Impact of organic compounds on the aerosol properties modelled in atmospheric studies

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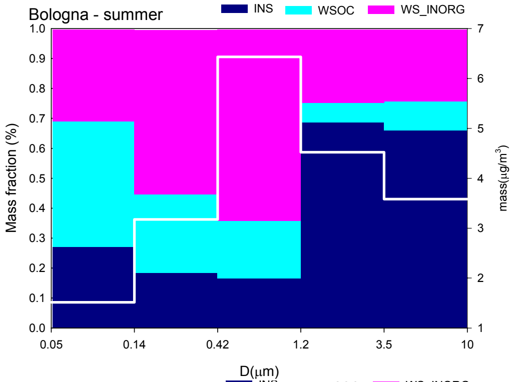
The aerosol properties required in atmospheric studies

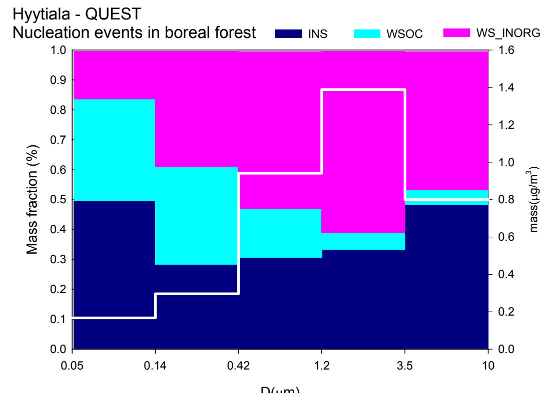
- **hygroscopic properties**
- **optical properties**
- **ability to form cloud condensation nuclei (CCN) and to growth as cloud droplets**

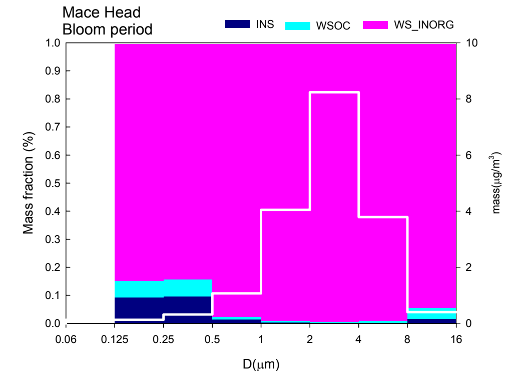
These properties are controlled by:

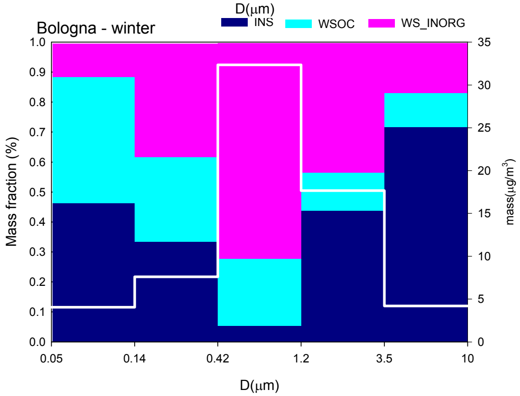
- chemical composition of aerosol, in particular the organic species, controls the number of soluble moles in solution, the surface tension of solution, deliquescence relative humidity (DRH) of aerosol particles, accommodation coefficient of water, refractive index of aerosol particles
- state of mixing of aerosol
- aerosol number size distribution

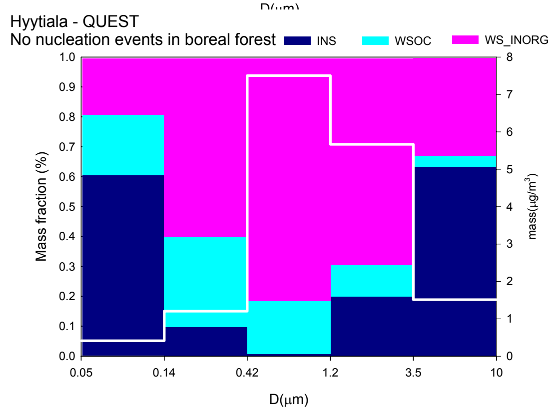
SIMPLIFIED REPRESENTATION OF THE SIZE SEGREGATED CHEMICAL COMPOSITION OF AEROSOL

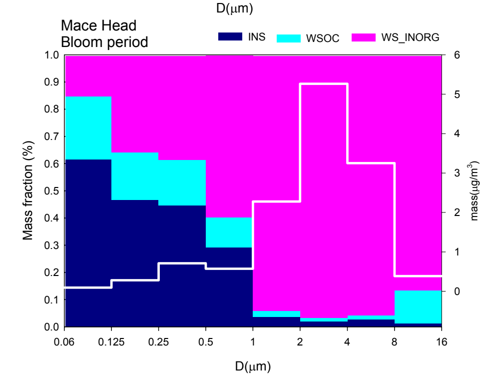


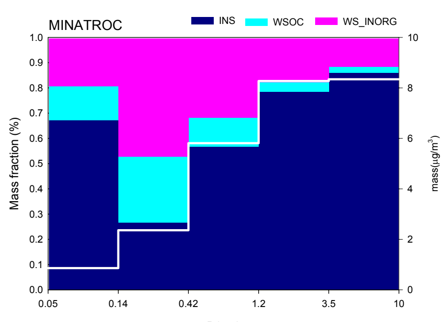


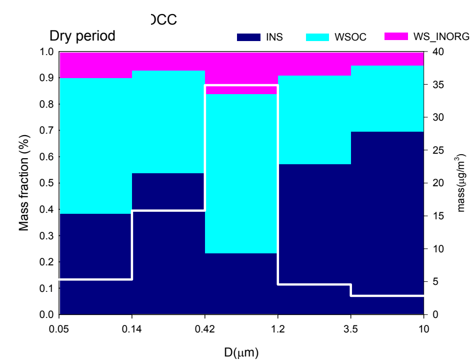












Water soluble organic compounds (WSOC) characterization

individual compound speciation accounts for less than 10% of total mass of organic carbon

•IC (ion chromatography), IEC(ion exclusion chromatography), IC-UV (ion chromatography ultraviolet detection)

•GC-MS(Gas Chromatography - mass spectrometry)

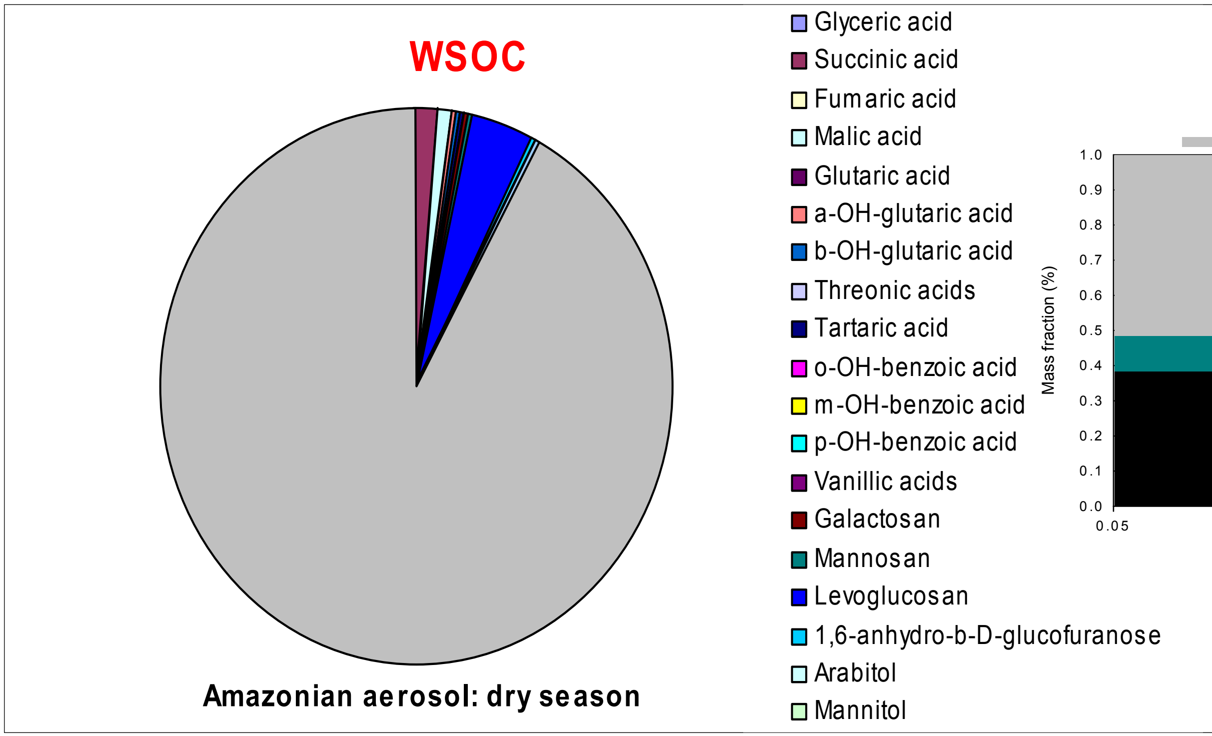
•HPLC-MS (High Performance Liquid Chromatography- mass spectrometry)

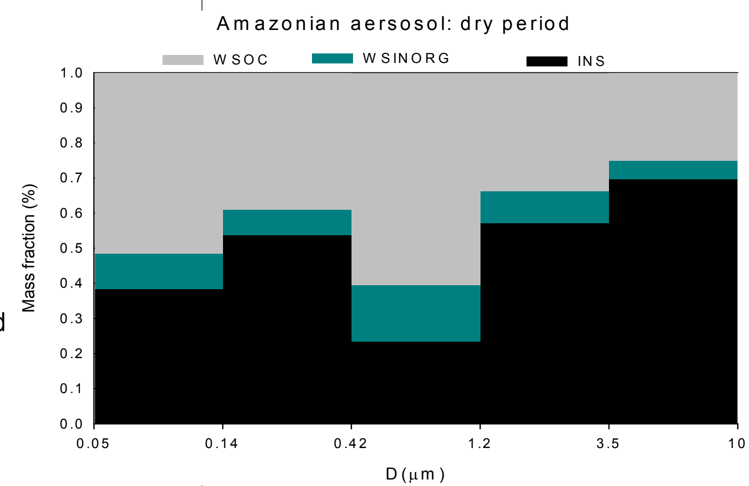
functional group analysis accounts on average for 80-90% of total mass of organic carbon

•separation in few main classes of compounds (chromatographic technique)

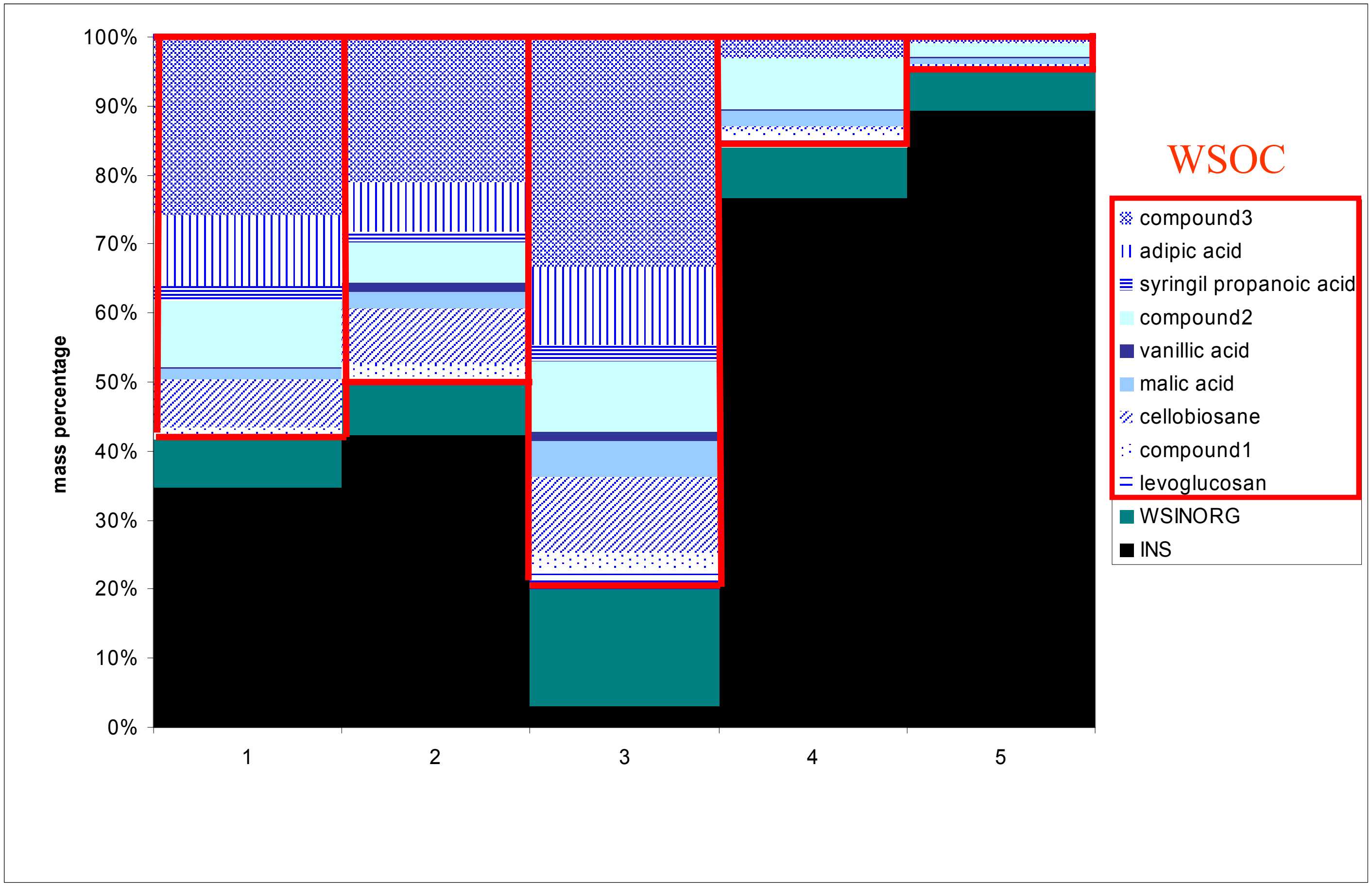
•nuclear magnetic resonance (NMR) spectroscopy or FTIR(Fourier Transform Infrared Spectroscopy)

WSOC: a complex reality…





…a simplification and a comprehensive characterization of WSOC: organic model compounds (Fuzzi et al., 2001)



WSOC

urban aerosol
marine aerosol
Amazonian aerosol
boreal forest aerosol

Organic model compounds open a way for more realistic laboratory and model studies on:

- aerosol – water interaction (aerosol growth and activation)

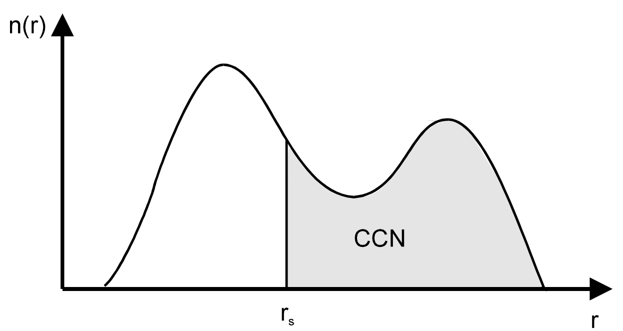
- aerosol – radiation interaction (optical properties)

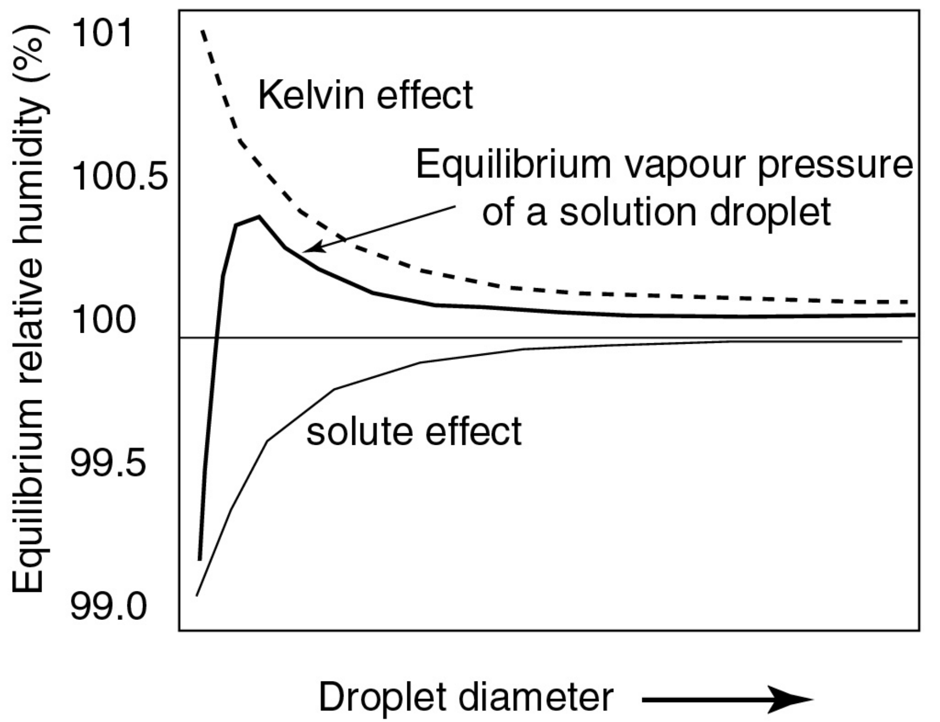
- aerosol – formation (nucleation) and interaction with gases

Kohler theory: hygroscopic growth and activation of aerosol

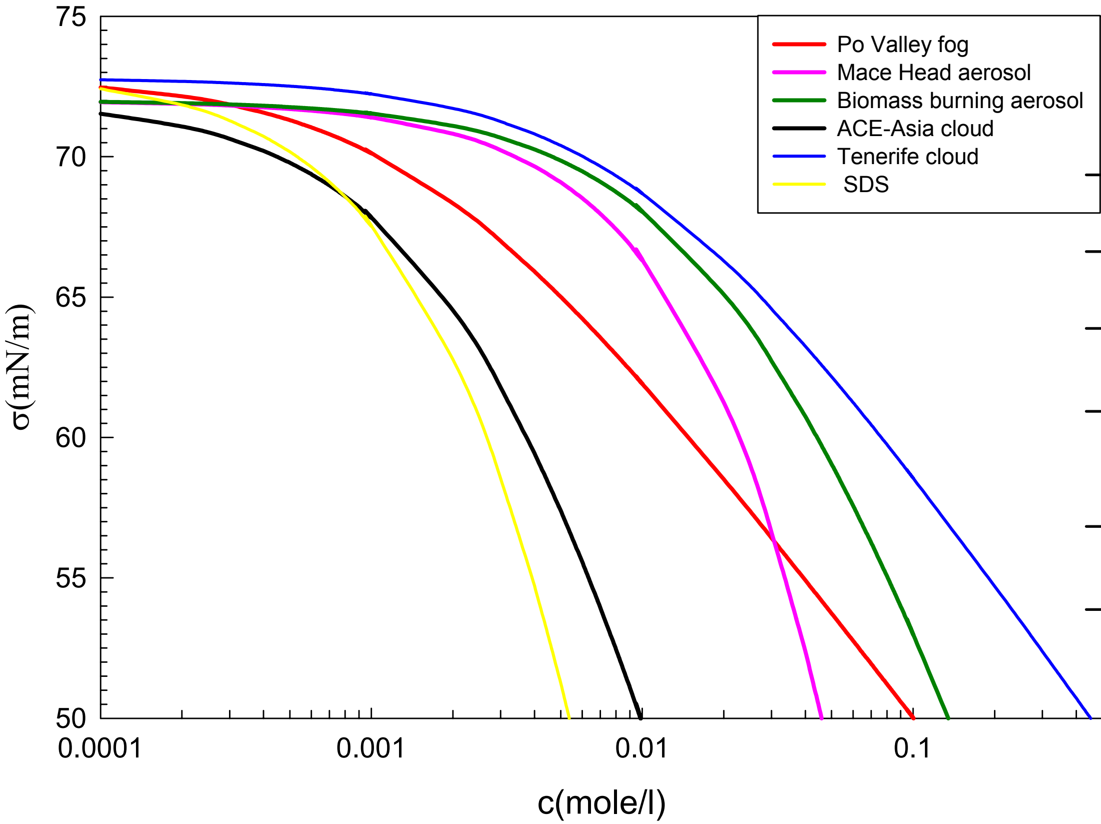
$$\frac{e}{e_s} = a_w \exp\left\{ \frac{2M_w \sigma_{sol}}{\rho_w RTr} \right\}$$

a_w is the water activity
M_w is the molecular mass of water
σ_{sol} is the surface tension of the solution
R is the universal gas constant
T is the droplet temperature
r is the particle radius.





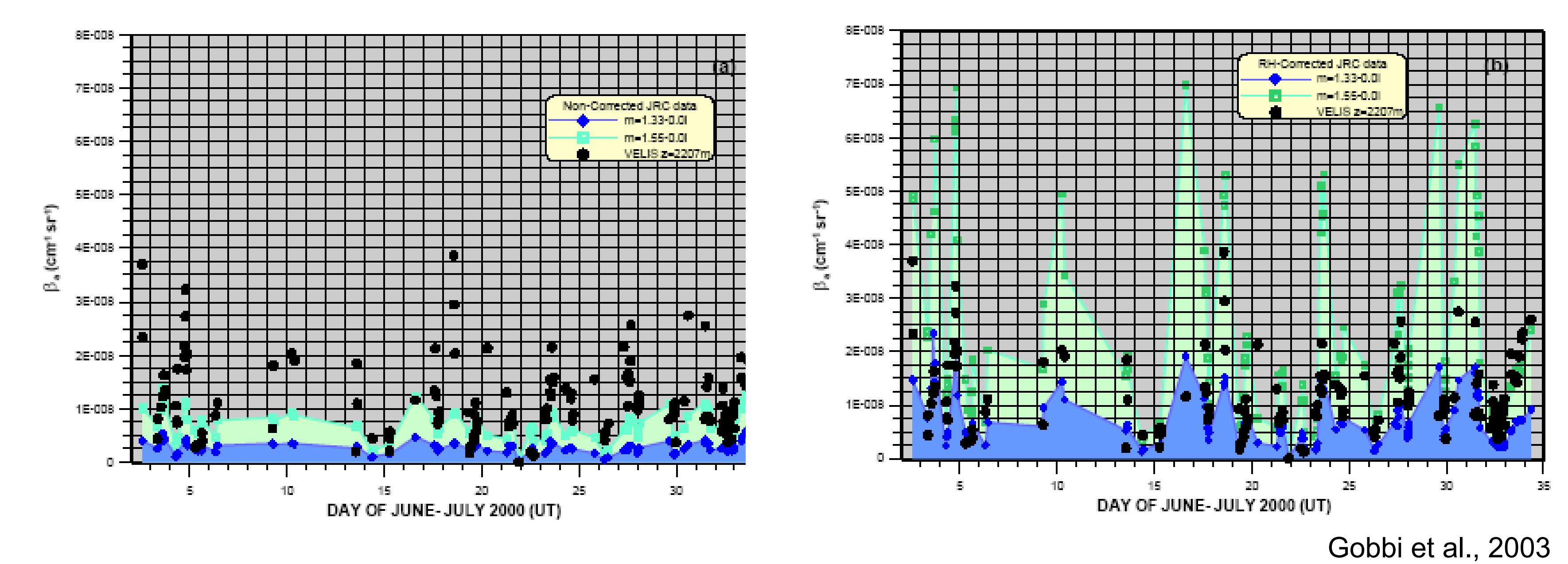
Influence of surface tension on aerosol activation



	$(s_{ST}-s_{H2O})/s_{H2O}(\%)$	$(D_{ST}-D_{H2O})/D_{H2O}(\%)$
Po Valley fog	-37.73	36.08
Tenerife cloud	-25.33	25.99
Mace Head aerosol	-40.10	71.45
Biomass burning aerosol	-30.49	36.08
ACE – Asia cloud	-59.69	116.01
SDS(sodium dodecyl sulfate)	-66.44	193.95

aerosol particle of 0.05μm dry diameter and the chemical composition was considered constant for the different cases (70 % soluble :40 % inorganic salts and 30% organic species).

Influence of aerosol hygroscopic growth on backscatter coefficients



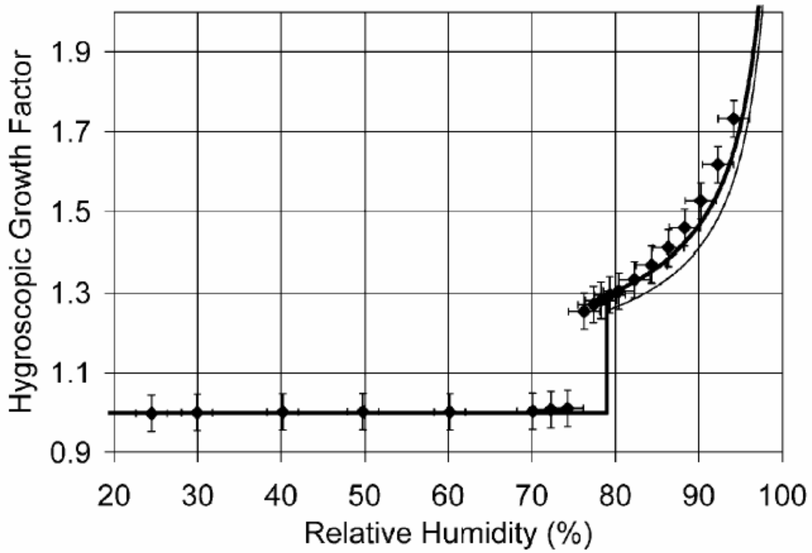
Gobbi et al., 2003

Lidar observed (black dots) and size distribution-derived backscatter coefficients for two values of the refractive index:1) m=1.33–0.0i (blue region), 2) m=1.55–0.0i (green region).
a) DMA “dry” aerosol size distributions; (b) ”wet” aerosol size distribution (RH and aerosol chemical composition and surface tension dependent growth)

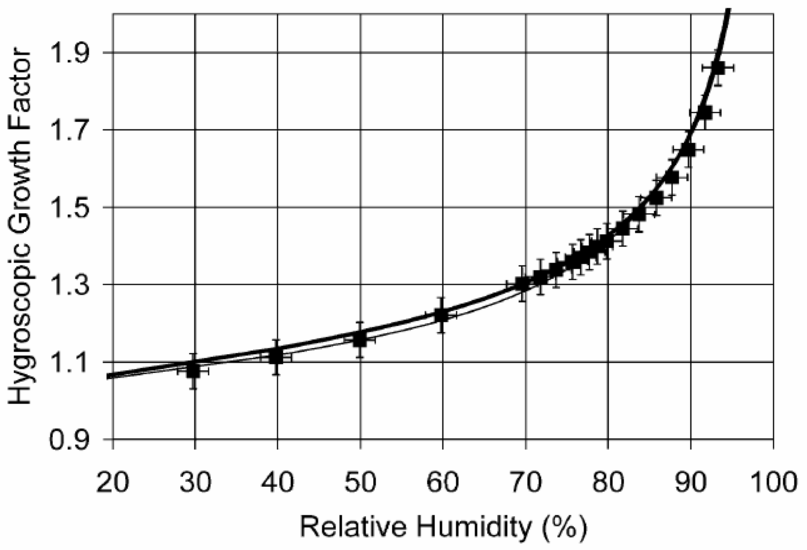
Refractive index of mixed aerosol particles is computed as mass weighted average of the refractive index of compounds

OM	1.53+0.005i
BC	1.75+0.45i
Sufate	1.53+0.000i

Effect of organic compounds on the deliquescence relative humidity (DRH) of mixed aerosol particles



Water uptake for 1:1 ammonium sulfate:succinic acid

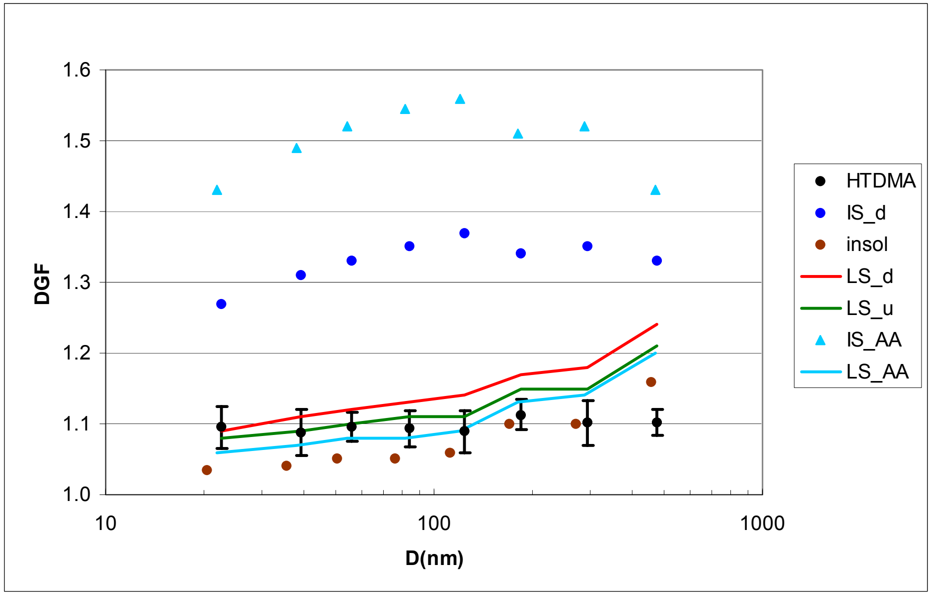


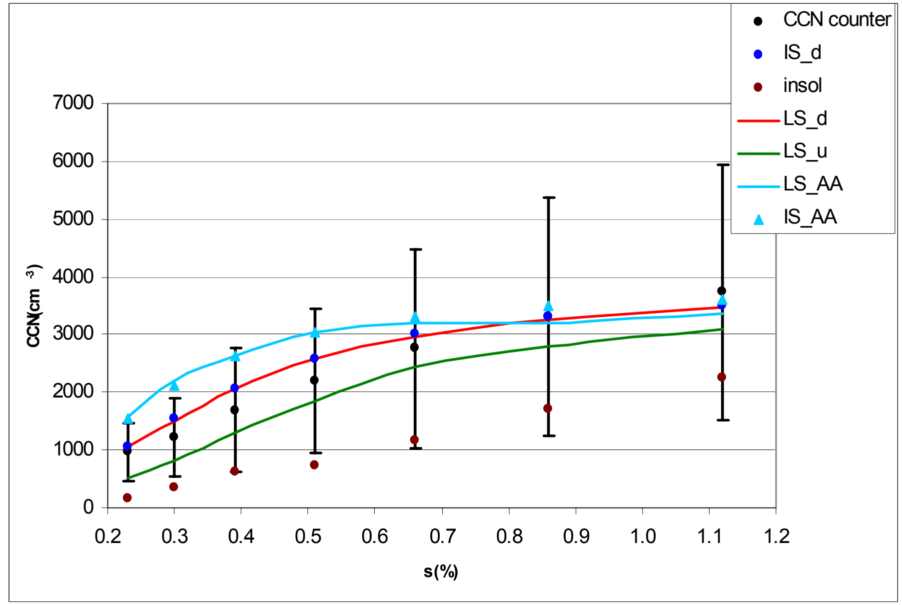
Water uptake for 1:1 ammonium sulfate:malonic acid

Prenni et al. (2003) Atmos. Environ., 37, 4243-4251

The effect of organic species on the deliquescence characteristic of mixed particle is not well understood.

Influence of slightly soluble organic compounds on aerosol growth and activation





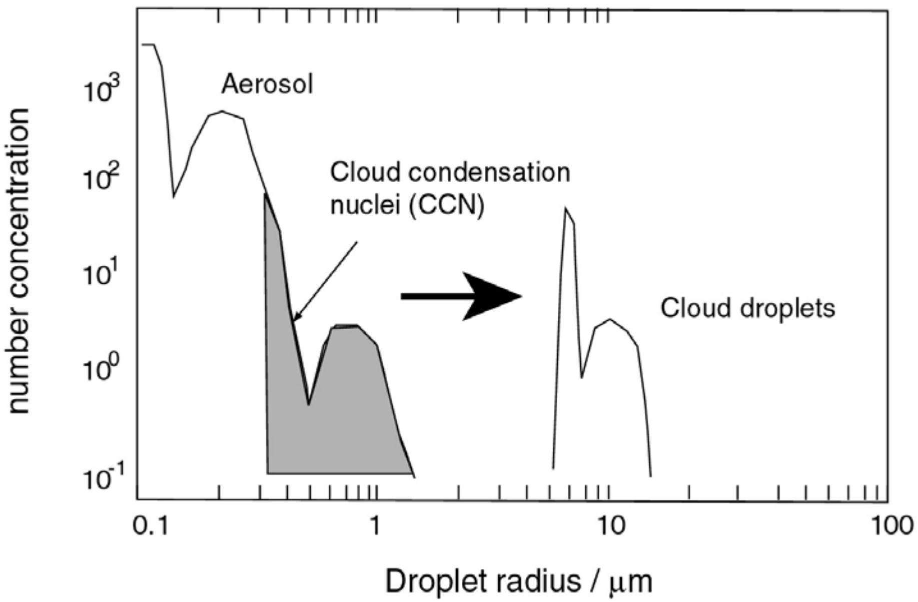
-the soluble organic compounds do not behave as salts

-the organic model compounds representative for WSOC aerosol fraction and their properties are indispensable for modeling aerosol water uptake in sub and super saturated conditions

Mircea et al. (ACPD, 2005)

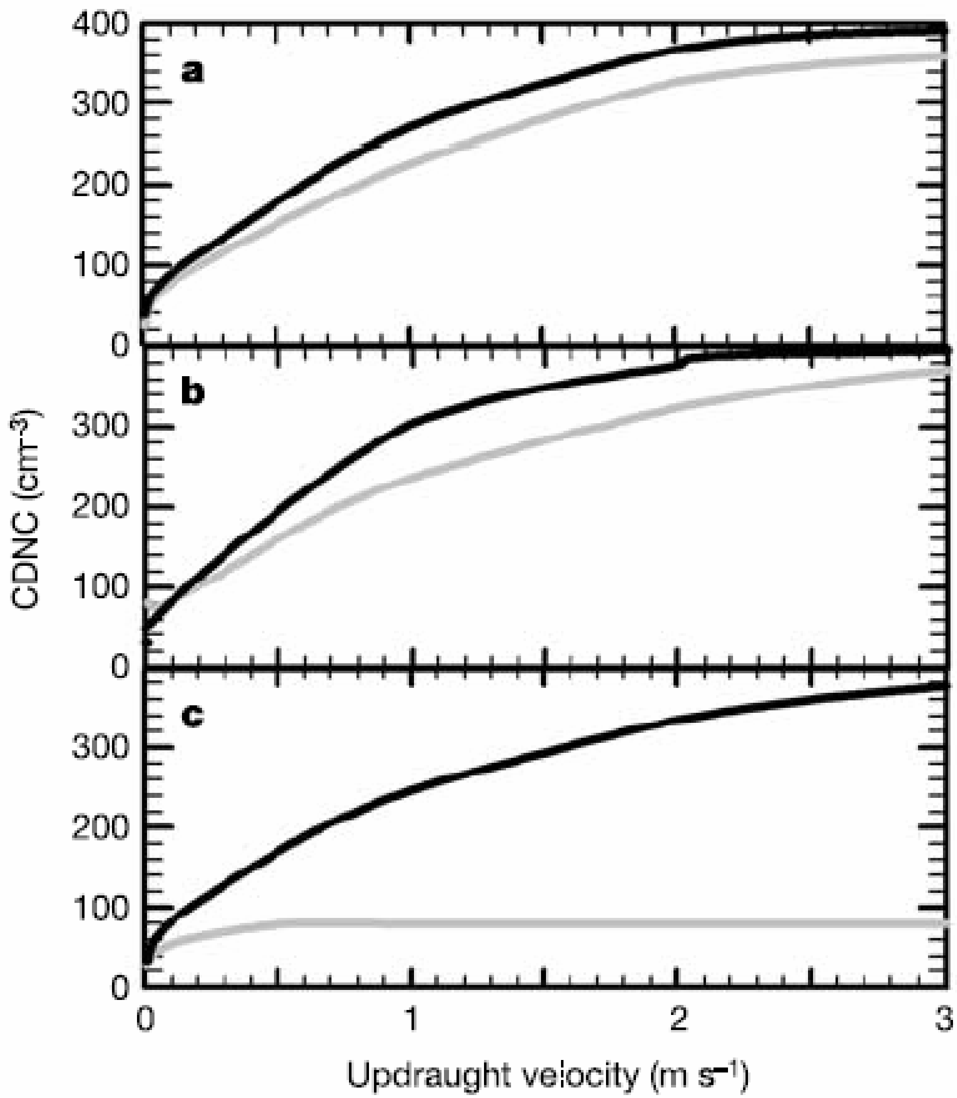
Cloud droplet number concentration (CDNC)

Droplet growth rate: $$D_i \frac{dD_i}{dt} = \frac{S_{v,\infty} - S_{eq.,i}}{\frac{\rho_w RT}{4 e_{sat} D_v^{'} M_w} + \frac{L_e \rho_w}{4 k_a^{'} T}\left(\frac{L_e M_w}{TR} - 1\right)}$$



$$\frac{ds_{v,w}}{dt} = \frac{M_{air}}{M_w}\frac{p}{e_{sat}}\frac{dw_v}{dt} - (1 + s_{v,w})\left[\frac{L_e M_w}{RT^2}\frac{dT}{dt} + \frac{g M_{air}}{RT} W\right]$$

Effect of the state of mixing of aerosol on CDNC



Increase in CDNC due to the addition of OM.

a) CDNC as a function of internally mixed sulphate and sea salt (base case) and as a function of OM internally mixed with sulphate and sea salt (base case plus OM).

b) CDNC as a function of an external mixture of sulphate and sea salt (base case) and of OM internally mixed with sea salt (base case plus OM).

c) Internal mixture of sulphate and sea salt (base case) and OM externally mixed (base case plus OM). In all panels the black line shows the base case plus OM, and the grey line the base case.

(O'Dowd et al., 2004)

The organic compounds delay the aerosol activation

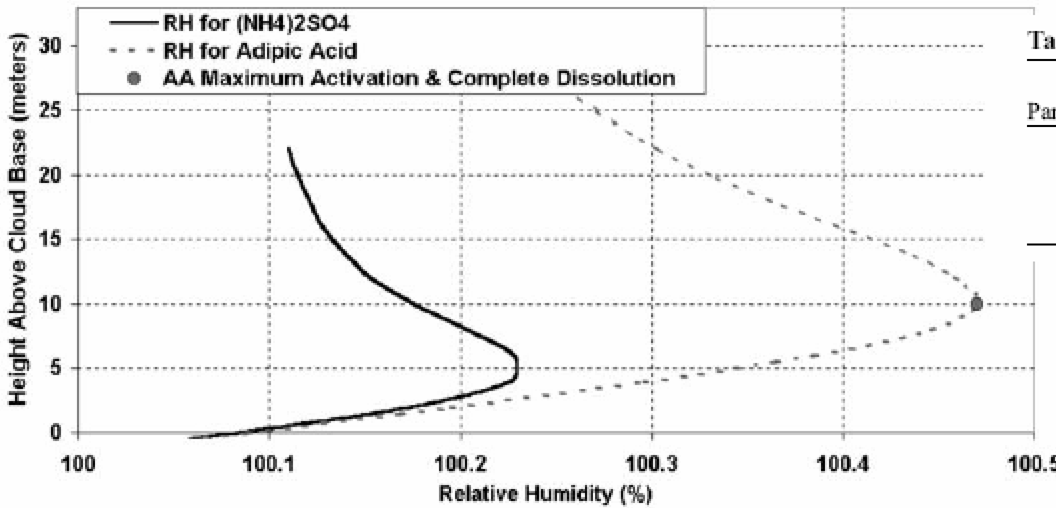
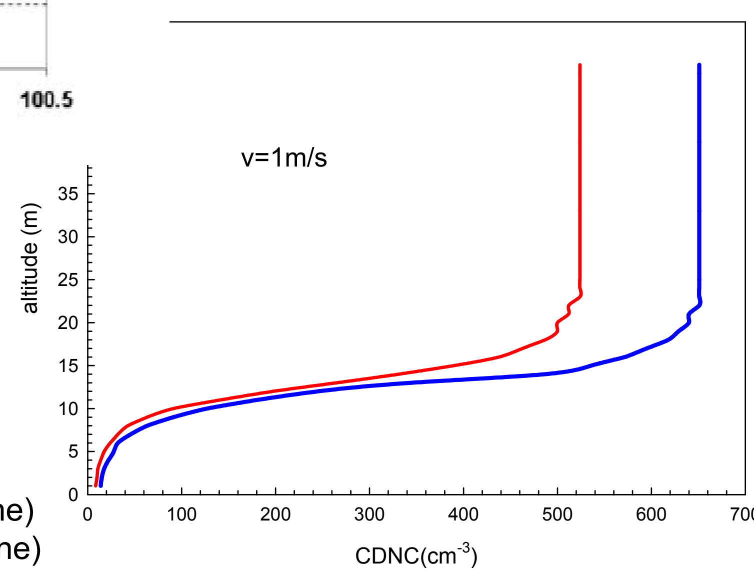


Table 2. Number of Cloud Droplets Activated		
Updraft Velocity, Initial Particle Number Concentration	Ammonium Sulfate	Adipic Acid
20 cm/sec, 100 #/cc	95	23
50 cm/sec, 100 #/cc	99	41
20 cm/sec, 500 #/cc	340	50
50 cm/sec, 500 #/cc	460	97

(Shantz et al., 2003)



Amazonian aerosol during wet season
Two representations for WSOC:
-more slightly soluble organic compounds (red line)
-less slightly soluble organic compounds (blue line)

Parameterization of water uptake by inorganic and organic fraction of aerosol using laboratory measurements

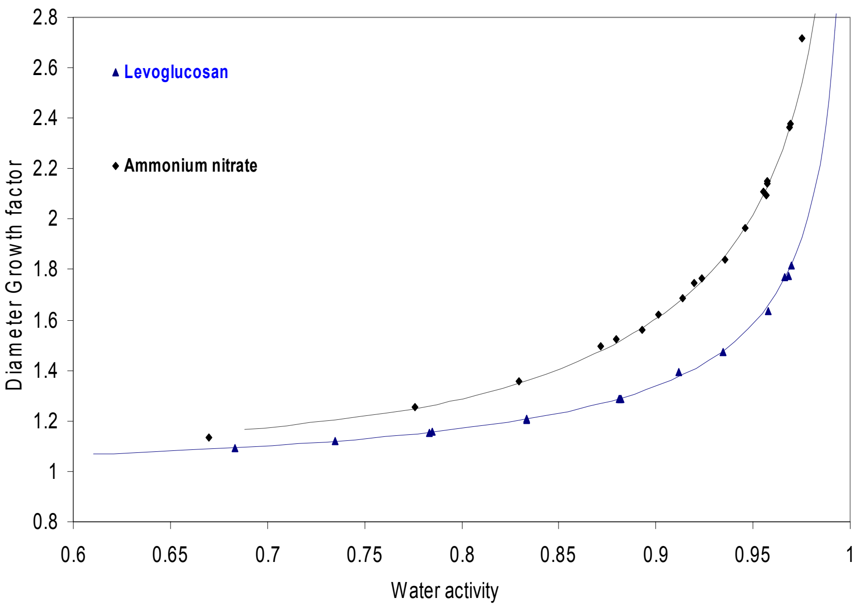
Water activity (solute effect) in Kohler equation:

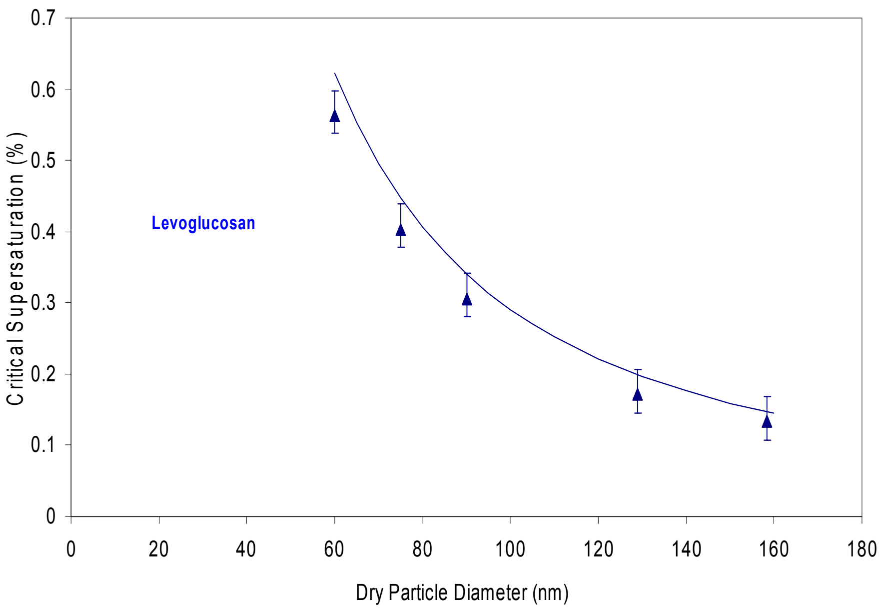
$$\frac{e}{e_s} = a_w \exp\left\{\frac{2M_w\sigma_{sol}}{\rho_w RTr}\right\}$$

I: water activity parameterizations for binary water-organic solutions
II: water activity calculations with ZSR rule for mixtures of organic and inorganic compounds

Water activity parameterizations using HTDMA data

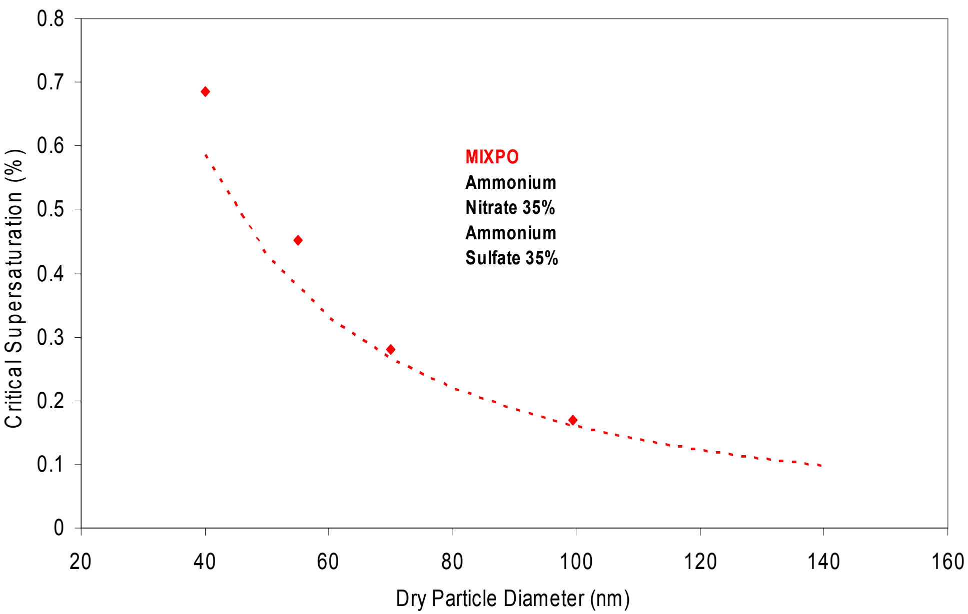
I: Pure organic compounds



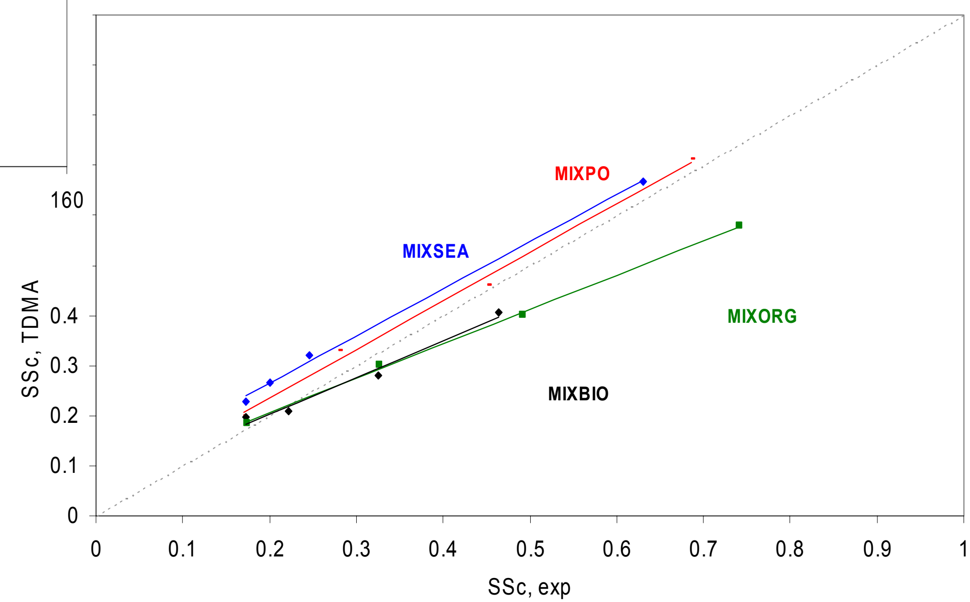


Svenningsson et al. (submitted to ACPD)

Water activity of single organic compounds and Zdanovskii-Stokes-Robinson (ZSR) mixing rule



II: Mixtures of organic and inorganic compounds



Svenningsson et al. (ACPD, 2005)

Alteration of aerosol properties by recently discovered aerosol processes

Source and transformation process:

- organic compounds can be produce by condensation and polymerization of SVOC (SOA formation) (Tolocka et al., 2004; Kalberer et al., 2004; Gao et al., 2004)

Sink:

- the organic fraction of aerosol can decay by oxidation initiated by hydroxyl radicals (OH) (Stephanou, 2005) – comparable with precipitation removal

Source

- SOA formation from vegetation emissions, marine natural emissions or from anthropogenic VOC

On-going or further work

- to identify and parameterize the sources (natural vs. anthropogenic, primary aerosols vs. secondary aerosols) of organic aerosol
- to assess the chemical composition of OC in different parts of the world
- to understand the interactions organic-organic and organic-inorganic compounds and to develop thermodynamics models for describing the properties of aerosols (hygroscopicity, water activity, surface tension, etc.);
- to understand and model the aging processes of organic aerosol (aging changes chemical composition, state of mixing and thermodynamic properties; aging may occur through gas-solid reactions or aqueous phase reactions)

On the purpose of developing a comprehensive *global model of aerosol*

a base for the aerosol-radiation and aerosol-cloud interactions in GCMs

ACKNOWLEDGEMENTS

- SMOCC, PHEONICS, QUEST: EU-projects
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