

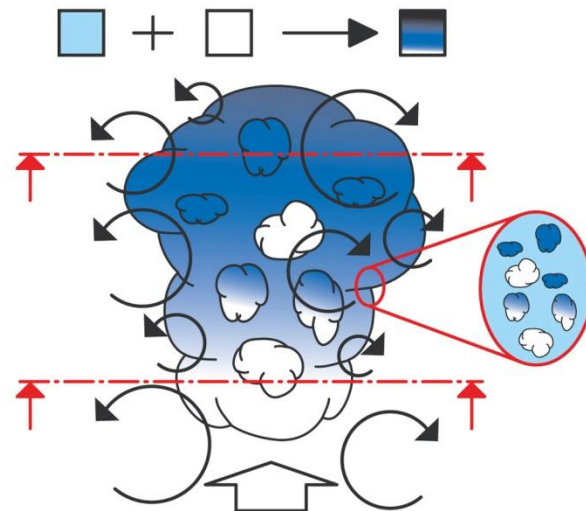
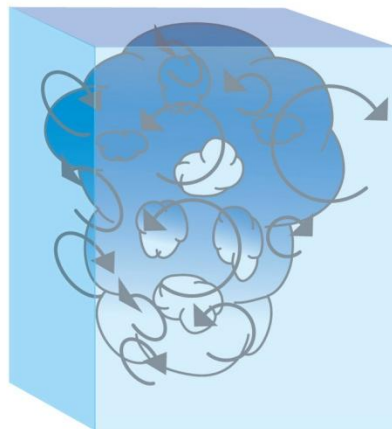
Gerhard Lammel: "Trends and Advances in Atmospheric and Environmental Chemistry"

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 $L = 0.1-2 \cdot 10^{-6} V_{\text{water}}/V_{\text{air}} = 0.1-2 \text{ g/m}^3$
 $= (0.1-2) \cdot 10^{-3} \text{ L/m}^3 < 10\%$ of total water content ($10-40 \text{ g/m}^3$!)
- only $\approx 10\%$ of clouds will rain out, while 90% will recycle aerosol particles
- lifetime of clouds hours-days, of cloud droplets ($D=5-50 \mu\text{m}$) minutes
- aqueous composition: dissolved ($c_i \approx 10^{-6} - 10^{-3} \text{ M}$) + 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 $c_{\text{H}_3\text{O}^+} = 10^{-7}$ M

Henry coefficients

Solubility increases with decreasing temperatures,

e.g. 78, 63 and 53% of O₂ 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	$(\Delta H_{\text{soln}}/R_g)$ /K	$R_g T K_H$	α^b	k_t ^c /s ⁻¹	τ_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 ₂ O ₂	1.0×10^5	6300	6.1×10^6	0.11	1.0×10^6	5.9	22
CH ₃ OOH	3.0×10^2	5300	1.6×10^4	0.004	1.8×10^5	4.5×10^{-2}	22
CH ₃ OO	6.0	–	1.4×10^2	0.01*	5.3×10^2	4.0×10^{-4}	23
CH ₃ OH	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 ₂ O 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
CH₃
for C
coeff

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>

¹ for
coeffs
law

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:

$$\begin{aligned}\epsilon_{i(g)} &= n_{i(aqu)} / (n_{i(aqu)} + n_{(g)}) = n_{i(aqu)} / [n_{i(aqu)} + p_i V_{air}/(R_g T)] = \\ &= n_{i(aqu)} / [n_{i(aqu)} + H_i n_{i(aqu)} V_{air}/(R_g T n_{H_2O})] = \\ &= [1 + H_i M_w / (R_g T L)]^{-1}\end{aligned}$$

with: Henry coefficient H_i [at] = $p_i n_{i(aqu)} / n_{H_2O} = p_i x_i = p_i / (c_i / 10^3 / M_w)$,
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:

$$K_H [M \text{ at}^{-1}] = 10^2 s / M_w p = (10^3 / M_w) \times \rho_{H_2O} / H$$

$$\text{solubility } s(T) [\text{mg/L}] = s(T_0) \times \exp[-\Delta H_{sol} / R_g \times (1/T - 1/T_0)]$$

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

$$\text{Air-water partitioning coefficient } K_{aw} [] = M_w p / (10^5 R_g T s) = 1 / (10^3 R_g T K_H)$$

$$\text{Henry coefficient } H' [\text{Pa m}^3/\text{mol}] = R_g T K_{aw} = 10^{-2} / K^H [\text{M/at}]$$

Tropospheric ozone and clouds

Ozone reactions

Ozone is a source of radicals and H_2O_2 in cloudwater:

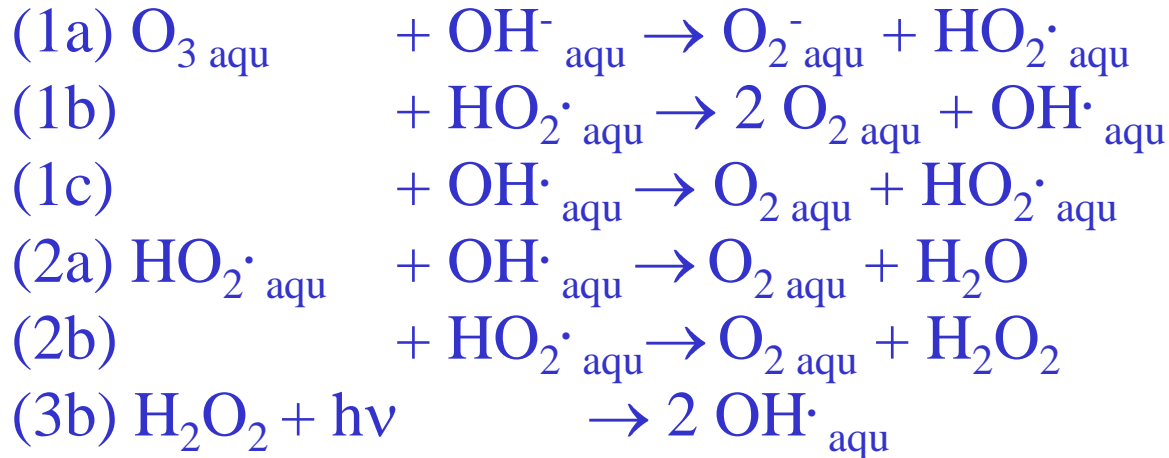


TABLE 1 Gas-phase, gas-liquid equilibrium and aqueous-phase reactions

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^{-6}	27	
G7	$CH_3OOH + h\nu + O_2 \rightarrow CH_2O + HO_2 + OH$	4.6×10^{-2}	27	
G8	$NO_3 + h\nu \rightarrow NO + O_2$	1.4×10^{-1}	27	
G9	$NO_3 + h\nu + O_2 \rightarrow NO_2 + O_3$	1.2×10^{-7}	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	$O_3 + NO \rightarrow NO_2 + O_2$	$2.0 \times 10^{-12} \exp(-1400/T)$	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	$HO_2 + OH \rightarrow H_2O + O_2$	$4.6 \times 10^{-11} \exp(230/T)$	27	
G20	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$3.3 \times 10^{-12} \exp(-200/T)$	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	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.4 \times 10^{-13} \exp(-2500/T)$	27	
G24	$NO + NO_3 \rightarrow 2NO_2$	$1.7 \times 10^{-11} \exp(150/T)$	27	
G25	$NO_2 + NO_3 (+M) \rightarrow N_2O_5 (+M)$	$8.1 \times 10^{-11} (7/300)^{-4.1}$	28	
G26	$N_2O_5 (+M) \rightarrow NO_2 + NO_3 (+M)$	$4.6 \times 10^{15} (7/300)^{-4.4} \exp(-11080/T)$	28	
G27	$CH_4 + OH + O_2 (+M) \rightarrow CH_3O_2 + H_2O (+M)$	$2.3 \times 10^{-12} \exp(-1700/T)$	27	
G28	$CH_2O_2 + NO + O_2 \rightarrow CH_2O + HO_2 + NO_2$	$4.2 \times 10^{-12} \exp(180/T)$	27	
G29	$CH_2O_2 + HO_2 \rightarrow CH_3OOH + O_2$	4.0×10^{-12}	29	
G30	$CH_2O_2 + HO_2 \rightarrow CH_2O + H_2O + O_2$	2.0×10^{-12}	29	
G31	$CH_2O + OH + O_2 \rightarrow HO_2 + H_2O + CO$	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	$CH_2O_2 + CH_2O_2 + O_2 \rightarrow 2CH_2O + 2HO_2$	$1.9 \times 10^{-13} \exp(220/T)$	27	
Gas-aqueous and aqueous-phase equilibria		K_{298}^\ddagger	$-\Delta H/R$	Ref.
E1	$HO_2(\text{gas}) \rightleftharpoons HO_2(\text{aq})$	2.0×10^3	6,600	31
E2	$HO_2(\text{aq}) \rightleftharpoons O_2 + H^+$	3.5×10^{-5}		32
E3	$H_2O_2(\text{gas}) \rightleftharpoons H_2O_2(\text{aq})$	7.4×10^4	6,615	33
E4	$O_3(\text{gas}) \rightleftharpoons O_3(\text{aq})$	1.1×10^{-2}	2,300	34
E5	$CH_2O(\text{gas}) \rightleftharpoons CH_2(OH)_2$	6.3×10^3	6,425	8
E6	$HCOOH(\text{gas}) \rightleftharpoons HCOOH(\text{aq})$	3.7×10^4	5,700	35
E7	$HCOOH(\text{aq}) \rightleftharpoons HCOO^- + H^+$	1.8×10^{-4}	-1,510	35
E8	$CH_3OOH(\text{gas}) \rightleftharpoons CH_3OOH(\text{aq})$	2.2×10^7	5,653	33
E9	$CH_2O_2(\text{gas}) \rightleftharpoons CH_2O_2(\text{aq})$	2.0×10^3	6,600	35
E10	$HNO_3(\text{gas}) \rightleftharpoons HNO_3(\text{aq})$	2.1×10^9	8,700	E9-E11
E11	$HNO_3(\text{aq}) \rightleftharpoons NO_3^- + H^+$	15.4		36
E12	$NO(\text{gas}) \rightleftharpoons NO(\text{aq})$	1.9×10^{-3}	1,480	36
E13	$NO_2(\text{gas}) \rightleftharpoons NO_2(\text{aq})$	6.4×10^{-3}	2,500	37
E14	$NO_3(\text{gas}) \rightleftharpoons NO_3(\text{aq})$	15.0		12
E15	$OH(\text{gas}) \rightleftharpoons OH(\text{aq})$	9.0×10^9		38
E16	$CO_2(\text{gas}) \rightleftharpoons CO_2(\text{aq})$	3.4×10^{-2}	2,420	39
E17	$CO_2(\text{aq}) \rightleftharpoons HCO_3^- + H^+$	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	$CH_2(OH)_2 + OH + O_2 \rightarrow H_2O + HCOOH + HO_2$	2.0×10^7	-1,500	40, 41
A4	$HCOOH + OH + O_2 \rightarrow CO_2 + H_2O + HO_2$	1.6×10^8	-1,500	42
A5	$HCOO^- + OH + O_2 \rightarrow CO_2 + OH^- + HO_2$	2.5×10^7	-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^{10}	-1,500	46
A8	$HO_2 + H \rightarrow H_2O_2$	5.0×10^{10}	-1,500	2
A9	$H_2O_2 + H \rightarrow HO_2 + H_2O$	2.7×10^7	-1,715	47
A10	$N_2O_5 + H_2O \rightarrow 2HNO_3$			1
A11	$CH_3O_2 + H_2O + H_2O \rightarrow CH_3OOH + O_2 + OH^-$	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	$HCO_3^- + OH \rightarrow H_2O + CO_3^{2-}$	1.0×10^7	-1,500	48
A15	$HCO_3^- + O_2^- \rightarrow HO_2 + CO_3^{2-}$	1.5×10^8	-1,500	48
A16	$CO_3^{2-} + H_2O_2 \rightarrow HO_2 + HCO_3^-$	8.0×10^9	-2,800	49
A17	$CO_3^{2-} + O_2^- \rightarrow O_2 + CO_3^{2-}$	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 adopted⁴⁶. 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 processes⁴, 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 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⁻¹ atm⁻¹ for Henry's law constants and in mol⁻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 N₂O₅ is limited by gas-phase diffusion and transfer through the interface. We assume that reaction A10 then occurs instantaneously, so that dissolution is irreversible.

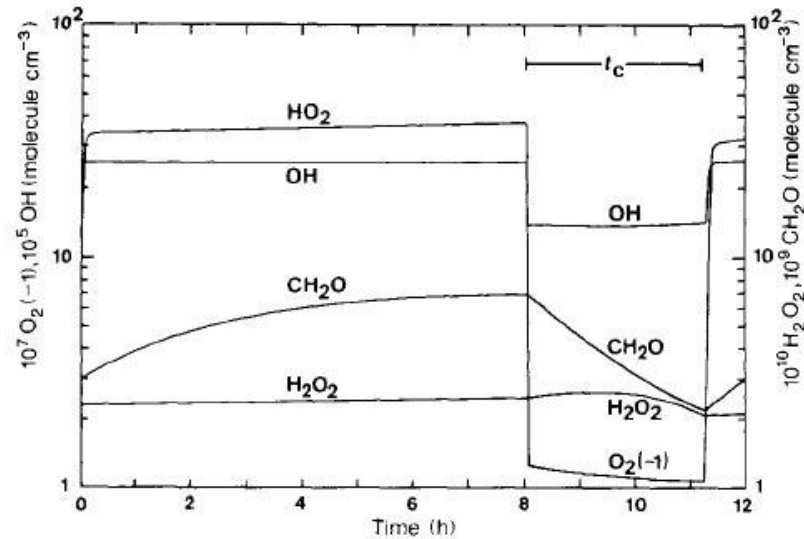
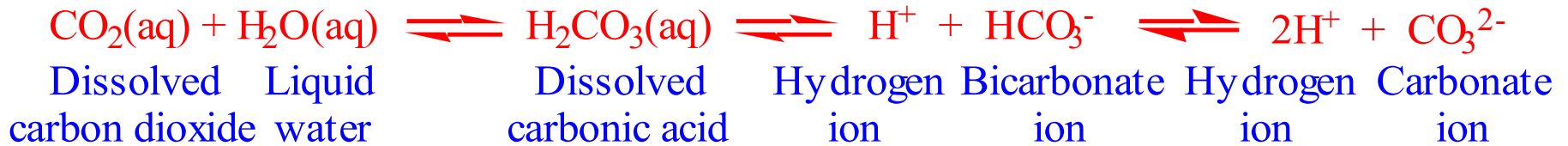


FIG. 2 Concentrations of some gases during sunlit hours of day 14 of the simulations, pertaining to the Equator at 3 km altitude (case 6, Table 2 and 3a), with NO_x fixed. For the cloudy period (t_c) total gas-phase plus aqueous-phase concentrations are depicted. $O_2(-1) = HO_2(\text{gas}) + HO_2(\text{aq})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

Differences in solubility and chemical reactivity in the aqueous phase result in changed (overall) chemistry of the atmosphere.

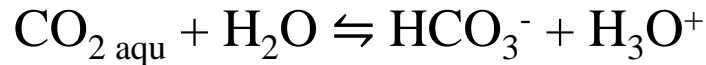
pH dependencies, e.g. O₃ sink A6 (O₃ + O₂⁻ + H₂O →) O₃, OH, NO_x overestimated when clouds are neglected

(Lelieveld & Crutzen, 1990)

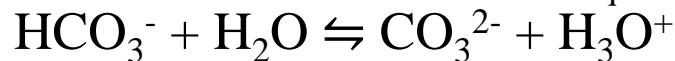


Solubility of $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_{2\text{aqu}} + 20 \text{ kJ/mol}$

$$(1) \quad K_H = c_{\text{CO}_2\text{aqu}} / p_{\text{CO}_2} = 3.4 \times 10^{-7} \text{ mol/L/Pa (298 K)}$$



$$(2) \quad K_{A1} = (c_{\text{HCO}_3^-} \cdot c_{\text{H}_3\text{O}^+}) / c_{\text{CO}_2\text{aqu}} = 10^{-6.35}$$



$$(3) \quad K_{A2} = (c_{\text{CO}_3^{2-}} \cdot c_{\text{H}_3\text{O}^+}) / c_{\text{HCO}_3^-} = 10^{-10.33}$$

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

$$K_{H\text{CO}_2}^* = (c_{\text{CO}_2\text{aqu}} + c_{\text{HCO}_3^-} + c_{\text{CO}_3^{2-}}) / p \quad (\text{mol/L/Pa})$$

$$K_H^* = K_H (1 + K_{A1} / c_{\text{H}_3\text{O}^+} + K_{A1} K_{A2} / c_{\text{H}_3\text{O}^+}^2)$$

pH of water in the atmosphere in equilibrium with CO_2 ($p_{\text{CO}_2} = 36 \text{ Pa}$):

$$(1) \quad \text{in (2):} \quad c_{\text{HCO}_3^-} \cdot c_{\text{H}_3\text{O}^+} = K_{A1} K_H p_{\text{CO}_2}$$

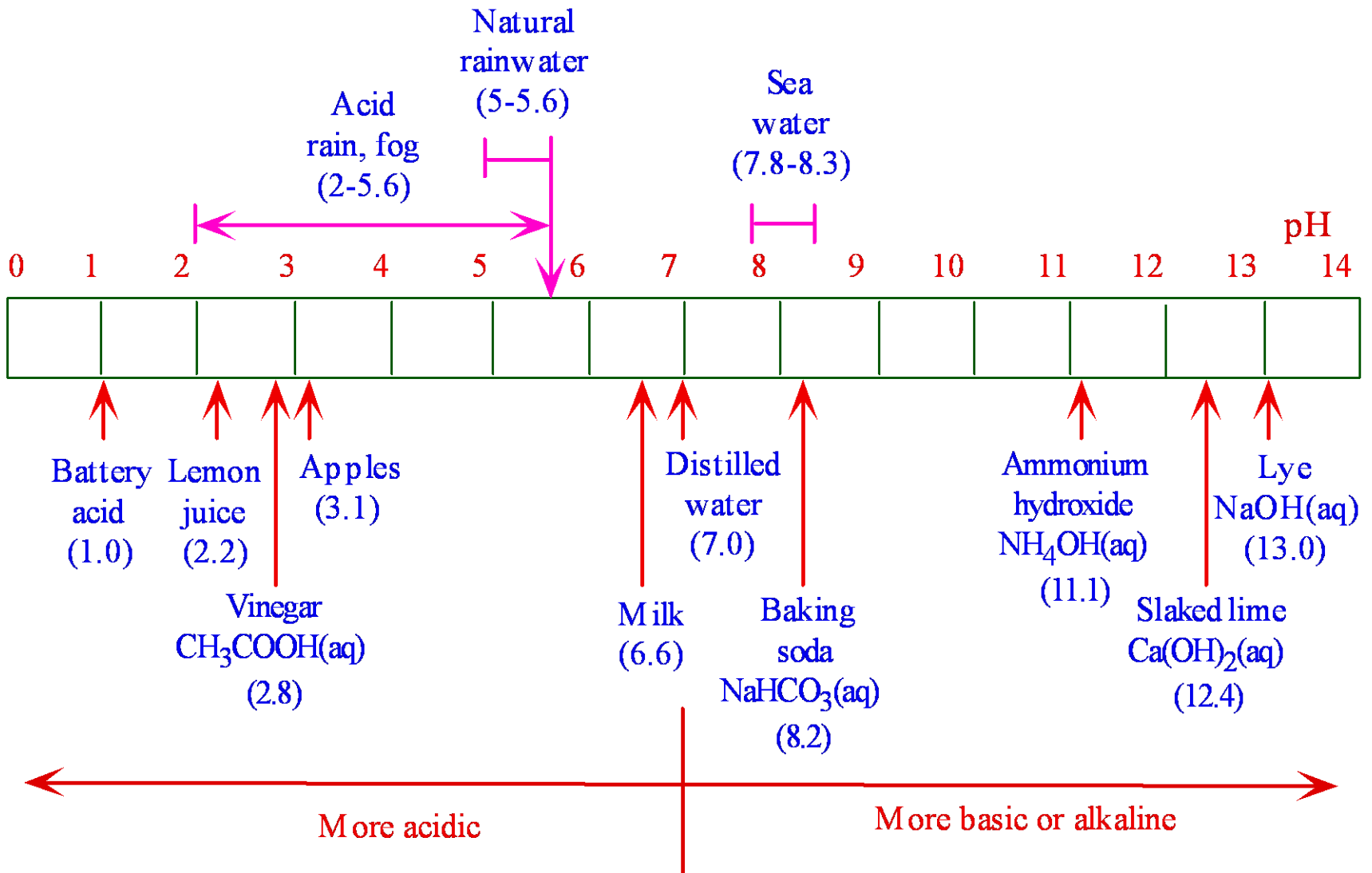
$$c_{\text{HCO}_3^-} = c_{\text{H}_3\text{O}^+}$$

$$c_{\text{H}_3\text{O}^+} = (K_{A1} K_H p_{\text{CO}_2})^{0.5}$$

$$\text{pH} = -0.5 (-\text{p}K_{A1} - \log K_H - \log p_{\text{CO}_2})$$

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

pH scale



Courtesy: Jacobson

Nitrogen compounds in the aqueous phase

Acidity formation in the troposphere: N



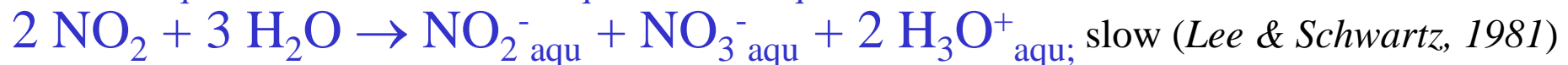
fast: $9.2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
(Mollner et al., 2010)



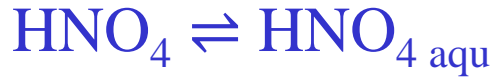
phase equilibria of N(-III), N(IV), N(V) species:



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



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



$$K^{\text{H}} = 50 \text{ M at}^{-1}$$

$$K^{\text{H}} = 1.4 \times 10^6 \text{ M at}^{-1}$$

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



$$K_{\text{A}} = 0.6 \times 10^{-5} \text{ M}$$



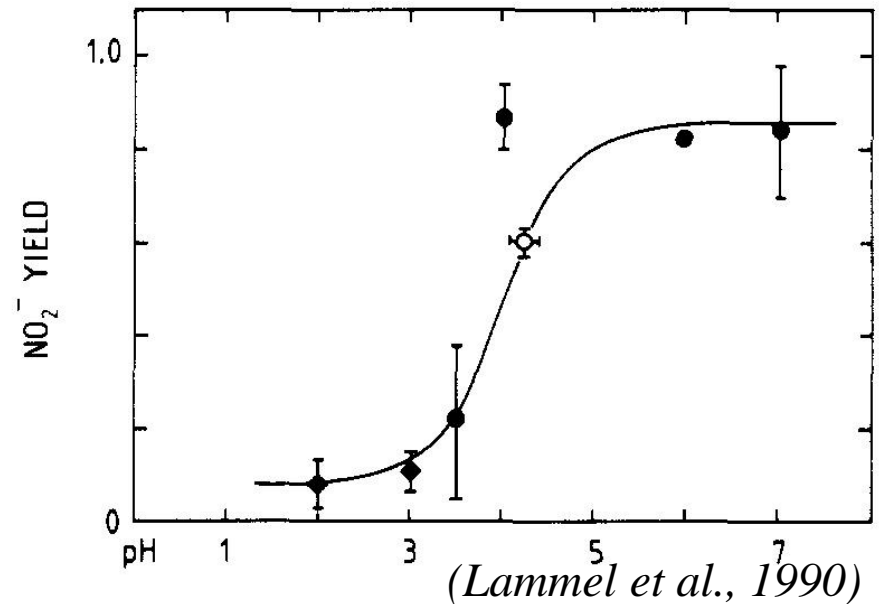
$$K_{\text{A}} = 1.0 \times 10^{-5} \text{ M}$$



$$K_{\text{A}} = 4.6 \times 10^{-10} \text{ M}$$



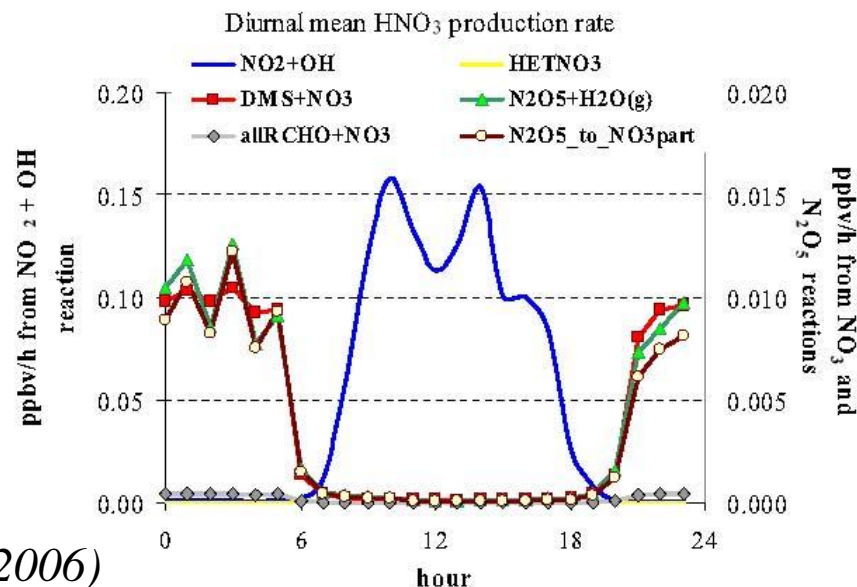
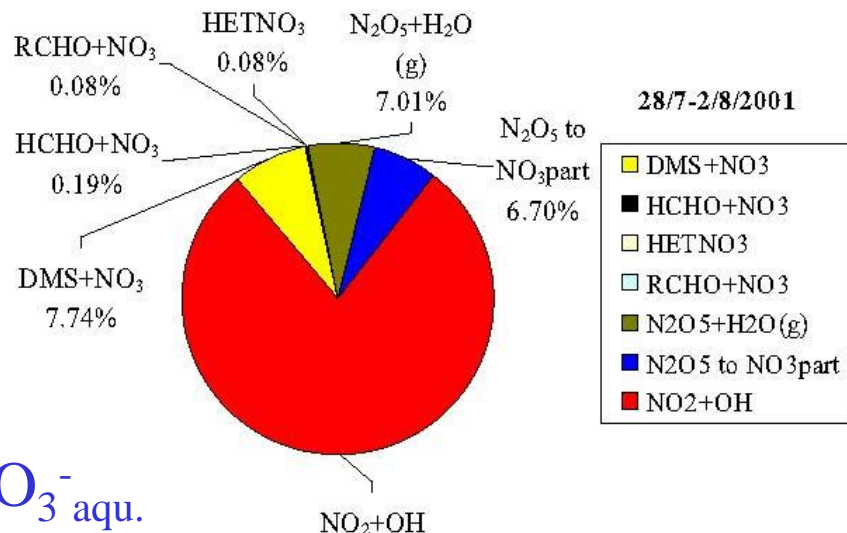
$$k = 1.4 \times 10^{-2} \text{ s}^{-1}$$



HNO₃ production: sources



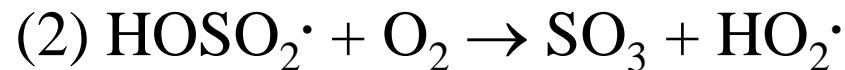
(2b) dissolution + hydration:



Acids: formation reactions and cloud chemistry

Sulfuric acid formation in the gas-phase

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

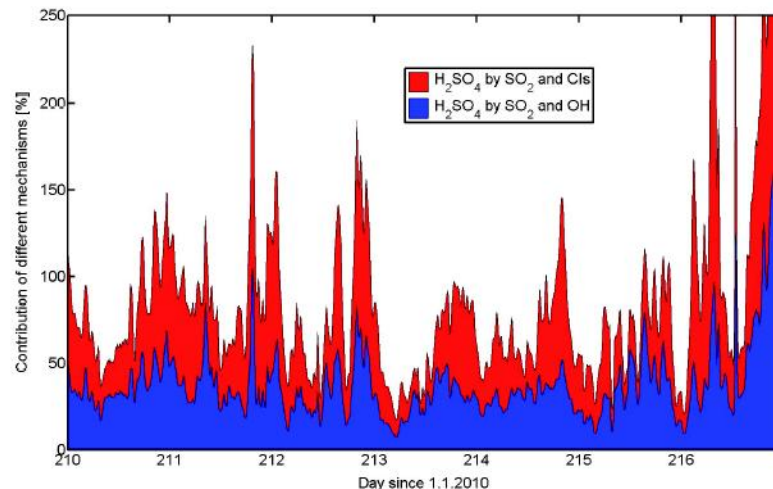
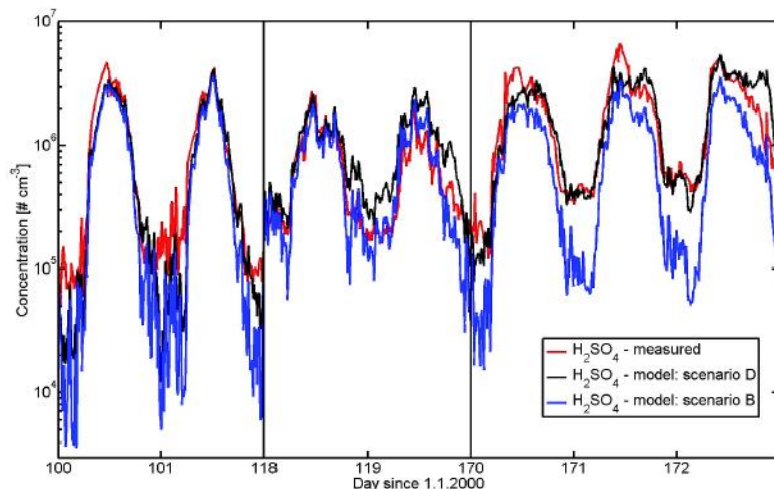
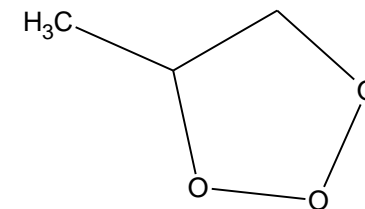
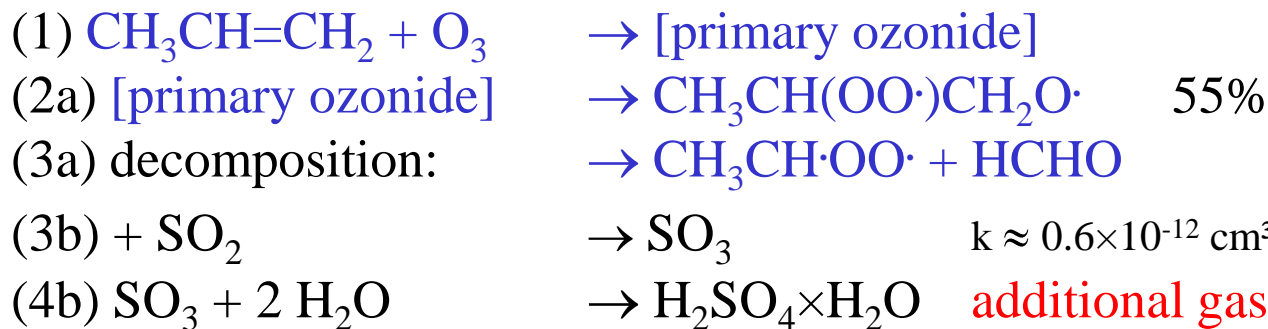


net:



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

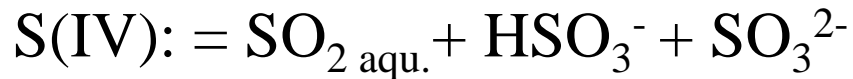
Alkenes react readily with ozone: $k \leq 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$



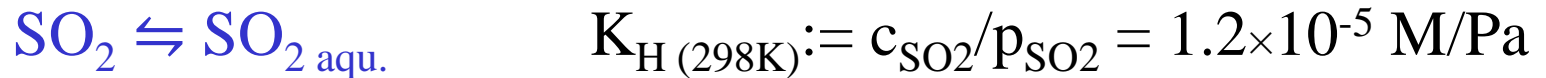
Chemical mechanism modified, Hohenpeissenberg data set; Boy et al., 2012

**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*



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



Dissociation equilibria:

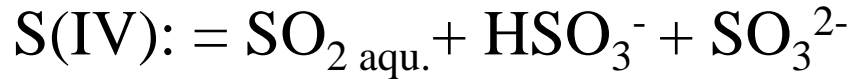


For substances which interact with water to form ions via acid-base dissociation equilibria K_H must be replaced by a modified coefficient K_H^* :

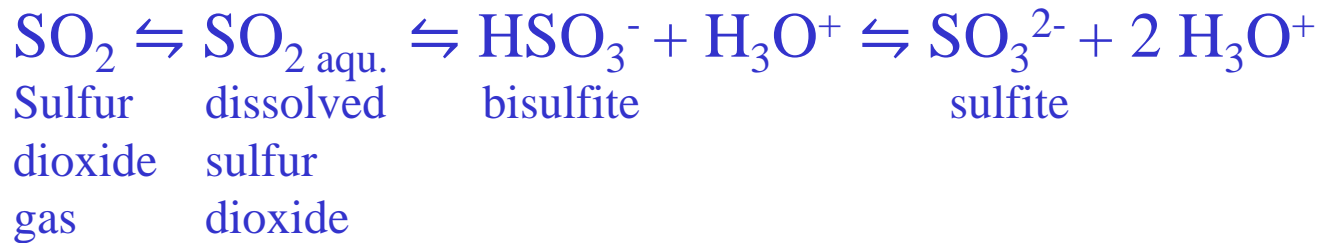
(,modified Henry coeff.):

$$K_{\text{H (298K)}}^* := c_{\text{S(IV)}} / p_{\text{SO}_2} = K_H (1 + K_{\text{A1}} / c_{\text{H}_3\text{O}^+} + K_{\text{A1}} K_{\text{A2}} / c_{\text{H}_3\text{O}^+}^2) = f(\text{pH})$$

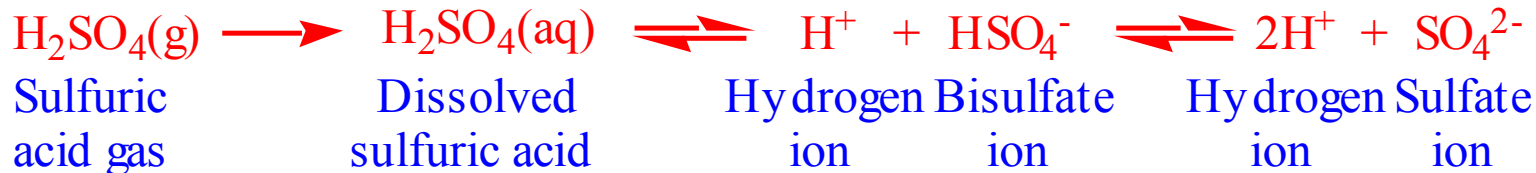
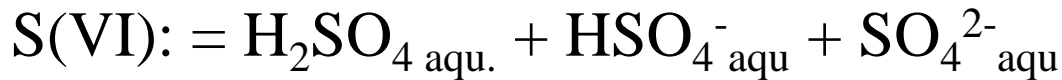
... and S(VI) phase equilibrium and dissociation



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



similarly:



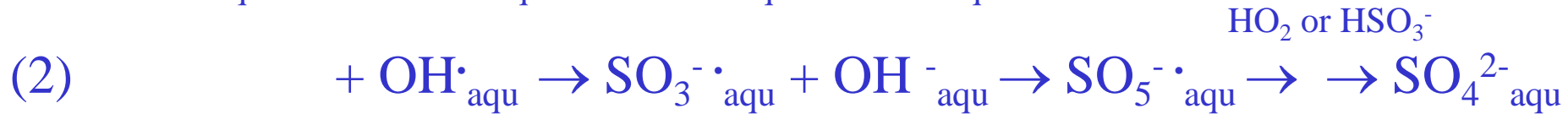
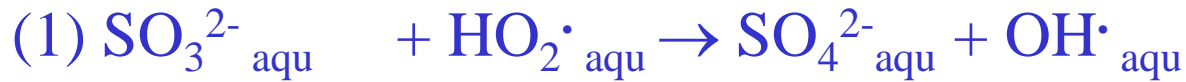
Acid-base dissociation equilibrium

Reaction	$K_{298}/\text{mol dm}^{-3}$	K_{285}
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	1.0×10^{-14}	3.6×10^{-15}
$\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$	1.6×10^{-5}	1.7×10^{-5}
$\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$	1.8×10^{-4}	1.8×10^{-4}
$\text{CO}_{2a} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	4.3×10^{-7}	3.6×10^{-7}
$\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	6.1×10^{-4}	4.6×10^{-4}
$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	1.5×10^1	1.5×10^1
$\text{HOONO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_4^-$	—	1.0×10^{-5}
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{NH}_4^+$	1.8×10^{-5}	1.7×10^{-5}
$\text{SO}_{2a} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	1.7×10^{-2}	2.2×10^{-2}
$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	6.5×10^{-8}	7.7×10^{-8}
$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	1.0×10^{-2}	1.5×10^{-2}

(Warneck, 1999)

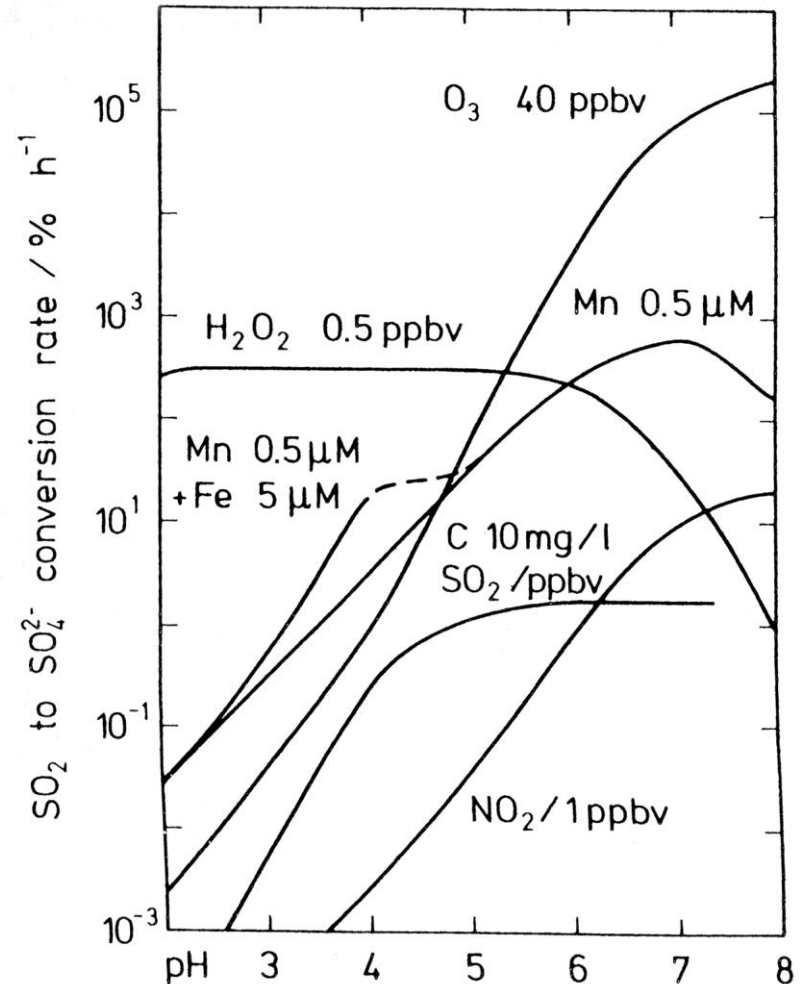
Dissociated / undissociated species exist in ratios determined by acidity (pH) and the dissociation constant, K_A . E.g. $\text{SO}_{2\text{ aqu.}}$ for $\text{pH} < -\log K_{A1} = 1.7$, SO_3^{2-} for $\text{pH} > -\log K_{A2} = 7.1$ and HSO_3^- in between.

S(IV) oxidation reactions



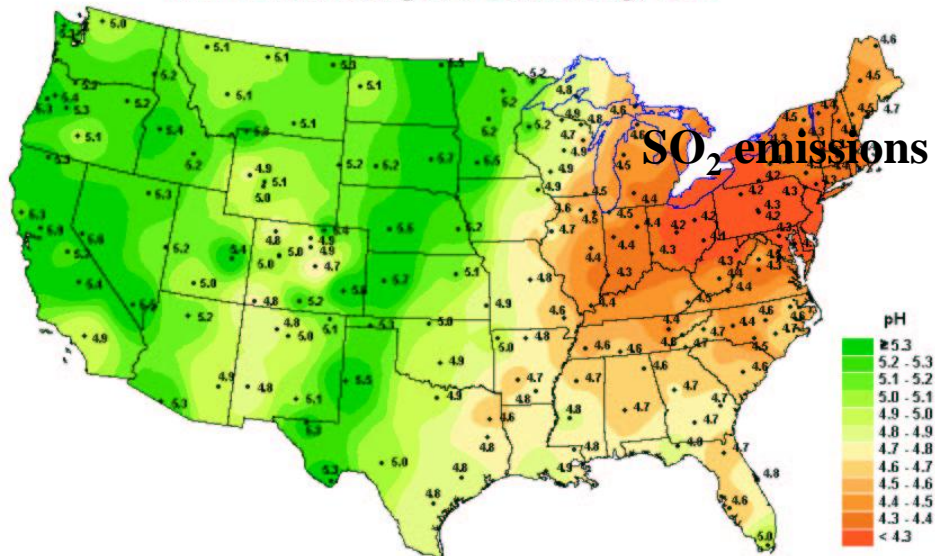
Acidity formation in the troposphere: sulfuric acid

Oxidations are pH dependent, because in individual steps of the reactions of $\text{SO}_{2\text{ aqu}}$, $\text{HSO}_3^-_{\text{ aqu}}$ and $\text{SO}_3^{2-}_{\text{ aqu}}$ (which are present in pH-dependent fractions according to K_{S1} , K_{S2}) is $\text{H}^+_{\text{ aqu}}$ consumed or formed.



for $L = V_{\text{H}_2\text{O}(l)}/V = 3 \times 10^{-6}$ (Seinfeld, Calvert)

pH Rain water pH nach Messungen
laboratory, 1994



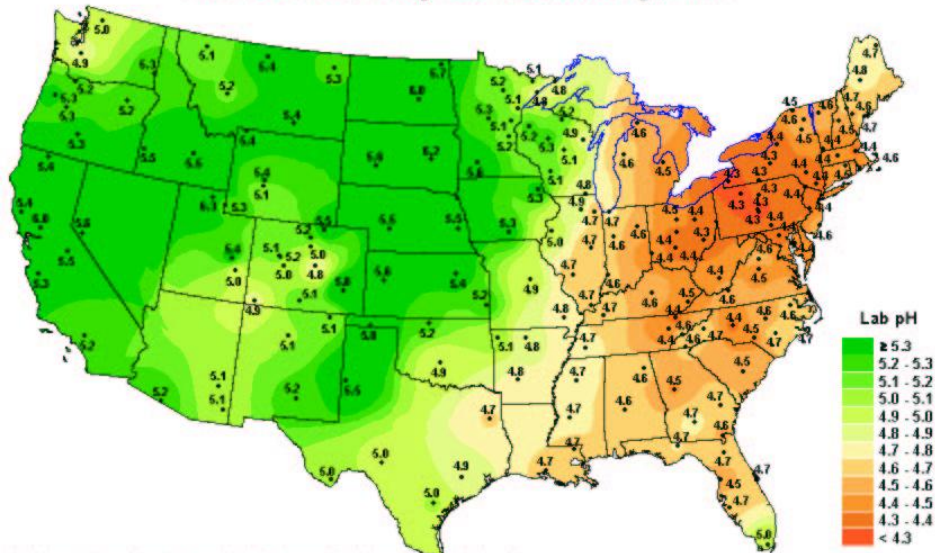
National Atmospheric Deposition Program/National Trends Network
<http://nadp.sws.uiuc.edu>

Tropospheric trace substances trends: pH, SO₂

Acidity of precipitation and SO₂ emissions

- discovery of acid rain 1852 (Smith)
- discovery of acidification of freshwater, Norway 1920
- effects on fishes, 1970

pH-Wert von Regenwasser nach Messungen
des Central Analytical Laboratory, 2000



National Atmospheric Deposition Program/National Trends Network
<http://nadp.sws.uiuc.edu>

Sulfuric acid: precursors other than anthropogenic SO₂

Aerosol constituents

McDonald Beach

[nmol/m³]

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, CH₃SCH₃
- MSA = methanesulfonate, CH₃SO₃⁻

Dimethylsulfide

Formation of carbonyl sulfide

(Gas-phase chemistry)

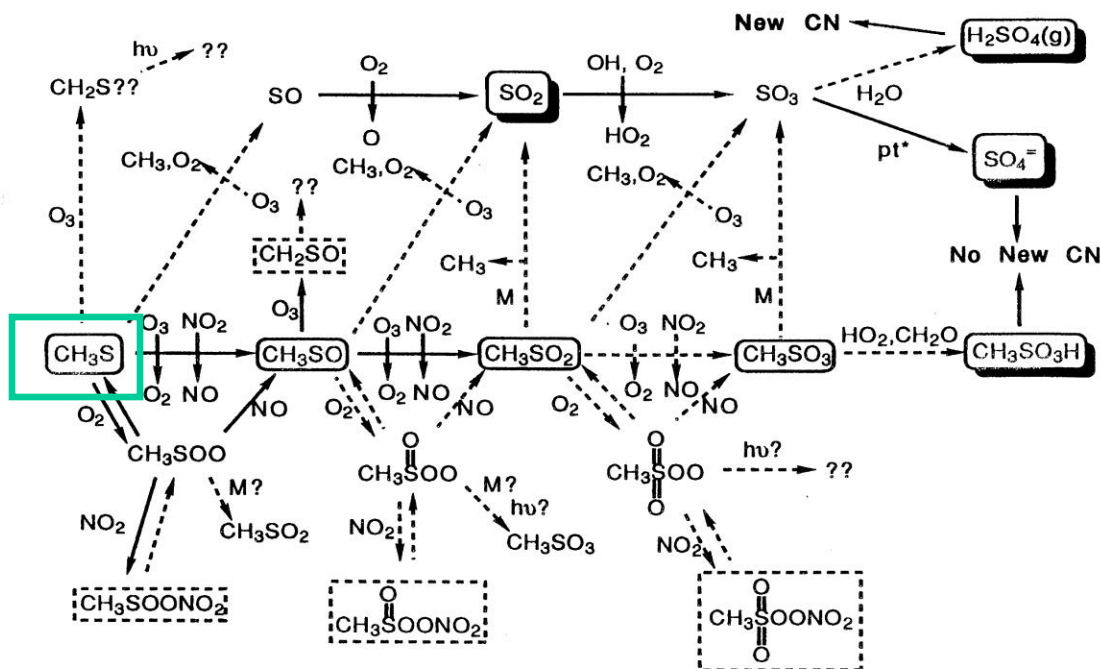
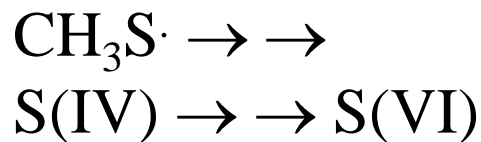
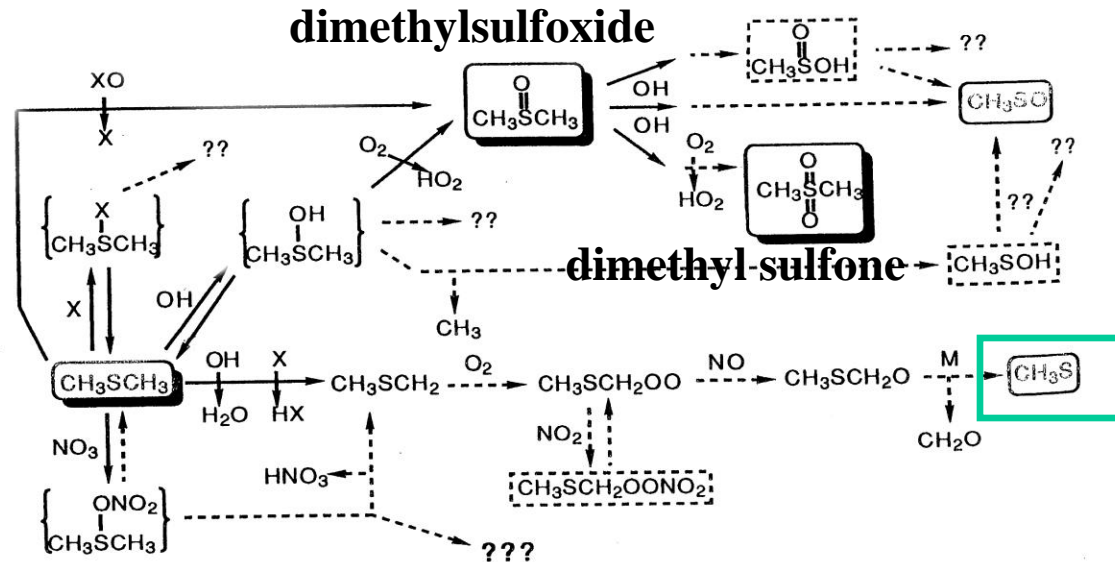
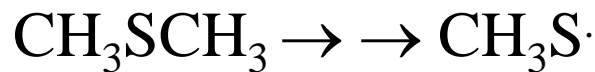


major

minor

Formation of SO₂

in the marine boundary layer:



Hypothetical negative feedback mechanism in the marine boundary layer:

CH_3SCH_3 emission

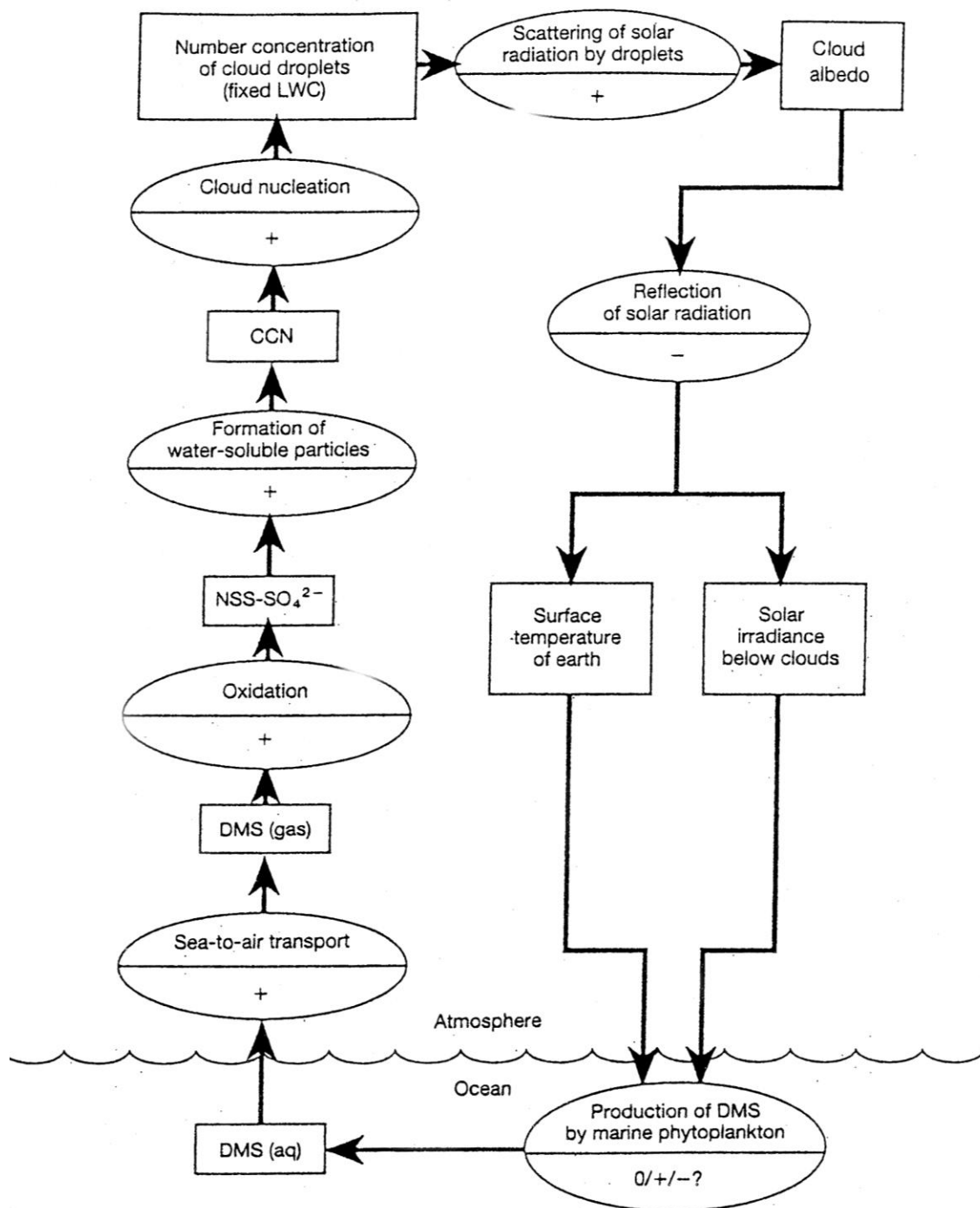
→ more clouds

→ 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: $c_{\text{SO}_2} = 2 \text{ nmol m}^{-3}$, $c_{\text{H}_2\text{O}_2} = 40 \text{ nmol m}^{-3}$, $T = 298 \text{ K}$
(near Bermuda 1988)

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

2. Aqueous phase ($L = 3 \times 10^{-8}$, $\text{pH} = 7$):

$$\begin{aligned} dc_{\text{SO}_4^{2-}}/dt &= k_4 p_{\text{H}_2\text{O}_2} K_{\text{H H}_2\text{O}_2} p_{\text{SO}_2} K_{\text{H SO}_2}^* (\text{M s}^{-1}) \\ &= (4 \times 10^7 \times 10^{-7}) \times 40 \times 10^{-9} \times 1 \times 10^5 \times 2 \times 10^{-9} \times 3.4 \times 10^5 \end{aligned}$$

$$\begin{aligned} K_{\text{H SO}_2}^* &= K_{\text{H SO}_2} \times (1 + K_{\text{A1}} / c_{\text{H}^+} + K_{\text{A1}} K_{\text{A2}} / c_{\text{H}^+}^2) = \\ &= 3.4 \times 10^5 \text{ M/atm} \end{aligned}$$

$$\begin{aligned} dc_{\text{S(VI)}}/dt &= dc_{\text{S(VI)}}/dt (\text{M s}^{-1}) \times L (\text{L m}^{-3}) \times 10^9 (\text{nmol mol}^{-1}) = \\ &= 32 \times 10^{-6} \text{ nmol m}^{-3} \text{ s}^{-1} \end{aligned}$$

Reactivity of organics in the aqueous phase: Overview OH reactions

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

Reaction	$k_{23^\circ\text{C}}$	[L/mol/s] reference
$\text{CH}_3 \cdot + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \cdot$	$(4.7 \pm 0.7) \times 10^9$	Thomas [1967]
$\text{R} \cdot + \text{O}_2 \rightarrow \text{RO}_2 \cdot$	$\sim 3 \times 10^9$	Howard [1973]
$\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CH}_2(\text{OH})_2$	(9.8 ± 0.8)	Sutton and Downes [1972]
$\text{HOCH}_2\text{O}_2 \cdot \rightarrow \text{HCHO} + \text{HO}_2 \cdot$	(9.9 ± 2.5)	Downes and Sutton [1973]
$\text{OH} \cdot + \text{CH}_4 \rightarrow \text{CH}_3 \cdot + \text{H}_2\text{O}$	$(1.2 \pm 0.4) \times 10^8$	FR
$\text{OH} \cdot + \text{HCHO} \rightarrow \text{CHO} \cdot + \text{H}_2\text{O}$	$(6.9 \pm 1.7) \times 10^8$	FR
$\text{OH} \cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} \cdot + \text{H}_2\text{O}$	$(9.4 \pm 2.3) \times 10^8$	FR
$\text{OH} \cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{HOCH}_2\text{CH}_2 \cdot$	$(4.8 \pm 1.2) \times 10^9$	FR
$\text{OH} \cdot + \text{CH}_3\text{CHO} \rightarrow \text{products}$	$(5.0 \pm 1.2) \times 10^8$	FR
$\text{OH} \cdot + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH} \cdot + \text{H}_2\text{O}$	$(1.8 \pm 0.5) \times 10^9$	FR
$\text{OH} \cdot + \text{CH}_3\text{C}(\text{O})\text{CH}_3 \rightarrow \text{products}$	$(9.7 \pm 2.4) \times 10^7$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{C}_6\text{H}_5\text{C}^\bullet\text{HO}$	$(7.0 \pm 1.8) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{O}^\bullet + \text{H}_2\text{O}$	$(3.0 \pm 0.8) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{CH}_2\text{OH} \rightarrow \text{products}$	$(2.0 \pm 0.5) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{CH}=\text{CH}_2 \rightarrow \text{products}$	$(7.7 \pm 1.9) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2 \rightarrow \text{products}$	$(7.7 \pm 1.9) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_3 \rightarrow \text{products}$	$(3.8 \pm 1.0) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_5 \rightarrow \text{products}$	$(9.0 \pm 2.2) \times 10^8$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{OH} \rightarrow \text{products}$	$(4.6 \pm 1.2) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_3(\text{OH})_2 \rightarrow \text{products}$	$(5.5 \pm 1.4) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_2(\text{OH})_3 \rightarrow \text{H}_2\text{O}$	$(3.0 \pm 0.8) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{OH} \rightarrow \text{products}$	$(5.9 \pm 1.5) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_3(\text{OH})_2\text{CH}_2\text{OH} \rightarrow \text{products}$	$(4.6 \pm 1.2) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CH}=\text{CH}_2 \rightarrow \text{H}_2\text{O}$	$(8.8 \pm 2.2) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_3(\text{OH})_2\text{CH}=\text{CH}_2 \rightarrow \text{H}_2\text{O}$	$(5.1 \pm 1.2) \times 10^9$	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

$\text{OH} \cdot + \text{C}_6\text{H}_6 \rightarrow \text{products}$	$(7.0 \pm 1.8) \times 10^9$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{products}$	$(1.1 \pm 0.3) \times 10^{10}$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_4(\text{OH})_2 \rightarrow \text{products}$	$(1.2 \pm 0.2) \times 10^{10}$	FR
$\text{OH} \cdot + \text{C}_6\text{H}_5\text{N} \rightarrow \text{products}$	$(4.4 \pm 0.5) \times 10^9$	Steenken and O'Neill [1979]
$\text{OH} \cdot + \text{C}_6\text{H}_4\text{N} \rightarrow \text{products}$	$(3.6 \pm 0.9) \times 10^9$	Steenken and O'Neill [1979]

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

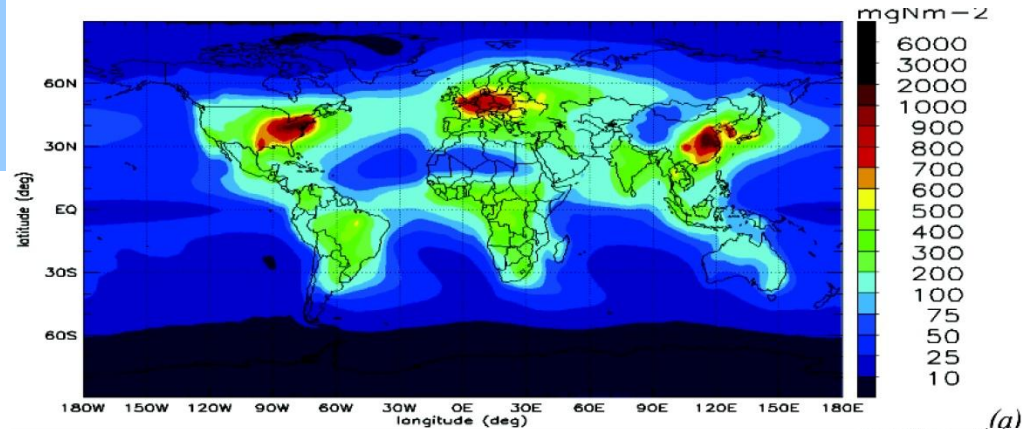
Less selectivity than in
the gas-phase

(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)

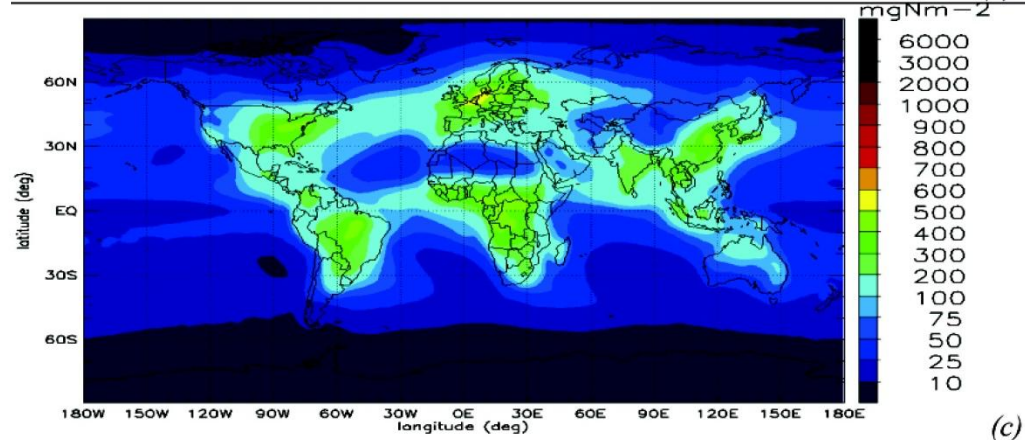


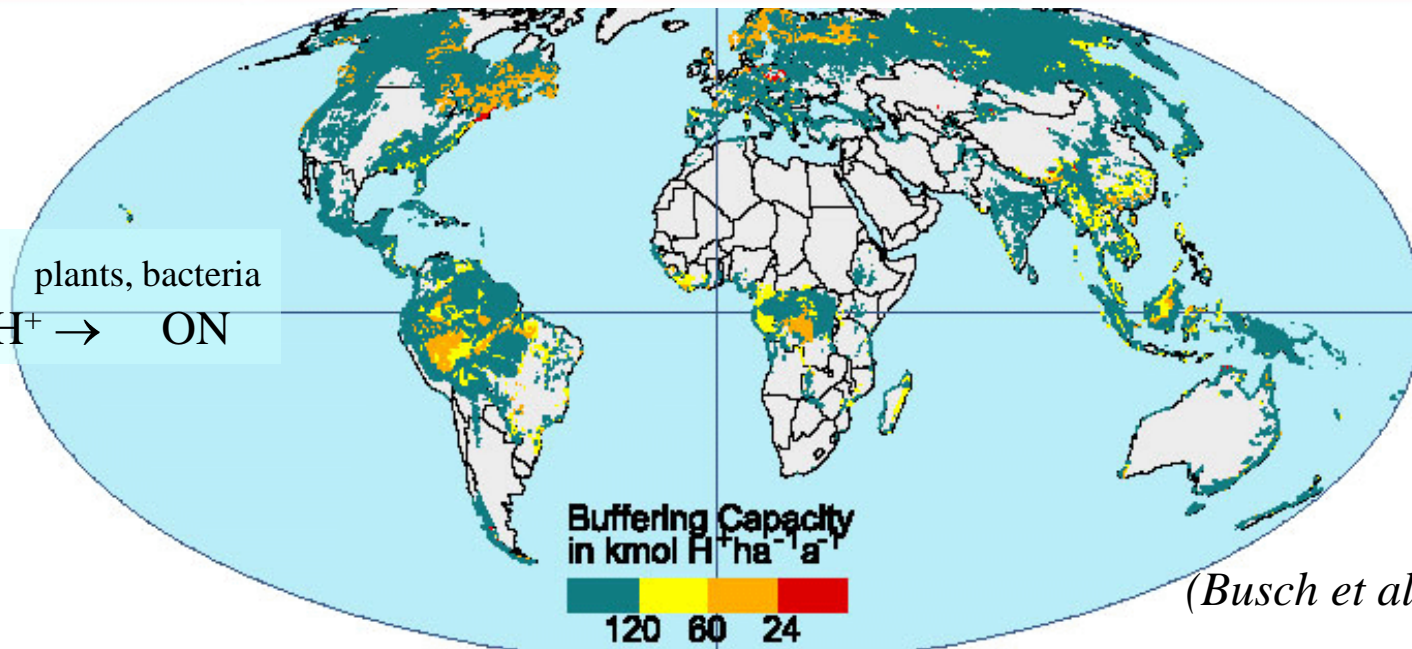
TABLE 1. Overview of Simulations, Prescribed Methane Volume Mixing Ratios, and Global Anthropogenic Emissions of CO, NMVOC, NO_x , SO_2 , and NH_3 ^a

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

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] ₂ SO ₄ /NH ₄ NO ₃	+2 / 0
NH ₄ ⁺	+1	H ₂ SO ₄ /HNO ₃	+2 / +0
NO ₃ ⁻	-1	H ₂ SO ₄ /NH ₄ NO ₃	+2 / 0
SO ₄ ²⁻	0	NH ₄ HSO ₄ /HNO ₃	+2 / +0



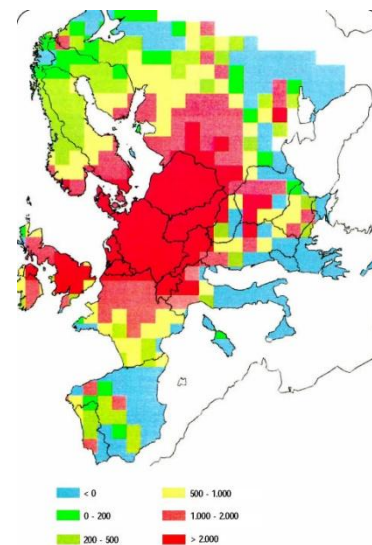
(Busch et al., 2001)

Critical loads concept to protect ecosystems

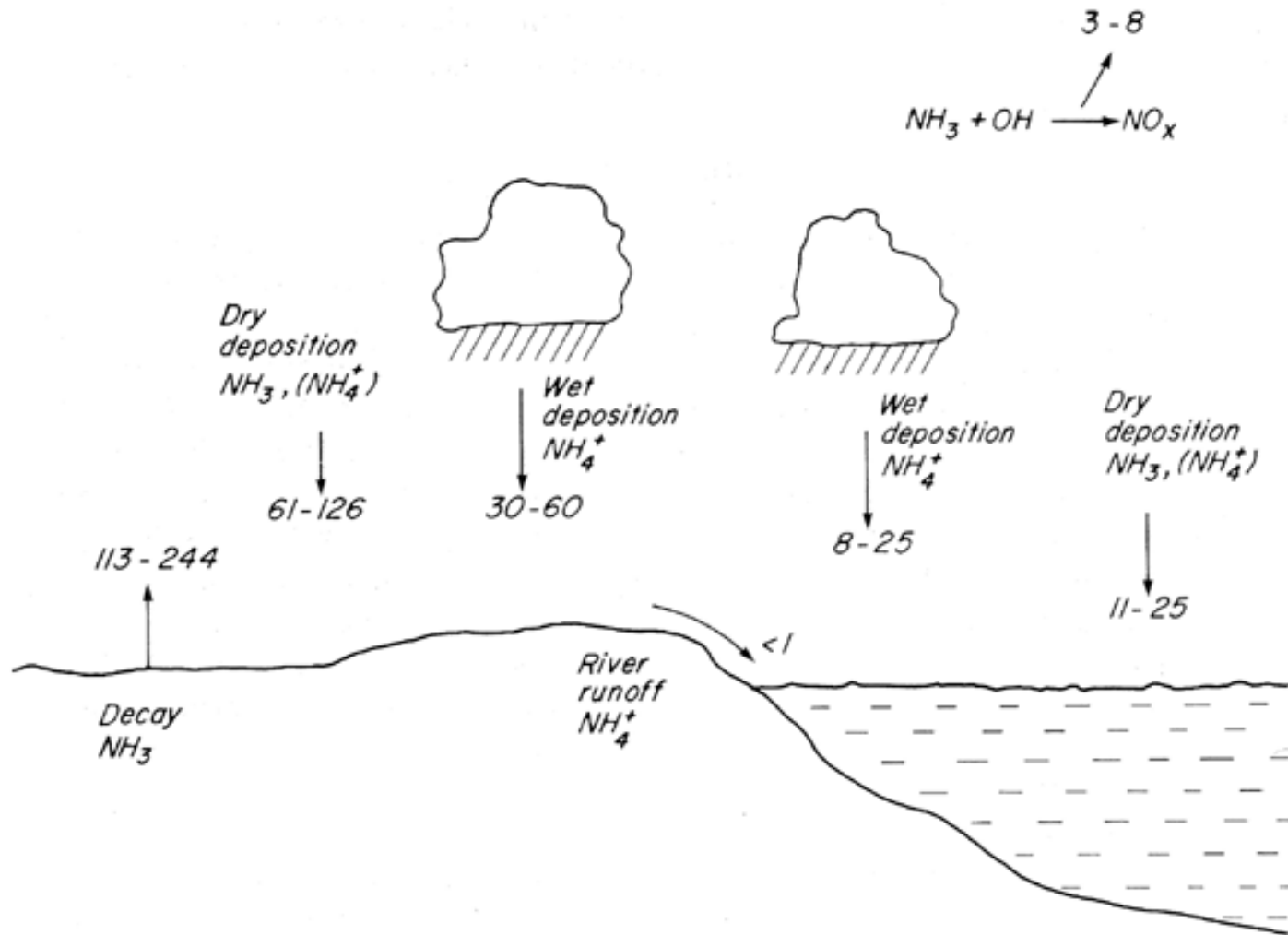
Mapping of critical loads „...below which harmful effects in ecosystem structure and function do not occur according to present knowledge“:

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*)

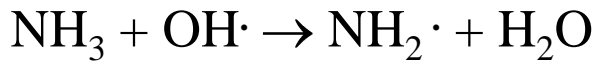


Cycling of ammonia

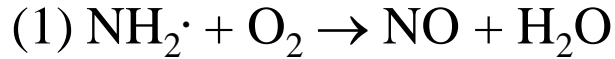


(following Manier)

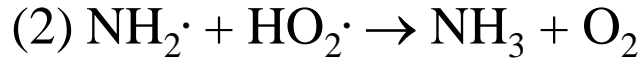
Gas-phase chemistry



$$k = 0.16 \times 10^{-12} \text{ cm}^3/\text{molec}/\text{s}$$



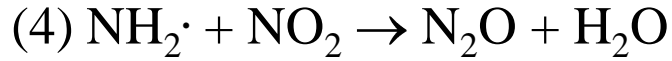
$$k_1 < 6 \times 10^{-21} \text{ cm}^3/\text{molec}/\text{s}$$



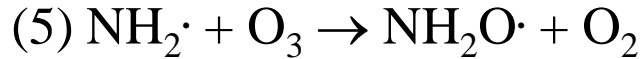
$$k_2 = 34 \times 10^{-12} \text{ cm}^3/\text{molec}/\text{s}$$



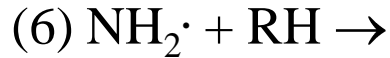
$$k_3 = 17 \times 10^{-12} \text{ cm}^3/\text{molec}/\text{s}$$



$$k_4 = 19 \times 10^{-12} \text{ cm}^3/\text{molec}/\text{s}$$



$$k_5 = 0.16 \times 10^{-12} \text{ cm}^3/\text{molec}/\text{s}$$



too slow to be of any significance

$$\begin{aligned} -dc_{\text{NH}_3}/dt &= k_{\text{OH}}^{(1)} c_{\text{NH}_3} = k_{\text{OH}}^{(2)} c_{\text{OH}} c_{\text{NH}_3}; \tau_{\text{OH}} = (k_{\text{OH}}^{(1)})^{-1} \\ &\approx 3 \text{ months for the global annual tropospheric mean } (1.16 \times 10^6 \text{ OH}/\text{cm}^3) \\ &\approx 10 \text{ days inner tropics near ground } (\approx 10^7 \text{ OH}/\text{cm}^3; \text{Spivakovsky et al., 2000}) \end{aligned}$$

$$-dc_{\text{NH}_3}/dt = k_{\text{OH}}^{(1)} c_{\text{NH}_3} + k_{\text{dep}}^{(1)} c_{\text{NH}_3}$$

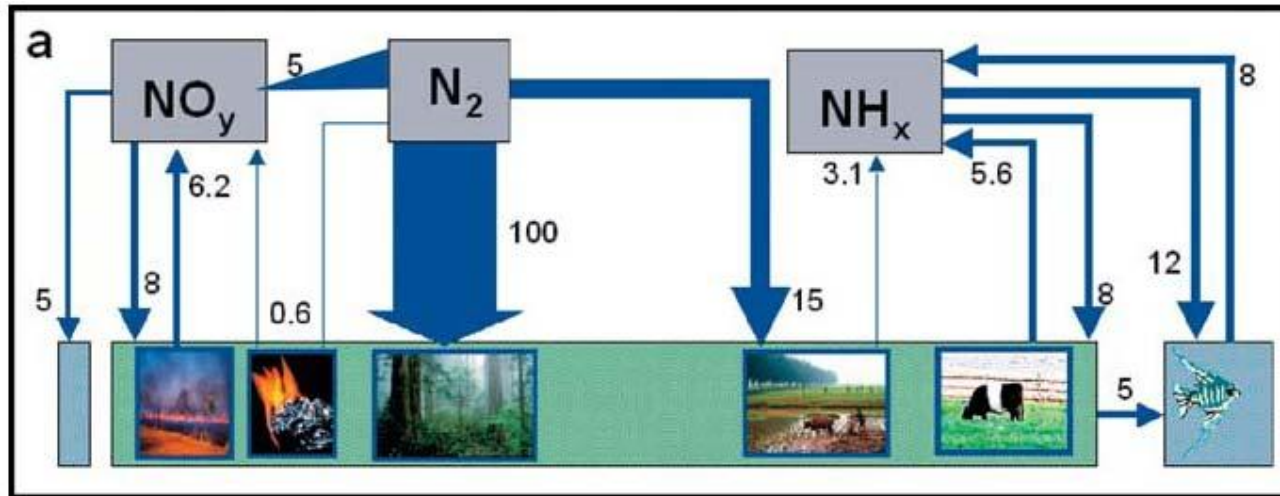
$$\tau_{\text{air}} = (k_{\text{OH}}^{(1)} + k_{\text{dep}}^{(1)})^{-1}$$

$$\text{Ammonia budget } dc_{\text{NH}_3}/dt = F_e - k_{\text{OH}}^{(1)} c_{\text{NH}_3} - k_{\text{dep}}^{(1)} c_{\text{NH}_3}$$

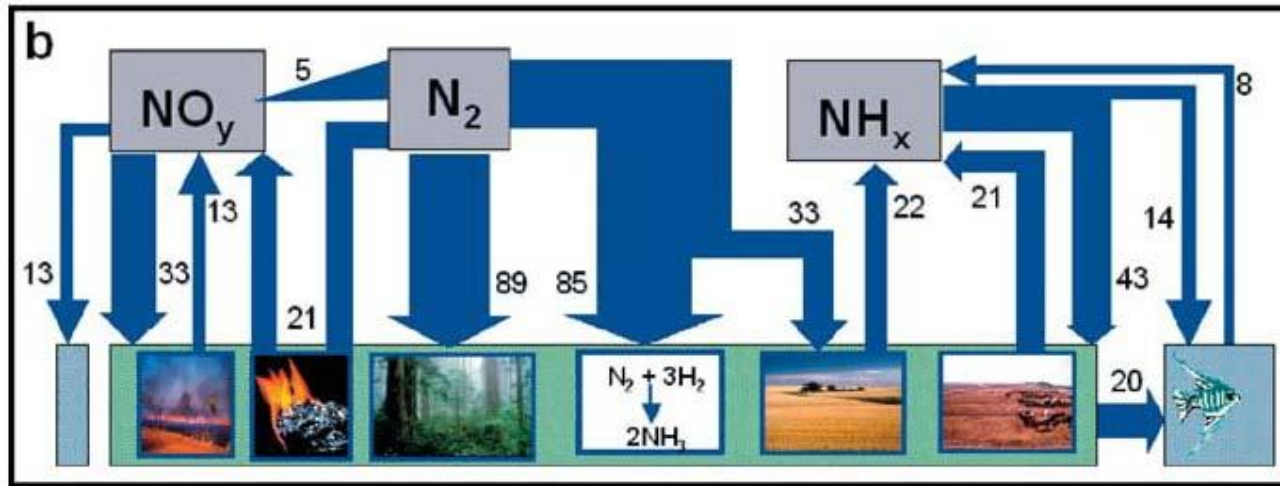
Global N cycle, fluxes (Tg/a)

+80%

1890



1990



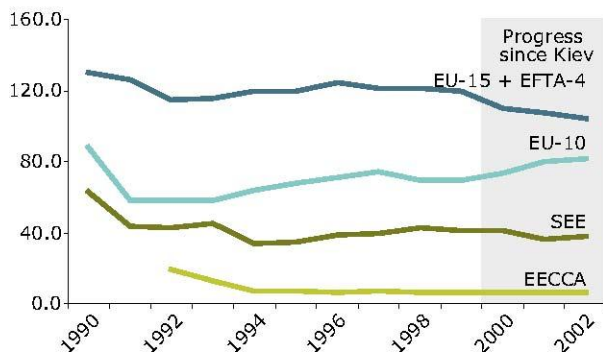
(Hibbard et al., 2006)

Ammonia trends Europe

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 %

Mean fertiliser consumption (kg/ha)



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.

Future

EU commitments

EU scenarios

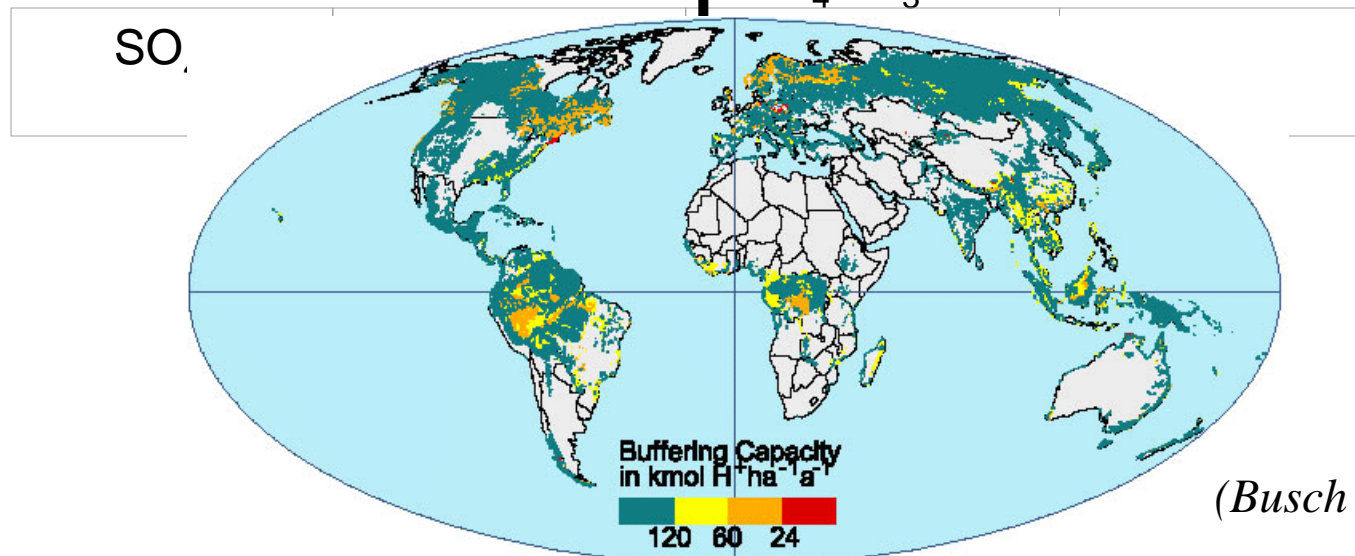
	2000	National Ceilings 2010	Climate Action 2020	Strategy on Air Poll. 2020	Base-line 2030	Climate Action 2030	Climate Action MFR 2030
NO _x	11,581	8,319	5,888	4,657	6,125	5,524	2,849
VOCs	10,654	8,150	5,915	5,251	5,863	5,877	4,101
SO ₂	8,736	6,543	2,806	1,602	2,851	2,371	1,130
			-4%	-28%	-6%		-43%

→ NO₃⁻/SO₄²⁻ and NH₄⁺/(SO₄²⁻ + NO₃⁻) are increasing in depositions

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] ₂ SO ₄ / NH ₄ NO ₃	+2 / 0
NH ₄ ⁺	+1	H ₂ SO ₄ /HNO ₃	+2 / 0
NO ₃ ⁻	-1	H ₂ SO ₄ / NH ₄ NO ₃	+2 / 0

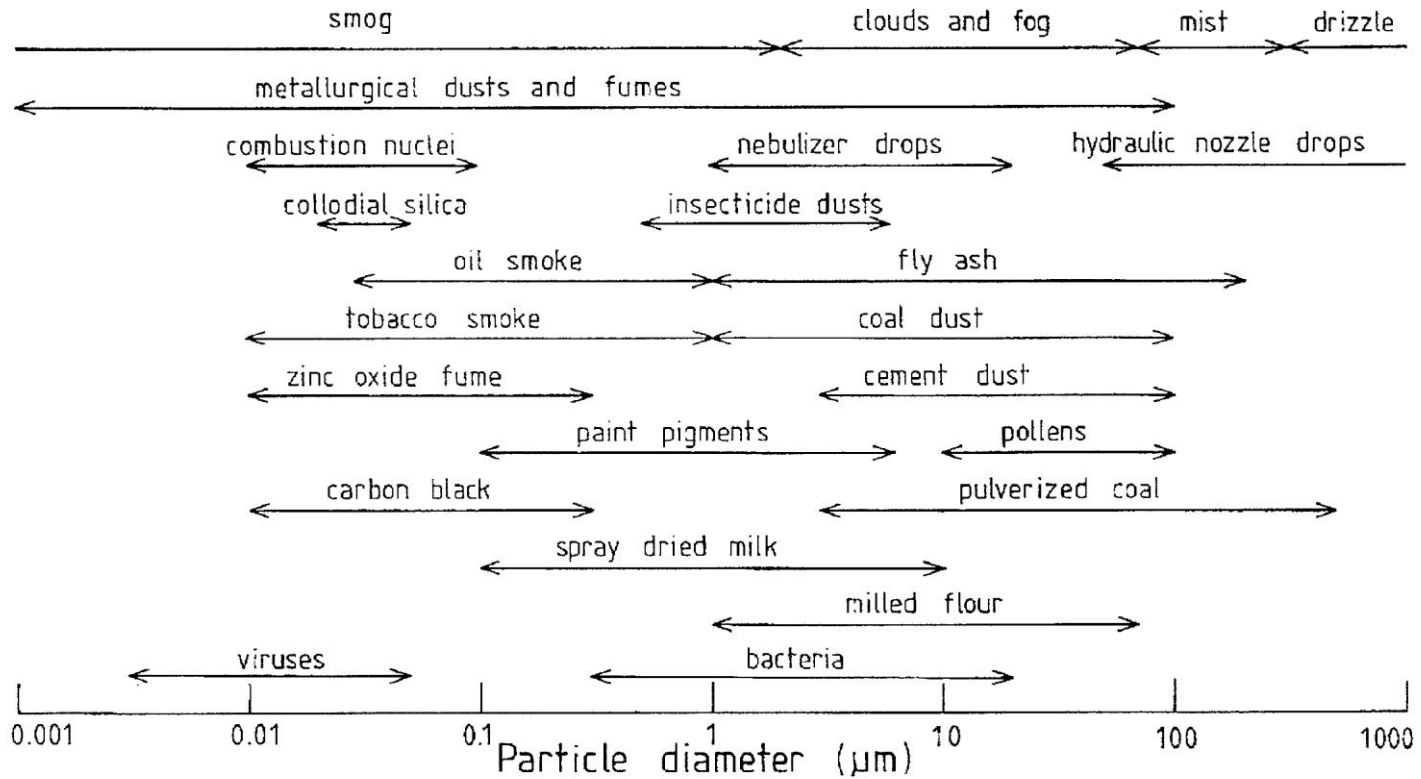


(Busch et al., 2001)

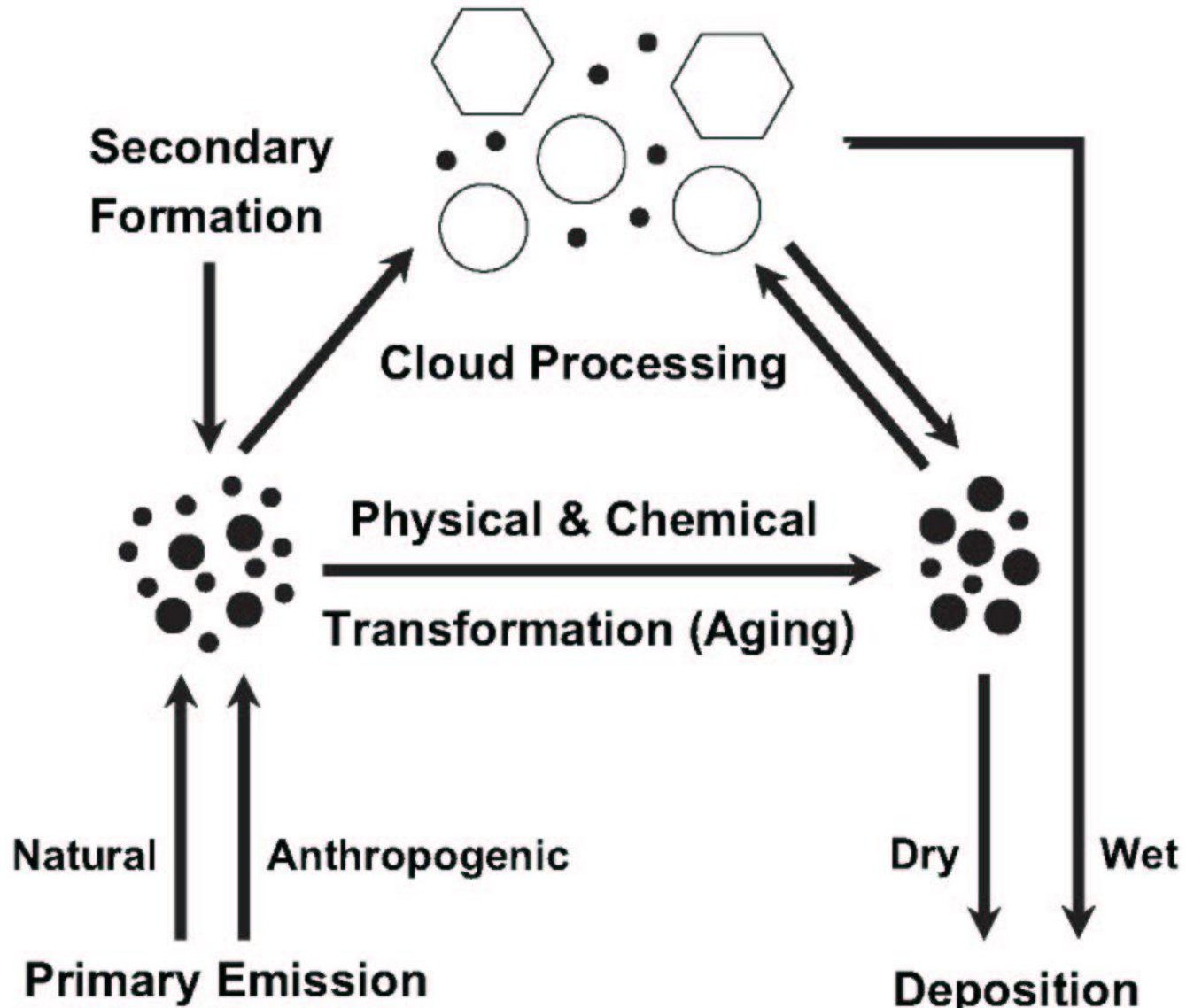
Critical loads concept to protect ecosystems

- 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

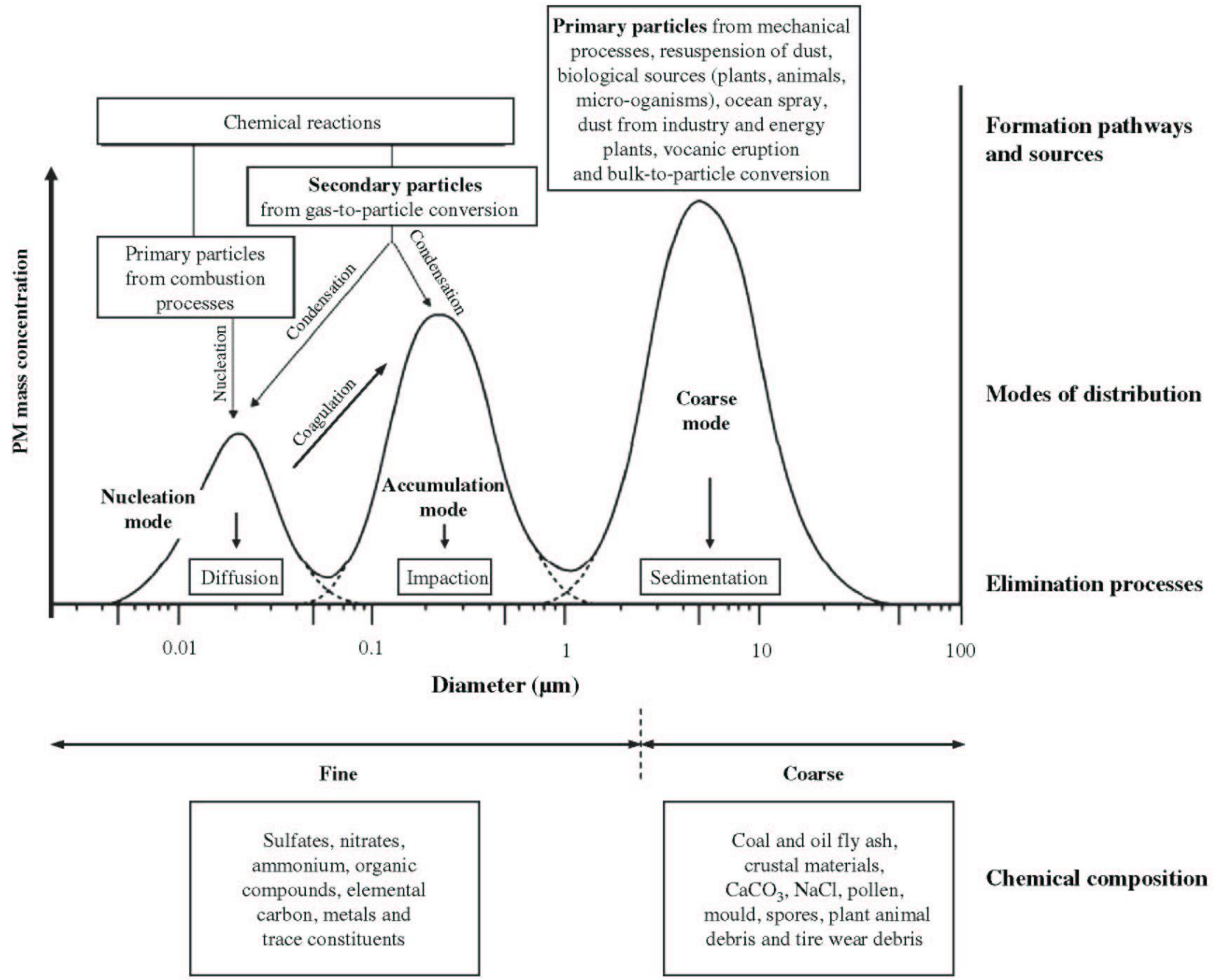
Aerosols = ?



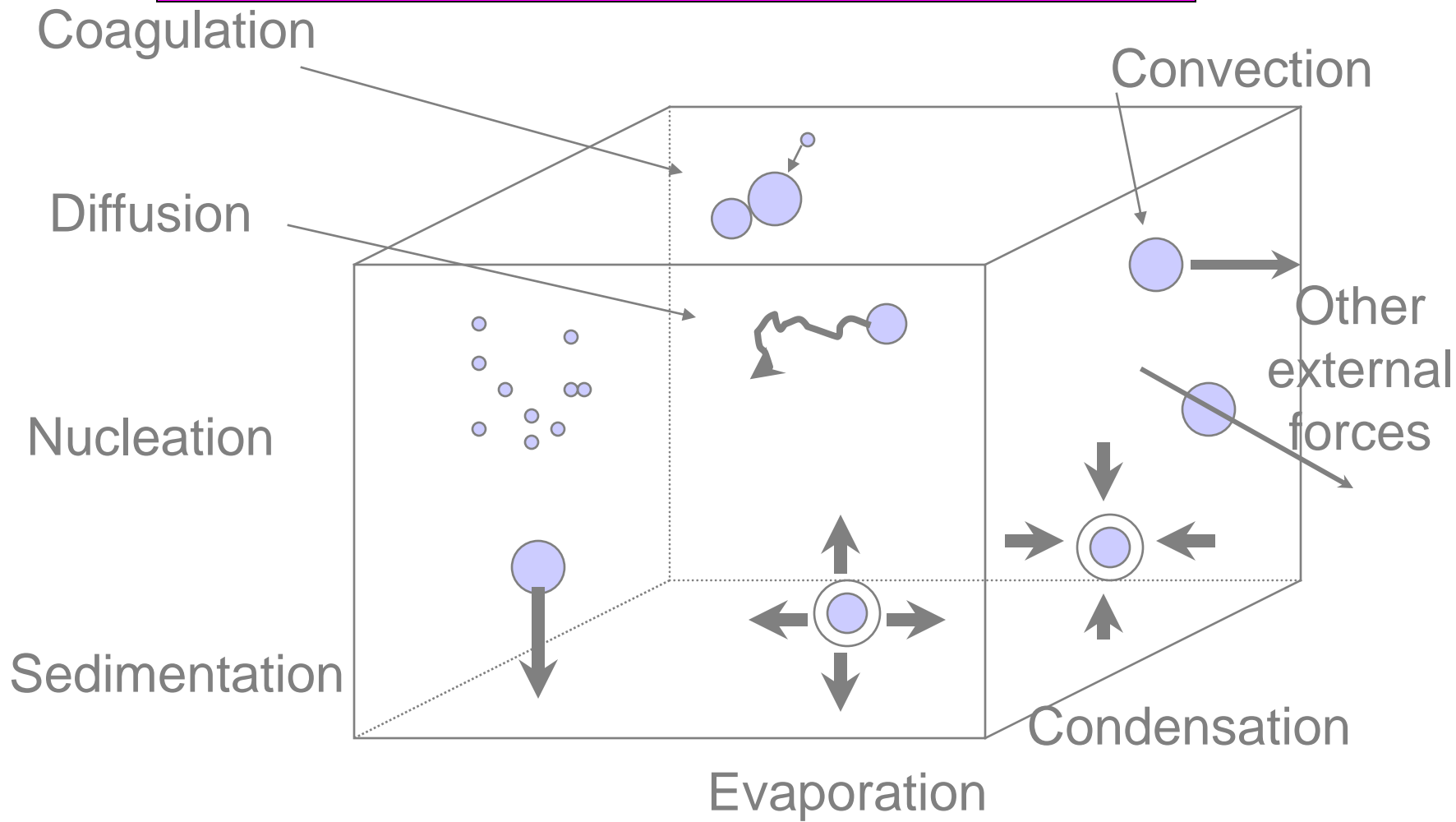
Aerosol processes



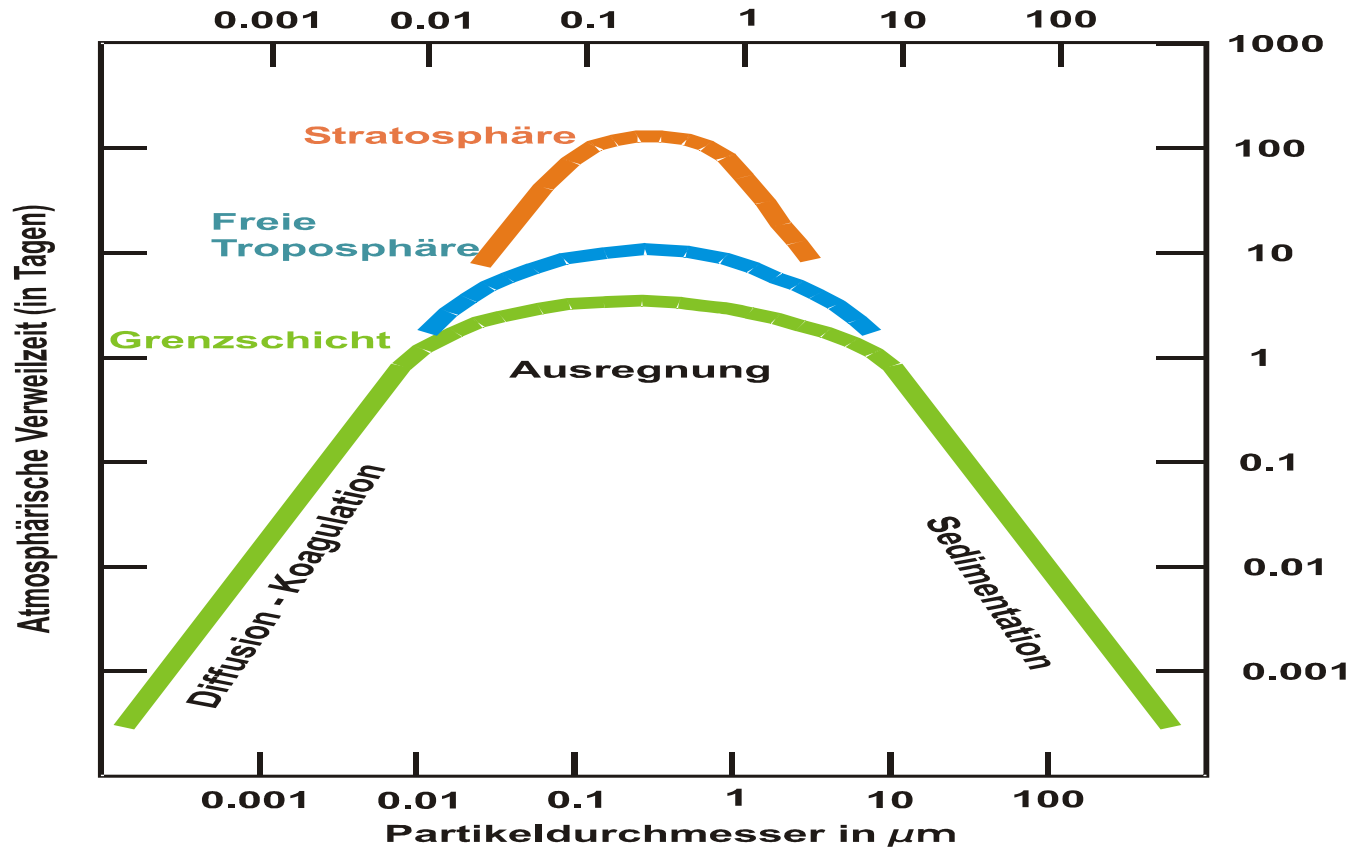
Courtesy of: Fuzzi et al., 2006



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

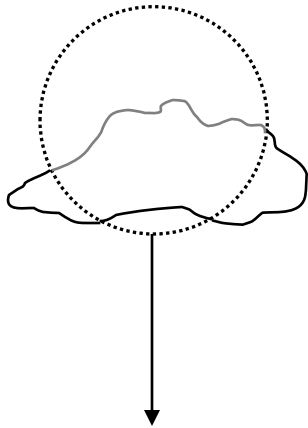
Particle size – not trivial !

Irregular particle

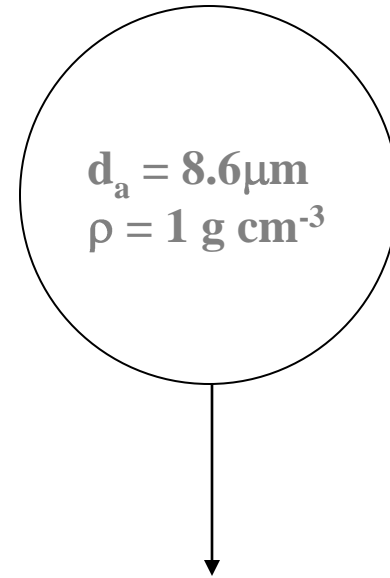
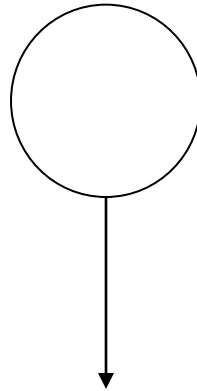
Stokes's equivalent sphere

**Aerodynamic
equivalent sphere**

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

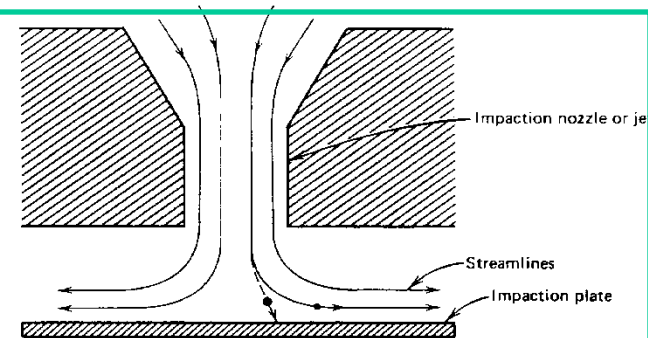


$$d_s = 4.3\mu\text{m}$$
$$\rho = 4\text{ g cm}^{-3}$$



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

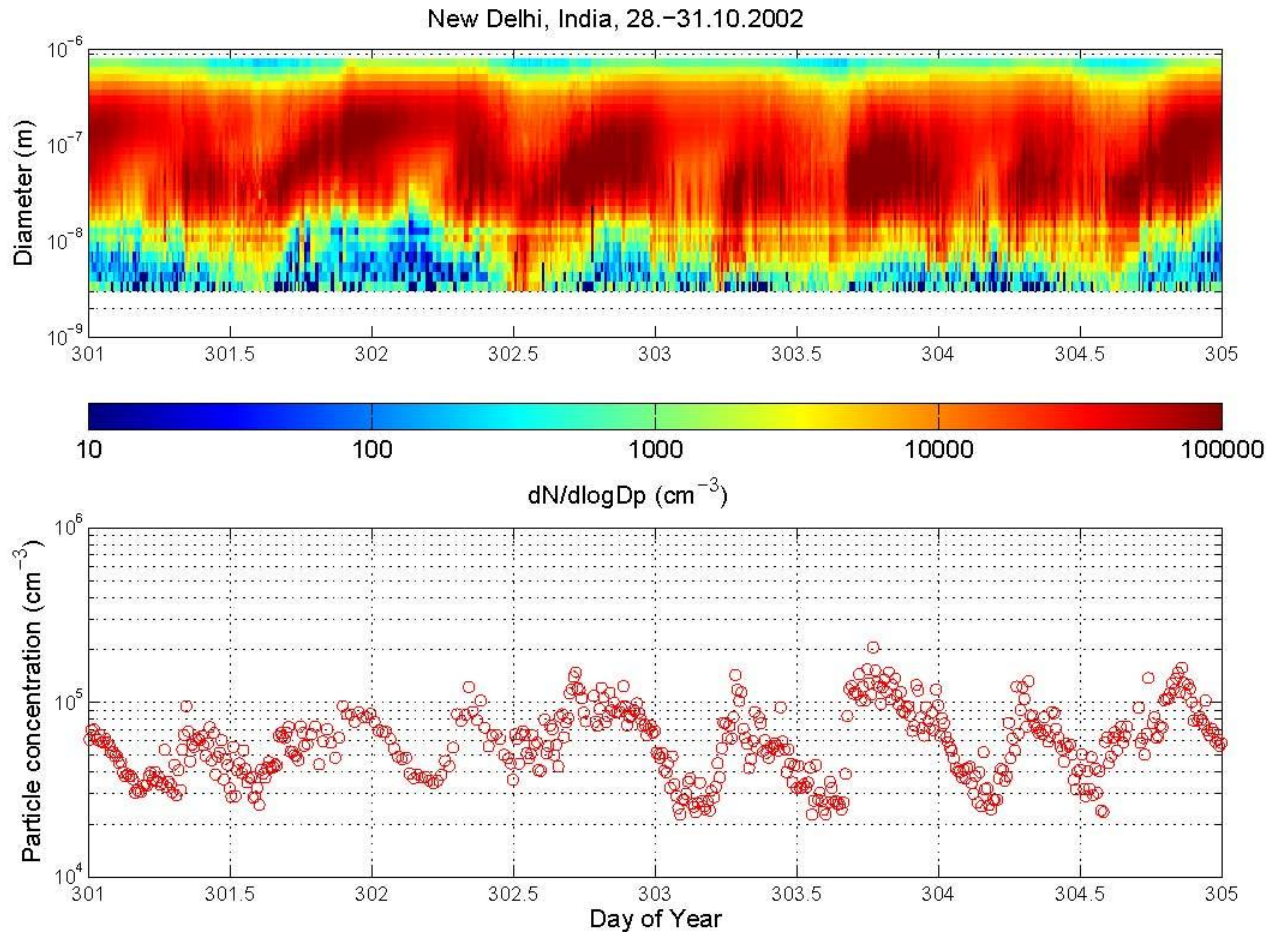


Fig. 2. Measured aerosol number size distribution **(a)** and number concentration **(b)**. The x-axis represents the time and y-axis in (a) particle diameter (m) and in (b) integrated particle concentration (cm^{-3}) for the same period. The color in the (a) represents particle concentration ($dN/d\log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

Primary particle formation (nucleation)

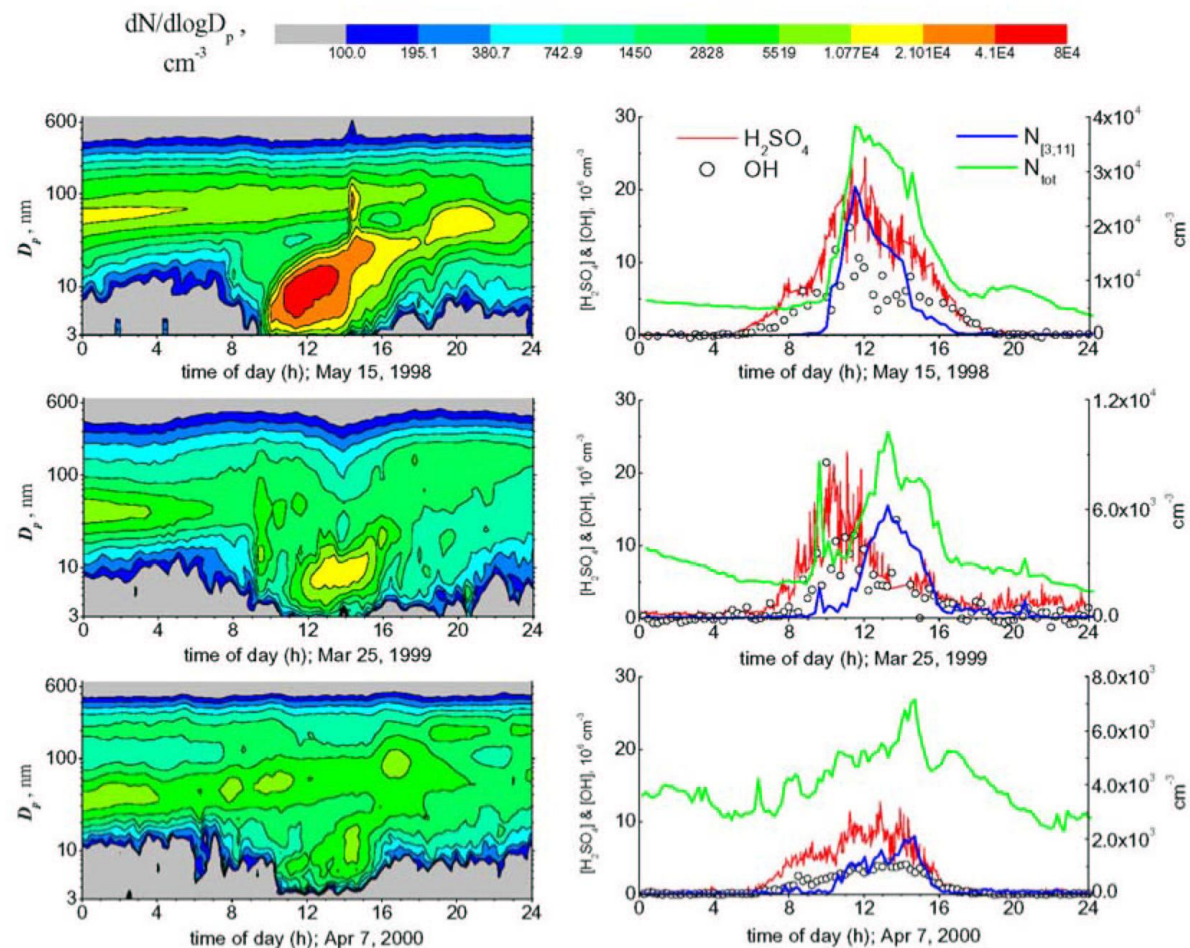
condensational growth



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:

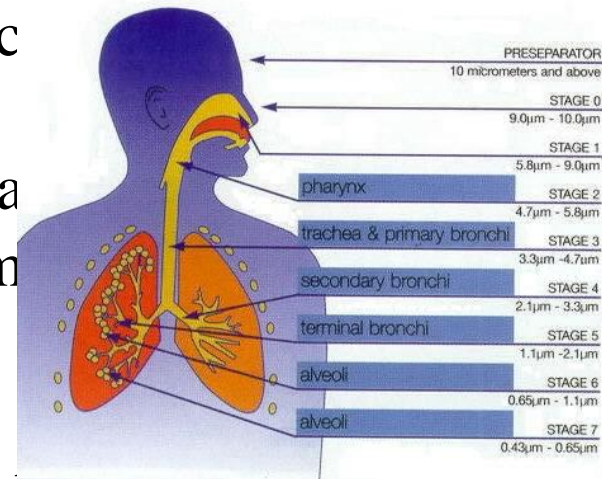
- Chemistry of the ozone hole is heterogeneous catalyzed by ice particles
- Formation of acidity in the marine boundary layer chemistry in the aqueous phase provided by humectant particles

Climate:

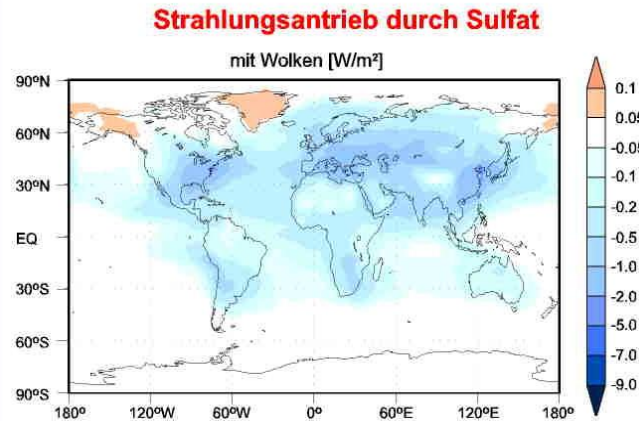
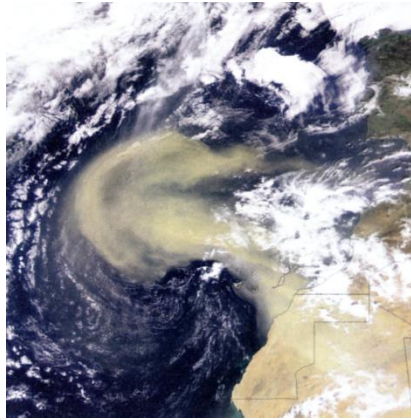
- strong climate sensitivity to aerosols, direct and more so indirect

Toxicology:

- fine particles $< 10 \mu\text{m}$ (PM_{10}) reach the lung
- constituents are partly toxic



Relevance of aerosols: Climate



Sulfate aerosols: cooling
(Feichter & Lammel, 1999)

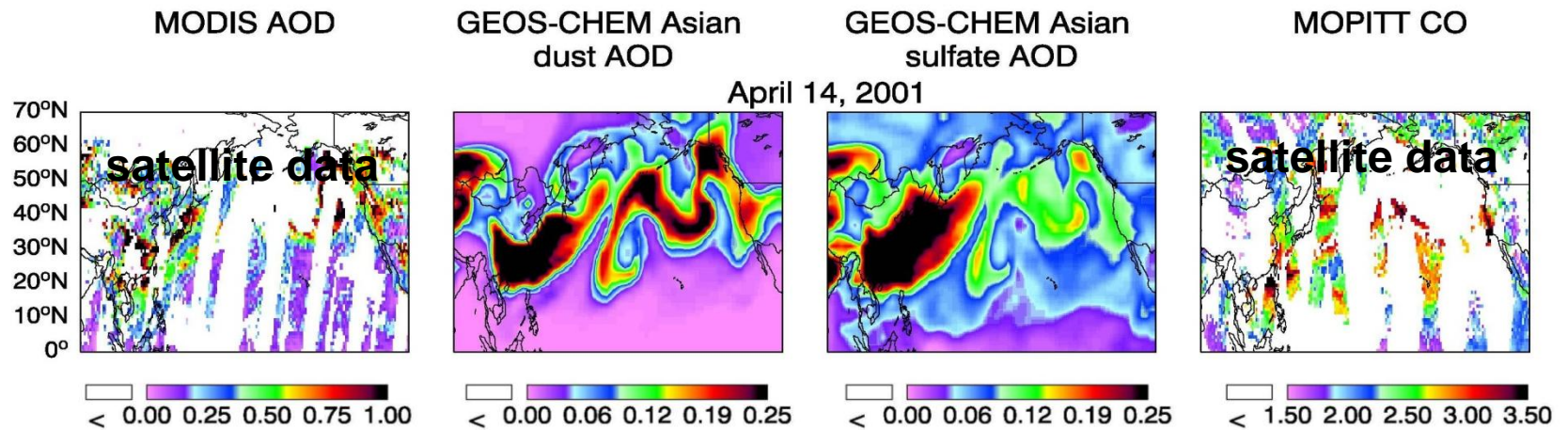
Optical and hygroscopic properties

- 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)

DUST STORMS PROVIDE VISIBLE EVIDENCE OF INTERCONTINENTAL TRANSPORT OF AEROSOLS



Glen Canyon, AZ/USA



PROVEN PATHWAYS OF REGIONAL AND INTERCONTINENTAL TRANSPORT OF AEROSOLS

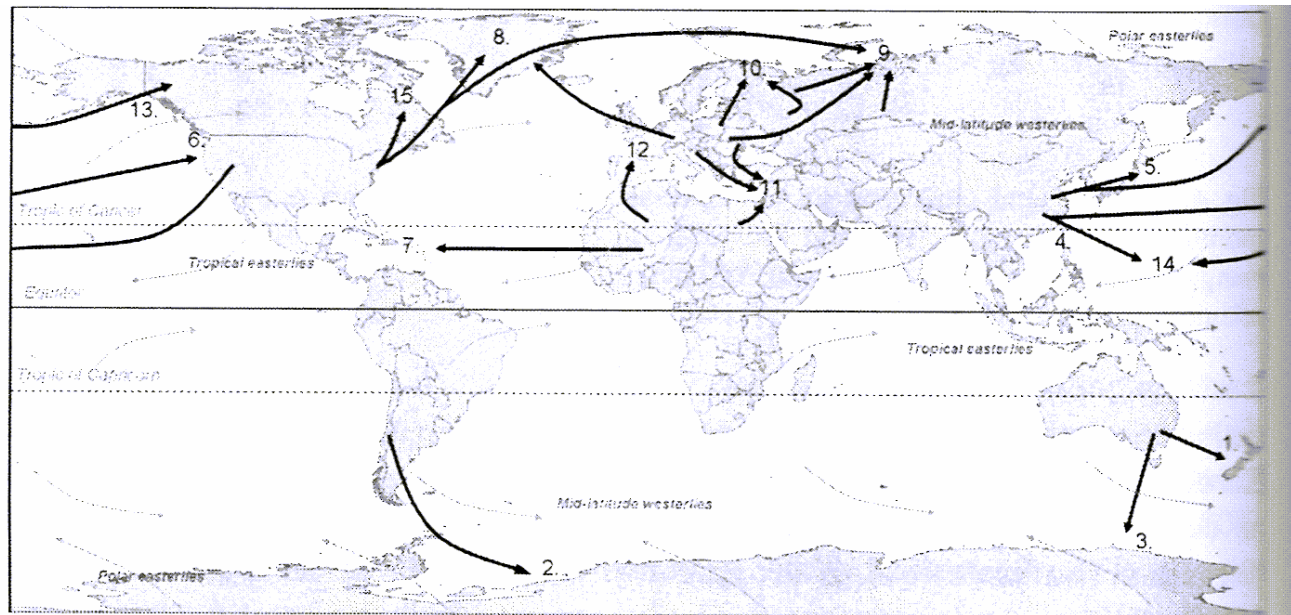
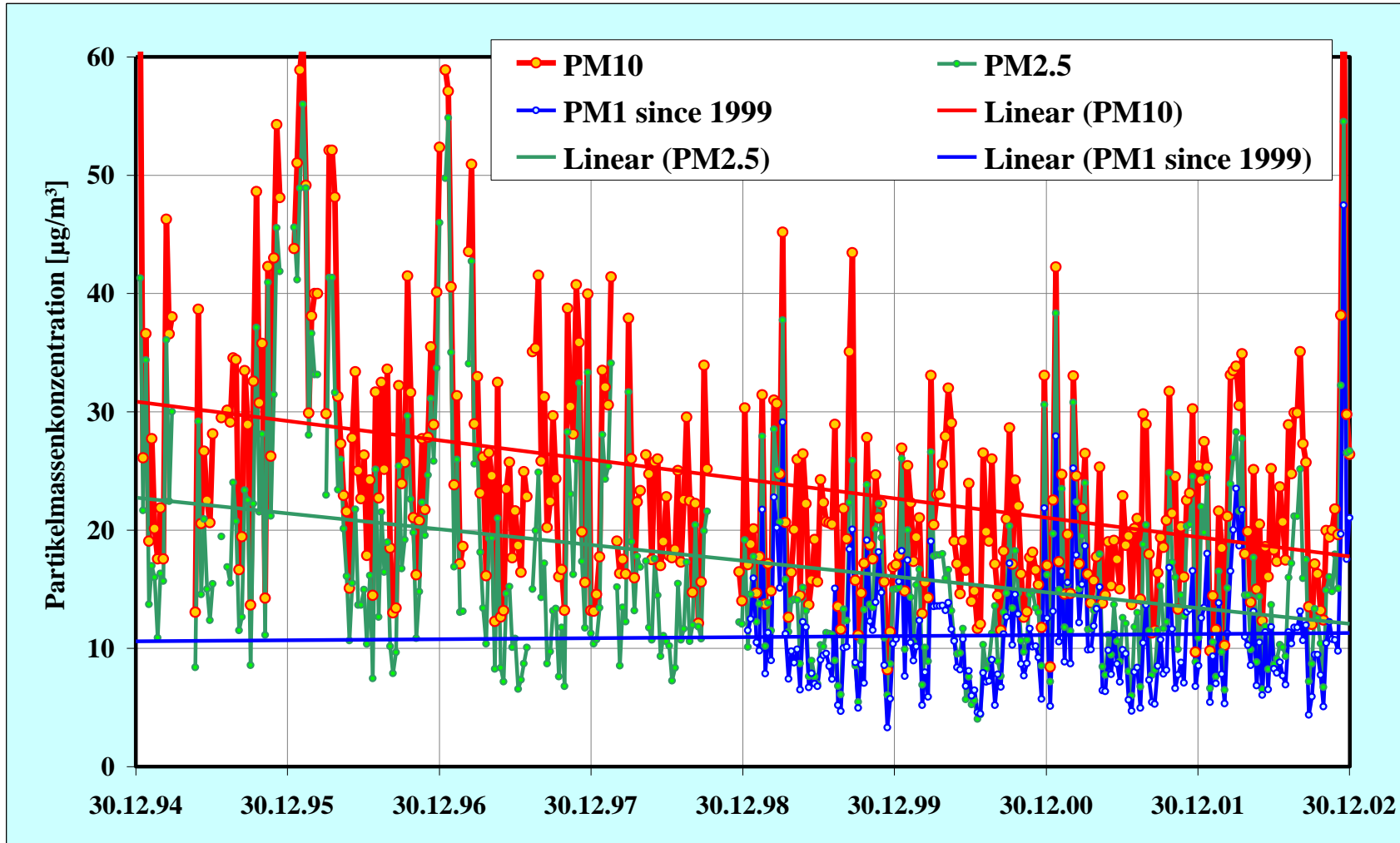


Fig. 5 The major documented pollution plume pathways over which the long-range transport of pollution occurs (as indicated by the *black arrows*). The main windfields are also indicated on the figure by the *grey arrows*. The *numbers* on the figure refer to representative studies documenting pollution 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. 1999; 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)

Main components – Trends

Weekly filter samples, PM₁₀, PM_{2.5} '95-'02 bzw. '99-'02 (PM₁)



Aerosol sources (globally, TgE/a oder Tg/a)

Precursors

		<i>anthr.</i>	<i>natural</i>
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)

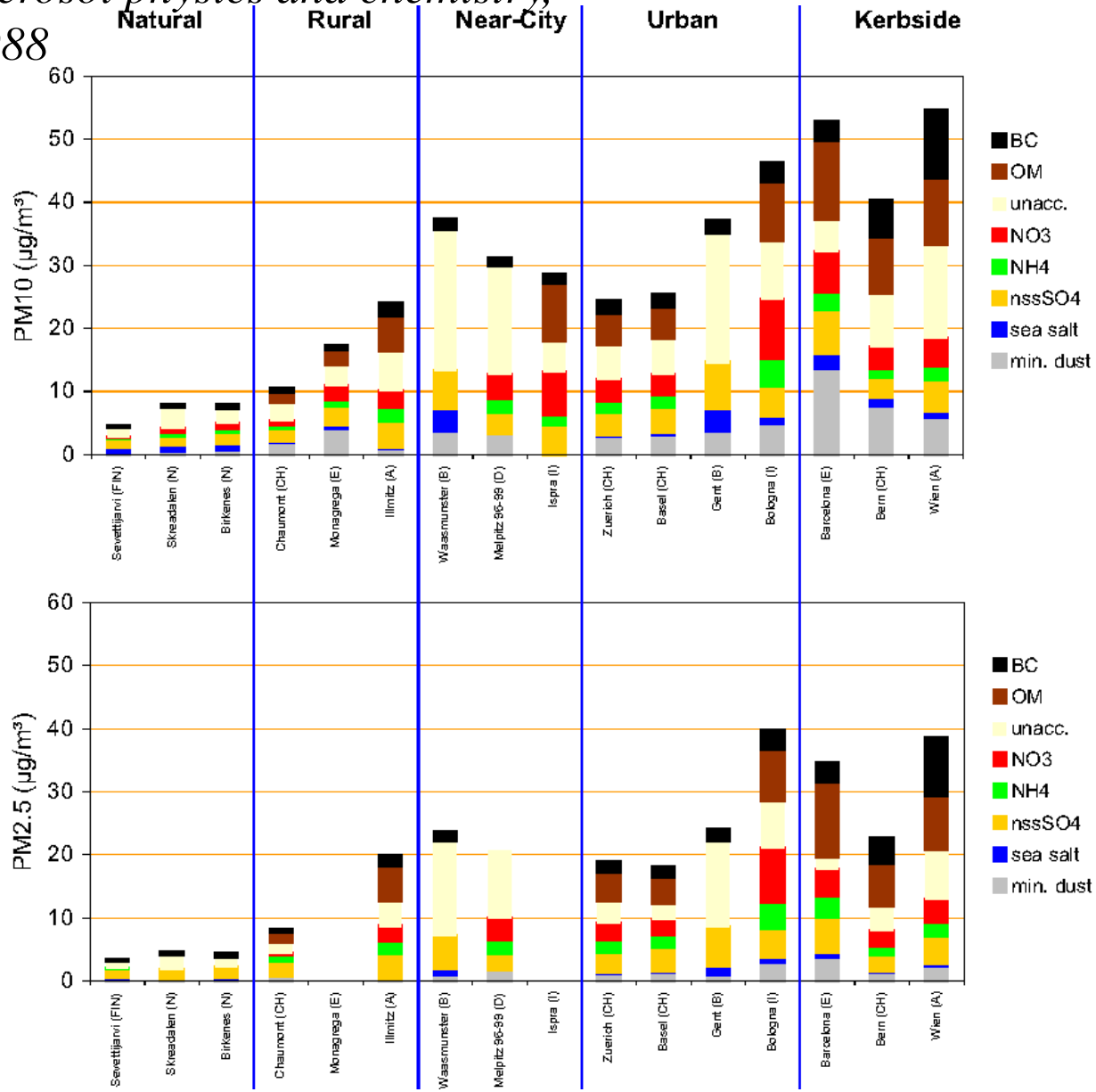
(Penner et al., in IPCC, 2001)

(UBA)

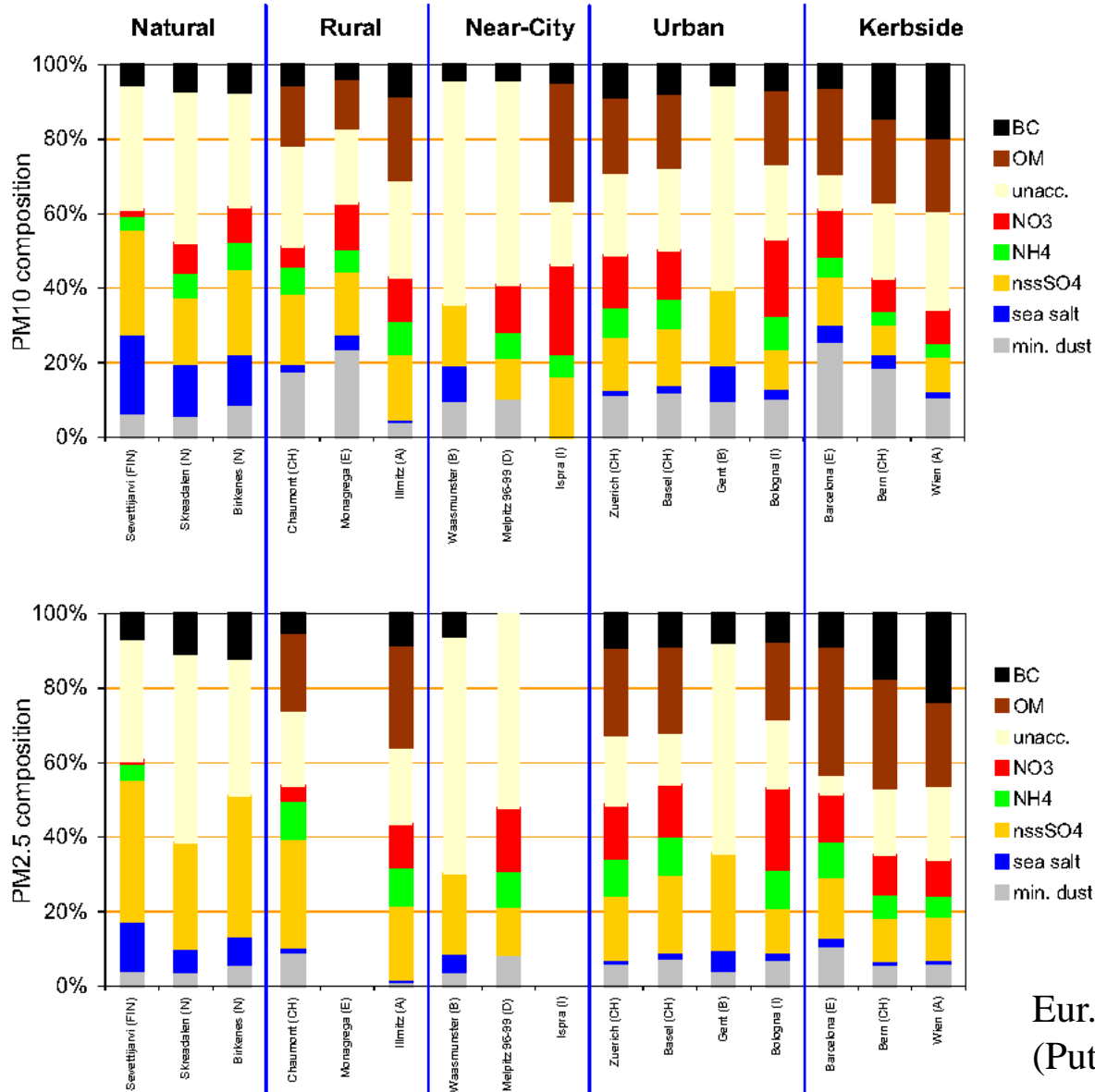
Chemical composition

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

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

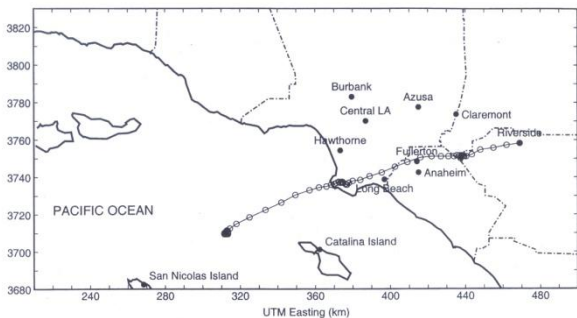


Aerosol chemical composition



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

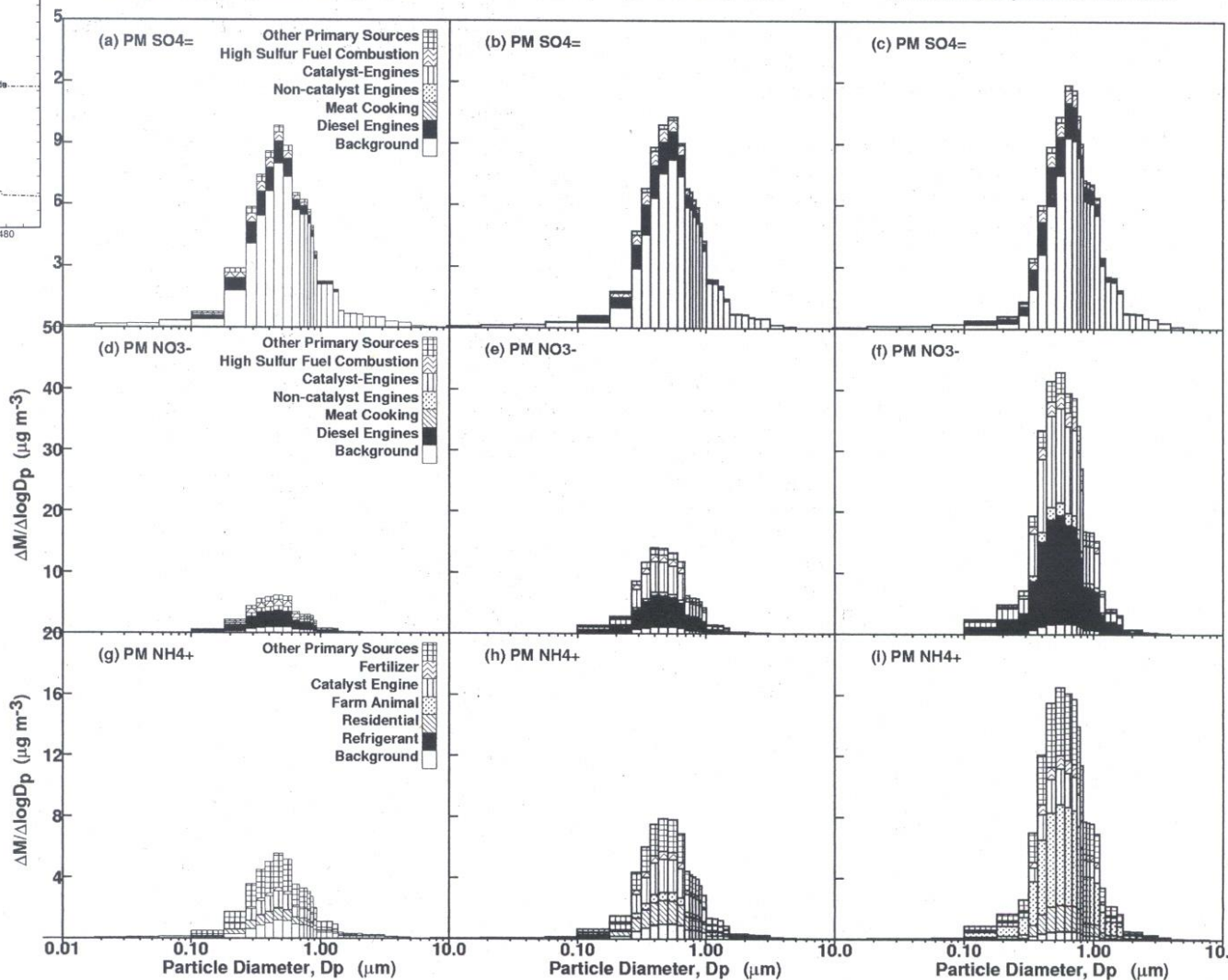
Sources for aerosol inorganic ions, Los Angeles 24.-25.9.1996 (Mysliwiec & Kleeman, 2002)



Long Beach, September 24, 1996

Fullerton, September 24, 1996

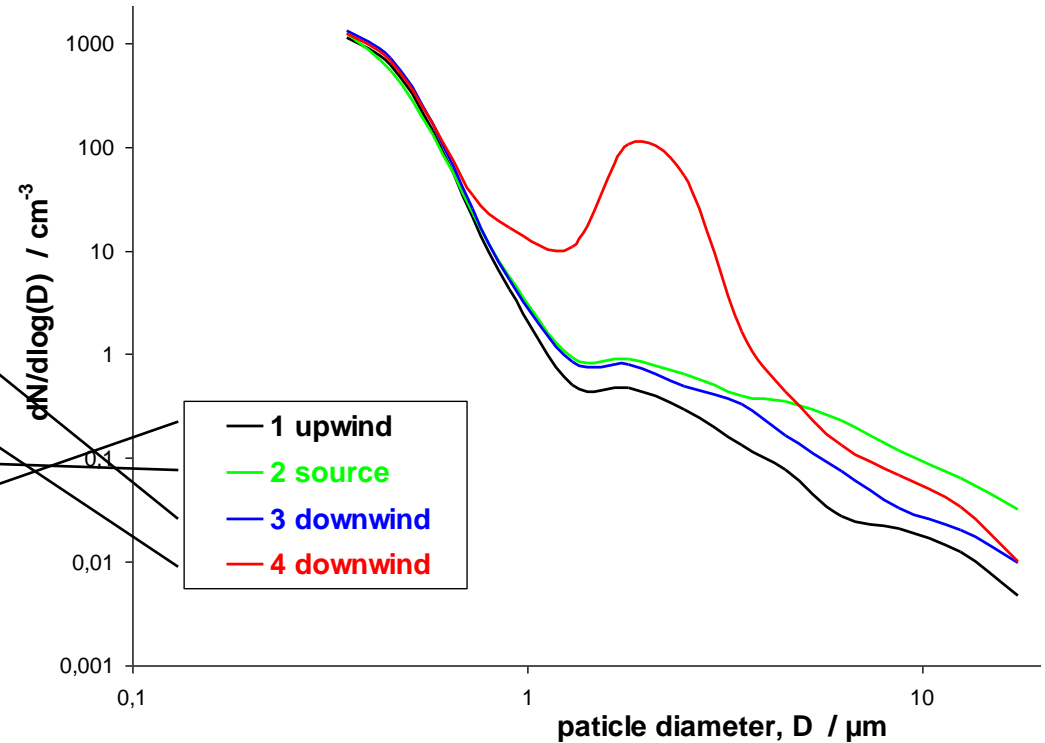
Riverside, September 25, 1996



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

Particle growth downwind of NH₃ 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: $\Delta n_{\text{CN}} = +(8-18) \cdot 10^3 \text{ cm}^{-3}$
- super- μm size range: very significant around 2 μm , $\Delta n_{1-4\mu\text{m}} = 14-21 \text{ cm}^{-3}$
- under humid conditions ((1) r.h. = 90%, T = 6-9 C; $rh \approx rh_D((\text{NH}_4)_2\text{SO}_4)$ and $rh > rh_D(\text{NH}_4\text{NO}_3)$) growth rate 0.2-0.7 $\mu\text{m min}^{-1}$



strong temperature dependence of
phase equilibrium $\text{NH}_3 + \text{HNO}_3 =$

for $\text{rh} < \text{rh}_D$:

$$P_{\text{NH}_3} * P_{\text{HNO}_3} = \begin{matrix} 0.12 \text{ ppbv}^2 \text{ (278 K),} \\ 2.0 \text{ ppbv}^2 \text{ (288 K),} \\ 28 \text{ ppbv}^2 \text{ (298 K)} \end{matrix}$$

$$Y = \frac{[\text{NH}_4\text{NO}_3]}{[\text{NH}_4\text{NO}_3] + 3 [\text{NH}_4(\text{SO}_4)_2]}$$

Humidity dependence:
(Stelson & Seinfeld, 1982)

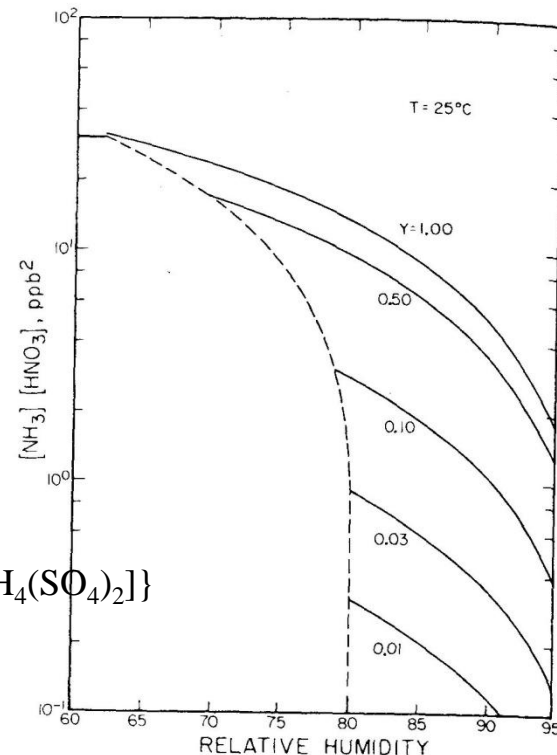
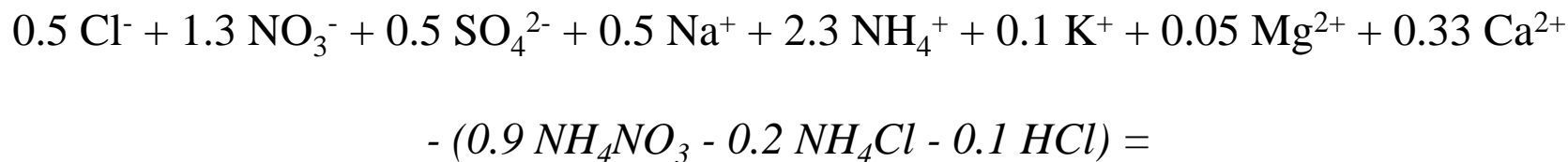


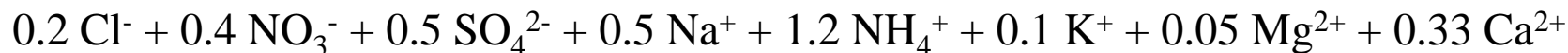
Fig. 2. The effect of $(\text{NH}_4)_2\text{SO}_4$ on the relative humidity dependence of the NH_4NO_3 dissociation constant.

Ions volatile, and non-volatile:

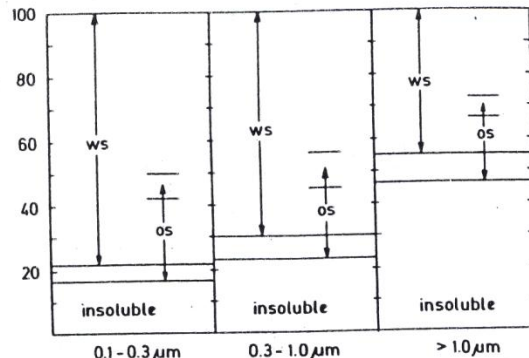
Winter



Summer



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



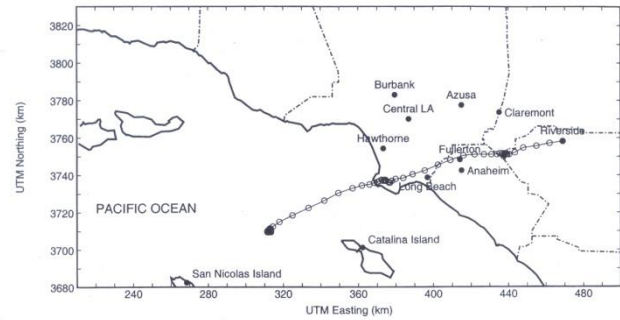
Continental aerosol (Winkler, 1974)

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

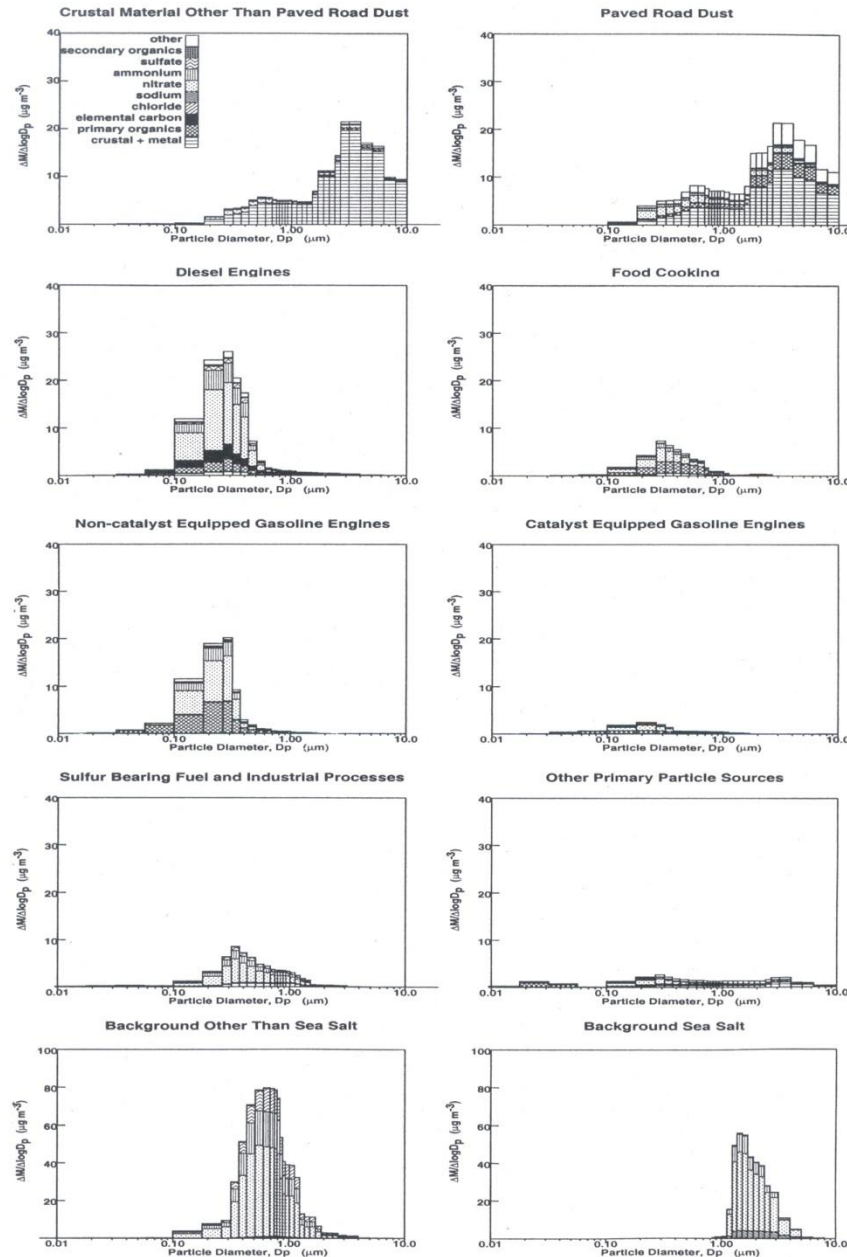
- aliphatic polyols (mostly sugars) and polyethers (polyphenols)
- low-molecular aliphatic and other multifunctional compounds, e.g. $\text{R}(\text{COOH})_{1-2}$
- unsaturated aliphatic and aromatic polyacids of various lipophilicity („humic-like“), $M = 200-500 \text{ Da}$, sources: Oxidation of soot,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



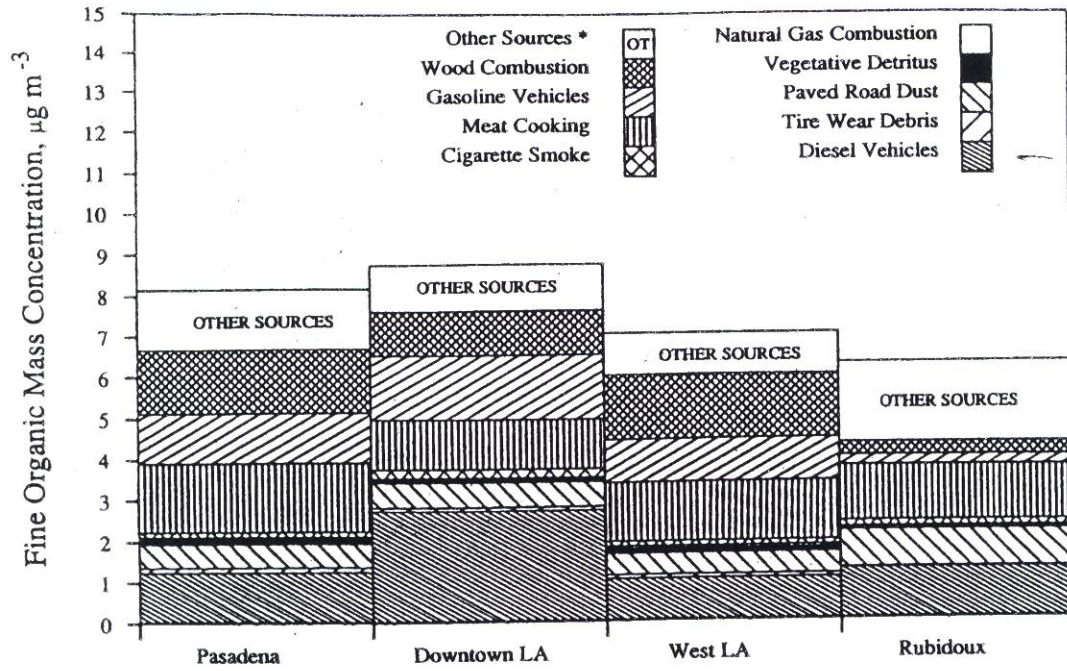
- Emission inventory (source distribution, characteristics)
- Atmosphere model covering transport and transformations



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

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

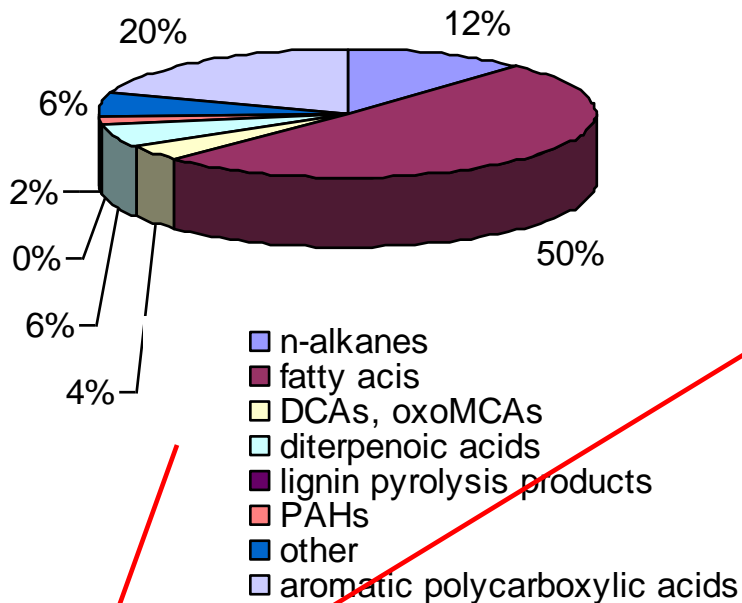
Source	Pasadena	Downtown LA	West Los Angeles	Rubidoux
Diesel exhaust	5.27 \pm 0.72	11.6 \pm 1.19	4.36 \pm 0.64	5.35 \pm 0.51
Tire wear debris	0.29 \pm 0.11	0.22 \pm 0.09	0.25 \pm 0.09	5.50 \pm 0.61
Paved road dust	3.46 \pm 0.43	3.62 \pm 0.46	3.00 \pm 0.39	0.18 \pm 0.08
Vegetative detritus	0.33 \pm 0.10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

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

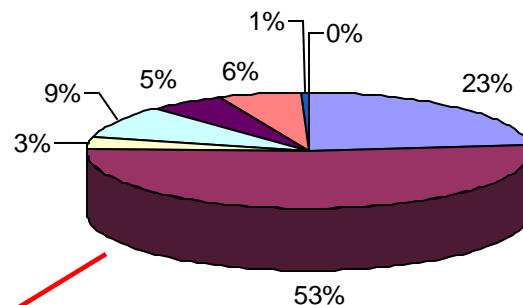
Southern California,
(Rogge et al., 1996; Schauer et al., 1996)

^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.

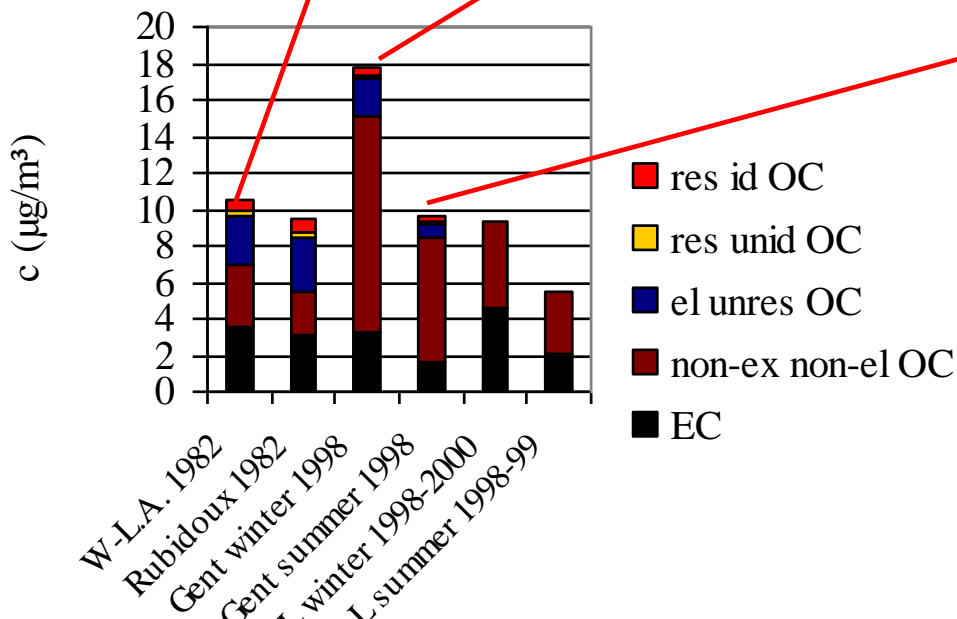
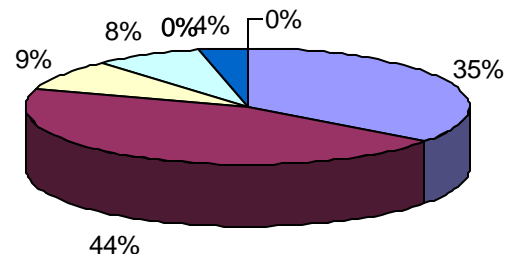
identified organics Los Angeles



identified organics Gent / winter



identified organics Gent / summer



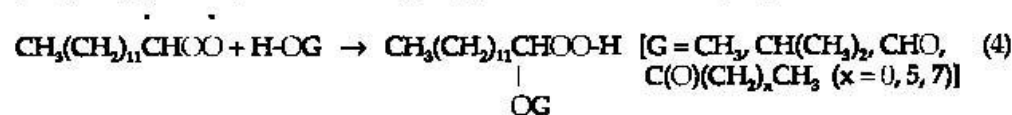
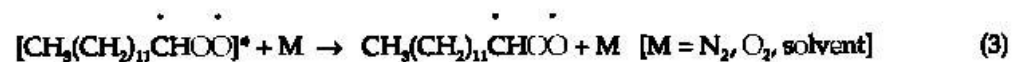
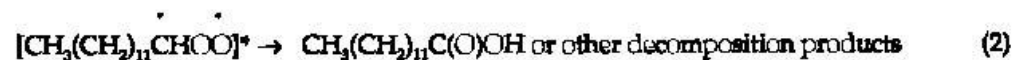
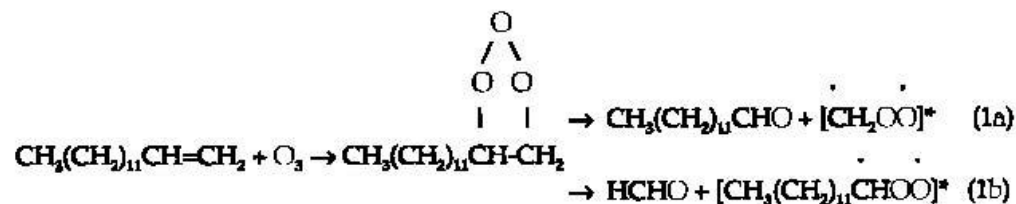
(Schauer et al, 1996; Kubátova et al., 2001)

Secondary particle sources: SOA formation

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

C₁₄-1-en: Smog chamber UCR (Ziemann et al., 2000):

C₁₄-1-en + O₃ →



→ SOA