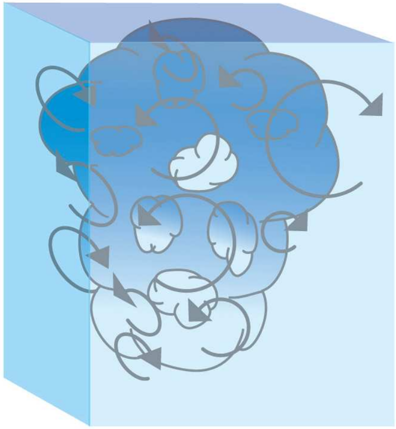
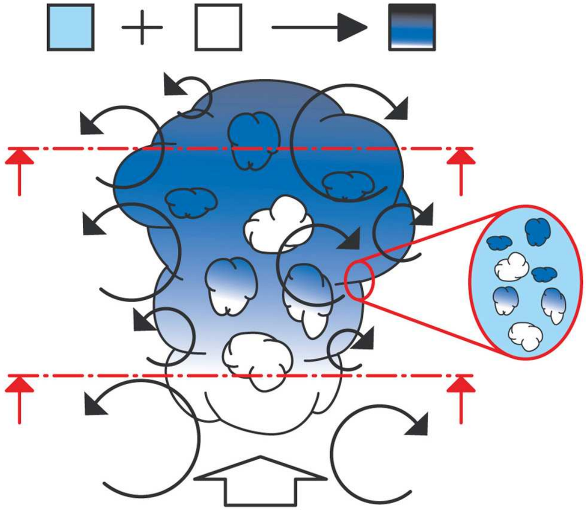
Gerhard Lammel: “Trends and Advances in Atmospheric and Environmental Chemistry"

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 $L = 0.1\text{-}2 \times 10^{-6}\ V_{water}/V_{air} = 0.1\text{-}2\ \text{g/m}^3$ $= (0.1\text{-}2) \times 10^{-3}\ \text{L/m}^3 < 10\%$ of total water content ($10\text{-}40\ \text{g/m}^3$!)
- only ≈ 10% of clouds will rain out, while 90% will recycle aerosol particles
- lifetime of clouds hours-days, of cloud droplets ($D = 5\text{-}50\ \mu\text{m}$) 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 ↔ $c_{H3O+} = 10^{-7}$ M

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) $+ HO_2\cdot_{aqu} \rightarrow 2\,O_{2\,aqu} + OH\cdot_{aqu}$

(1c) $+ OH\cdot_{aqu} \rightarrow O_{2\,aqu} + HO_2\cdot_{aqu}$

(2a) $HO_2\cdot_{aqu} + OH\cdot_{aqu} \rightarrow O_{2\,aqu} + H_2O$

(2b) $+ HO_2\cdot_{aqu} \rightarrow O_{2\,aqu} + H_2O_2$

(3b) $H_2O_2 + h\nu \rightarrow 2\,OH\cdot_{aqu}$

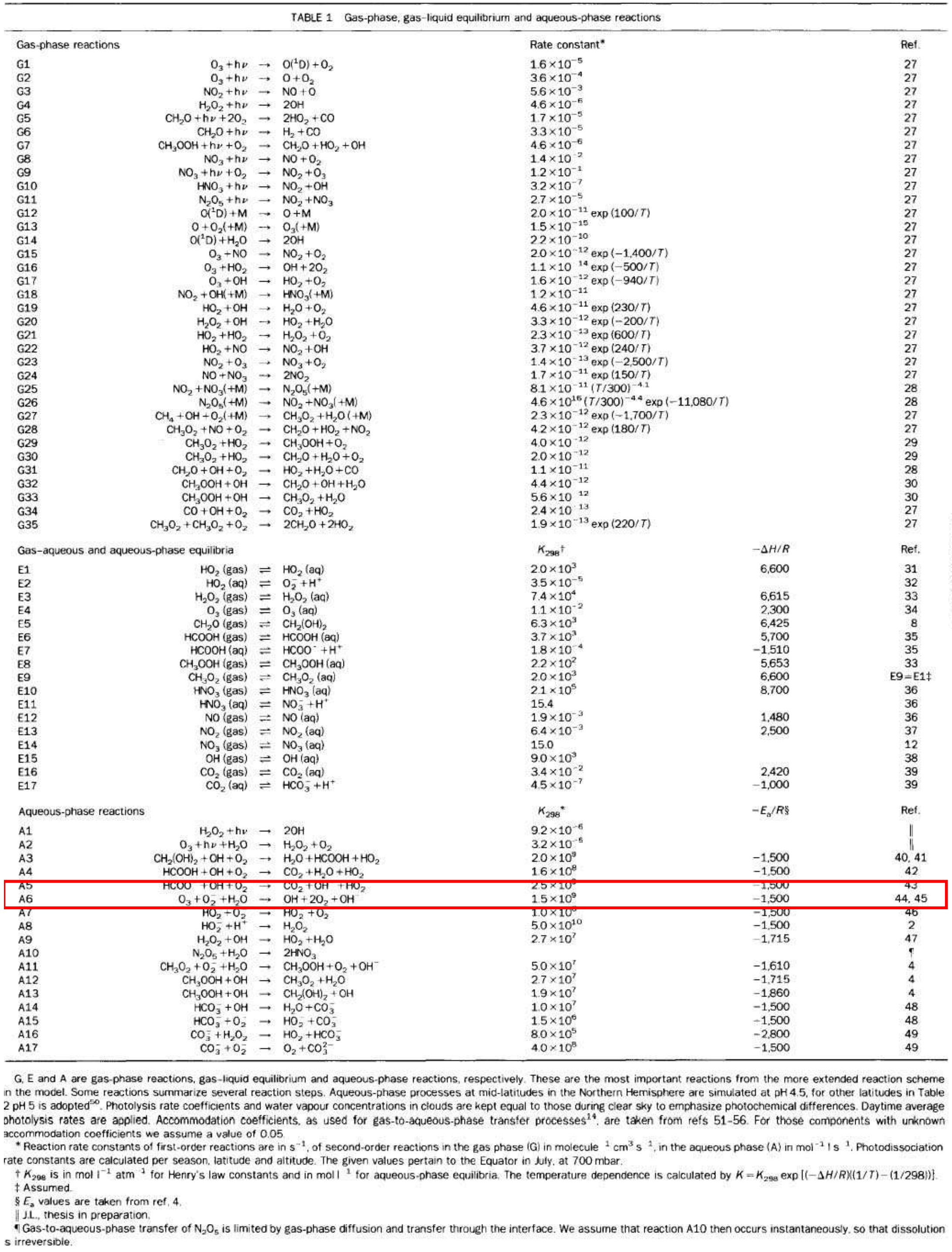


TABLE 1 Gas-phase, gas–liquid equilibrium and aqueous-phase reactions

Gas-phase reactions				Rate constant*		Ref.
G1	$O_3 + h\nu$	→	$O(^1D) + O_2$	1.6×10^{-5}		27
G2	$O_3 + h\nu$	→	$O + O_2$	3.6×10^{-4}		27
G3	$NO_2 + h\nu$	→	$NO + O$	5.6×10^{-3}		27
G4	$H_2O_2 + h\nu$	→	$2OH$	4.6×10^{-6}		27
G5	$CH_2O + h\nu + 2O_2$	→	$2HO_2 + CO$	1.7×10^{-5}		27
G6	$CH_2O + h\nu$	→	$H_2 + CO$	3.3×10^{-5}		27
G7	$CH_3OOH + h\nu + O_2$	→	$CH_2O + HO_2 + OH$	4.6×10^{-6}		27
G8	$NO_3 + h\nu$	→	$NO + O_2$	1.4×10^{-2}		27
G9	$NO_3 + h\nu + O_2$	→	$NO_2 + O_3$	1.2×10^{-1}		27
G10	$HNO_3 + h\nu$	→	$NO_2 + OH$	3.2×10^{-7}		27
G11	$N_2O_5 + h\nu$	→	$NO_2 + NO_3$	2.7×10^{-5}		27
G12	$O(^1D) + M$	→	$O + M$	$2.0 \times 10^{-11} \exp(100/T)$		27
G13	$O + O_2(+M)$	→	$O_3(+M)$	1.5×10^{-15}		27
G14	$O(^1D) + H_2O$	→	$2OH$	2.2×10^{-10}		27
G15	$O_3 + NO$	→	$NO_2 + O_2$	$2.0 \times 10^{-12} \exp(-1{,}400/T)$		27
G16	$O_3 + HO_2$	→	$OH + 2O_2$	$1.1 \times 10^{-14} \exp(-500/T)$		27
G17	$O_3 + OH$	→	$HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-940/T)$		27
G18	$NO_2 + OH(+M)$	→	$HNO_3(+M)$	1.2×10^{-11}		27
G19	$HO_2 + OH$	→	$H_2O + O_2$	$4.6 \times 10^{-11} \exp(230/T)$		27
G20	$H_2O_2 + OH$	→	$HO_2 + H_2O$	$3.3 \times 10^{-12} \exp(-200/T)$		27
G21	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	$2.3 \times 10^{-13} \exp(600/T)$		27
G22	$HO_2 + NO$	→	$NO_2 + OH$	$3.7 \times 10^{-12} \exp(240/T)$		27
G23	$NO_2 + O_3$	→	$NO_3 + O_2$	$1.4 \times 10^{-13} \exp(-2{,}500/T)$		27
G24	$NO + NO_3$	→	$2NO_2$	$1.7 \times 10^{-11} \exp(150/T)$		27
G25	$NO_2 + NO_3(+M)$	→	$N_2O_5(+M)$	$8.1 \times 10^{-11} (T/300)^{-4.1}$		28
G26	$N_2O_5(+M)$	→	$NO_2 + NO_3(+M)$	$4.6 \times 10^{15} (T/300)^{-4.4} \exp(-11{,}080/T)$		28
G27	$CH_4 + OH + O_2(+M)$	→	$CH_3O_2 + H_2O\ (+M)$	$2.3 \times 10^{-12} \exp(-1{,}700/T)$		27
G28	$CH_3O_2 + NO + O_2$	→	$CH_2O + HO_2 + NO_2$	$4.2 \times 10^{-12} \exp(180/T)$		27
G29	$CH_3O_2 + HO_2$	→	$CH_3OOH + O_2$	4.0×10^{-12}		29
G30	$CH_3O_2 + HO_2$	→	$CH_2O + H_2O + O_2$	2.0×10^{-12}		29
G31	$CH_2O + OH + O_2$	→	$HO_2 + H_2O + CO$	1.1×10^{-11}		28
G32	$CH_3OOH + OH$	→	$CH_2O + OH + H_2O$	4.4×10^{-12}		30
G33	$CH_3OOH + OH$	→	$CH_3O_2 + H_2O$	5.6×10^{-12}		30
G34	$CO + OH + O_2$	→	$CO_2 + HO_2$	2.4×10^{-13}		27
G35	$CH_3O_2 + CH_3O_2 + O_2$	→	$2CH_2O + 2HO_2$	$1.9 \times 10^{-13} \exp(220/T)$		27
Gas–aqueous and aqueous-phase equilibria				K_{298}†	$-\Delta H/R$	Ref.
E1	HO_2 (gas)	⇌	HO_2 (aq)	2.0×10^{3}	6,600	31
E2	HO_2 (aq)	⇌	$O_2^- + H^+$	3.5×10^{-5}		32
E3	H_2O_2 (gas)	⇌	H_2O_2 (aq)	7.4×10^{4}	6,615	33
E4	O_3 (gas)	⇌	O_3 (aq)	1.1×10^{-2}	2,300	34
E5	CH_2O (gas)	⇌	$CH_2(OH)_2$	6.3×10^{3}	6,425	8
E6	HCOOH (gas)	⇌	HCOOH (aq)	3.7×10^{3}	5,700	35
E7	HCOOH (aq)	⇌	$HCOO^- + H^+$	1.8×10^{-4}	−1,510	35
E8	CH_3OOH (gas)	⇌	CH_3OOH (aq)	2.2×10^{2}	5,653	33
E9	CH_3O_2 (gas)	⇌	CH_3O_2 (aq)	2.0×10^{3}	6,600	E9 = E1‡
E10	HNO_3 (gas)	⇌	HNO_3 (aq)	2.1×10^{5}	8,700	36
E11	HNO_3 (aq)	⇌	$NO_3^- + H^+$	15.4		36
E12	NO (gas)	⇌	NO (aq)	1.9×10^{-3}	1,480	36
E13	NO_2 (gas)	⇌	NO_2 (aq)	6.4×10^{-3}	2,500	37
E14	NO_3 (gas)	⇌	NO_3 (aq)	15.0		12
E15	OH (gas)	⇌	OH (aq)	9.0×10^{3}		38
E16	CO_2 (gas)	⇌	CO_2 (aq)	3.4×10^{-2}	2,420	39
E17	CO_2 (aq)	⇌	$HCO_3^- + H^+$	4.5×10^{-7}	−1,000	39
Aqueous-phase reactions				K_{298}*	$-E_a/R$§	Ref.
A1	$H_2O_2 + h\nu$	→	$2OH$	9.2×10^{-6}		‖
A2	$O_3 + h\nu + H_2O$	→	$H_2O_2 + O_2$	3.2×10^{-5}		‖
A3	$CH_2(OH)_2 + OH + O_2$	→	$H_2O + HCOOH + HO_2$	2.0×10^{9}	−1,500	40, 41
A4	$HCOOH + OH + O_2$	→	$CO_2 + H_2O + HO_2$	1.6×10^{8}	−1,500	42
A5	$HCOO^- + OH + O_2$	→	$CO_2 + OH^- + HO_2$	2.5×10^{9}	−1,500	43
A6	$O_3 + O_2^- + H_2O$	→	$OH + 2O_2 + OH^-$	1.5×10^{9}	−1,500	44, 45
A7	$HO_2 + O_2^-$	→	$HO_2^- + O_2$	1.0×10^{8}	−1,500	46
A8	$HO_2^- + H^+$	→	H_2O_2	5.0×10^{10}	−1,500	2
A9	$H_2O_2 + OH$	→	$HO_2 + H_2O$	2.7×10^{7}	−1,715	47
A10	$N_2O_5 + H_2O$	→	$2HNO_3$			¶
A11	$CH_3O_2 + O_2^- + H_2O$	→	$CH_3OOH + O_2 + OH^-$	5.0×10^{7}	−1,610	4
A12	$CH_3OOH + OH$	→	$CH_3O_2 + H_2O$	2.7×10^{7}	−1,715	4
A13	$CH_3OOH + OH$	→	$CH_2(OH)_2 + OH$	1.9×10^{7}	−1,860	4
A14	$HCO_3^- + OH$	→	$H_2O + CO_3^-$	1.0×10^{7}	−1,500	48
A15	$HCO_3^- + O_2^-$	→	$HO_2^- + CO_3^-$	1.5×10^{6}	−1,500	48
A16	$CO_3^- + H_2O_2$	→	$HO_2 + HCO_3^-$	8.0×10^{5}	−2,800	49
A17	$CO_3^- + O_2^-$	→	$O_2 + CO_3^{2-}$	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 adopted[50]. Photolysis rate coefficients and water vapour concentrations in clouds 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 processes[14], 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} cm^3 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.

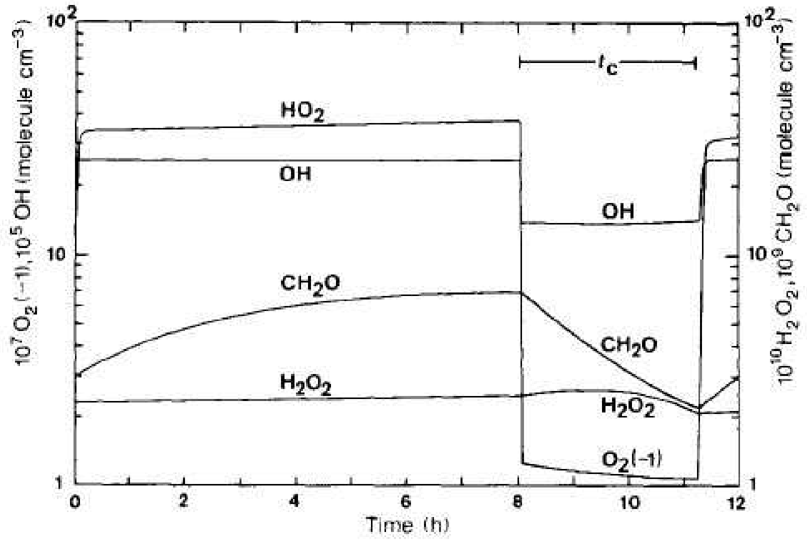


FIG. 2 Concentrations of some gases during sunlit hours of day 14 of the simulations, pertaining to the Equator at 3 km altitude (case 6, Table 2 and 3*a*), with NO_x fixed. For the cloudy period (t_c) total gas-phase plus aqueous-phase concentrations are depicted. $O_2(-1) = HO_2(gas) + HO_2(aq) + O_2^-$.

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*)

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:

$HNO_2 \rightleftharpoons HNO_{2\,aqu}$ $K^H = 50$ M/at

$HNO_4 \rightleftharpoons HNO_{4\,aqu}$ $K^H = 1.4\times10^6$ M/at

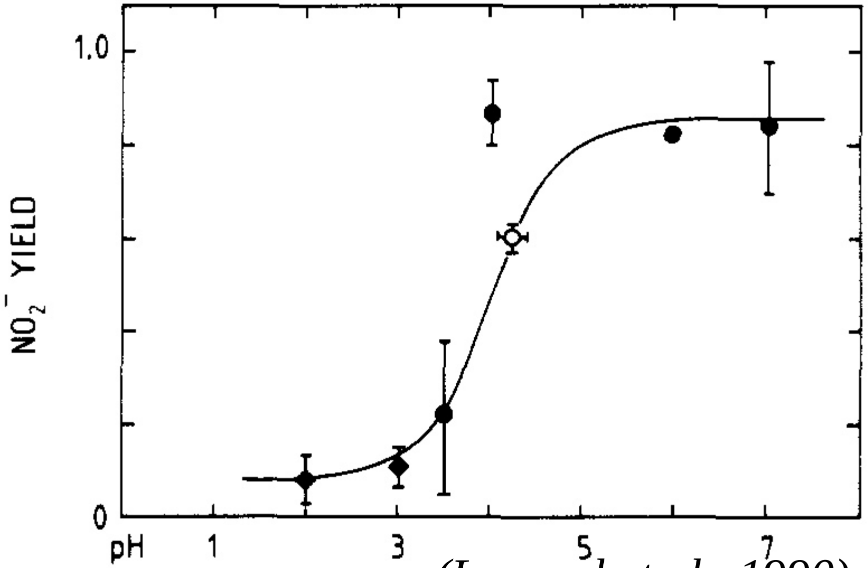
dissociation, hydration N(-III), N(V):

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

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

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

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



(Lammel et al., 1990)

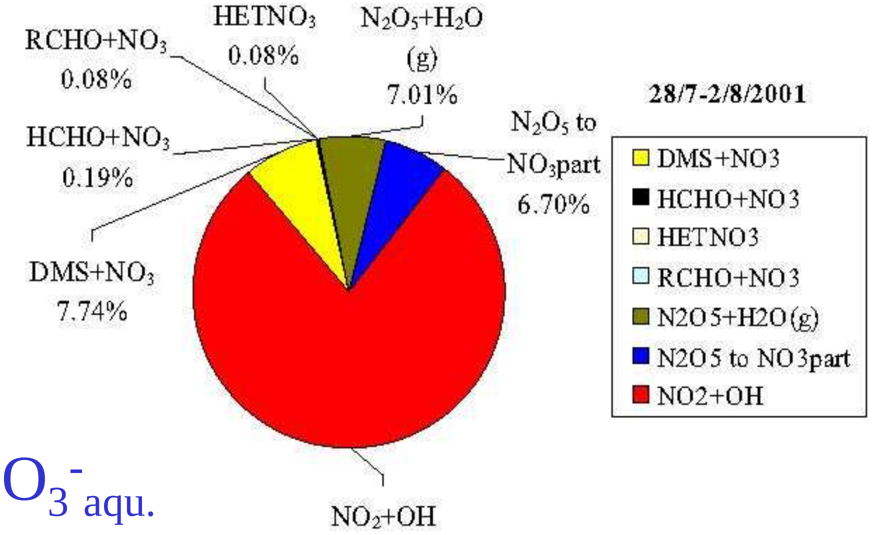
HNO_3 production: sources

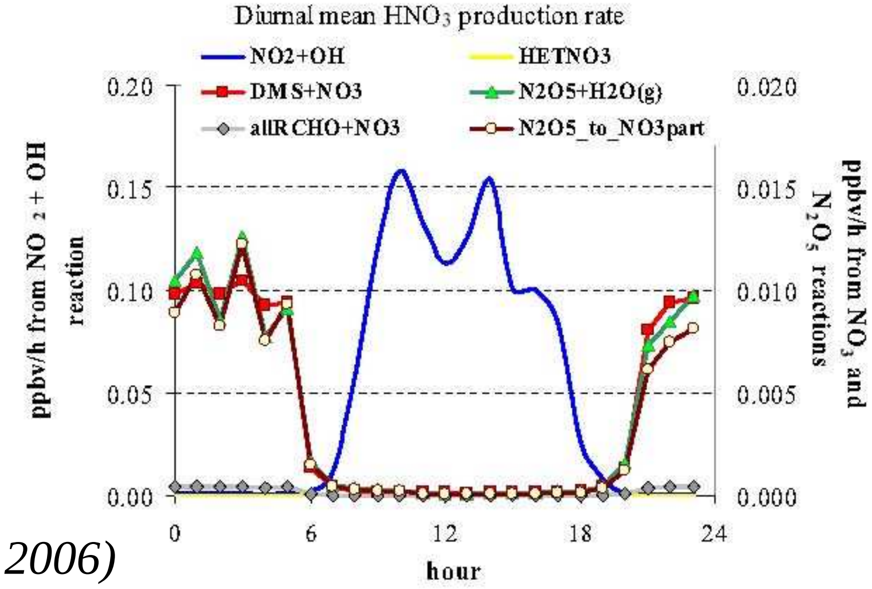
(1a) $NO_2 + {\cdot}OH \rightarrow HNO_3$ *(day)*

(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 (→*3.1 Aer*) and subsequent condensation

However, only 15% of S(VI) is formed in the gas-phase globally,

85% is formed (B) in cloud droplets and humid aerosol particles

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/m^3]
gas constant $R_g = 8.206\times10^{-5}$ m^3 at/mol/K, M_w[g/mol], 10^3[cm^3/L]

(*Warneck, 1986*)

Another, more common Henry coefficient:

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

... 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 m^3/mol] = $RTK_{aw} = 10^{-2}/K^H$[M/at]

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.

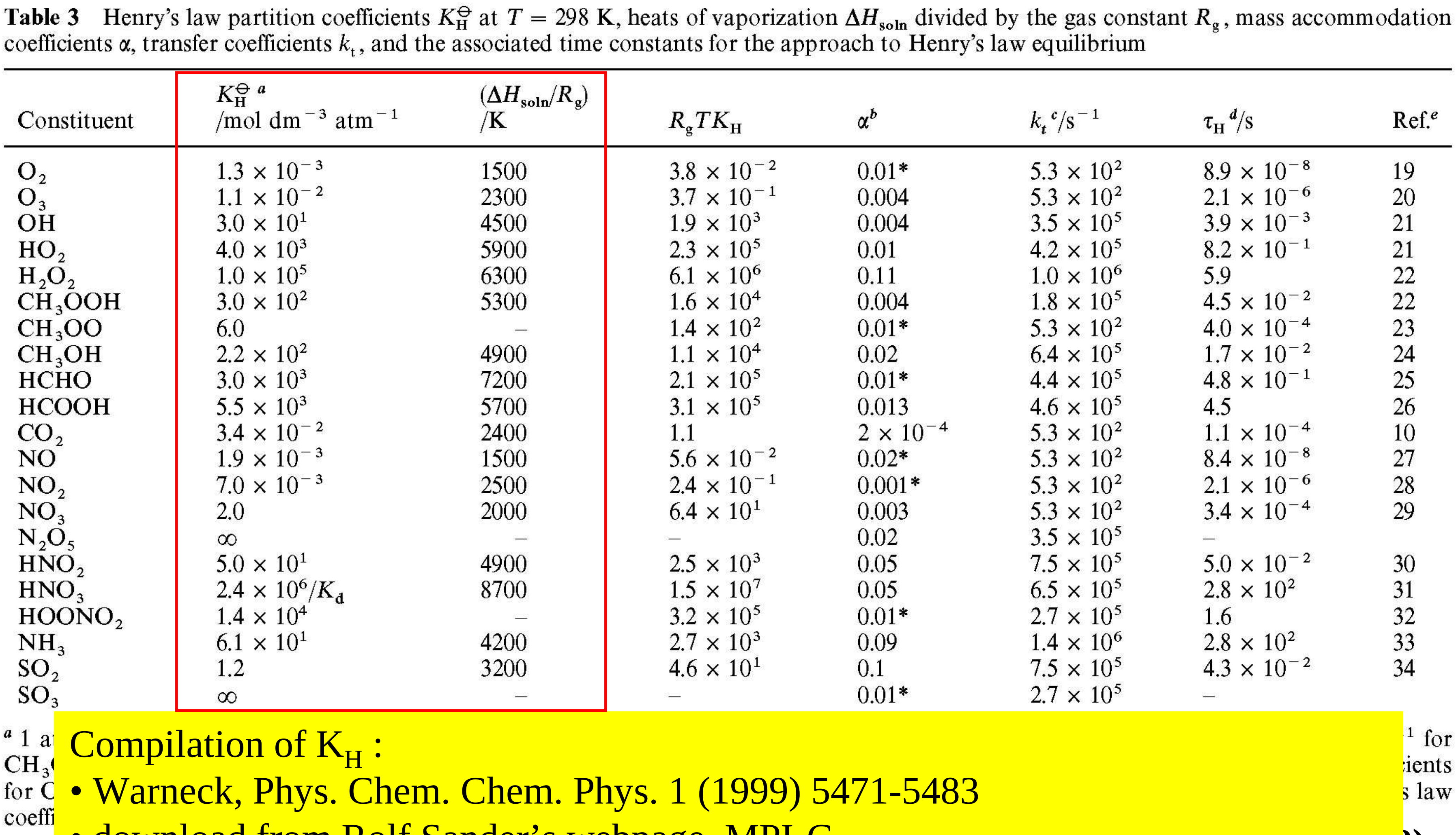


Table 3 Henry's law partition coefficients $K_H^\ominus$ at $T = 298$ K, heats of vaporization ΔH_{soln} divided by the gas constant R_g, mass accommodation coefficients α, transfer coefficients k_t, and the associated time constants for the approach to Henry's law equilibrium

Constituent	$K_H^\ominus$ [a] /mol dm^{-3} atm^{-1}	$(\Delta H_{soln}/R_g)$ /K	R_gTK_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	–	

[a] 1 a … ^{1} for
CH_3 … ients
for C … s law
coeffi …

9)

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

$CO_2(aq)$	$+ H_2O(aq)$	$\rightleftharpoons H_2CO_3(aq)$	$\rightleftharpoons H^+$	$+ HCO_3^-$	$\rightleftharpoons 2H^+$	$+ CO_3^{2-}$
Dissolved carbon dioxide	Liquid water	Dissolved carbonic acid	Hydrogen ion	Bicarbonate ion	Hydrogen ion	Carbonate ion

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

(1) $K_H = c_{CO2\ aqu} / p_{CO2} = 3.4\times10^{-7}$ mol/L/Pa (298 K)

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

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

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

(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):

$c_{HCO3-}\ \ c_{H3O+} = K_{A1}\ K_H\ p_{CO2}$

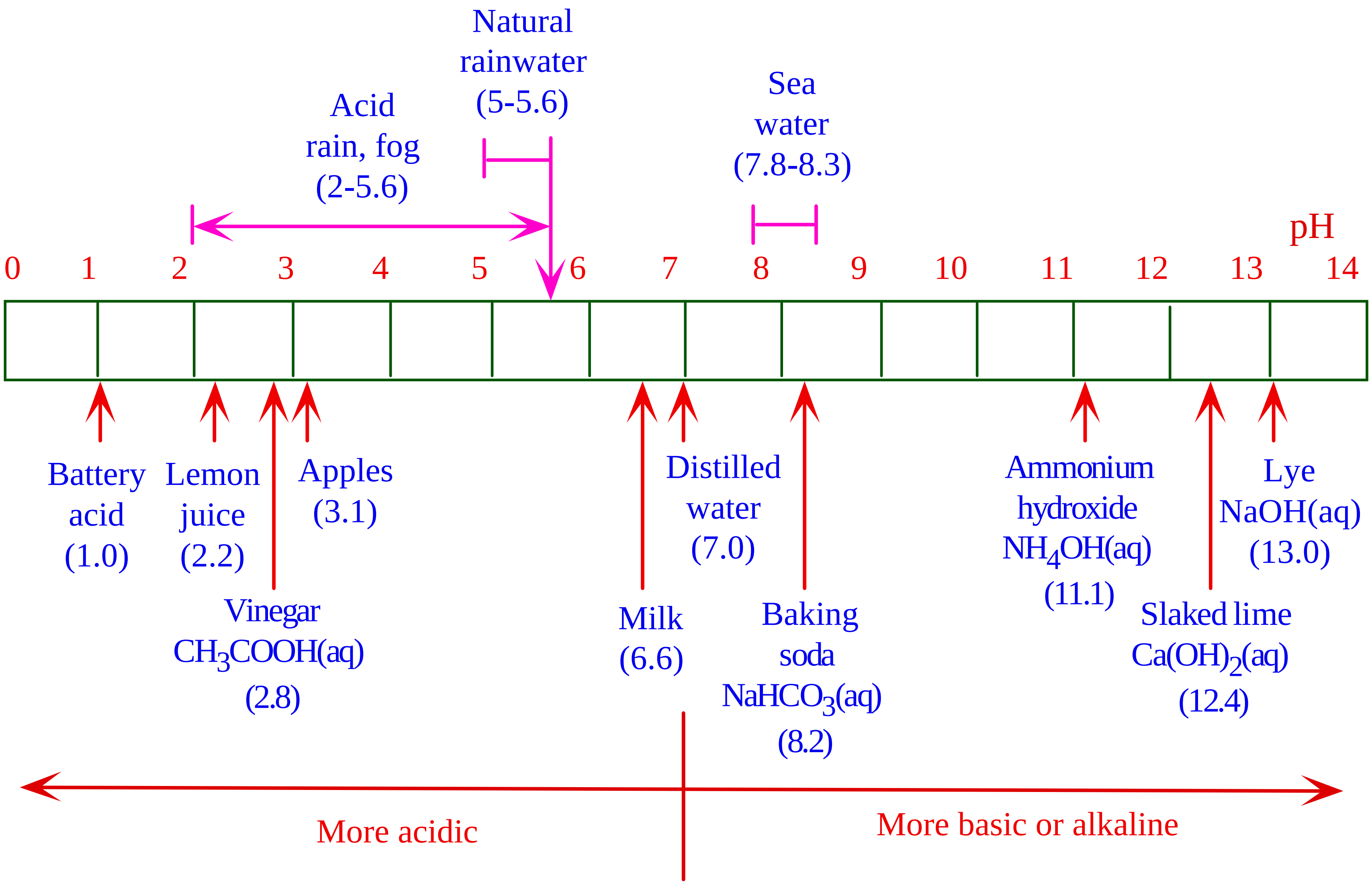
$c_{HCO3-} = c_{H3O+}$

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

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

$pH = 0.5\ (6.35 - \log 3.4\times10^{-7} - \log 36) = 5.63$

pH scale



Acid rain, fog (2-5.6)

Natural rainwater (5-5.6)

Sea water (7.8-8.3)

Battery acid (1.0)

Lemon juice (2.2)

Vinegar $CH_3COOH(aq)$ (2.8)

Apples (3.1)

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

S(IV) phase equilibrium and reactions

determined by Henry coeff. K_H, pH, T

$S(IV)\text{:} = SO_{2\ \text{aqu.}} + HSO_3^- + SO_3^{2-}$

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

$SO_2 \rightleftharpoons SO_{2\ \text{aqu.}}$ $K_{H\ (298K)} := c_{SO2}/p_{SO2} = 1.2\times10^{-5}$ M/Pa

Dissociation equilibria:

$SO_{2\ \text{aqu.}} + 2\ H_2O \rightleftharpoons HSO_3^- + H_3O^+$ $K_{A1\ (298K)} = 1.7\times10^{-2}$ M

$HSO_3^-{}_{.} + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$ $K_{A2\ (298K)} = 6.5\times10^{-8}$ 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:

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

SO_2	$SO_{2\ aqu.}$	HSO_3^-	SO_3^{2-}
Sulfur dioxide gas	dissolved sulfur dioxide	bisulfite	sulfite

similarly:

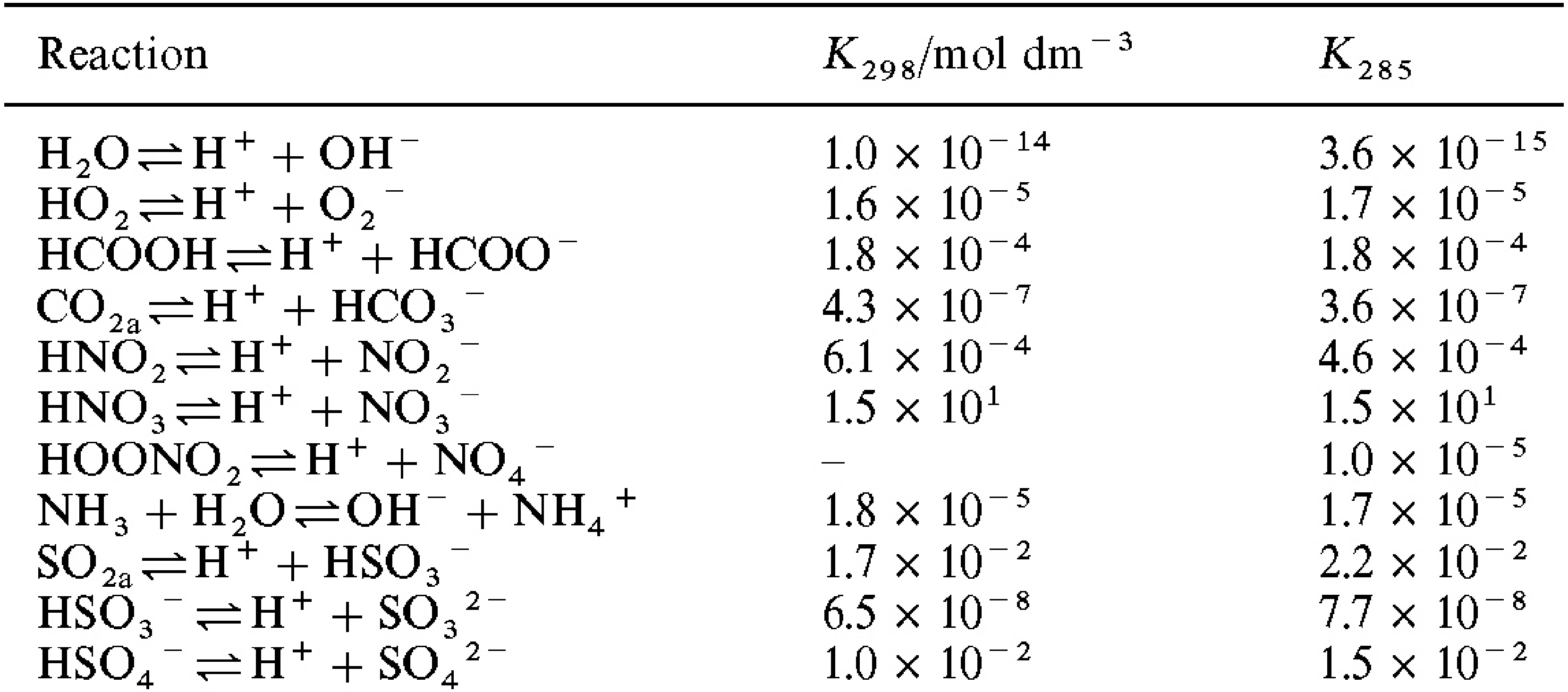
$S(VI): = H_2SO_{4\ aqu.} + HSO_{4\ aqu}^- + SO_{4\ aqu}^{2-}$

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

$H_2SO_4(g)$	$H_2SO_4(aq)$	H^+	HSO_4^-	$2H^+$	SO_4^{2-}
Sulfuric acid gas	Dissolved sulfuric acid	Hydrogen ion	Bisulfate ion	Hydrogen ion	Sulfate ion

Bulk aqueous phase chemistry

Acid-base dissociation equilibrium



Reaction	K_{298}/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. $SO_{2\ \text{aqu.}}$ 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) $SO_{3\,aqu}^{2-} + HO_{2\,aqu}^{\cdot} \rightarrow SO_{4\,aqu}^{2-} + OH_{aqu}^{\cdot}$

(2) $+ OH_{aqu}^{\cdot} \rightarrow SO_{3\,aqu}^{-\,\cdot} + OH_{aqu}^{-} \rightarrow SO_{5\,aqu}^{-\,\cdot} \xrightarrow{HO_2 \text{ or } HSO_3^-} \rightarrow SO_{4\,aqu}^{2-}$

(3a) $HSO_{3\,aqu}^{-} + O_{3\,aqu} \rightarrow HSO_{4\,aqu}^{-} + H_2O$ $k_{3a} = 3.2\times10^5\ M^{-1}s^{-1}$

(3b) $SO_{3\,aqu}^{2-} + O_{3\,aqu} \rightarrow SO_{4\,aqu}^{2-} + H_2O$ $k_{3b} = 1.5\times10^9\ M^{-1}s^{-1}$

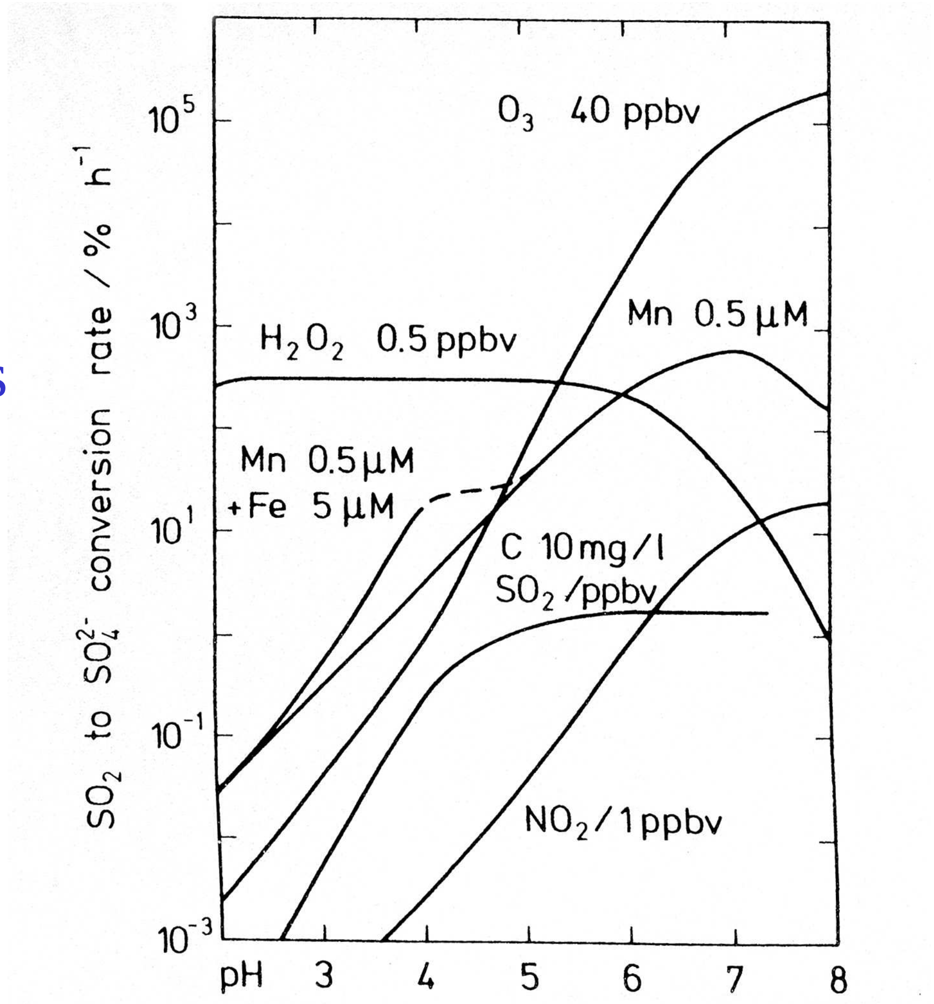
(4) $HSO_{3\,aqu}^{-} + H_2O_{2\,aqu} \rightarrow HSO_{4\,aqu}^{-} + H_2O$ $k_4 = 4.0\times10^7\ c_{H+}\ M^{-1}s^{-1}$

(5) $2\ HSO_{3\,aqu}^{-} + O_{2\,aqu} \xrightarrow{<M^{n+}>} 2\ HSO_{4\,aqu}^{-}$ “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 $SO_{3\ aqu}^{2-}$ (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)

Tropospheric trace substances trends: pH, SO_2

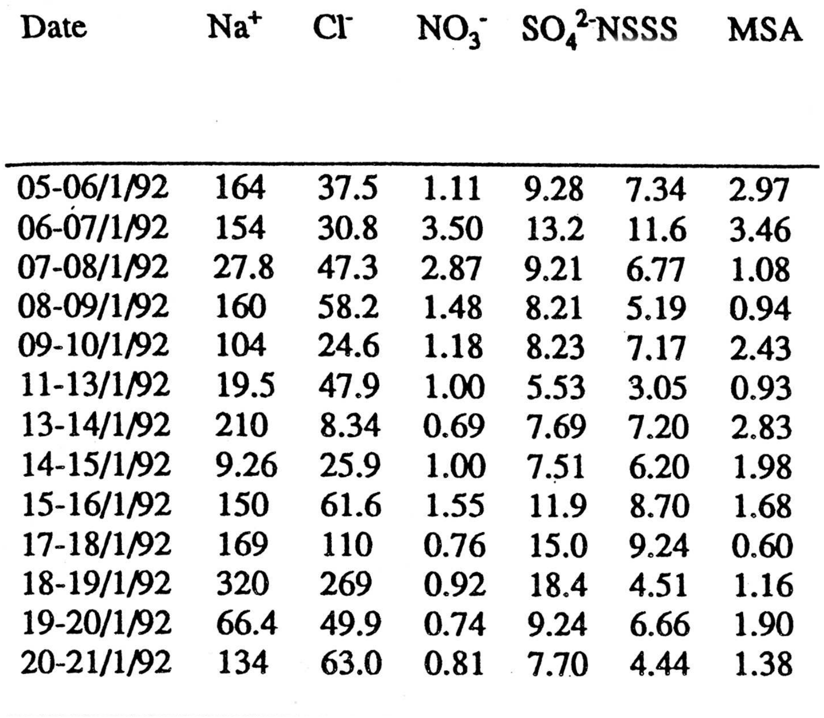
Rain water pH

SO_2 emissions

Sulfuric acid: precursors other than anthropogenic SO_2

Aerosol constituents
McDonald Beach
[nmol/m^3]

seasalt-S(VI)/Cl^- = 0.051



Date	Na^+	Cl^-	NO_3^-	SO_4^{2-}	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 carbonyl sulfide

(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) $CH_3SCH_2OO\cdot + NO \rightarrow CH_3SCH_2O\cdot + NO_2$

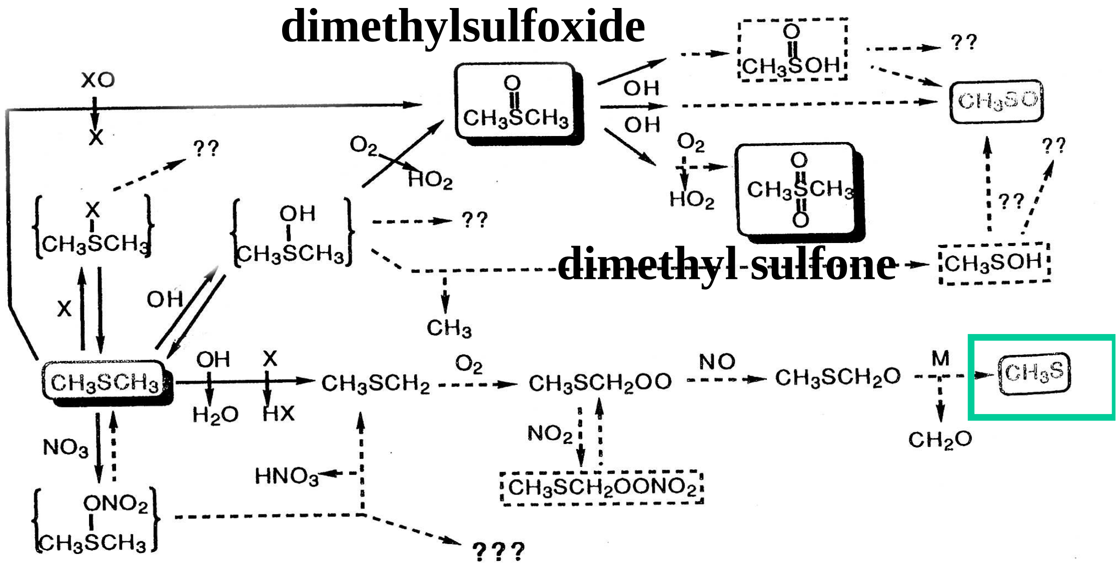
(3a) $CH_3SCH_2O\cdot \rightarrow HCHO + \boxed{CH_3S\cdot}$ **major**

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

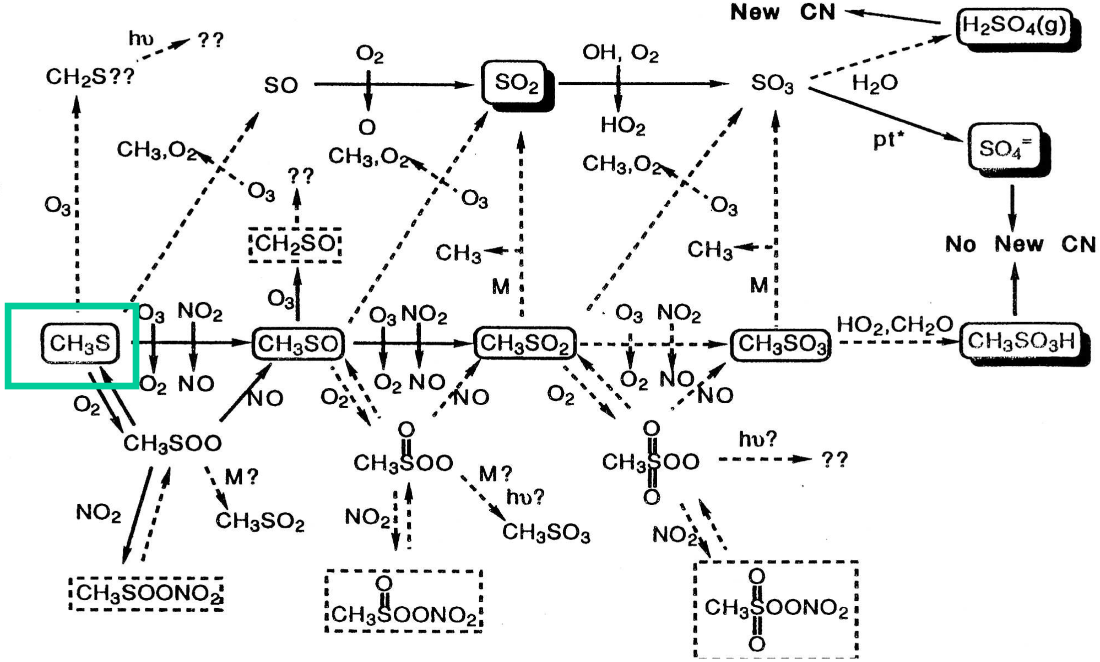
(4b) $CH_3SCHO + OH\cdot \rightarrow CH_3\cdot + COS + H_2O$

Formation of SO_2

in the marine boundary layer:
$CH_3SCH_3 \rightarrow \rightarrow CH_3S^{\cdot}$



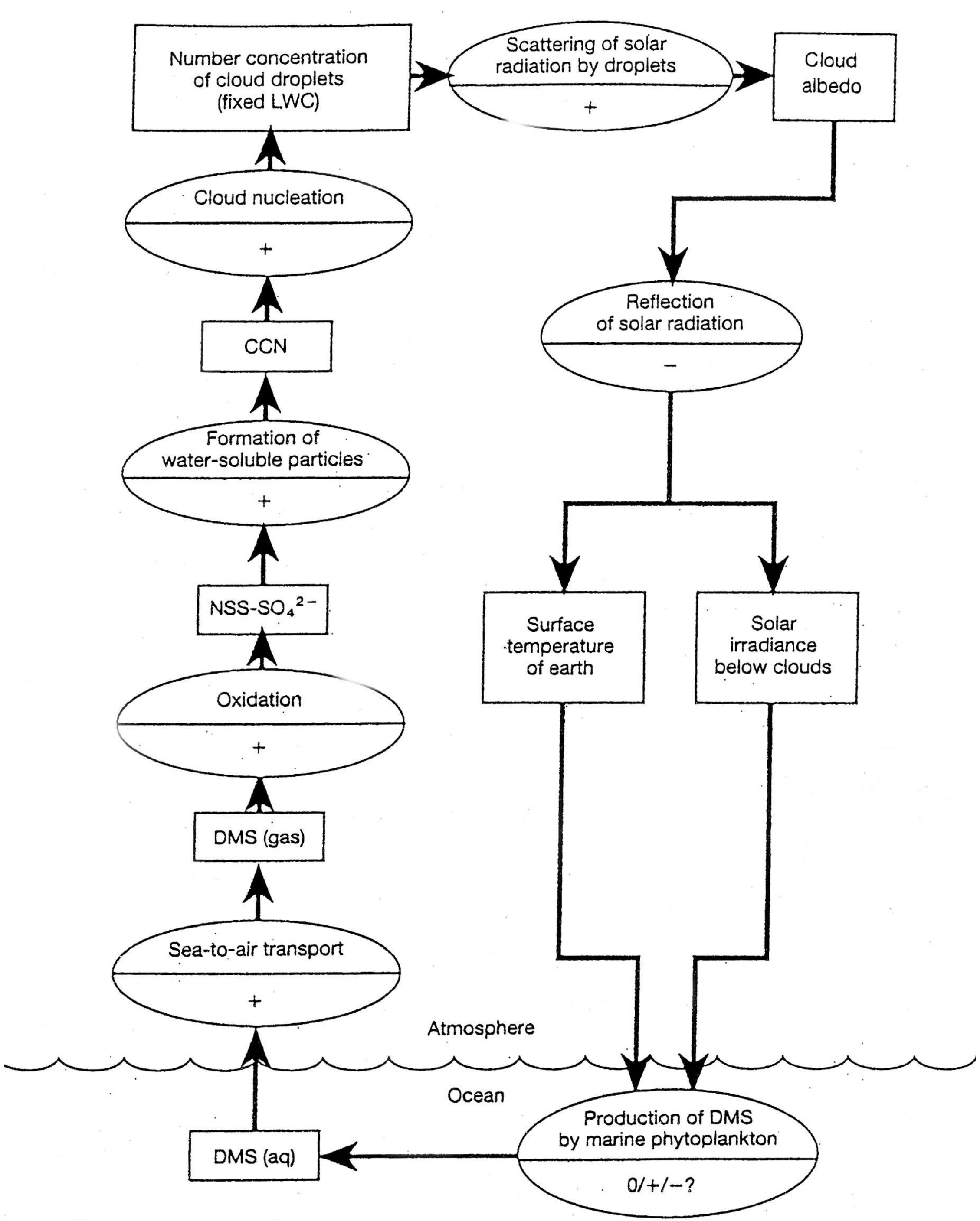
$CH_3S^{\cdot} \rightarrow \rightarrow$
$S(IV) \rightarrow \rightarrow S(VI)$



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*)



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: $dc_{S(VI)}/dt = 5.6\times10^{-6}$ nmol m^{-3} s^{-1}

2. Aqueous phase (L $=3\times10^{-8}$, pH=7):

$$dc_{SO4--}/dt = k_4\, p_{H2O2}\, K_{H\ H2O2}\, p_{SO2}\, K^*_{H\ SO2}\ (M\ s^{-1})$$

$$= (4\times10^7\times 10^{-7}) \times 40\times10^{-9}\times 1\times10^5\times 2\times10^{-9}x3.4x10^5$$

$$K^*_{H\ SO2} = K_{H\ SO2} \times (1 + K_{A1} / c_{H+} + K_{A1}K_{A2} / c^2_{H+}) =$$

$$= 3.4\times10^5\ M/atm$$

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

$$= 32\times10^{-6}\ nmol\ m^{-3}\ s^{-1}$$

Reactivity of organics in the aqueous phase: Overview OH reactions

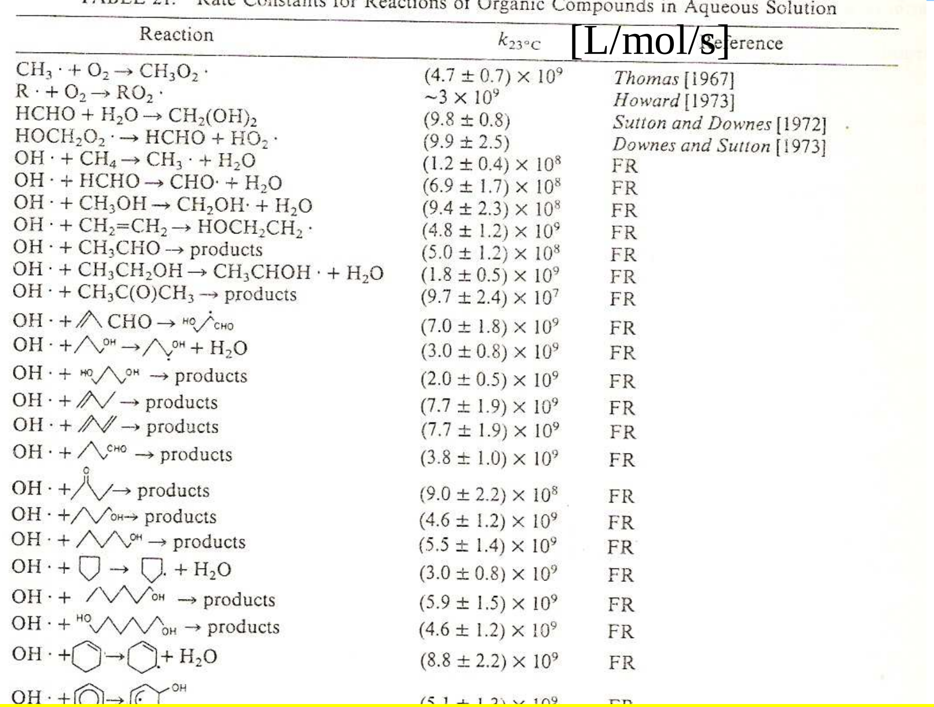


TABLE 21. Rate Constants for Reactions of Organic Compounds in Aqueous Solution

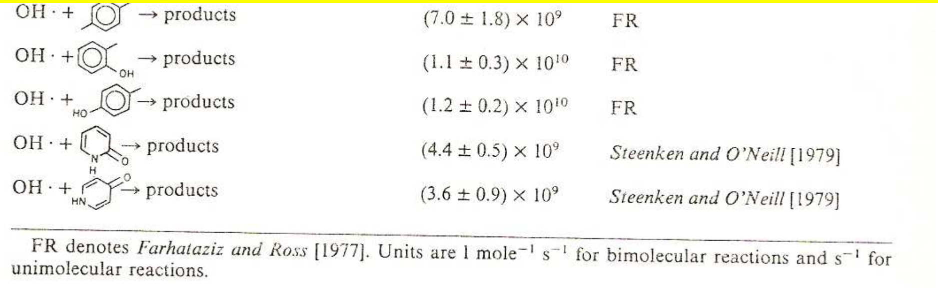
Reaction	$k_{23°C}$ [L/mol/s]	Reference
$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$	$(4.7 \pm 0.7) \times 10^9$	*Thomas* [1967]
$R\cdot + O_2 \rightarrow RO_2\cdot$	$\sim 3 \times 10^9$	*Howard* [1973]
$HCHO + H_2O \rightarrow CH_2(OH)_2$	(9.8 ± 0.8)	*Sutton and Downes* [1972]
$HOCH_2O_2\cdot \rightarrow HCHO + HO_2\cdot$	(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
$OH\cdot +$ CHO → HO CHO	$(7.0 \pm 1.8) \times 10^9$	FR
$OH\cdot +$ OH → OH $+ H_2O$	$(3.0 \pm 0.8) \times 10^9$	FR
$OH\cdot +$ HO OH → products	$(2.0 \pm 0.5) \times 10^9$	FR
$OH\cdot +$ → products	$(7.7 \pm 1.9) \times 10^9$	FR
$OH\cdot +$ → products	$(7.7 \pm 1.9) \times 10^9$	FR
$OH\cdot +$ CHO → products	$(3.8 \pm 1.0) \times 10^9$	FR
$OH\cdot +$ O → products	$(9.0 \pm 2.2) \times 10^8$	FR
$OH\cdot +$ OH → products	$(4.6 \pm 1.2) \times 10^9$	FR
$OH\cdot +$ OH → products	$(5.5 \pm 1.4) \times 10^9$	FR
$OH\cdot +$ → $+ H_2O$	$(3.0 \pm 0.8) \times 10^9$	FR
$OH\cdot +$ OH → products	$(5.9 \pm 1.5) \times 10^9$	FR
$OH\cdot +$ HO OH → products	$(4.6 \pm 1.2) \times 10^9$	FR
$OH\cdot +$ → $+ H_2O$	$(8.8 \pm 2.2) \times 10^9$	FR
$OH\cdot +$ → OH	$(5.1 \pm 1.2) \times 10^9$	FR

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



Reaction	$k_{23°C}$ [L/mol/s]	Reference
$OH\cdot +$ → products	$(7.0 \pm 1.8) \times 10^9$	FR
$OH\cdot +$ OH → products	$(1.1 \pm 0.3) \times 10^{10}$	FR
$OH\cdot +$ HO → products	$(1.2 \pm 0.2) \times 10^{10}$	FR
$OH\cdot +$ N H O → products	$(4.4 \pm 0.5) \times 10^9$	*Steenken and O'Neill* [1979]
$OH\cdot +$ HN O → products	$(3.6 \pm 0.9) \times 10^9$	*Steenken and O'Neill* [1979]

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

Less selectivity than in the gas-phase

(Graedel & Weschler, 1981)

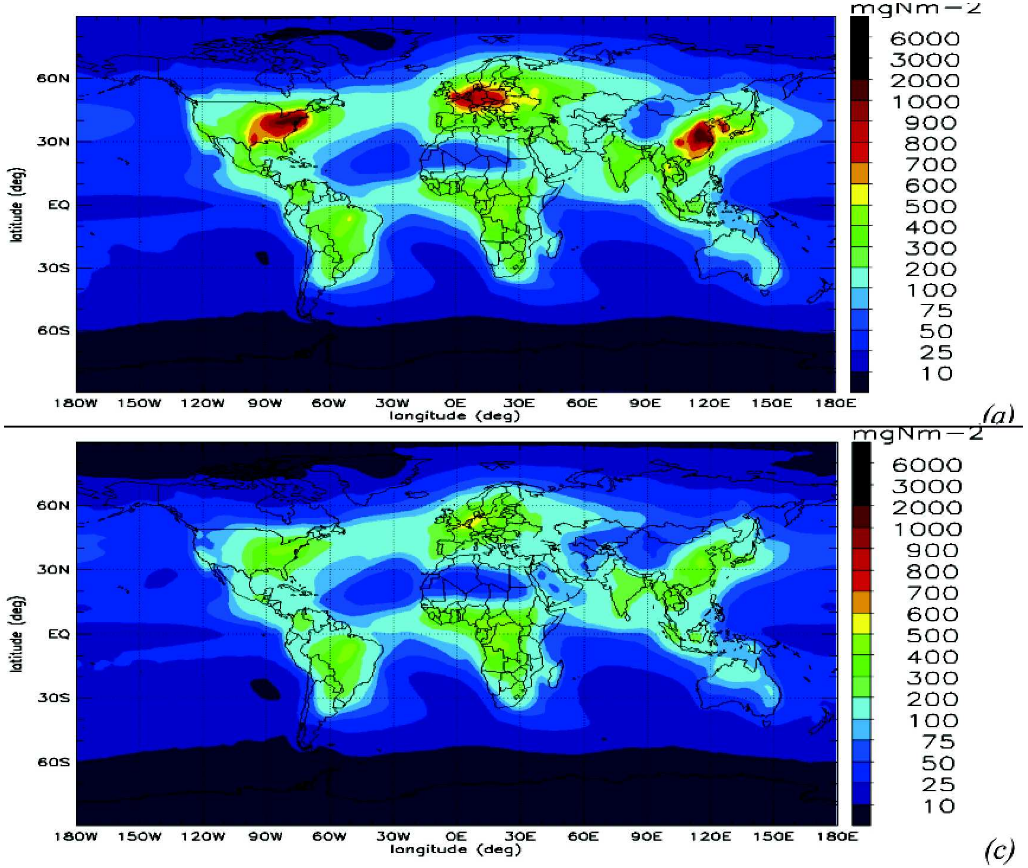
Impacts of atmospheric acidity in ecosystems

acid deposition,
example NO_y trends

2000

2030 under MFR

[mg N/m²/a]
(Dentener et al., 2006)



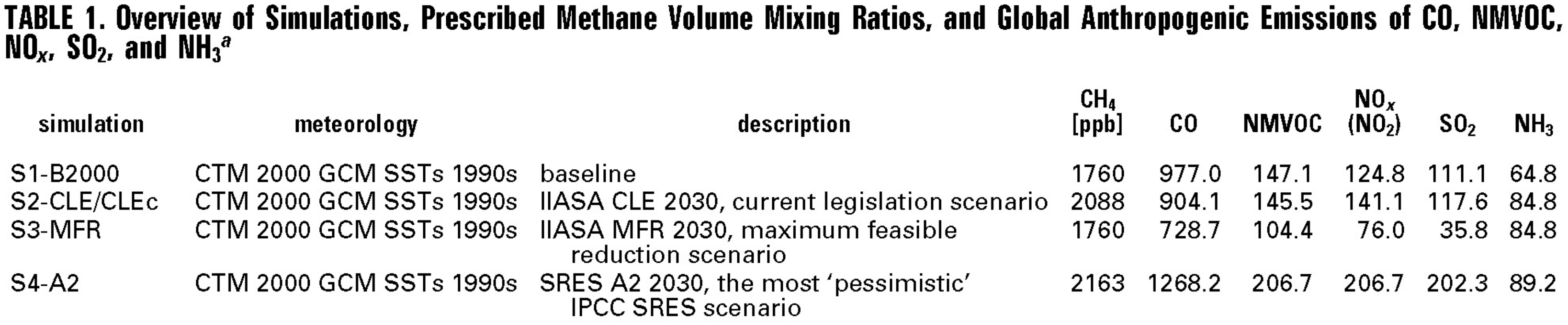


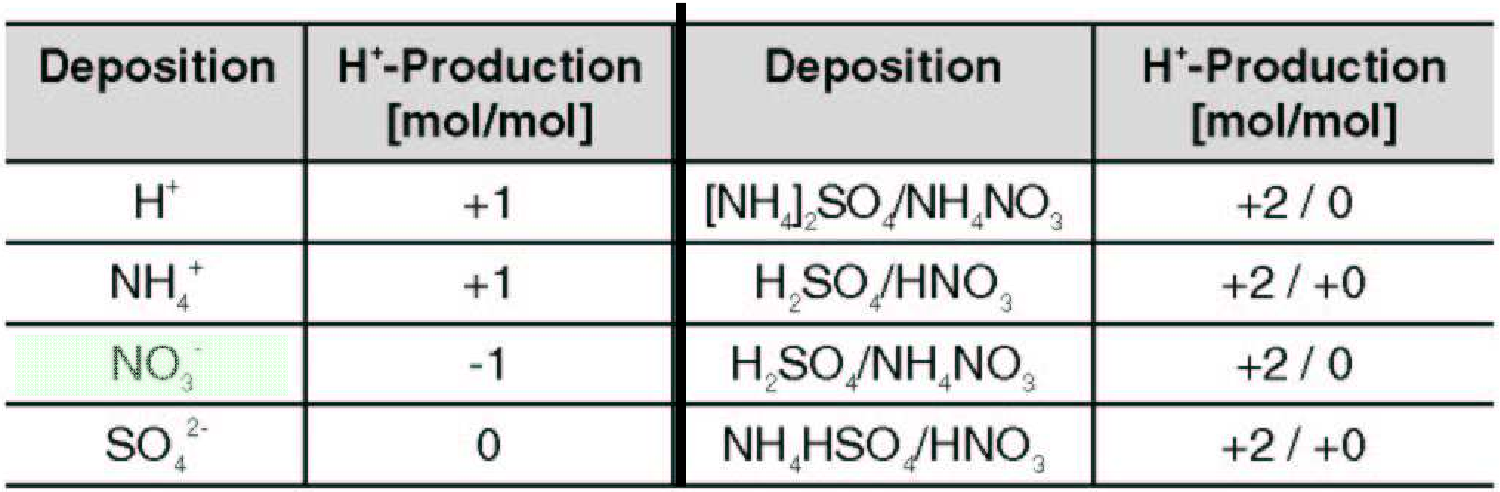
TABLE 1. Overview of Simulations, Prescribed Methane Volume Mixing Ratios, and Global Anthropogenic Emissions of CO, NMVOC, NO_x, SO_2, and NH_3[a]

simulation	meteorology	description	CH_4 [ppb]	CO	NMVOC	NO_x (NO_2)	SO_2	NH_3
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

[Tg/a]

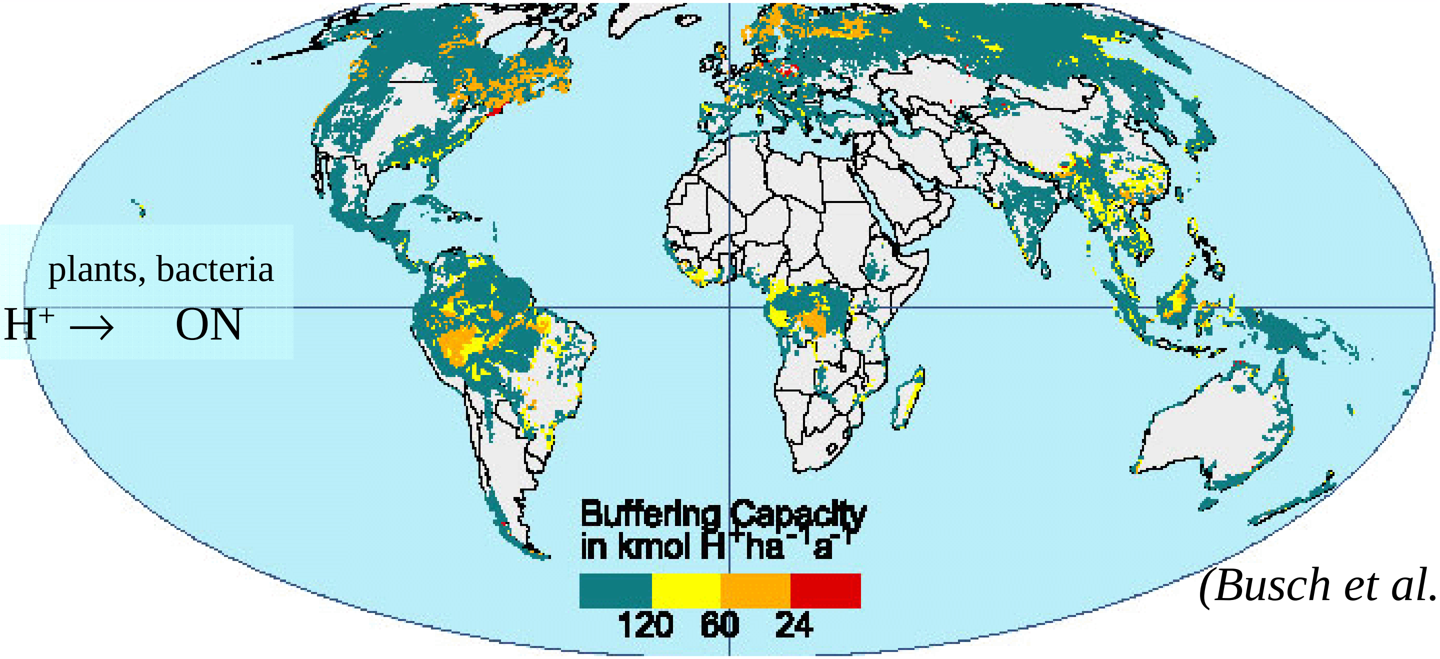
Impacts of atmospheric acidity: acidification of soils

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

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

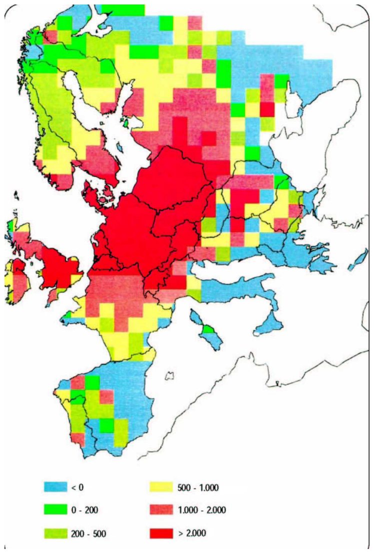


(Busch et al., 2001)

Critical loads concept to protect ecosystems

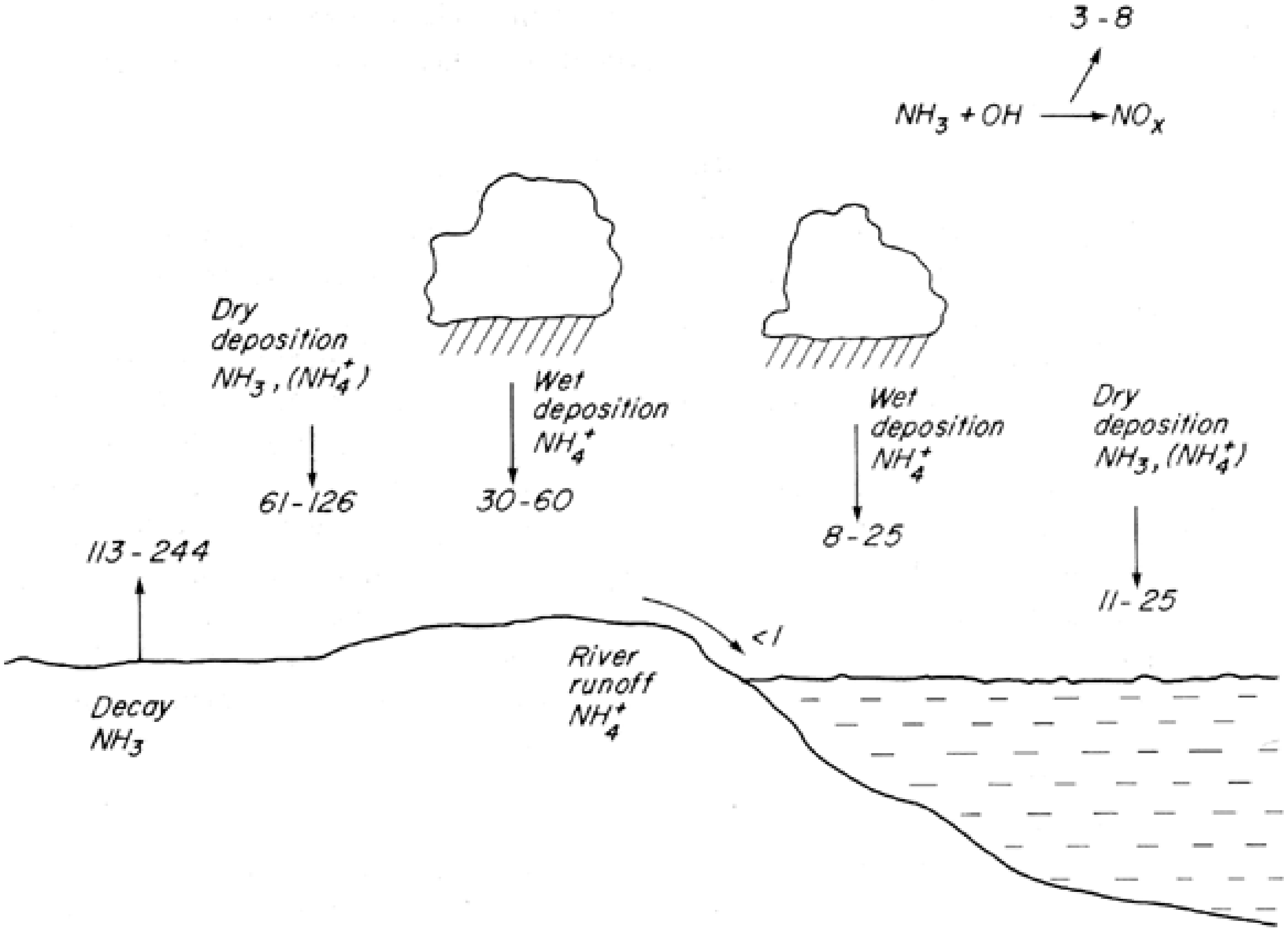
Mapping of critical loads „...below which harmful effects in ecosystem structure and function do not occur according to present knowledge“:
Determines which loads of pollutants and combinations thereof will not cause adverse effects, do not exceed ecosystem resilience (*PNEC*).

- + 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)

Cycling of ammonia



(following Manier)

Gas-phase chemistry

$NH_3 + OH\cdot \rightarrow NH_2\cdot + H_2O$	$k = 0.16\times10^{-12}\ cm^3/molec/s$
(1) $NH_2\cdot + O_2 \rightarrow NO + H_2O$	$k_1 < 6\times10^{-21}\ cm^3/molec/s$
(2) $NH_2\cdot + HO_2\cdot \rightarrow NH_3 + O_2$	$k_2 = 34\times10^{-12}\ cm^3/molec/s$
(3) $NH_2\cdot + NO \rightarrow N_2 + H_2O$	$k_3 = 17\times10^{-12}\ cm^3/molec/s$
(4) $NH_2\cdot + NO_2 \rightarrow N_2O + H_2O$	$k_4 = 19\times10^{-12}\ cm^3/molec/s$
(5) $NH_2\cdot + O_3 \rightarrow NH_2O\cdot + O_2$	$k_5 = 0.16\times10^{-12}\ cm^3/molec/s$
(6) $NH_2\cdot + RH \rightarrow$	too slow to be of any significance

$-dc_{NH3}/dt = k_{OH}^{(1)}\, c_{NH3} = k_{OH}^{(2)}\, c_{OH}\, c_{NH3;}\ \ \tau_{OH} = (k_{OH}^{(1)})^{-1}$

$\approx$ 3 months for the global annual tropospheric mean (1.16×10^6 OH/cm^3)

$\approx$ 10 days inner tropics near ground ($\approx 10^7$ OH/cm^3; *Spivakovsky et al., 2000*)

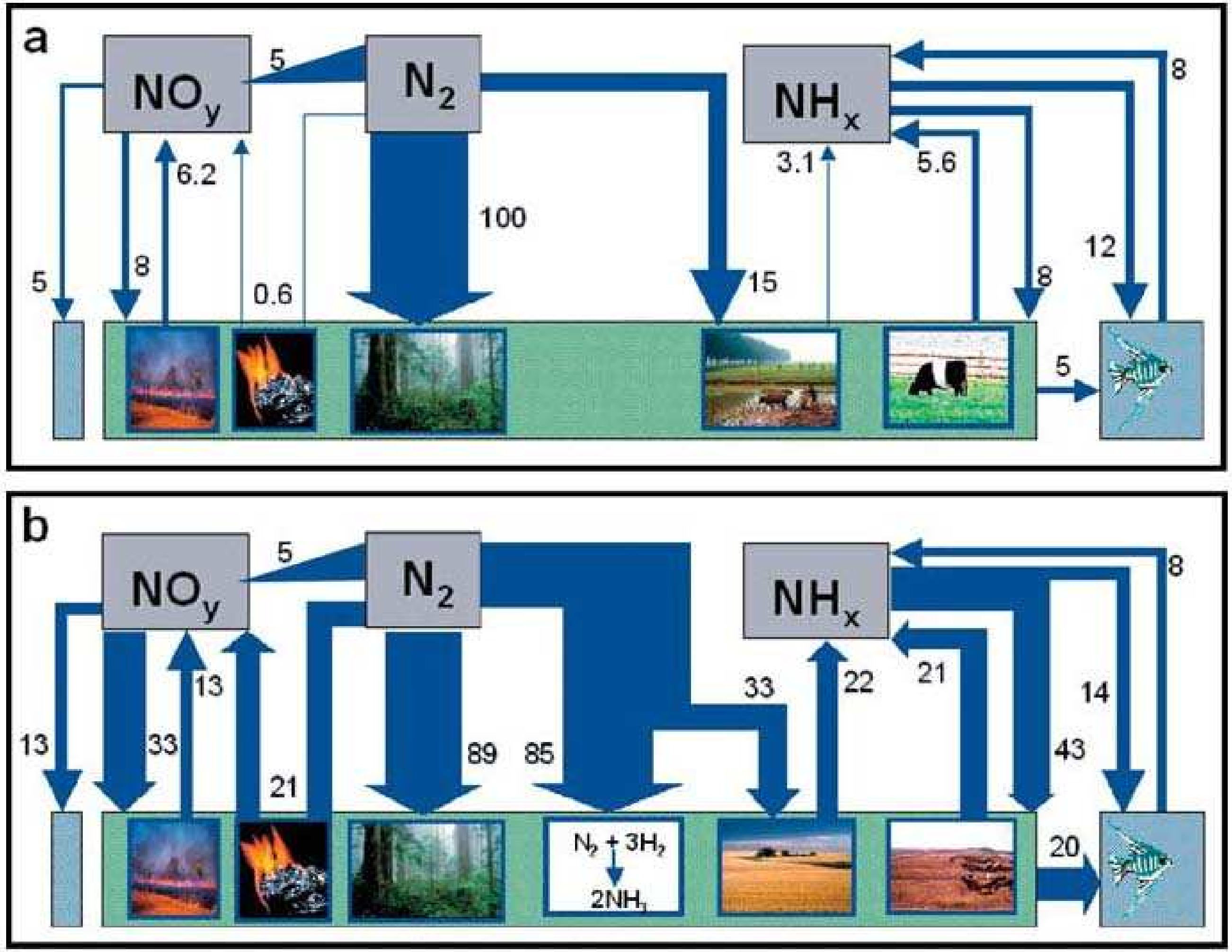
$-dc_{NH3}/dt = k_{OH}^{(1)}\, c_{NH3} + k_{dep}^{(1)}\, c_{NH3}$

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

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

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

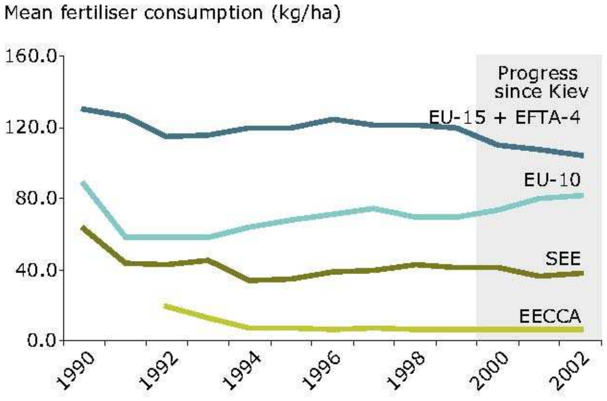
1890



1990

(Hibbard et al., 2006)

Ammonia trends Europe

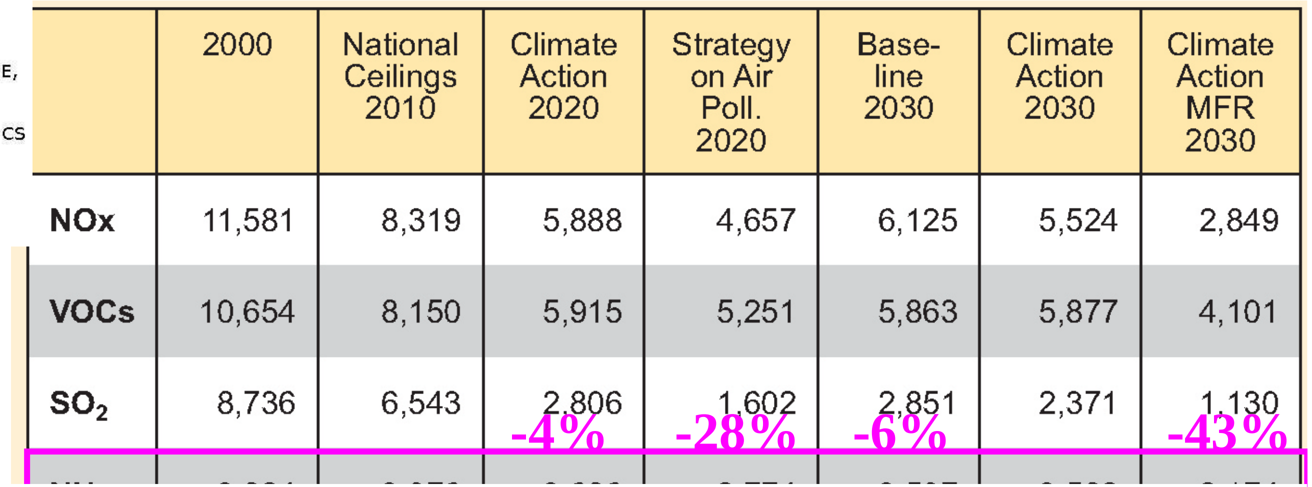


Note: EU-15 + EFTA-4: no data for LI; no data for BE, LU for 2000–2002.
EU-10: no data for SK, CZ for 1990–1992; no data for EE, LV, LT, SI for 1990–1991.
SEE: no data for BA for 1990-1994; no data for HR for 1990–1992; no data for MK for 1990–1992; no data for CS for 1990–1991.
EECCA countries: no data for 1990–1991.

Source: FAO.

Past emissions in Europe and adjacent seas (Mt/a)	1980	2004	Δ
NH_3	7.64	5.74	-25 %
SO_2	54.3	15.1	-72 %
NO_x	25.7	20.2	-21 %

Future **EU commitments** **EU scenarios**



	2000	National Ceilings 2010	Climate Action 2020	Strategy on Air Poll. 2020	Base-line 2030	Climate Action 2030	Climate Action MFR 2030
NOx	11,581	8,319	5,888	4,657	6,125	5,524	2,849
VOCs	10,654	8,150	5,915	5,251	5,863	5,877	4,101
SO_2	8,736	6,543	2,806	1,602	2,851	2,371	1,130

-4% -28% -6% -43%

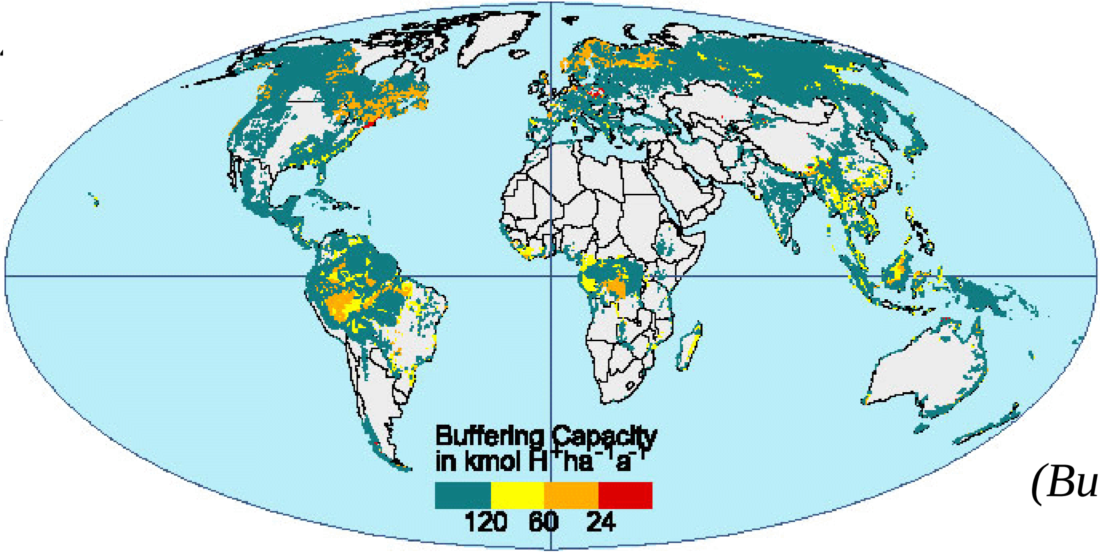
→ NO_3^-/SO_4^{2-} and $NH_4^+/(SO_4^{2-} + NO_3^-)$ are increasing in depositions

Emission trends (kt) in the EU-25 (*EEA, 2006*)

Impacts of atmospheric acidity: acidification of soils

Deposition of nitrogen and sulphur compounds and their corresponding production of acidity in a nitrogen unsaturated plant-soil-system

Deposited individual ion	H^+-Production [mol/mol]	Deposited species	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			

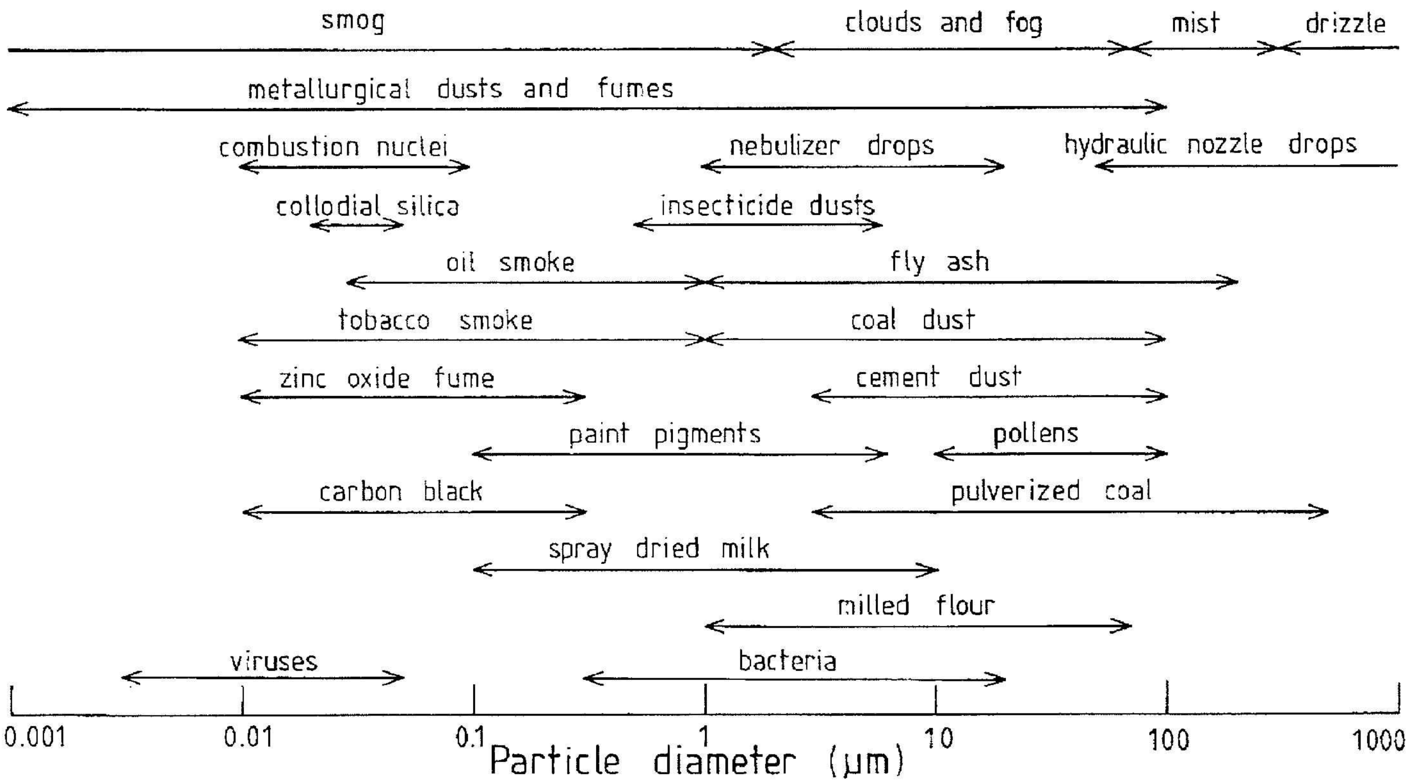


(Busch et al., 2001)

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“
- 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 (→ *Sustainability*), 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

Aerosols = ?


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)

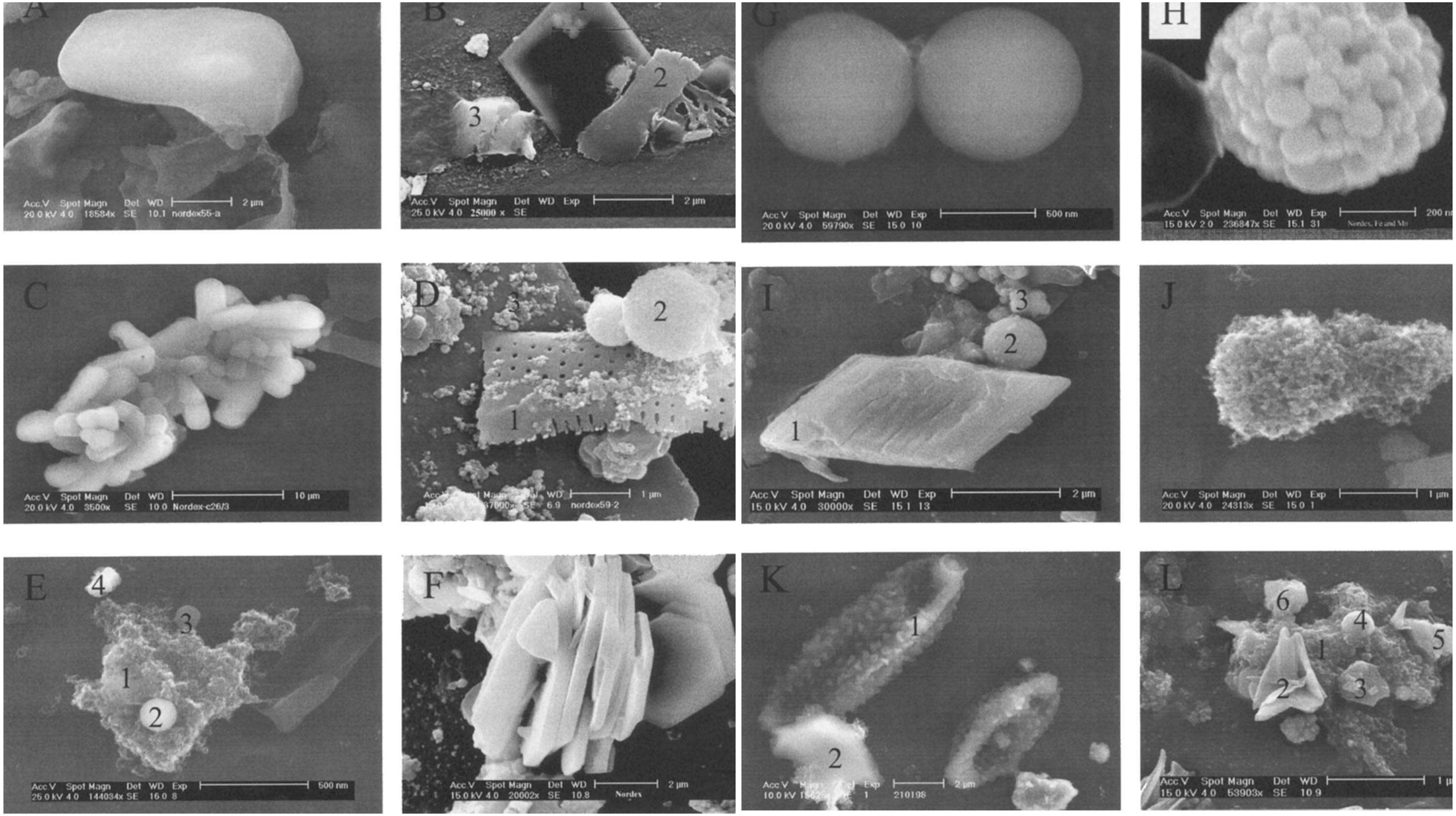


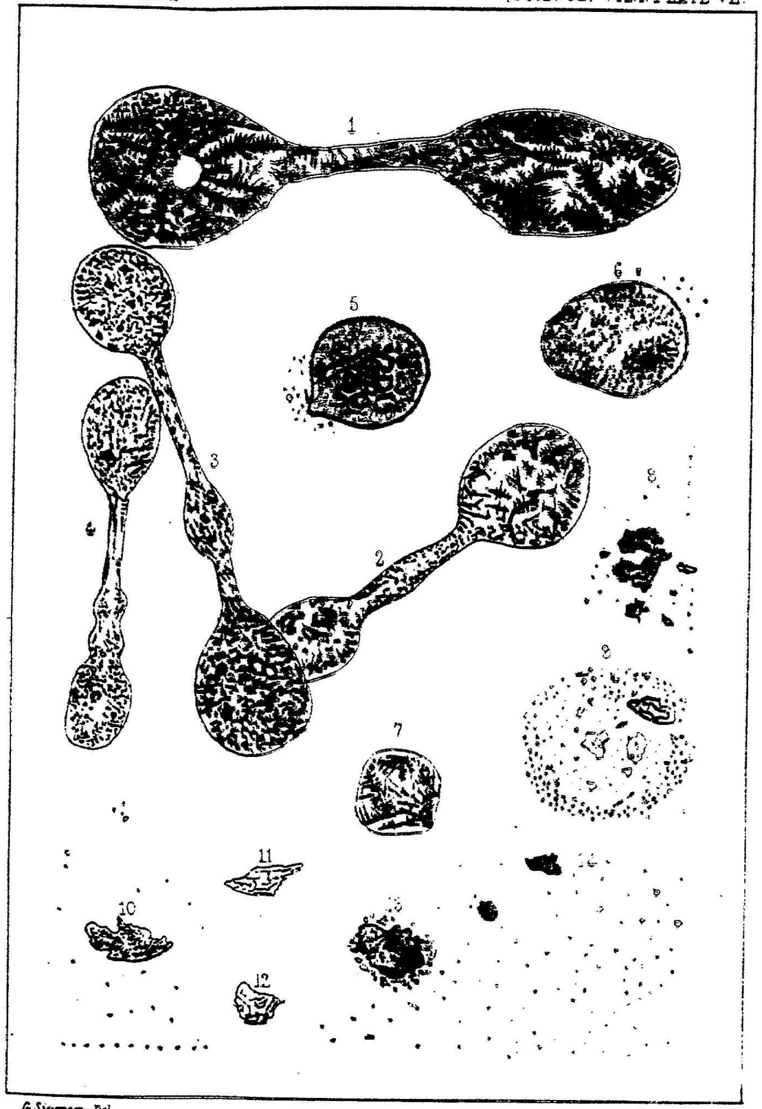
Fig. 1(A–F). Secondary electron image of North Sea aerosol particles: (A) Irregularly shaped sea-salt particle; (B) sea-salt particle with typical cubic morphology (1), irregularly-shaped sea-salt particle (2), and alumosilicate particle (3); (C) aged sea-salt particle; (D) biological particle (1), Si-rich 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

Sigerson 1870 Proc Roy Irish Acad Sci

CITY AIR.

R.I.A. PROC. SER. II. (SCIENCE) VOL. I. PLATE VII.

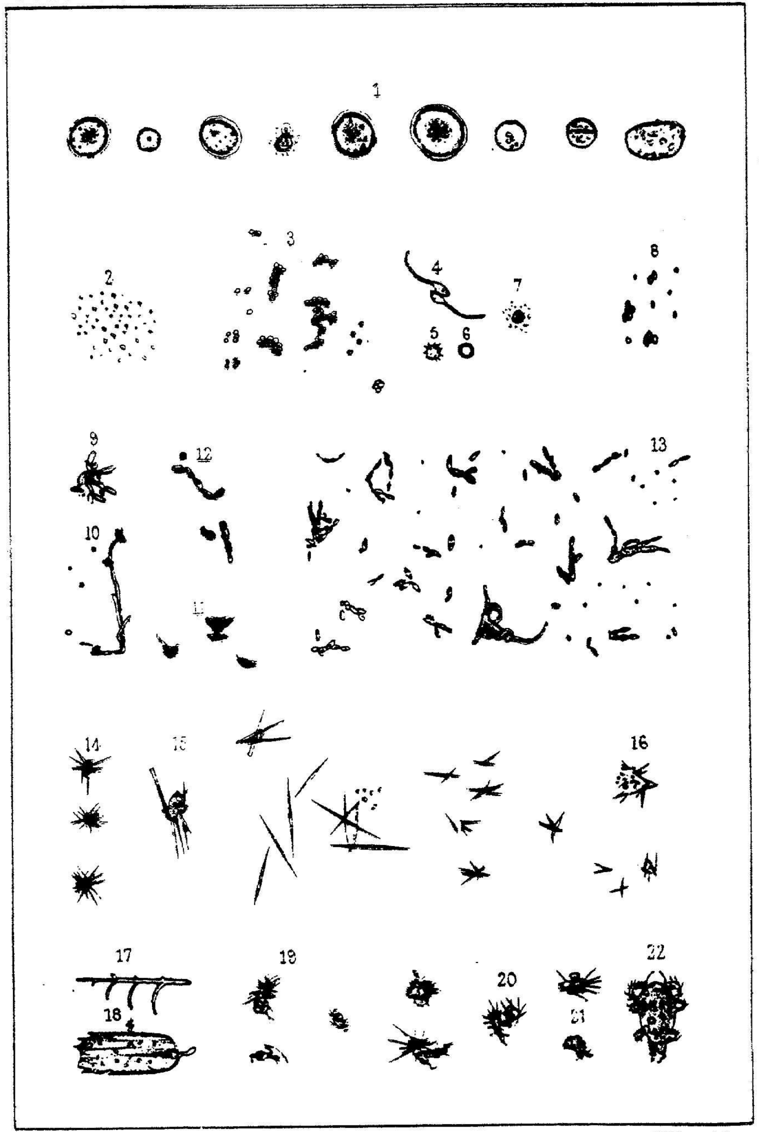


G. Sigerson. Del. F. W. Swan Lith

DR. SIGERSON on the Atmosphere.

COUNTRY AIR.

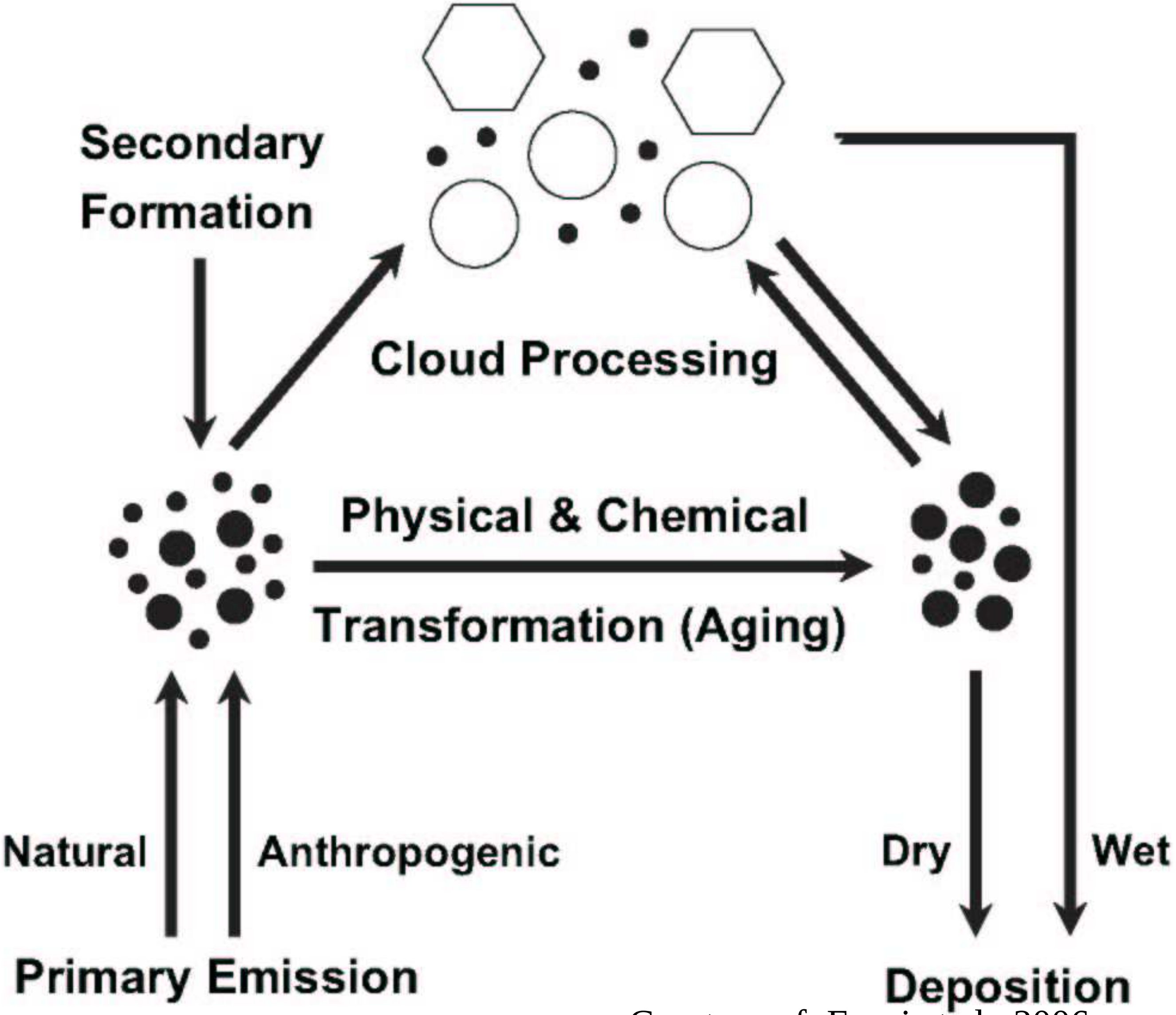
R.I.A. PROC. SER. II. (SCIENCE) VOL. I. PLATE V.



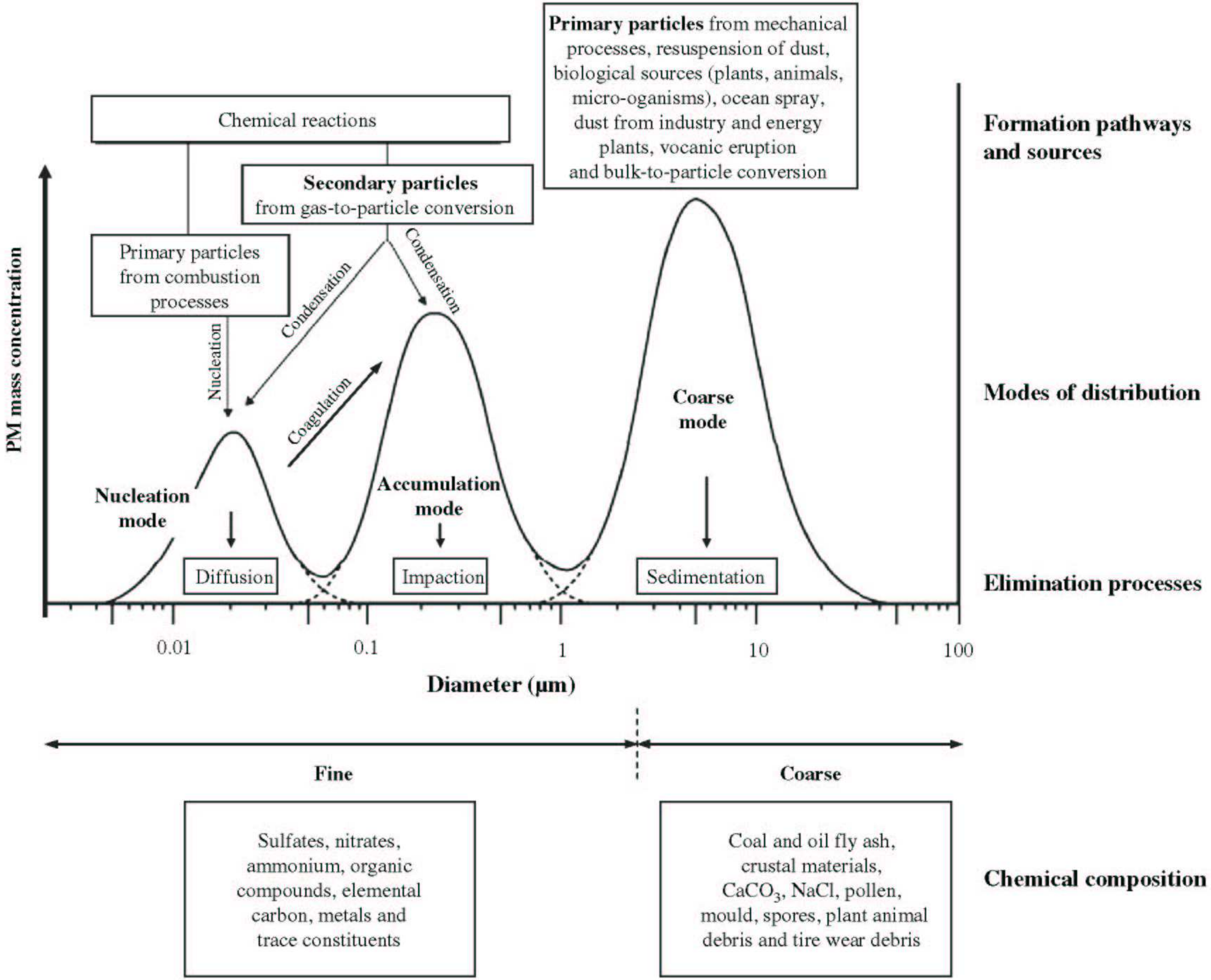
G. Sigerson. Del. P. W. Swan. Lith.

DR. SIGERSON on the Atmosphere.

Aerosol processes

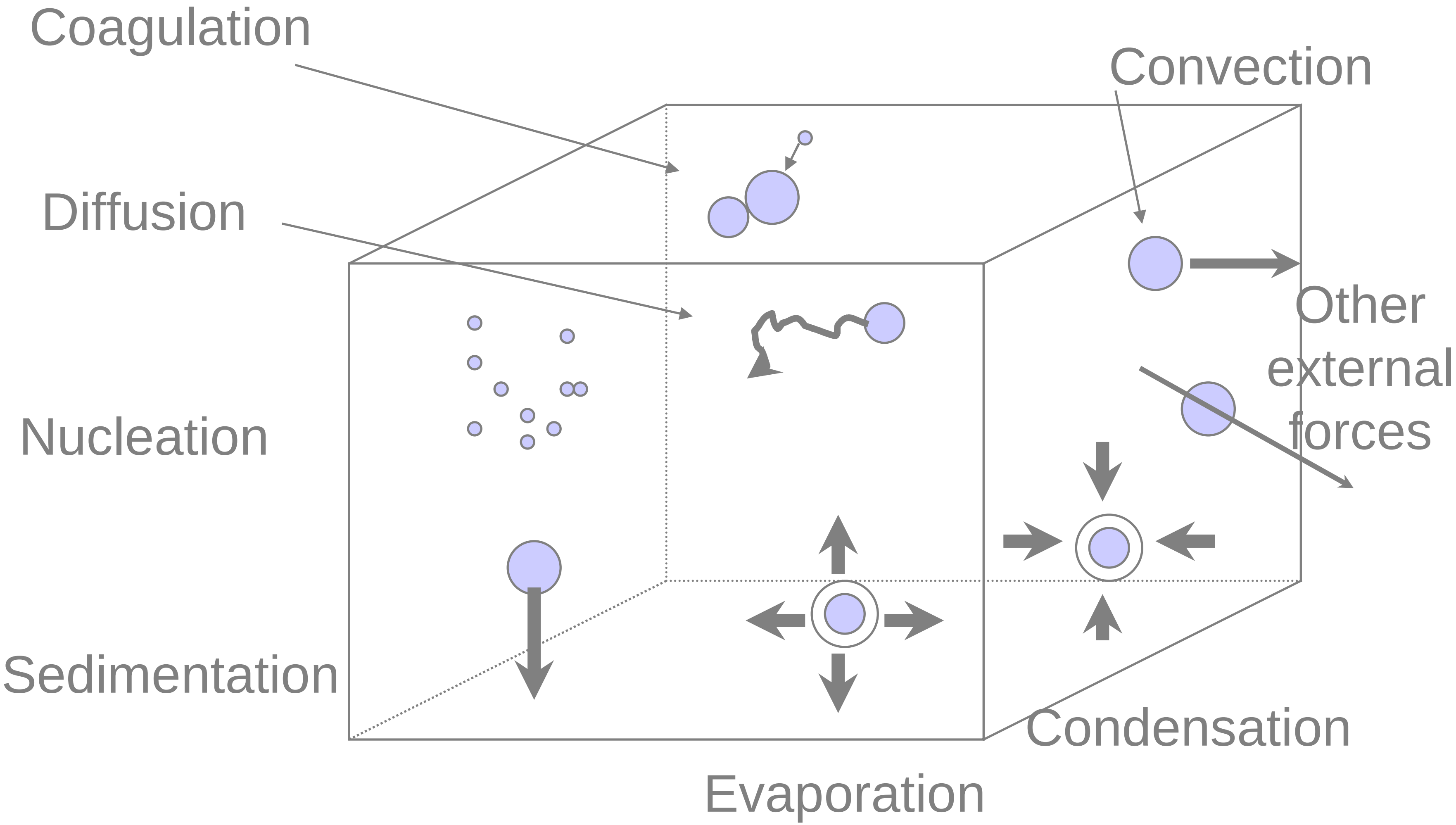


Courtesy of: Fuzzi et al., 2006

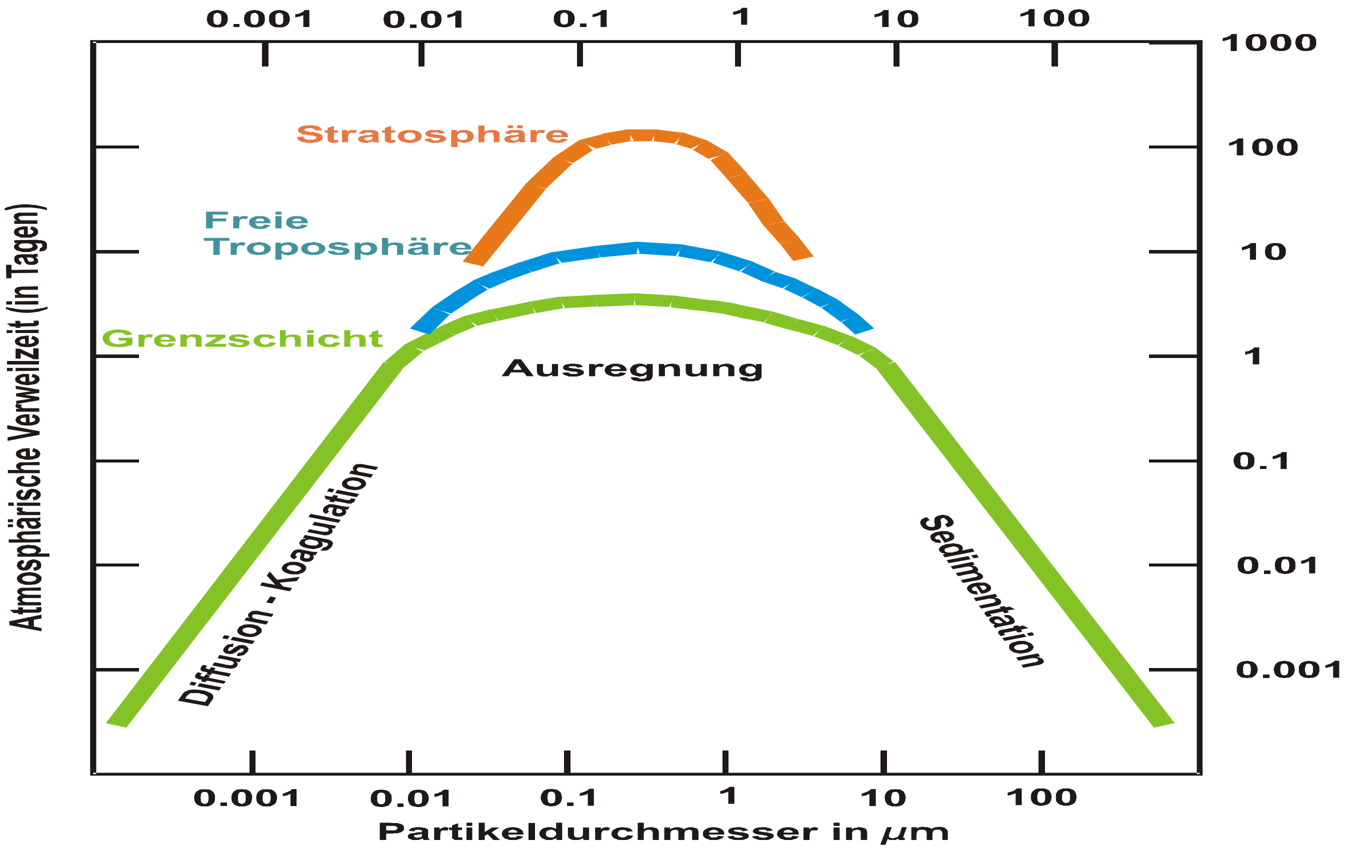


Courtesy of: Cambra-López et al., 2010

Aerosol microphysical processes



Atmospheric residence time $\tau = f(D)$:



Atmospheric residence time / dry deposition

Diameter (µm)	Time to Fall 1 km	Diameter (µm)	Time to Fall 1 km
0.0005	9630 y	4	23 d
0.02	226 y	5	14.5 d
0.1	36 y	10	3.6 d
0.5	3.2 y	20	23 h
1	326 d	100	1.1 h
2	89 d	1000	4 m
3	41 d	5000	1.8 m

Particle size – not trivial !

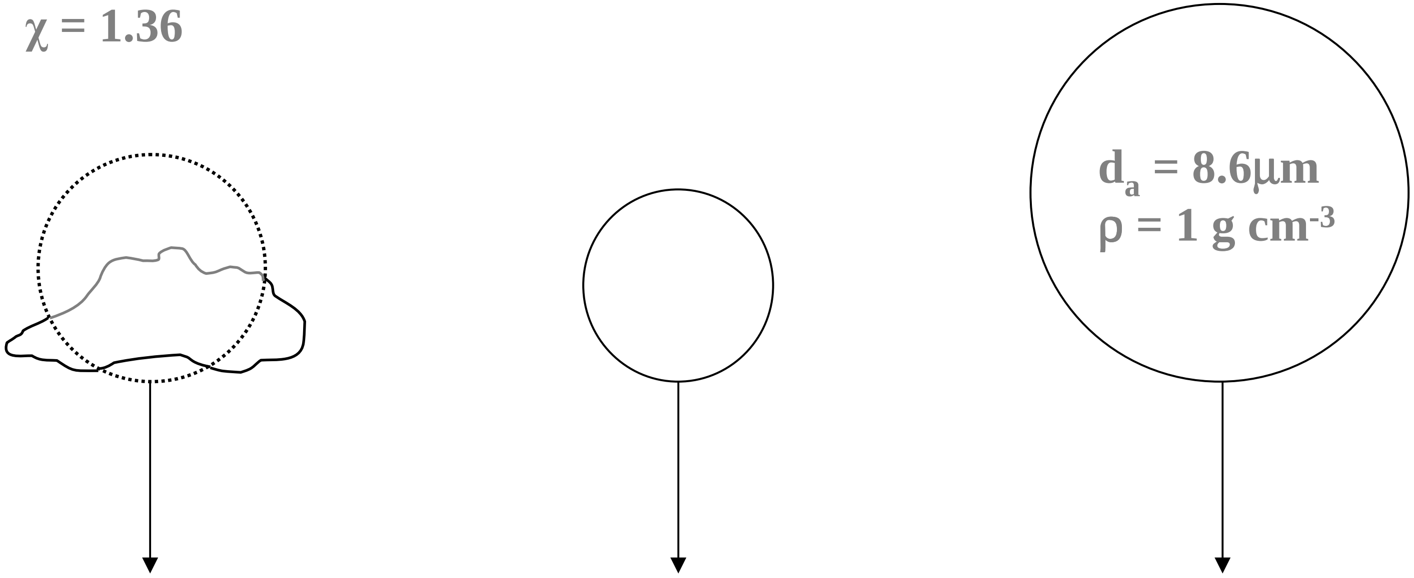
Irregular particle

Stokes’s equivalent sphere

Aerodynamic equivalent sphere

$d_e = 5.0\mu m$
$\rho = 4\ g\ cm^{-3}$
$\chi = 1.36$

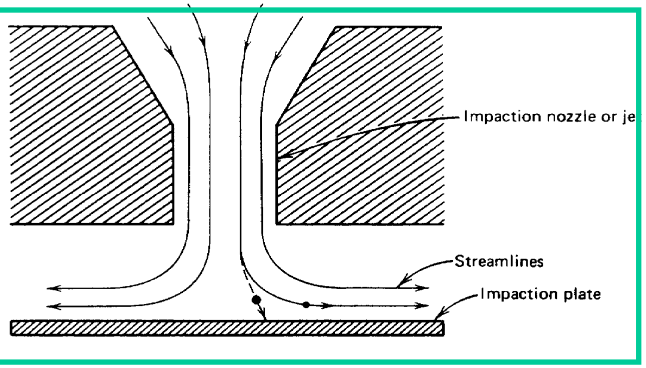
$d_s = 4.3\mu m$
$\rho = 4\ g\ cm^{-3}$



$d_a = 8.6\mu m$
$\rho = 1\ g\ cm^{-3}$

Terminal velocity of all three particles = 0.22 cm s^{-1}

The aerodynamic diameter is the diameter of the unit density sphere that has the same settling velocity as the particle



Nucleation events in polluted air

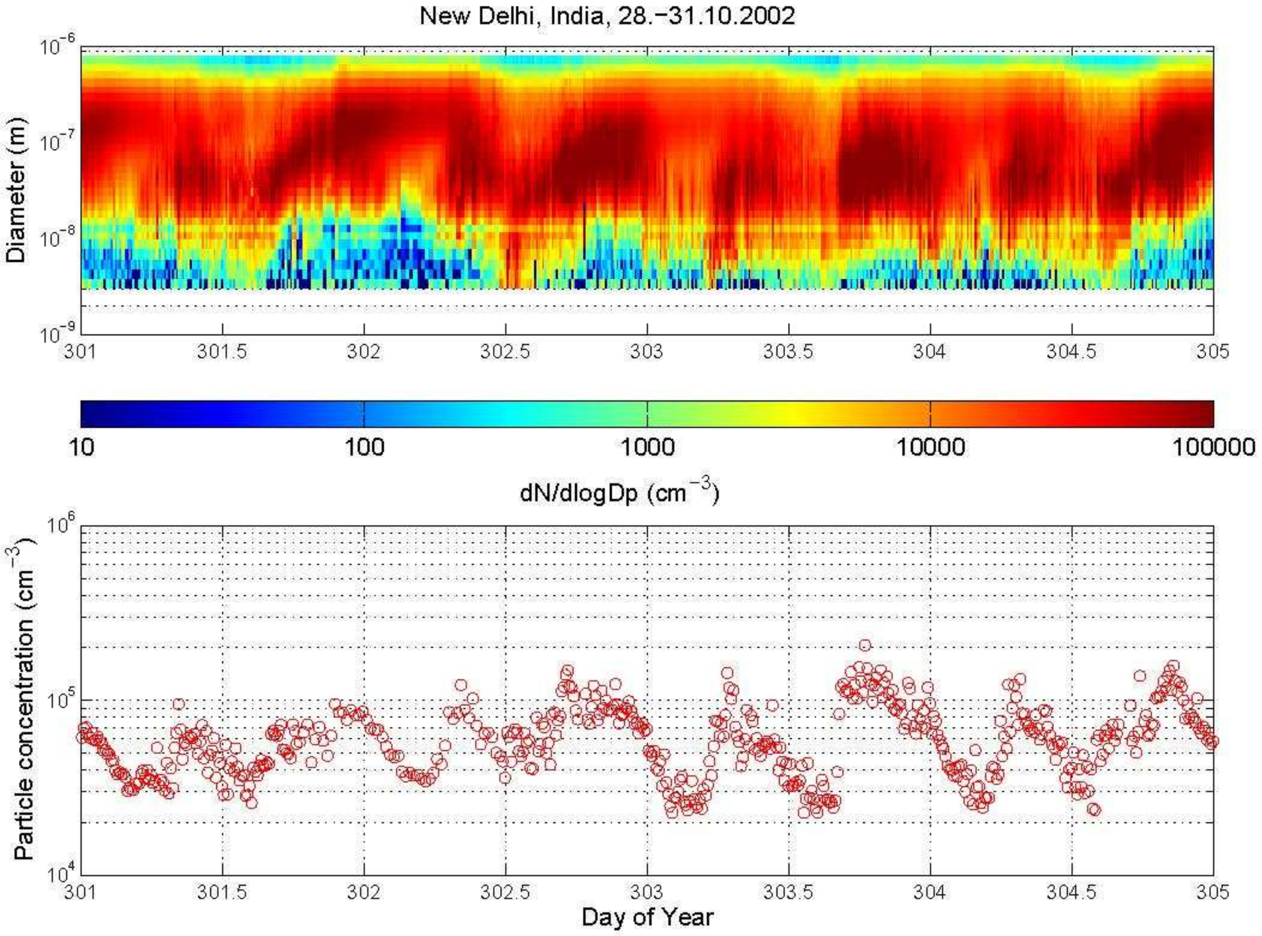


Fig. 2. Measured aerosol number size distribution **(a)** and number concentration **(b)**. The x-axis represents the time and y-axis in (a) particle diameter (m) and in (b) integrated particle concentration (cm^{-3}) for the same period. The color in the (a) represents particle concentration ($dN/d\log D_p$).

Mönkkönen et al., 2004

Primary particle formation (nucleation)

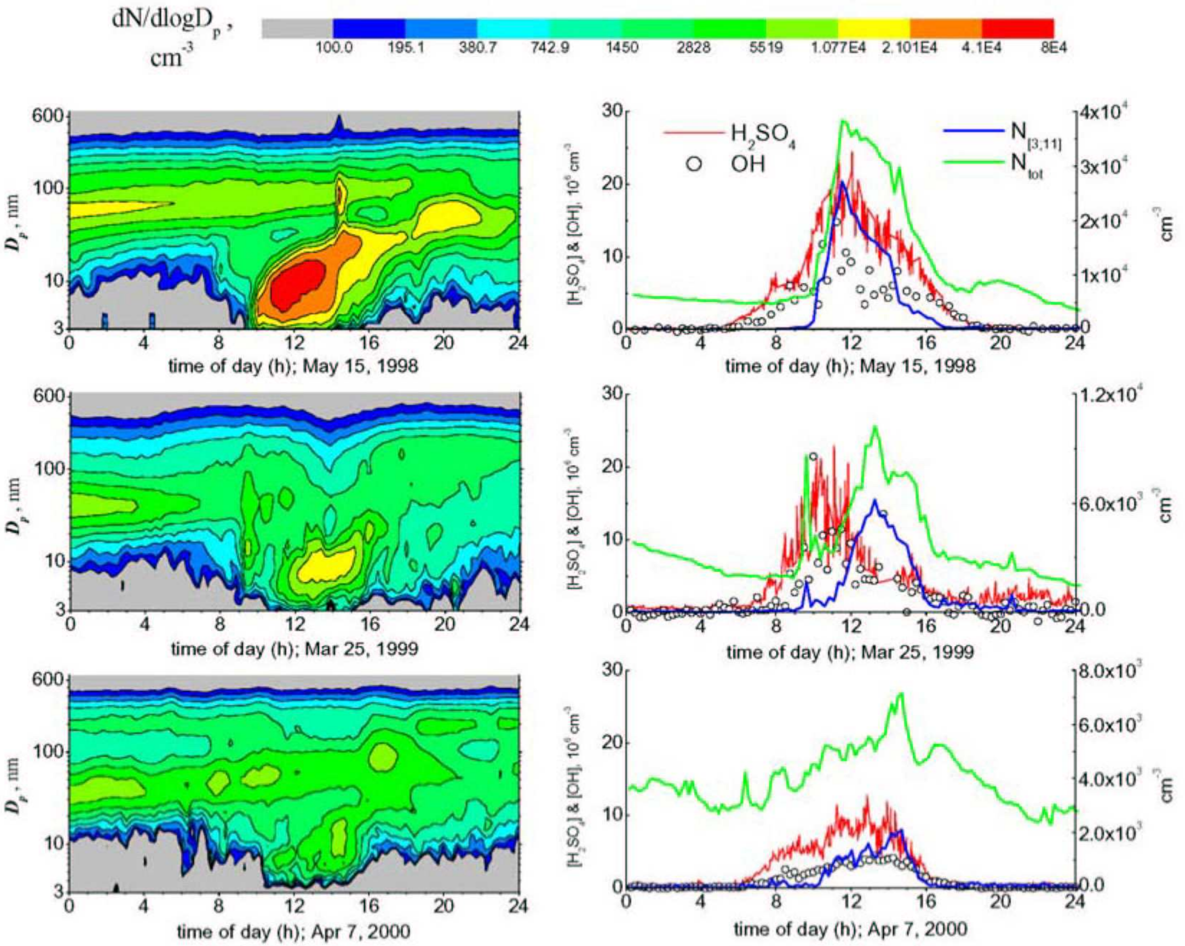
$$n_1\,H_2SO_4 + n_2\,H_2O + n_3\,NH_3\ (?) + RCOOH\ (??) \rightarrow \text{critical cluster} \xrightarrow{\text{condensational growth}} \text{ultrafine particle}$$

Nucleation events:

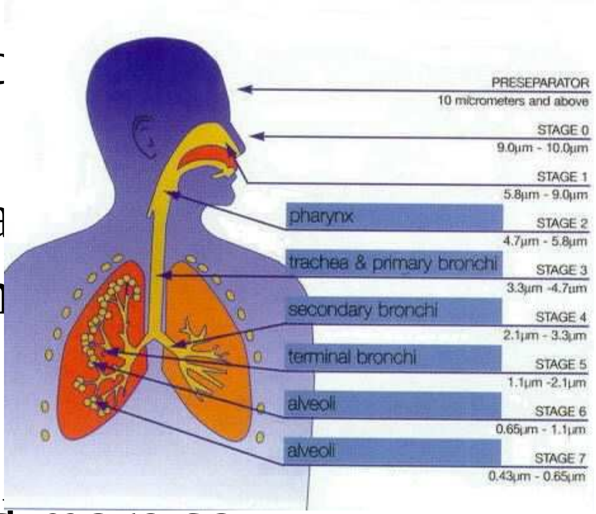
Reasons for occurrence of nucleation events unclear. No simple correlations, key factors unknown. Example: 3 different events on Hohenpeissenberg 1998-2000 (*Birmili et al., 2003*).

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*).



Aerosol effects



Atmospheric chemistry:

- Chemistry of the ozone hole is heterogeneous c ice particles
- Formation of acidity in the marine boundary la chemistry in the aqueous phase provided by hum particles

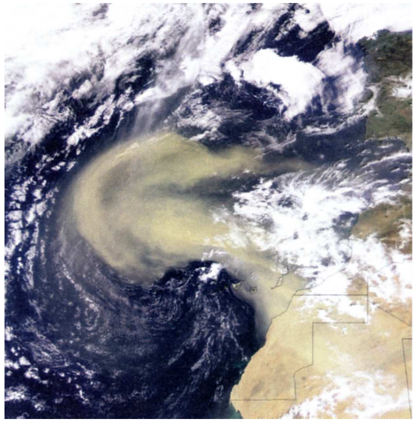
Climate:

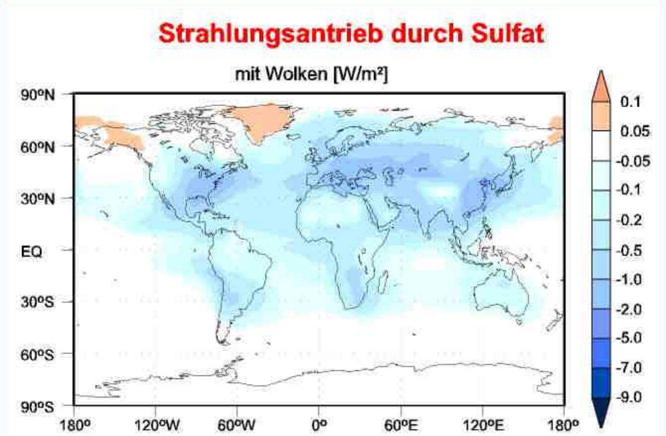
- strong climate sensitivity to aerosols, direct and more so indirect

Toxicology:

- fine particles < 10 µm (PM_{10}) reach the lung
- consitutents are partly toxic

Relevance of aerosols: Climate





Sulfate aerosols: cooling (Feichter & Lammel, 1999)

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: –1.5 ± 0.5 W/m² (Lohmann & Feichter, 2001; Lohmann et al., 2001)

PROVEN PATHWAYS
OF REGIONAL AND INTERCONTINENTAL TRANSPORT OF AEROSOLS

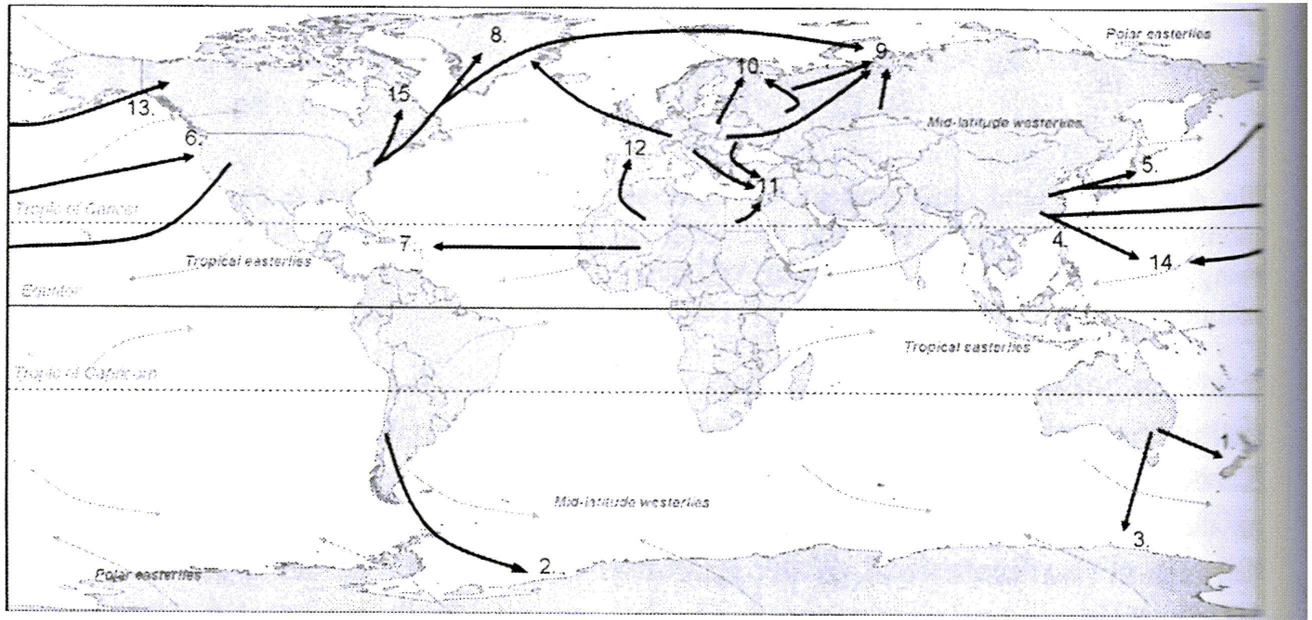
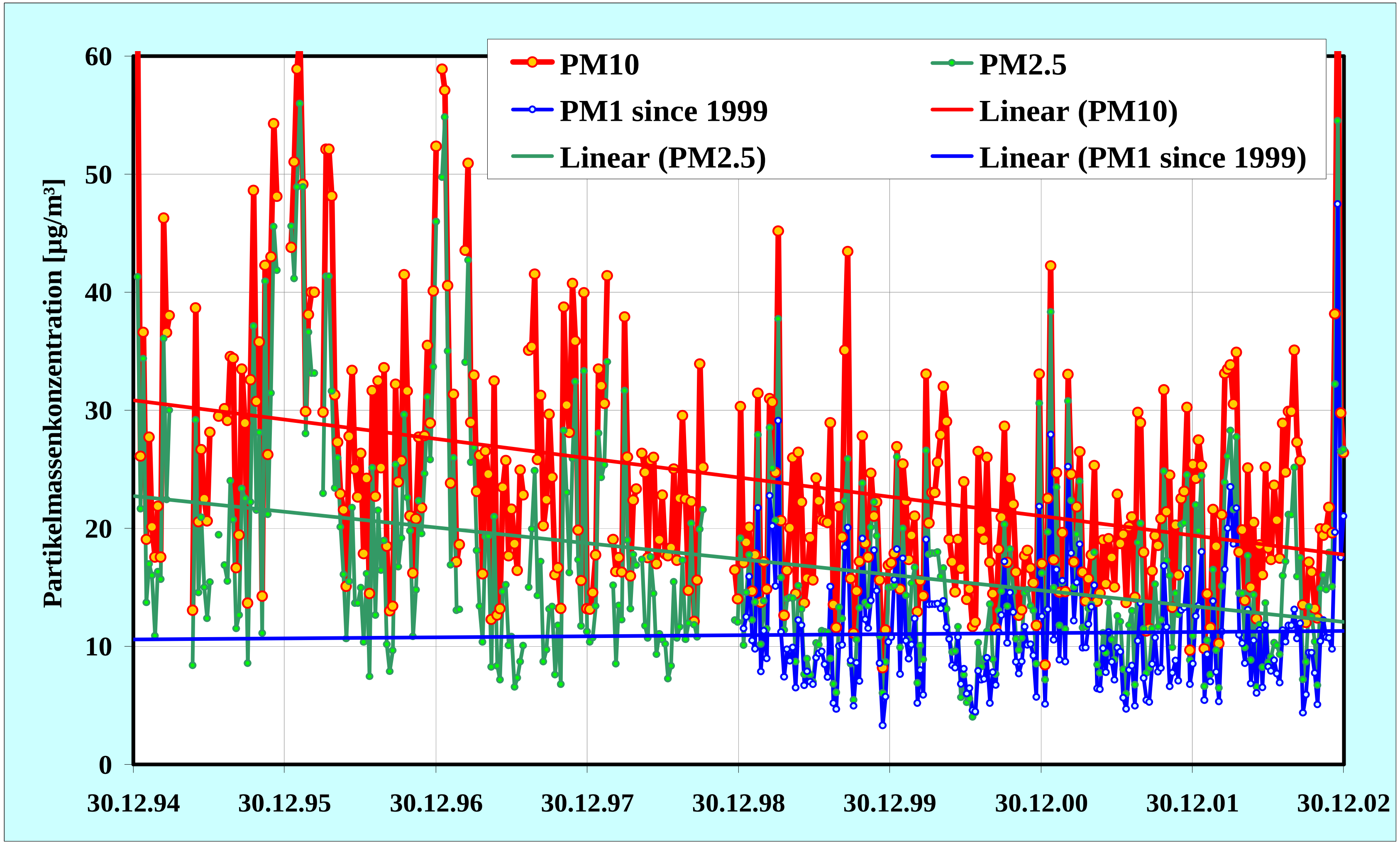


Fig. 5 The major documented pollution plume pathways over which the long-range transport of pollution occurs (as indicated by the *black arrows*). The main windfields are also indicated on the figure by the *grey arrows*. The *numbers* on the figure refer to representative studies documenting pollution 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)

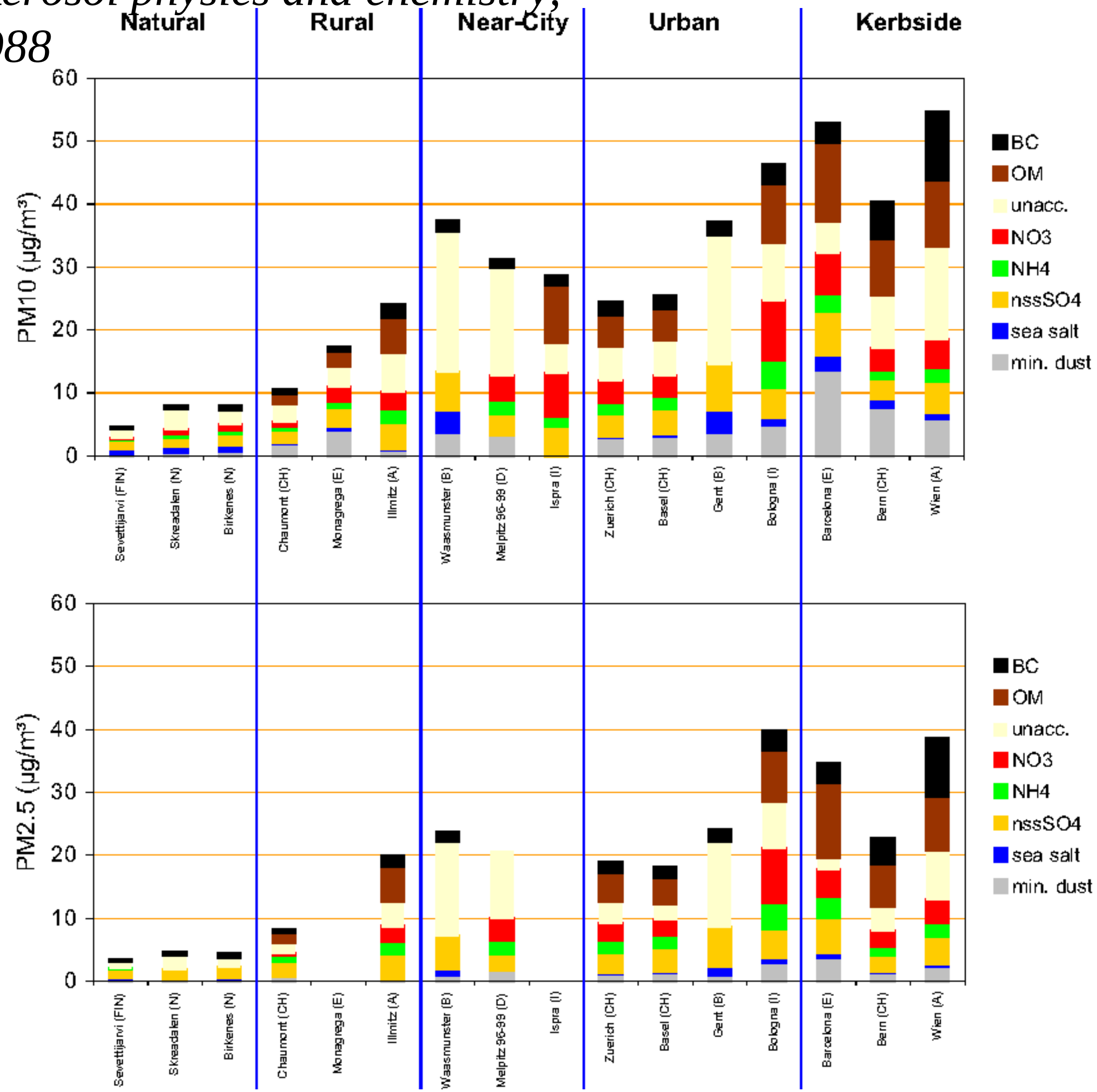
Precursors			*anthr.*	*natural*
	NO_x	41	31	10
	NH_3	54 (40-70)	43	11
	SO_2	88 (67-130)	79	9
	DMS	25 (12-42)	0	25
	VOCs	236 (100-560)	109	127 (only terpenes)
Primary				
	Carbonaceous (OC)			
		Biomass burning	54 (45-80)	
		Fossil fuel burning	28 (10-30)	
		biogenic		56 (0 – 90)
	Black carbon (soot)			
		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)*

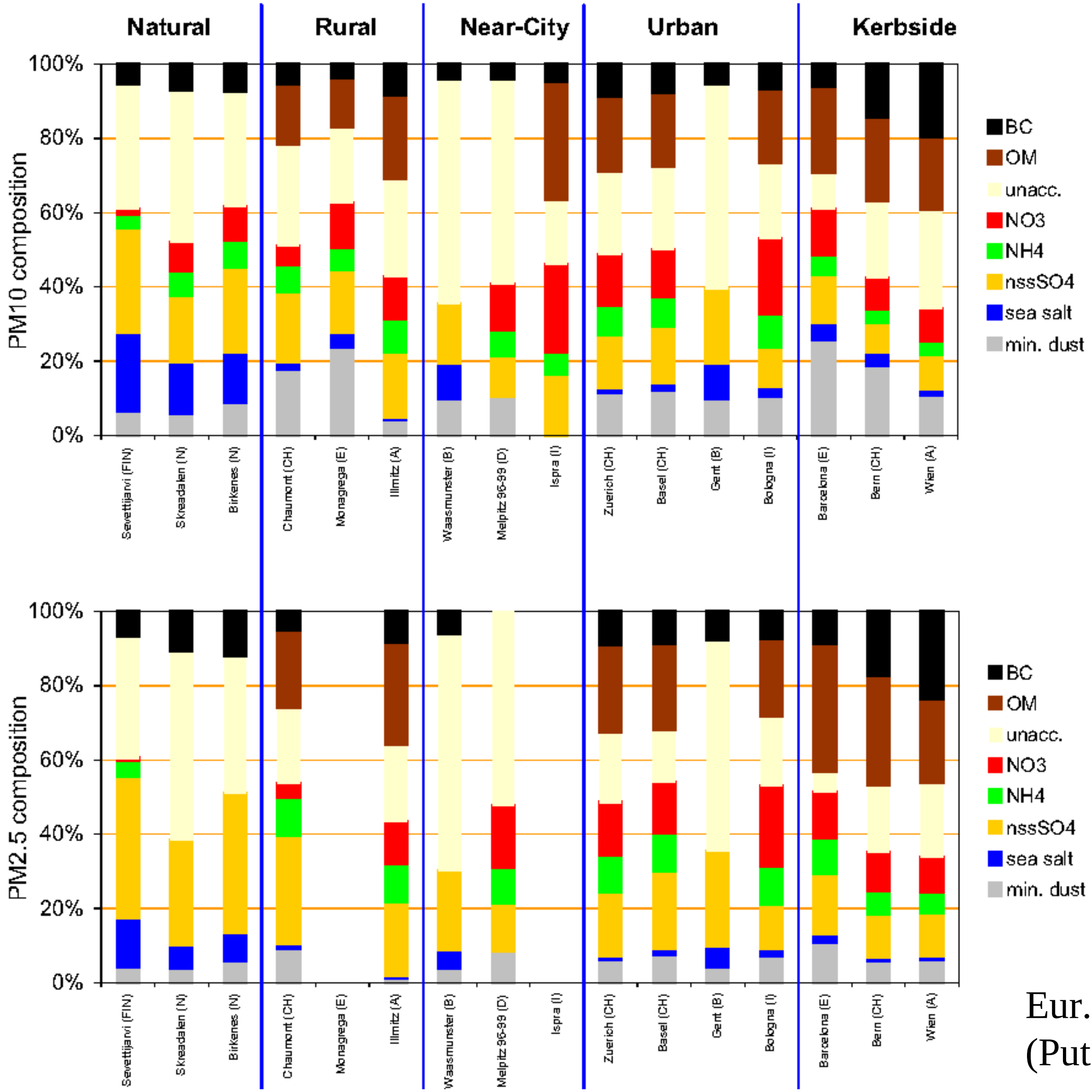
Chemical composition

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

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



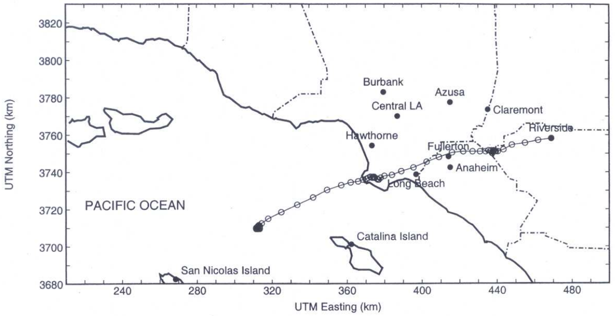
Aerosol chemical composition



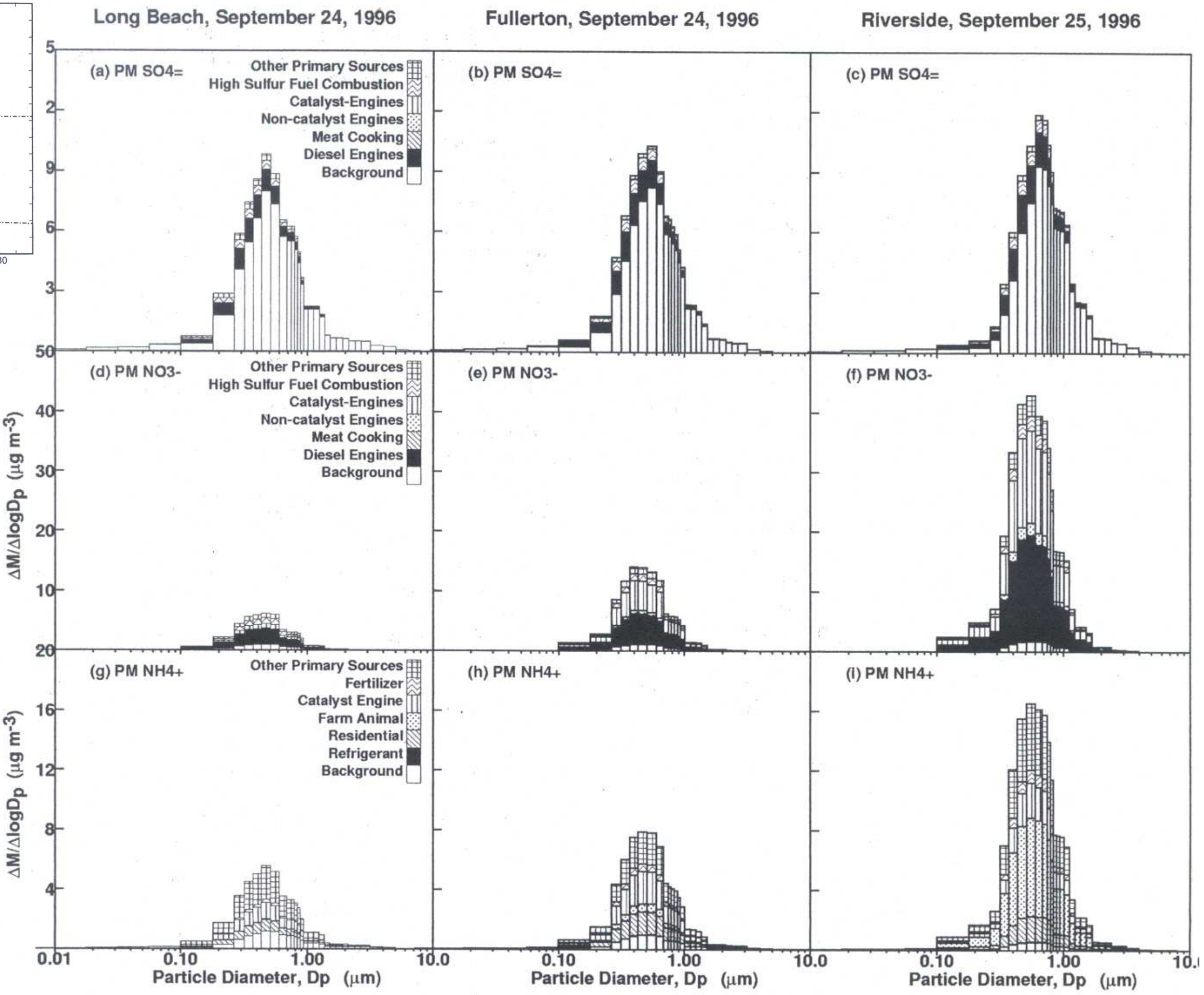
Eur. Aer. Phenomenology
(Putaud et al., 2002)

Sources for aerosol inorganic ions,

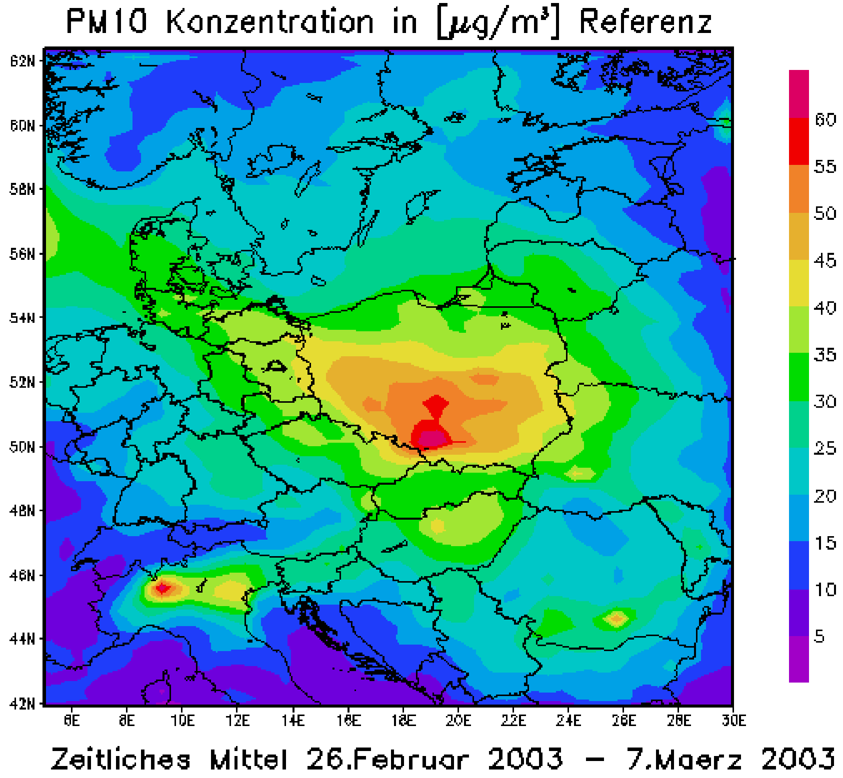
Los Angeles 24.-25.9.1996 (Mysliwiec & Kleeman, 2002)



- Emission inventory (source distribution, characteristics)
- Atmosphere model covering transport and transformations

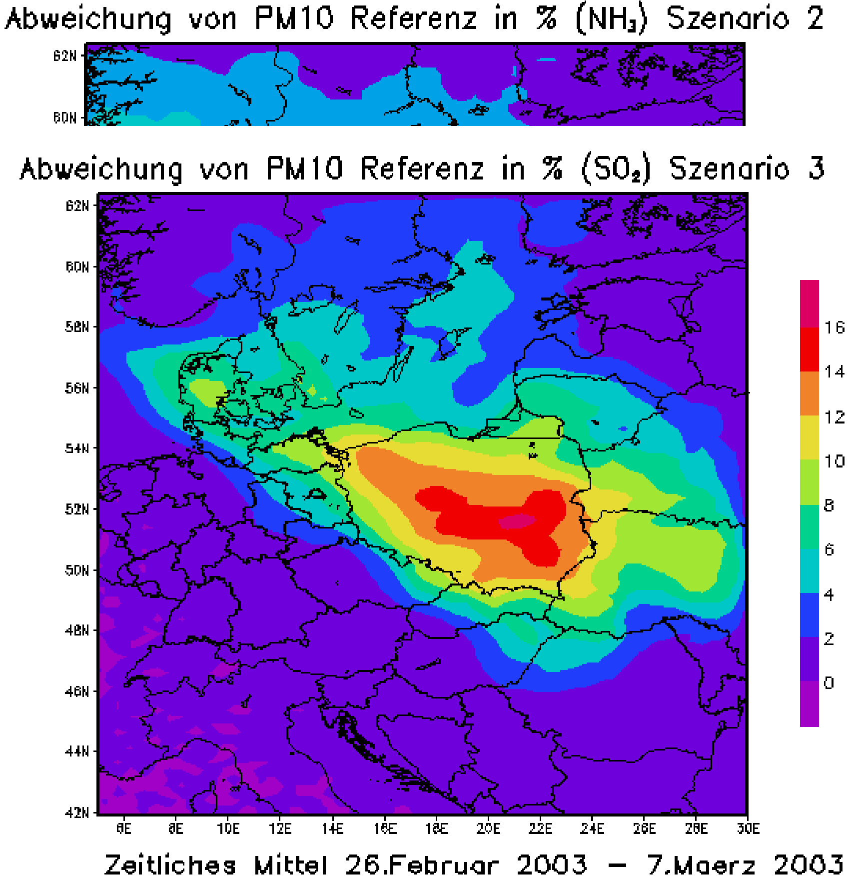


Reduction potentials fine particulate matter ? - NH_3



NH_3 emissions are underestimated

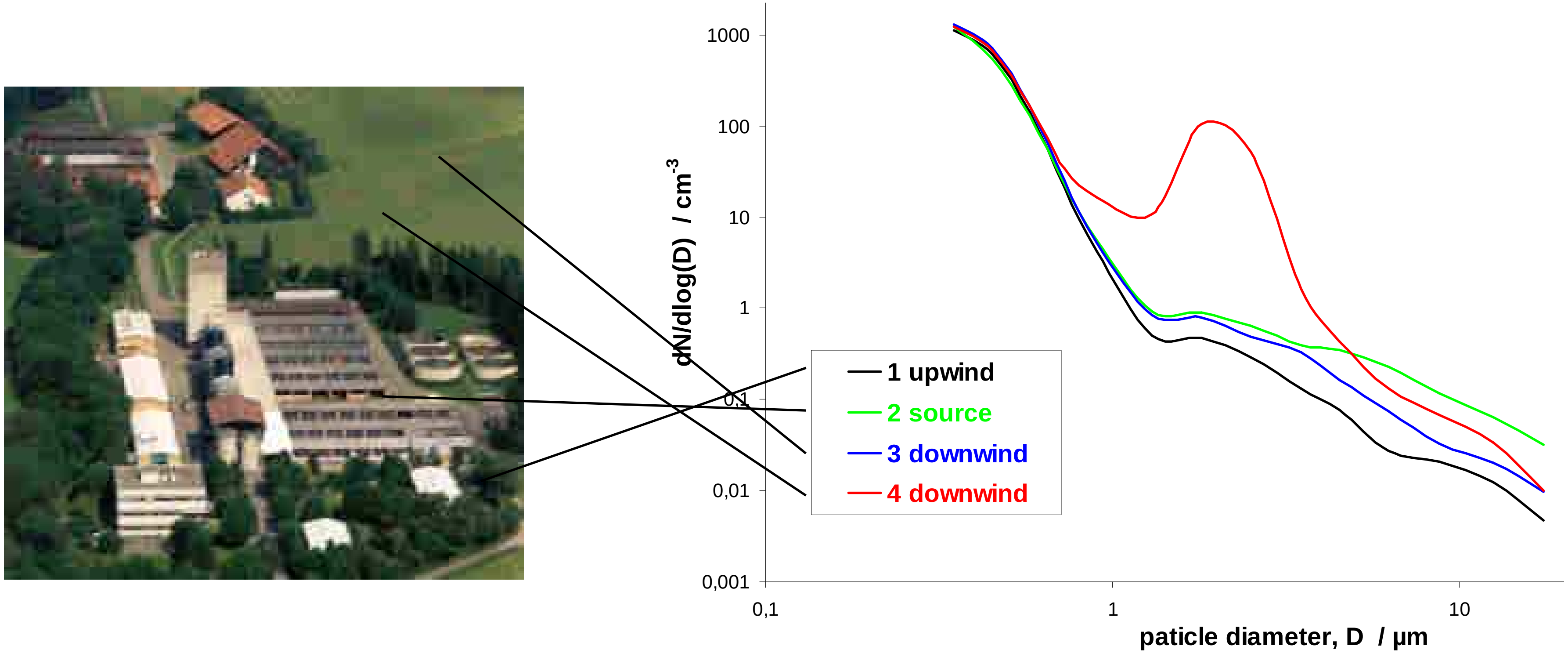
No NH_3 emissions in E D, PL, UA



(courtesy of Reimer, FU Berlin 2006)

Particle growth downwind of NH_3 sources:

- plumes downwind < 300 m of open liquid manure pits and other more or less open sources (animal houses, feed stocks)
- sub-µm size range: $\Delta n_{CN} = +(8\text{-}18)*10^3\ \mathrm{cm}^{-3}$
- super-µm size range: very significant around 2 µm, $\Delta n_{1\text{-}4\mu m} = 14\text{-}21\ \mathrm{cm}^{-3}$
- under humid conditions ((1) r.h. = 90%, T = 6-9°C; $rh \approx rh_D((NH_4)_2SO_4)$ and $rh > rh_D(NH_4NO_3)$) growth rate 0.2-0.7 $\mu m\ min^{-1}$



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

for rh < $rh_{D:}$

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

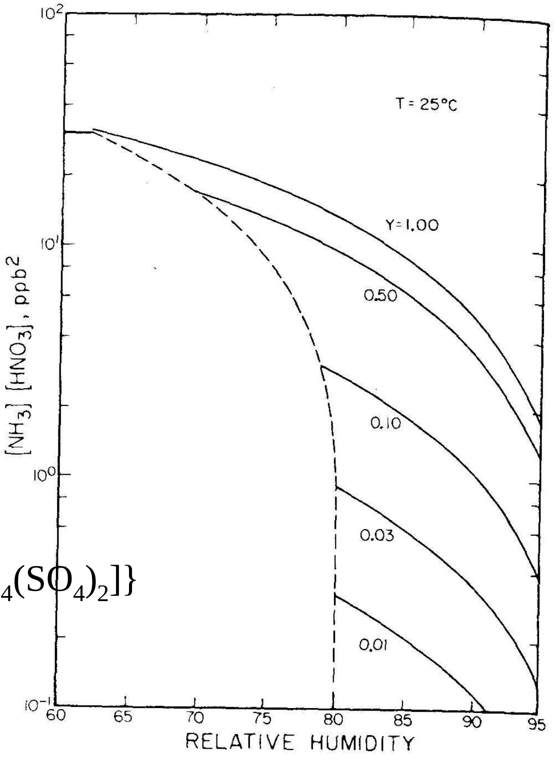


Fig. 2. The effect of $(NH_4)_2SO_4$ on the relative humidity dependence of the NH_4NO_3 dissociation constant.

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

Humidity dependence:

(Stelson & Seinfeld, 1982)

Ions volatile, and non-volatile:

Winter

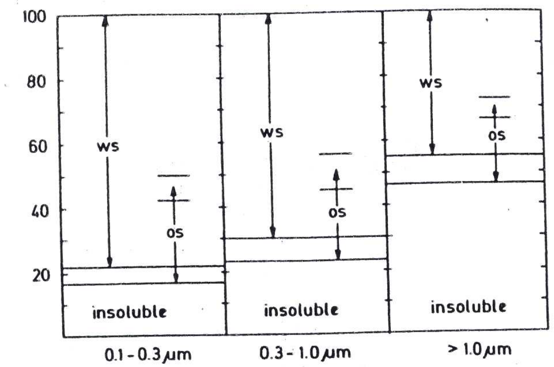
$0.5\ Cl^- + 1.3\ NO_3^- + 0.5\ SO_4^{2-} + 0.5\ Na^+ + 2.3\ NH_4^+ + 0.1\ K^+ + 0.05\ Mg^{2+} + 0.33\ Ca^{2+}$

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

Summer

$0.2\ Cl^- + 0.4\ NO_3^- + 0.5\ SO_4^{2-} + 0.5\ Na^+ + 1.2\ NH_4^+ + 0.1\ K^+ + 0.05\ Mg^{2+} + 0.33\ Ca^{2+}$

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



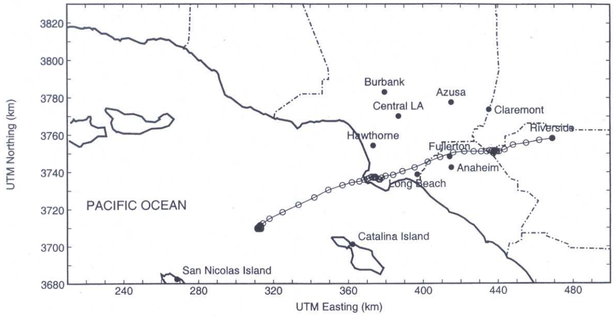
Continental aerosol (Winkler, 1974)

Continental aerosol consists of (each 25-50%):

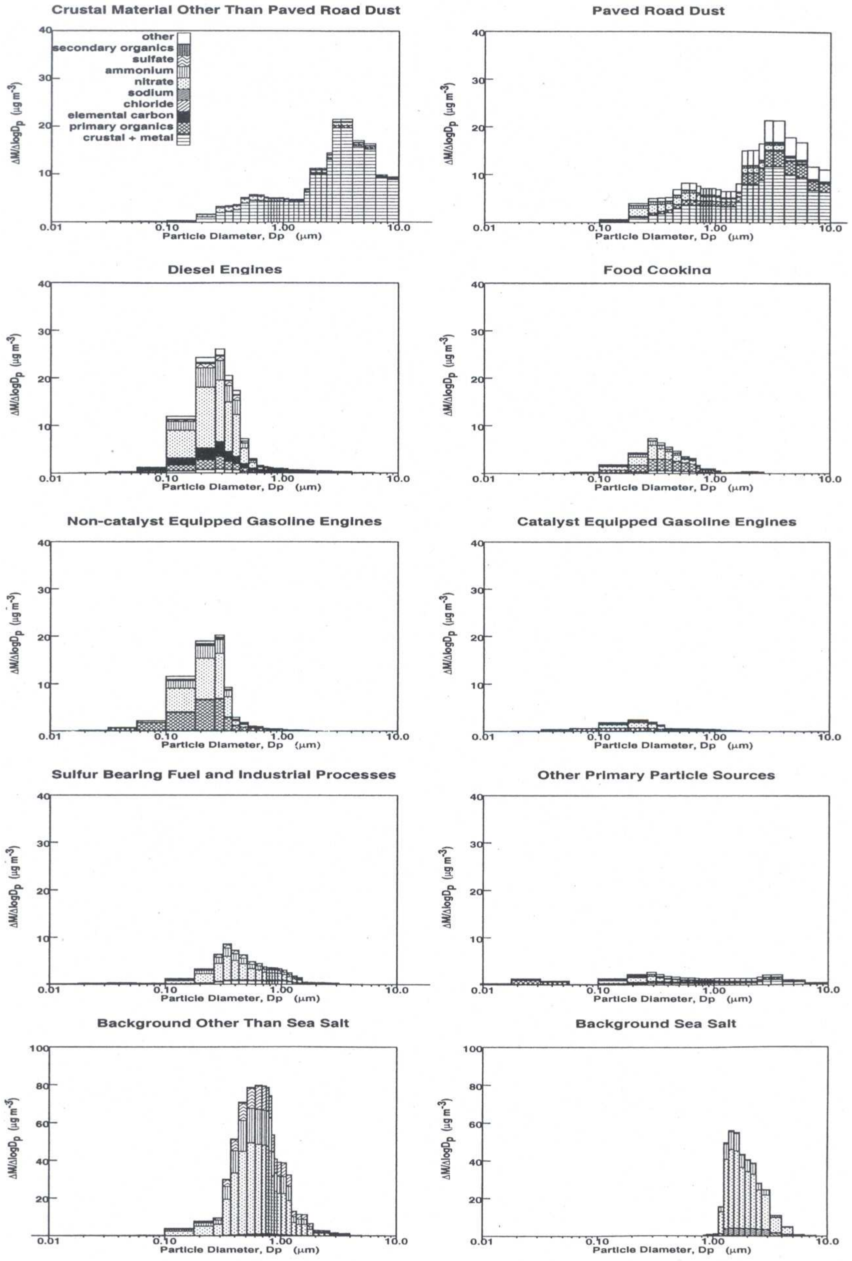
- aliphatic polyols (mostly sugars) and polyethers (polyphenols)
- low-molecular aliphatic and other multifunctional compounds, e.g. $R(COOH)_{1-2}$
- unsaturated aliphatic and aromatic polyacids of various lipophilicity („humic-like“), M = 200-500 Da, sources: Oxidation of soot, acid catalyzed polymerisation 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)



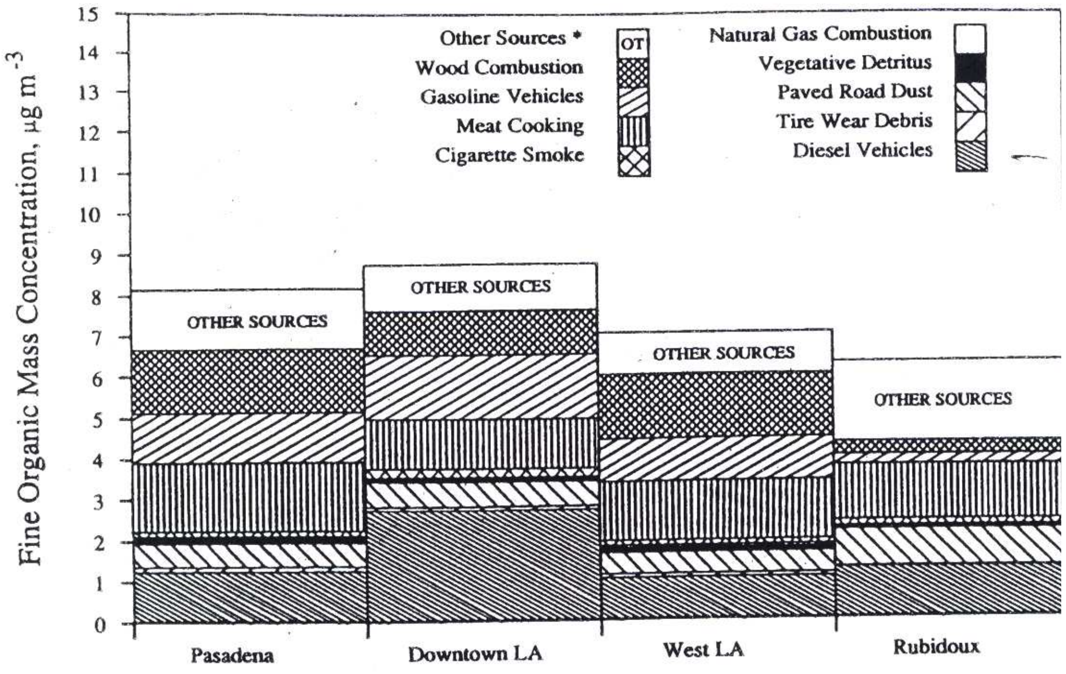
- Emission inventory (source distribution, characteristics)
- Atmosphere model covering transport and transformations



Source contributions to OC: urban

Total fine part. OC emitt. 30 t/d

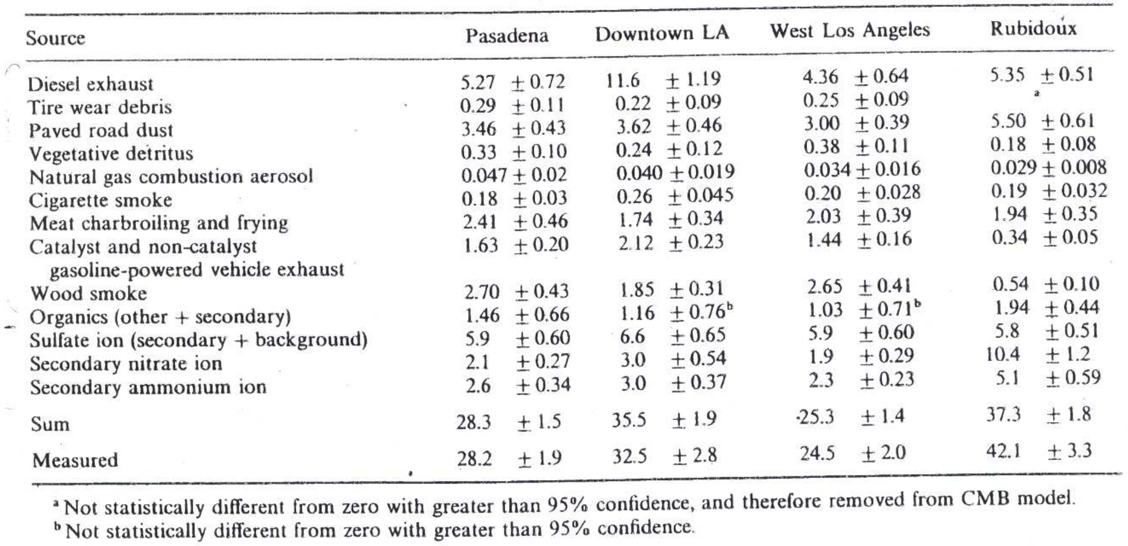
Meat cooking	21%
Road abrasion	16%
Open fires	14%
Vehicles without cat. converter	12%
Diesel vehicles	6.2%
Lacquing	4.8%
Forest fires	2.9%
Vehicles without cat. converter	2.9%
Tobacco smoke	2.7%



* Other Sources include secondary formation

ıt of ambient fine organic aerosol mass concentration — 1982 annual average

Table 4. Source apportionment of fine particulate mass concentration: 1982 annual average determined by chemical mass balance (avg ± std in μg m⁻³)



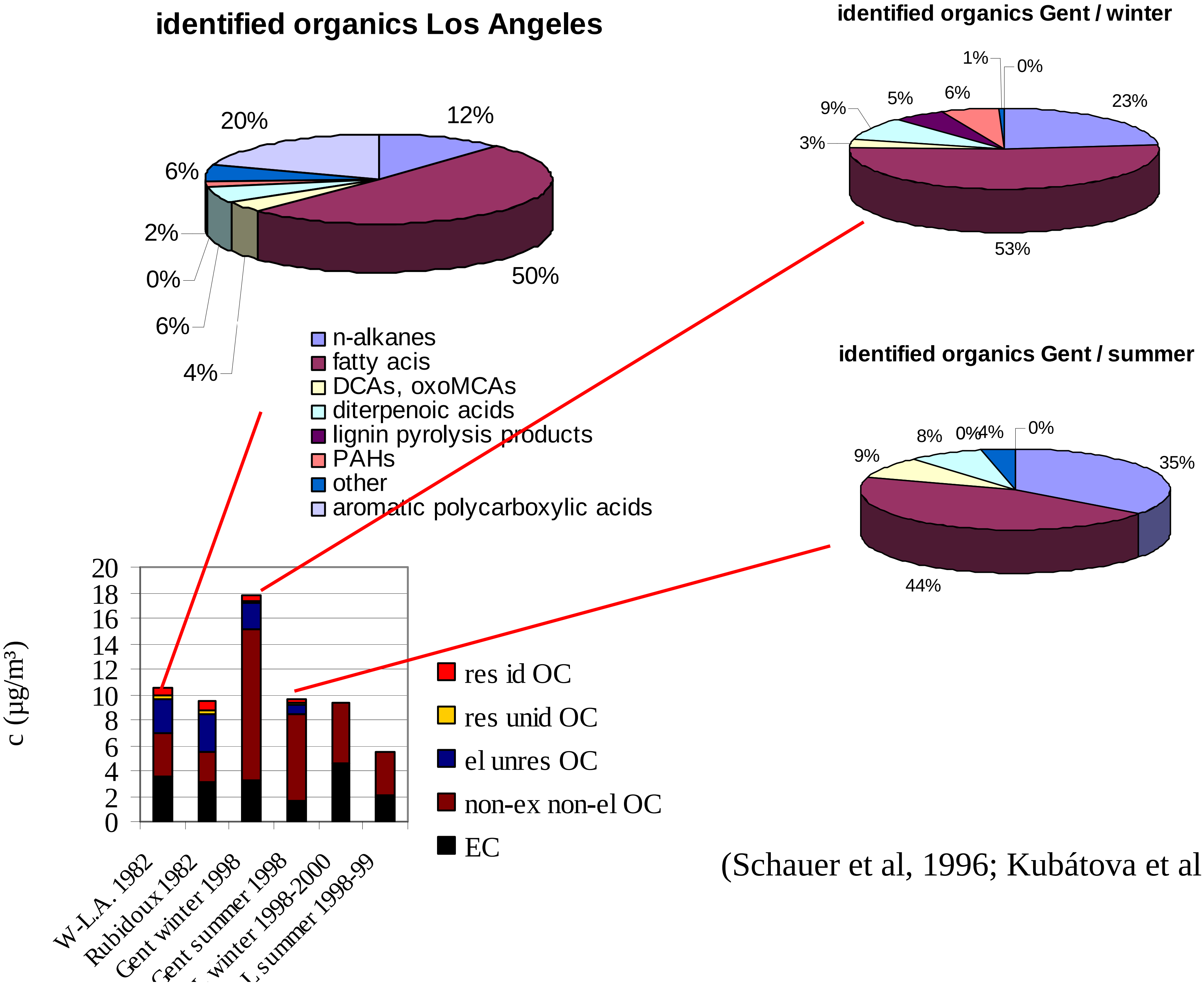
Source	Pasadena	Downtown LA	West Los Angeles	Rubidoux
Diesel exhaust	5.27 ± 0.72	11.6 ± 1.19	4.36 ± 0.64	5.35 ± 0.51
Tire wear debris	0.29 ± 0.11	0.22 ± 0.09	0.25 ± 0.09	[a]
Paved road dust	3.46 ± 0.43	3.62 ± 0.46	3.00 ± 0.39	5.50 ± 0.61
Vegetative detritus	0.33 ± 0.10	0.24 ± 0.12	0.38 ± 0.11	0.18 ± 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

[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.

Southern California,

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



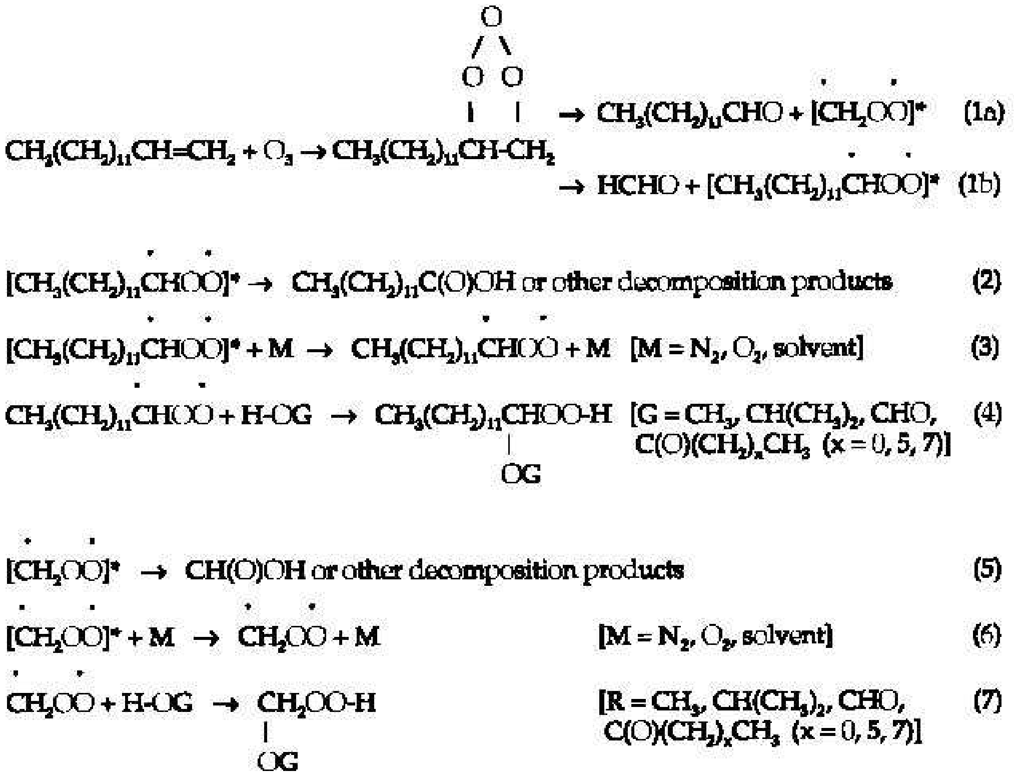
(Schauer et al, 1996; Kubátova et al., 2001)

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 →



$$CH_3(CH_2)_{11}CH{=}CH_2 + O_3 \rightarrow CH_3(CH_2)_{11}\underset{}{\overset{\begin{array}{c}O\\ /\ \backslash\\ O\quad O\\ |\qquad |\end{array}}{CH-CH_2}} \quad \begin{array}{ll}\rightarrow CH_3(CH_2)_{11}CHO + [\dot{C}H_2O\dot{O}]^* & (1a)\\ \rightarrow HCHO + [CH_3(CH_2)_{11}\dot{C}HO\dot{O}]^* & (1b)\end{array}$$

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

$$[CH_3(CH_2)_{11}\dot{C}HO\dot{O}]^* + M \rightarrow CH_3(CH_2)_{11}\dot{C}HO\dot{O} + M \quad [M = N_2, O_2, \text{solvent}] \qquad (3)$$

$$CH_3(CH_2)_{11}\dot{C}HO\dot{O} + H\text{-}OG \rightarrow CH_3(CH_2)_{11}\underset{\begin{array}{c}|\\ OG\end{array}}{C}HOO\text{-}H \quad [G = CH_3, CH(CH_3)_2, CHO, C(O)(CH_2)_xCH_3\ (x = 0, 5, 7)] \qquad (4)$$

$$[\dot{C}H_2O\dot{O}]^* \rightarrow CH(O)OH \text{ or other decomposition products} \qquad (5)$$

$$[\dot{C}H_2O\dot{O}]^* + M \rightarrow \dot{C}H_2O\dot{O} + M \quad [M = N_2, O_2, \text{solvent}] \qquad (6)$$

$$\dot{C}H_2O\dot{O} + H\text{-}OG \rightarrow \underset{\begin{array}{c}|\\ OG\end{array}}{C}H_2OO\text{-}H \quad [R = CH_3, CH(CH_3)_2, CHO, C(O)(CH_2)_xCH_3\ (x = 0, 5, 7)] \qquad (7)$$

→ SOA