Gerhard Lammel: "Trends and Advances in Atmospheric and Environmental Chemistry"

Cloud chemistry: Ozone, acidity formation, dimethyl sulphide
Atmospheric aerosol, its composition, surface and bulk particle reactions

Cloudwater - introduction, significance

- 15% of the volume of the troposphere filled with clouds
- liquid water content $L = 0.1\text{-}2 \times 10^{-6}\ V_{water}/V_{air} = 0.1\text{-}2$ g/m³
$= (0.1\text{-}2) \times 10^{-3}$ L/m³ $< 10\%$ of total water content (10-40 g/m³!) only $\approx 10\%$ of clouds will rain out, while 90% will recycle aerosol particles
- lifetime of clouds hours-days, of cloud droplets (D=5-50 µm) minutes
- aqueous composition: dissolved ($c_i \approx 10^{-6}$ - 10^{-3} M) + eventually non-dissolved constituents, droplet-size dependent, $c_i(D)$
- humidity/supersaturation S (:=rh-1) is altitude (above cloud base)-dependent
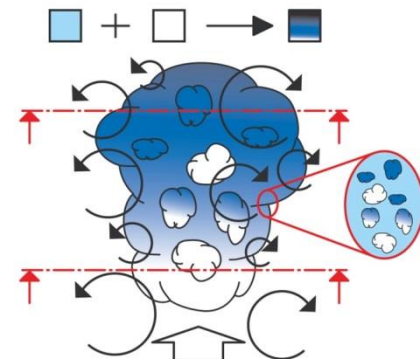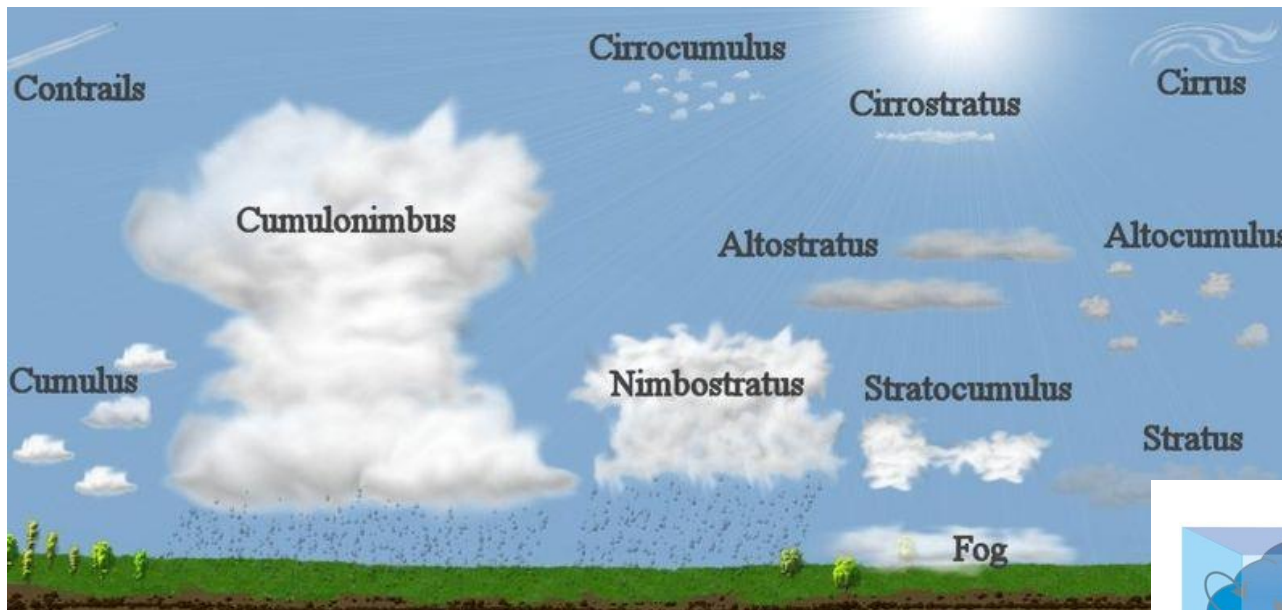
Terminology:

- Hydrometeors = cloud droplets + ice particles + rain droplets + snow flakes + graupel + ...
- Wet deposition = rain + snow fall + rime
- Wash-out = below-cloud scavenging + in-cloud scavenging of both gases and particles
- in-cloud scavenging of gases = dissolution
- Occult deposition = droplet deposition from clouds, fogs else than rain or snow fall

some units:

- 1 M = 1 mol/L
- pH 7 $\leftrightarrow c_{H3O+} = 10^{-7}$ M

Henry coefficients

**Solubility increases with decreasing temperatures,
e.g. 78, 63 and 53% of O_2 at 0°C is soluble at 10, 20 and 30°C, respectively.**

Table 3 Henry's law partition coefficients $K_H^\ominus$ at $T = 298$ K, heats of vaporization ΔH_{soln} divided by the gas constant R_g, mass accommodation coefficients α, transfer coefficients k_t, and the associated time constants for the approach to Henry's law equilibrium

Constituent	$K_H^{\ominus\,a}$ /mol dm^{-3} atm^{-1}	$(\Delta H_{soln}/R_g)$ /K	$R_g T K_H$	α^b	$k_t{}^c$/s^{-1}	$\tau_H{}^d$/s	Ref.^{e}
O_2	1.3×10^{-3}	1500	3.8×10^{-2}	0.01*	5.3×10^2	8.9×10^{-8}	19
O_3	1.1×10^{-2}	2300	3.7×10^{-1}	0.004	5.3×10^2	2.1×10^{-6}	20
OH	3.0×10^1	4500	1.9×10^3	0.004	3.5×10^5	3.9×10^{-3}	21
HO_2	4.0×10^3	5900	2.3×10^5	0.01	4.2×10^5	8.2×10^{-1}	21
H_2O_2	1.0×10^5	6300	6.1×10^6	0.11	1.0×10^6	5.9	22
CH_3OOH	3.0×10^2	5300	1.6×10^4	0.004	1.8×10^5	4.5×10^{-2}	22
CH_3OO	6.0	–	1.4×10^2	0.01*	5.3×10^2	4.0×10^{-4}	23
CH_3OH	2.2×10^2	4900	1.1×10^4	0.02	6.4×10^5	1.7×10^{-2}	24
HCHO	3.0×10^3	7200	2.1×10^5	0.01*	4.4×10^5	4.8×10^{-1}	25
HCOOH	5.5×10^3	5700	3.1×10^5	0.013	4.6×10^5	4.5	26
CO_2	3.4×10^{-2}	2400	1.1	2×10^{-4}	5.3×10^2	1.1×10^{-4}	10
NO	1.9×10^{-3}	1500	5.6×10^{-2}	0.02*	5.3×10^2	8.4×10^{-8}	27
NO_2	7.0×10^{-3}	2500	2.4×10^{-1}	0.001*	5.3×10^2	2.1×10^{-6}	28
NO_3	2.0	2000	6.4×10^1	0.003	5.3×10^2	3.4×10^{-4}	29
N_2O_5	∞	–	–	0.02	3.5×10^5	–	
HNO_2	5.0×10^1	4900	2.5×10^3	0.05	7.5×10^5	5.0×10^{-2}	30
HNO_3	$2.4 \times 10^6/K_d$	8700	1.5×10^7	0.05	6.5×10^5	2.8×10^2	31
$HOONO_2$	1.4×10^4	–	3.2×10^5	0.01*	2.7×10^5	1.6	32
NH_3	6.1×10^1	4200	2.7×10^3	0.09	1.4×10^6	2.8×10^2	33
SO_2	1.2	3200	4.6×10^1	0.1	7.5×10^5	4.3×10^{-2}	34
SO_3	∞	–	–	0.01*	2.7×10^5	–	

Compilation of K_H :
• Warneck, Phys. Chem. Chem. Phys. 1 (1999) 5471-5483
• download from Rolf Sander's webpage, MPI-C
          http://www.mpch-mainz.mpg.de/~sander/res/henry.html

Sulfuric acid formation in the aqueous phase
Dissolution of gases - thermodynamic equilibrium

...with diluted solutions (ideal behaviour).
The in-cloud scavenged fraction of gaseous molecules is dependent on water solubility:

$\varepsilon_{i(g)}$ $= n_{i(aqu)} / (n_{i(aqu)} + n_{(g)}) = n_{i(aqu)} / [n_{i(aqu)} + p_i V_{air}/(R_g T)] =$
$= n_{i(aqu)} / [n_{i(aqu)} + H_i n_{i(aqu)} V_{air}/(R_g T n_{H2O})] =$
$= [1 + H_i M_w/(R_g T L)]^{-1}$

with: Henry coefficient H_i [at] $= p_i n_{i(aqu)}/n_{H2O} = p_i x_i = p_i/(c_i/10^3/M_w)$,
liquid water content L [g/m³]
gas constant $R_g = 8.206 \times 10^{-5}$ m³ at/mol/K, M_w[g/mol], 10^3[cm³/L]

(*Warneck, 1986*)

Another, more common Henry coefficient:

K_H [M at^{-1}] $= 10^2$ s/M_wp $= (10^3/M_w) \times \rho_{H2O}/H$
solubility s(T) [mg/L] $= s(T_0) \times \exp[-\Delta H_{sol}/R_g \times (1/T-1/T_0)]$

... confusing: there are more common so-called 'Henry coefficients':

Air-water partitioning coefficient K_{aw} [ ] $= M_w p/(10^5 R_g Ts) = 1/ (10^3 R_g T K_H)$
Henry coefficient H' [Pa m³/mol] $= R_g T K_{aw} = 10^{-2}/K^H$[M/at]

Tropospheric ozone and clouds

Ozone reactions
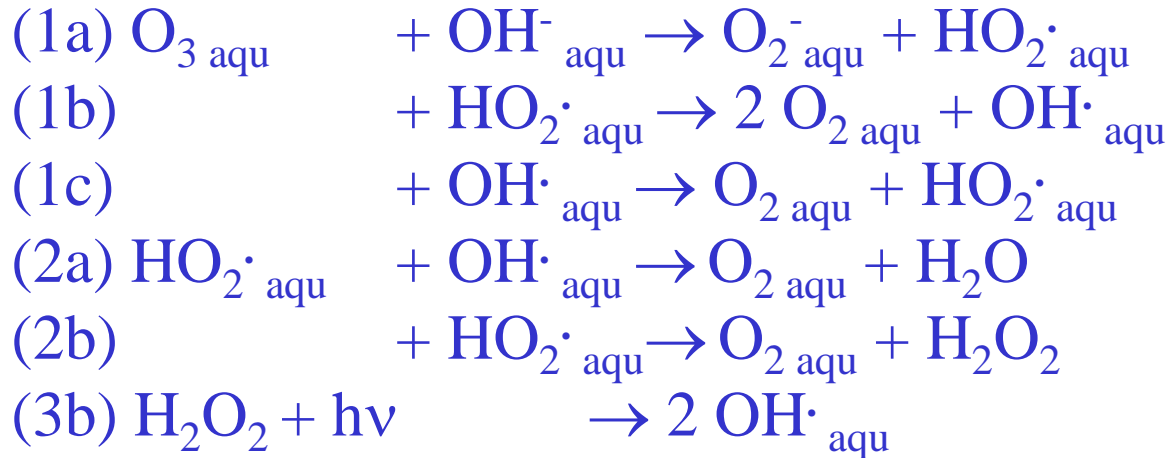
Ozone is a source of radicals and H_2O_2 in cloudwater:

(1a) $O_{3\ aqu}$ $+ OH^-_{\ aqu} \rightarrow O^-_{2\ aqu} + HO_2^{\cdot}{}_{aqu}$

(1b) $\qquad\qquad + HO_2^{\cdot}{}_{aqu} \rightarrow 2\ O_{2\ aqu} + OH^{\cdot}{}_{aqu}$

(1c) $\qquad\qquad + OH^{\cdot}{}_{aqu} \rightarrow O_{2\ aqu} + HO_2^{\cdot}{}_{aqu}$

(2a) $HO_2^{\cdot}{}_{aqu}$ $+ OH^{\cdot}{}_{aqu} \rightarrow O_{2\ aqu} + H_2O$

(2b) $\qquad\qquad + HO_2^{\cdot}{}_{aqu} \rightarrow O_{2\ aqu} + H_2O_2$

(3b) $H_2O_2 + h\nu$ $\qquad \rightarrow 2\ OH^{\cdot}{}_{aqu}$

TABLE 1. Gas-phase, gas–liquid equilibrium and aqueous-phase reactions

Gas-phase reactions		Rate constant*		Ref.
G1	$O_3 + h\nu \rightarrow O(^1D) + O_2$	1.6×10^{-5}		27
G2	$O_3 + h\nu \rightarrow O + O_2$	3.6×10^{-4}		27
G3	$NO_2 + h\nu \rightarrow NO + O$	5.6×10^{-3}		27
G4	$H_2O_2 + h\nu \rightarrow 2OH$	4.6×10^{-6}		27
G5	$CH_2O + h\nu + 2O_2 \rightarrow 2HO_2 + CO$	1.7×10^{-5}		27
G6	$CH_2O + h\nu \rightarrow H_2 + CO$	3.3×10^{-5}		27
G7	$CH_3OOH + h\nu + O_2 \rightarrow CH_2O + HO_2 + OH$	4.6×10^{-6}		27
G8	$NO_3 + h\nu \rightarrow NO + O_2$	1.4×10^{-2}		27
G9	$NO_3 + h\nu + O_2 \rightarrow NO_2 + O_3$	1.2×10^{-1}		27
G10	$HNO_3 + h\nu \rightarrow NO_2 + OH$	3.2×10^{-7}		27
G11	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	2.7×10^{-5}		27
G12	$O(^1D) + M \rightarrow O + M$	$2.0 \times 10^{-11} \exp(100/T)$		27
G13	$O + O_2(+M) \rightarrow O_3(+M)$	1.5×10^{-15}		27
G14	$O(^1D) + H_2O \rightarrow 2OH$	2.2×10^{-10}		27
G15	$O_3 + NO \rightarrow NO_2 + O_2$	$2.0 \times 10^{-12} \exp(-1,400/T)$		27
G16	$O_3 + HO_2 \rightarrow OH + 2O_2$	$1.1 \times 10^{-14} \exp(-500/T)$		27
G17	$O_3 + OH \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-940/T)$		27
G18	$NO_2 + OH(+M) \rightarrow HNO_3(+M)$	1.2×10^{-11}		27
G19	$HO_2 + NO \rightarrow NO_2 + OH$	$4.6 \times 10^{-11} \exp(230/T)$		27
G20	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$3.3 \times 10^{-12} \exp(-200/T)$		27
G21	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.3 \times 10^{-13} \exp(600/T)$		27
G22	$HO_2 + NO \rightarrow NO_2 + OH$	$3.7 \times 10^{-12} \exp(240/T)$		27
G23	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.4 \times 10^{-13} \exp(-2,500/T)$		27
G24	$NO + NO_3 \rightarrow 2NO_2$	$1.7 \times 10^{-11} \exp(150/T)$		27
G25	$NO_2 + NO_3(+M) \rightarrow N_2O_5(+M)$	$8.1 \times 10^{-11} (T/300)^{-4.1}$		28
G26	$N_2O_5(+M) \rightarrow NO_2 + NO_3(+M)$	$4.6 \times 10^{16} (T/300)^{-4.4} \exp(-11,080/T)$		28
G27	$CH_4 + OH + O_2(+M) \rightarrow CH_3O_2 + H_2O(+M)$	$2.3 \times 10^{-12} \exp(-1,700/T)$		27
G28	$CH_3O_2 + NO + O_2 \rightarrow CH_2O + HO_2 + NO_2$	$4.2 \times 10^{-12} \exp(180/T)$		27
G29	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	4.0×10^{-12}		29
G30	$CH_3O_2 + HO_2 \rightarrow CH_2O + H_2O + O_2$	2.0×10^{-12}		29
G31	$CH_2O + OH + O_2 \rightarrow H_2O + HO_2 + CO$	1.1×10^{-11}		28
G32	$CH_3OOH + OH \rightarrow CH_2O + OH + H_2O$	4.4×10^{-12}		30
G33	$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	5.6×10^{-12}		30
G34	$CO + OH + O_2 \rightarrow CO_2 + HO_2$	2.4×10^{-13}		27
G35	$CH_3O_2 + CH_3O_2 + O_2 \rightarrow 2CH_2O + 2HO_2$	$1.9 \times 10^{-13} \exp(220/T)$		27

Gas–aqueous and aqueous-phase equilibria		K_{298}†	$-\Delta H/R$	Ref.
E1	$HO_2 (gas) \rightleftharpoons HO_2 (aq)$	2.0×10^3	6,600	31
E2	$HO_2 (aq) \rightleftharpoons O_2^- + H^+$	3.5×10^{-5}		32
E3	$H_2O_2 (gas) \rightleftharpoons H_2O_2 (aq)$	7.4×10^4	6,615	33
E4	$O_3 (gas) \rightleftharpoons O_3 (aq)$	1.1×10^{-2}	2,300	34
E5	$CH_2O (gas) \rightleftharpoons CH_2(OH)_2$	6.3×10^3	6,425	8
E6	$HCOOH (gas) \rightleftharpoons HCOOH (aq)$	3.7×10^3	5,700	35
E7	$HCOOH (aq) \rightleftharpoons HCOO^- + H^+$	1.8×10^{-4}	-1,510	35
E8	$CH_3OOH (gas) \rightleftharpoons CH_3OOH (aq)$	2.2×10^2	5,653	33
E9	$CH_3O_2 (gas) \rightleftharpoons CH_3O_2 (aq)$	2.0×10^3	6,600	E9=E1‡
E10	$HNO_3 (gas) \rightleftharpoons HNO_3 (aq)$	2.1×10^5	8,700	36
E11	$HNO_3 (aq) \rightleftharpoons NO_3^- + H^+$	15.4		36
E12	$NO (gas) \rightleftharpoons NO (aq)$	1.9×10^{-3}	1,480	36
E13	$NO_2 (gas) \rightleftharpoons NO_2 (aq)$	6.4×10^{-3}	2,500	37
E14	$NO_3 (gas) \rightleftharpoons NO_3 (aq)$	15.0		12
E15	$OH (gas) \rightleftharpoons OH (aq)$	9.0×10^3		38
E16	$CO_2 (gas) \rightleftharpoons CO_2 (aq)$	3.4×10^{-2}	2,420	39
E17	$CO_2 (aq) \rightleftharpoons HCO_3^- + H^+$	4.5×10^{-7}	-1,000	39

Aqueous-phase reactions		K_{298}*	$-E_a/R$§	Ref.
A1	$H_2O_2 + h\nu \rightarrow 2OH$	9.2×10^{-6}		‖
A2	$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2$	3.2×10^{-6}		‖
A3	$CH_2(OH)_2 + OH + O_2 \rightarrow H_2O + HCOOH + HO_2$	2.0×10^9	-1,500	40, 41
A4	$HCOOH + OH + O_2 \rightarrow CO_2 + H_2O + HO_2$	1.6×10^8	-1,500	42
A5	$HCOO^- + OH + O_2 \rightarrow CO_2 + OH^- + HO_2$	2.5×10^9	-1,500	43
A6	$O_3 + O_2^- + H_2O \rightarrow OH + 2O_2 + OH^-$	1.5×10^9	-1,500	44, 45
A7	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$	1.0×10^8	-1,500	46
A8	$HO_2^- + H^+ \rightarrow H_2O_2$	5.0×10^{10}	-1,500	2
A9	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	2.7×10^7	-1,715	47
A10	$N_2O_5 + H_2O \rightarrow 2HNO_3$			¶
A11	$CH_3O_2 + O_2^- + H_2O \rightarrow CH_3OOH + O_2 + OH^-$	5.0×10^7	-1,610	4
A12	$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	2.7×10^7	-1,715	4
A13	$CH_3OOH + OH \rightarrow CH_2(OH)_2 + OH$	1.9×10^7	-1,860	4
A14	$HCO_3^- + OH \rightarrow H_2O + CO_3^-$	1.0×10^7	-1,500	48
A15	$HCO_3^- + O_2^- \rightarrow HO_2^- + CO_3^-$	1.5×10^6	-1,500	48
A16	$CO_3^- + H_2O_2 \rightarrow HO_2 + HCO_3^-$	8.0×10^5	-2,800	49
A17	$CO_3^- + O_2^- \rightarrow O_2 + CO_3^{2-}$	4.0×10^8	-1,500	49

G, E and A are gas-phase reactions, gas–liquid equilibrium and aqueous-phase reactions, respectively. These are the most important reactions from the more extended reaction scheme in the model. Some reactions summarize several reaction steps. Aqueous-phase processes at mid-latitudes in the Northern Hemisphere are simulated at pH 4.5, for other latitudes in Table 2 pH 5 is adopted⁵⁰. Photolysis rate coefficients and water vapour concentrations are kept equal to those during clear sky to emphasize photochemical differences. Daytime average photolysis rates are applied. Accommodation coefficients, as used for gas-to-aqueous-phase transfer processes¹⁴, are taken from refs 51–56. For those components with unknown accommodation coefficients we assume a value of 0.05.

* Reaction rate constants of first-order reactions are in s⁻¹, of second-order reactions in the gas phase (G) in molecule⁻¹ cm³ s⁻¹, in the aqueous phase (A) in mol⁻¹ l s⁻¹. Photodissociation rate constants are calculated per season, latitude and altitude. The given values pertain to the Equator in July, at 700 mbar.

† K_{298} is in mol l⁻¹ atm⁻¹ for Henry's law constants and in mol l⁻¹ for aqueous-phase equilibria. The temperature dependence is calculated by $K = K_{298} \exp[(-\Delta H/R)((1/T) - (1/298))]$.

‡ Assumed.

§ E_a values are taken from ref. 4.

‖ J.L., thesis in preparation.

¶ Gas-to-aqueous-phase transfer of N_2O_5 is limited by gas-phase diffusion and transfer through the interface. We assume that reaction A10 then occurs instantaneously, so that dissolution is irreversible.
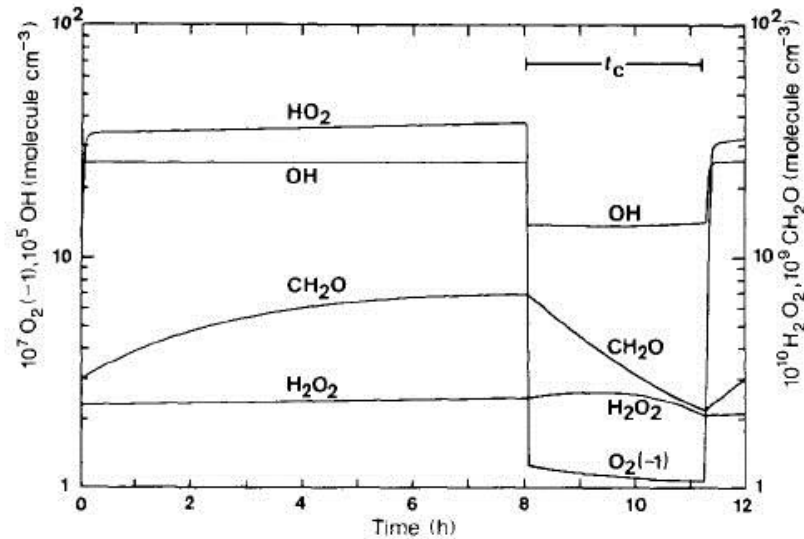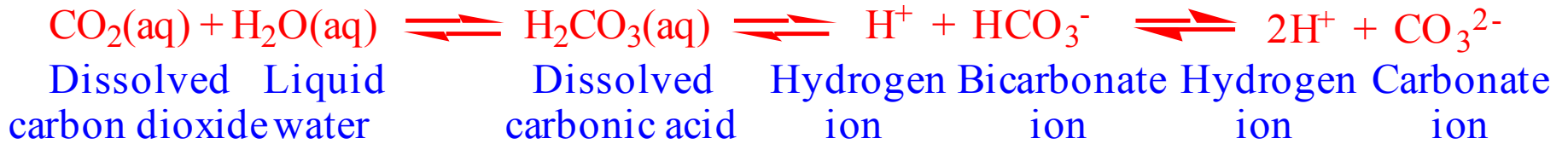

FIG. 2 Concentrations of some gases during sunlit hours of day 14 of the simulations, pertaining to the Equator at 3 km altitude (case 6, Table 2 and 3a), with NO_x fixed. For the cloudy period (t_c) total gas-phase plus aqueous-phase concentrations are depicted. $O_2(-1) = HO_2(gas) + HO_2(aq) + O_2^-$.

Differences in solubility and chemical reactivity in the aqueous phase result in changed (overall) chemistry of the atmosphere.
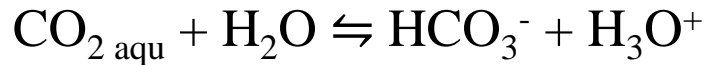
pH dependencies, e.g. O_3 sink A6 $(O_3 + O_2^- + H_2O \rightarrow)$

O_3, OH, NO_x overestimated when clouds are neglected
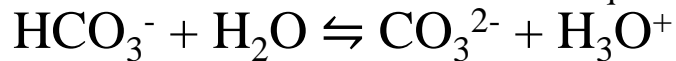
(*Lelieveld & Crutzen, 1990*)

$$CO_2(aq) + H_2O(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

Dissolved carbon dioxide | Liquid water | Dissolved carbonic acid | Hydrogen ion | Bicarbonate ion | Hydrogen ion | Carbonate ion

Solubility of CO_2 (g) $\rightleftharpoons$ $CO_{2\,aqu}$ + 20 kJ/mol

(1) $K_H = c_{CO2\,aqu} / p_{CO2} = 3.4 \times 10^{-7}$ mol/L/Pa (298 K)

$$CO_{2\,aqu} + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

(2) $K_{A1} = (c_{HCO3-}\, c_{H3O+}) / c_{CO2\,aqu} = 10^{-6.35}$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

(3) $K_{A2} = (c_{CO3--}\, c_{H3O+}) / c_{HCO3-} = 10^{-10.33}$

Dissolved fraction is pH dependent, expressed as the effective Henry coeff. H*:

$K_{H\,CO2}{}^* = (c_{CO2\,aqu} + c_{HCO3-} + c_{CO3--}) / p$ (mol/L/Pa)

$K_H{}^* = K_H (1 + K_{A1} / c_{H3O+} + K_{A1}K_{A2} / c_{H3O+}{}^2)$

pH of water in the atmosphere in equilibrium with CO_2 (p_{CO2} = 36 Pa):

(1) in (2): $c_{HCO3-}\, c_{H3O+} = K_{A1}\, K_H\, p_{CO2}$

$c_{HCO3-} = c_{H3O+}$

$c_{H3O+} = (K_{A1}\, K_H\, p_{CO2})^{0.5}$

pH = $-0.5\,(-pK_{A1} - \log K_H - \log p_{CO2})$

pH = $0.5\,(6.35 - \log 3.4 \times 10^{-7} - \log 36) = 5.63$

pH scale

Natural rainwater (5-5.6)

Acid rain, fog (2-5.6)

Sea water (7.8-8.3)

pH

0   1   2   3   4   5   6   7   8   9   10   11   12   13   14

Battery acid (1.0)

Lemon juice (2.2)

Apples (3.1)

Vinegar $CH_3COOH(aq)$ (2.8)

Milk (6.6)

Distilled water (7.0)

Baking soda $NaHCO_3(aq)$ (8.2)

Ammonium hydroxide $NH_4OH(aq)$ (11.1)

Slaked lime $Ca(OH)_2(aq)$ (12.4)

Lye $NaOH(aq)$ (13.0)

More acidic   More basic or alkaline
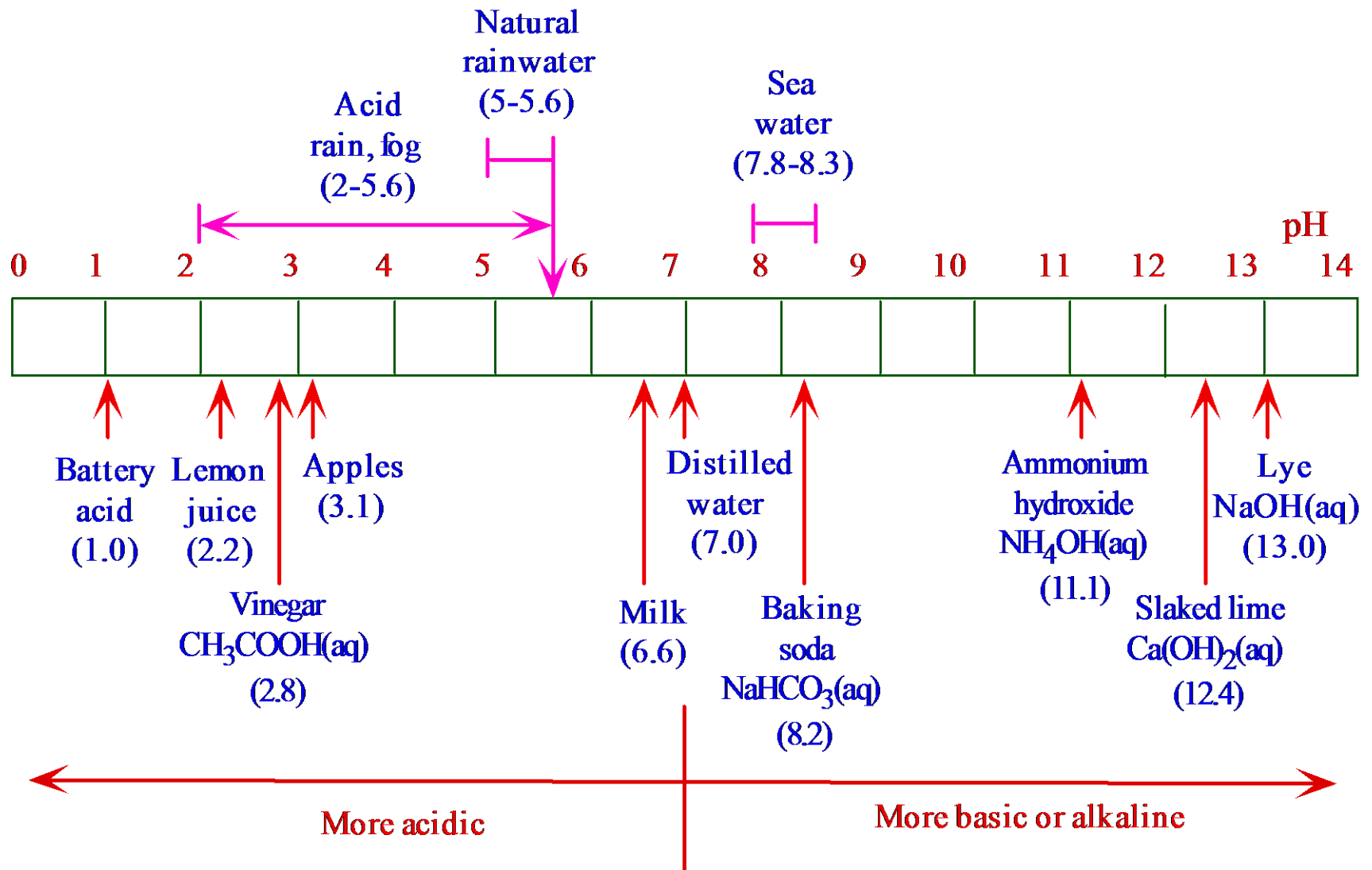
Courtesy: Jacobson

Nitrogen compounds in the aqueous phase

Acidity formation in the troposphere: N

during the day: $NO_2 + OH \rightarrow HNO_3$ fast: 9.2×10^{-12} cm³ molec^{-1} s^{-1}

(Mollner et al., 2010)

during night: $NO_2 + NO_3 \rightleftharpoons N_2O_5$

phase equilibria of N(-III), N(IV), N(V) species:

$NH_3 \rightleftharpoons NH_{3\ aqu.}$
$NO_2 \rightleftharpoons NO_{2\ aqu}$
$HNO_3 \rightleftharpoons HNO_{3\ aqu}$
$N_2O_5 \rightleftharpoons N_2O_{5\ aqu}$

dissociation, hydration N(-III), N(V):

$NH_{3\ aqu} + H_2O \rightarrow NH_{4\ aqu}^+ + OH_{aqu}^-$
$HNO_{3\ aqu} + H_2O \rightarrow H_3O_{aqu}^+ + NO_{3\ aqu}^-$
$2\ NO_2 + 3\ H_2O \rightarrow NO_{2\ aqu}^- + NO_{3\ aqu}^- + 2\ H_3O_{aqu}^+;$ slow *(Lee & Schwartz, 1981)*
$N_2O_{5\ aqu} + 3\ H_2O \rightarrow 2\ H_3O_{aqu}^+ + 2\ NO_{3\ aqu}^-$
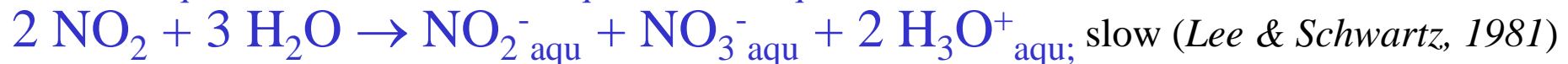
more phase equilibria of N(-III), N(V) species:

$HNO_2 \rightleftharpoons HNO_{2\ aqu}$ $\qquad\qquad\qquad\qquad K_H = 50$ M at^{-1}

$HNO_4 \rightleftharpoons HNO_{4\ aqu}$ $\qquad\qquad\qquad\qquad K_H = 1.4\times10^6$ M at^{-1}

dissociation, hydration N(-III), N(V):

$HNO_{2\ aqu} + H_2O \rightleftharpoons H_3O^+_{\ aqu} + NO_2^-{}_{aqu}$ $\qquad K_A = 0.6\times10^{-5}$ M

$HNO_{4\ aqu} + H_2O \rightleftharpoons H_3O^+_{\ aqu} + NO_4^-{}_{aqu}$ $\qquad K_A = 1.0\times10^{-5}$ M

$HNO_{4\ aqu} \qquad\quad \rightleftharpoons HO_2\cdot_{\ aqu} + NO_{2\ aqu}$ $\qquad K_A = 4.6\times10^{-10}$ M

$NO_4^-{}_{aqu} \qquad\quad \rightarrow O_{2\ aqu} + NO_2^-{}_{aqu}$ $\qquad k = 1.4\times10^{-2}$ s^{-1}

(Lammel et al., 1990)
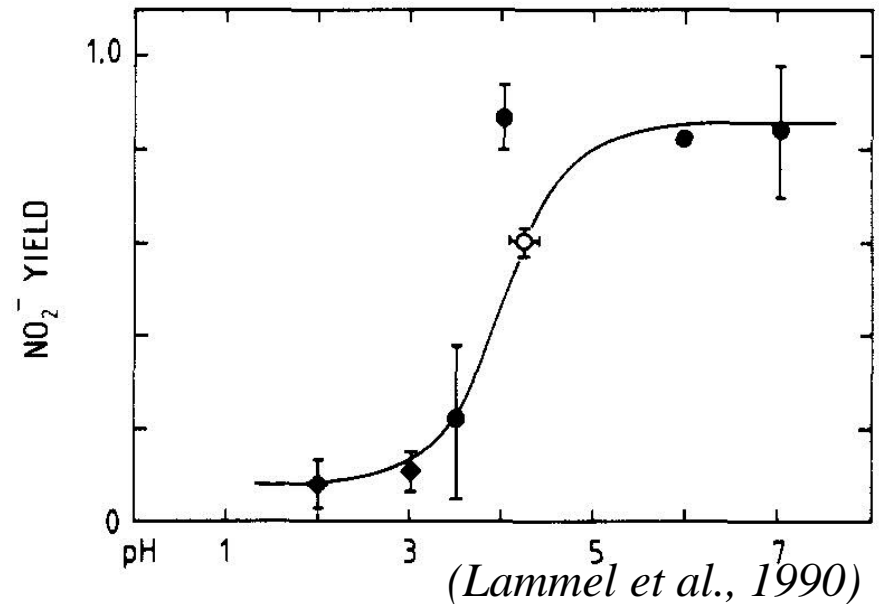
HNO$_3$ production: sources

(1a) $NO_2 + \cdot OH \rightarrow HNO_3$ *(day)*

(1b) $NO_2 + NO_3 \cdot \rightleftharpoons N_2O_5$ *(night)*

(2b) dissolution + hydration:
$N_2O_5 + 3\,H_2O \rightarrow 2\,H_3O^+_{aqu.} + 2\,NO_3^-_{aqu.}$

Crete, 2001-03 *(Vrekoussis et al., 2006)*
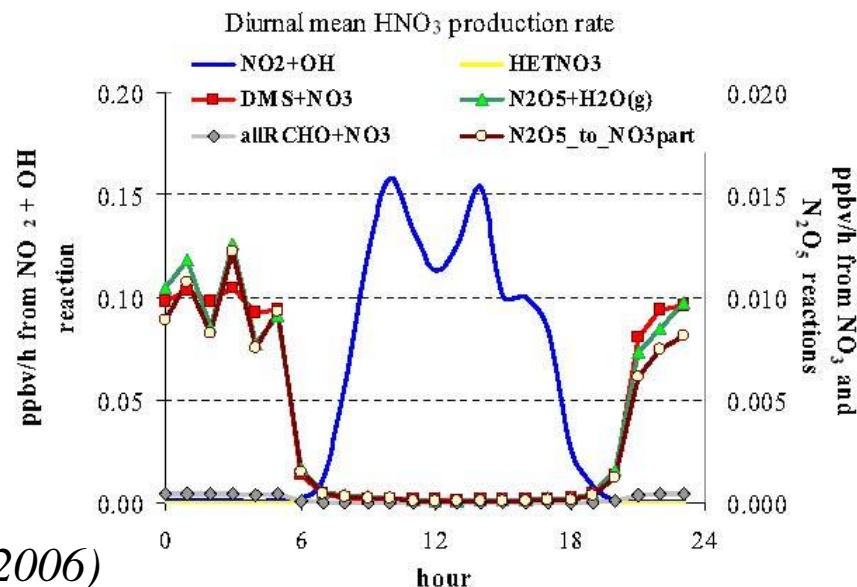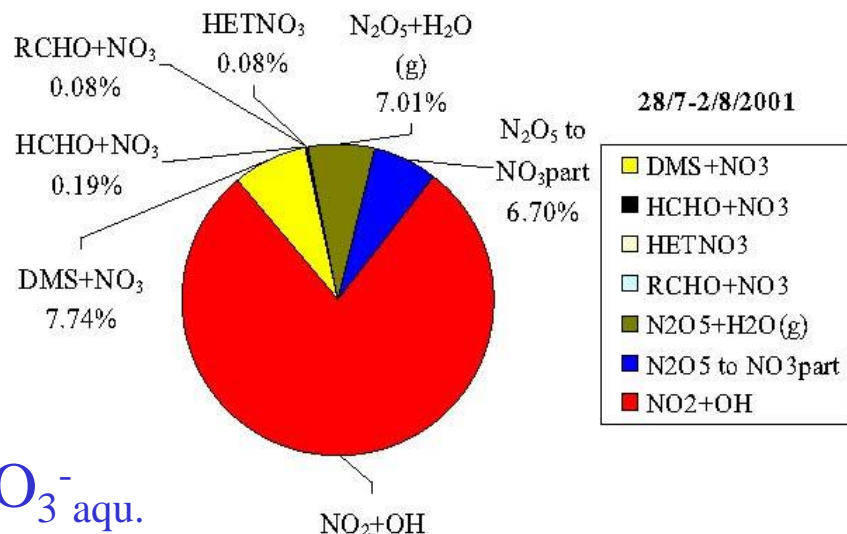
Acids: formation reactions and cloud chemistry
Sulfuric acid formation in the gas-phase

Formation of sulfuric acid in the (**A**) gas-phase:

(1) $SO_2 + OH\cdot \rightarrow HOSO_2\cdot$

(2) $HOSO_2\cdot + O_2 \rightarrow SO_3 + HO_2\cdot$

(3) $SO_3 + 2\ H_2O \rightarrow H_2SO_4 \times H_2O$

net:

(1-3) $SO_2 + OH\cdot + O_2 + 2\ H_2O \rightarrow H_2SO_4 \times H_2O + HO_2\cdot$

Then very fast phase change by nucleation ($\rightarrow$ *3.1 Aer*) and subsequent condensation

Alkenes react readily with ozone: $k \leq 10^{-10}$ cm³ molec⁻¹ s⁻¹

(1) $CH_3CH=CH_2 + O_3$ $\rightarrow$ [primary ozonide]

(2a) [primary ozonide] $\rightarrow CH_3CH(OO\cdot)CH_2O\cdot$ 55%

(3a) decomposition: $\rightarrow CH_3CH\cdot OO\cdot + HCHO$

(3b) + SO_2 $\rightarrow SO_3$ $k \approx 0.6\times10^{-12}$ cm³/molec/s (estimate)

(4b) $SO_3 + 2 H_2O$ $\rightarrow H_2SO_4\times H_2O$ additional gas-phase source for H_2SO_4!
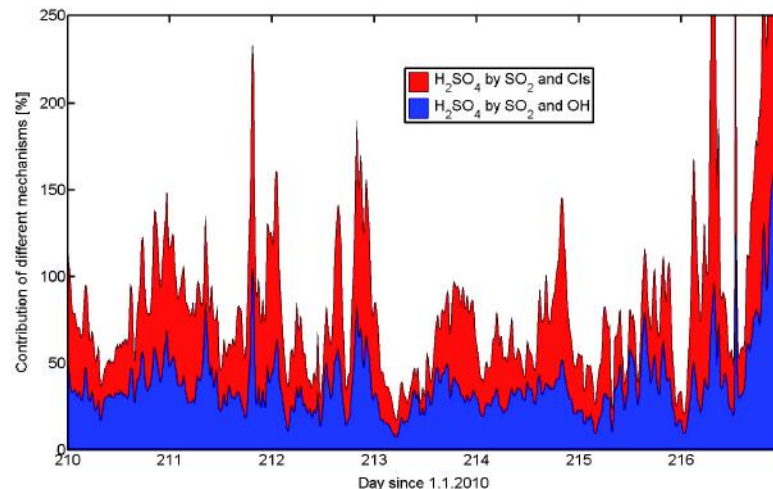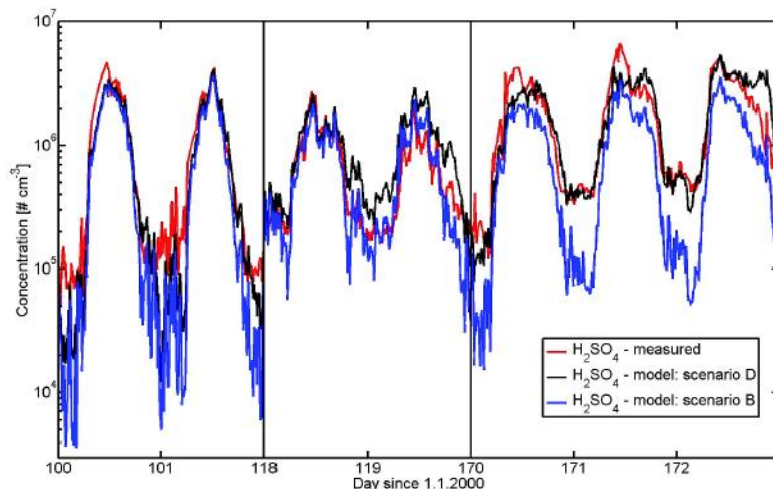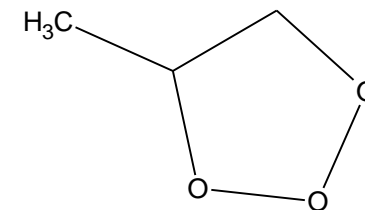
Chemical mechanism modified, Hohenpeissenberg data set; Boy et al.., 2012

However, only 15% of S(VI) is formed in the gas-phase globally,
85% is formed (B) in cloud droplets and humid aerosol particles

S(IV) phase equilibrium and reactions
determined by Henry coeff. K_H, pH, T
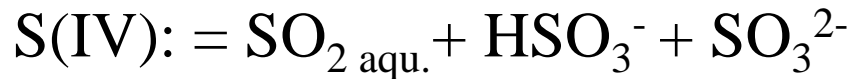
$S(IV): = SO_{2\ aqu.} + HSO_3^- + SO_3^{2-}$

Phase equilibrium (Henry coeff., physical solubility of SO_2):

$$SO_2 \leftrightharpoons SO_{2\ aqu.} \qquad K_{H\ (298K)} := c_{SO2}/p_{SO2} = 1.2 \times 10^{-5}\ M/Pa$$

Dissociation equilibria:

$$SO_{2\ aqu.} + 2\ H_2O \leftrightharpoons HSO_3^- + H_3O^+ \qquad K_{A1\ (298K)} = 1.7 \times 10^{-2}\ M$$

$$HSO_3^-. + H_2O \leftrightharpoons SO_3^{2-} + H_3O^+ \qquad K_{A2\ (298K)} = 6.5 \times 10^{-8}\ M$$
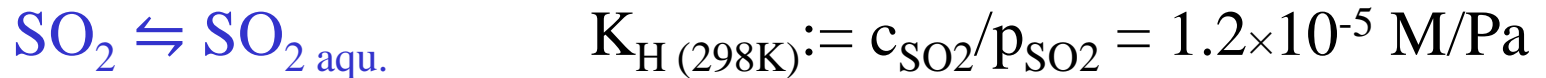
For substances which interact with water to form ions via acid-base dissociation equilibria K_H must be replaced by a modified coefficient K_H^*: („modified Henry coeff.'):

$$K_{H\ (298K)}^* := c_{S(IV)}/p_{SO2} = K_H\ (1 + K_{A1}/c_{H3O+} + K_{A1}K_{A2}/c_{H3O+}^2) = f(pH)$$

... and S(VI) phase equilibrium and dissociation

$S(IV): = SO_{2\ aqu.} + HSO_3^- + SO_3^{2-}$
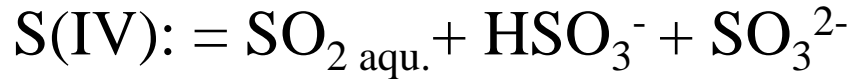
Phase equilibrium (Henry coeff., physical solubility of SO_2), subsequent dissociation:

$$SO_2 \leftrightharpoons SO_{2\ aqu.} \leftrightharpoons HSO_3^- + H_3O^+ \leftrightharpoons SO_3^{2-} + 2\ H_3O^+$$

Sulfur	dissolved	bisulfite	sulfite
dioxide	sulfur		
gas	dioxide		

similarly:

$S(VI): = H_2SO_{4\ aqu.} + HSO_{4\ aqu}^- + SO_{4\ aqu}^{2-}$

$$H_2SO_4(g) \longrightarrow H_2SO_4(aq) \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

Sulfuric	Dissolved	Hydrogen Bisulfate	Hydrogen Sulfate
acid gas	sulfuric acid	ion ion	ion ion
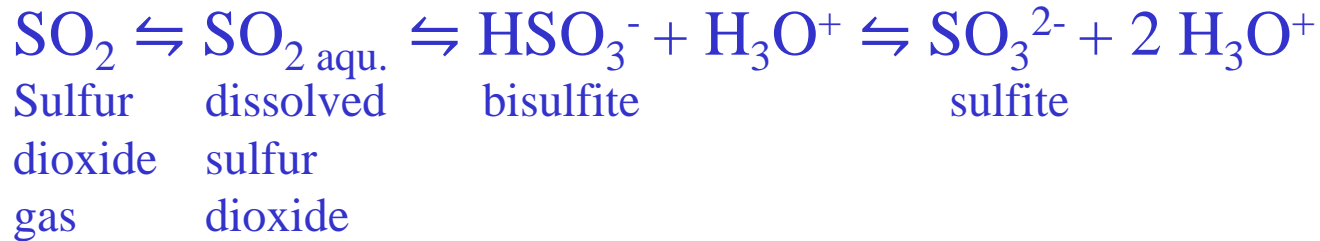
Bulk aqueous phase chemistry
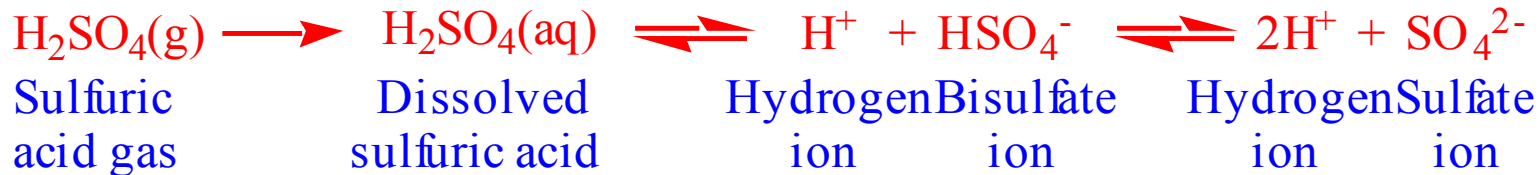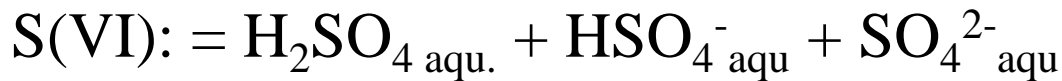
Acid-base dissociation equilibrium

Reaction	$K_{298}/\text{mol dm}^{-3}$	K_{285}
$H_2O \rightleftharpoons H^+ + OH^-$	1.0×10^{-14}	3.6×10^{-15}
$HO_2 \rightleftharpoons H^+ + O_2^-$	1.6×10^{-5}	1.7×10^{-5}
$HCOOH \rightleftharpoons H^+ + HCOO^-$	1.8×10^{-4}	1.8×10^{-4}
$CO_{2a} \rightleftharpoons H^+ + HCO_3^-$	4.3×10^{-7}	3.6×10^{-7}
$HNO_2 \rightleftharpoons H^+ + NO_2^-$	6.1×10^{-4}	4.6×10^{-4}
$HNO_3 \rightleftharpoons H^+ + NO_3^-$	1.5×10^1	1.5×10^1
$HOONO_2 \rightleftharpoons H^+ + NO_4^-$	$-$	1.0×10^{-5}
$NH_3 + H_2O \rightleftharpoons OH^- + NH_4^+$	1.8×10^{-5}	1.7×10^{-5}
$SO_{2a} \rightleftharpoons H^+ + HSO_3^-$	1.7×10^{-2}	2.2×10^{-2}
$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	6.5×10^{-8}	7.7×10^{-8}
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.0×10^{-2}	1.5×10^{-2}

(Warneck, 1999)

Dissociated / undissociated species exist in ratios determined by acidity (pH) and the dissociation constant, K_A. E.g., $SO_{2\ aqu.}$ for pH < -log K_{A1}= 1.7, SO_3^{2-} for pH > -log K_{A2} = 7.1 and HSO_3^- in between.

S(IV) oxidation reactions

(1) $SO_3^{2-}{}_{aqu}$ + $HO_2^\bullet{}_{aqu}$ → $SO_4^{2-}{}_{aqu}$ + $OH^\bullet{}_{aqu}$

HO_2 or HSO_3^-

(2) + $OH^\bullet{}_{aqu}$ → $SO_3^{-\bullet}{}_{aqu}$ + $OH^-{}_{aqu}$ → $SO_5^{-\bullet}{}_{aqu}$ → → $SO_4^{2-}{}_{aqu}$

(3a) $HSO_3^-{}_{aqu}$ + $O_3{}_{aqu}$ → $HSO_4^-{}_{aqu}$ + H_2O k_{3a} = 3.2×10^5 $M^{-1}s^{-1}$

(3b) $SO_3^{2-}{}_{aqu}$ + $O_3{}_{aqu}$ → $SO_4^{2-}{}_{aqu}$ + H_2O k_{3b} = 1.5×10^9 $M^{-1}s^{-1}$

(4) $HSO_3^-{}_{aqu}$ + $H_2O_2{}_{aqu}$ → $HSO_4^-{}_{aqu}$ + H_2O k_4 = 4.0×10^7 c_{H+} $M^{-1}s^{-1}$

$<M^{n+}>$

(5) 2 $HSO_3^-{}_{aqu}$ + $O_2{}_{aqu}$ → 2 $HSO_4^-{}_{aqu}$ "autoxidation" reactions

(Graedel & Weschler, 1981; Warneck, 1999)
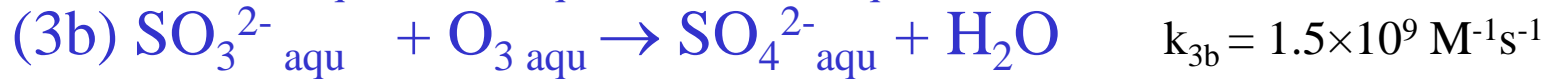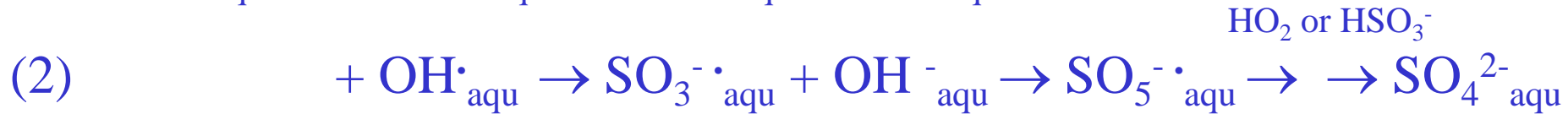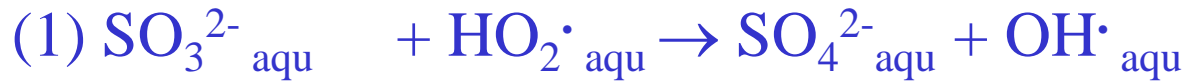
Acidity formation in the troposphere: sulfuric acid

Oxidations are pH dependent, because in individual steps of the reactions of $SO_{2\ aqu}$, $HSO_3^-{}_{aqu}$ and $SO_3^{2-}{}_{aqu}$ (which are present in pH-dependent fractions according to K_{S1}, K_{S2}) is $H^+{}_{aqu}$ consumed or formed.
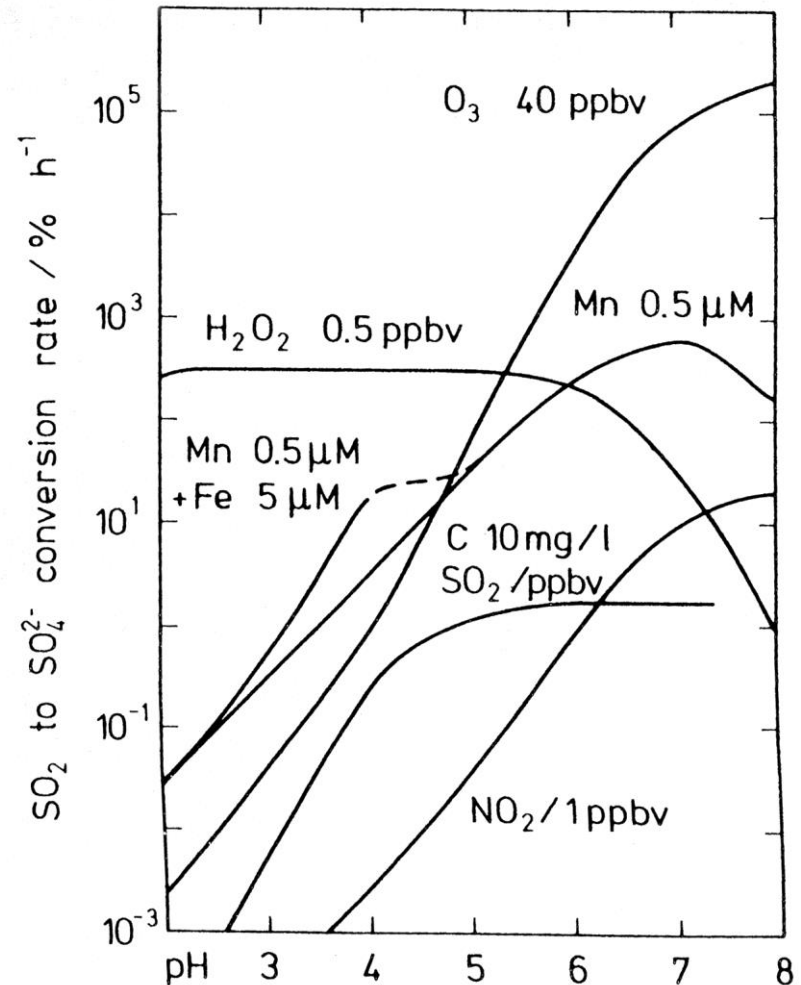
for $L = V_{H2O(l)}/V = 3\times10^{-6}$ (Seinfeld, Calvert)

Rain water pH
SO₂ emissions

pH nach Messungen ... aboratory, 1994
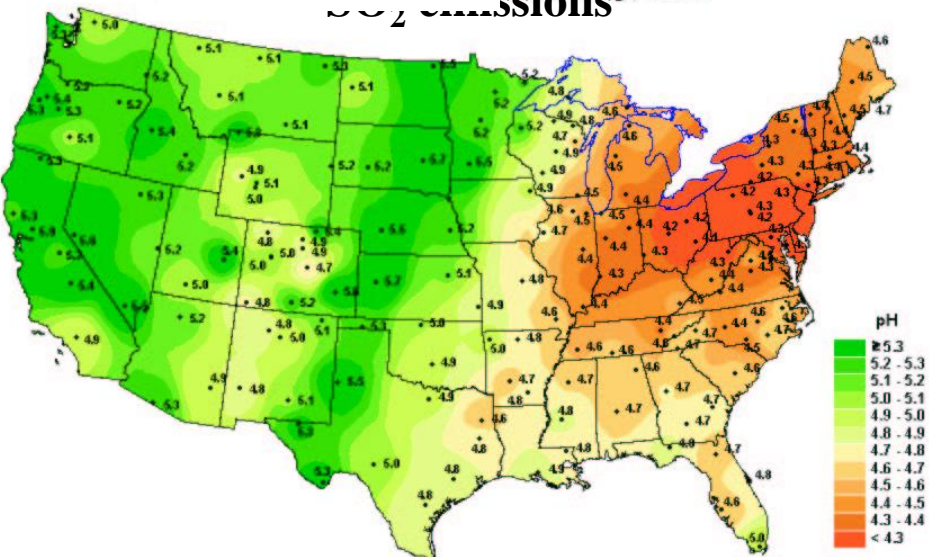
National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

pH-Wert von Regenwasser nach Messungen
des Central Analytical Laboratory, 2000
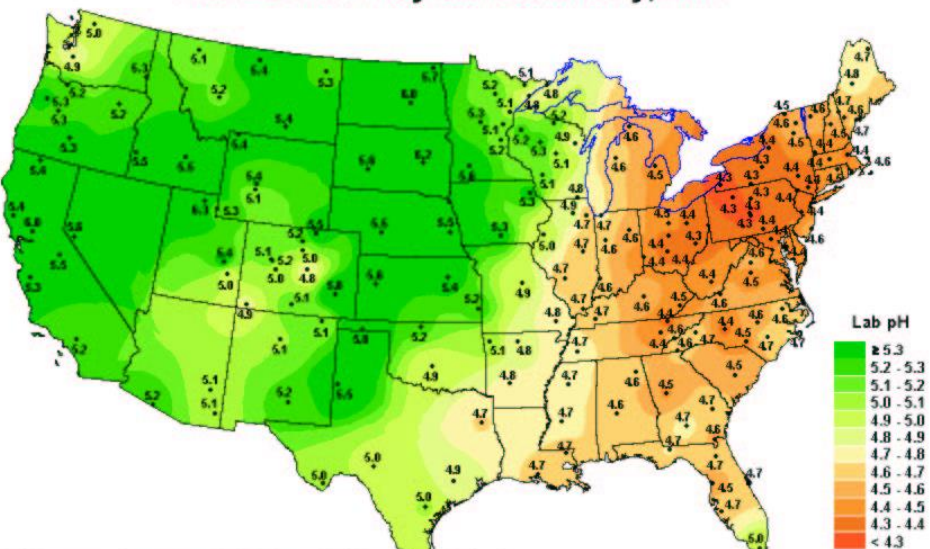
National Atmospheric ...
http://nadp.sws.ed...

Reduction 60% 2010 vs. 1990

Tropospheric trace substances trends: pH, SO₂

Aciditiy of precipitation and SO_2 emissions

- discovery of acid rain 1852 (Smith)
- discovery of acidification of freshwater, Norway 1920
- effects on fishes, 1970
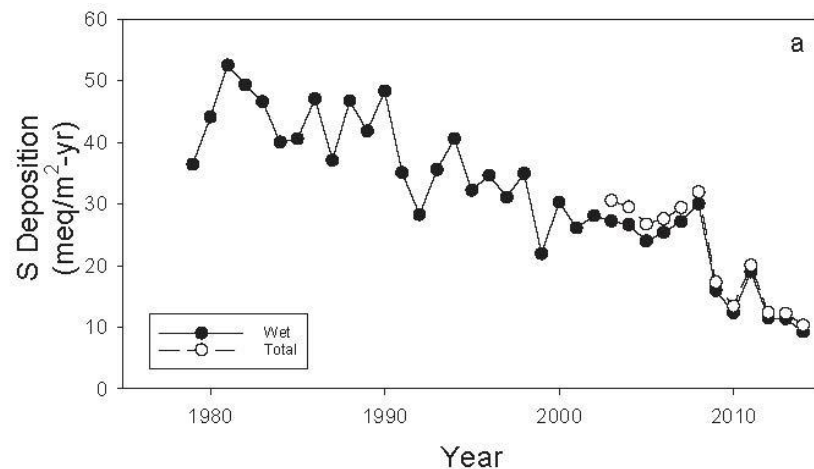
Annual S wet deposition (NADP) and estimated total (USEPA) deposition at Huntington Forest in the central Adirondacks (*Driscoll et al., 2016*)

Tropospheric trace substances trends: pH, SO₂
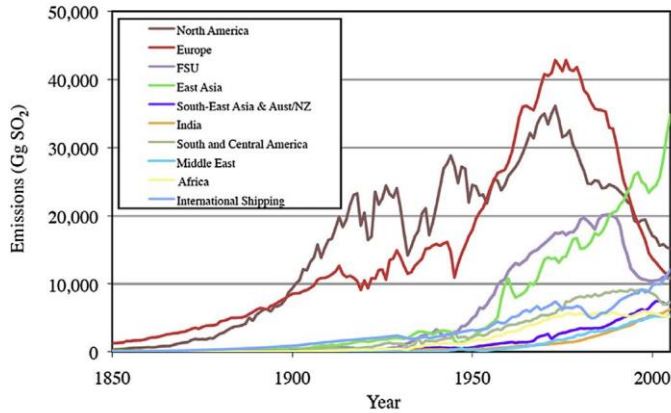
Aciditiy of precipitation and SO_2 emissions

SO₂ emissions

Rain water pH

Duan et al., 2016
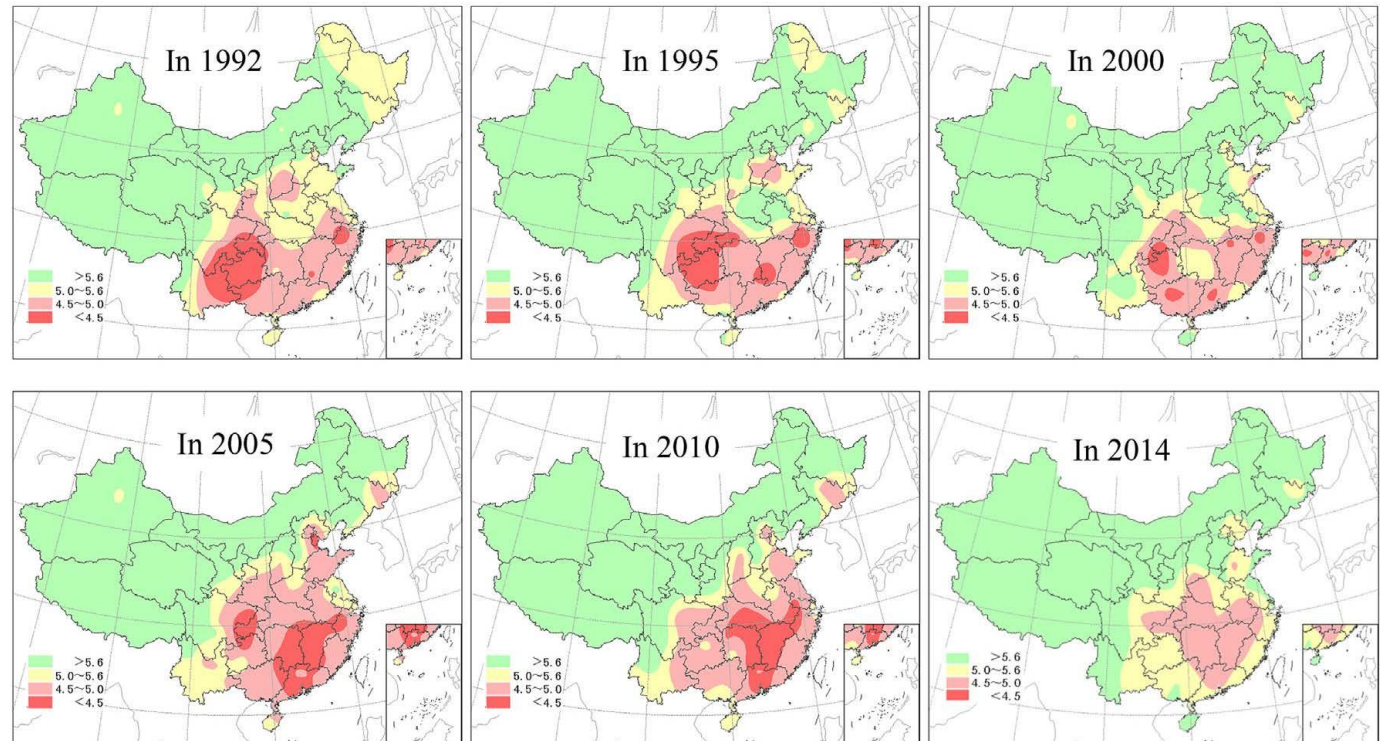
Sulfuric acid: precursors other than anthropogenic SO_2

Aerosol constituents
McDonald Beach
[nmol/m³]

seasalt-S(VI)/Cl⁻ = 0.051

Date	Na⁺	Cl⁻	NO₃⁻	SO₄²⁻	NSSS	MSA
05-06/1/92	164	37.5	1.11	9.28	7.34	2.97
06-07/1/92	154	30.8	3.50	13.2	11.6	3.46
07-08/1/92	27.8	47.3	2.87	9.21	6.77	1.08
08-09/1/92	160	58.2	1.48	8.21	5.19	0.94
09-10/1/92	104	24.6	1.18	8.23	7.17	2.43
11-13/1/92	19.5	47.9	1.00	5.53	3.05	0.93
13-14/1/92	210	8.34	0.69	7.69	7.20	2.83
14-15/1/92	9.26	25.9	1.00	7.51	6.20	1.98
15-16/1/92	150	61.6	1.55	11.9	8.70	1.68
17-18/1/92	169	110	0.76	15.0	9.24	0.60
18-19/1/92	320	269	0.92	18.4	4.51	1.16
19-20/1/92	66.4	49.9	0.74	9.24	6.66	1.90
20-21/1/92	134	63.0	0.81	7.70	4.44	1.38

Terminology:
- NSSS = non-sea salt sulfate
- DMS = dimethylsulfide, CH_3SCH_3
- MSA = methanesulfonate, $CH_3SO_3^-$

Dimethylsulfide

Formation of SO$_2$

(Gas-phase chemistry)

(1) $CH_3SCH_3 + OH \rightarrow CH_3SCH_2\cdot + H_2O$

$CH_3SCH_2\cdot + O_2 + M \rightarrow CH_3SCH_2OO\cdot + M$

(2) $CH_3SCH_2OO\cdot + NO \rightarrow CH_3SCH_2O\cdot + NO_2$
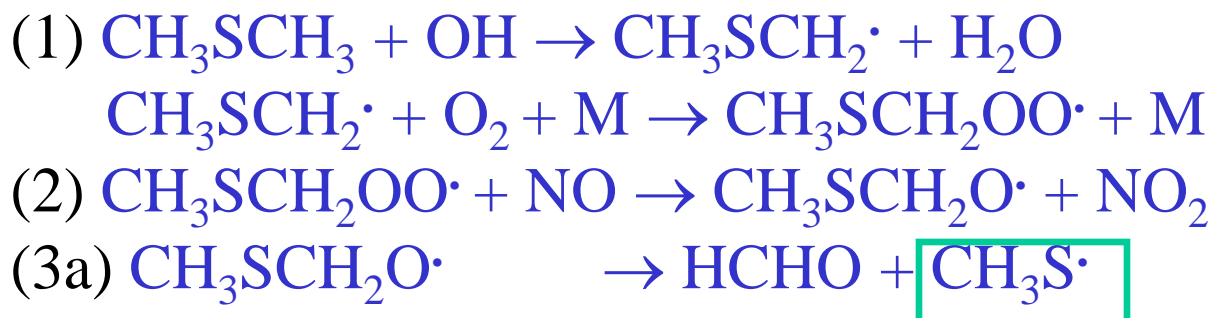
(3a) $CH_3SCH_2O\cdot \rightarrow HCHO + \boxed{CH_3S\cdot}$ **major**

Formation of SO$_2$

in the marine
boundary layer:
CH$_3$SCH$_3$ $\rightarrow$ $\rightarrow$ CH$_3$S$^.$
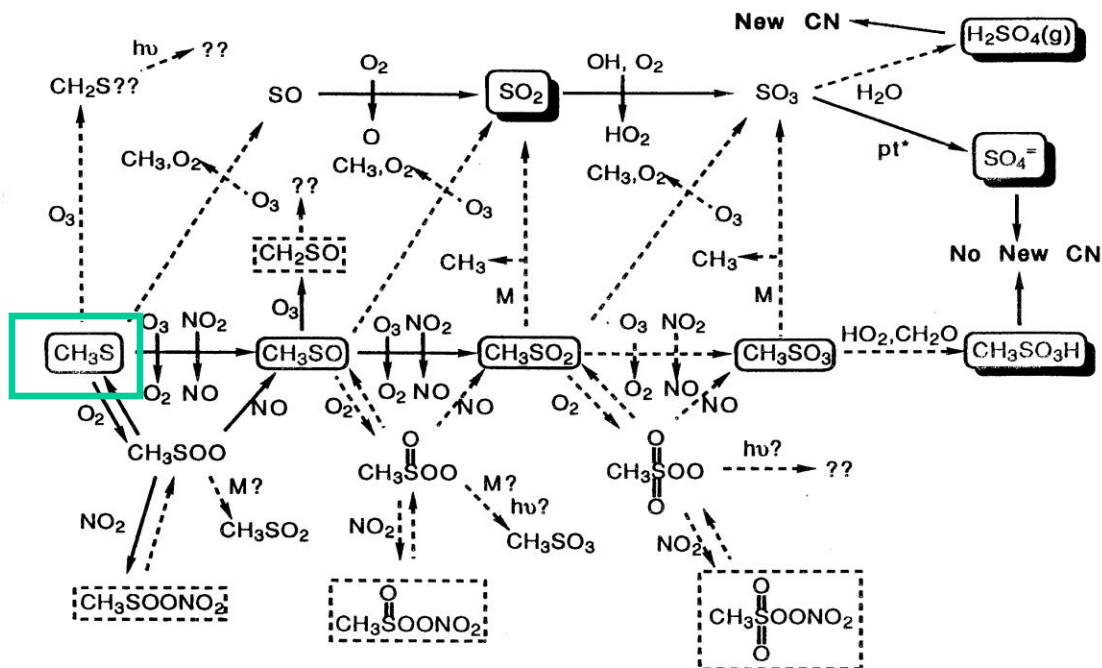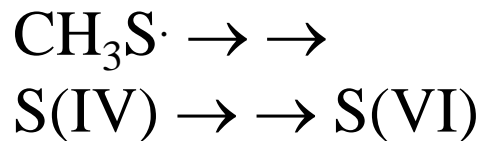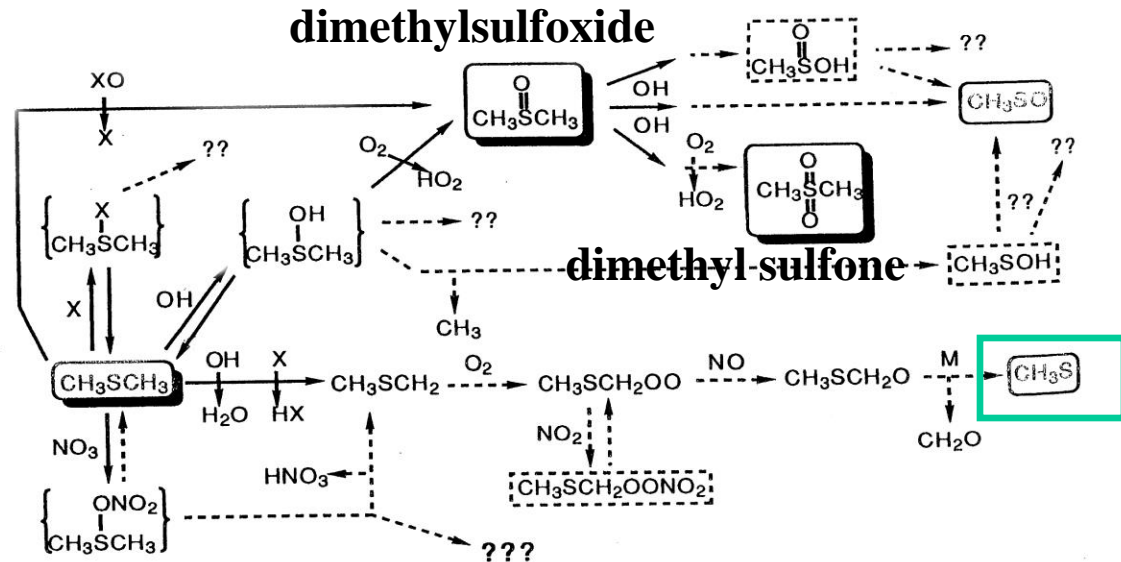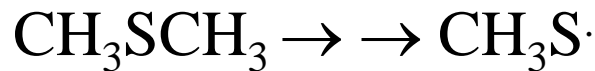
CH$_3$S$^.$ $\rightarrow$ $\rightarrow$
S(IV) $\rightarrow$ $\rightarrow$ S(VI)

Hypothetical negative feedback mechanism in the marine boundary layer:

CH_3SCH_3 emission
→ more clouds
→ less radiative flux
→ less phytoplankton
→ less CH_3SCH_3 emission

(CLAW hypothesis; *Charlson et al., 1987*)

Number concentration of cloud droplets (fixed LWC)

Scattering of solar radiation by droplets +

Cloud albedo

Cloud nucleation +

Reflection of solar radiation −

CCN

Formation of water-soluble particles +

NSS-SO₄²⁻

Surface temperature of earth

Solar irradiance below clouds

Oxidation +

DMS (gas)

Sea-to-air transport +

Atmosphere

Ocean

DMS (aq)

Production of DMS by marine phytoplankton
0/+/−?

Formation of carbonyl sulfide, COS

(Gas-phase chemistry)

(1) $CH_3SCH_3 + OH \rightarrow CH_3SCH_2{\cdot} + H_2O$

$\quad\ CH_3SCH_2{\cdot} + O_2 + M \rightarrow CH_3SCH_2OO{\cdot} + M$

(2) $CH_3SCH_2OO{\cdot} + NO \rightarrow CH_3SCH_2O{\cdot} + NO_2$

(3a) $CH_3SCH_2O{\cdot} \qquad\ \rightarrow HCHO + CH_3S{\cdot}$ **major**

(3b) $\qquad\qquad\ + O_2 \rightarrow CH_3SCHO + HO_2{\cdot}$ **minor**

(4b) $CH_3SCHO + OH{\cdot} \rightarrow CH_3{\cdot} + COS + H_2O$

The COS yield is much smaller than 1 molecule per CH_3SCH_3 molecule, because of
- decomposition of the alkoxy radical CH_3SCH_2O (3a) and
- much of the intermediate products are washed out ($\tau <$ week).

Stratospheric aerosol

As $\tau_{COS} \approx$ years it is transported globally and reaches the stratosphere.

COS stratospheric chemistry:

Its photolysis there produces SO_2:

(1a) COS $+ h\nu$ $\rightarrow S^*$
(2) S^* $+ O_2$ $\rightarrow SO + O\cdot$
(1b) $O\cdot$ $+ COS$ $\rightarrow SO + CO$
(3) SO $+ O_2$ $\rightarrow SO_2 + O\cdot$ (Crutzen, 1983)
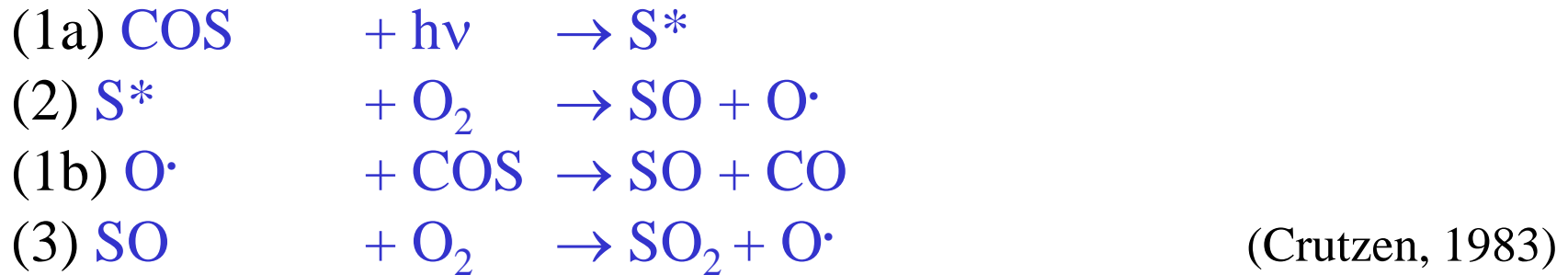
From SO_2 H_2SO_4 is formed which explains the <u>stratospheric sulfate layer</u> during periods of low volcanic activity

Other carbonyl sulfide, COS, sources, else than CH_3SCH_3 chemistry

(1a) CS_2 $+ OH + O_2$ $\rightarrow COS + SO_2 + H\cdot$
(1b) $+ h\nu$ $\rightarrow CS_2^*$
(2b) CS_2^* $+ O_2$ $\rightarrow COS + O\cdot$ (Crutzen, 1983)
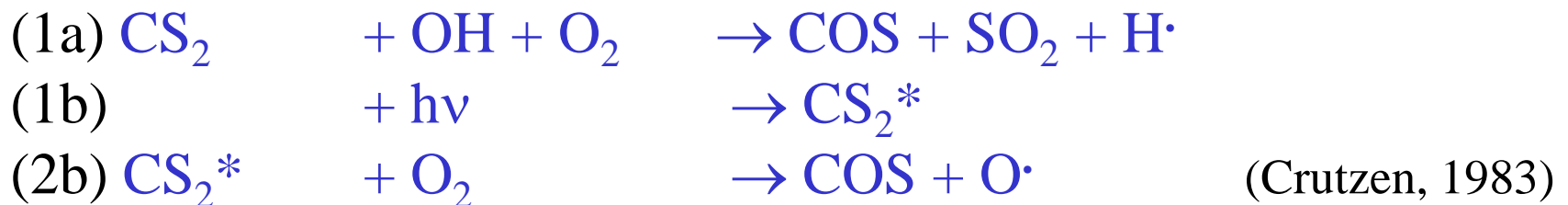
Heterogeneous reactions in the gas/water droplet system
In phase equilibrium

Acidity formation in the troposphere: sulfuric acid

Example: c_{SO2} = 2 nmol m^{-3}, c_{H2O2} = 40 nmol m^{-3}, T = 298 K
(near Bermuda 1988)

1. Gas-phase: $dc_{S(VI)}/dt$ = 5.6×10^{-6} nmol m^{-3} s^{-1}

2. Aqueous phase (L =3×10^{-8}, pH=7):

$dc_{SO4--}/dt = k_4\, p_{H2O2}\, K_{H\,H2O2}\, p_{SO2}\, K^*_{H\,SO2}$ (M s^{-1})
$= (4×10^7× 10^{-7}) × 40×10^{-9}× 1×10^5× 2×10^{-9}× 3.4×10^5$

$K^*_{H\,SO2} = K_{H\,SO2} × (1 + K_{A1}\, /\, c_{H+} + K_{A1}K_{A2}\, /\, c^2_{H+}) =$
$= 3.4×10^5$ M/atm

$dc_{S(VI)}/dt = dc_{S(VI)}/dt$ (M s^{-1}) × L (L m^{-3}) × 10^9 (nmol mol^{-1}) =
$= 32×10^{-6}$ nmol m^{-3} s^{-1}

Reactivity of organics in the aqueous phase: Overview OH reactions

TABLE 21. Rate Constants for Reactions of Organic Compounds in Aqueous Solution

Reaction	$k_{23°C}$ [L/mol/s]	Reference
$CH_3 \cdot + O_2 \rightarrow CH_3O_2 \cdot$	$(4.7 \pm 0.7) \times 10^9$	Thomas [1967]
$R \cdot + O_2 \rightarrow RO_2 \cdot$	$\sim 3 \times 10^9$	Howard [1973]
$HCHO + H_2O \rightarrow CH_2(OH)_2$	(9.8 ± 0.8)	Sutton and Downes [1972]
$HOCH_2O_2 \cdot \rightarrow HCHO + HO_2 \cdot$	(9.9 ± 2.5)	Downes and Sutton [1973]
$OH \cdot + CH_4 \rightarrow CH_3 \cdot + H_2O$	$(1.2 \pm 0.4) \times 10^8$	FR
$OH \cdot + HCHO \rightarrow CHO \cdot + H_2O$	$(6.9 \pm 1.7) \times 10^8$	FR
$OH \cdot + CH_3OH \rightarrow CH_2OH \cdot + H_2O$	$(9.4 \pm 2.3) \times 10^8$	FR
$OH \cdot + CH_2=CH_2 \rightarrow HOCH_2CH_2 \cdot$	$(4.8 \pm 1.2) \times 10^9$	FR
$OH \cdot + CH_3CHO \rightarrow products$	$(5.0 \pm 1.2) \times 10^8$	FR
$OH \cdot + CH_3CH_2OH \rightarrow CH_3CHOH \cdot + H_2O$	$(1.8 \pm 0.5) \times 10^9$	FR
$OH \cdot + CH_3C(O)CH_3 \rightarrow products$	$(9.7 \pm 2.4) \times 10^7$	FR
$OH \cdot + \triangle CHO \rightarrow$	$(7.0 \pm 1.8) \times 10^9$	FR
$OH \cdot + \wedge^{OH} \rightarrow \wedge^{OH} + H_2O$	$(3.0 \pm 0.8) \times 10^9$	FR
$OH \cdot + {}^{HO}\wedge^{OH} \rightarrow products$	$(2.0 \pm 0.5) \times 10^9$	FR
$OH \cdot + \wedge \rightarrow products$	$(7.7 \pm 1.9) \times 10^9$	FR
$OH \cdot + \wedge \rightarrow products$	$(7.7 \pm 1.9) \times 10^9$	FR
$OH \cdot + \wedge^{CHO} \rightarrow products$	$(3.8 \pm 1.0) \times 10^9$	FR
$OH \cdot + \rightarrow products$	$(9.0 \pm 2.2) \times 10^8$	FR
$OH \cdot + \wedge_{OH} \rightarrow products$	$(4.6 \pm 1.2) \times 10^9$	FR
$OH \cdot + \wedge\wedge^{OH} \rightarrow products$	$(5.5 \pm 1.4) \times 10^9$	FR
$OH \cdot + \square \rightarrow \square \cdot + H_2O$	$(3.0 \pm 0.8) \times 10^9$	FR
$OH \cdot + \wedge\wedge_{OH} \rightarrow products$	$(5.9 \pm 1.5) \times 10^9$	FR
$OH \cdot + {}^{HO}\wedge\wedge_{OH} \rightarrow products$	$(4.6 \pm 1.2) \times 10^9$	FR
$OH \cdot + \bigcirc \rightarrow \bigcirc + H_2O$	$(8.8 \pm 2.2) \times 10^9$	FR
$OH \cdot + \bigcirc \rightarrow \bigcirc^{OH}$	$(5.1 \pm 1.3) \times 10^9$	FR
$OH \cdot + \bigcirc \rightarrow products$	$(7.0 \pm 1.8) \times 10^9$	FR
$OH \cdot + \bigcirc_{OH} \rightarrow products$	$(1.1 \pm 0.3) \times 10^{10}$	FR
$OH \cdot + {}_{HO}\bigcirc \rightarrow products$	$(1.2 \pm 0.2) \times 10^{10}$	FR
$OH \cdot + \rightarrow products$	$(4.4 \pm 0.5) \times 10^9$	Steenken and O'Neill [1979]
$OH \cdot + \rightarrow products$	$(3.6 \pm 0.9) \times 10^9$	Steenken and O'Neill [1979]

FR denotes *Farhataziz and Ross* [1977]. Units are 1 mole^{-1} s^{-1} for bimolecular reactions and s^{-1} for unimolecular reactions.

Compilation of k_{aqu} can be found in
N, S chemistry: Warneck, Phys Chem Chem Phys 1 (1999) 5471-5483
                   Herrmann, Chem Rev 103 (2003) 4691-4716
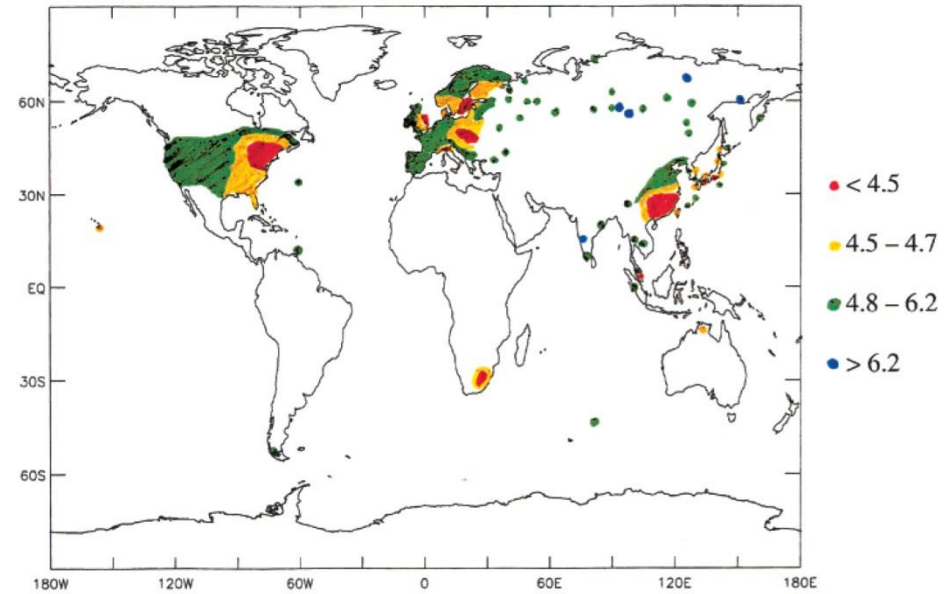HC_x chemistry: Herrmann, Chem Rev 103 (2003) 4691-4716

Less selectivity than in the gas-phase

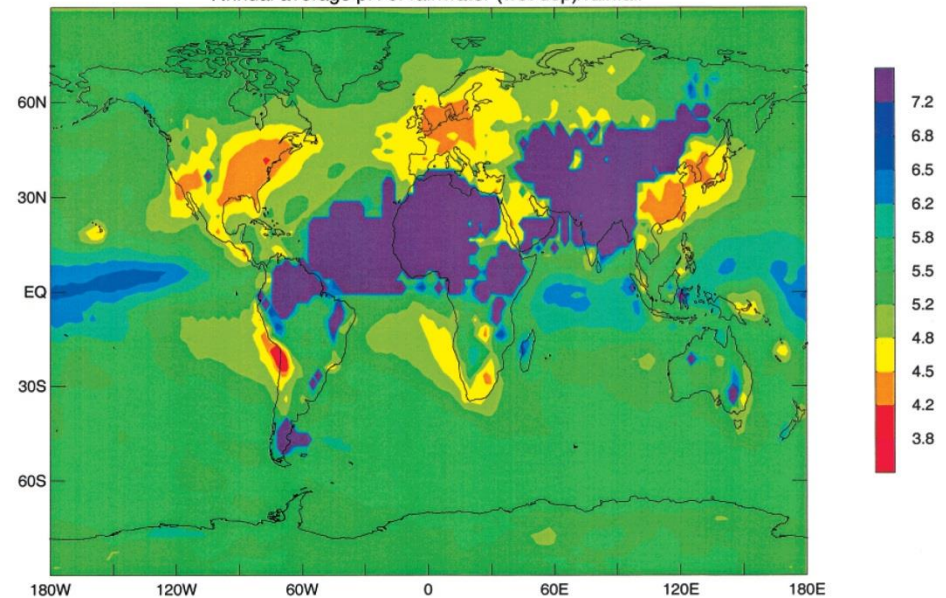*(Graedel & Weschler, 1981)*

Impacts of atmospheric acidity in ecosystems

acid deposition trends

Observed pH in precipitation
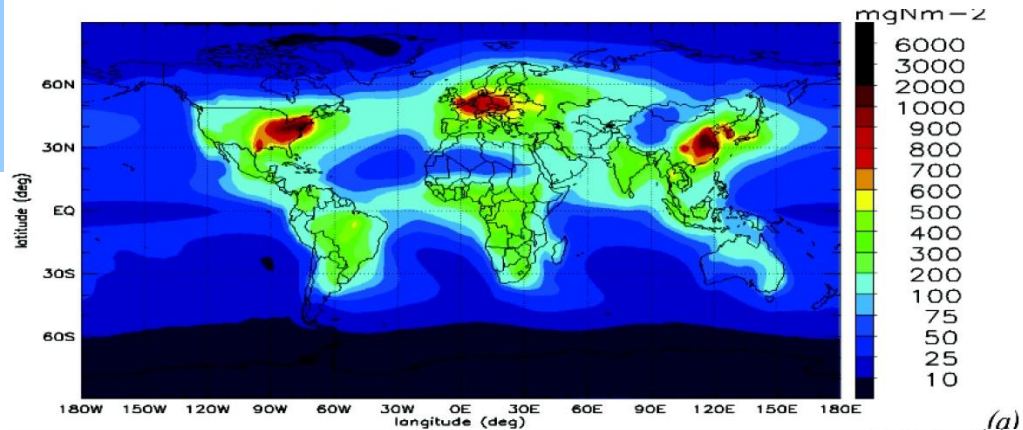

Annual average pH of rainwater (wet dep)/rainfall

Model (TM3) prediction

(Rodhe et al., 2002)

acid deposition, example NO$_y$ trends

2000
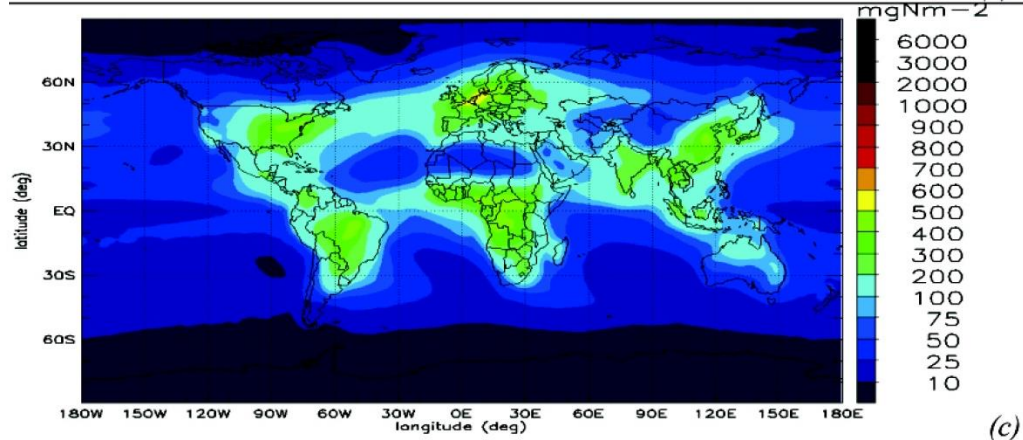
2030 under MFR

[mg N/m²/a]
(Dentener et al., 2006)

TABLE 1. Overview of Simulations, Prescribed Methane Volume Mixing Ratios, and Global Anthropogenic Emissions of CO, NMVOC, NO$_x$, SO$_2$, and NH$_3$[a]

simulation	meteorology	description	CH$_4$ [ppb]	CO	NMVOC	NO$_x$ (NO$_2$)	SO$_2$	NH$_3$	[Tg/a]
S1-B2000	CTM 2000 GCM SSTs 1990s	baseline	1760	977.0	147.1	124.8	111.1	64.8	
S2-CLE/CLEc	CTM 2000 GCM SSTs 1990s	IIASA CLE 2030, current legislation scenario	2088	904.1	145.5	141.1	117.6	84.8	
S3-MFR	CTM 2000 GCM SSTs 1990s	IIASA MFR 2030, maximum feasible reduction scenario	1760	728.7	104.4	76.0	35.8	84.8	
S4-A2	CTM 2000 GCM SSTs 1990s	SRES A2 2030, the most 'pessimistic' IPCC SRES scenario	2163	1268.2	206.7	206.7	202.3	89.2	

Ammonia budget $dc_{NH3}/dt = F_e - k_{OH}^{(1)} c_{NH3} - k_{dep}^{(1)} c_{NH3}$

Global N cycle, fluxes (Tg/a)   **+80%**

1890
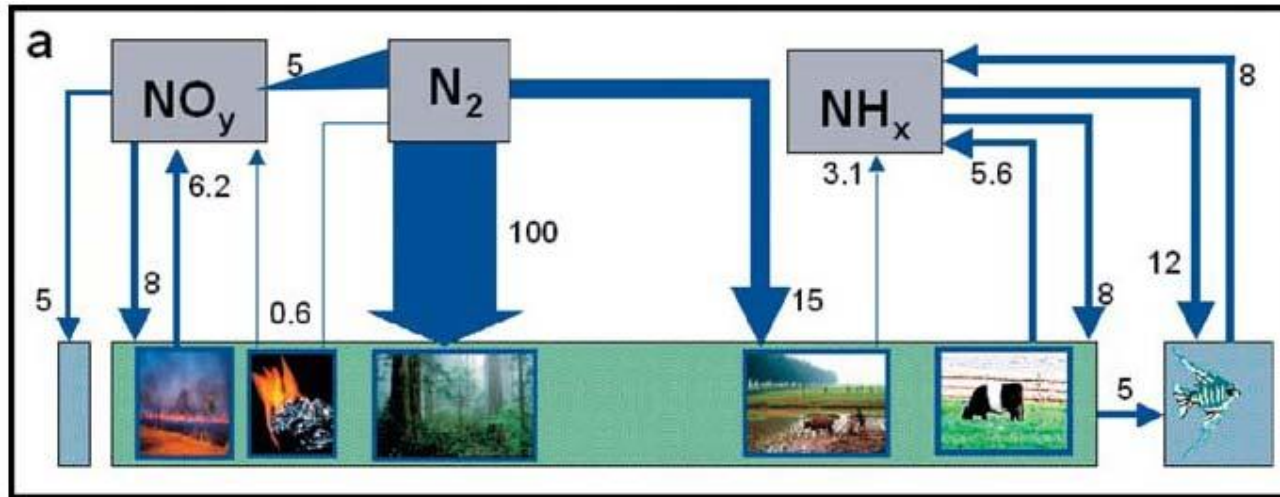
$NH_x = NH_3 + NH_4^*$

1990
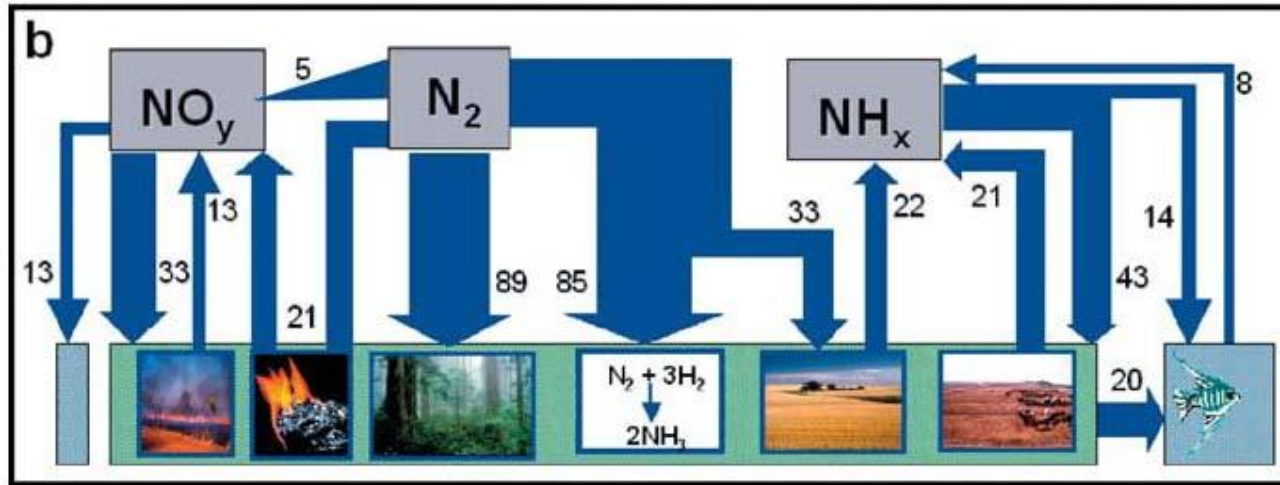
(Hibbard et al., 2006)

Ammonia and acidifying ions trends Europe
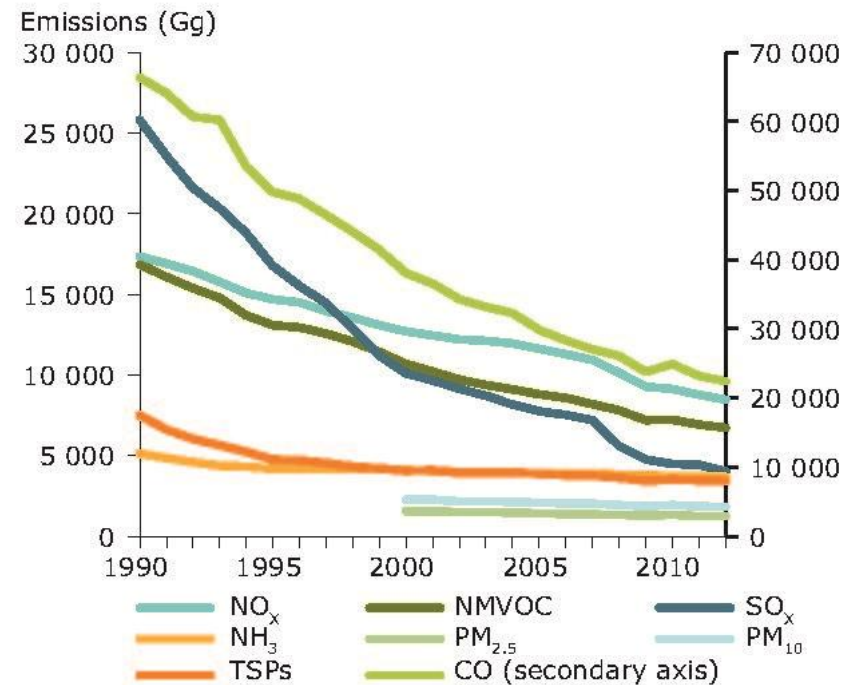
Pollutant	Unit	1990	1995	2000	2005	2006	2007	2008	2009	2010	2011	2012	Change 1990– 2012
NO_x	Gg	17 358	14 707	12 702	11 611	11 296	10 940	10 133	9 275	9 116	8 775	8 479	− 51 %
NMVOC	Gg	16 853	13 088	10 668	8 800	8 567	8 183	7 803	7 180	7 216	6 904	6 707	− 60 %
SO_x	Gg	25 835	16 766	10 103	7 733	7 529	7 188	5 573	4 769	4 484	4 434	4 005	− 84 %
NH_3	Gg	5 103	4 171	4 102	3 881	3 886	3 897	3 811	3 776	3 712	3 724	3 668	− 28 %
TSPs	Gg	7 492	4 760	4 030	3 877	3 777	3 750	3 633	3 432	3 504	3 455	3 404	− 55 %
CO	Gg	66 407	49 799	38 096	29 833	28 345	27 055	26 113	23 755	24 907	23 144	22 401	− 66 %

→ NO_3^-/SO_4^{2-} and $NH_4^+/(SO_4^{2-} + NO_3^-)$ are increasing in depositions

Emission trends (kt/a) in the EU-28 (*EEA, 2014*)

Ammonia and acid precursor gases trends Asia
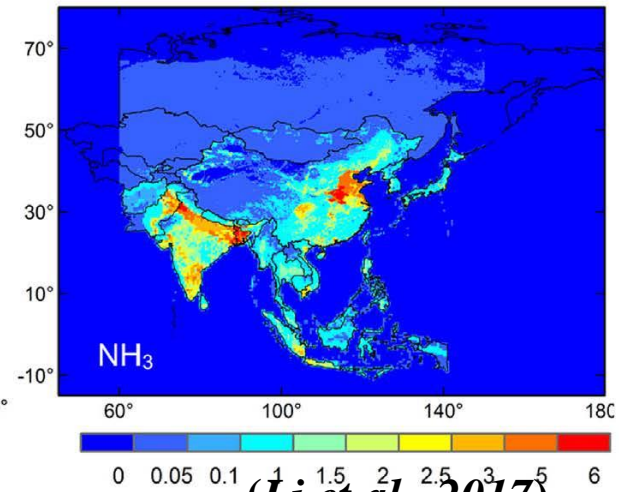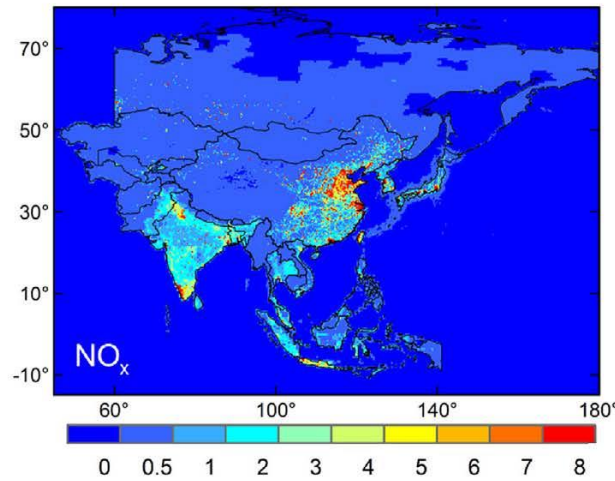
(*Li et al., 2017*)
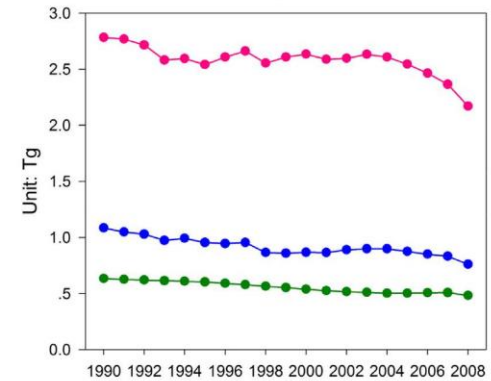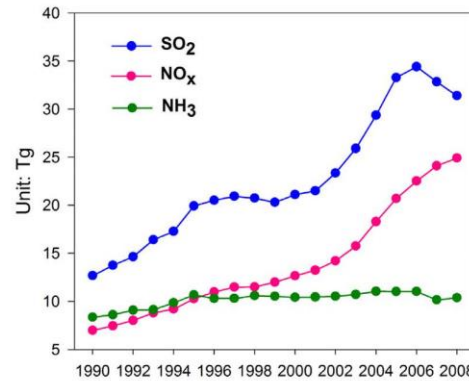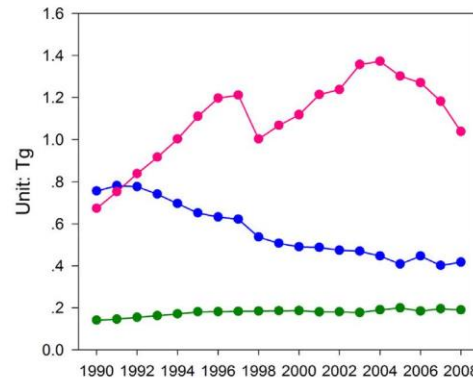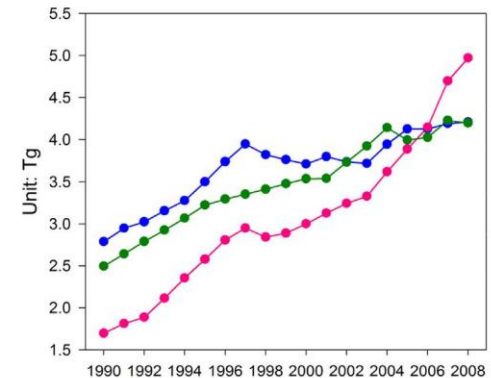
→ **No negative NH₃ emission trend**

(*Duan et al., 2016*)

Gas-phase chemistry

$NH_3 + OH\cdot \rightarrow NH_2\cdot + H_2O$ $\qquad\qquad$ $k = 0.16\times10^{-12}$ cm³/molec/s
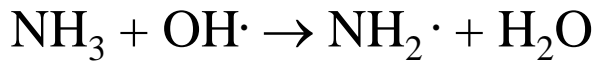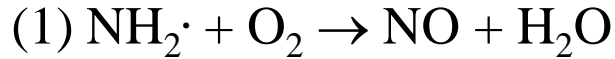
(1) $NH_2\cdot + O_2 \rightarrow NO + H_2O$ $\qquad$ $k_1 < 6\times10^{-21}$ cm³/molec/s
(2) $NH_2\cdot + HO_2\cdot \rightarrow NH_3 + O_2$ $\qquad$ $k_2 = 34\times10^{-12}$ cm³/molec/s
(3) $NH_2\cdot + NO \rightarrow N_2 + H_2O$ $\qquad$ $k_3 = 17\times10^{-12}$ cm³/molec/s
(4) $NH_2\cdot + NO_2 \rightarrow N_2O + H_2O$ $\qquad$ $k_4 = 19\times10^{-12}$ cm³/molec/s
(5) $NH_2\cdot + O_3 \rightarrow NH_2O\cdot + O_2$ $\qquad$ $k_5 = 0.16\times10^{-12}$ cm³/molec/s
(6) $NH_2\cdot + RH \rightarrow$ $\qquad\qquad$ too slow to be of any significance
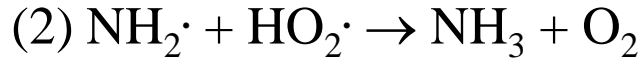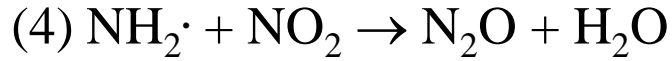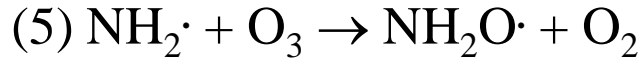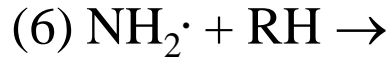
$-dc_{NH3}/dt = k_{OH}^{(1)}\, c_{NH3} = k_{OH}^{(2)}\, c_{OH}\, c_{NH3;}\ \tau_{OH} = (k_{OH}^{(1)})^{-1}$
$\qquad\quad \approx 3$ months for the global annual tropospheric mean (1.16×10^6 OH/cm³)
$\qquad\quad \approx 10$ days inner tropics near ground ($\approx 10^7$ OH/cm³; *Spivakovsky et al., 2000*)
$-dc_{NH3}/dt = k_{OH}^{(1)}\, c_{NH3} + k_{dep}^{(1)}\, c_{NH3}$

$\tau_{air} = (k_{OH}^{(1)} + k_{dep}^{(1)})^{-1}$

Cycling of ammonia

$3-8$

$NH_3 + OH \longrightarrow NO_x$

Dry
deposition
NH_3, (NH_4^+)

Wet
deposition
NH_4^+

Wet
deposition
NH_4^+

Dry
deposition
NH_3, (NH_4^+)

$61-126$

$30-60$

$8-25$

$113-244$

$11-25$

<1
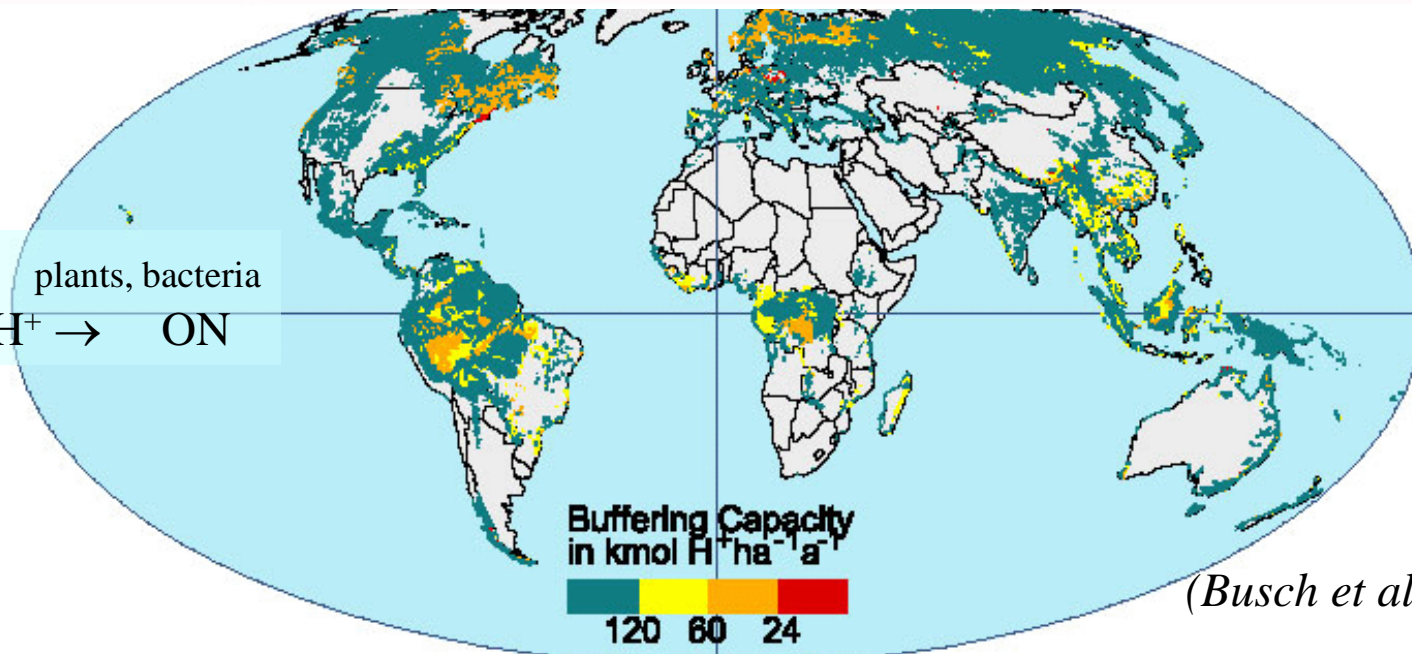
Decay
NH_3

River
runoff
NH_4^+
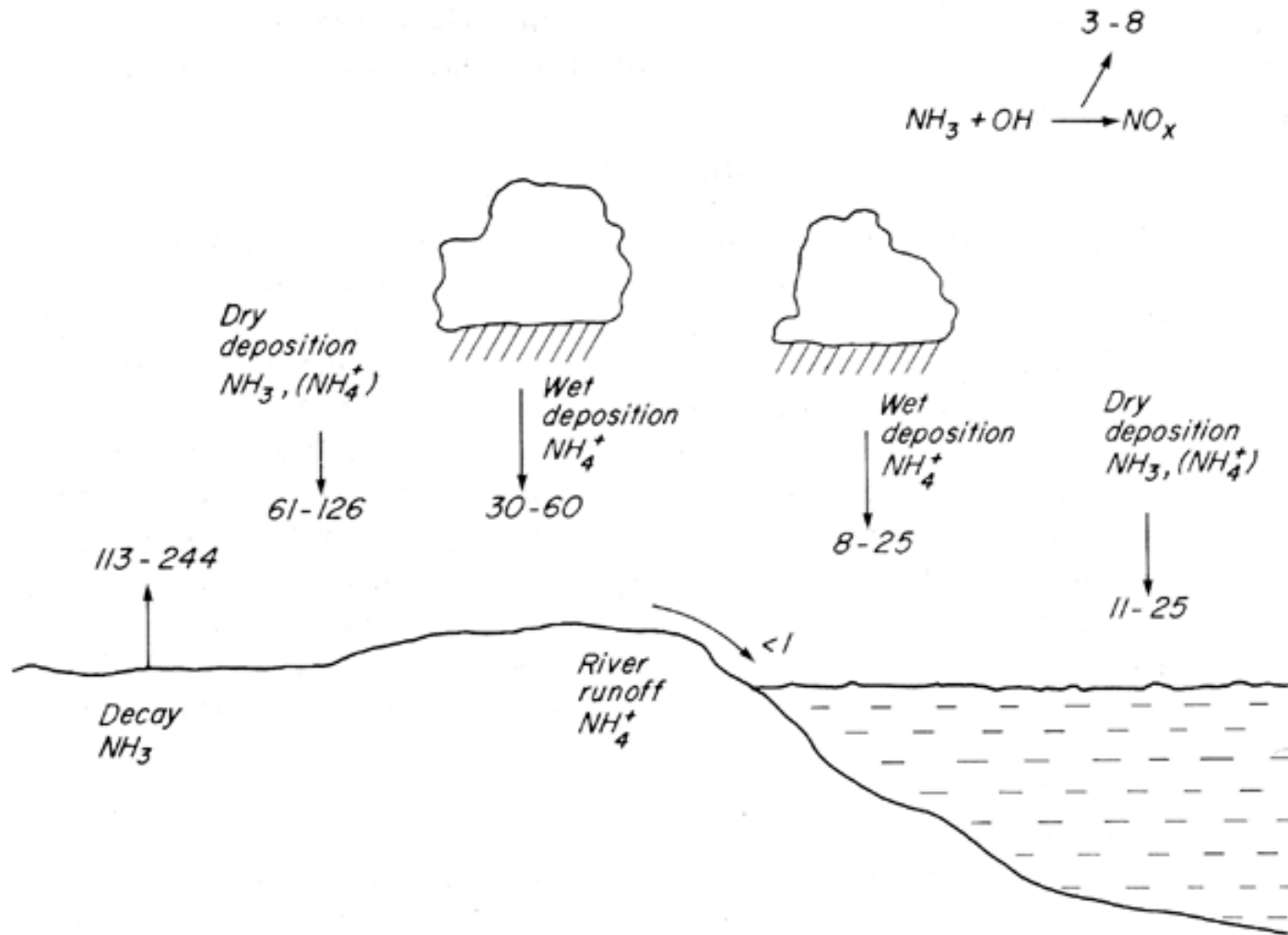
(following Manier)

Impacts of atmospheric acidity: acidification of soils

**Table 3:** Deposition of nitrogen and sulphur compounds and their corresponding production of acidity in a nitrogen unsaturated plant-soil-system
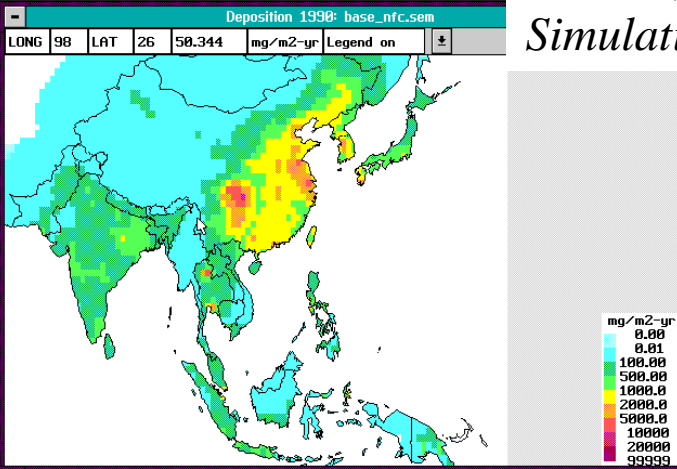
Deposition	H$^+$-Production [mol/mol]	Deposition	H$^+$-Production [mol/mol]
H$^+$	+1	$[NH_4]_2SO_4/NH_4NO_3$	+2 / 0
NH$_4^+$	+1	H_2SO_4/HNO_3	+2 / +0
NO$_3^-$	-1	H_2SO_4/NH_4NO_3	+2 / 0
SO$_4^{2-}$	0	NH_4HSO_4/HNO_3	+2 / +0

$$NO_3^- + H^+ \xrightarrow{\text{plants, bacteria}} ON$$

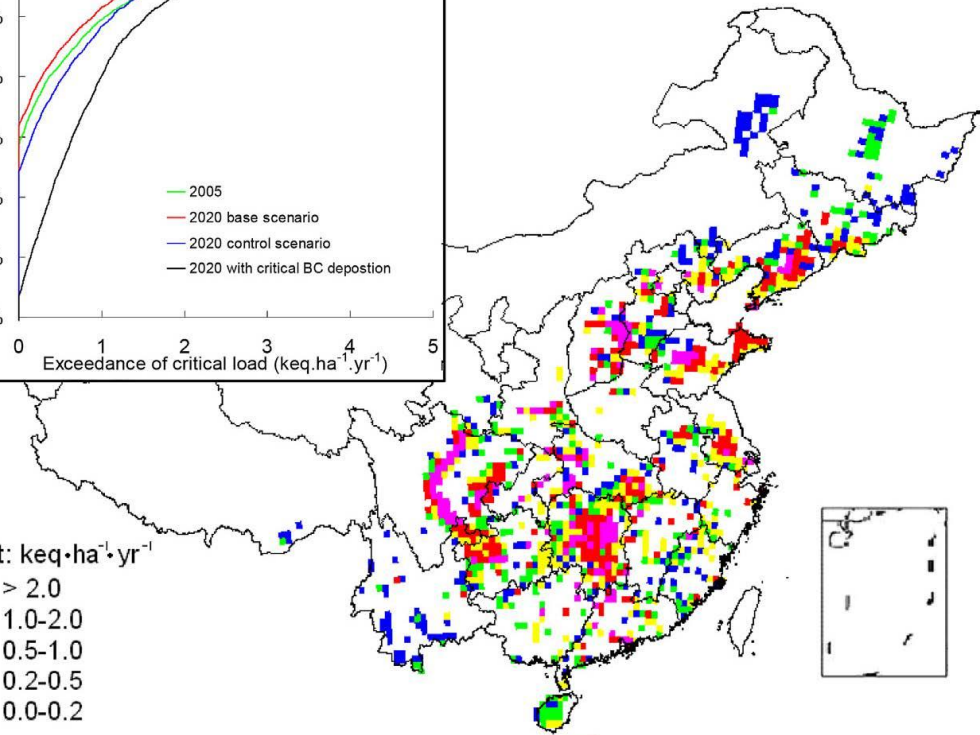Buffering Capacity in kmol H$^+$ha^{-1}a^{-1}

120   60   24

(Busch et al., 2001)

Deposition of acid: Effects in soils

RAINS (Regional Air Pollution Information and Simulation Model) Asia project, IIASA
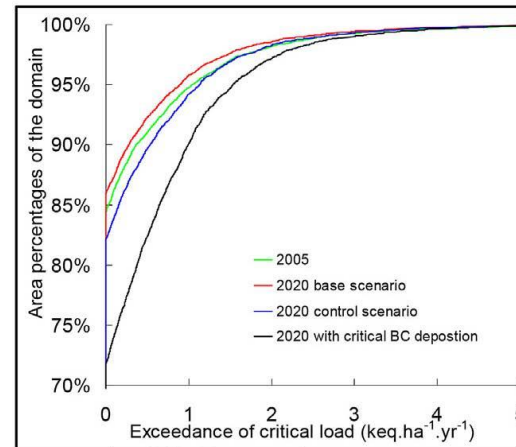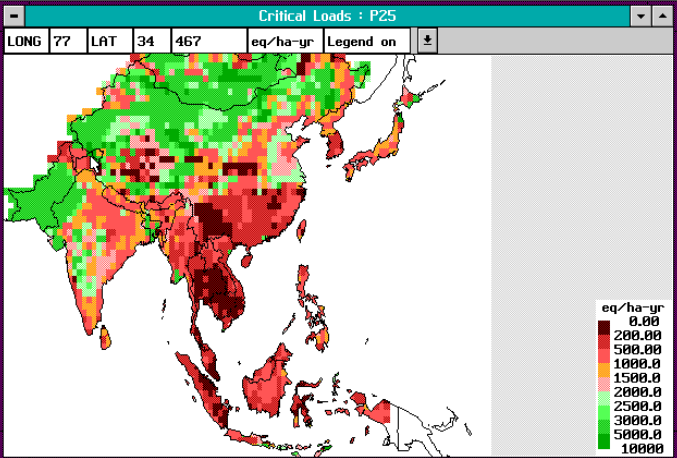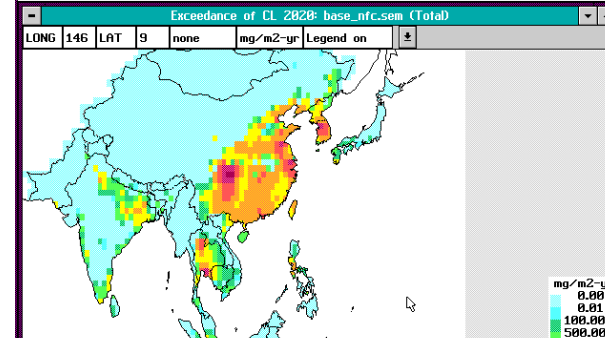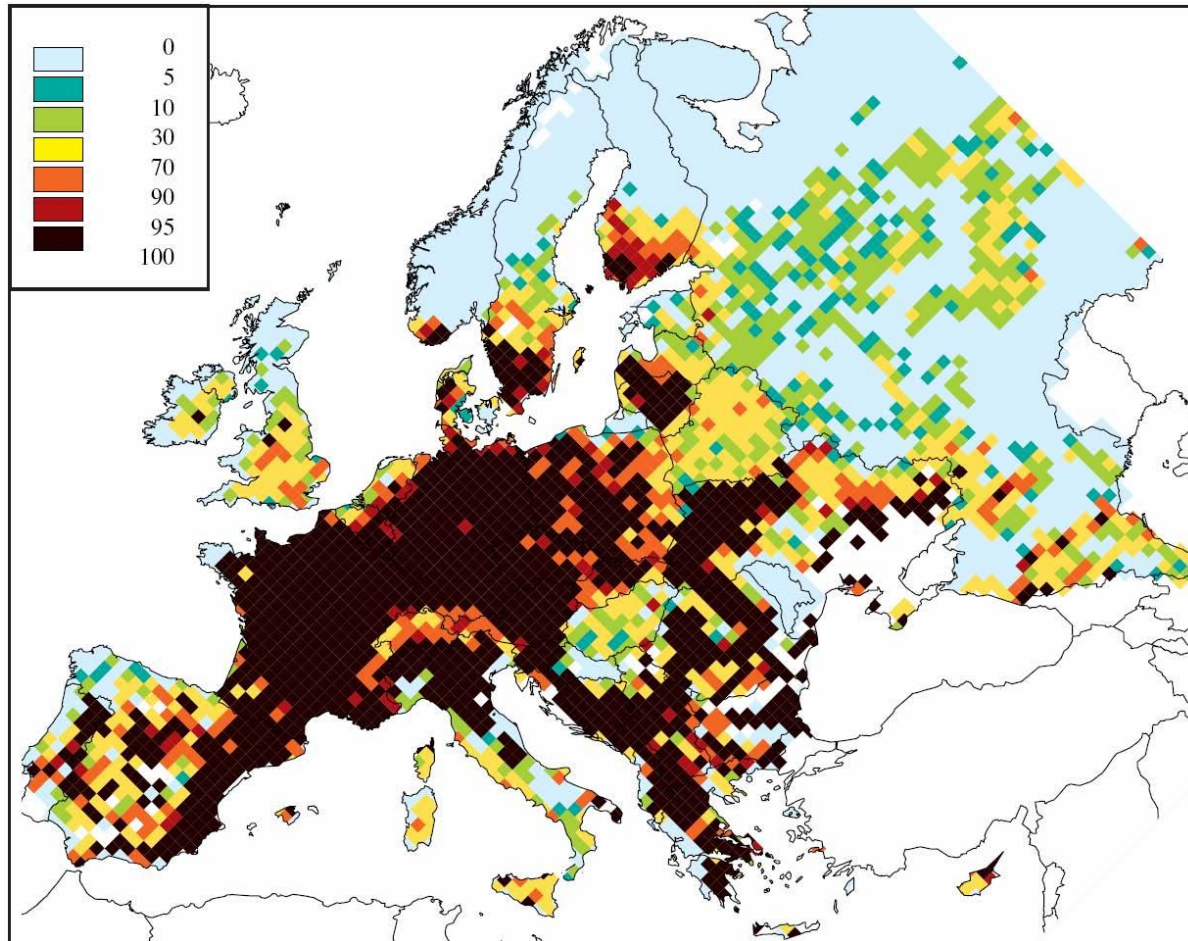

Critical loads exceedances in China 2005 (mapped) and cumulative distribution of the critical load exceedances under various future scenarios (Zhou et al., 2011; Duan et al., 2016)

Ecosystem response to nutrient N: Eutrophication (or: hyper-)

Percentage of total ecosystems area ~~...~~
for eutrophication for the emissions ~~...~~
(Sverd...)

**Ammonification := biotic $ON \rightarrow NH_3$ or NH_4^+**

mass balance

$$F_{\text{critical load}} := F_{\text{N uptake by biomass}} + F_{\text{N immobilisation}} + F_{\text{acceptable N leaching}} + F_{\text{denitrification}}$$

Critical loads concept to protect ecosystems

Mapping of critical loads „...below which harmful effects in ecosystem structure and function do not occur according to present knowledge":
Determines which loads of pollutants and combinations thereof will not cause adverse effects, do not exceed ecosystem resilience (*PNEC*).

• + Protection of vulnerable areas is possible (protection of 95% of the area is common)

• + Accounts for dynamics, mostly however based on steady state-assumption and therefore neglecting the very slow dynamics of the soils

• – Scale problems when matching exposure (deposition model output) and vulnerabilities (mapped ecosystems)

• – normative steps are not transparent

• Integrated Assessment Modelling (IAM) under the auspices of the Convention on Long-range Transboundary Air Pollution (CLRTAP): Study various scenarios of emissions and related abatement costs + depositions and related exceedances of thresholds (*Alcamo et al., 1987*, besides others)

< 0	500 - 1.000
0 - 200	1.000 - 2.000
200 - 500	> 2.000
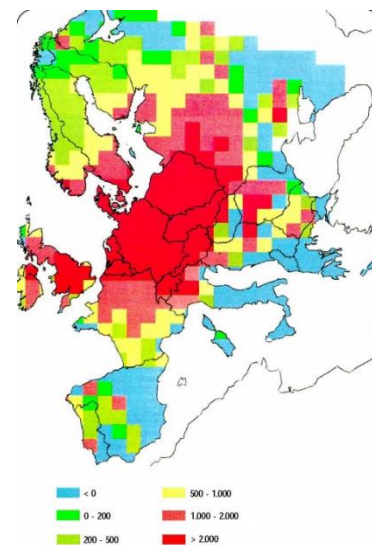
Atmospheric aerosol, its composition, surface and bulk particle reactions

Introduction, significance, sources

Global atmospheric particulate matter sources (Tg/a)

1. Precursors

n: Vegetation	**1000 (825-1150)**	*(Guenther et al., 1995)*
n: Oceans	**26**	*(Eichmann et al., 1980)*
a: Industry, transport	**100 (90-100)**	*(Ehhalt, 1986; Müller, 1992)*

Gas-to-particle-conversion efficiencies

n: ≈ 5%	**55 (40-200)**	*(Andreae, 1995)*
n: ≈ 2%	**18.5**	*(Griffin et al., 1999)*
a: ≈ 6%	**10 (5-25)**	*(Andreae, 1995)*

Aerosol = particles dispersed in air + gas-phase
Directly emitted = primary particles / aerosols
Formed in air (by gas-to-particle-conversion processes) = secondary particles / aerosols

2. direct emission

n: Vegetation	**50 (26-80)**	
n: Soils	**11**	
a: Biomass burning	**80 (50-140)**	
a: Industrial dust	**100 (40-130)**	
n: Sea salt	**3340 (1000-6000)**	
n: Mineral dust	**2150 (1000-3000)**	*(Penner et al., 2001)*

3340 (1000-6000) Tg/a **sea salt**, 2150 (1000-3000) Tg/a **mineral dust**, 450 (260-840) Tg/a **secondary particles**, ...
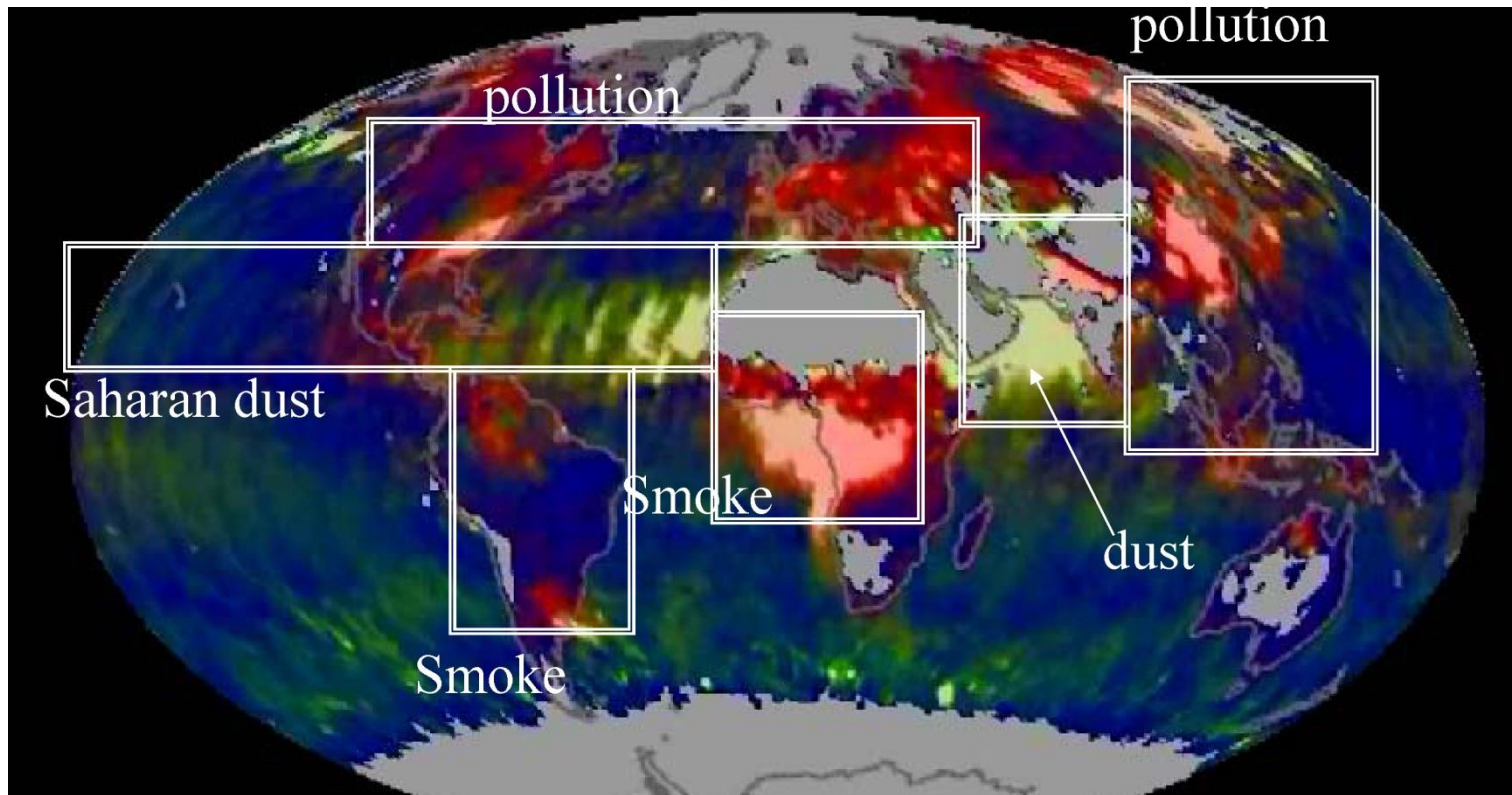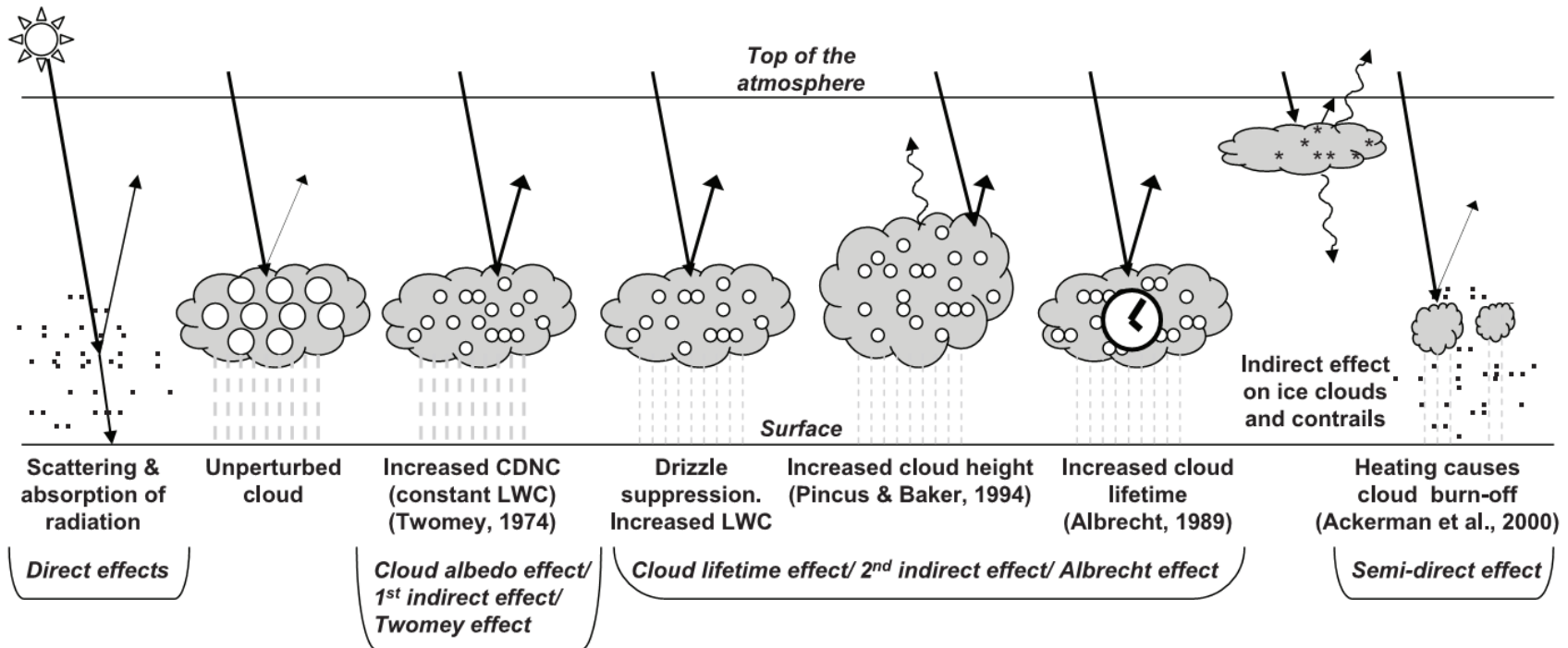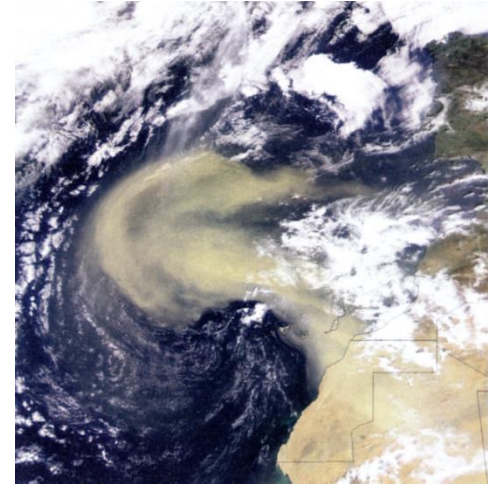

Aerosol distributions (on 3.8.01) with low and high sub-micron mass fraction

**(MODIS aerosol optical density, *Martin & Kaufman, NASA*)**

Why is the atmospheric aerosol relevant ?

1. **Human health: Respiratory and cardiovascular diseases and short-term effects**
2. **Provides matrix for heterogeneous reactions and is carrier for semivolatile compounds → 3.1.4**
3. **Radiative and cloud nucleation effects (climate, so-called direct and indirect aerosol effects)**


Scattering & absorption of radiation	Unperturbed cloud	Increased CDNC (constant LWC) (Twomey, 1974)

Top of the atmosphere

Surface

Indirect effect on ice clouds and contrails

| Scattering & absorption of radiation | Unperturbed cloud | Increased CDNC (constant LWC) (Twomey, 1974) | Drizzle suppression. Increased LWC | Increased cloud height (Pincus & Baker, 1994) | Increased cloud lifetime (Albrecht, 1989) | Heating causes cloud burn-off (Ackerman et al., 2000) |

Direct effects

Cloud albedo effect/ 1st indirect effect/ Twomey effect

Cloud lifetime effect/ 2nd indirect effect/ Albrecht effect

Semi-direct effect

→ Potential to affect insolation, precipitation, temperatures IPCC, 2007

Radiative and cloud nucleation effects (climate, so-called direct and indirect aerosol effects)


IPCC, 2013
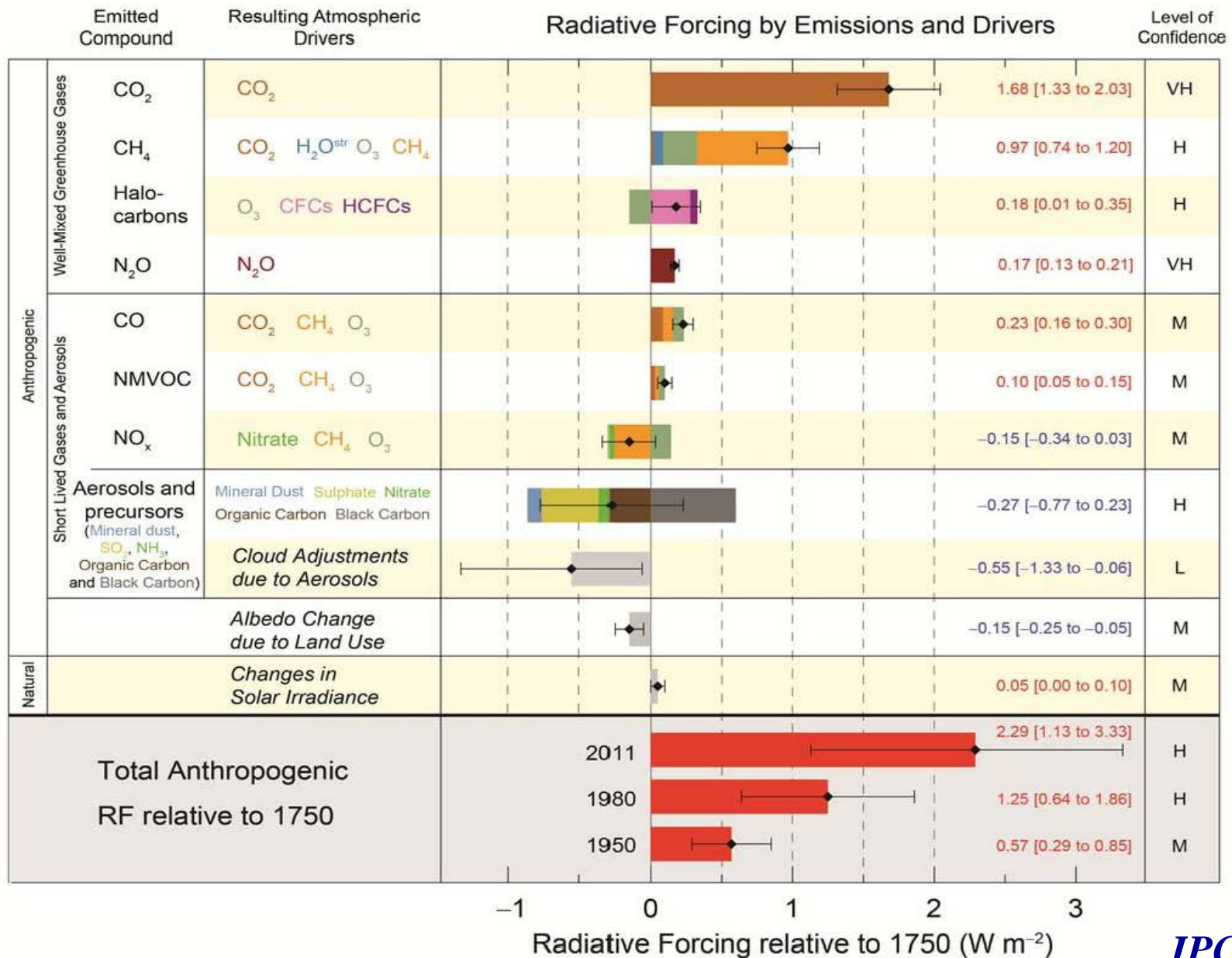
3. Radiative and cloud nucleation effects (climate, so-called direct and indirect aerosol effects)

Sulfate aerosols: cooling
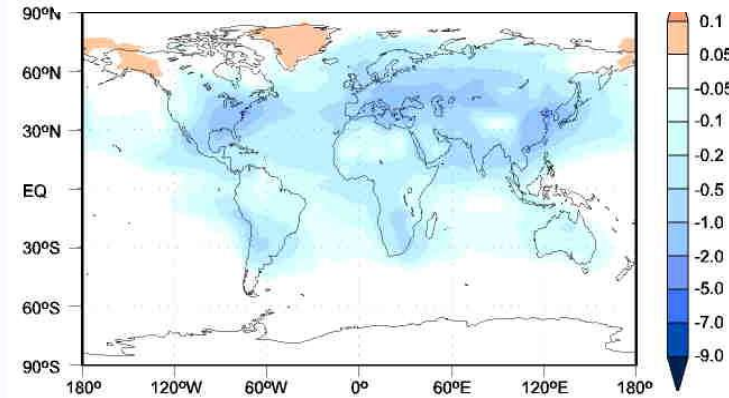
Optical and hygroscopic properties

• **Scattering ('direct effect') + warming due to absorption ('semi-direct effect'):**
−1.2 W/m² (earth surface)

• **Clouds: increase optical thickness and albedo due to increased droplet number concentration ('1ˢᵗ indirect effect'): −1.5 ± 0.5 W/m²** *(Lohmann & Feichter, 2001)*

→ Instead of ≈ +0.7°C global warming we had without anthropogenic aerosols ≈ +
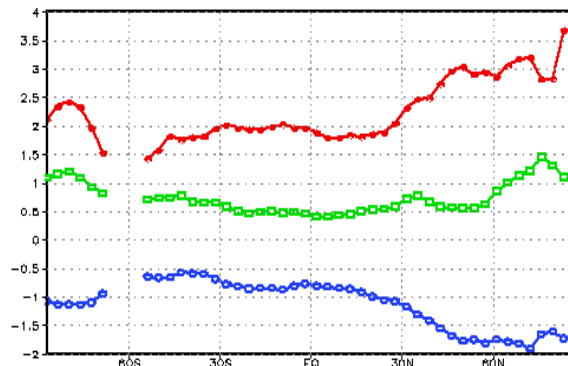
Zonal (S pole – N pole) mean temperature changes 1990-1850:
GHG, aerosols, GHG + aerosols
(Feichter et al., 2004)

Gerhard Lammel: "Trends and Advances in Atmospheric and Environmental Chemistry"

Where: **Bohunice campus A29, room 411**
When: **25.9., 27.9., 26.10., 27.10. 10:00, 20.11.(?), 21.11.(?)17**

Introduction: pressure, law of mass action
Thermal reactions, radiation, photochemical processes
Tropospheric ozone: hydrocarbon chemistry, role of nitrogen oxides
Cloud chemistry: Ozone, acidity formation, dimethyl sulphide
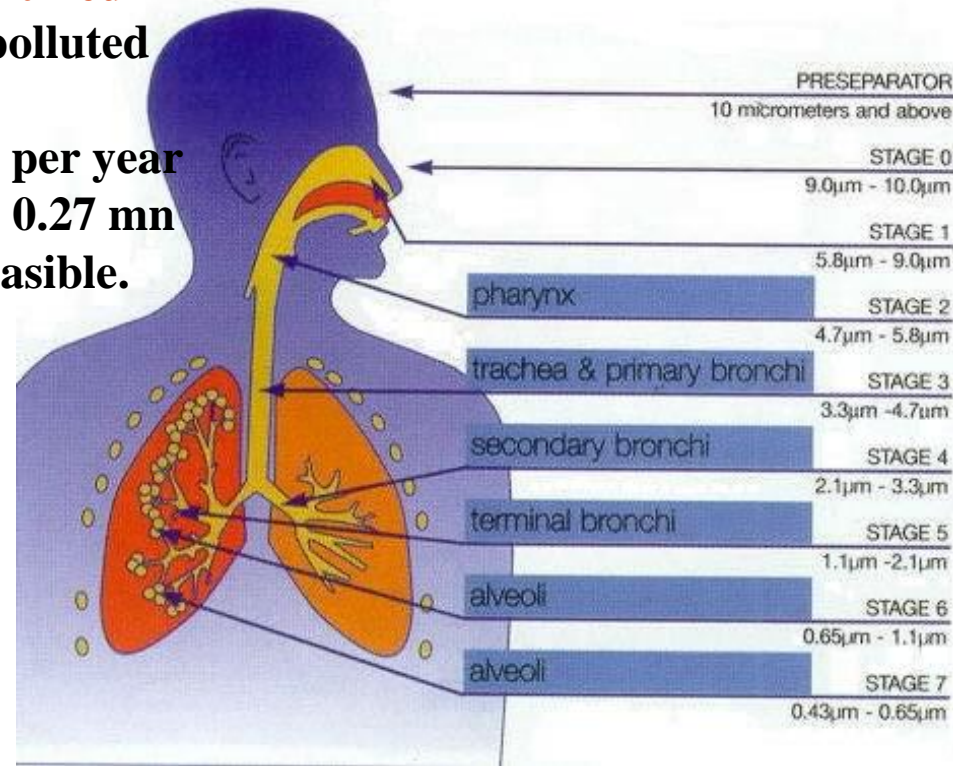**Atmospheric aerosol, its composition, surface and bulk particle reactions**
Trace substance mass budgets, surface cycling: Emissions, deposition, re-volatilisation
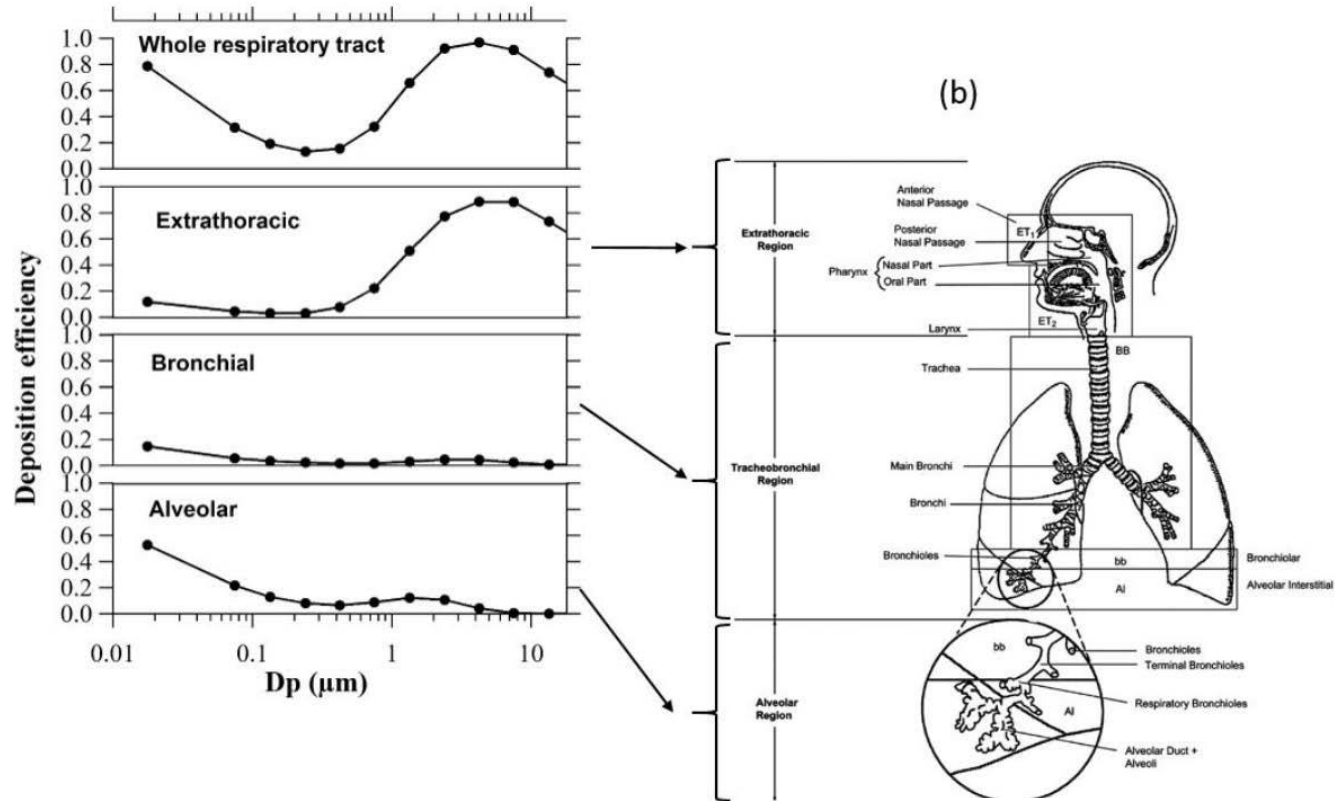
Aerosol ↔ Health

Adverse health effects

• Fine PM reaches the lung: < 10 μm (PM_{10}), at least < 5 μm, macrophages remove 1/3 (the larger), rest remains in the alveolar region or even reaches into the lymphatic and blood circulations

• $PM_{2.5}$ carries numerous organic and inorganic substances, including toxics (nitro-PAHs, dioxins, …) → pulmonary and cardiovascular diseases (e.g., elevated fatal stroke risk), mutagenic, nervous system impairment. A no-effect-concentration/threshold value cannot be identified

• WHO estimate (2006): Mortality in most polluted cities could be reduced by 15%

• EU Comm. (2007): 2 mn premature deaths per year globally, 0.39 mn in EU (2007). Reduction to 0.27 mn in 2020 under current legislation, 0.19 mn feasible.

PM_x = particulate matter smaller than x μm by size
TSP = total suspended particulate matter

PRESEPARATOR
10 micrometers and above

STAGE 0
9.0μm - 10.0μm

STAGE 1
5.8μm - 9.0μm

pharynx

STAGE 2
4.7μm - 5.8μm

trachea & primary bronchi

STAGE 3
3.3μm -4.7μm

secondary bronchi

STAGE 4
2.1μm - 3.3μm

terminal bronchi

STAGE 5
1.1μm -2.1μm

alveoli

STAGE 6
0.65μm - 1.1μm

alveoli

STAGE 7
0.43μm - 0.65μm

Particle size dependent deposition in the respiratory tract

(Dombu & Betbeder, 2013)

Protection through deposition from
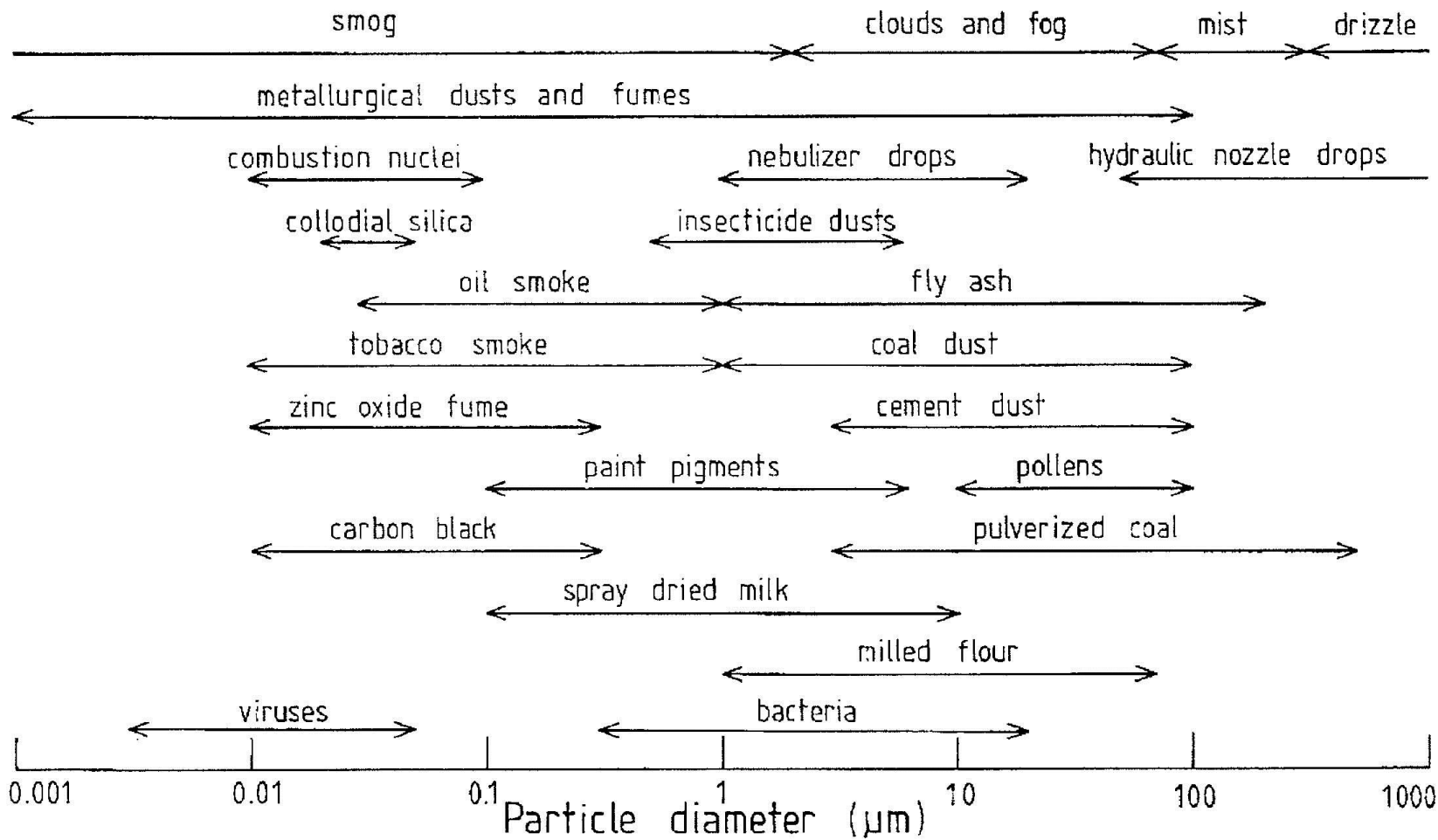**<0.1 μm: ineffective**
Macrophages and innate immune system need to react

PREMATURE DEATHS ASSOCIATED WITH ENVIRONMENTAL RISK
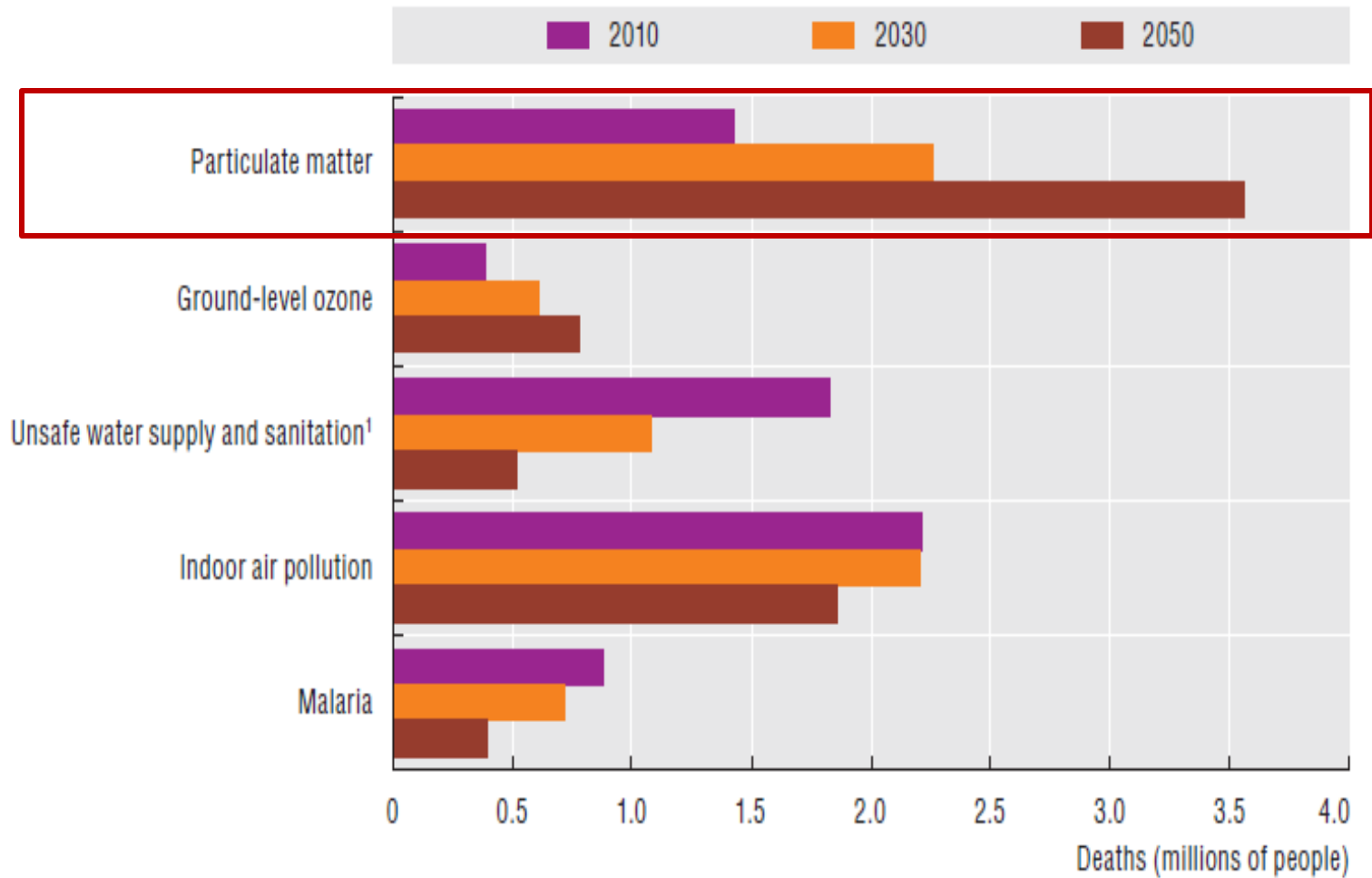
[OECD, 2012]

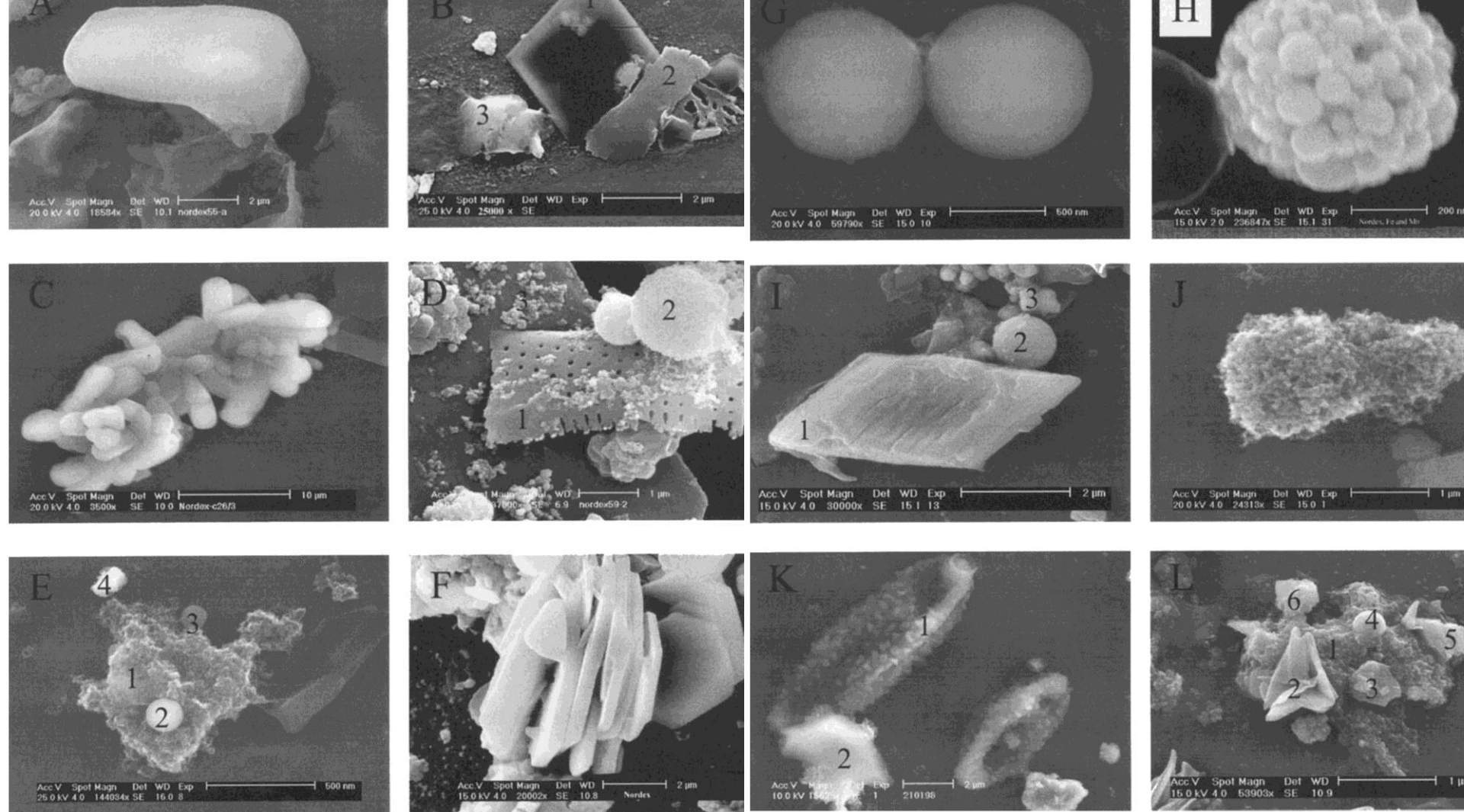**By 2030, PM surpasses unsafe water as the leading environmental cause of premature deaths.**

smog | clouds and fog | mist | drizzle

metallurgical dusts and fumes

combustion nuclei | nebulizer drops | hydraulic nozzle drops

collodial silica | insecticide dusts

oil smoke | fly ash

tobacco smoke | coal dust

zinc oxide fume | cement dust

paint pigments | pollens

carbon black | pulverized coal

spray dried milk

milled flour

viruses | bacteria

0.001   0.01   0.1   1   10   100   1000

Particle diameter (μm)

← ← ← **fine** → ← **coarse** → → →

Fig. 1(A–F). Secondary electron image of North Sea aerosol particles: (A) Irregularly shaped sea-salt particle; (B) sea-salt particle with typical cubic morphology (1), irregularly-shaped sea-salt particle (2), and alumosilicate particle (3); (C) aged sea-salt particle; (D) biological particle (1), Si-rich fly ash particle (2), and various soot particles (diameter of primary particles below 100 nm); (E) soot agglomerate (1) with alumosilicate particles (2, 4), and carbonaceous material (3); (F) alumosilicate particle (clay mineral); (G) two alumosilicate fly ash particles; (H) agglomeration of iron oxide spheres; (I) calcium sulphate (presumably gypsum) particle (1), spherical iron oxide particle (2), and titanium oxide particle (3); (J) typical soot agglomerate; (K) biological particle (1) and sea-salt (2); (L) agglomerate of carbonaceous material (1, 2), alumosilicates (3), Si-rich fly-ash (4), and calcium sulphate (5, 6).

M.Ebert, S.Weinbruch et al., 2000
TU Darmstadt

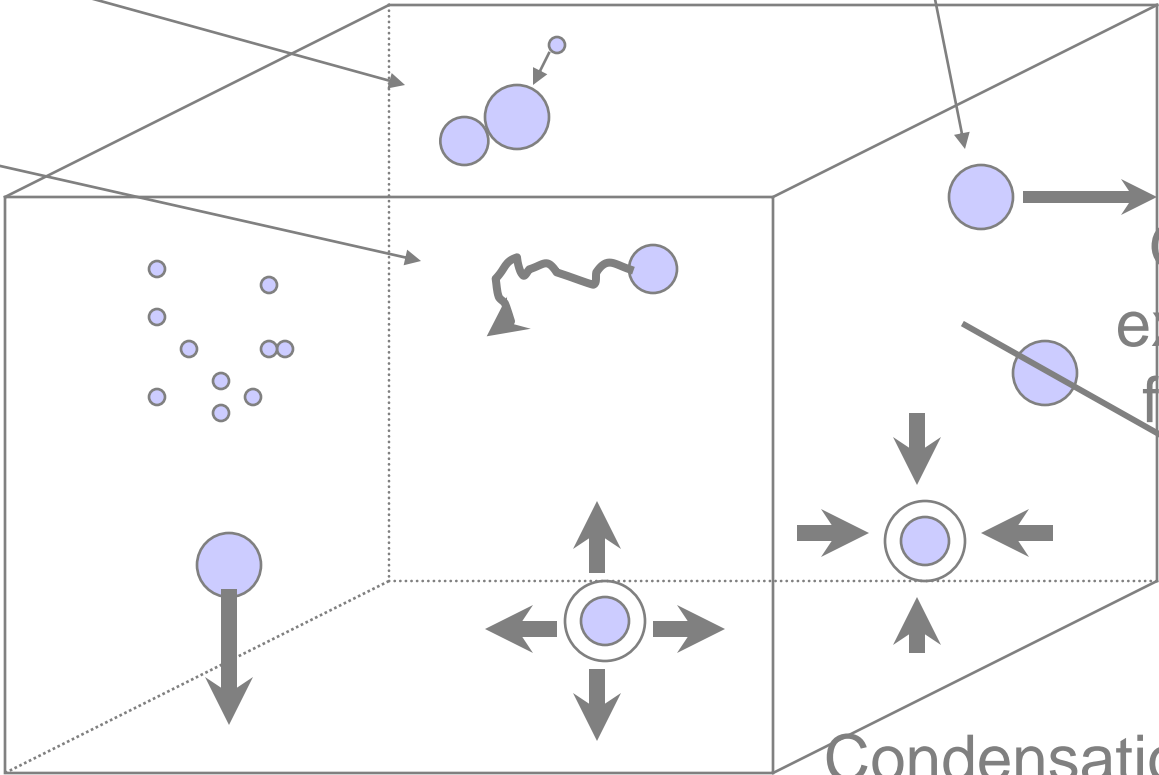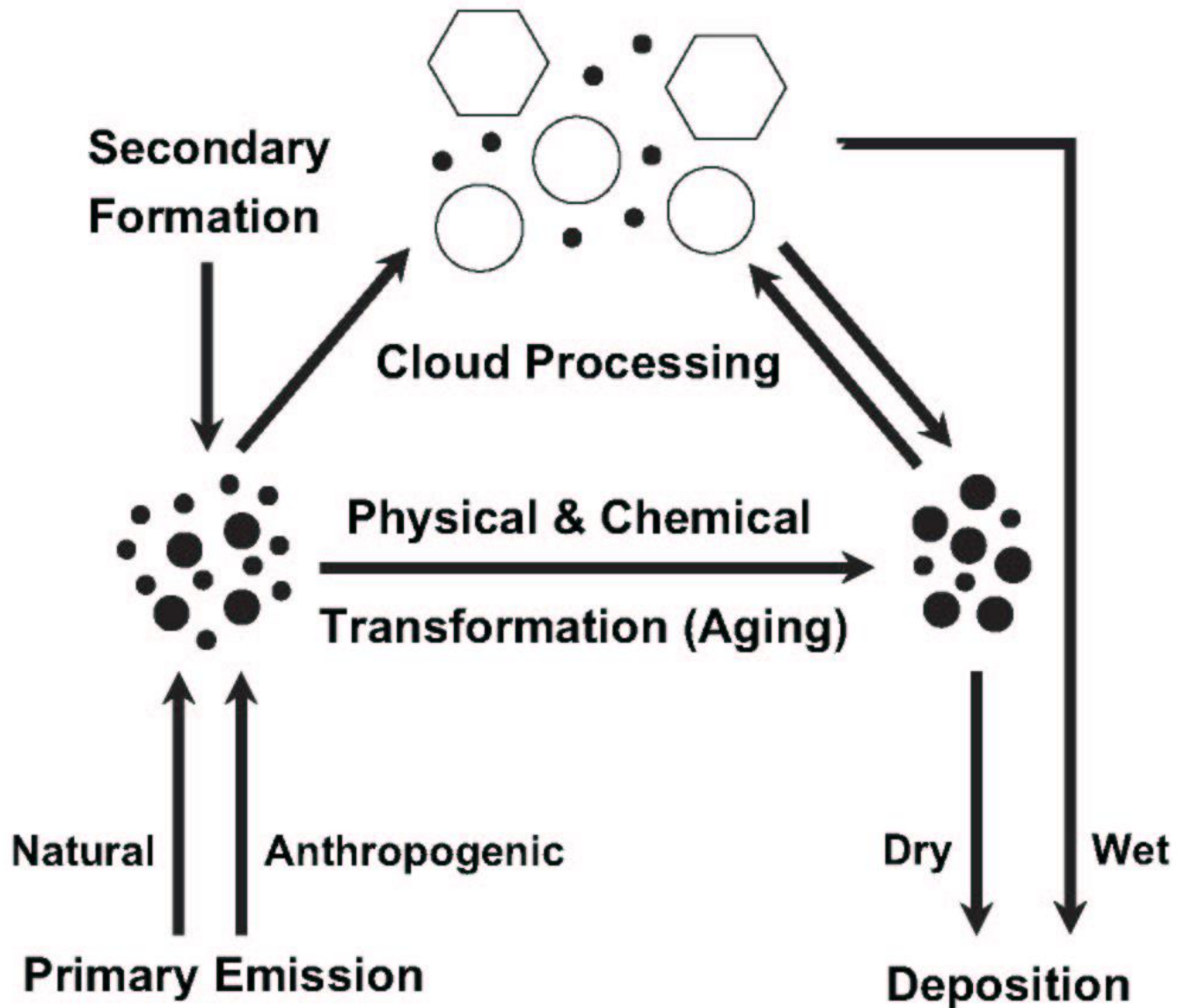# Aerosol microphysical processes

Coagulation

Convection

Diffusion

Other external forces

Nucleation

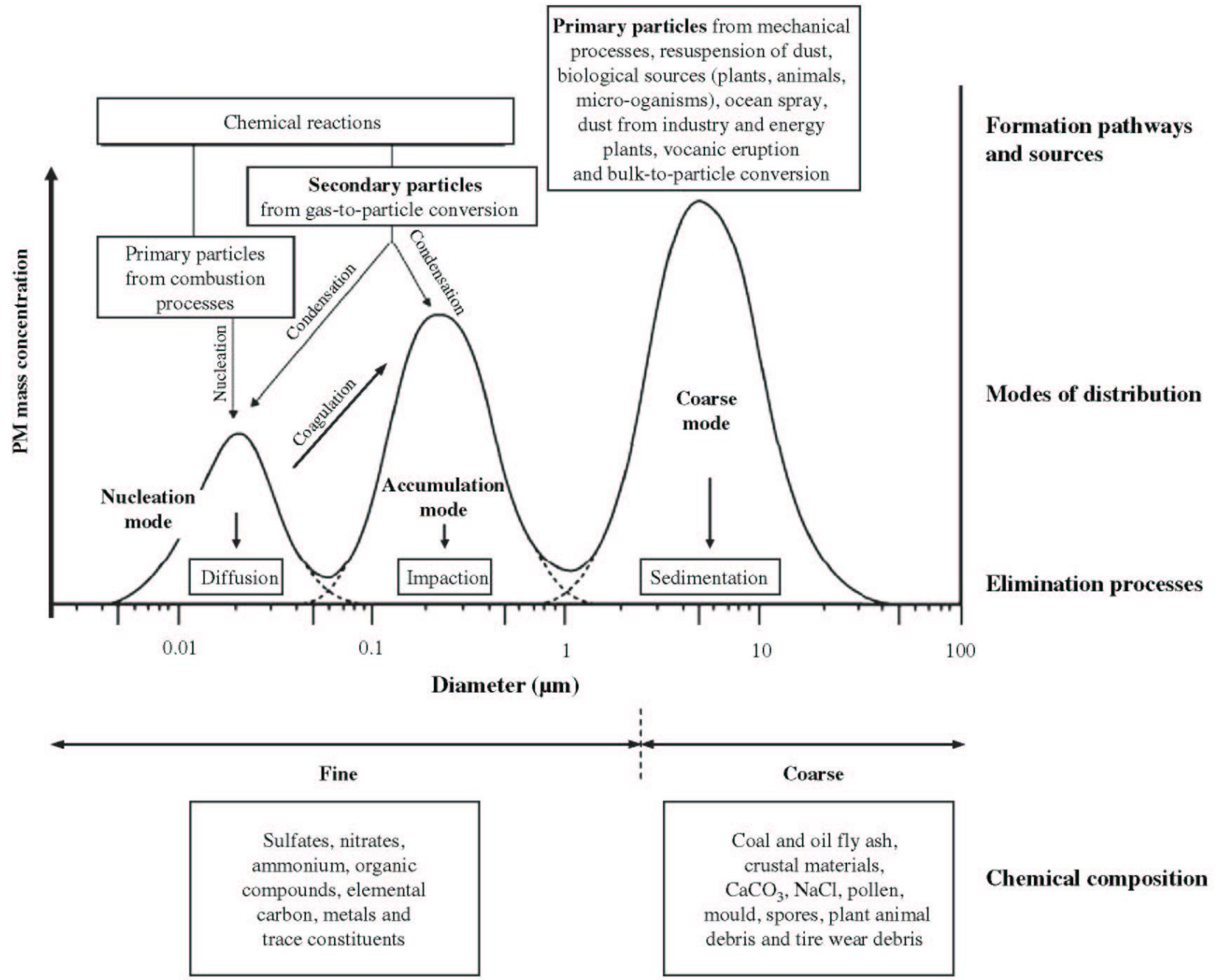Sedimentation

Condensation

Evaporation

Aerosol processes

Fuzzi et al., 2006

Courtesy of: Cambra-López et al., 2010

Primary particle formation (nucleation)

condensational growth

$n_1 H_2SO_4 + n_2 H_2O + n_3 NH_3 (?) + RCOOH (??) \rightarrow$ critical cluster $\rightarrow$ ultrafine particle

Nucleation events:

Reasons for occurrence of nucleation events unclear. No simple correlations, key factors unknown. Example: 3 different events on Hohenpeissenberg 1998-2000 (*Birmili et al., 2003*).

The nucleation rate is mostly 2nd order in H_2SO_4, in general 1st to 2nd. This suggests the prevalence of a bimolecular reaction (collision) of 2 clusters with each one H_2SO_4 molecule for formation of the critical cluster
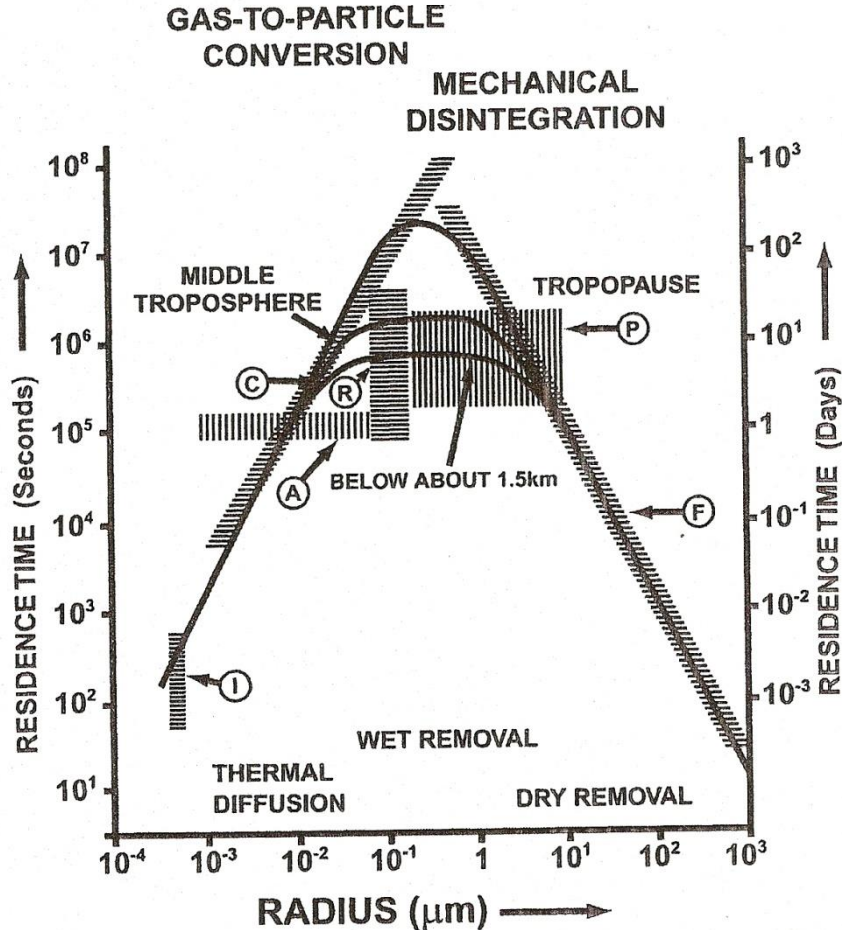
(*Weber et al., 2006*).
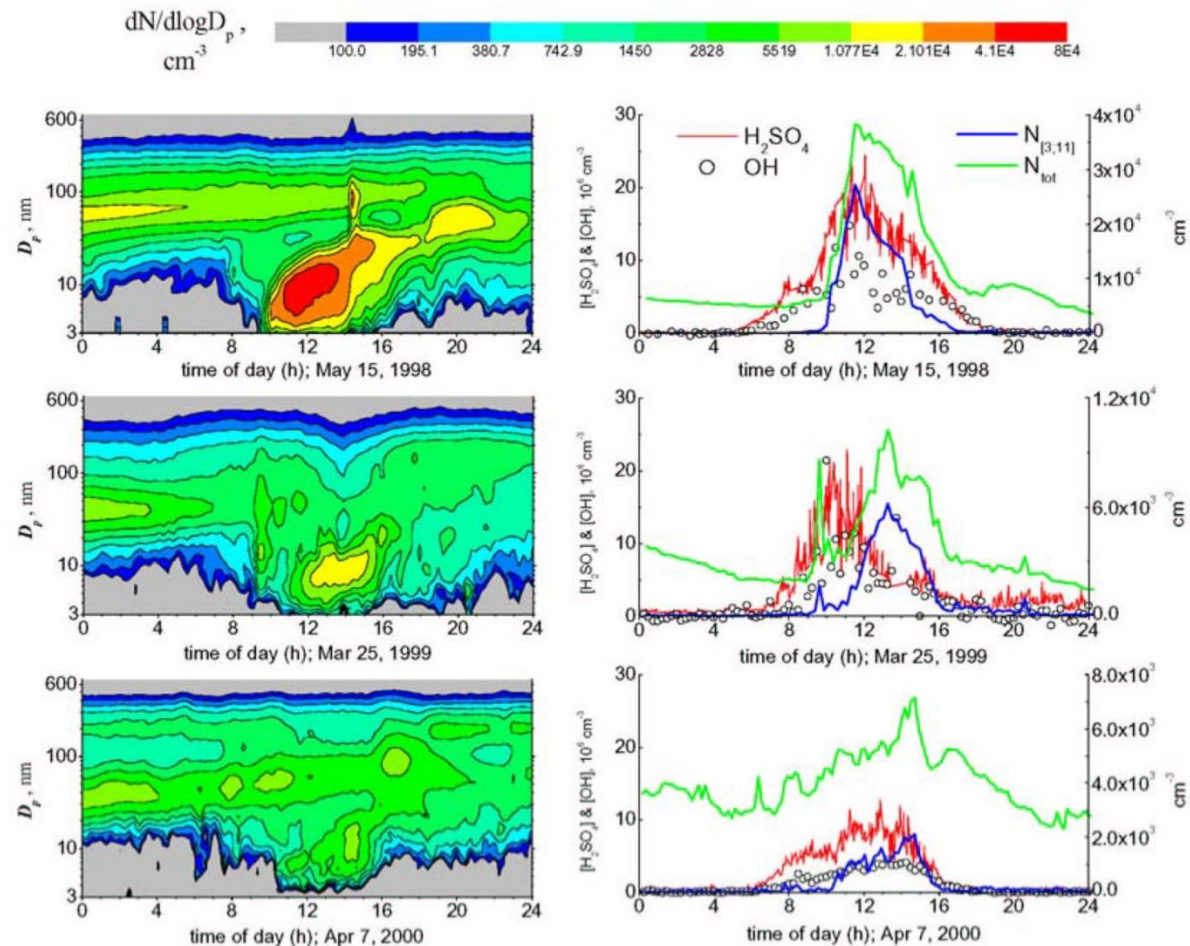
Removal processes - size dependent residence time
empirical expression:

$$\tau_{dry} = f(D) = \beta/[(D/0.6)^2 + (D/0.6)^{-2}]; \quad D \text{ [µm]}, \quad \beta = 1.28 \times 10^8 \text{ s}$$

$$\tau_{wet} < 10^6 \text{ s } (\textit{Jaenicke, 1988})$$

D/2 [µm]	τ [d]	Δs [km]	Δz [m]
0.001	0.01	8	20
0.01	1	800	2000
0.1	10	8000	20000
1	10	8000	20000
10	1	800	2000
100	0.01	8	20

Figure 2-6 Residence time of tropospheric aerosols as a function of particle diameter. Figure taken from Jaenicke (1987) and reprinted with permission from Dechema e.V. The hatched areas represent published estimates for: small ions (I); Aitken particles (A); coagulation by thermal diffusion (C); radioactivity (R); precipitation (P); and sedimentation (F). The major production mechanisms and removal processes are indicated in the most important size ranges.

(*Franklin et al., 2000*)

PROVEN PATHWAYS
OF REGIONAL AND INTERCONTINENTAL TRANSPORT OF AEROSOLS
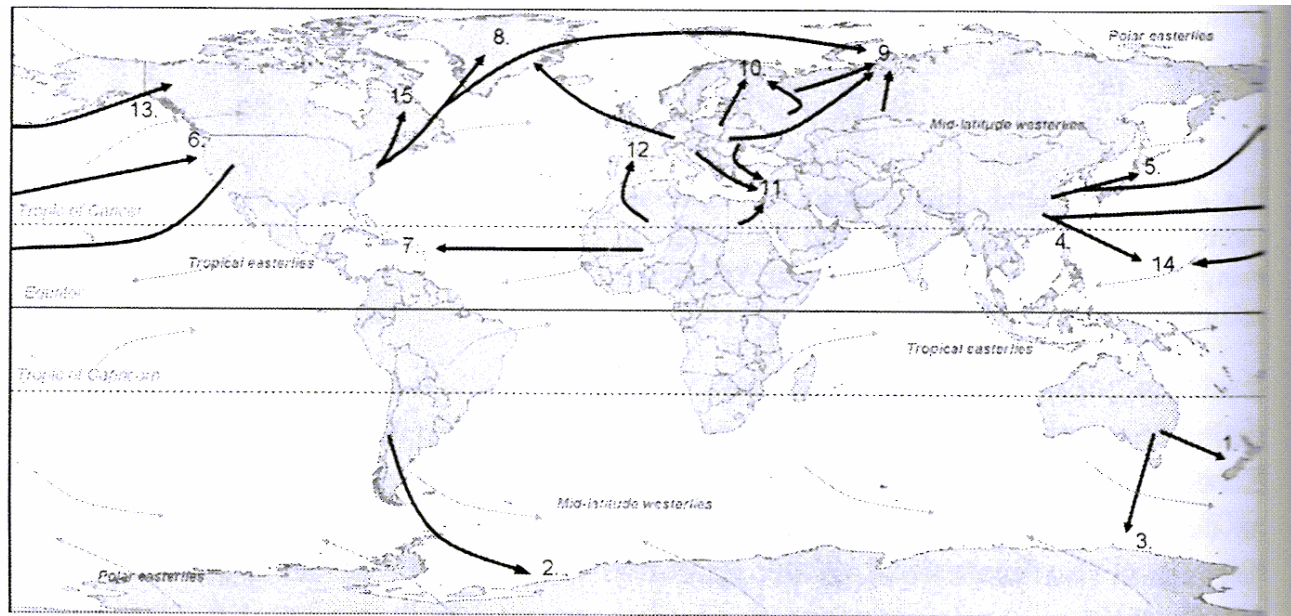

Fig. 5 The major documented pollution plume pathways over which the long-range transport of pollution occurs (as indicated by the *black arrows*). The main windfields are also indicated on the figure by the *grey arrows*. The *numbers* on the figure refer to representative studies documenting pollution transport over these pathways. *1* Australia to New Zealand (Marx et al. 2008); *2* South America to Antarctica (Wolff et al. 1999); *3* Australia to Antarctica (Vallelonga et al. 2002); *4* Asia to Taiwan (Lin 2001); *5* Asia to Japan and Korea (Kim et al. 2009; Okuda et al. 2006); *6* Asia to North America (Jaffe et al. 2003; Osterberg et al. 2008); *7* northern Africa to central America (Arimoto et al. 1992); *8* Europe and North America to Greenland (Hong et al. 1996; McConnell and Edwards 2008); *9* North America, Europe and Russia to the Russian Arctic (Shevchenko et al. 2003); *10* western and eastern Europe to Scandinavia (Brännvall et al. 1999); *11* Europe and North Africa to the Middle East (Erel et al. 2007); *12* North Africa to Spain (Bacardit and Camarero 2009); *13* Asia to the North American Arctic (Osterberg et al. 2008); *14* Asia and North America to the central north Pacific (Settle and Patterson 1982); *15* North America to the remote Canadian Arctic (Outridge et al. 2002)

Marx & McGowan, 2010

Main components – Trends

Weekly filter samples, PM_{10}, $PM_{2.5}$ '95-'02 bzw. '99-'02 (PM_1)

Spindler et al., 2004
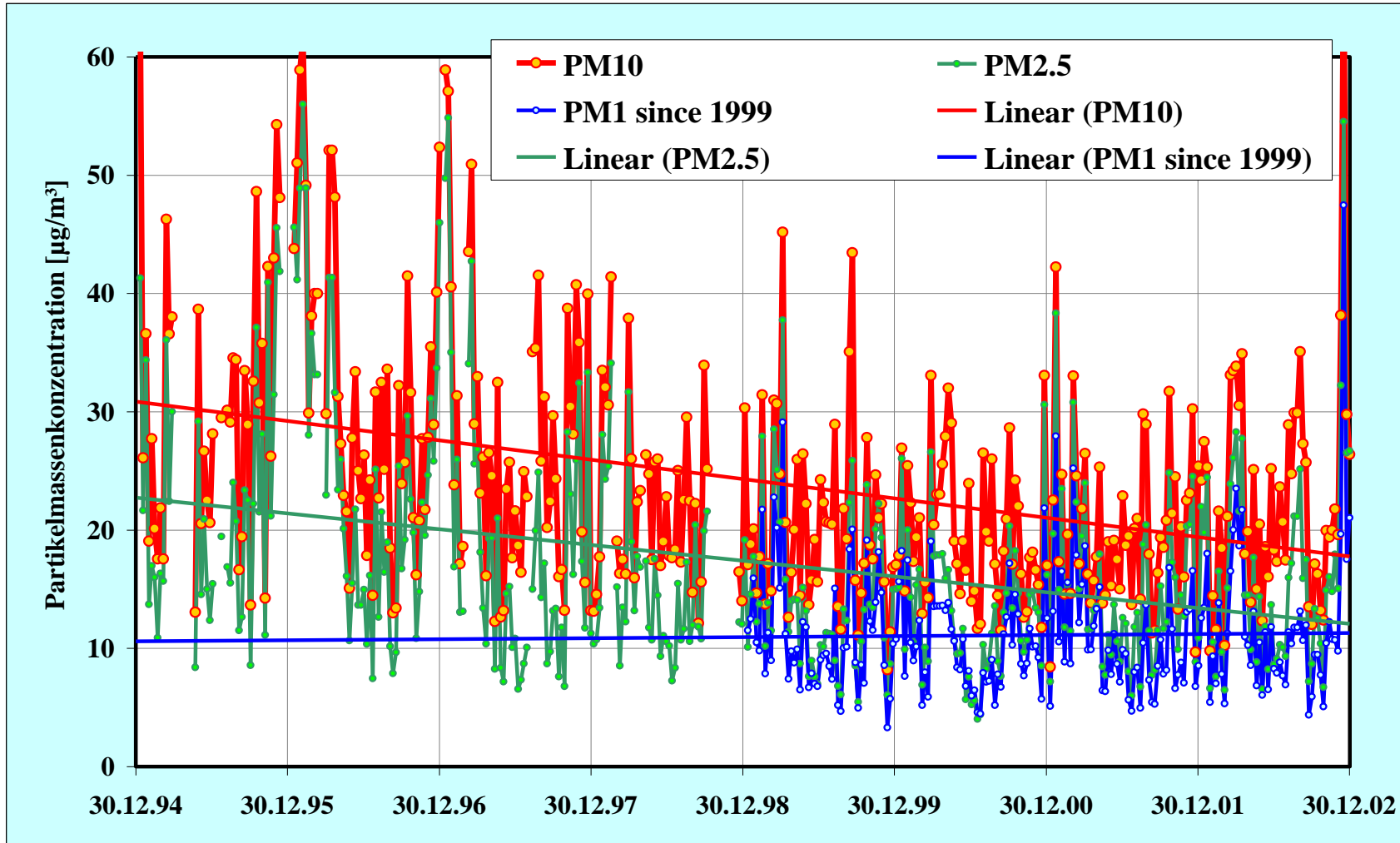
Aerosol sources (globally, TgE/a oder Tg/a)

Precursors   *anthr.*   *natural*

		anthr.	natural
NO_x	41	31	10
NH_3	54 (40-70)	43	11
SO_2	88 (67-130)	79	9
DMS	25 (12-42)	0	25
VOCs	236 (100-560)	109	127 (only terpenes)

Primary

   Carbonaceous (OC)

     Biomass burning   54 (45-80)

     Fossil fuel burning   28 (10-30)

     biogenic   56 (0 – 90)

   Black carbon (soot)

     Biomass burning   5.7 (5-9)

     Fossil fuel burning   6.6 (6-8)

   Industrial dust   100 (40-130)

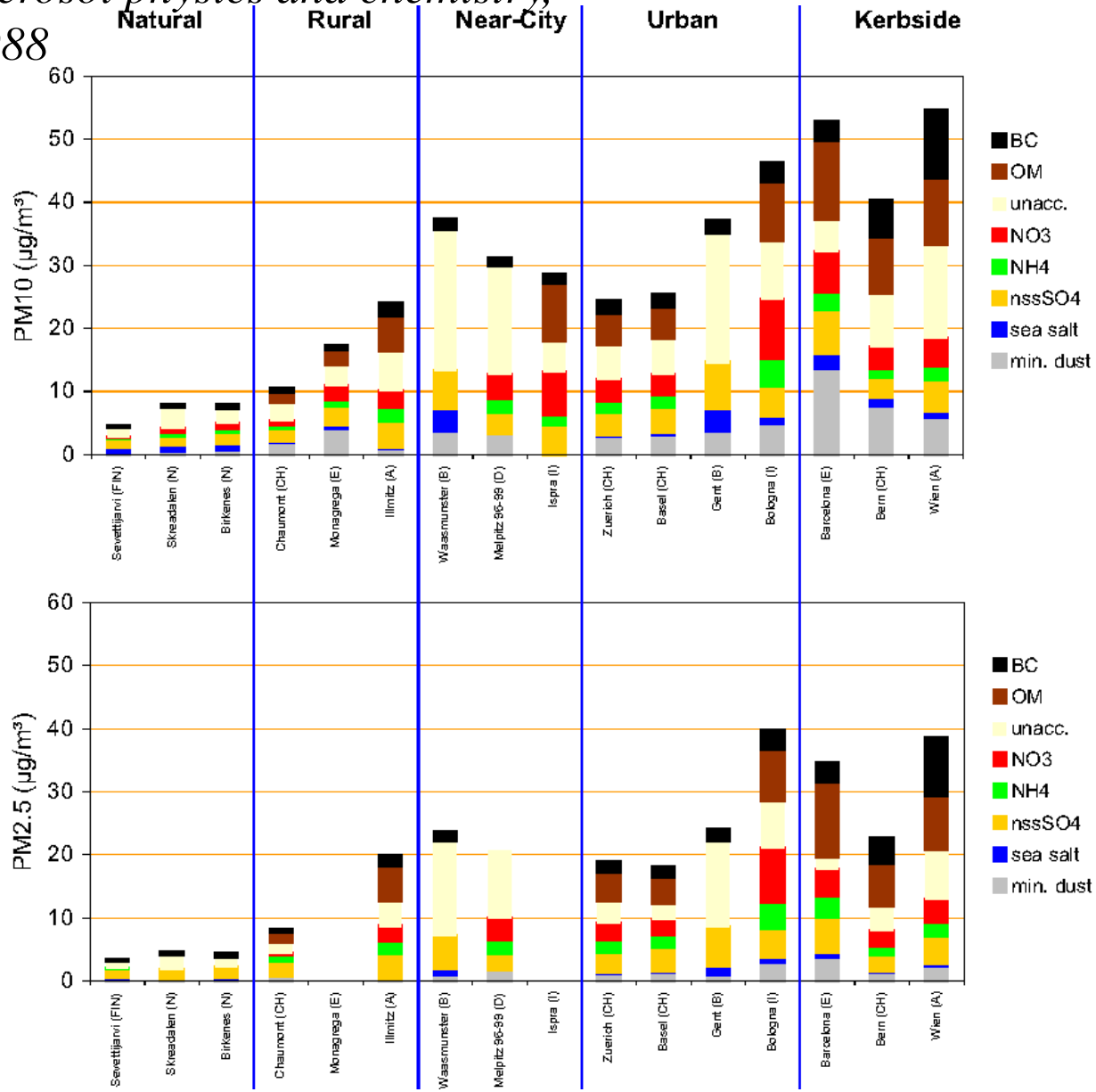   Sea salt   3340 (1000-6000)

   Mineral dust   2150 (1000-3000)
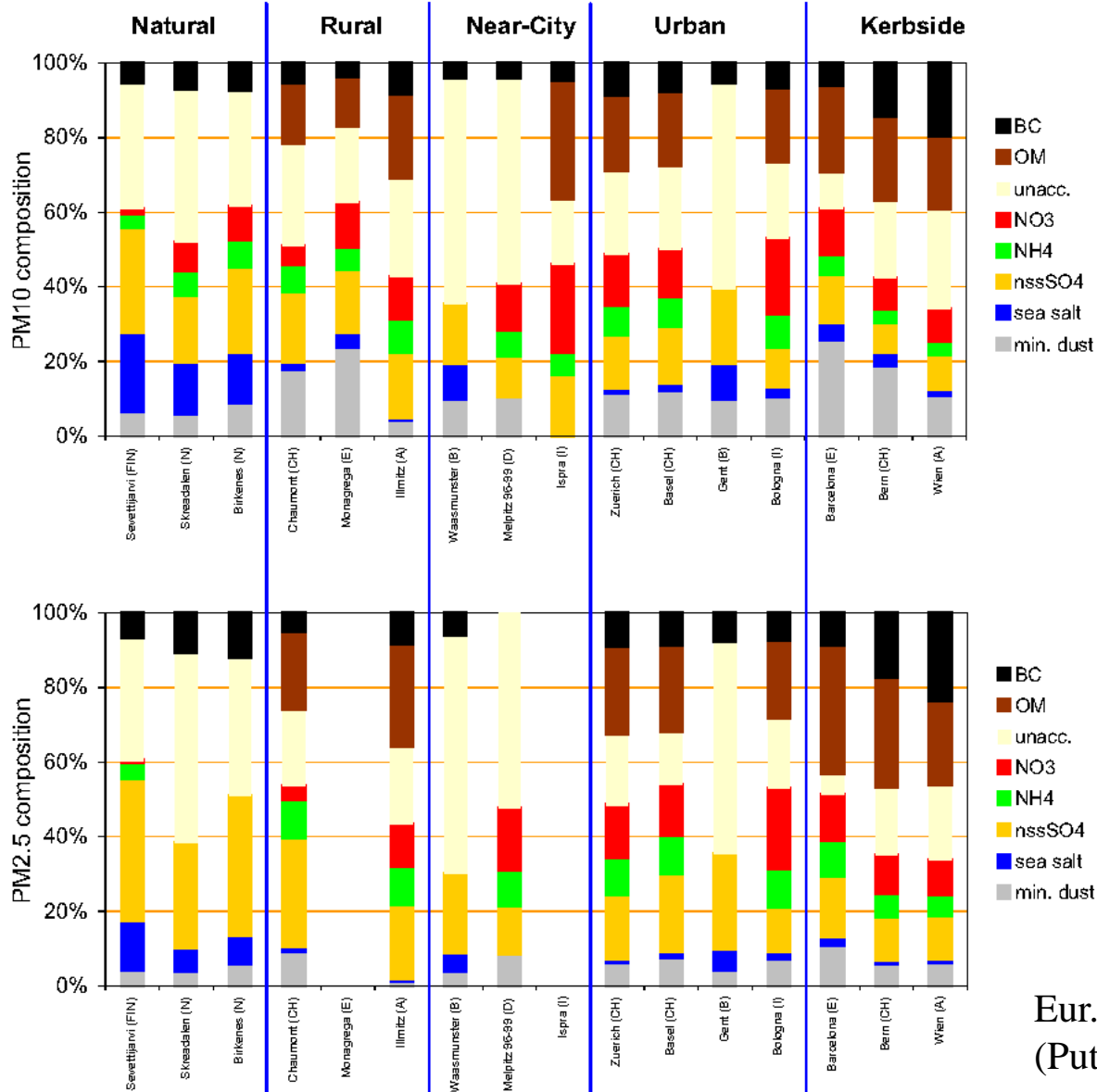
      (Penner et al., in IPCC, 2001)   *(UBA)*

Chemical composition

Globally: Jaenicke: Aerosol physics and chemistry, Landolt-Börnstein, 1988

Europe:
Putaud et al.,
EU-Report 2002 =
van Dingenen et al.,
Atmos. Environ. 2004

Aerosol chemical composition

Eur. Aer. Phenomenology
(Putaud et al., 2002)

strong temperature dependence of phase equilibrium $NH_3 + HNO_3 =$

for rh < $rh_{D:}$

$$p_{NH3} * p_{HNO3} = \quad 0.12 \text{ ppbv}^2 \text{ (278 K)},$$
$$2.0 \text{ ppbv}^2 \text{ (288 K)},$$
$$28 \text{ ppbv}^2 \text{ (298 K)}$$

$Y = [NH_4NO_3]/\{[NH_4NO_3] + 3 [NH_4(SO_4)_2]\}$

Humidity dependence:
(Stelson & Seinfeld, 1982)
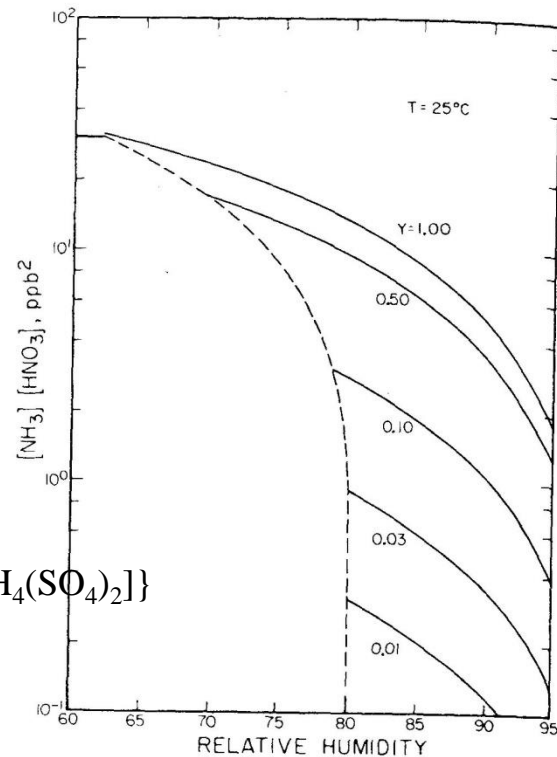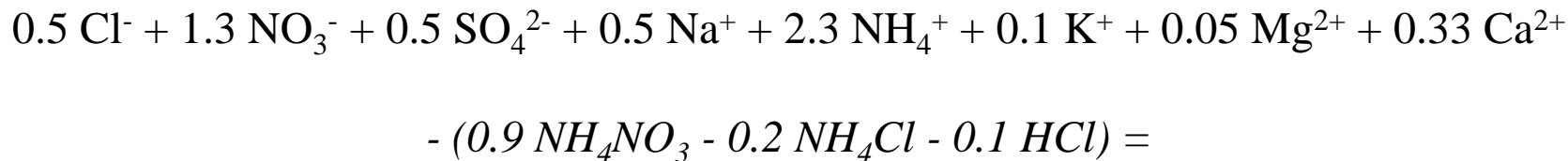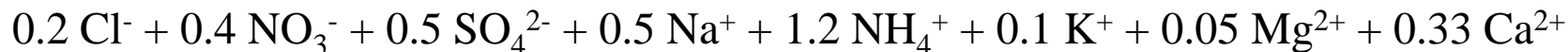

Fig. 2. The effect of $(NH_4)_2SO_4$ on the relative humidity dependence of the NH_4NO_3 dissociation constant.

Ions volatile, and non-volatile:

Winter

$$0.5 \text{ Cl}^- + 1.3 \text{ NO}_3^- + 0.5 \text{ SO}_4^{2-} + 0.5 \text{ Na}^+ + 2.3 \text{ NH}_4^+ + 0.1 \text{ K}^+ + 0.05 \text{ Mg}^{2+} + 0.33 \text{ Ca}^{2+}$$

- (0.9 NH_4NO_3 - 0.2 NH_4Cl - 0.1 HCl) =

Summer

$$0.2 \text{ Cl}^- + 0.4 \text{ NO}_3^- + 0.5 \text{ SO}_4^{2-} + 0.5 \text{ Na}^+ + 1.2 \text{ NH}_4^+ + 0.1 \text{ K}^+ + 0.05 \text{ Mg}^{2+} + 0.33 \text{ Ca}^{2+}$$
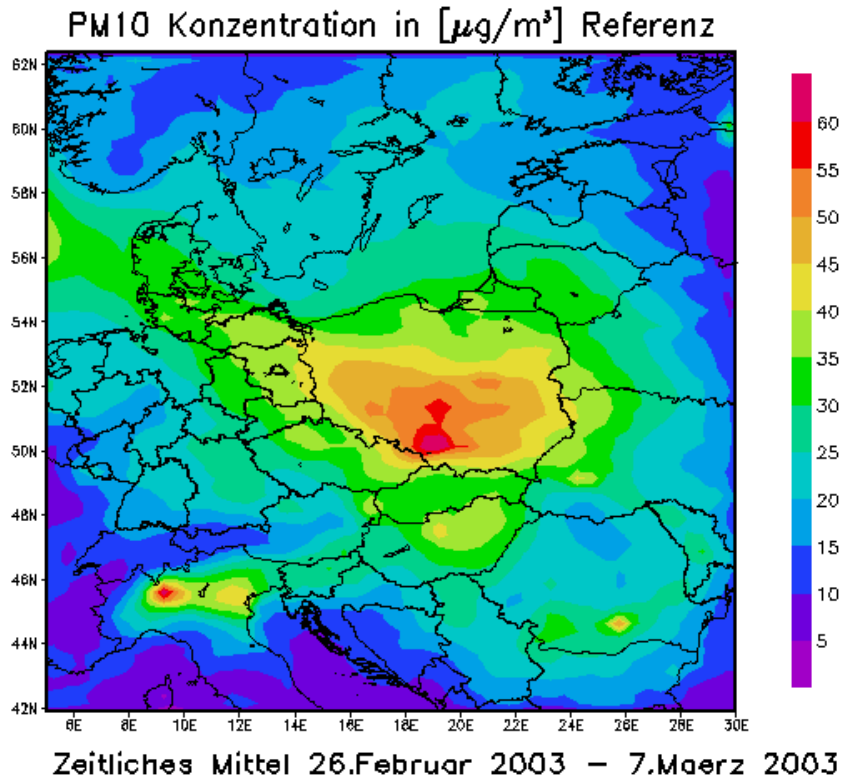
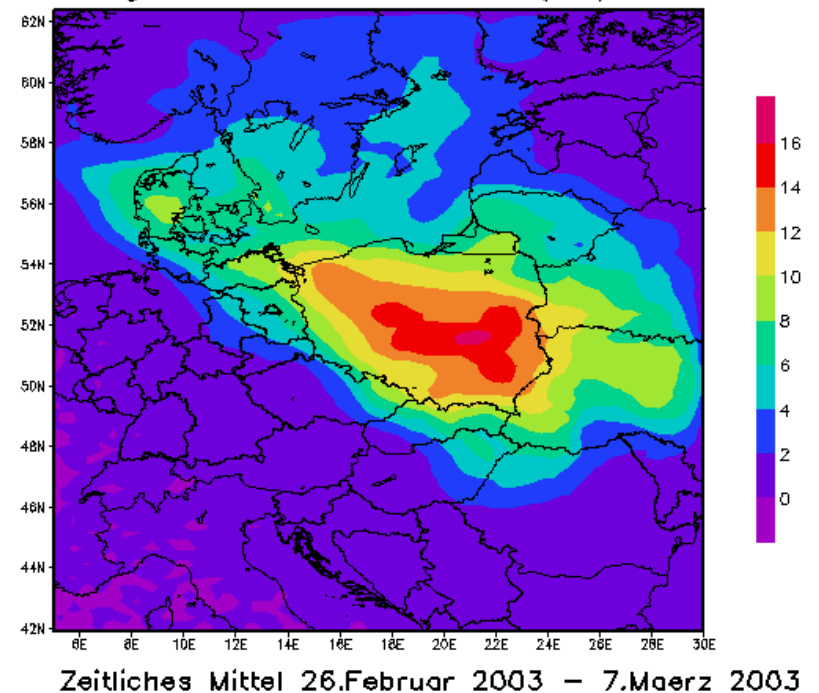# Potential to reduce fine particulate matter (PM) ?

Example emission reductions NH_3

ΔPM_{10} (% reduction) for scenario of 0 **NH_3** emissions in eastern Germany, Poland and Ukraine

PM10 Konzentration in [µg/m³] Referenz

Zeitliches Mittel 26.Februar 2003 – 7.Maerz 2003

Abweichung von PM10 Referenz in % (NH_3) Szenario 2

Abweichung von PM10 Referenz in % (SO_2) Szenario 3

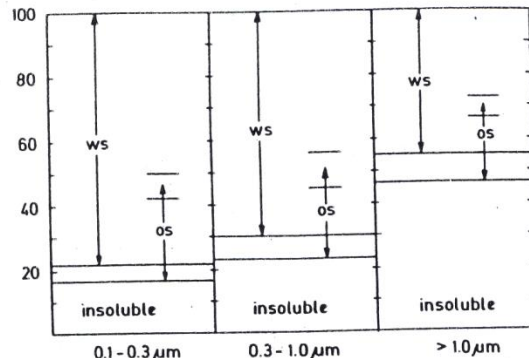Zeitliches Mittel 26.Februar 2003 – 7.Maerz 2003

(courtesy of Reimer, FU Berlin 2006)

Expected effects are not very large

NH_3 emissions are underestimated

A large fraction of the organic carbon (OC, POM) is water soluble (WSOC)
(...and, hence, suitable as cloud condensation nucleus (CCN))


Continental aerosol (Winkler, 1974)

Continental aerosol consists of (each 25-50%):
• aliphatic polyols (mostly sugars) and polyethers (polyphenols)
• low-molecular aliphatic and other multifunctional compounds, e.g. $R(COOH)_{1-2}$
• unsaturated aliphatic and aromatic polyacids of various lipophilicity („humic-like"), M = 200-500 Da, sources: Oxidation of soot, acid catalyzed polymerisation of terpenes (Havers et al., 1998; Fuzzi et al., 2001; Krivacsy et al., 2001; Decesari et al., 2002; Gelencser et al., 2003; Puxbaum et al., 2003)

Aerosol sources, size segregated
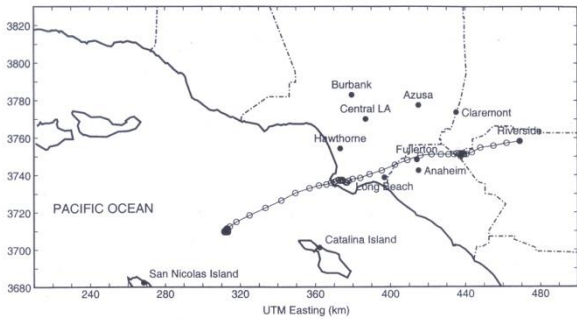## Air in Riverside, CA, 25.9.1996 (Kleeman et al., 1999)
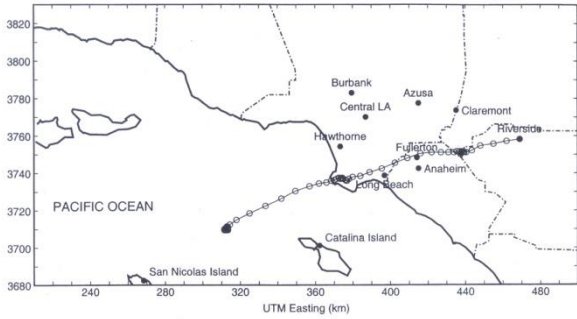
• Emission inventory (source distribution, characteristics)
• Atmosphere model covering transport and transformations
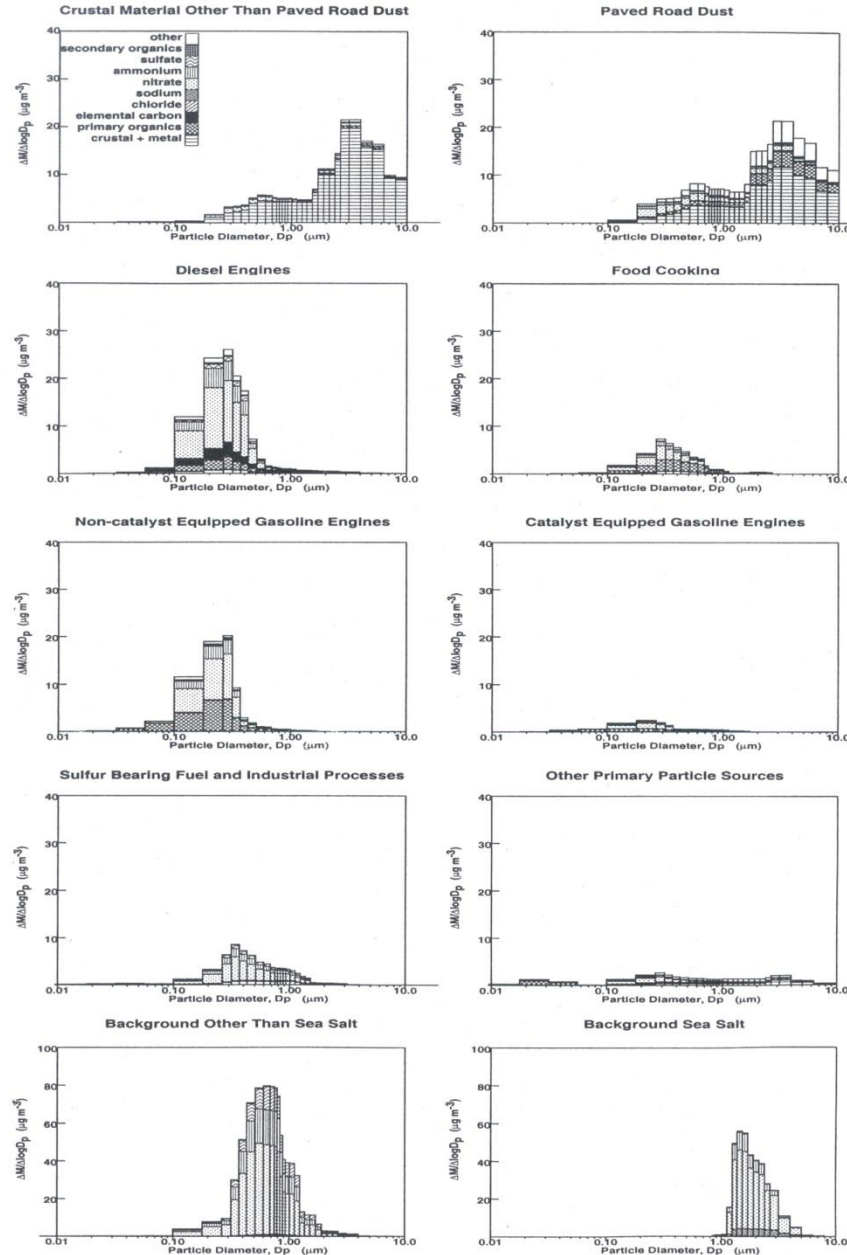
Sources for aerosol inorganic ions,
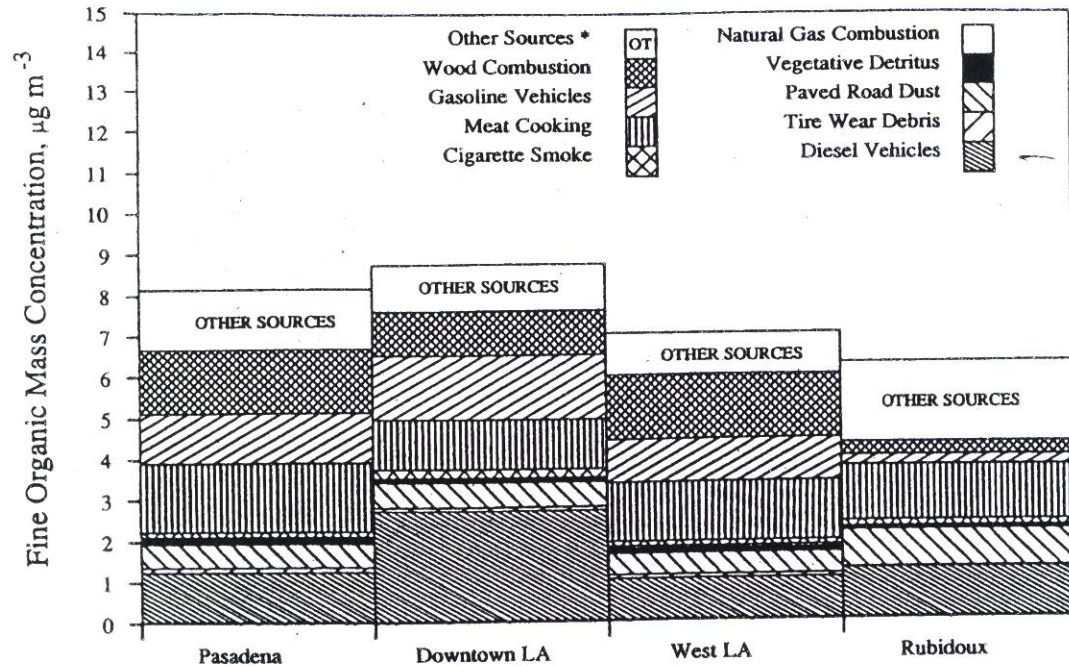Los Angeles 24.-25.9.1996 (Mysliwiec & Kleeman, 2002)

• Emission inventory
(source distribution,
characteristics)
• Atmosphere model
covering transport and
transformations
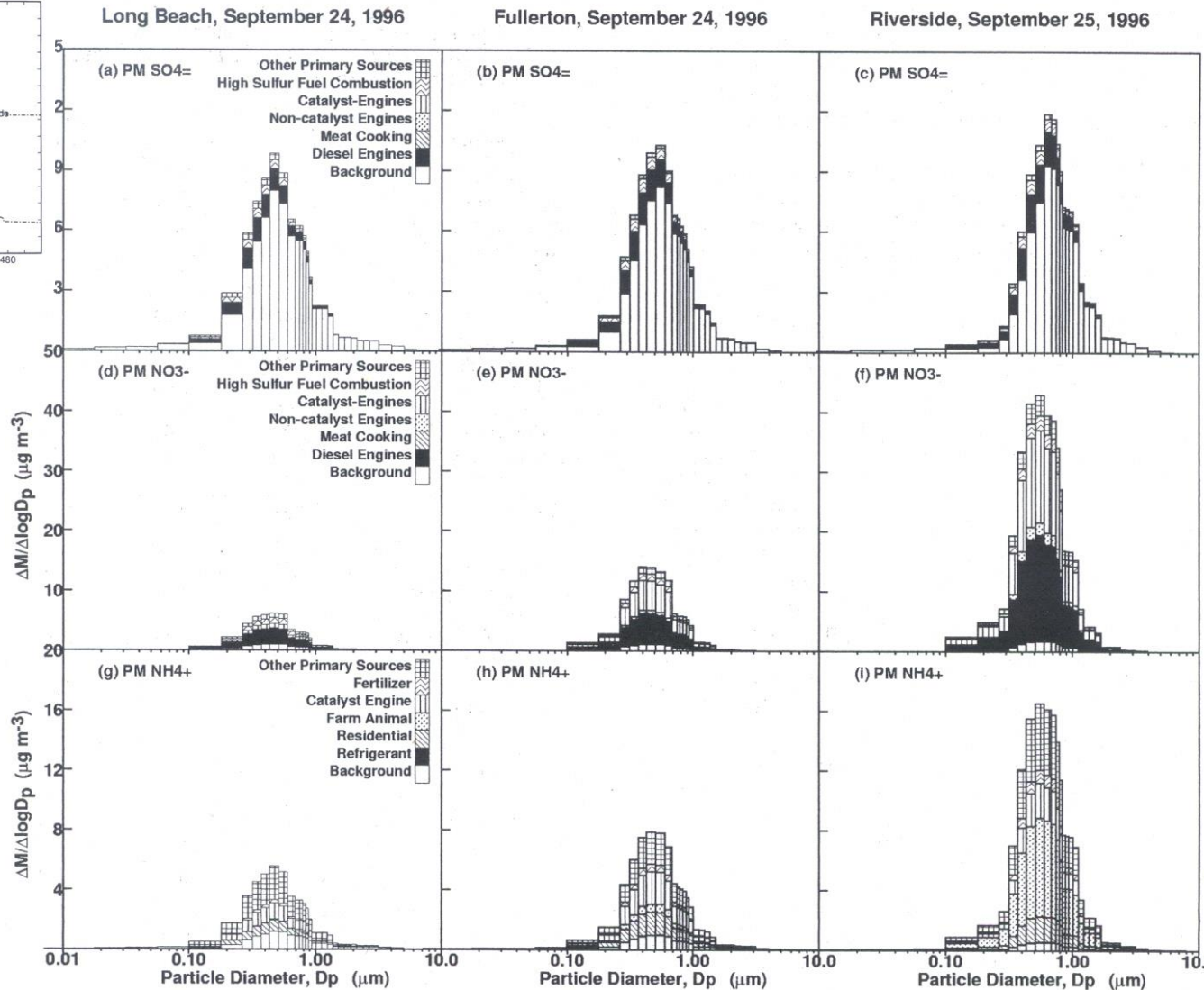
Source contributions to OC: urban

Total fine part. OC emitt. 30 t/d

Meat cooking   21%
Road abrasion   16%
Open fires   14%
Vehicles without cat.
          converter 12%
Diesel vehicles   6.2%
Lacquing   4.8%
Forest fires   2.9%
Vehicles without cat.
          converter 2.9%
Tobacco smoke   2.7%

Legend: Other Sources *, Wood Combustion, Gasoline Vehicles, Meat Cooking, Cigarette Smoke, Natural Gas Combustion, Vegetative Detritus, Paved Road Dust, Tire Wear Debris, Diesel Vehicles

Y-axis: Fine Organic Mass Concentration, $\mu g\ m^{-3}$

Categories: Pasadena, Downtown LA, West LA, Rubidoux

* Other Sources include secondary formation

Table 4. Source apportionment of fine particulate mass concentration: 1982 annual average determined by chemical mass balance (avg ± std in $\mu g\ m^{-3}$)

...t of ambient fine organic aerosol mass concentration — 1982 annual average

Source	Pasadena	Downtown LA	West Los Angeles	Rubidoux
Diesel exhaust	5.27 ± 0.72	11.6 ± 1.19	4.36 ± 0.64	5.35 ± 0.51
Tire wear debris	0.29 ± 0.11	0.22 ± 0.09	0.25 ± 0.09	[a]
Paved road dust	3.46 ± 0.43	3.62 ± 0.46	3.00 ± 0.39	5.50 ± 0.61
Vegetative detritus	0.33 ± 0.10	0.24 ± 0.12	0.38 ± 0.11	0.18 ± 0.08
Natural gas combustion aerosol	0.047 ± 0.02	0.040 ± 0.019	0.034 ± 0.016	0.029 ± 0.008
Cigarette smoke	0.18 ± 0.03	0.26 ± 0.045	0.20 ± 0.028	0.19 ± 0.032
Meat charbroiling and frying	2.41 ± 0.46	1.74 ± 0.34	2.03 ± 0.39	1.94 ± 0.35
Catalyst and non-catalyst gasoline-powered vehicle exhaust	1.63 ± 0.20	2.12 ± 0.23	1.44 ± 0.16	0.34 ± 0.05
Wood smoke	2.70 ± 0.43	1.85 ± 0.31	2.65 ± 0.41	0.54 ± 0.10
Organics (other + secondary)	1.46 ± 0.66	1.16 ± 0.76[b]	1.03 ± 0.71[b]	1.94 ± 0.44
Sulfate ion (secondary + background)	5.9 ± 0.60	6.6 ± 0.65	5.9 ± 0.60	5.8 ± 0.51
Secondary nitrate ion	2.1 ± 0.27	3.0 ± 0.54	1.9 ± 0.29	10.4 ± 1.2
Secondary ammonium ion	2.6 ± 0.34	3.0 ± 0.37	2.3 ± 0.23	5.1 ± 0.59
Sum	28.3 ± 1.5	35.5 ± 1.9	25.3 ± 1.4	37.3 ± 1.8
Measured	28.2 ± 1.9	32.5 ± 2.8	24.5 ± 2.0	42.1 ± 3.3

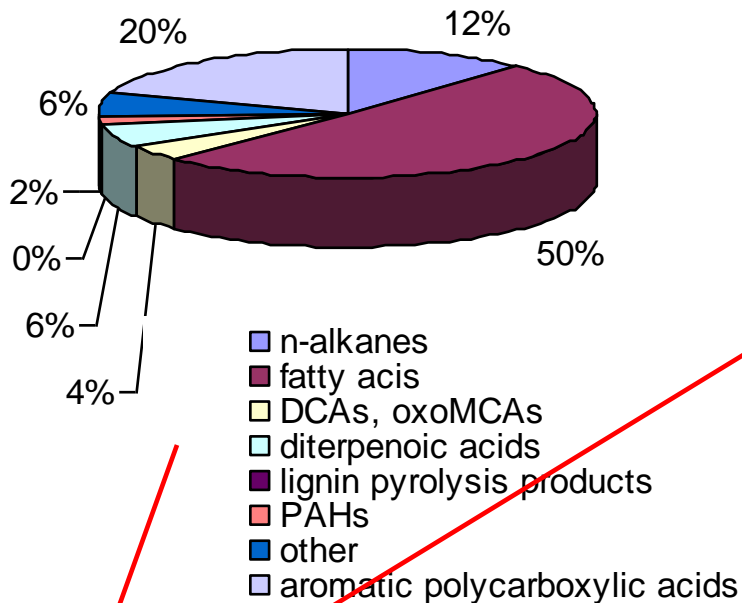Southern California,
(Rogge et al., 1996; Schauer et al., 1996)

[a] Not statistically different from zero with greater than 95% confidence, and therefore removed from CMB model.
[b] Not statistically different from zero with greater than 95% confidence.
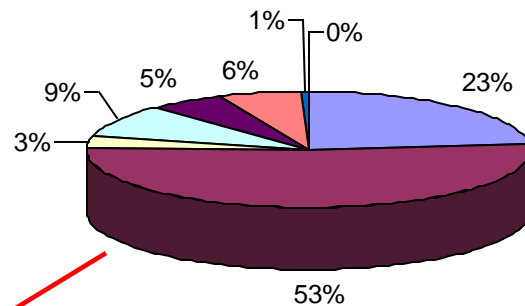
identified organics Los Angeles

identified organics Gent / winter

identified organics Gent / summer

- n-alkanes
- fatty acis
- DCAs, oxoMCAs
- diterpenoic acids
- lignin pyrolysis products
- PAHs
- other
- aromatic polycarboxylic acids

- res id OC
- res unid OC
- el unres OC
- non-ex non-el OC
- EC

c ($\mu g/m^3$)

W.-L.A. 1982
Rubidoux 1982
Gent winter 1998
Gent summer 1998
winter 1998-2000
summer 1998-99
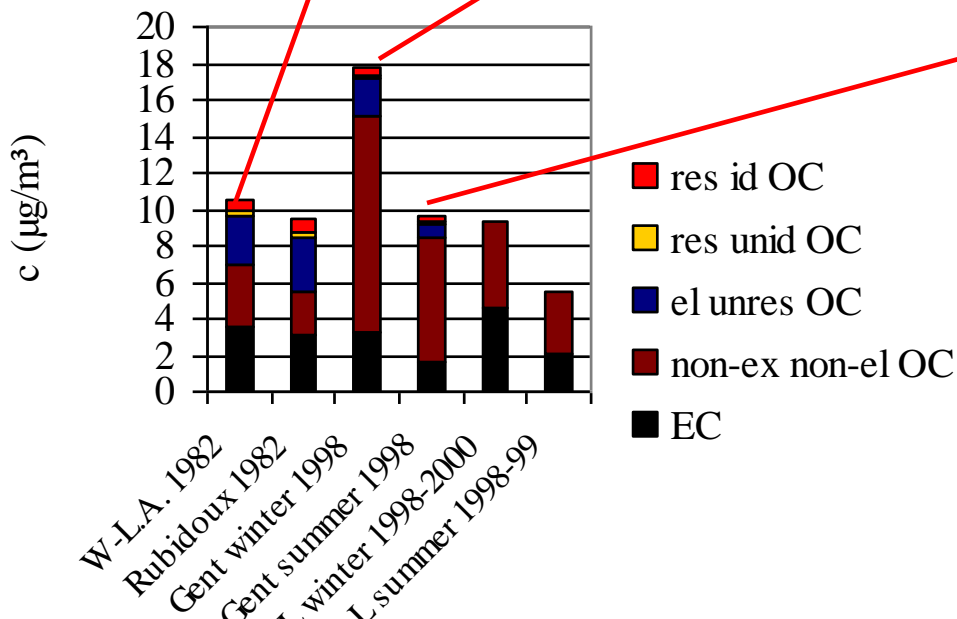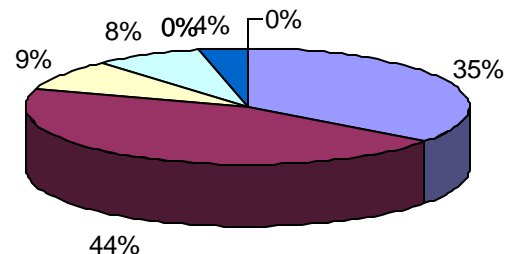
(Schauer et al, 1996; Kubátova et al., 2001)

Secondary particle sources: SOA formation

Ozonolysis of alkenes:　　　Terpenes (Griffin et al., 1999ff; Iinuma et al., 2004)

C_{14}-1-en: Smog chamber UCR (Ziemann et al., 2000):

C_{14}-1-en + O_3 →

$$CH_3(CH_2)_{11}CH=CH_2 + O_3 \rightarrow CH_3(CH_2)_{11}\overset{O-O}{\overset{|\ \ |}{CH-CH_2}}$$

$\rightarrow CH_3(CH_2)_{11}CHO + [CH_2OO]^*$　　(1a)

$\rightarrow HCHO + [CH_3(CH_2)_{11}CHOO]^*$　　(1b)

$[CH_3(CH_2)_{11}CHOO]^* \rightarrow CH_3(CH_2)_{11}C(O)OH$ or other decomposition products　　(2)

$[CH_3(CH_2)_{11}CHOO]^* + M \rightarrow CH_3(CH_2)_{11}CHOO + M$　$[M = N_2, O_2, solvent]$　(3)

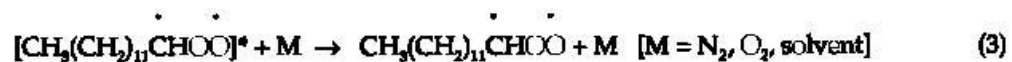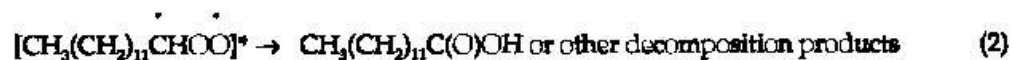$CH_3(CH_2)_{11}CHOO + H\text{-}OG \rightarrow CH_3(CH_2)_{11}\underset{\overset{|}{OG}}{CHOO\text{-}H}$　$[G = CH_3, CH(CH_3)_2, CHO, C(O)(CH_2)_xCH_3\ (x = 0, 5, 7)]$　(4)

$[CH_2OO]^* \rightarrow CH(O)OH$ or other decomposition products　　(5)

$[CH_2OO]^* + M \rightarrow CH_2OO + M$　　　$[M = N_2, O_2, solvent]$　(6)

$CH_2OO + H\text{-}OG \rightarrow CH_2\underset{\overset{|}{OG}}{OO\text{-}H}$　　　$[R = CH_3, CH(CH_3)_2, CHO, C(O)(CH_2)_xCH_3\ (x = 0, 5, 7)]$　(7)

→ SOA

POM molecular weight:

A large fraction of the water insoluble fraction is high molecular

• biogenic primary emitted, including biologically effective substances (proteins, toxins)

	EC/TC	Protein/TC
Urban:	~ 60 %	~ 4 %
Rural:	~ 30 %	~ 30 %
Alpine:	~ 30 %	~ 20 %

(Franze et al., 2003; Fehrenbach, 2007)

• biogenic secondary (formed from terpenes, besides other)
• biopolymers and fragments thereof, eventually photochemically formed polymers (*Gelencser et al., 2003*)

for example, $x_{cellulose}$ = 1-2 % in Wien (*Kunit & Puxbaum, 1996*);

• microorganisms, fragments thereof, macroscopic particles (hairs, droplets,...)
• anthropogenic primary (cooking vapours, tobacco smoke…)
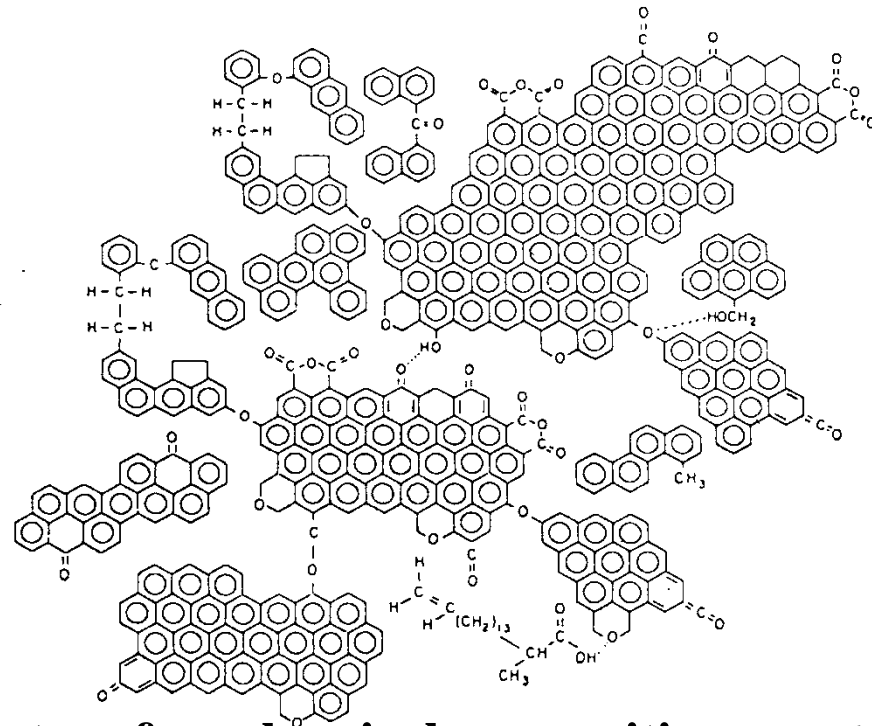• anthropogenic secondary

3.4.2.4 Soot

**= amorphous C + shell of adsorbed molecules and/or partly oxygenated C
+ adsorbed water molecules**
- **Strong sorbent**
- **Light absorbing**
- **Hydrophobic (initially**
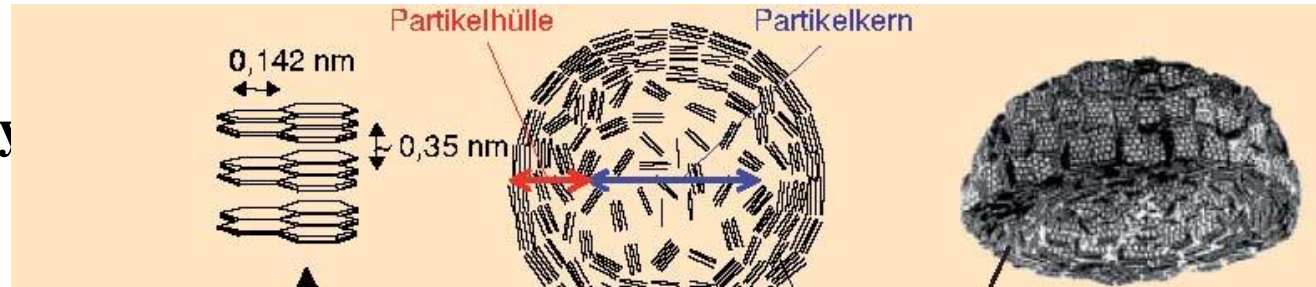
soot particle shell, core *(Hoffmann et al., 2007)*

flame soot surface chemical composition *(Smith et al.,*

= nanosphere-soot particles
Curvature probably caused by 5-ring structures (fullerenes!) or by lacking
C atoms
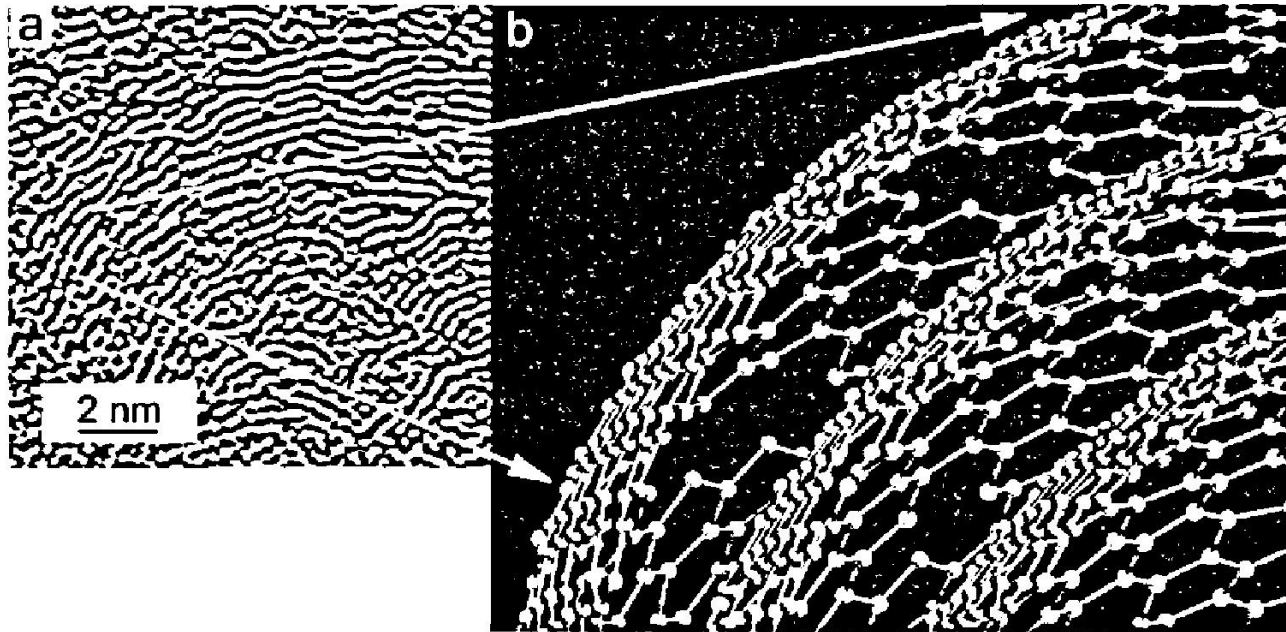
FIG. 8. (a) Part of Figure 5b, with the contrast of graphene-like layers in ns-soot enhanced digitally. (b) A schematic model for three layers. They are graphene-like, but some C atoms are missing from the hexagonal nets. The missing atoms break the periodic order and presumably cause the misalignment of layer segments relative to one another, resulting in the layer curvature. H in ns-soot can be accommodated around the sites of missing C atoms, where some C atoms can be bonded to two C and one H.

(Buseck et al., 2014)

- **Soot and POM distributions are not easily available**
- **In most aerosol models: Hygroscopic soot is formed from lipophilic soot (BC) after a fixed time („aging'). Example: ECHAM5-HAM Aerosol Model**

4 size modes
7 chemical components

Species	Total Sources [Tg yr^{-1}]	Burden [Tg]	Lifetime [days]
SU	76.1	0.80	3.9
BC	7.7	0.11	5.4
POM	66.1	0.99	5.4
SS	5032.2	10.50	0.8
DU	662.4	8.28	4.6
SO$_2$	92.0	0.67	2.7
SU$_{gas}$	28.0	0.00088	0.01
DMS	23.4	0.077	1.2

+ PAHs

(Stier et al., 2005)
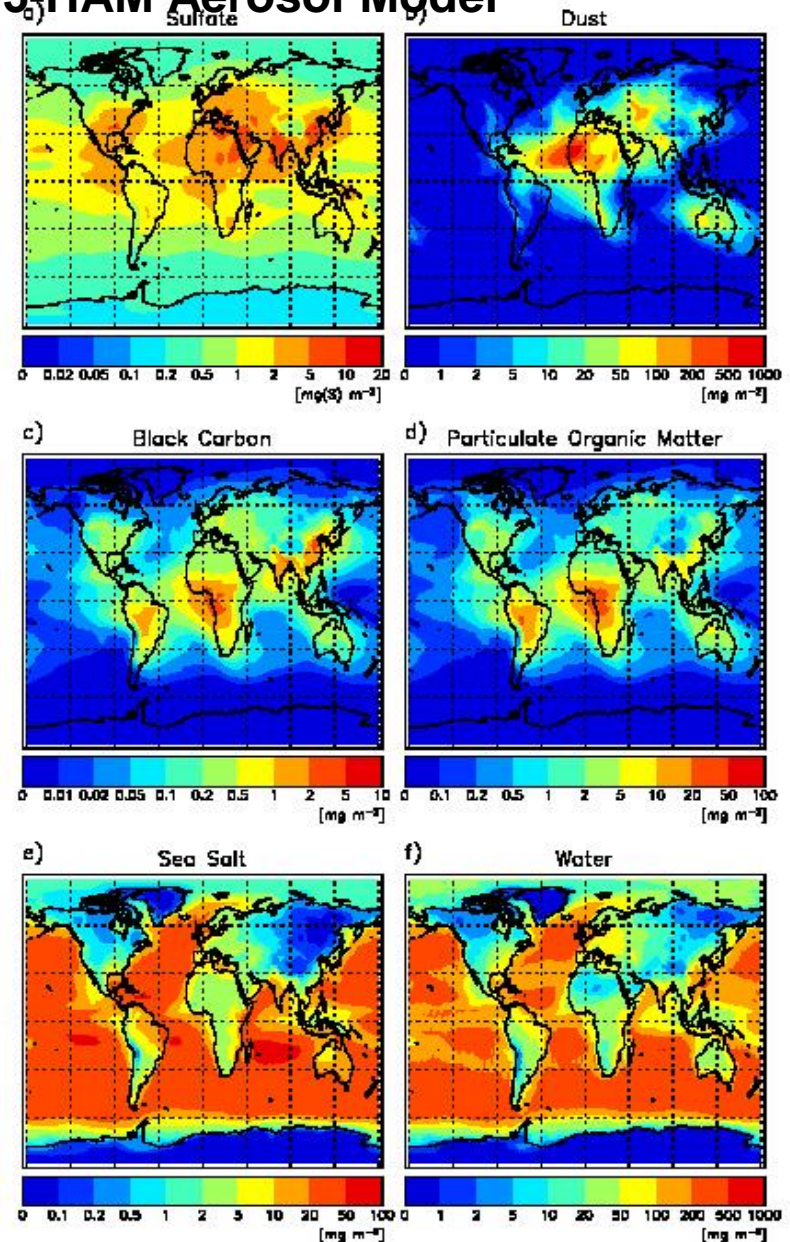
3.4.2.5 Water

Particulate matter water uptake:

Growth of particulate matter containing inorganic salts is smooth (unlike for pure salts)
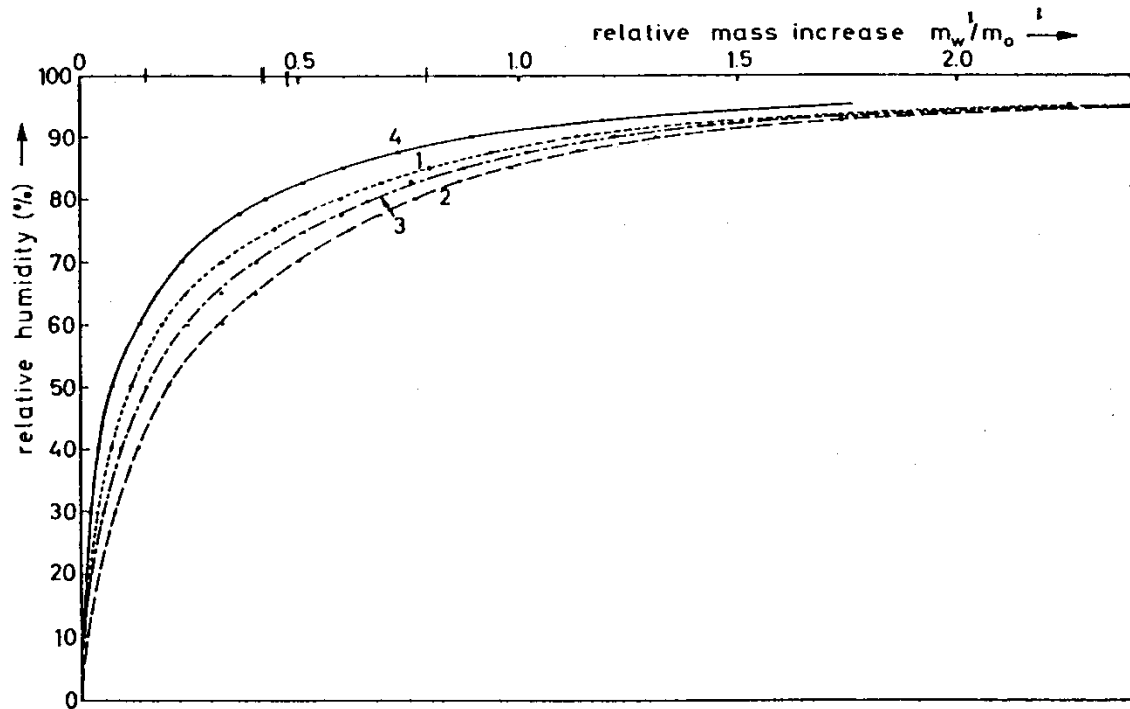
FIG. 5. — Average growth curves of atmospheric aerosols.
Curve 1 : 0.1 μm < r < 1.0 μm Deuselbach, 14 samples.
Curve 2 : r > 1.0 μm Deuselbach, 14 samples.
Curve 3 : Calculated mean from 1 and 2 for r > 0.1 μm.
Curve 4 : r > 0.1 μm Mainz, 28 samples.

(Tang, 1976; Winkler & Junge, 1972)

dt: Liqueszenzfeuchte

	Deliquescence humidity, rh_D	Density [g cm^{-3}]
NaCl	75%	2.16
$CaCO_3$	-	1.77
$(NH_4)_2SO_4$	80%	1.77
NH_4HSO_4	39%	1.78
NH_4NO_3	62%	1.72

Particulate matter provides an aqueous phase: Overview trace species concentrations

TABLE 8. Typical Concentrations of Selected Gases in the Atmosphere and in the Aqueous Phase of Atmospheric Aerosols at 25°C

Species	Urban			Rural		
	Gas Concentration, ppb	Reference	Aqueous Concentration, M	Gas Concentration, ppb	Reference	Aqueous Concentration, M
O_2	2×10^8		3×10^{-4}	2×10^8		3×10^{-4}
O_3	70	1	2×10^{-11}	30	1	9×10^{-12}
H_2	2×10^3	1	2×10^{-9}	600	1	5×10^{-10}
H_2O_2	20	2, 3	3×10^{-6}	1	4, 5	3×10^{-7}
CO	8×10^3	1	7×10^{-9}	120	1	1×10^{-10}
CO_2	5×10^5	6	2×10^{-5}	3.3×10^5	7	1×10^{-5}
NO	10	1	2×10^{-11}	0.1	1	2×10^{-13}
HNO_3	1	1, 8	5×10^{-5}	0.3	1, 8	1×10^{-6}
NH_3	25	1	2×10^{-6}	1.5	1	1×10^{-7}
H_2S	2	1	2×10^{-10}	0.1	1	1×10^{-11}
CS_2	0.15	9	3×10^{-12}	0.04	9	9×10^{-13}
OCS	0.6	10	1×10^{-11}	0.6	10	1×10^{-11}
SO_2	50	1	7×10^{-8}	1	1	2×10^{-9}
HCl	6	1	1×10^{-7}	0.7	1	1×10^{-8}
HCHO	6	11	5×10^{-8}	0.2	11	2×10^{-9}

References are to the gas phase concentration except for H_2O_2 and HNO_3, where references to both gas phase and aqueous phase concentrations are given: (1) *Graedel* [1980], (2) *Kok et al.* [1978], (3) *Kok* [1980], (4) *Kelly et al.* [1979], (5) *Bufalini et al.* [1979], (6) *McRae and Graedel* [1979], (7) *Woodwell* [1978], (8) *Likens et al.* [1979], (9) *Maroulis and Bandy* [1980], (10) *Torres et al.* [1980], (11) *Platt et al.* [1979].

$$-dc_1/dt = k^{(2)} c_1 c_2; \quad k^{(2)} [1/M/s]$$

(Graedel & Weschler, 1981)