollution from industrial emission
  (iron and steel industry, copper foundry, zinc-plating)
- Pollutants stagnation in the valley
- 17 people dead after 1 week

London, December 1952

- Pollution from domestic heating emissions
- Persistent fog
- Synergy between pollutants (SO_2 + particulates)
- Association between SO_2 concentration and deaths time patterns



Photochemical smog

Primary smog

Linfen, China - 2007

- Pollution from industrial emissions (coal and iron industry) and automotive
- 196 iron foundries and 153 coal processing plants
- nearly 3,000,000 people affected from very low air quality
- death rate 10 times higher than China's average

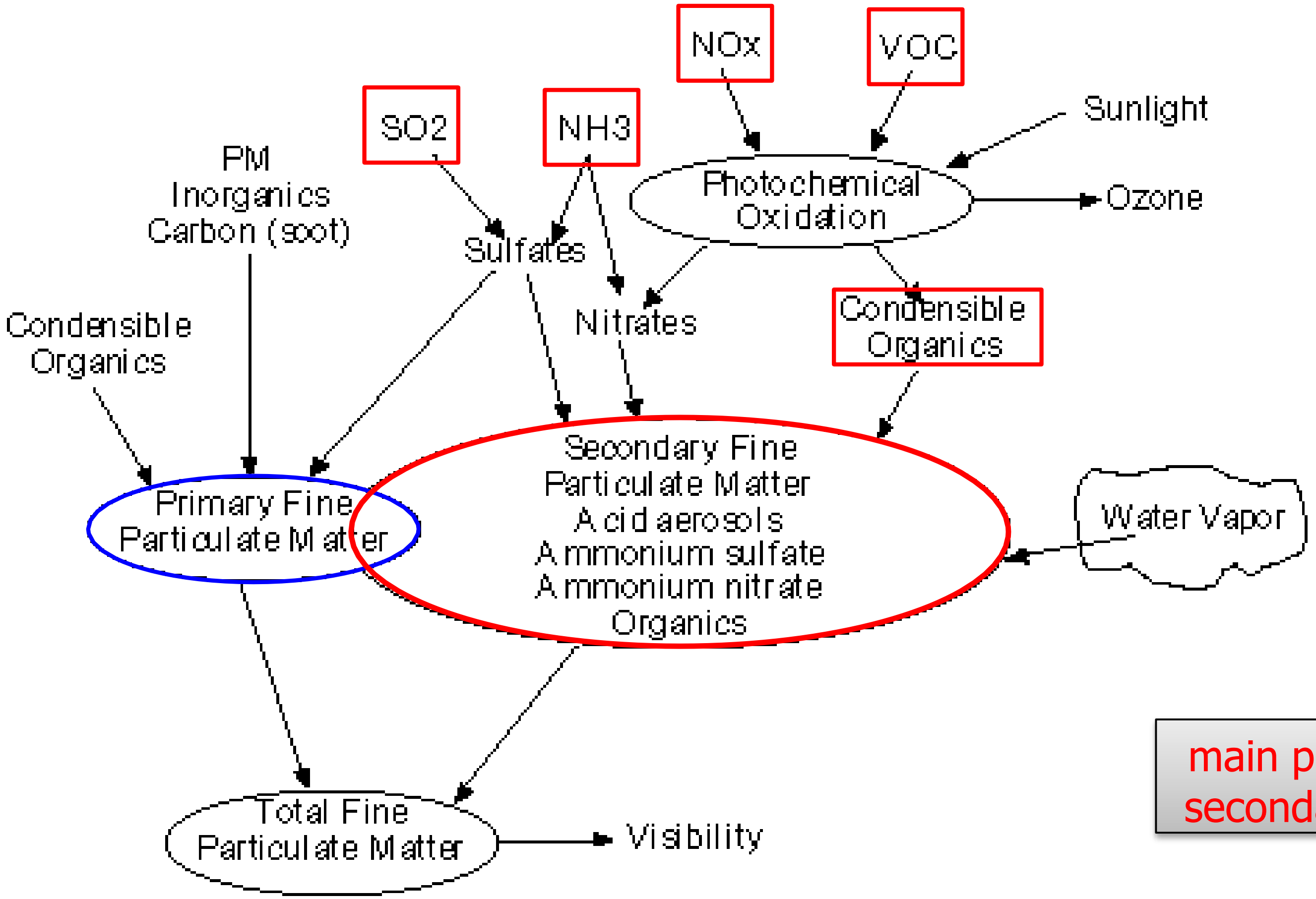
Photochemical smog

Photochemical smog

Photochemical smog

Fine particles ($PM_{2.5}$ and smaller)

- complex mixture of primary and secondary particles



main precursors of secondary particles

Photochemical smog

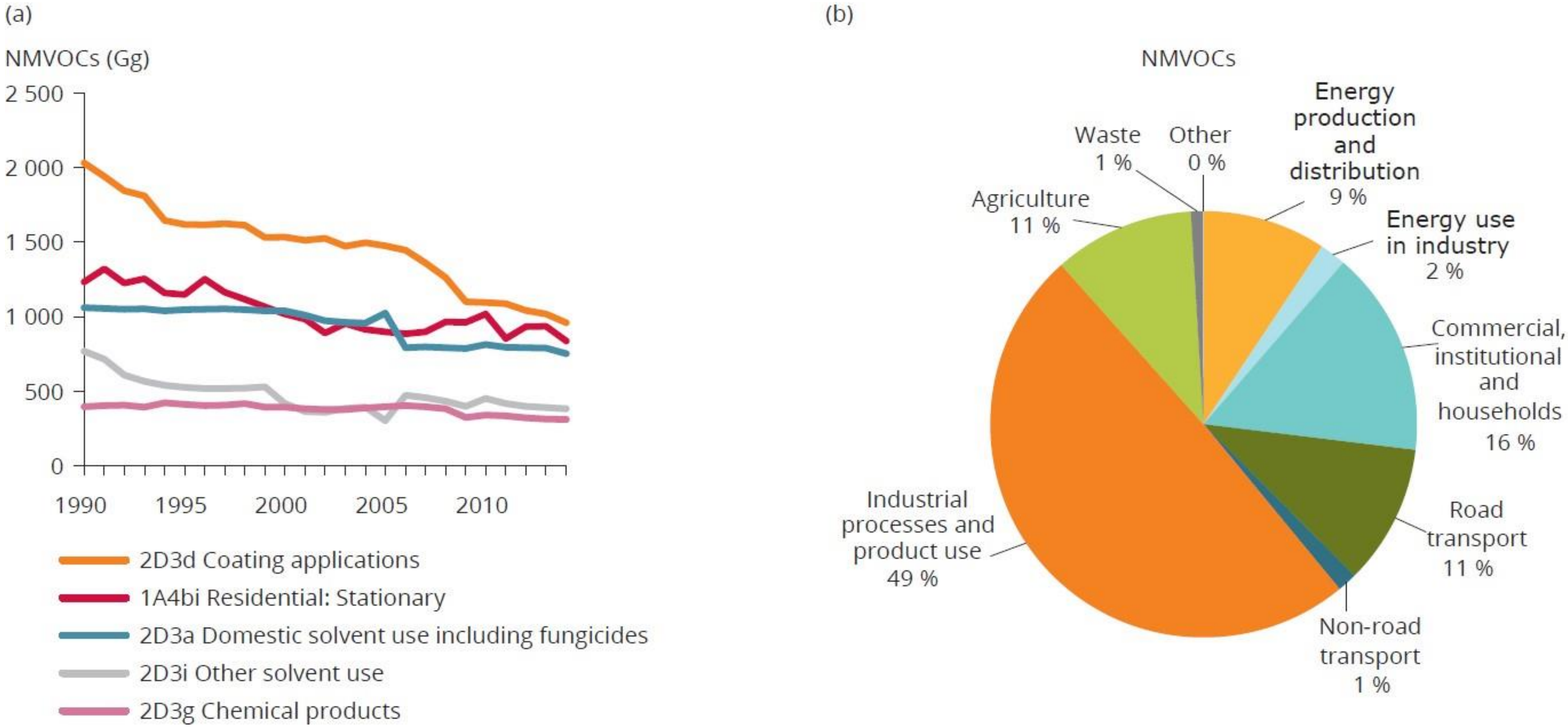
- Health hazards
  - throat/lung/eyes irritation, difficulty in breathing, premature aging of the lungs
  - modifications/reductions of immune system from excess O_3
  - toxicity from trace ROGS (aldehydes)

- Direct effects
  - materials vulnerability from O_3 oxidation (natural and synthetic rubbers)
  - enhanced loss of vegetation and forests for excess O_3 levels
  - visibility reductions

Photochemical smog

Source category inventories

Figure 3.6 NMVOC emissions in the EU-28: (a) trend in emissions from the five most important key categories, 1990–2014; (b) share by sector group, 2014; (c) sectoral trends in emissions



HEALTH EFFECT

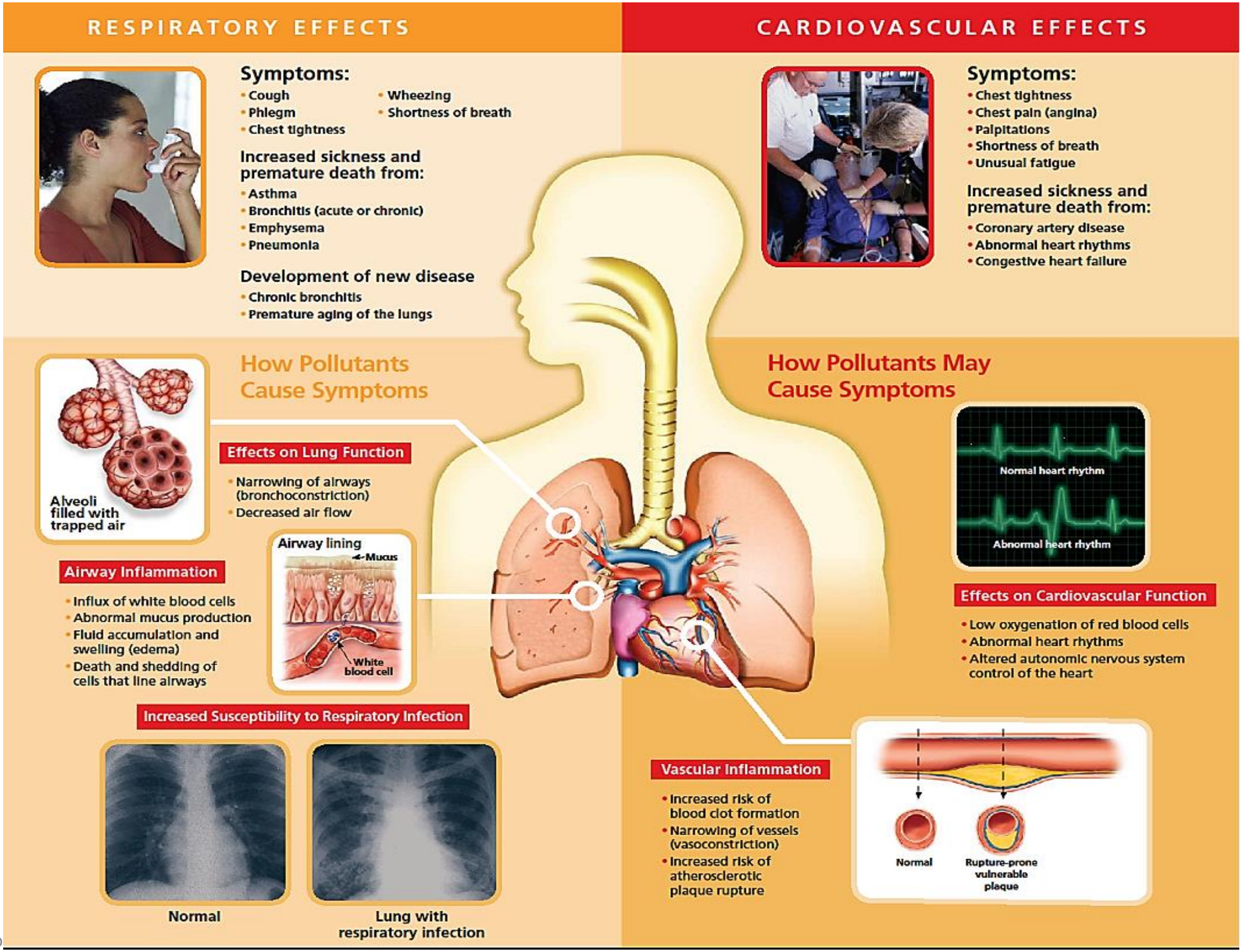
Air pollution Effects: ***Human health***

Air pollution is a major environmental risk to health.

- ***Premature death*** — ***Heart disease*** and ***stroke*** are responsible for 80% of cases of premature death and the most common reasons for premature death attributable to air pollution; lung diseases and lung cancer follow (WHO, 2016).
- ***Long and short-term health effects*** — In addition to causing premature death, air pollution ***increases the incidence of a wide range of diseases*** (e.g. respiratory and cardiovascular diseases and cancer), with both long and short-term health effects (WHO, 2016).
- ***Carcinogenic effect*** — Air pollution as a whole, as well as PM (Particulate Matter) as a separate component of air pollution mixtures, have recently been classified as ***carcinogenic*** (IARC, 2013).
- ***Health-related costs*** — The effect of air pollution on health also has considerable ***economic impacts***, cutting lives short, increasing medical costs and reducing productivity. Total health-related external costs for EU in 2010 were in the range of EUR 330–940 billion per year, including direct economic damages of EUR 15 billion from lost work days, EUR 4 billion from healthcare costs, EUR 3 billion from crop yield loss and EUR 1 billion from damage to buildings (EEA, 2015 and 2017).

Health effects

Effects of common pollutants



Health effects

❍ SO_2

- acute and chronic damage to respiratory system
  - ➢ alteration of mechanical function of the upper airways (increase in nasal flow resistance, decrease in nasal mucus flow rate)
  - ➢ acute bronchial constriction on inhalation when exposing strenuously exercising even to relatively low levels of SO_2 (0.25-0.50 ppm)
- some of health effects most likely result from its conversion to fine-particle sulfate aerosols such as H_2SO_4 (sulfuric acid)

❍ CO

- acute effects on respiration formation of carboxyhemoglobin (CO affinity for hemoglobin is 200 times greater than for O_2) decreasing O_2 delivery to body's organs & tissues
- highly toxic at concentrations > 1000 ppm, leading to death from asphyxiation

Health effects

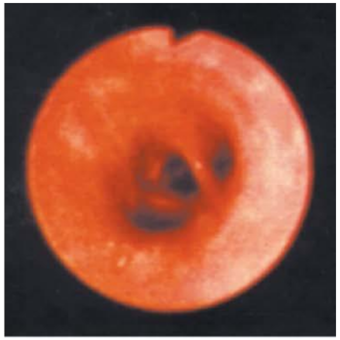
❍ NO_2

- highly reactive gas, leads to respiratory illness (bronchitis, pneumonia)

❍ O_3

- major component of photochemical smog
- throat/lung irritation, difficulty in breathing → increased respiratory rate, increased pulmonary resistance, decreased tidal volume (rise and fall) of air intake, changes in respiratory mechanics, premature aging of the lungs
- interference or inhibition with immune system → microbial infections
- inflammation of lung's lining

Healthy lung airway

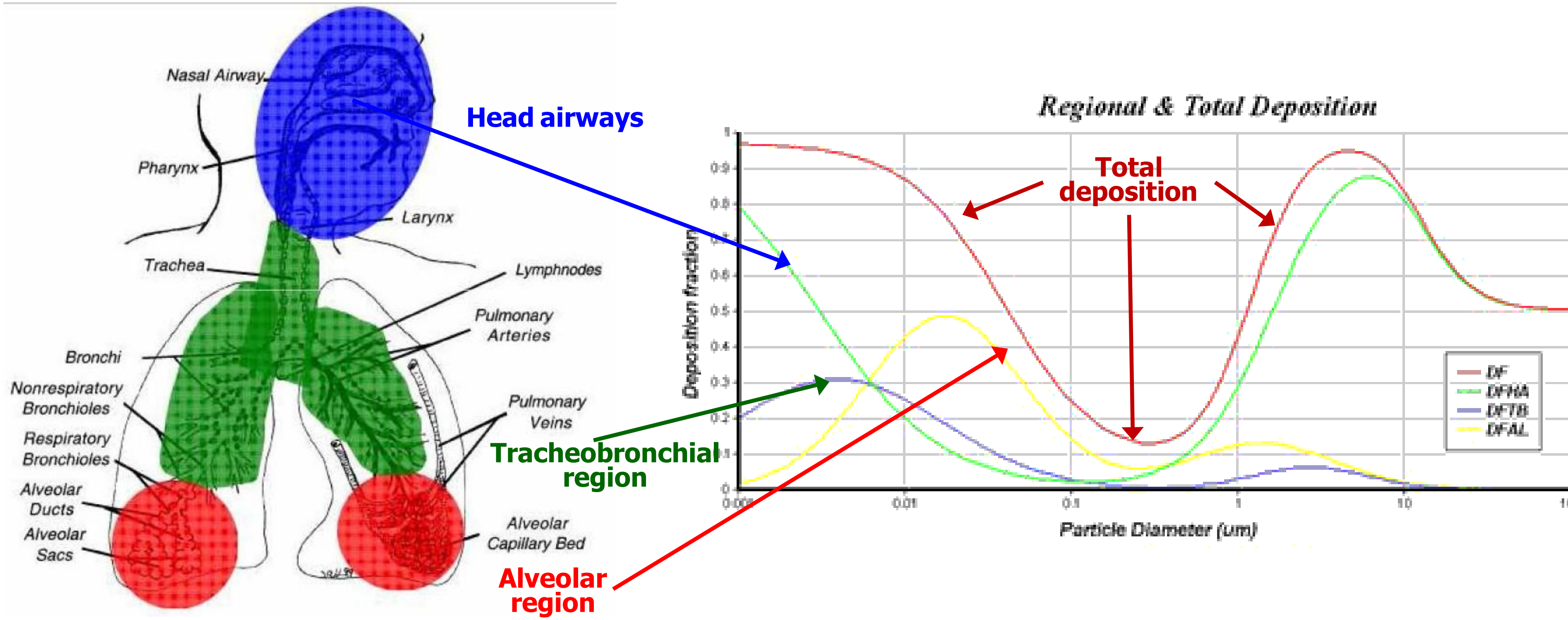


Inflamed lung airway

Health effects

❍ Particulate matter

- effects depending on penetration into respiratory system regions → particle dimensions



- inverse dependence of penetration with particle dimensions → deeper penetration for finer particles ($PM_{2.5}$, PM_1, ultrafines, nanoparticles)

Health effects

- Particulate matter
  - breathing and respiratory symptoms
  - increased respiratory illnesses (bronchitis)
  - exacerbate effects of other cardiovascular diseases
  - toxic effects for finer fractions: deeper penetration + surface enrichment (trace metals and/or organics)

- Toxic trace compounds (metals, NMVOC)
  - chronic toxicity effects from long term exposures
    - non carcinogenic (for ex., lead, mercury, toluene)
    - carcinogenic (for ex., benzene, cadmium, some PAHs)

Health effects

The annual excess mortality rate from ambient air pollution in Europe is **790 000** [95% confidence interval (95% CI) 645 000–934 000], and **659 000** (95% CI 537 000–775 000) in the EU-28. Between 40% and 80% are due to cardiovascular events, which dominate health outcomes. The upper limit includes events attributed to other non-communicable diseases, which are currently not specified.
It is estimated that air pollution reduces the mean life expectancy in Europe by about 2.2 years with an annual, attributable per capita mortality rate in Europe of 133/100 000 per year.

Table 1 Estimated annual excess mortality attributed to air pollution[a]

	All risks	From air pollution[b]							
	Total CVD mortality ($\times 10^3$)	CEV ($\times 10^3$)	IHD ($\times 10^3$)	CVD[c] ($\times 10^3$)	Other NCD[c] ($\times 10^3$)	All diseases[d] ($\times 10^3$)	Deaths per 100 000	YLL ($\times 10^6$)	LLE (years)
Europe	2138	64	313	377 (48%)	255 (32%)	790	133	14	2.2
EU-28	1849	48	216	264 (40%)	249 (38%)	659	129	11.5	2.1
Germany	330	7	42	49 (40%)	48 (39%)	124	154	2.1	2.4
Italy	221	6	23	29 (36%)	35 (43%)	81	136	1.2	1.9
Poland	180	6	27	33 (57%)	13 (22%)	58	150	1.1	2.8
United Kingdom	147	3	14	17 (27%)	29 (45%)	64	98	1.1	1.5
France	144	3	13	16 (24%)	38 (57%)	67	105	1.1	1.6

[a]Data for all EU countries, including 95% CI, are given in the Supplementary material online (overall uncertainty about ±50%).
[b]CEV is cerebrovascular disease, IHD is ischaemic heart disease, CVD are total cardiovascular diseases (CEV + IHD), NCD are non-communicable diseases. YLL are years of life lost. LLE is loss of life expectancy.
[c]Percentages refer to fractional contributions of CVD and other NCD to attributable mortality from all diseases.
[d]All diseases refer to NCD + LRI according to Burnett *et al.*[13]

Lelieveld, J., Klingmüller, K., Pozzer, A., Pöschl, U., Fnais, M., Daiber, A., Münzel, T., 2019. Cardiovascular disease burden from ambient air pollution in Europe reassessed using novel hazard ratio functions. Eur. Heart J. 40, 1590–1596. doi:10.1093/eurheartj/ehz135

NEGATIVE EFFECTS OF AIR POLLUTANTS ON MATERIALS AND CULTURAL HERITAGE

Sandstone portal Figure on Herten Castle in Ruhr district of Germany. Sculpted 1702; photo in 1908.

Same sandstone portal figure photo in 1969.

After chemical attack by acid rain, mostly by sulfuric acid, but also by nitric acid.

Materials tested in an ozone chamber

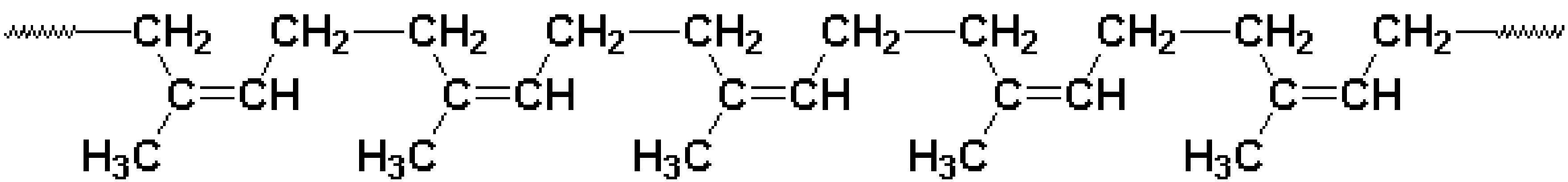
Ozone testing is particularly effective for rubber and is a routine test for suppliers to the automotive and transportation industries.

Polymers, silicones, and other elastomers can also be effectively tested in an ozone chamber.

Natural rubber (NR) consists almost exclusively of the cis-1,4 polymer

Because contains an unsaturated backbone, natural rubber can be easily attacked by ozone and UV radiation.

Ozone degradation, which is primarily a surface phenomenon, results in discoloration and cking of rubber, particularly of the natural one.

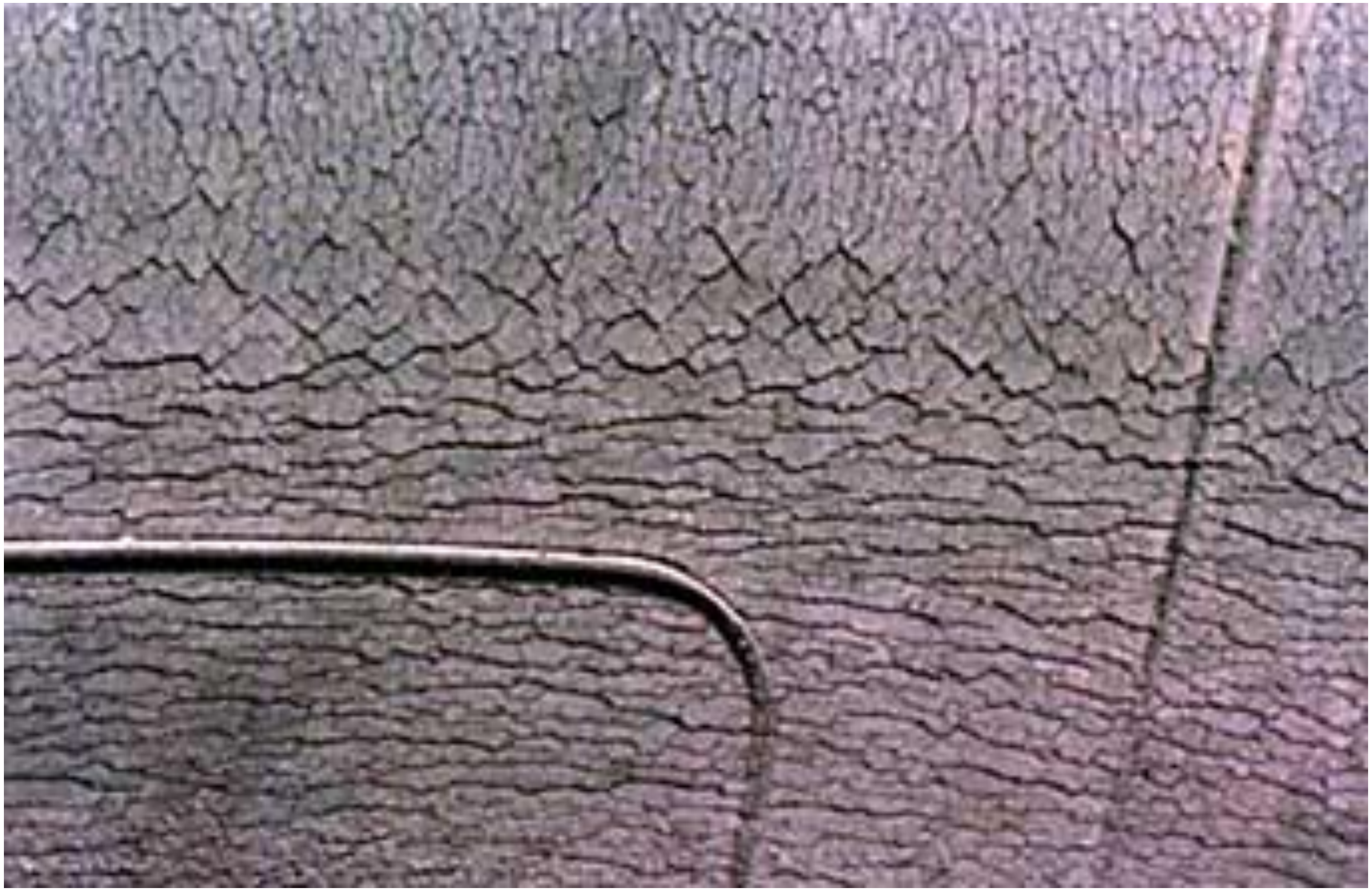


UV and O_3 ATTACK TO THE DOUBLE C=C BOND

OZONE CRACKING

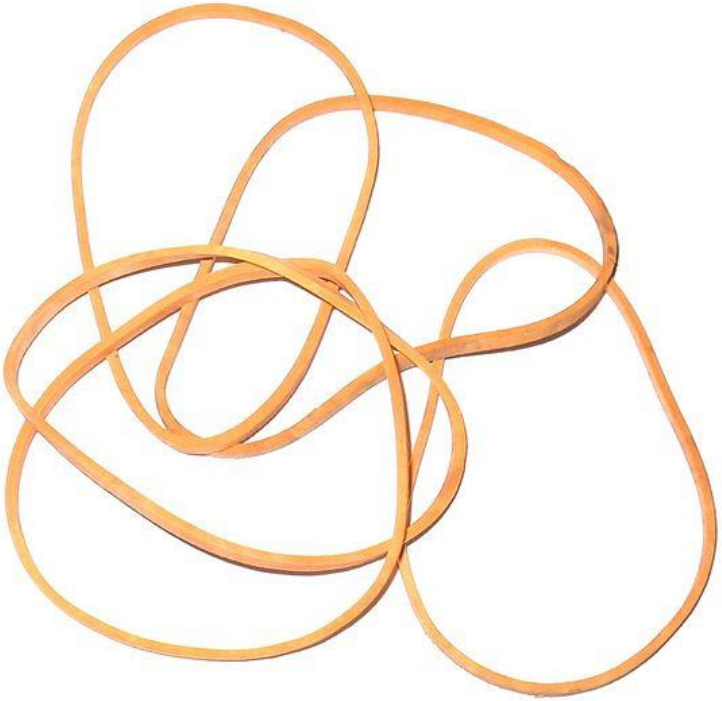
Because all tires are made of rubber, all TIRES will eventually exhibit some type of cracking condition, usually late in their life. However, this cracking can be accelerated by too much exposure to heat, vehicle exhaust, ozone and sunlight,

Anti-aging chemicals are used in the rubber compounds (ex. in tires), particularly with natural rubber..)



Ozone can damage rubber bands and through a comparison, you will be able to determine the relative ozone levels for different locations.

Rubber bands deteriorate and develop cracks



MATERIAL DEGRADATION PREVENTION CAN BE ACHIEVED BY USING:

METALS

SPECIAL PROTECTION AND/OR MORE RESISTANT MATERIAL (COPPER OR STAINLESS STEEL …INSTEAD OF GALVANISED IRON….) gutters /download spouts from houses roofs

CATHODIC PROTECTION OF ACTIVE METALS (IRON, STEEL)

POLYMERS

SATURATED ORGANIC POLYMERS INSTEAD OF UNSATURATED ORGANIC POLYMERS …..

A wide variety of fillers such as antioxidants (Chain Terminating), carbon black, are often used in the rubber industry (e.g. tires)

Thank you!