3.4 Atmospheric aerosol, its composition, surface and bulk particle reactions

3.4.1 Introduction, significance, sources

Global atmospheric particulate matter sources

1. Precursors

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

Gas-to-particle-conversion efficiencies

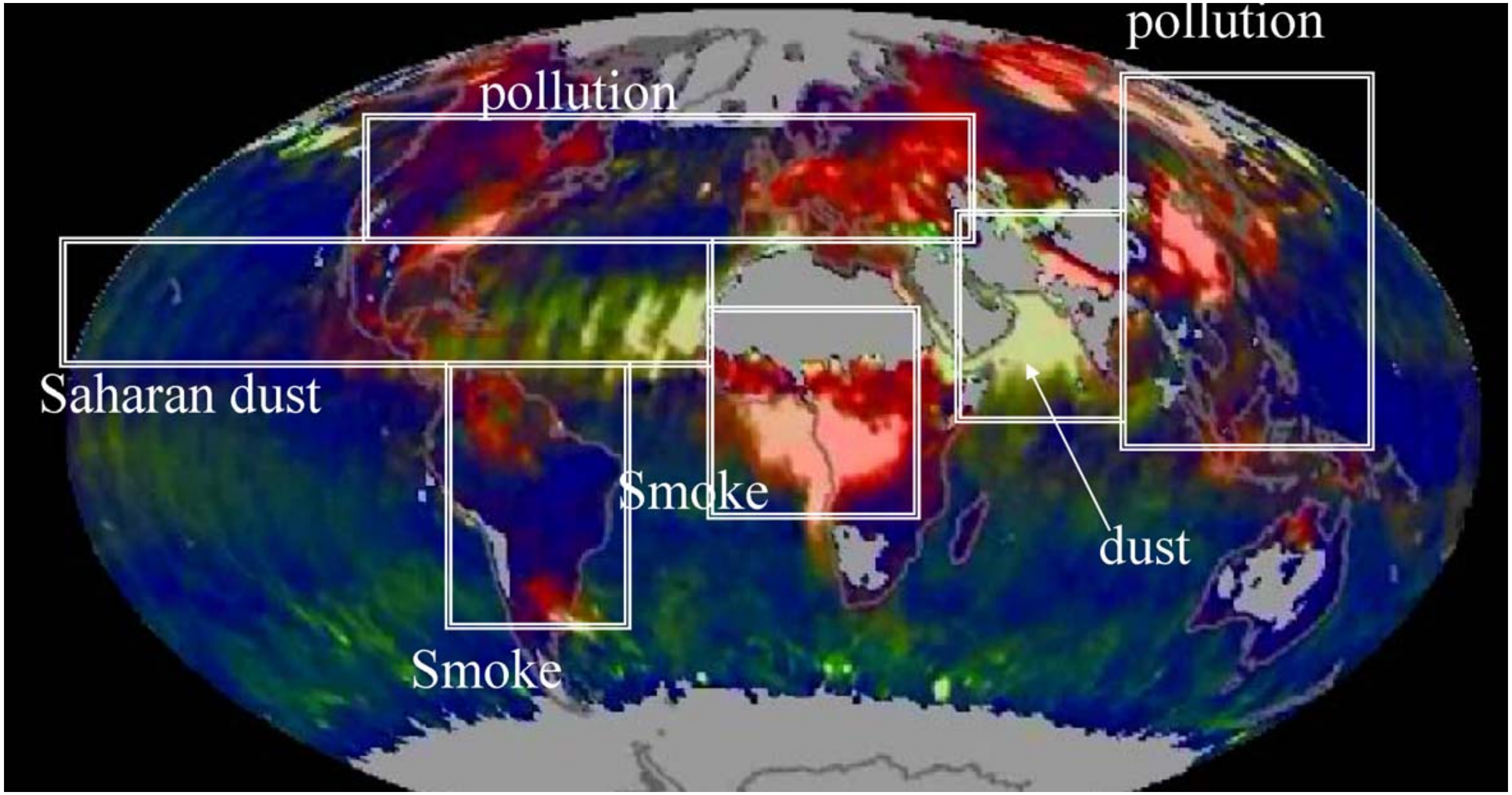
n: ≈ 5%	55 (40-200)	(Andreae, 1995)
n: ≈ 2%	18.5	(Griffin et al., 1999)
a: ≈ 6%	10 (5-25)	(Andreae, 1995)

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

2. direct emission

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

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



Aerosol distributions (on 3.8.01) with **low** and **high** sub-micron mass fraction
(MODIS aerosol optical density, *Martin & Kaufman, NASA*)

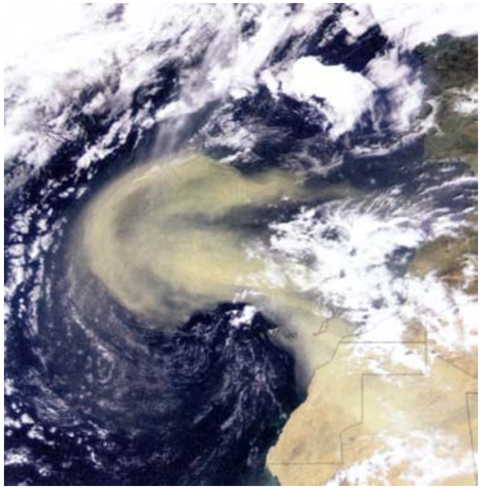
Why is the atmospheric aerosol relevant ?

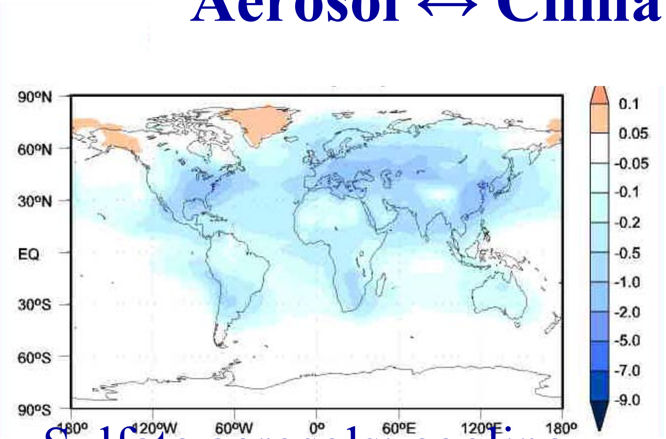
1. **Provides matrix for heterogeneous reactions and is carrier for semivolatile compounds → 3.1.4**
2. **Radiative and cloud nucleation effects (climate, so-called direct and indirect aerosol effects)**
3. **Human health: Respiratory diseases, besides other**

(3)

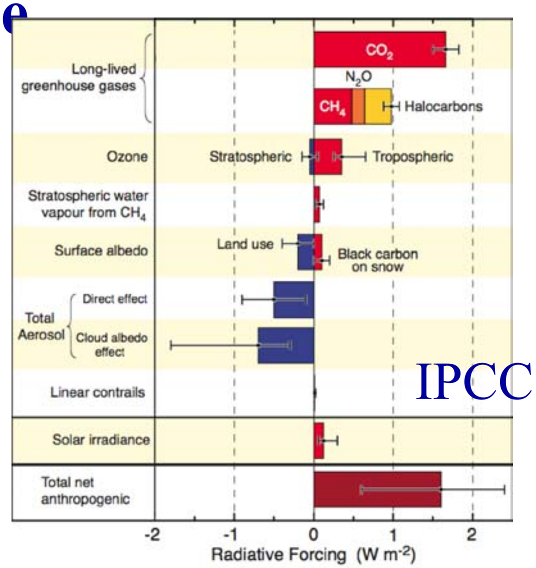
(4)

Aerosol ↔ Climate





Sulfate aerosols: cooling

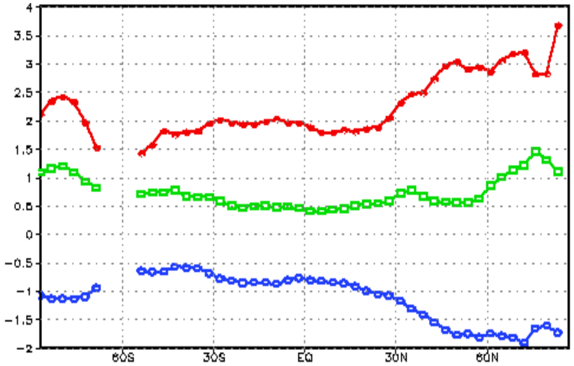


IPCC, 2007

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 (‚indirect effect‘): –1.5 ± 0.5 W/m² *(Lohmann & Feichter, 2001)*

→ Instead of ≈ +0.7°C global warming we had without anthropogenic aerosols ≈ +1.7°C !



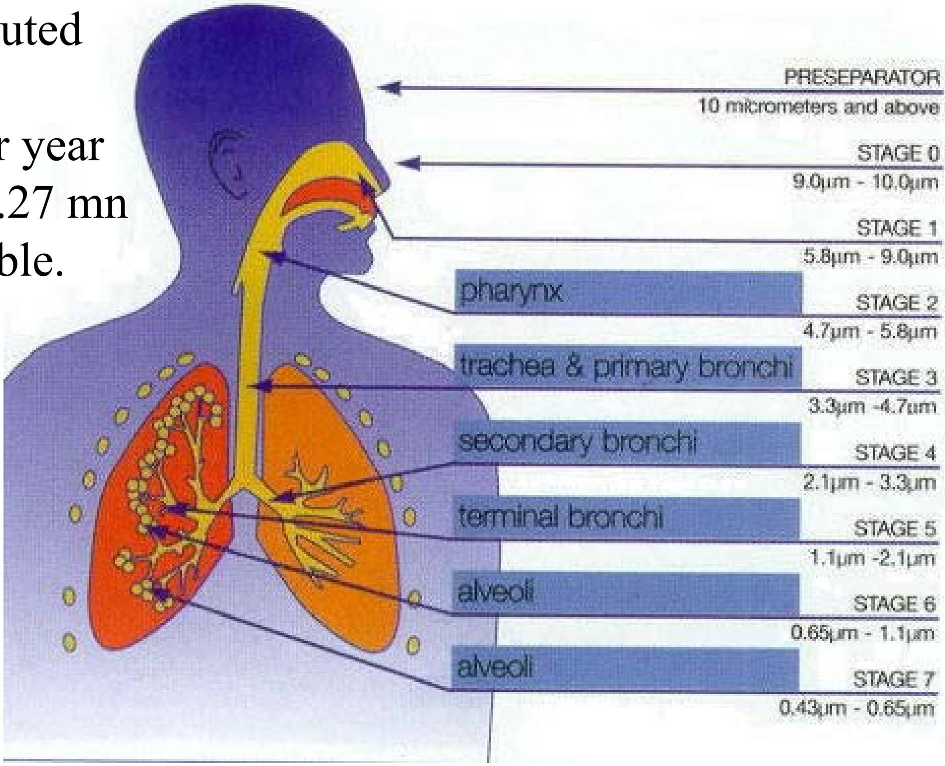
Zonal (S pole – N pole) mean temperature changes 1990-1850:
GHG, aerosols, GHG + aerosols
(Feichter et al., 2004)

Aerosol ↔ Health

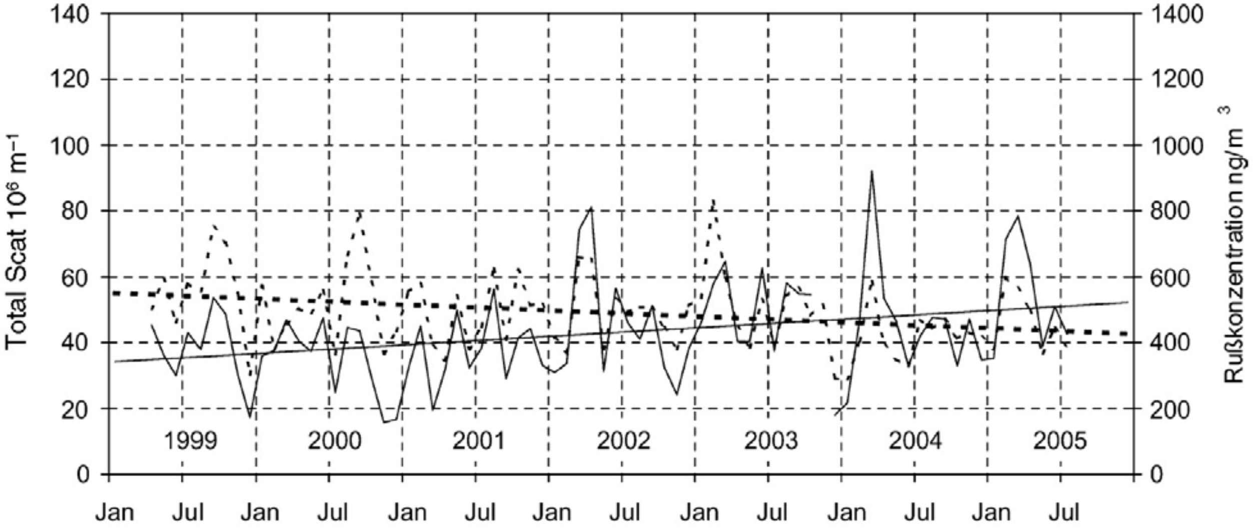
Adverse health effects

- Fine PM reaches the lung: < 10 µm (PM_{10}), at least < 5 µm, macrophages remove 1/3 (the larger), rest remains in the alveolar region or even reaches into the lymphatic and blood circulations
- $PM_{2.5}$ carries numerous organic and inorganic substances, including toxics → pulmonary and cardivascular diseases (e.g., elevated fatal stroke risk), mutagenic, nervous system impairment. A no-effect-concentration/threshold value cannot be identified
- WHO estimate (2006): Mortality in most polluted cities could be reduced by 15%
- EU Comm. (2007): 2 mn premature deaths per year globally, 0.39 mn in EU (2007). Reduction to 0.27 mn in 2020 under current legislation, 0.19 mn feasible.

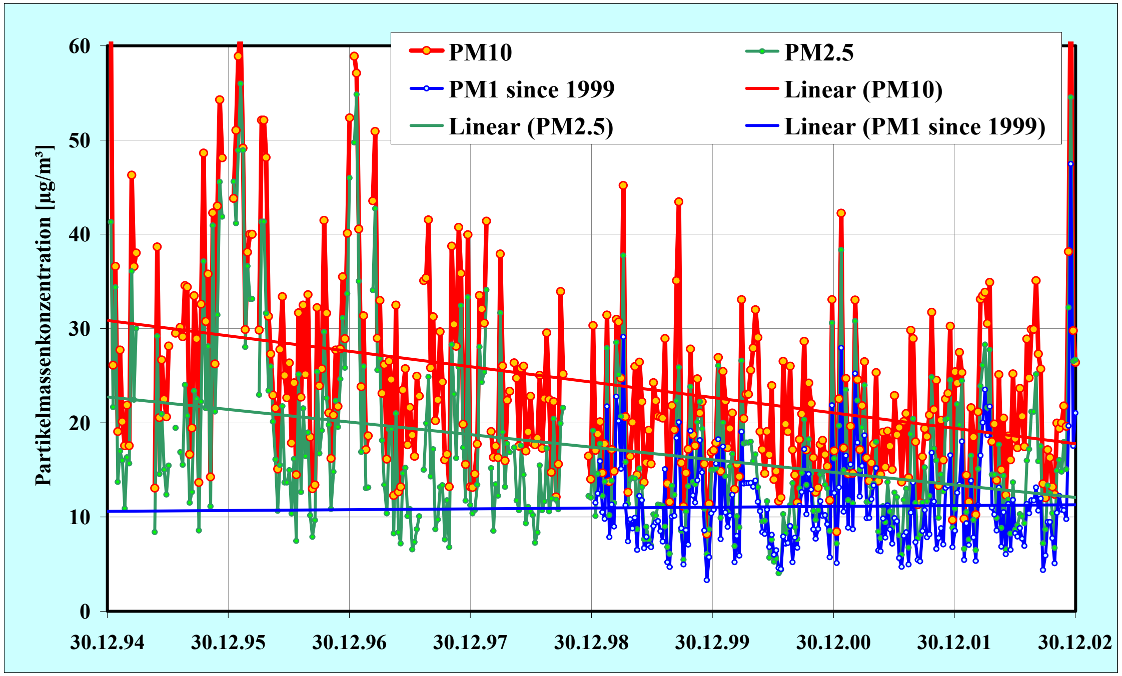
PM_x = particulate matter smaller than x µm by size
TSP = total suspended particulate matter



Trends of particulate matter (PM) and PM size fractions



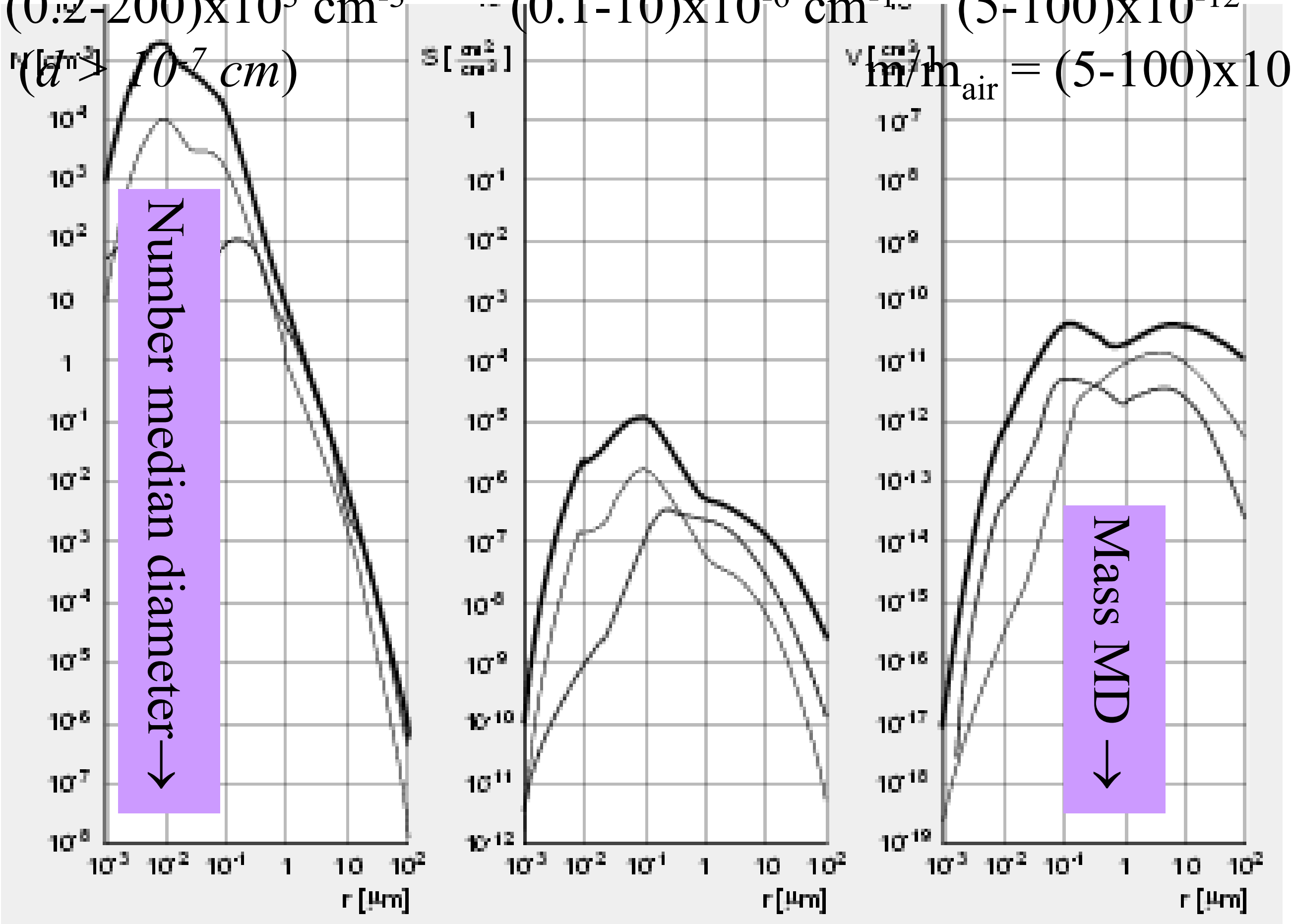
GAW Hohenpeissenberg, D
1000 m a.s.l.;
(Kaminski, 2006)



rural central Germany
(Spindler et al., 2004)

Aerosol size distributions

- size dependent number, surface and volume concentrations



Number

$(0.2\text{-}200)\times10^3\ \mathrm{cm}^{-3}$

($d > 10^{-7}$ *cm*)

Surface

$(0.1\text{-}10)\times10^{-6}\ \mathrm{cm}^{-1}$

Volume

$(5\text{-}100)\times10^{-12}$

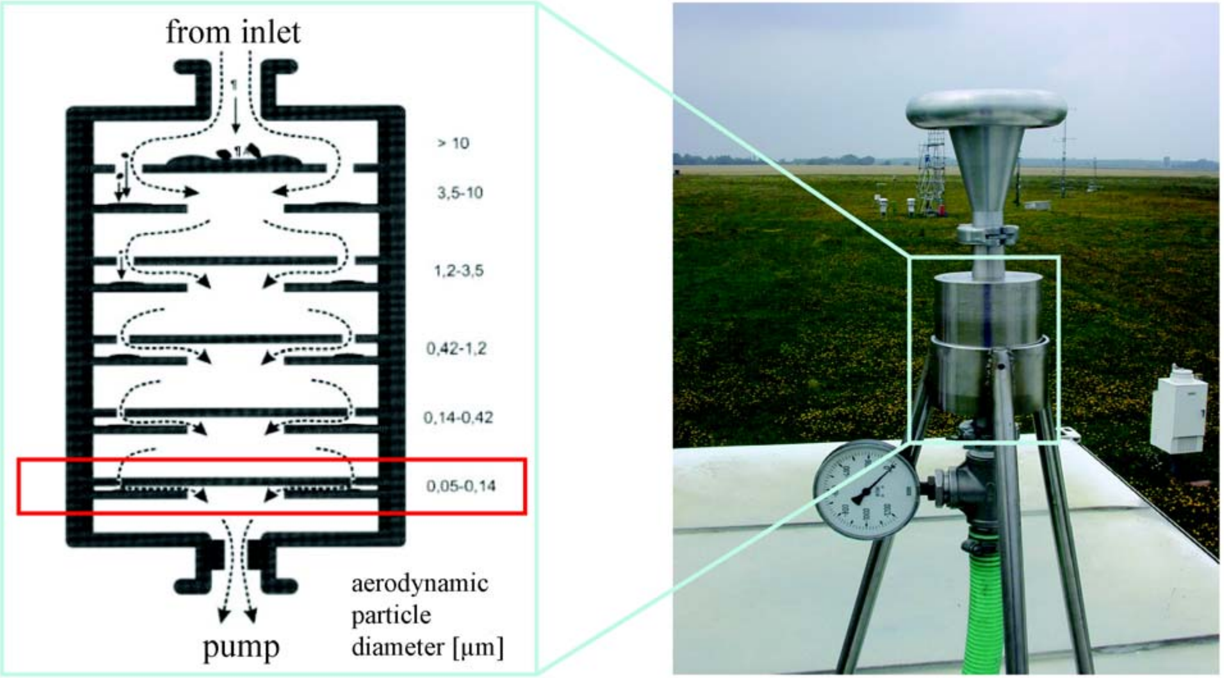
$m/m_{air} = (5\text{-}100)\times10^{-9}$

Urban

Rural

Continental background

In most cases, inherent to sampling techniques (impactor), r (D) refers to the aerodynamic radius (diameter), i.e. the particle size provided its density equals 1 g cm^{-3}! Impactor:



Berner round nozzle impactor (courtesy of Herrmann, IfT)

Removal processes
- size dependent residence time

$\tau = f(D)$:

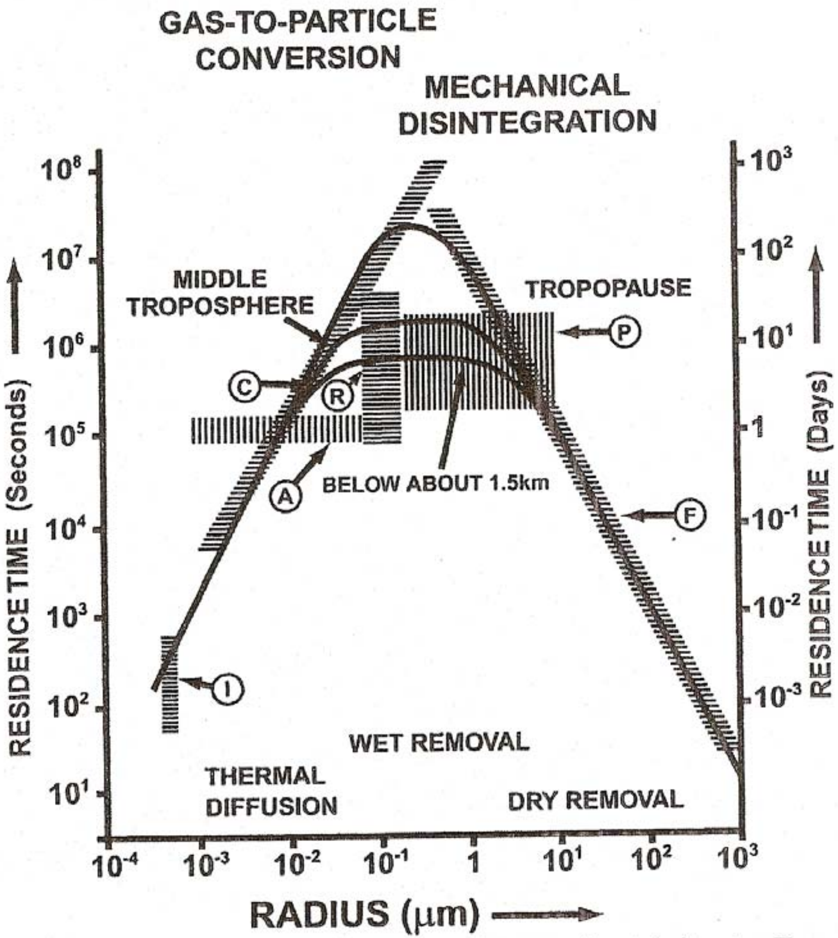


Figure 2-6 Residence time of tropospheric aerosols as a function of particle diameter. Figure taken from Jaenicke (1987) and reprinted with permission from Dechema e.V. The hatched areas represen published estimates for: small ions (I); Aitken particles (A); coagulation by thermal diffusion (C); radioactivity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

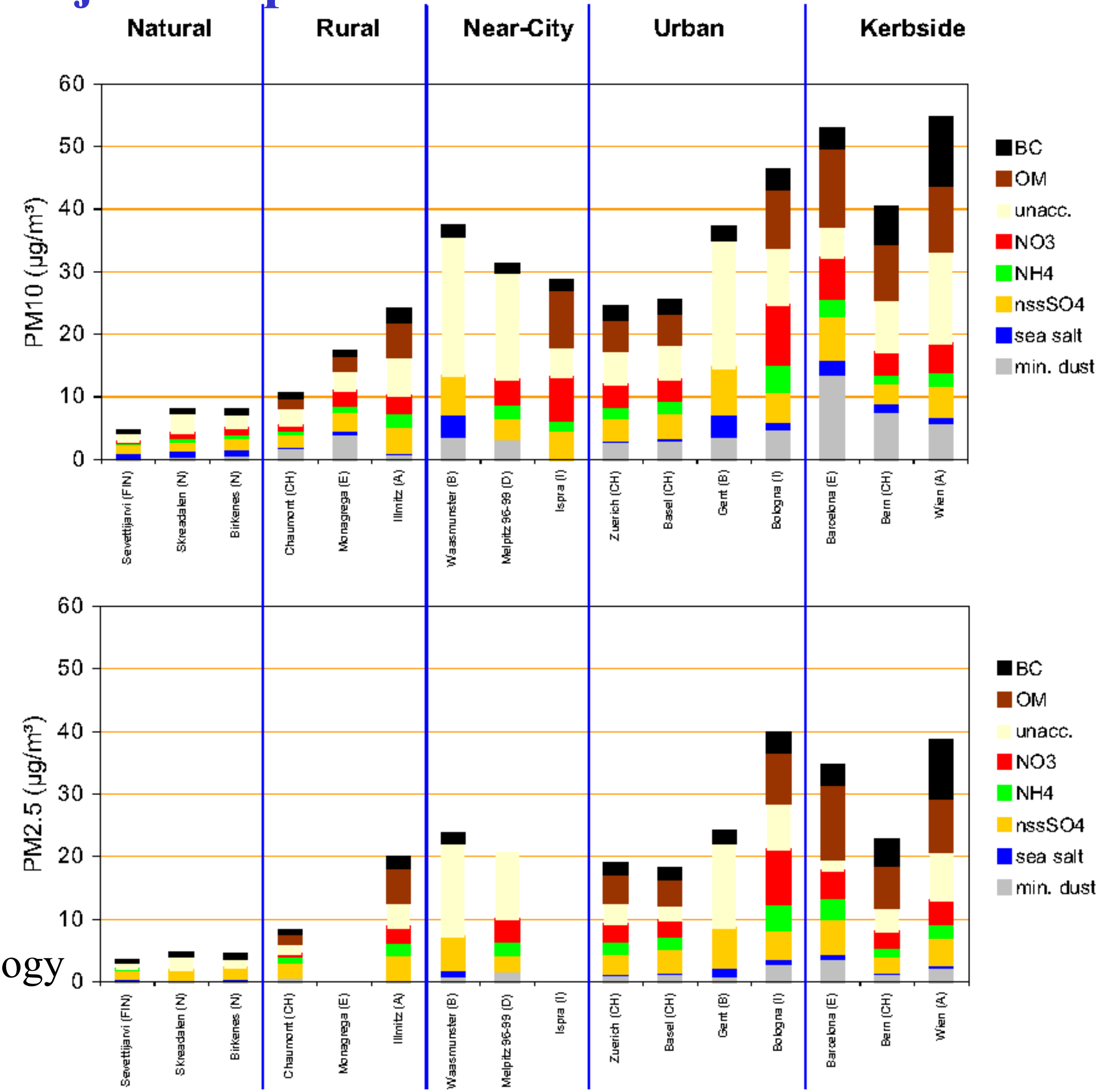
(Franklin et al., 2000)

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

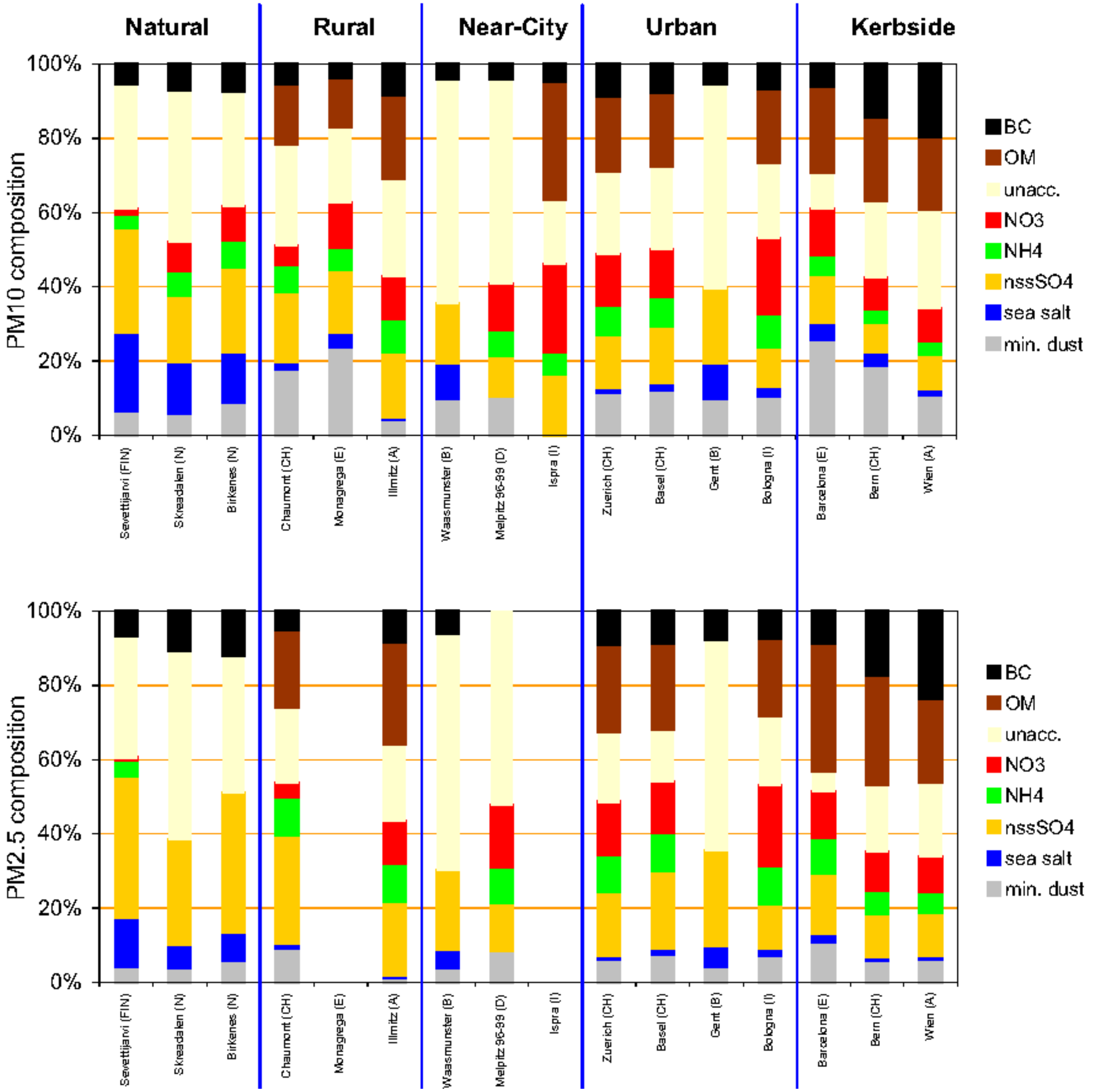
3.4.2 Chemical composition

3.4.2.1 Inorganic, major components

- size dependent



European aerosol phenomenology
(van Dingenen et al., 2004)



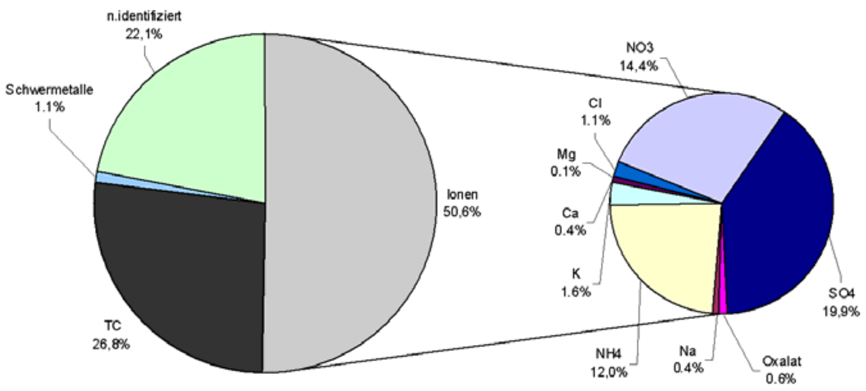
(van Dingenen et al., 2004)

Chemical composition, 2 size ranges, 2 urban sites in Austria 2000/01

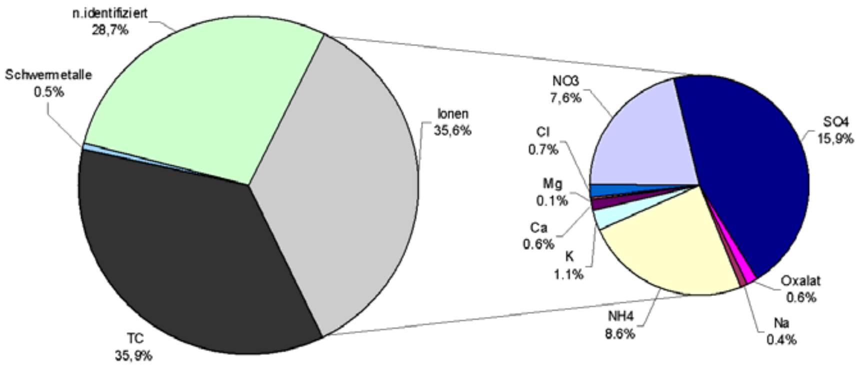
(Hauck et al., 2004)

$PM_{2.5}$

Linz AUPHEP- 3

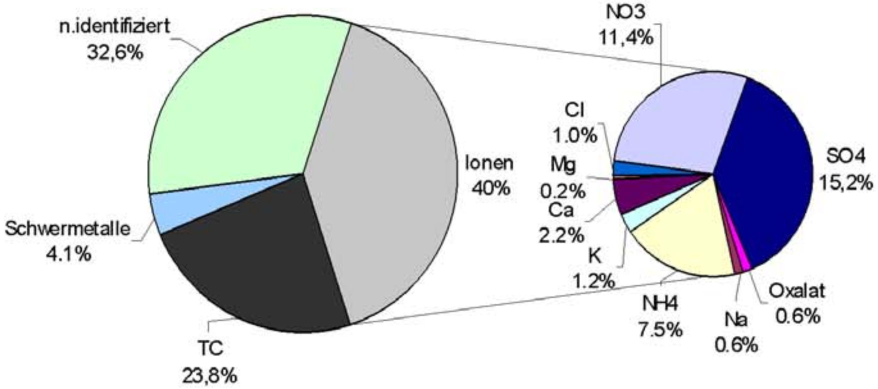


Graz AUPHEP- 4

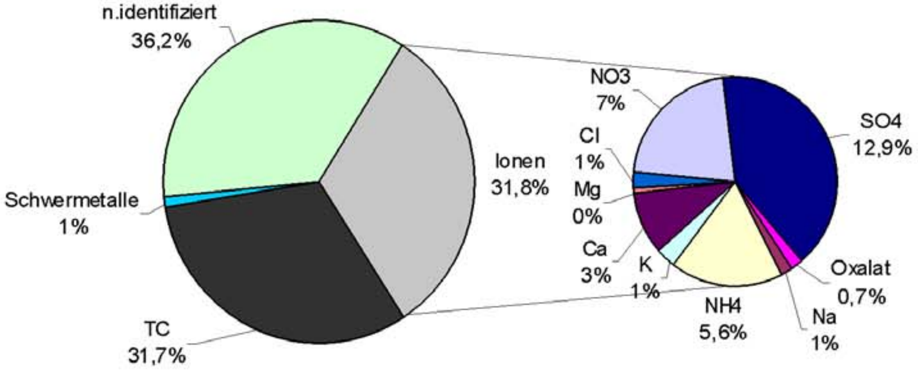


PM_{10}

Linz AUPHEP- 3



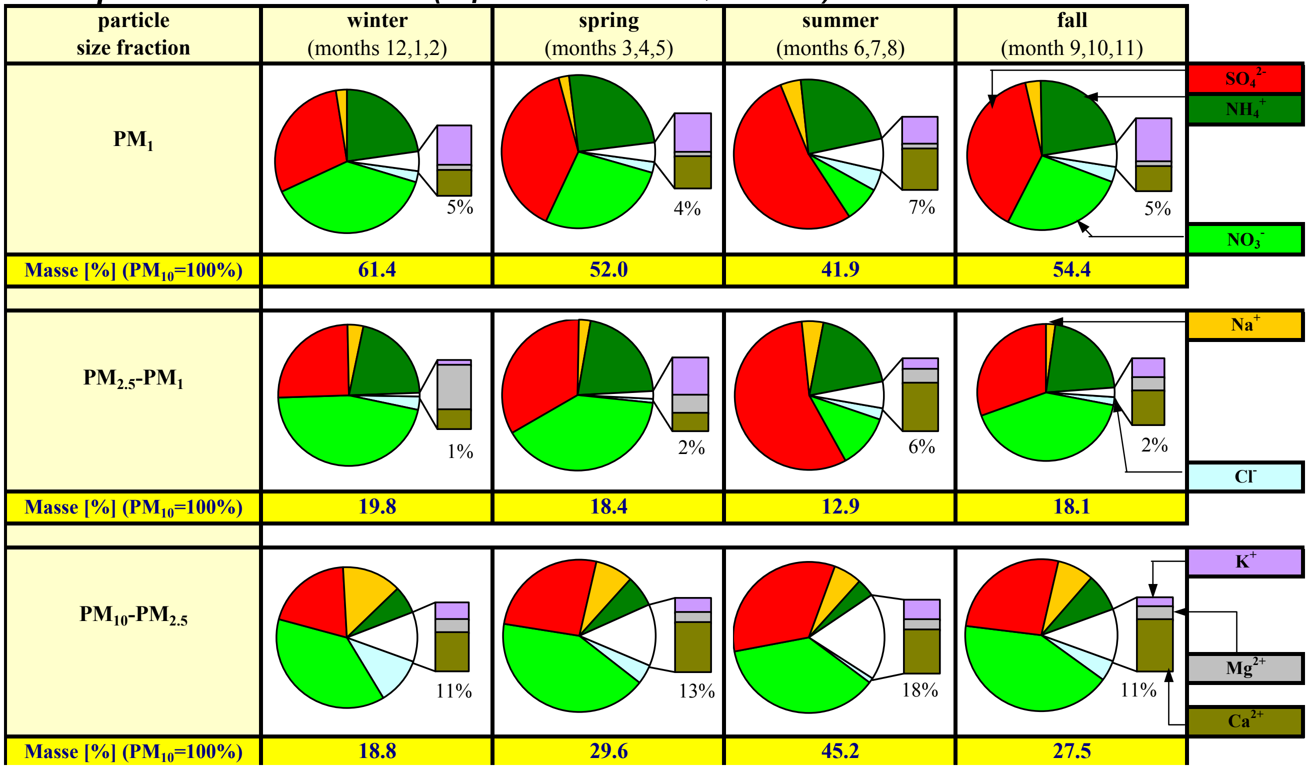
Graz AUPHEP- 4



→ Particle size matters!

Seasonal varibaility of chemical composition (water soluble ions only)

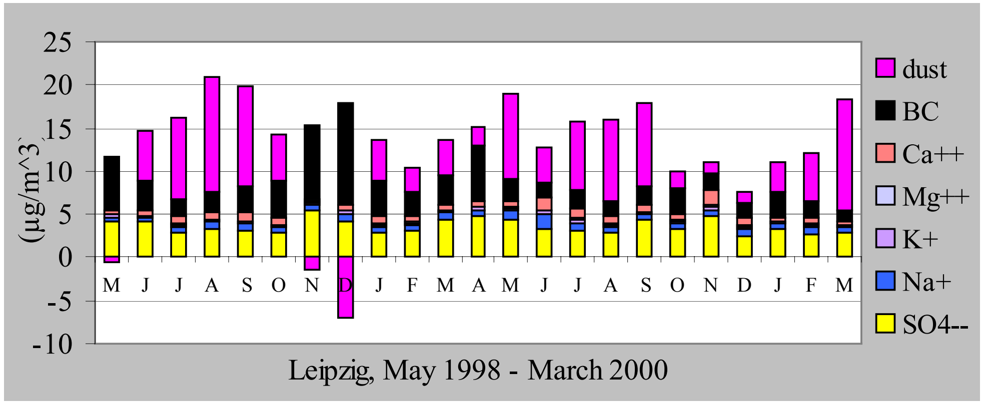
Melpitz 1999-2002 (Spindler et al., 2004)



particle size fraction	winter (months 12,1,2)	spring (months 3,4,5)	summer (months 6,7,8)	fall (month 9,10,11)
PM_1	5%	4%	7%	5%
Masse [%] (PM_{10}=100%)	**61.4**	**52.0**	**41.9**	**54.4**
$PM_{2.5}$-PM_1	1%	2%	6%	2%
Masse [%] (PM_{10}=100%)	**19.8**	**18.4**	**12.9**	**18.1**
PM_{10}-$PM_{2.5}$	11%	13%	18%	11%
Masse [%] (PM_{10}=100%)	**18.8**	**29.6**	**45.2**	**27.5**

Seasonality (ions of non-volatile salts, black carbon, and mineral dust)

Leipzig 1998-2000 (Lammel et al., unpubl.)

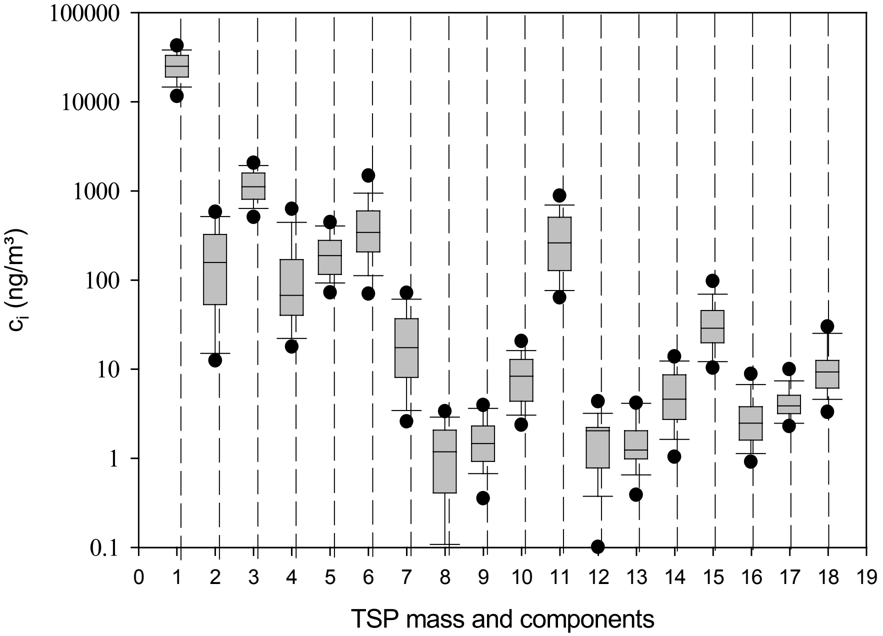


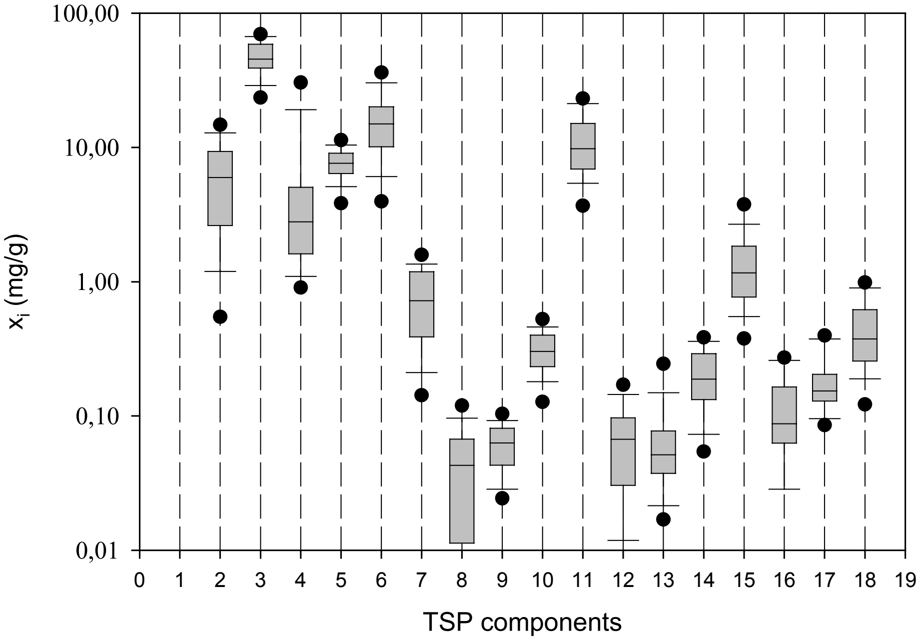
3.4.2.2 Inorganic, minor components

Elemental composition

TSP 1 = mass,
2 = Al, 3 = S, 4 = Cl, 5 = K, 6 = Ca, 7 = Ti, 8 = V, 9 = Cr, 10 = Mn,
11 = Fe, 12 = Co, 13 = Ni, 14 = Cu, 15 = Zn, 16 = As, 17 = Br, 18 = Pb

c_i urban Leipzig 1998-99 (1-100 ng/m³) **x_i** **(0.01-1 %)**





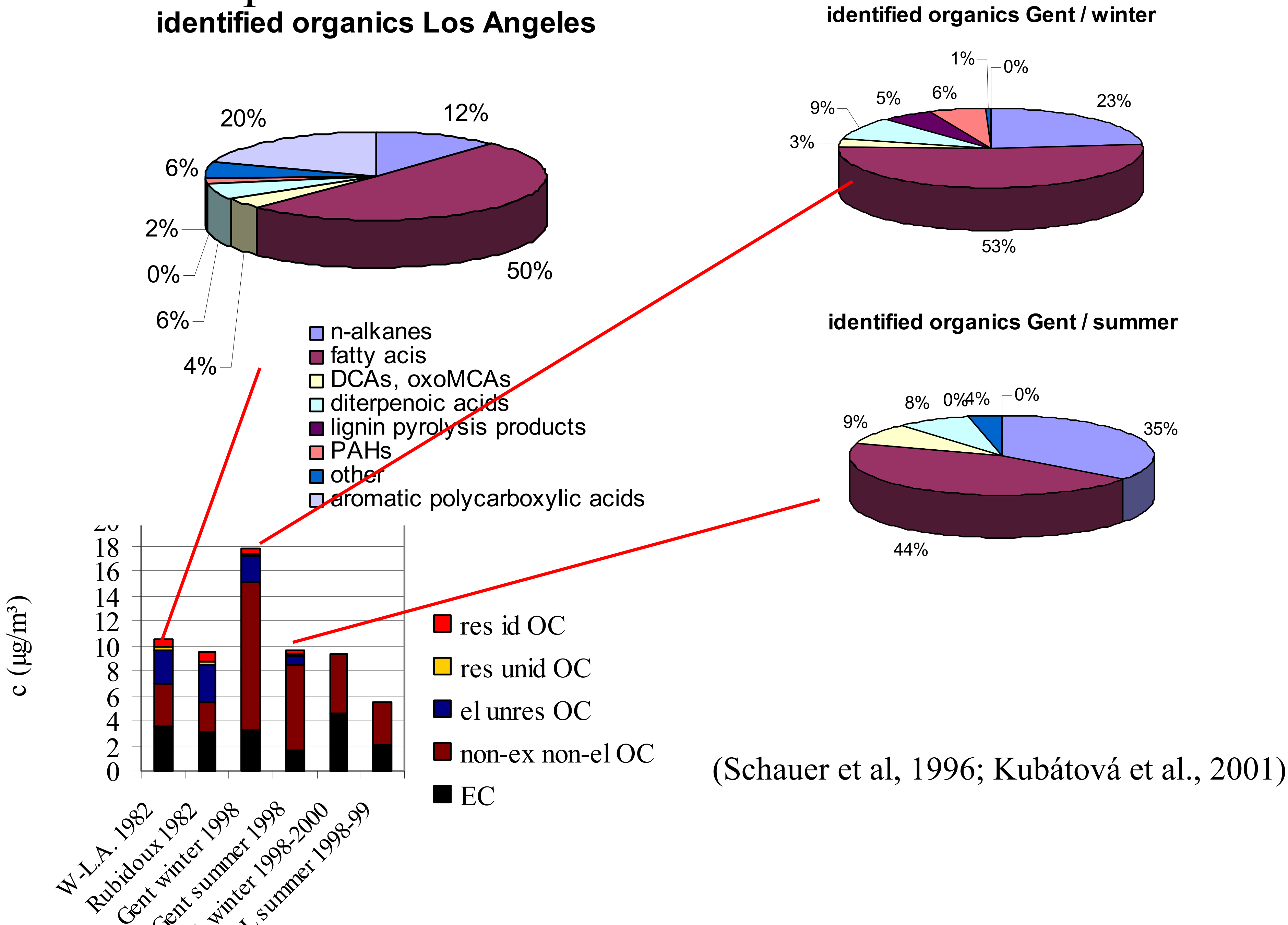
(Lammel et al., 2003)

3.4.2.3 Particulate organic matter

Mean atmospheric concentrations of particulate organic matter (POM or ‚OC‘)

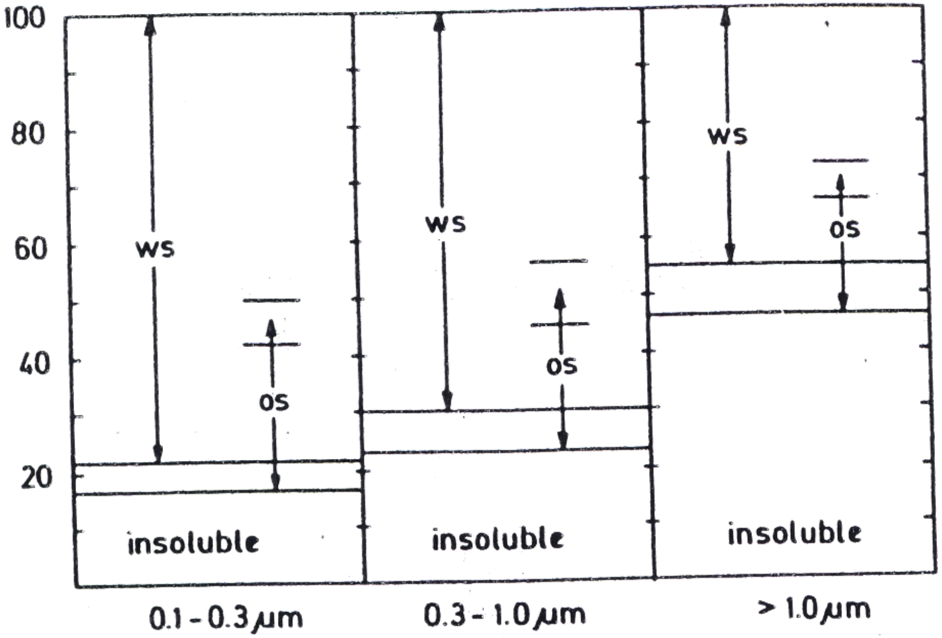
	µg/m³	
Marine		
Puerto Rico	0.66	(Novakov & Penner, 1993)
Hawaii	0.05	(Liousse et al., 1996)
Geenland	0.16	(Liousse et al., 1996)
Oki/trop.Pazifik	1.4	(Liousse et al., 1996)
SargassoSea	0.44	(Liousse et al., 1996)
Mace Hd./IRL	1.0	(Liousse et al., 1996)
Continental		
Abastumani/GEO	2.4	(Dzubay et al., 1984)
USA, *20 sites*	2.4	(Shah et al., 1986)
K-puszta	4.7	(Molnár et al., 1999)
Aspverten/S	2.2	(Zappoli et al., 1999)
Urban/industrial		
USA, *46 sites*	6.6	(Shah et al., 1986)
Detroit	5.5	(Dasch & Cadle, 1989)
Nagoya	13-22	(Kadowaki, 1990)
Estarrejo/P	16	(Nunes & Pio, 1993)
Birmingham	5	(Harrison & Jones, 1995)
S.Pietro Capofiume/I	6.2	(Zappoli et al., 1999)
Leipzig	4.1	(Lammel et al., unpubl.)

POM composition in urban air



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

POM water solubility:
A large fraction is water soluble – size dependent



Continental aerosol particulate matter *(Winkler, 1974)*

POM **in the continental background** consists of (25-50% each):

- aliphatic polyols (mostly sugars) and polyethers (polyphenols)
- low-molecular aliphatic and other multifunctional compounds, $R(COOH)_{1-2}$ besides others
- unsaturated aliphatic and aromatic polyacids of varying lipophilicity („humic-like“), M_g = 200-500 Da, sources: Oxidation of soot, acid catalyzed polymerisation of terpenes *(Havers et al., 1998; Fuzzi et al., 2002; Krivacsy et al., 2001; Decesari et al., 2002; Gelencser et al., 2003)*

POM molecular weight:
A large fraction of the water insoluble fraction is high molecular

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

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

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

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

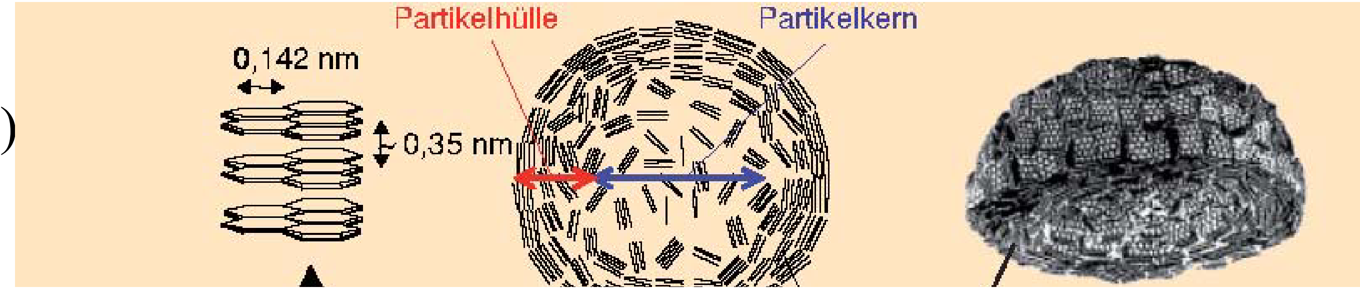
For example: $x_{cellulose}$ = 1-2 % in Wien *(Kunit & Puxbaum, 1996)*;

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

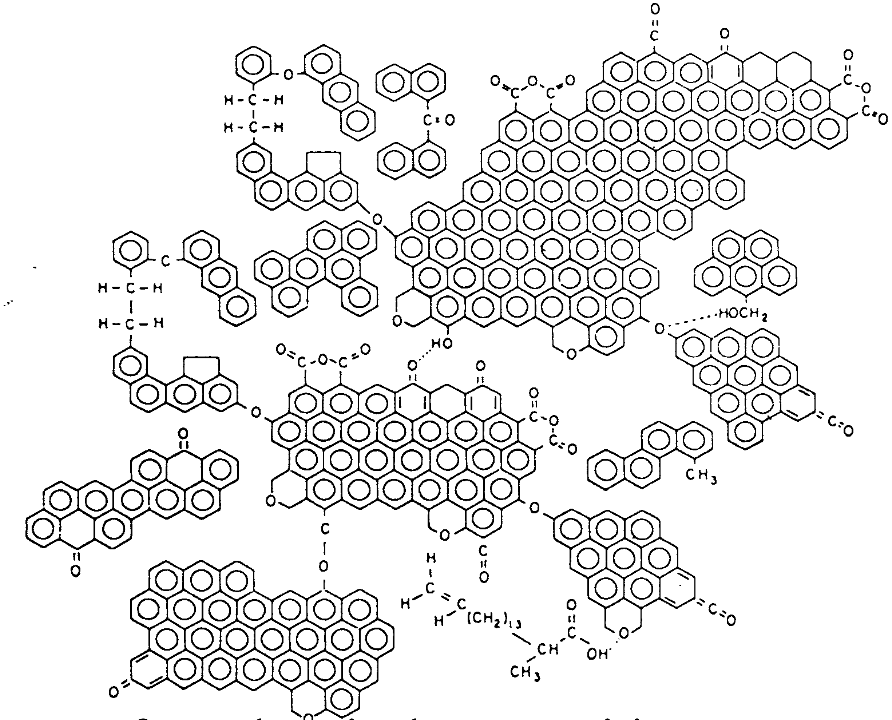
3.4.2.4 Soot

= amorphous C + shell of adsorbed molecules and/or partly oxygenated C + adsorbed water molecules

- Strong sorbent
- Light absorbing
- Hydrophobic (initially)



soot particle shell, core *(Hoffmann et al., 2007)*

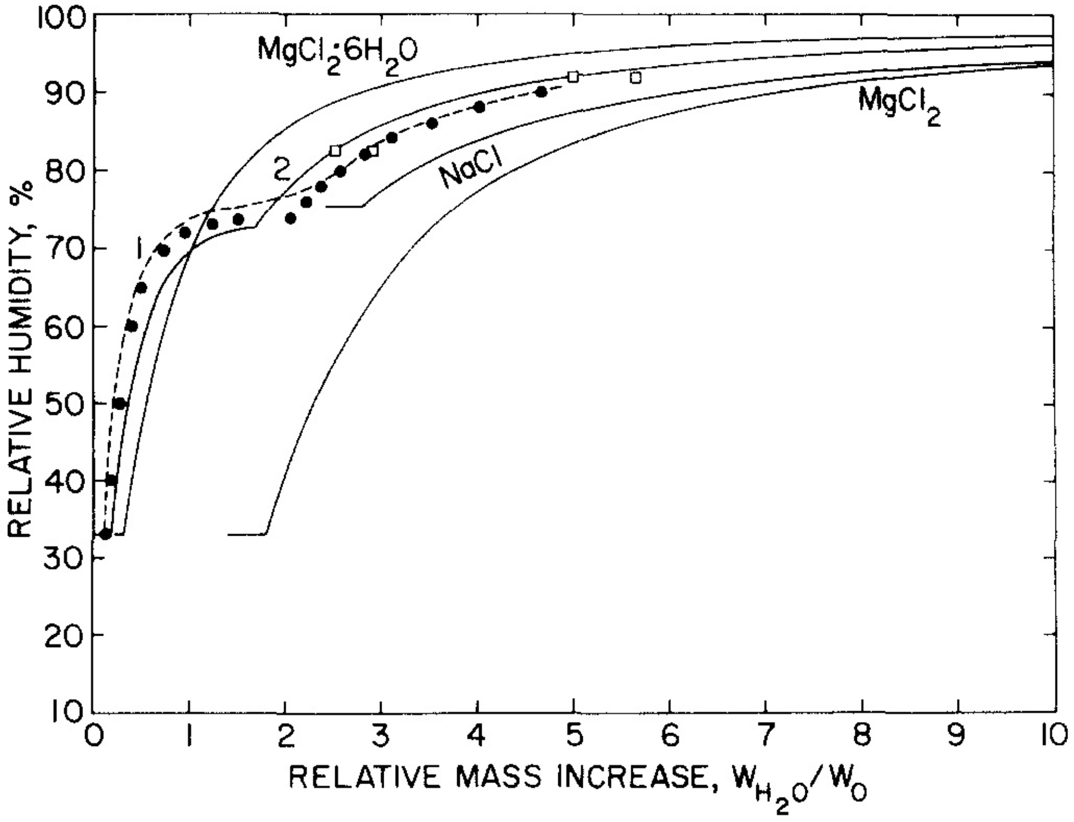


flame soot surface chemical composition *(Smith et al., 1989)*

3.4.2.5 Water

Particulate matter water uptake:

Growth of particulate matter containing inorganic salts is smooth (unlike for pure salts)



(Tang, 1976; Winkler & Junge, 1972)

dt: Liqueszenzfeuchte

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

Particulate matter provides an aqueous phase: Overview trace species concentrations

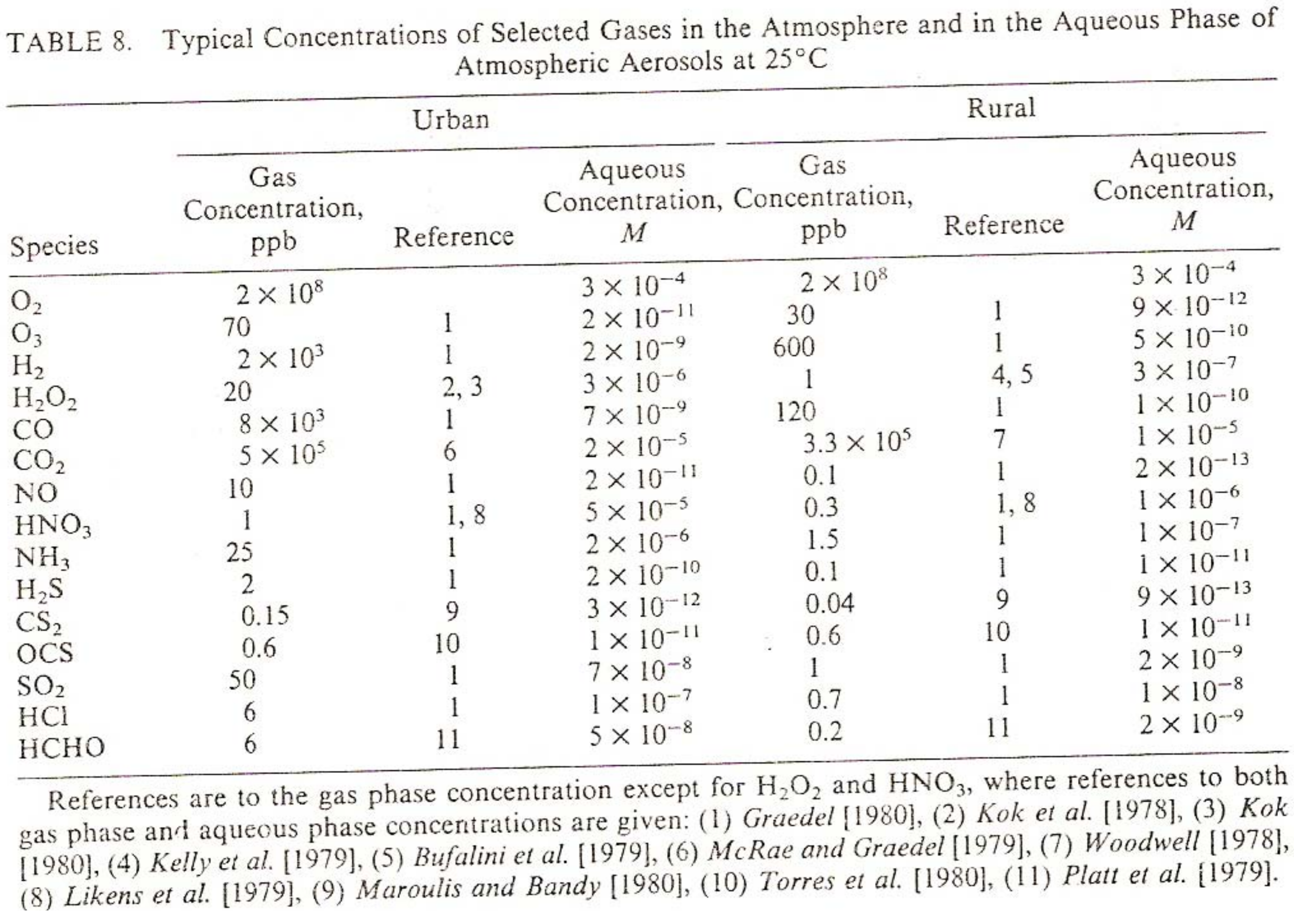


TABLE 8. Typical Concentrations of Selected Gases in the Atmosphere and in the Aqueous Phase of Atmospheric Aerosols at 25°C

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

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

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

(Graedel & Weschler, 1981)

3.4.3 Heterogeneous chemistry in atmospheric aerosols

- Particulate products are formed from gaseous precursors in surface or bulk (aqueous) reactions
- Some products volatilise back into the gas-phase (e.g. reactions in polar stratospheric clouds)
- Rate laws are complex: series of reaction steps including mass transfer between phases
- The diversity of heterogeneous chemistry is enormous due to the particles‘ chemical composition and surface properties, but because of $V_{part}/V < 10^{-10}$ reactions need to be fast to make a difference for the multiphase system (aerosol)

3.4.3.1 Secondary inorganic aerosol (SIA)

3.4.3.1.1 Condensation and thermodynamic equilibrium composition

$$HNO_3 \overset{\text{condensation/volatilization}}{=} HNO_{3\ ads}$$

Strong temperature dependence of the N(V) phase equilibrium

$NH_3 + HNO_3 = NH_4NO_3\,(s)$

for rh < $rh_{D:}$

$p_{NH3} * p_{HNO3} =$ 0.12 ppbv² (278 K),
2.0 ppbv² (288 K),
28 ppbv² (298 K)

Humidity dependence:

(Stelson & Seinfeld, 1982; Stelson et al., 1984)

$NH_3 + HNO_3 = NH_4{}^+{}_{aqu} + NO_3{}^-{}_{aqu}$

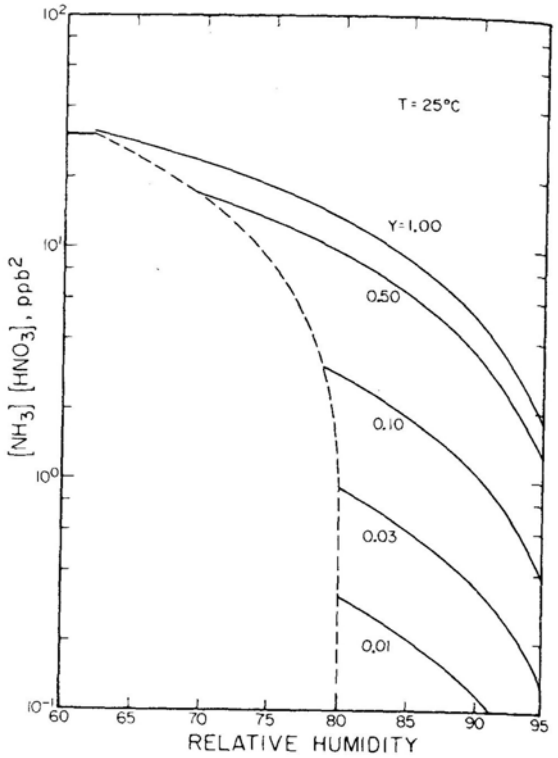


Fig. 2. The effect of $(NH_4)_2SO_4$ on the relative humidity dependence of the NH_4NO_3 dissociation constant.

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

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

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

Thermodynamic equilibrium composition

→ Predict gas-particle partitioning of ‚volatile‘ inorganic species (i.e., NH_3, HNO_3, NH_4NO_3, H_2O), i.e. including the water content.
Needed: Knowledge of phase diagrams
Treated as aqueous solution thermodynamics, with equilibrium water activity, a_w, equal to the relative humidity. Approximation methods exist for $a_w = f(a_{\text{pure salts}}, I)$, with I = ionic strength. *(Stelson & Seinfeld, 1982; Stelson et al., 1984)*

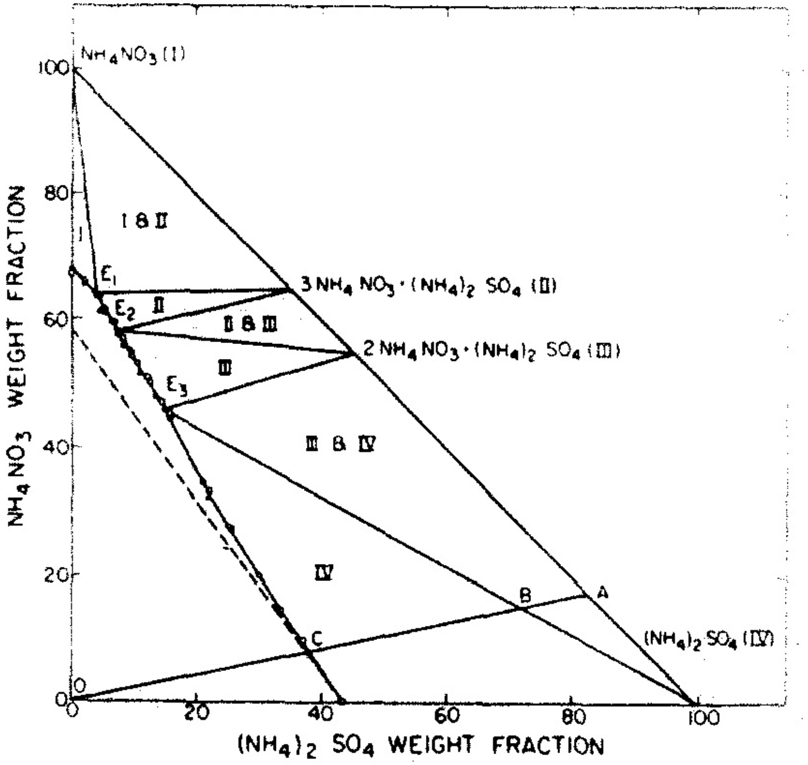


Fig. 1. NH_4NO_3–$(NH_4)_2SO_4$–H_2O phase diagram at 25 °C. □, Emons and Hahn (1970); ○, +, Δ, Silcock (1979).

Activity = activity coefficient * concentration

$\mathbf{a_i = \gamma_i \, c_i}$
$\gamma_i = 1$ for diluted (ideal) solutions

Relaxation to equilibrium

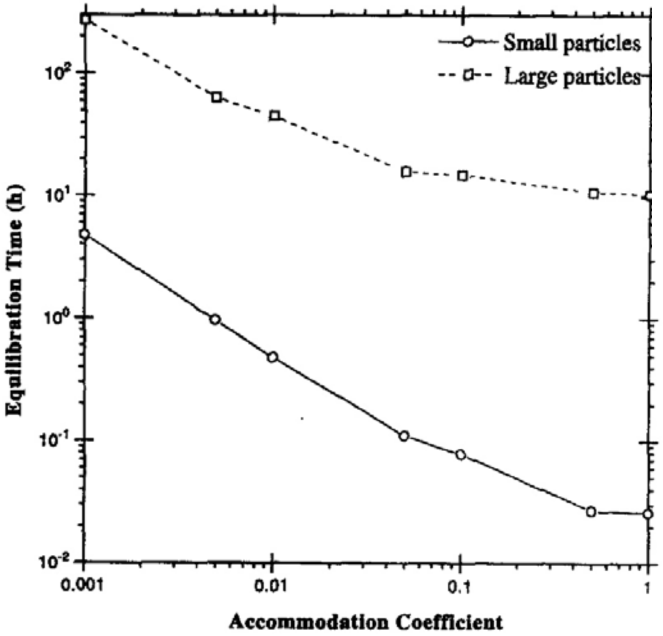
$\tau = f(p_i(T), N_{part}(D), S_{part}/V, \lambda_i, \alpha_i)$

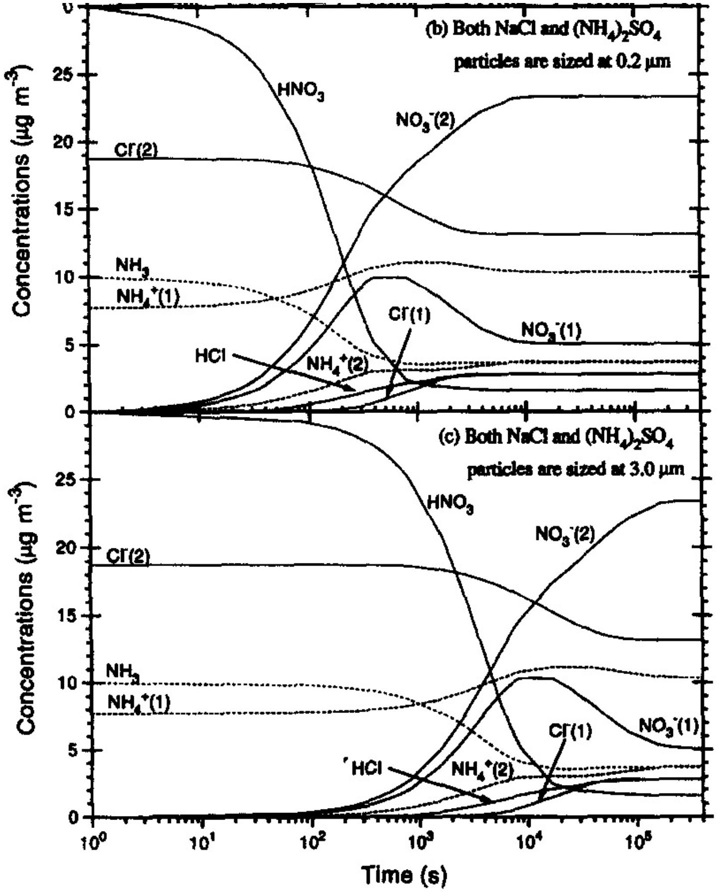
mass flux of gaseous i to single particle

$F_i = 2\pi D_{i\,part} D_{i\,g} (c_{i\,aqu} - c_{i\,g})/(2\lambda_i/\alpha_i D_{i\,part} - 1)$

(with air mean free path λ, accommodation coefficient α_i)

Ammonium salts in the gas and particulate phases are not always in equilibrium, especially under low aerosol loading, cooler conditions, low α_i and for large D *(Wexler & Seinfeld, 1990; Meng & Seinfeld, 1996)*.

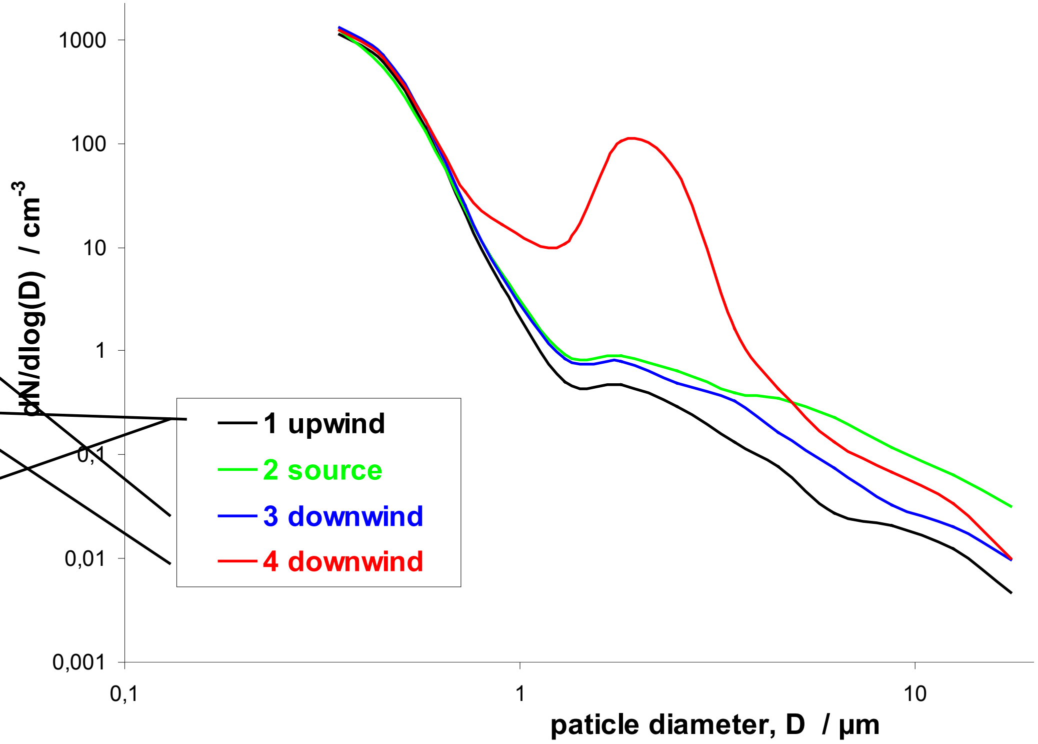




Particel sizes: (1) = 0.2, (2) = 1.5 µm (b) or 3.0 µm (c), 80% rh

SIA formation can be very fast:

- super-µm plume 2-5 min (< 300 m) downwind of open liquid manure pits and other more or less open sources (animal houses, feed stocks), around 2 µm, $\Delta n_{1\text{-}4\mu m} = 14\text{-}21\ cm^{-3}$
- sub-µm size range: $\Delta n_{CN} = +(8\text{-}18)*10^3\ cm^{-3}$
- under humid conditions (r.h. = 90%, T = 6-9°C; $rh \approx rh_D((NH_4)_2SO_4)$ and $rh > rh_D(NH_4NO_3)$)



(Lammel et al., 2004)

3.4.3.1.2 SIA formation through radical or ionic reactions

Examples

- SO_2 oxidation in marine air

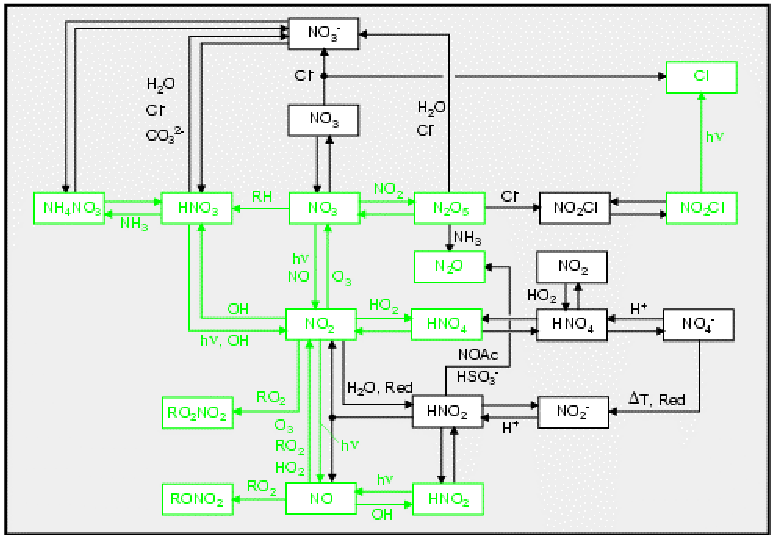
$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$$

- formation of nitric acid, nitrogen oxides chemistry

$$HNO_3 + NaCl\,(s) \rightarrow NaNO_3\,(s) + HCl$$

$$N_2O_5 + 2\,H_2O(l) \rightarrow 2\,NO_3^-{}_{(aqu)} + 2\,H_3O^+{}_{(aqu)}$$

$$NO_2 + H_2O_{ads.} \xrightarrow{<NO_2>} HNO_2 + HNO_{3\,ads.}$$



3.4.3.1.3 SIA formation through catalysis by particle surfaces

on soot:

$$SO_2 + H_2O + O_2 \xrightarrow{\text{<soot>}} 2\,HSO^{-}_{4\ \text{aqu}}$$

“autoxidation“ reactions, heavy metal ions (if present) catalyze mostly more than soot

$$NO_3 \xrightarrow{\text{<soot>}} NO$$

(1) $$NO_2 \xrightarrow{\text{<soot>}} HNO_2$$

(2) $$2\,HNO_2 \xrightarrow{\text{<soot>}} H_2O + NO + NO_{2\ \text{ads.}}$$

NO/HNO$_2$ yield depending on fuel/O$_2$ ratio upon soot generation

in the presence of heavy metals:

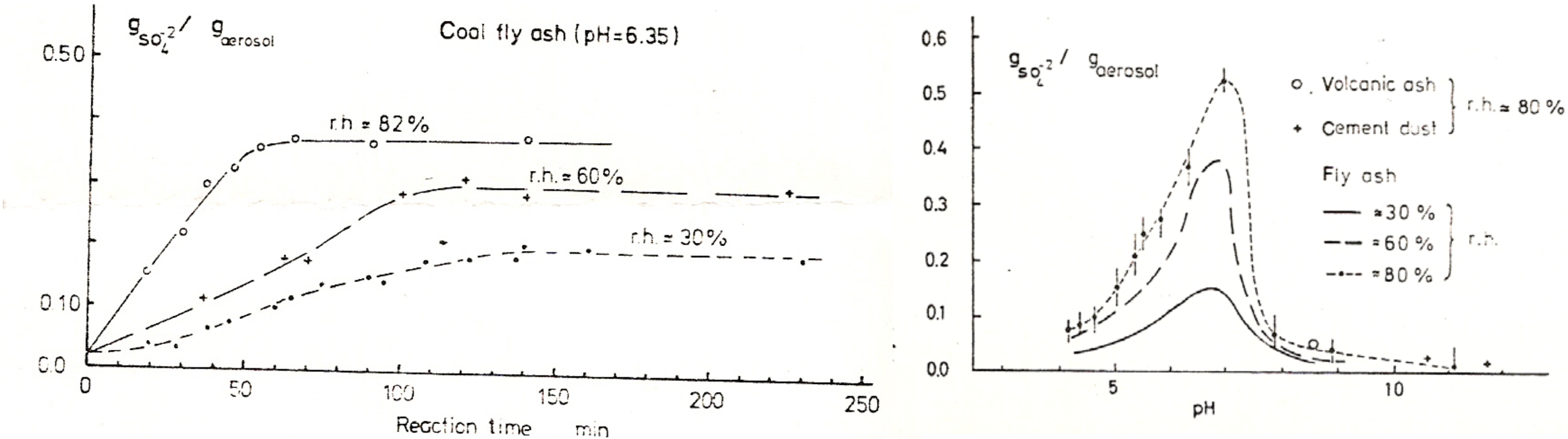
similar reactions, synergisms with action of soot → fly ash

on fly ash, volcanic ash, cement:

$$SO_2 + H_2O + O_2 \xrightarrow{\text{<particle>}} 2\ HSO_{4\ aqu}^{-}$$

- yield strongly dependent on particle type (composition, pH and morphology) and humidity
- surface coverage by reaction products inhibits reaction:

$$dc_{S(VI)}/dt = k^{het}\ c_{SO2}^{a}\ (V_{part}/V)\ [1 - c_{S(VI)}(t)/c_{S(VI)}^{\infty}]^2 \qquad a = 0.5\text{-}0.8$$



(Dlugi & Jordan, 1982)

- Surface reaction kinetics of organics on suspended particulate matter depends on the surface chemical properties, strongly on the availability of heavy metal ions and soot *(Judeikis et al., 1979; Dlugi & Jordan, 1982; besides others)*
- Significant uncertainties with regard to yields result, in particular in urban air and on small spatial scales

3.4.3.1.4 SIA formation through homogeneous nucleation

Def.: The formation of clusters of molecules which are large enough to undergo condensational growth subsequently (so-called critical clusters, typically consisting of 20-200 molecules) is called homogeneous nucleation.*

See textbooks on aerosol chemistry and physics, e.g. Seinfeld & Pandis, 2006, for details

$$H_2SO_4{*}H_2O + n\ NH_3 + m\ H_2O \xrightarrow{\text{(Nucleation)}} \text{droplet} \rightarrow (NH_4)_2SO_4$$

(drying to aerosol particle)

→ mostly, but not always ternary (i.e., 3 different gas molecules involved; *Napari et al., 2002)*

→ Neutral molecules, while the contribution from ion-induction is minor in most ambient cases *(Kulmala et al., 2007)*

* In contrast, te growth of particles of sub-µm size to cloud droplets is called heterogeneous nucleation.

3.4.3.2 Secondary organic aerosol (SOA)

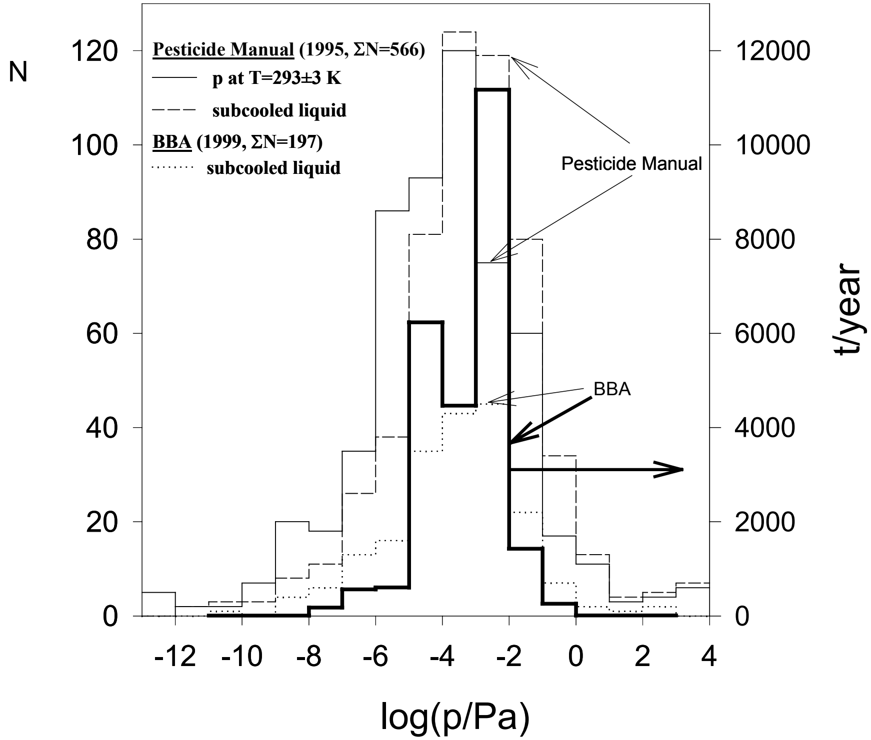
3.4.3.2.1 SOA formation through condensation of semivolatile organic compounds (SOC)

SOC ↔ $p_{sat} = 10^{-6} - 10^{-2}$ Pa

Polar low-molecular weight and/or mid to high-molecular weight organics

1. Oxygenated hydrocarbons, e.g. dicarboxylic acids, hydroxyaldehydes and ketones
2. Polycyclic aromatic hydrocarbons (PAH)
3. Pesticides (chlorinated cyclic aliphatics and aromatics, amides, triazines, phosphoric acid esters, ...)

Example:
Number distribution of pesticide saturated vapour pressures registered in Germany *(Franklin et al., 2000)*



3.4.4 Gas-particle partitioning of organics

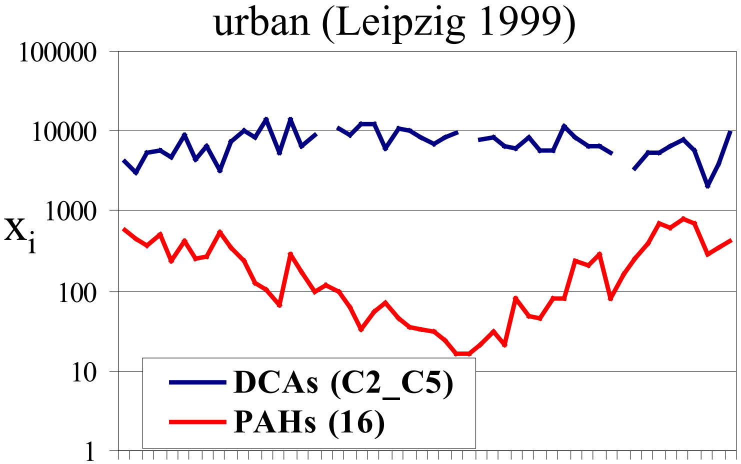
Definitions:

Fraction sorbed to aerosol particles, $\theta := c_{part}/(c_{gas} + c_{part}) = [1 + 1/(K_p\, c_{TSP})]^{-1}$

Particle-gas partitioning coefficient $K_p = c_{i(part)}/(c_{i(g)}\, c_{TSP})[m^3/\mu g]$

Condensation under low temperatures →
may be reflected as seasonal variation of gas-particle partitioning (minimum θ in summer).
Example: Polycyclic aromatic hydrocarbons (PAHs)

Caution: A lack of seasonality of SOC's concentration may be due to conversion of the SOC into a non-volatile species.
Example: Dicarboxylic acids (DCAs) dissociate into, typically, the mono-anion under ambient pHs. Ions are non-volatile.



(unpubl., courtesy of Müller/IfT, Lammel/MPIM)

Gas-particle partitioning – Which molecular processes contribute ?

3.4.4.1 Condensation

1. Adsorption to any type of surface (unspecific)

Empiric finding (Junge, 1977): $\theta = c\,(S/V) \,/\, [c\,(S/V) + p]$,

$c \approx 17.2$ Pa cm related to heat of desorption from particle surface, (S/V) [cm^{-1}], p [Pa], enthalpy of vapourisation ΔH_{vap} [$\mathrm{J\ mol}^{-1}$],

$p(T) = p_0 \exp[(-\Delta H_{vap}/R)(1/T - 1/T_0)]$ (Clausius-Clapeyron)

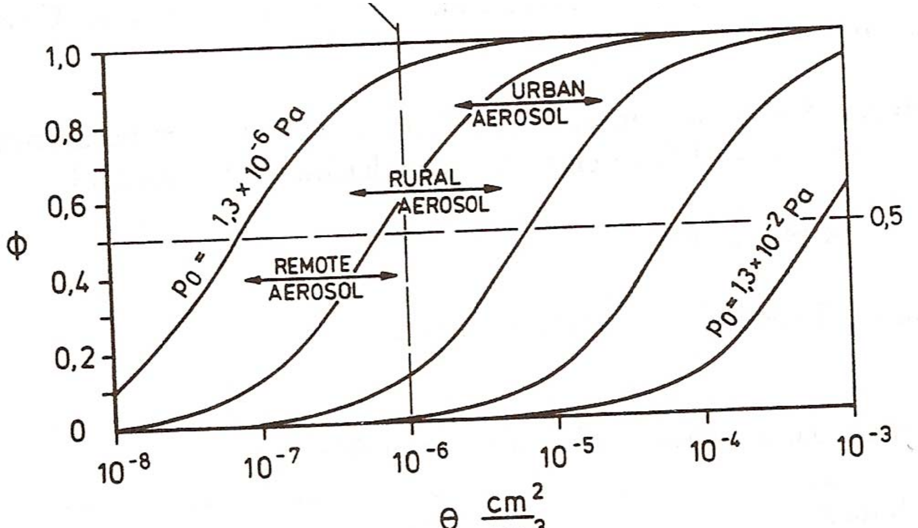
p_0 saturation vapour pressure at T_0

p should be saturation vapour pressure over sub-cooled liquid rather than solid, because heat of crystallization should not interfere *(Pankow, 1987)*

→ ‚Junge-Pankow‘:

$\theta = c\,(S/V) / [c\,(S/V) + p\, e^{6.8\,(T\_melt - T)/T}]$

example: θ_{PAH} should double per 4.9 K

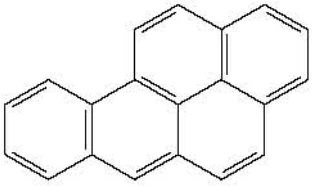


Model predicted (ECHAM-HAM; *Sehili &Lammel, 2007*) spatial and seasonal variations of ground-level θ_{PAH} due to adsorption only:

$$\theta = c\,(S/V) / [c\,(S/V) + p\,e^{6.8\,(T\_melt - T)/T}]$$

Benzo[a]-pyrene

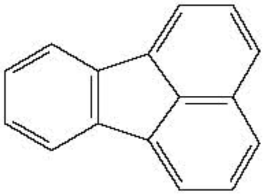
$p_{298K} = 7 \times 10^{-7}$ Pa



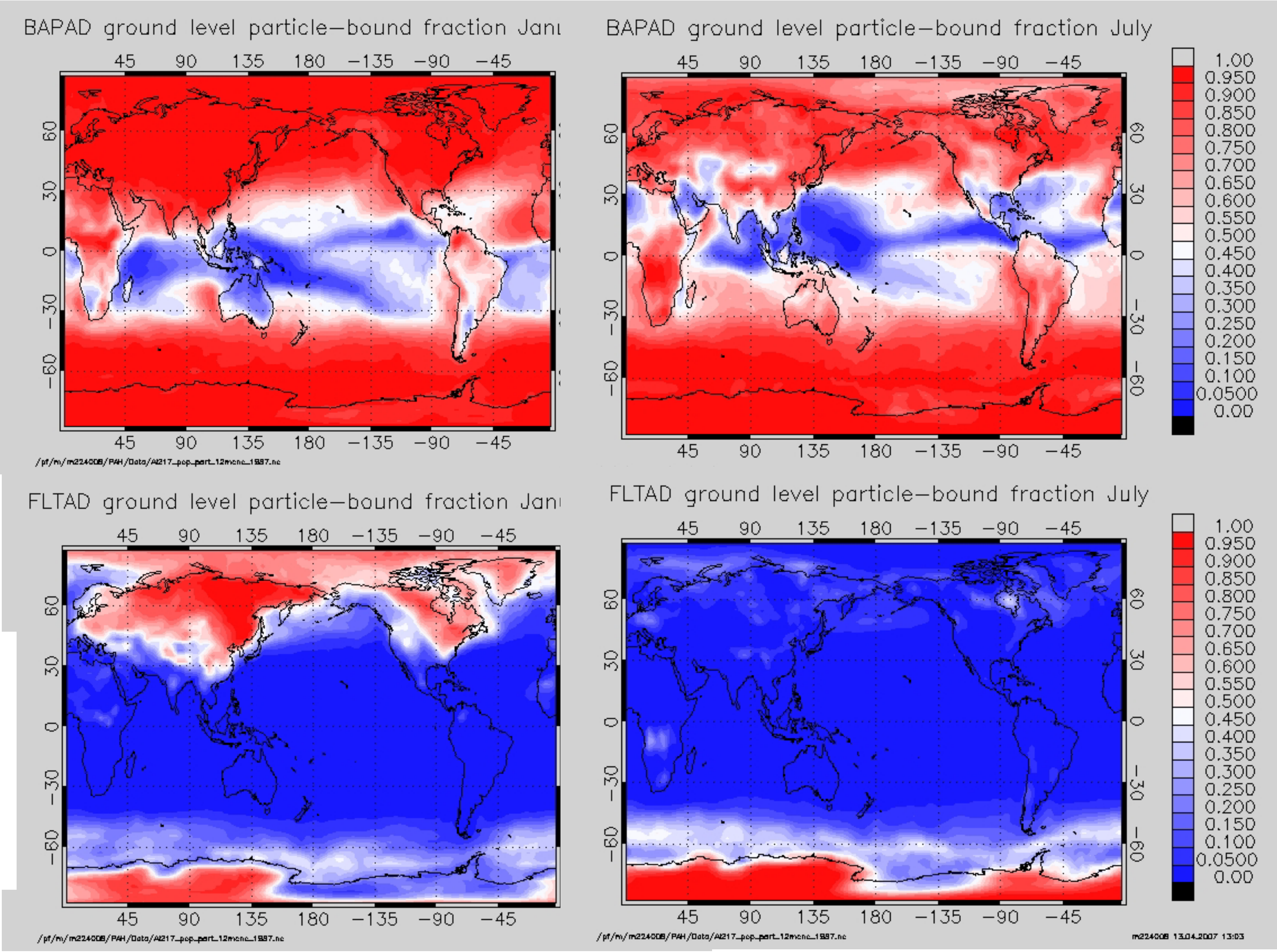
Benzo(a)pyren ($C_{20}H_{12}$)*

Fluoranthene

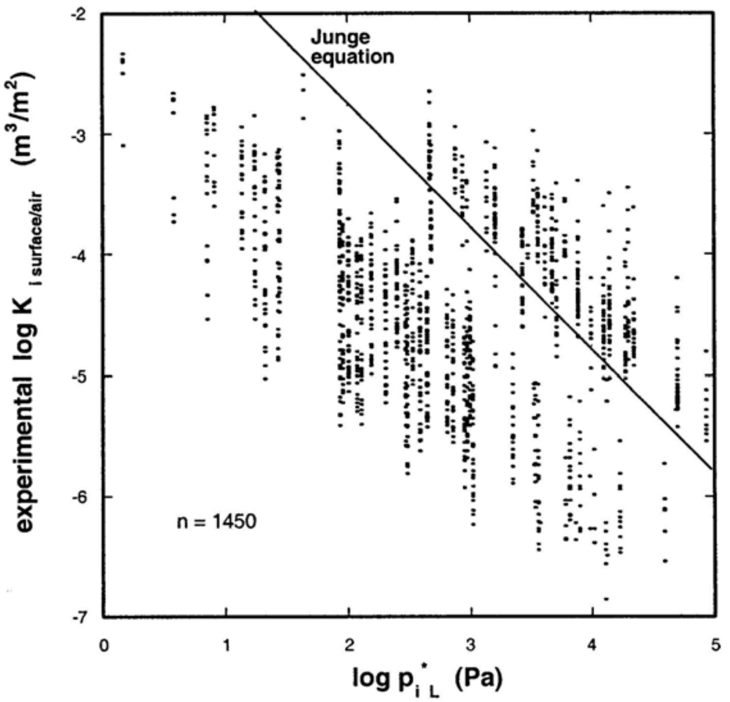
$p_{298K} = 2 \times 10^{-3}$ Pa



Fluoranthen ($C_{16}H_{10}$)*



PAH (number of rings)	p_{sat} (298 K)	Urban mean	$\theta = c_{part}/c_{total}$			
	Ng m^{-3}	ng m^{-3}	Winter	Spring	Summer	Winter
Napthalene (2)	6.7 x 10^8		0 %			0.0 %
Acenapthylene (3)	8.6 x 10^6	2.1				
Acenapthene (3)	2.7 x 10^7	1.1				
Fluorene (3)	7.4 x 10^6	5.1				
Anthracene (3)	6.2 x 10^4	1.4				
Phenanthrene (3)	0.015 Pa = 1.4 x 10^6	20				
Fluoranthene (4)	6.7e-4 Pa = 1.3x10^5	4.8				
Pyrene (4)	6e-4 Pa =3.6 x 10^4	4.0				
Benz[a]anthracene (4)	1.9 x 10^2	0.49				
Chrysene (4)	8.3e-7 Pa = 1.3 x 10^2	1.0				
Benzo[b]fluoranthene(5)	1.0 x 10^2	0.63				
Benzo[a]pyrene (5)	7e-7 Pa = 5.4	0.29				
Perylene (5)	1.9					
Dibenz[ac]anthracene (5)	0.64	0.08				
Dibenz[ah]anthracene (5)	0.55	0.08				
Benzo[ghi]perylene (6)	1.1	0.93	100 %	100%	100%	
Coronene (7)	0.035		100 %	100%	100%	



(EC-PAHWG, 2001)

Gas-particle partitioning – Which molecular processes contribute ?

3.4.4.2 Absorption

If the substance is significantly lipophilic, then absorption by particulate organic matter may occur (dissolution in an organic phase).

$\log K_p = 0.55 \log K_{oa} - 8.23$

with:

$K_p = c_{i(part)}/(c_{i(g)}\ c_{TSP})[m^3/\mu g]$ particle-gas partitioning coefficient

$K_{oa} = \ = c_{i(octanol)}/c_{i(air)}$ [ ] octanol-air partitioning coefficient

$\theta = [1 + 1/(K_p\ c_{TSP})]^{-1}$

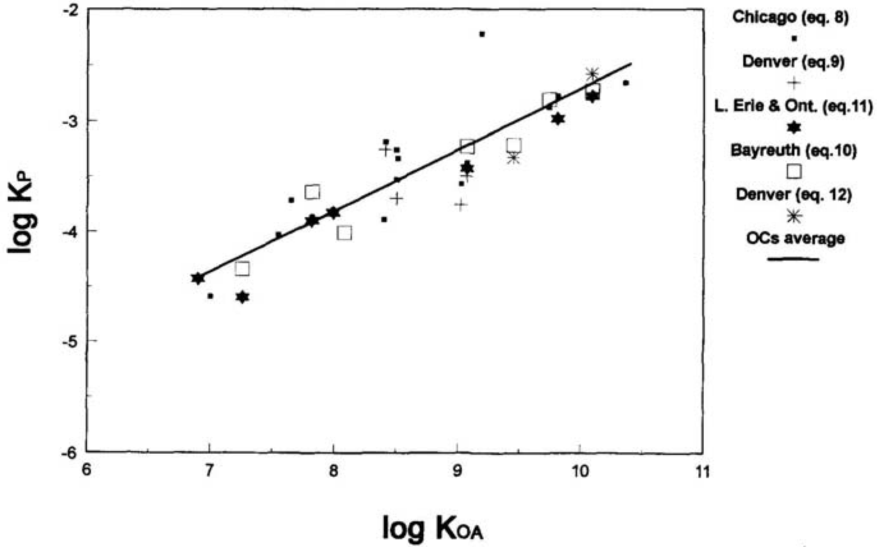
c_{TSP} = total suspended particulate matter concentration [$\mu g\ m^{-3}$]

examples:

polychlorinated biphenyls (PCB),

organochlorine pesticides (OCP)

$\theta_{DDT} = 0.1\text{-}0.3$ *(Kaupp & Umlauf, 1992)*



(Finizio et al. 1997; Harner & Bidleman, 1998)

Fig. 2. Plot of log K_P ($m^3\ \mu g^{-1}$) vs log K_{OA} for OC compounds (PCBs and OC pesticides).

Gas-particle partitioning – Which molecular processes contribute ?

3.4.4.3 Adsorption

to soot

PAHs: Absorption in POM + adsorption to soot *(Lohmann & Lammel, 2004)*:

$\theta = [1 + 1/(K_p\, c_{TSP})]^{-1}$

$\log K_p = 10^{-12}\, [K_{oa}\, f_{OM}/\rho_{oct} + K_{soot\text{-}air}\, f_{BC} S_{BC}/(\rho_{BC} S_{soot})]$

With:

$\log K_p = 0.55 \log K_{oa} - 8.23$; with:

$K_p = c_{i(part)}/(c_{i(g)}\, c_{TSP})$[m³/µg] particle-gas partitioning coefficient

c_{TSP} = total suspended particulate matter concentration (µg m^{-3})

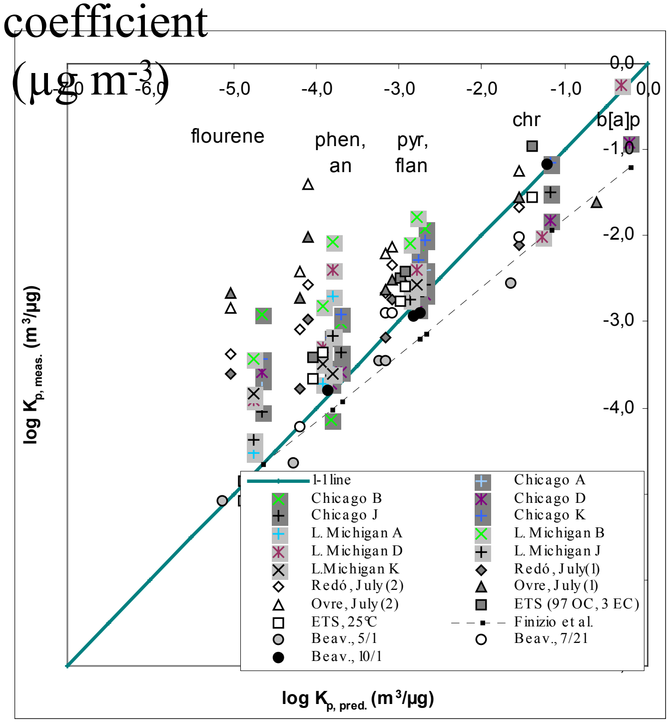
f_{BC}, f_{OM} = mass fractions of soot and POM, respectively in TSP

S_{BC}, S_{soot} = surface of black carbon and soot (cm²)

ρ_{oct} = density of octanol

$K_{soot\text{-}air}$ = diesel soot-air partitioning coefficient (-)

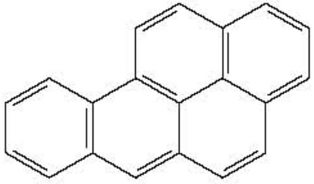
K_{oa} = octanol-air partitioning coefficient (-)



Model predicted (ECHAM-HAM; *Sehili &Lammel, 2007*) spatial and seasonal variations of ground-level θ_{PAH} due to absorption in POM + adsorption to soot:

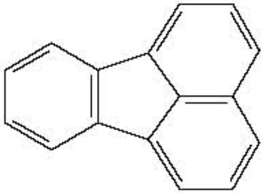
$$\theta = [1 + 1/(K_p\, c_{TSP})]^{-1};\ \log K_p = 10^{-12}\, [K_{oa}\, f_{OM}/\rho_{oct} + K_{soot\text{-}air}\, f_{BC} S_{BC}/(\rho_{BC} S_{soot})]$$

Benzo[a]-pyrene

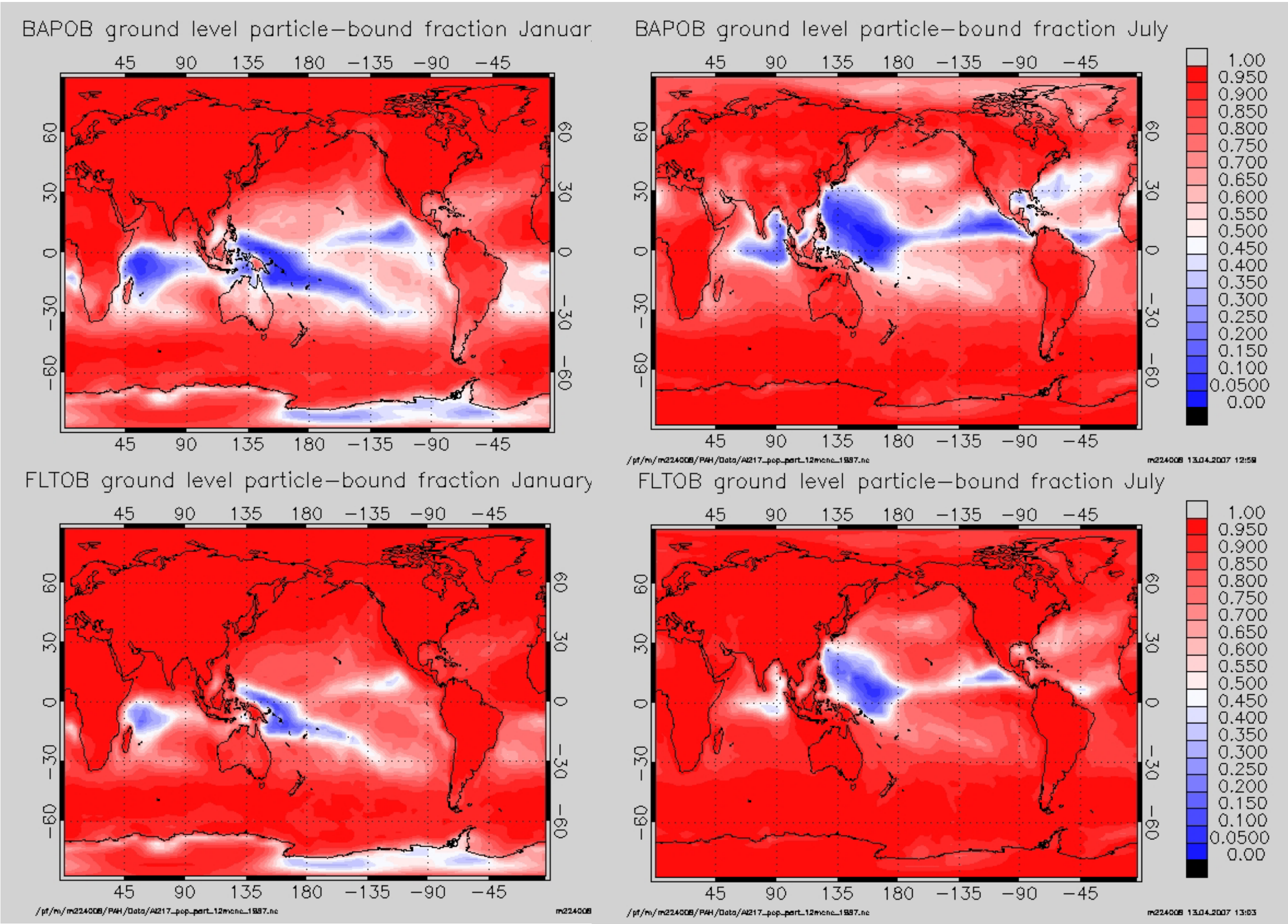


Benzo(a)pyren ($C_{20}H_{12}$)*

Fluor-anthene



Fluoranthen ($C_{16}H_{10}$)*



Gas-particle partitioning – Which molecular processes contribute ?

Common: double-logarithmic correlations, 1-parameter linear free-energy relationships (LFER), e.g. $\log K_p = 0.55 \log K_{oa} - 8.23$

→ *Can only predict compound variability <u>within</u> a substance class.*

→ *Provides no means to account for variability between classes or different organic phases.*

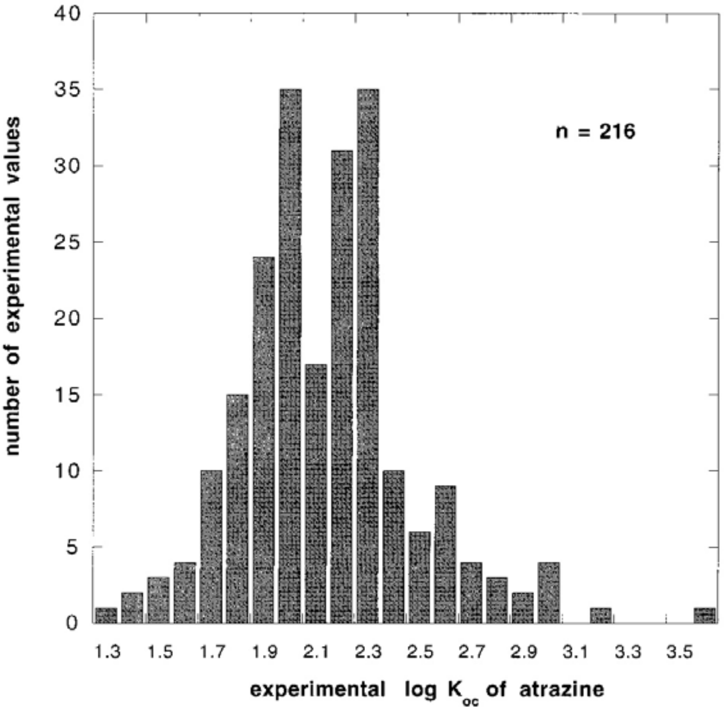


FIGURE 3. Variability of experimental K_{oc}-values of atrazine for different soils and sediments. (Note: this also includes the variance coming from different research groups and different experimental protocols) (data compilation from (*63*)).

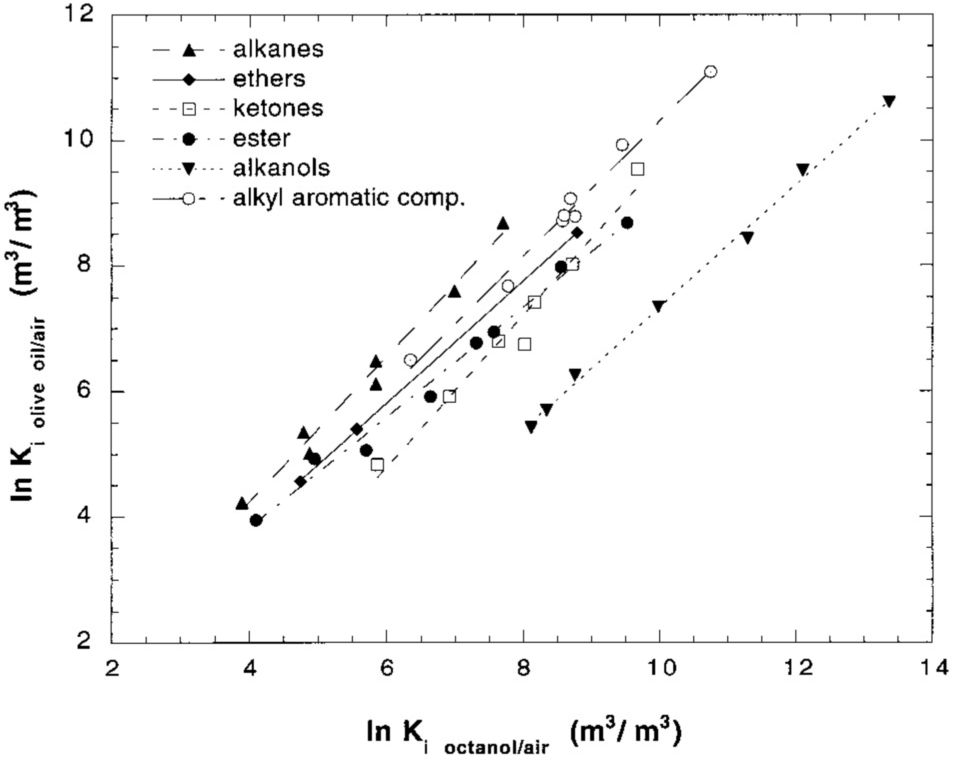


FIGURE 2. Plot of one-parameter LFERs between the logarithmic olive oil/air partition constant of different compound classes and the logarithmic octanol/air partition constant (25 °C, data for olive oil from ref *62* extrapolated from 37 to 25 °C; data for octanol/air partitioning were calculated from Henry's Law constants (*27*) and octanol/water partition constants (*22*)).

(Goss & Schwarzenbach, 1991)

3.4.4.4 Complete approach: poly-parameter linear free-energy relationship (LFER)

employing so-called Abraham parameters *(Abraham et al., 1991; Abraham, 1993):*

$$\ln K_{i\,12} = -(E^{vdW}_{12} + E^{H}_{12} + c)/RT$$

$$\log K_{i\,12} = a_{12} \bullet vdW_i + b_{12} \bullet HD_i + d_{12} \bullet HA_i + e_{12} \bullet V_i + c$$

With:

E^{vdW}_{12}, E^{H}_{12} =van der Waals and H bond component of intermolecular interaction of i

$K_{i\,12}$ = partitioning coefficient of i between phases 1and 2

vdW_i, HD_i, HA_i = variables describing van der Waals, H donor and H acceptor properties of i, respectively

a_{12} = difference between van der Waals properties of i in phases 1 and 2

b_{12} = difference between H-donor properties of i in phases 1 and 2

c = constant

d_{12} = difference between H-acceptor properties of i in phases 1 and 2

e_{12} = cohesive energy parameter (difference due to cavity formation in phases 1

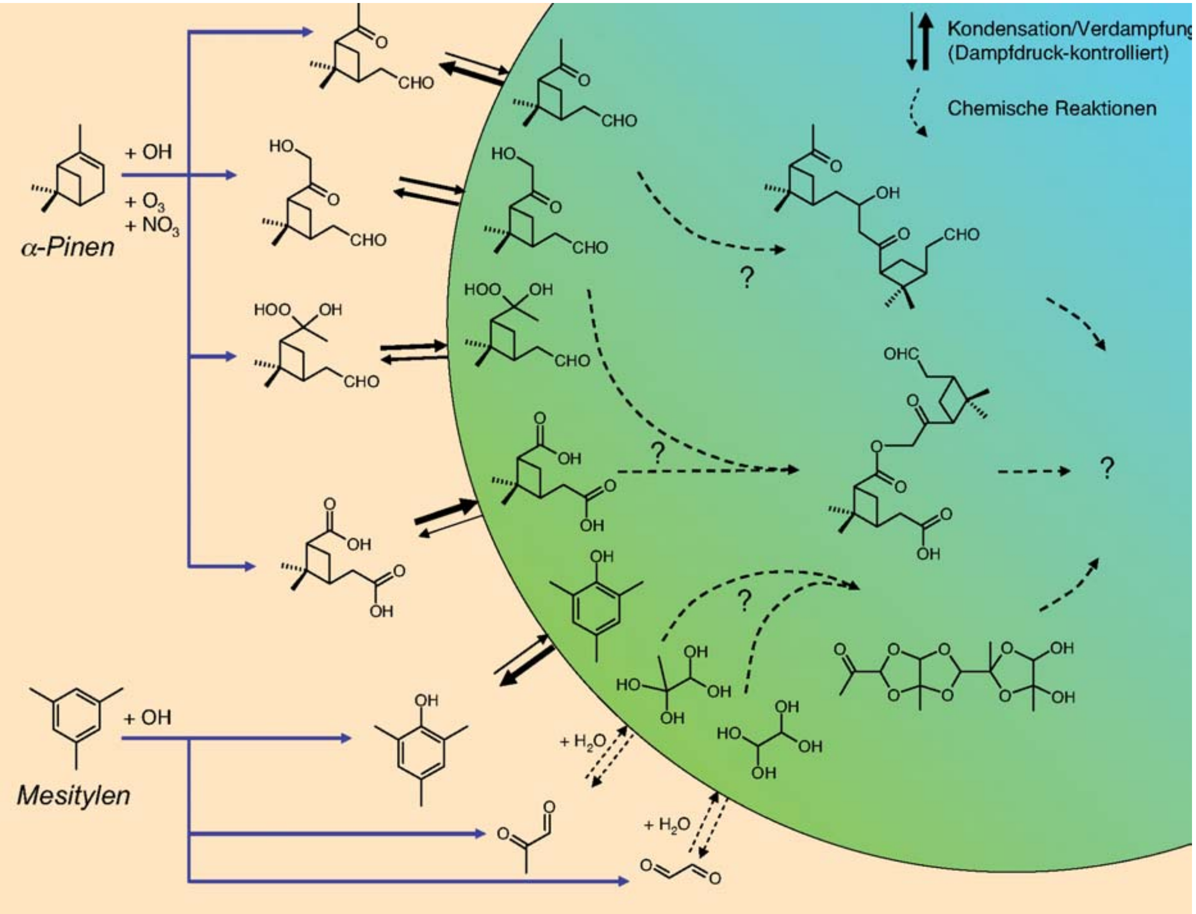
Abraham parameters to predict phase equilibria → *Goss, Crit. Rev. Environ. Sci. Technol. 34 (2004) 339-389; Roth et al., 2004; Ciani et al., 2005*

However, many relevant data are still lacking.

3.4.3.2.2 SOA formation through oxidation of volatile organic compounds (VOCs) to SOCs and subsequent condensation

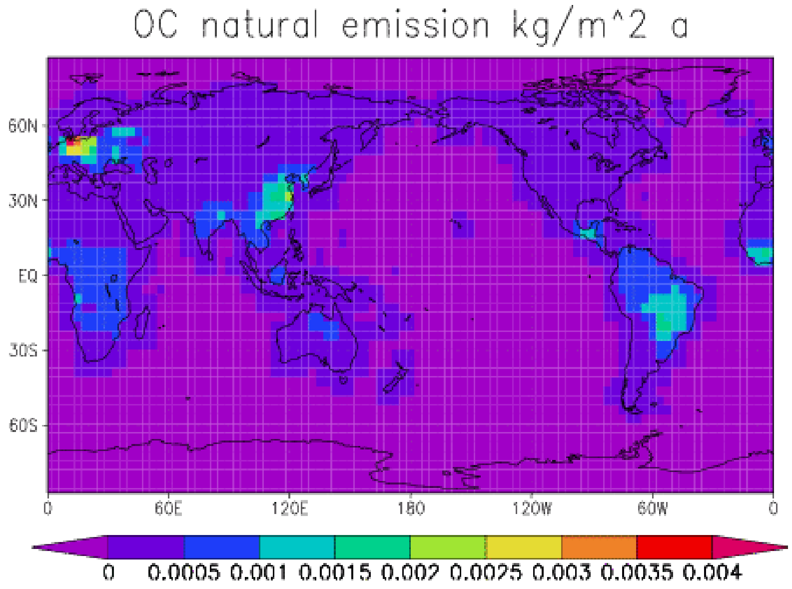
3.4.3.2.2 Aliphatic hydrocarbons

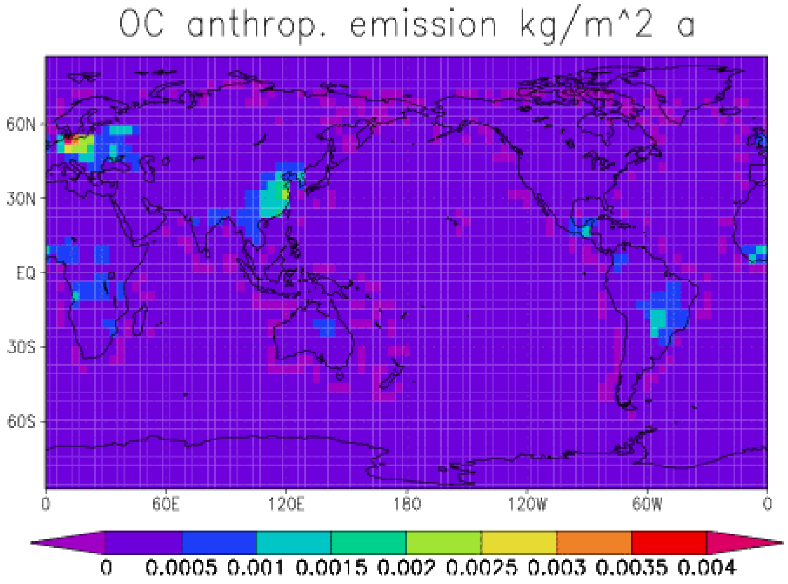
Example: oligomerisation of partly oxygenated natural (pinene) and anthropogenic (trimethylbenzene, mesitylene) VOCs

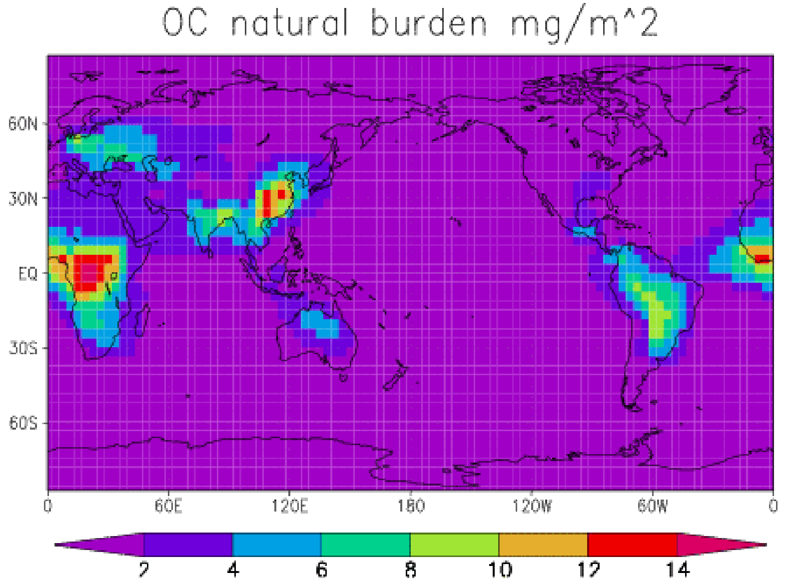


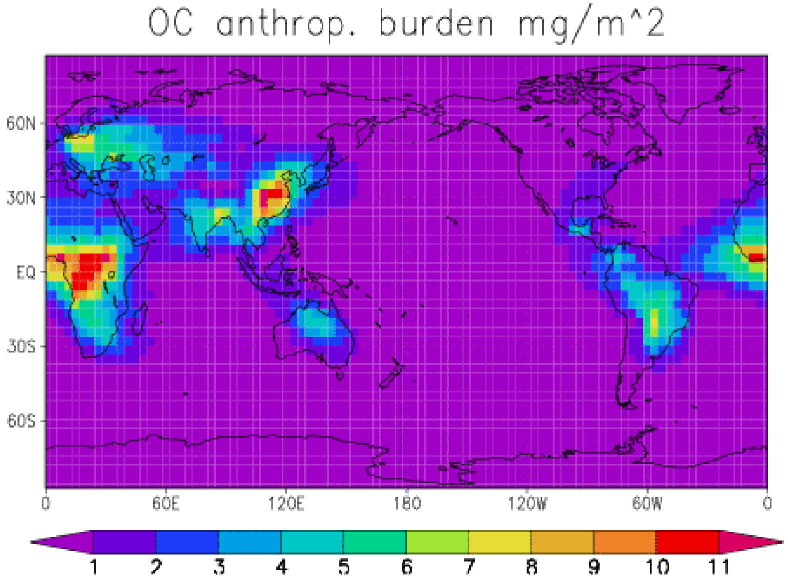
(Hoffmann et al., 2007)

Particulate Organic Matter - globally


OC natural emission kg/m^2 a


OC anthrop. emission kg/m^2 a


OC natural burden mg/m^2


OC anthrop. burden mg/m^2

3.4.3.2.2.2 Aromatic hydrocarbons

Example: di(2-ethylhexyl)phthalate

$\phi(C(O)OCH_2CH(CH_2CH_3)C_4H_9)_2 + OH\cdot_{aqu} \rightarrow$

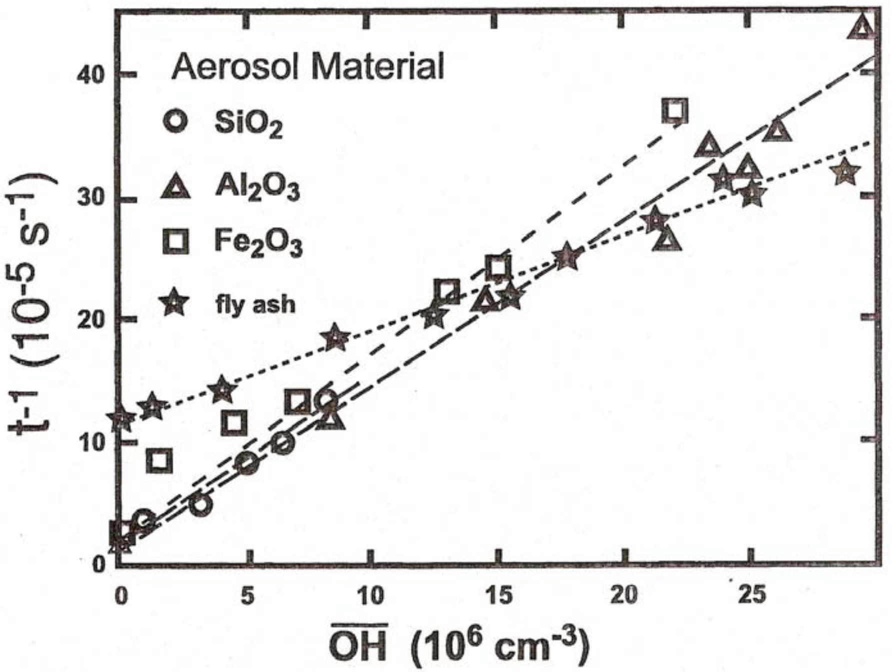


Figure 2-8 Decay rate of a monolayer of di(2-ethylhexyl)phthalate, adsorbed on various types of aerosols (SiO_2: Aerosil 200, DEGUSSA, Al_2O_3: type C, DEGUSSA, Fe_2O_3: Sicotram Orange, BASF) at various concentrations of OH in the smog chamber. Figure taken from Behnke et al. 1987c and reprinted with permission (©1987 Elsevier Science).

(Behnke et al., 1987)

- Surface reaction kinetics of organics on suspended particulate matter depends on surface chemical properties
- Significant uncertainties with regard to yields result

Polycyclic aromatic hydrocarbons (PAH)

Radical attack

$RH_{part} + OH\cdot_{part} \rightarrow R\cdot_{part} + H_2O$

$+ NO_3\cdot_{part} \rightarrow \quad + HNO_3$

in both gas-phase and particulate phases

Oxidation to oxyaromatics:

$RH + O_3 \rightarrow R(O)$

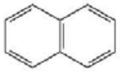
Nitration to nitroaromatics:

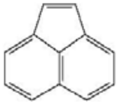
$RH + NO_2 \rightarrow RNO_2$

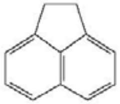
$+ HNO_3 \rightarrow RNO_2$

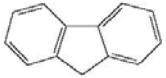
in both gas-phase and particulate phases

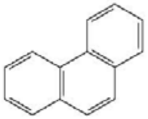
selection of PAHs, the 16 so-called EPA PAHs) RH =

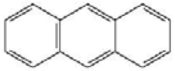

Naphthalin ($C_{10}H_8$)

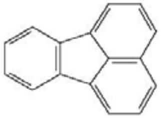

Acenaphtylen ($C_{12}H_8$)

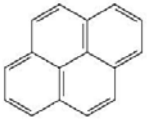

Acenaphthen ($C_{12}H_{10}$)

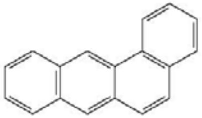

Fluoren ($C_{13}H_{10}$)

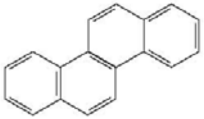

Phenanthren ($C_{14}H_{10}$)

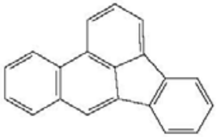

Anthracen ($C_{14}H_{10}$)

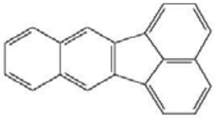

Fluoranthen ($C_{16}H_{10}$)*

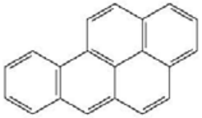

Pyren ($C_{16}H_{10}$)

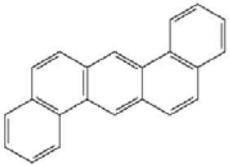

Benz(a)anthracen ($C_{18}H_{12}$)

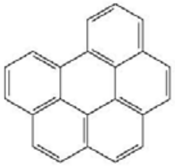

Chrysen ($C_{18}H_{12}$)

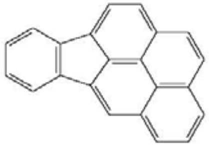

Benzo(b)fluoranthen ($C_{20}H_{12}$)*


Benzo(k)fluoranthen ($C_{20}H_{12}$)*


Benzo(a)pyren ($C_{20}H_{12}$)*


Dibenz(a,h)anthracen ($C_{22}H_{14}$)


Benzo(ghi)perylen ($C_{22}H_{12}$)*


Indeno(1,2,3-cd)pyren ($C_{22}H_{12}$)*

Polycyclic aromatic hydrocarbons (PAH) emitted with ash atmospheric lifetime (OH attack + photolysis)

	Classification of ash (a)							
PAH (number of rings)	“White group”		“Red group”		“Grey group”		“Black group”	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
Fluoranthene (4)	7.7 hr	23 hr	1.5 day	4.5 day	1.9 day	5.7 day	1.2 day	3.6 day
Pyrene (4)	3.7 hr	11 hr	17 hr	2.1 day	1.6 day	4.8 day	1.1 day	3.3 day
Benz[a]anthracene (4)	15 min	45 min	6.6 hr	20 hr	17 hr	2.1 day	1.1 day	3.3 day
Chrysene (4)	10 hr	1.3 day	2.6 day	7.8 day	2.3 day	6.9 day	1.0 day	3.0 day
Benzo[e]pyrene (5)	9.1 hr	1.1 day	2.4 day	7.2 day	2.5 day	7.5 day	1.1 day	3.3 day
Benzo[a]pyrene (5)	15 min	45 min	8.0 hr	1.0 day	18 hr	2.3 day	20 hr	2.5 day
Perylene (5)	24 min	1.2 hr	7.0 hr	21 hr	18 hr	2.3 day	21 hr	2.6 day
Indeno[123,cd]pyrene (6)	6.5 hr	20 hr	2.5 day	7.5 day	1.1 day	3.3 day	1.0 day	3.0 day
Benzo[ghi]perylene (6)	1.9 hr	5.7 hr	2.0 day	6.0 day	2.5 day	7.5 day	23 hr	2.9 day
Anthranthrene (6)	3.0 min	9.0 min	2.9 hr	8.7 hr	9.0 hr	1.1 day	23 hr	2.9 day
Coronene (7)	12.7 hr	38 hr	2.5	7.5	2.2	6.6	21 hr	2.6

k_{OH} and other rate constants of PAHs → *Finlayson-Pitts & Pitts, 1998*

However, laboratory-based rates are not necessarily representative for ambient air as particulate matter matrix in many cases obviously shields against radical attack.

European Commission, PAH Working Group, 2001