The Abdus Salam International Centre for Theoretical Physics

The International Union of Geodesy and Geophysics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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Workshop on Atmospheric Deposition: Processesand Environmental Impacts

21 - 25 May 2012

Processes in wet deposition: In-cloud and below cloud scavenging

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Processes in wet deposition:
In-cloud and below cloud scavenging

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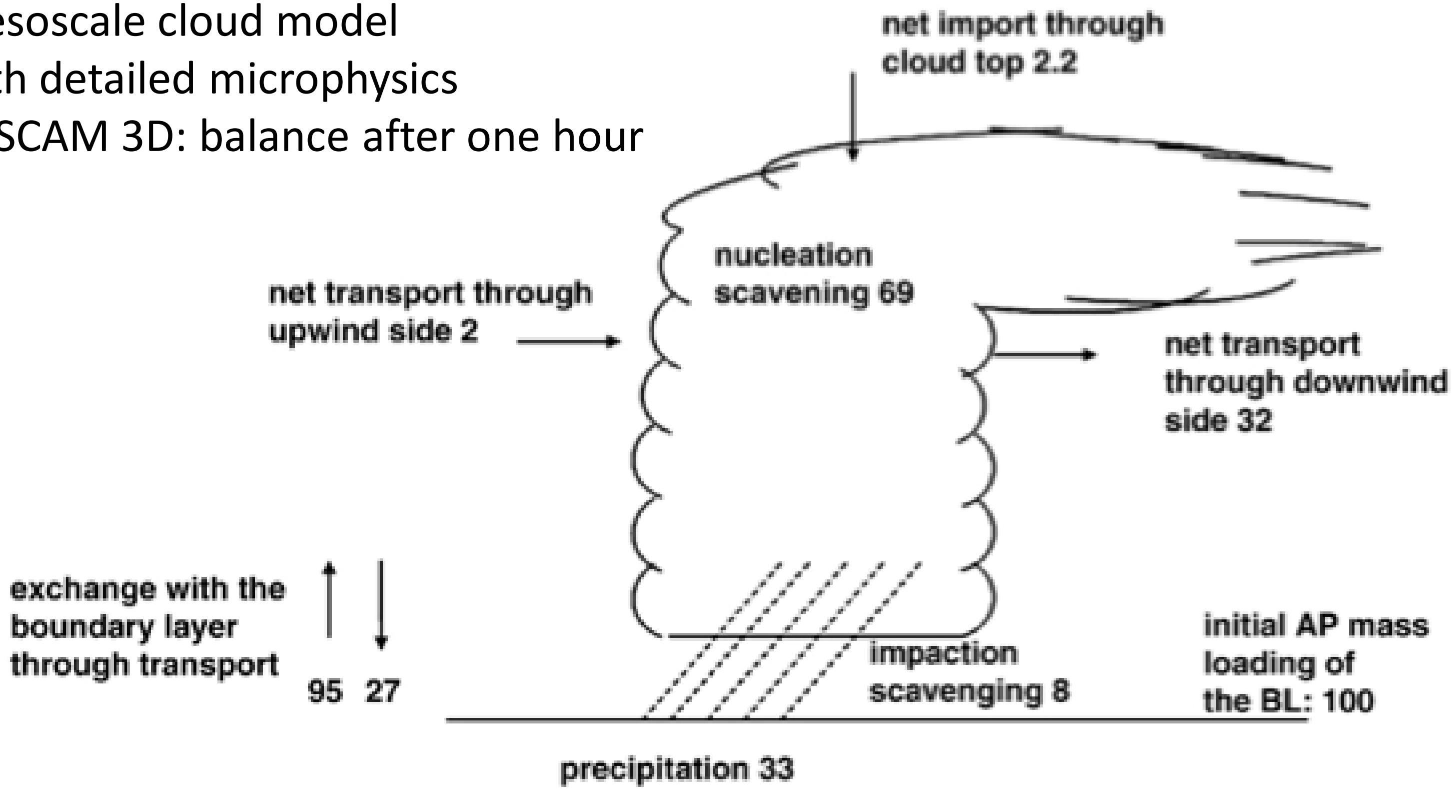
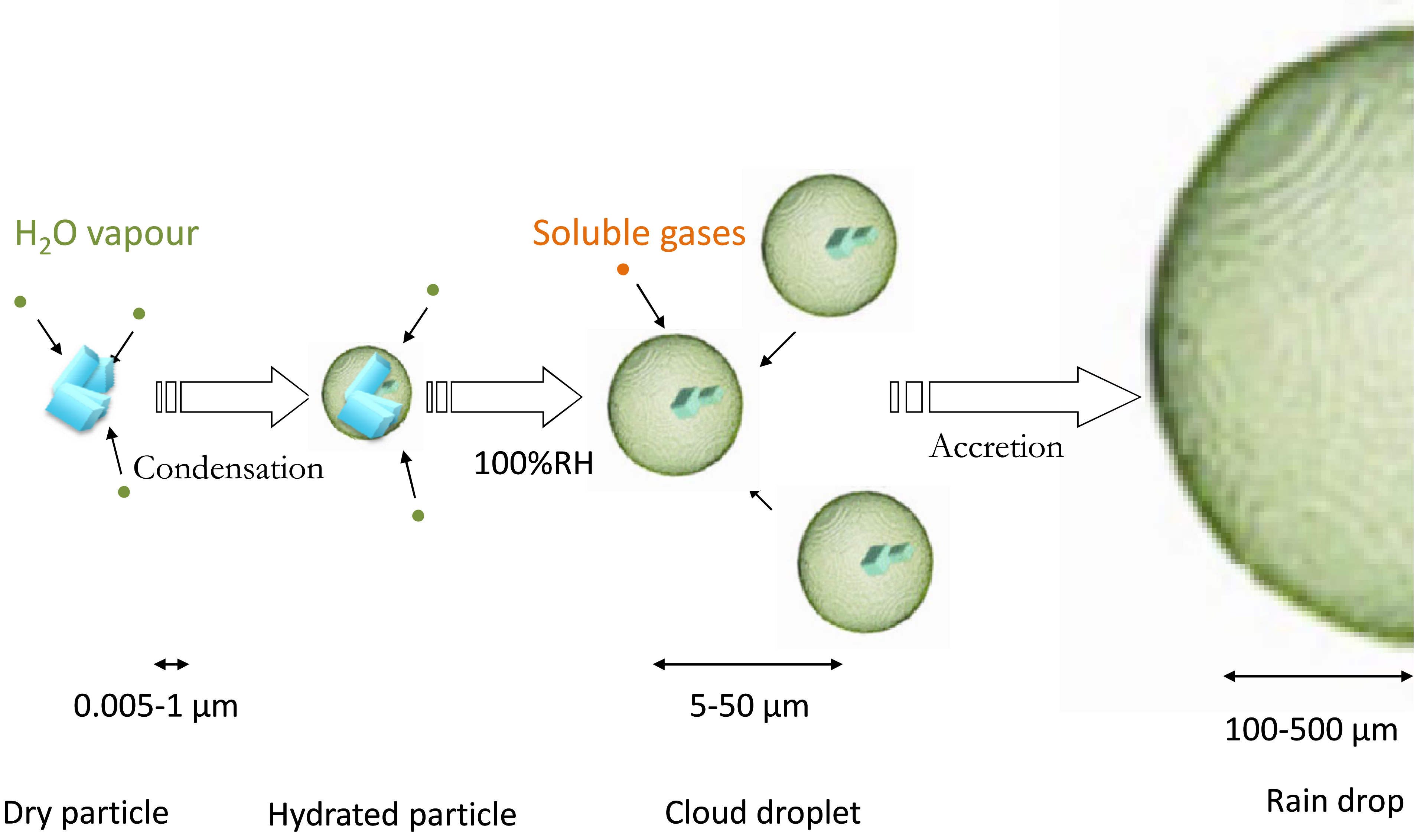
Relative contribution of in-cloud and below-cloud scavenging

Aerosol mass transfer using
Mesoscale cloud model
with detailed microphysics
DESCAM 3D: balance after one hour



Adapted from Flossmann (1998), *in Flossmann and Wobrock, Atm. Res. 2010*

General processes involved in clouds



In-cloud scavenging: Cloud droplet formation

Köhler theory: Equilibrium between aqueous solution and humid air

Surface tension

Soluble fraction

Particle radius

$$S = \frac{P}{P_{sat}} = \exp\left[\frac{2M_e\sigma}{RTr_g\rho_e} - \frac{\upsilon\Phi_s\varepsilon M_e\rho r_p^3}{M_s\rho_e(r_g^3 - r_p^3)}\right]$$

Saturation vapour pressure/flat surface

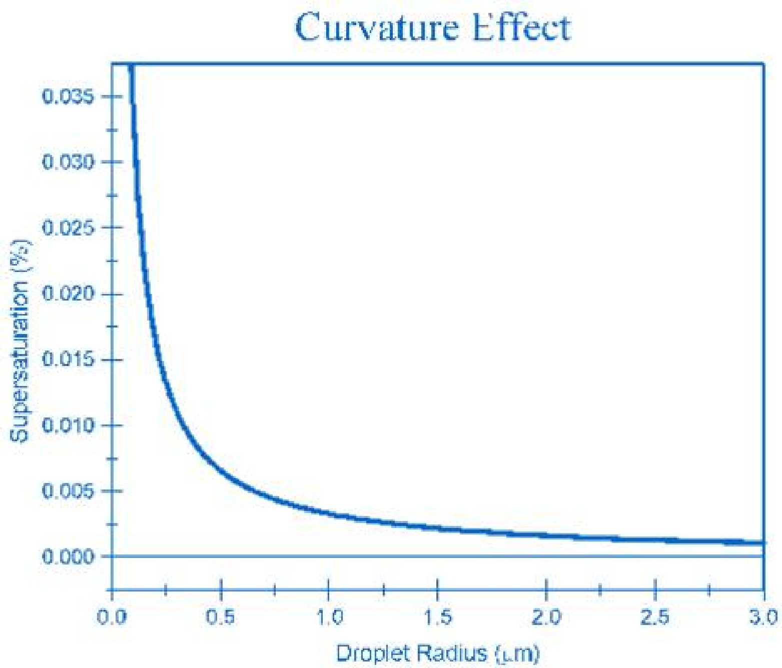
Droplet radius

Curvature (Kelvin) Effect: the saturation vapour pressure increases with increasing curvature

Solute (Raoult) Effect: the presence of solutes in the drop decreases the saturation vapour pressure

Curvature (Kelvin) effect

The smaller the droplet, the greater the supersaturation (with respect to a flat surface) is needed to keep the droplet from evaporating

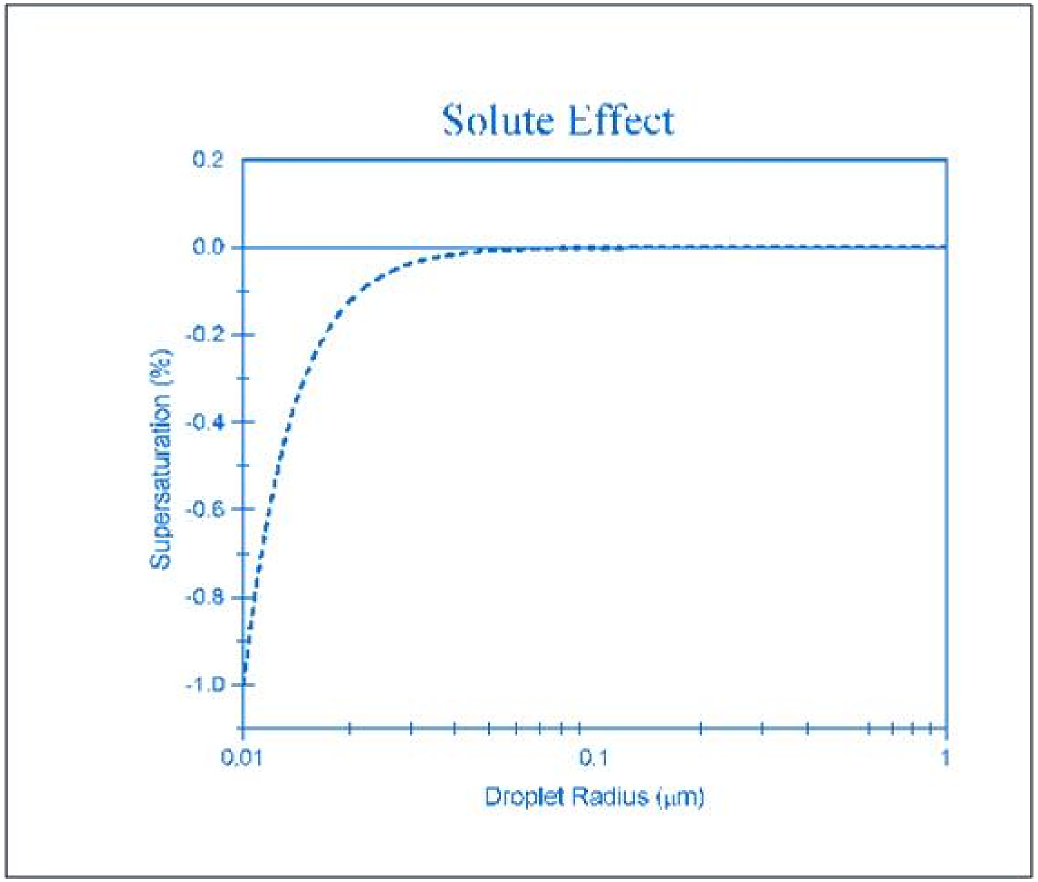


Raoult effect

The vapor pressure for a solution drop is less than that for a plane of pure water

The vapor pressure required to maintain equilibrium *decreases* as the drop radius decreases.

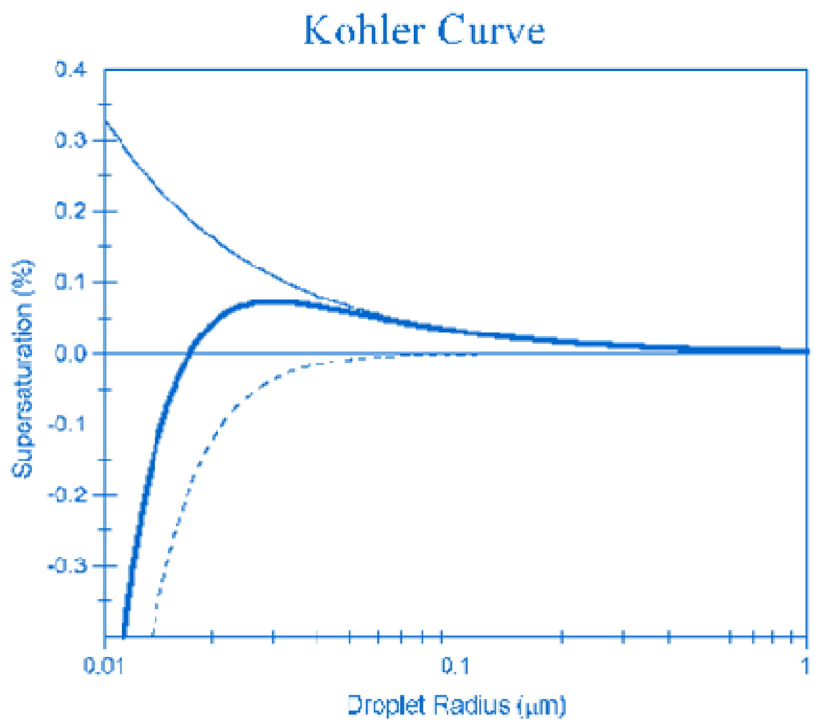
This is opposite of the effect for curvature.



Köhler curve

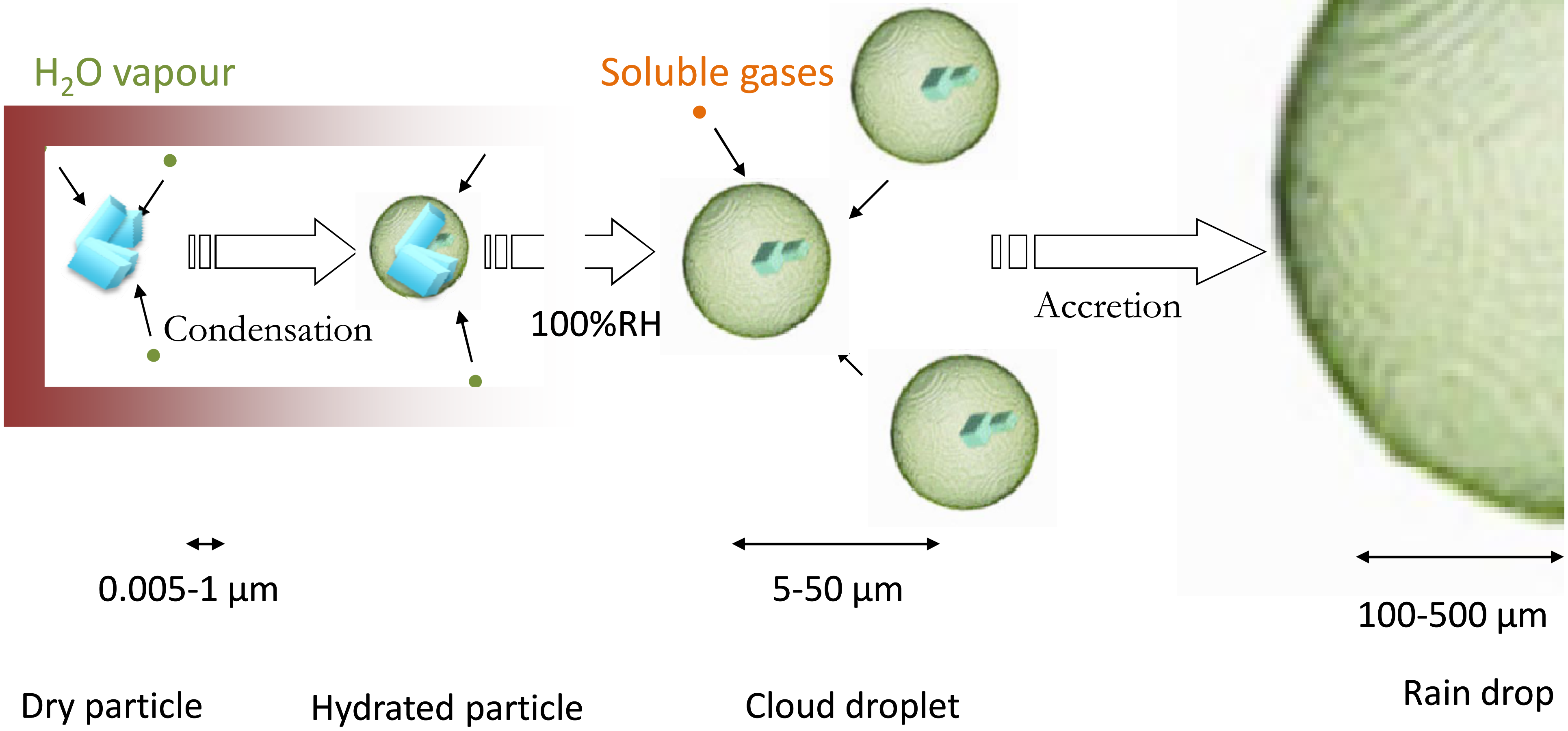
Initially the solution effect dominates, but as the drop gets bigger, the curvature effect takes over.

When the drop is very large, neither effect dominates and the surface of the drop, to the water molecules, appears as a flat surface.



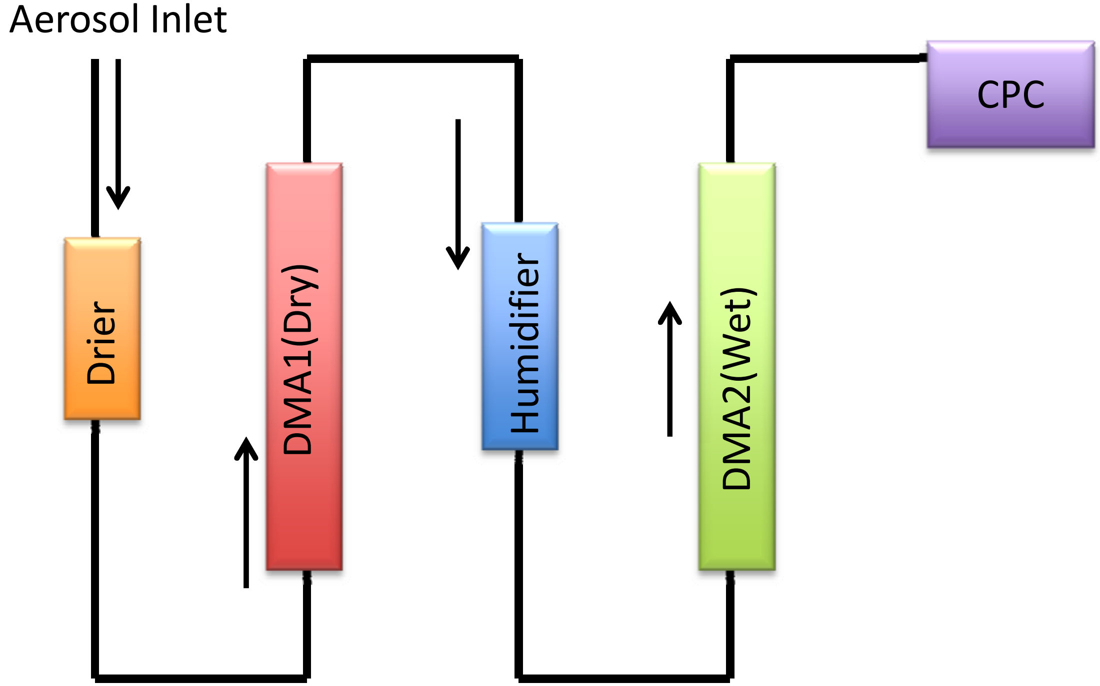
Is this equilibrium theory observed in reality?

Processes in the subsaturation regime

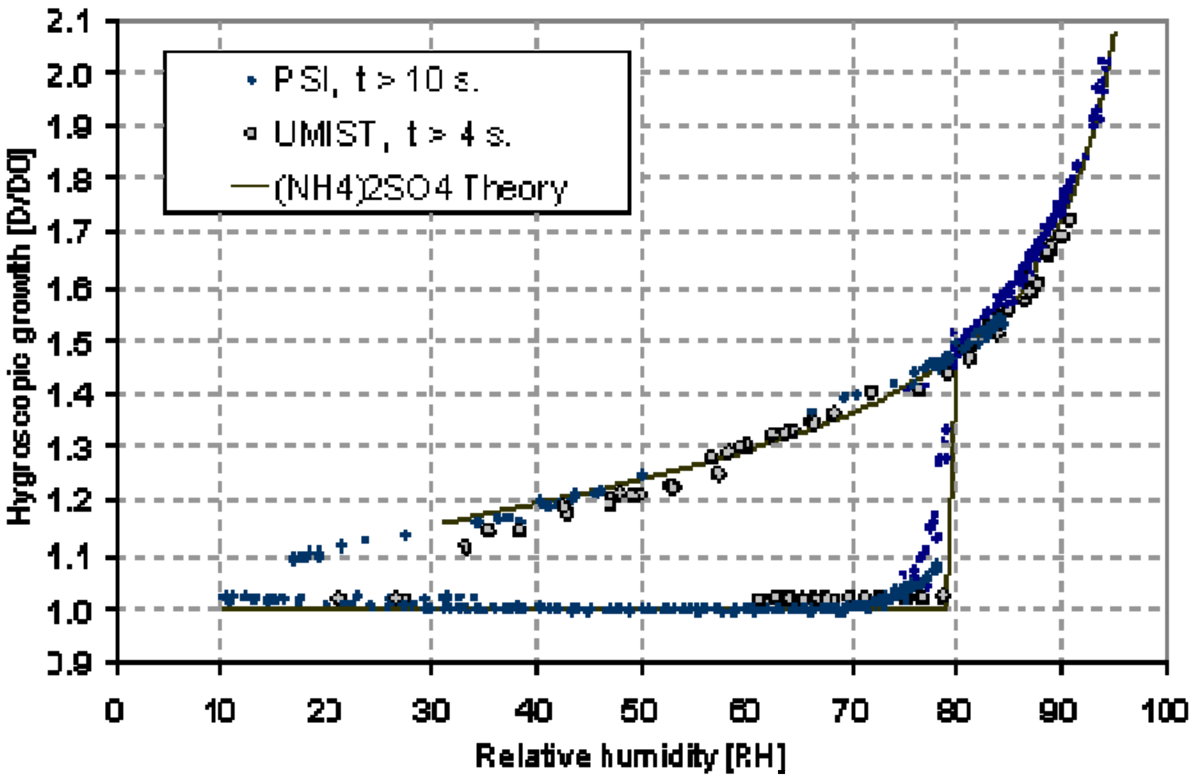


Aerosol-water vapour interactions: controlled humidification systems

HTDMA: Humiditidy Tandem Differencial Mobility Analyser

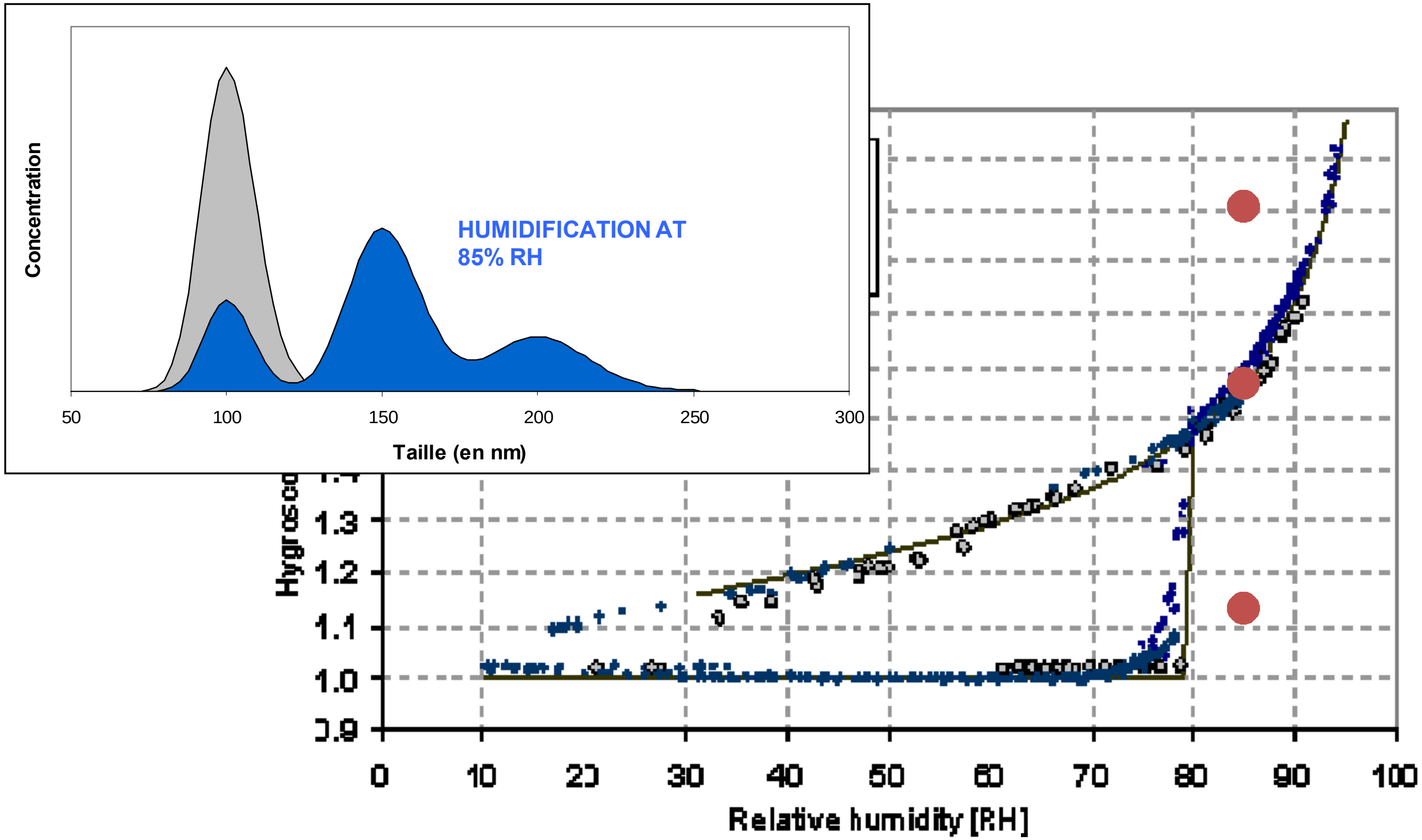


Hygroscopic growth for a known inorganic aerosol

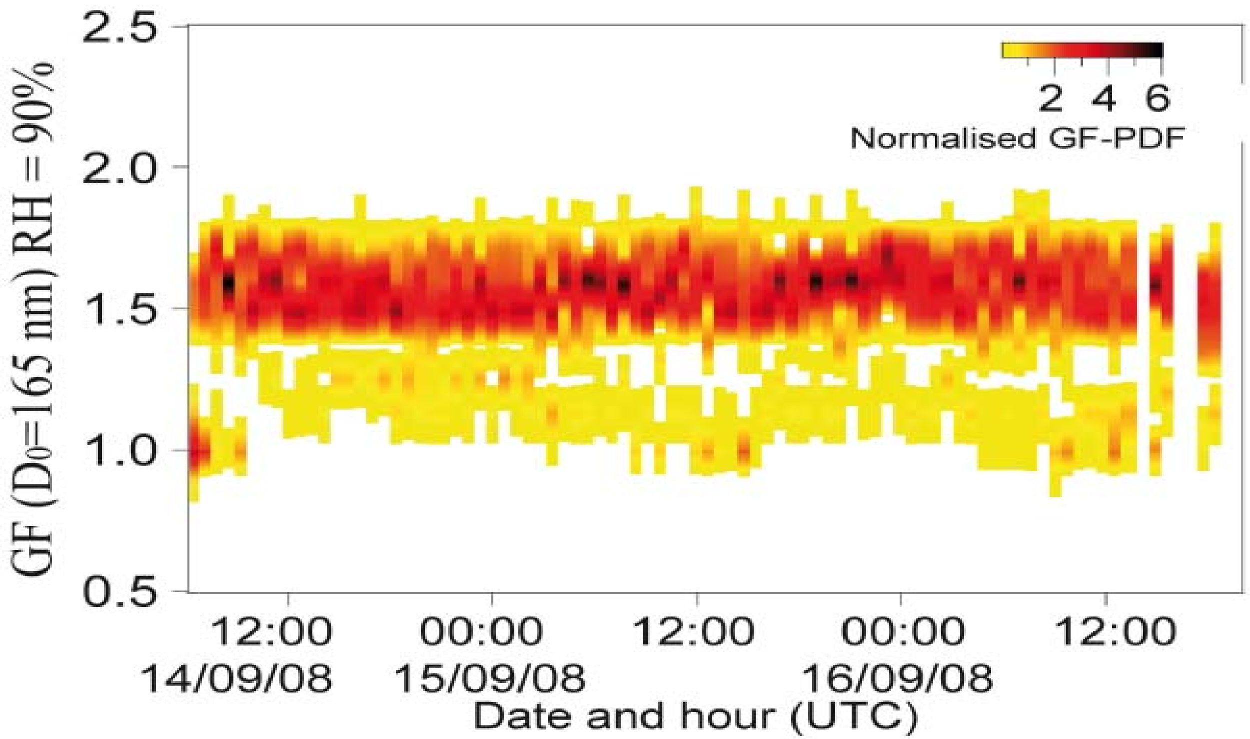


Theory works well for simple inorganic aerosols, even for residence time of a few seconds

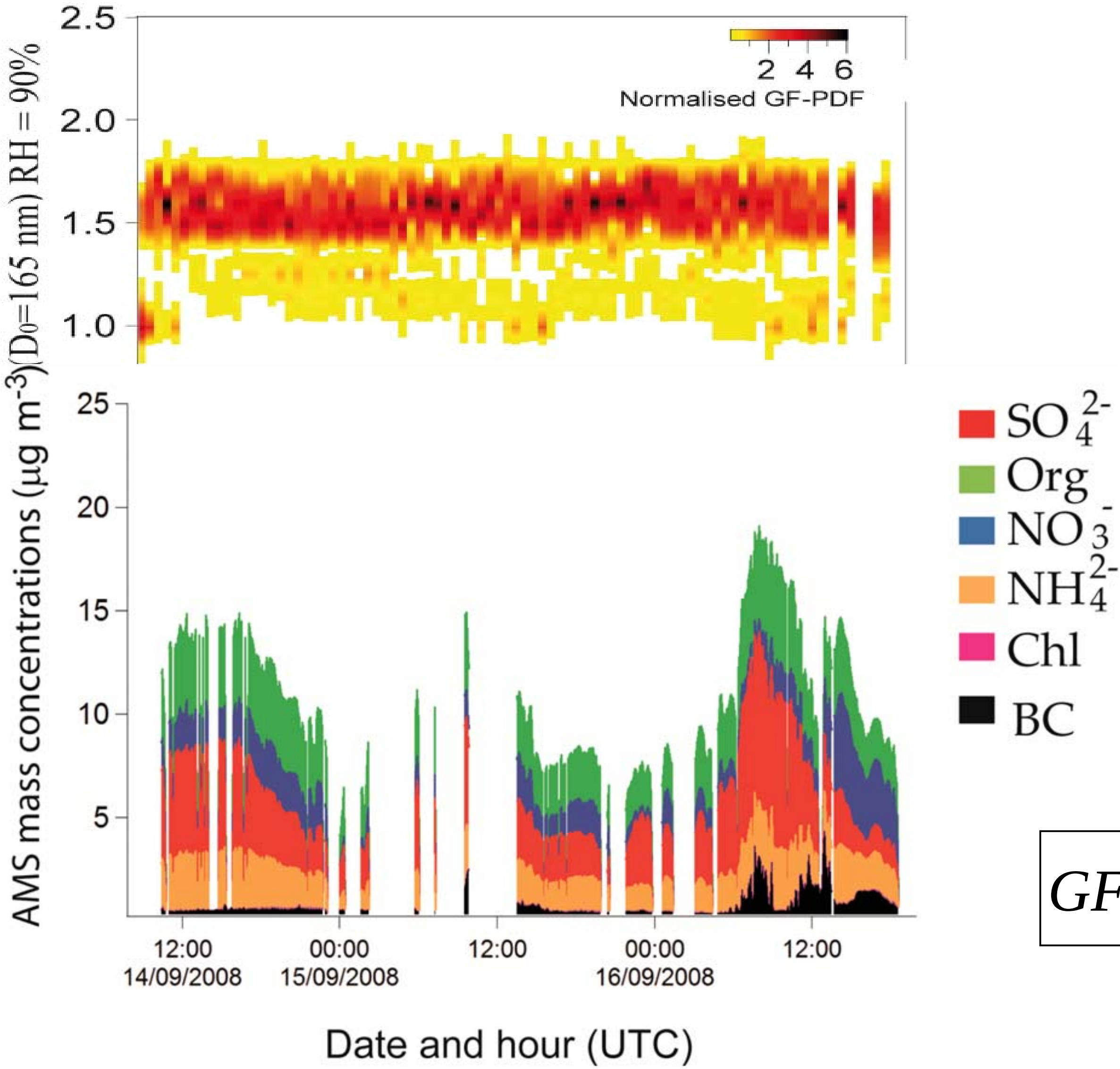
Water vapour uptake of a mixture of different aerosol types at a given size



Example of results for atmospheric aerosols: time series at a background station (puy de Dôme)



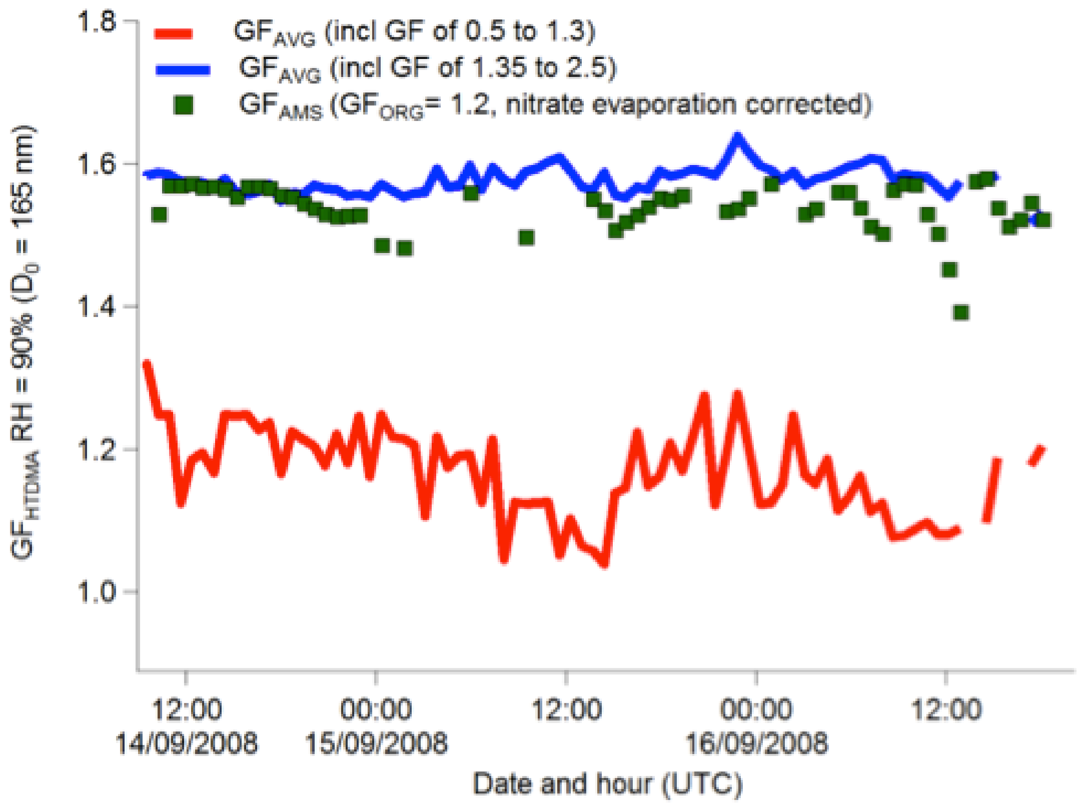
Can hygroscopic growth be accurately predicted from chemistry?



ZSR Theory (Zdanovskii-Stokes-Robinson): approximates the GF of a chemical mixture with the hypothesis that no interaction exist between chemicals, no surface and kinetic effects

$$GF_{global} = \sqrt[3]{(\varepsilon_a GF_a^3 + \varepsilon_b GF_b^3)}$$

Can hygroscopic growth be accurately predicted from chemistry?

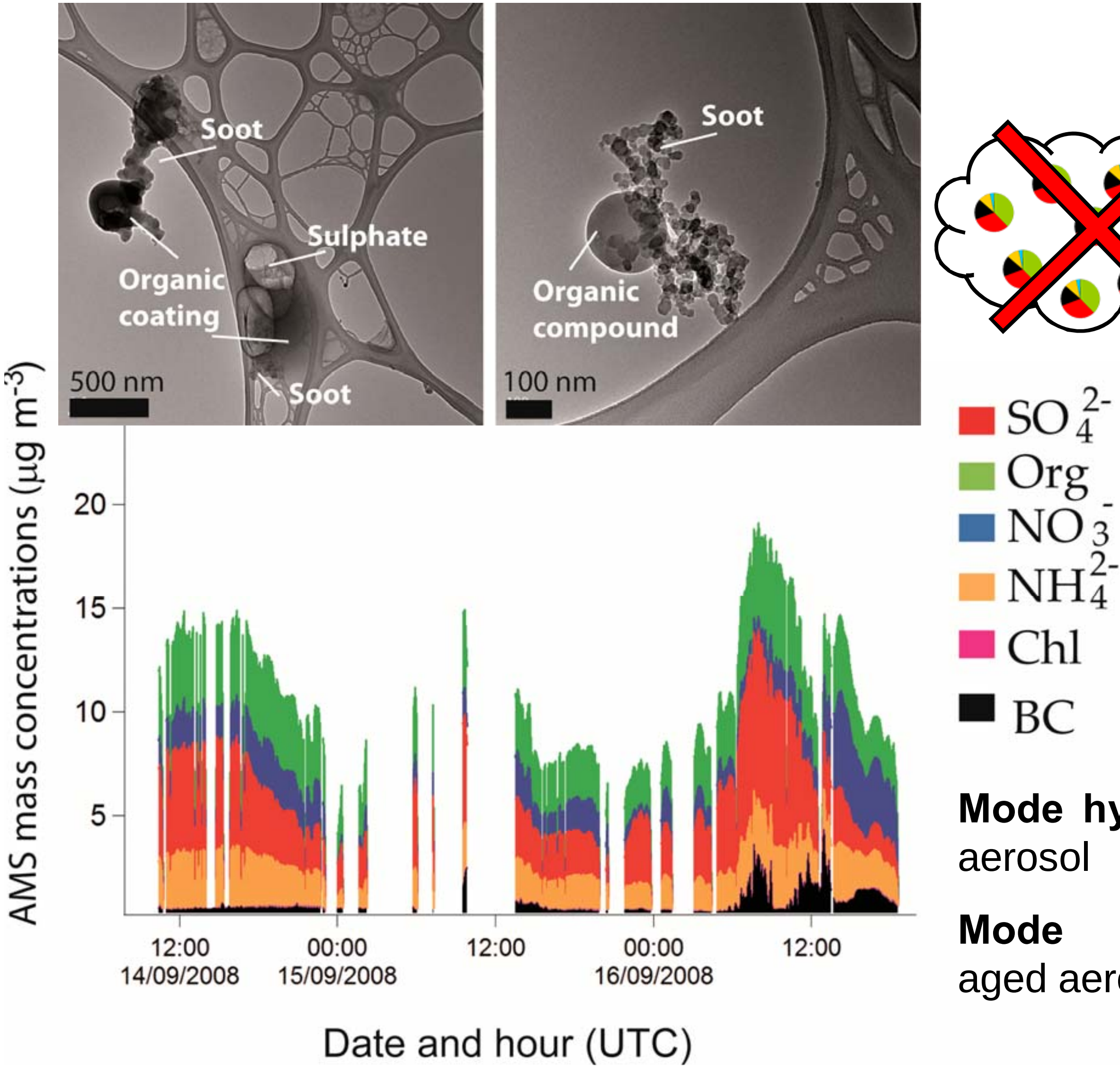


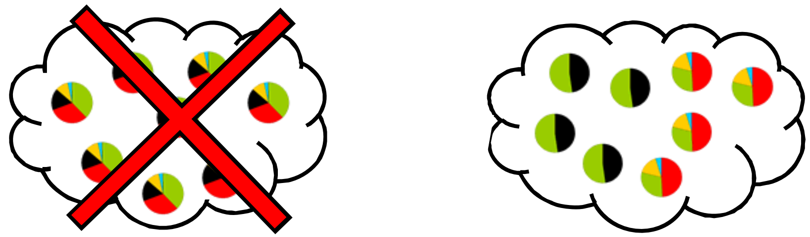
Theory ZSR (Zdanovskii-Stokes-Robinson): approximates the GF of a chemical mixture with the hypothesis that no interaction exist between chemicals, no surface and kinetic effects

The model predicts that the aerosol population is uptaking water as if only the more hygroscopic mode existed

$$GF_{global} = \sqrt[3]{(\varepsilon_a GF_a^3 + \varepsilon_b GF_b^3)}$$

Can hygroscopic growth be accurately predicted from chemistry?





BC hydrophobic ($GF_{90\%}$=1.00)

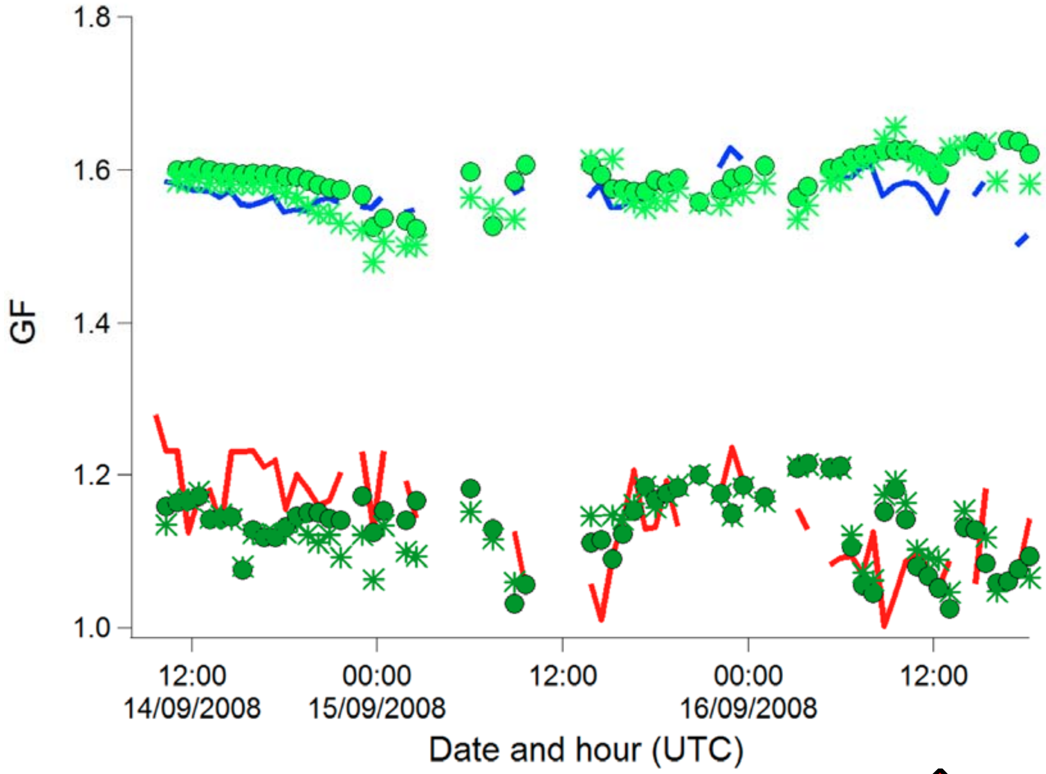
SO_4+NH_4+NO_3 ($GF_{90\%}$=1.7)

Organics : variable GF= 1.1-1.4

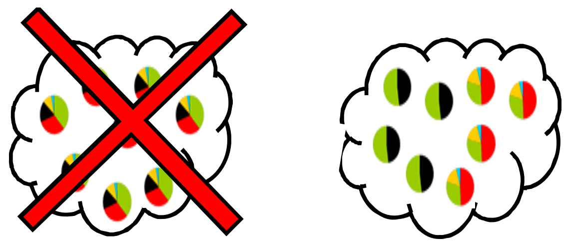
Mode hydrophobic (BC + org) : combustion aerosol

Mode hygroscopic (NH_4+SO_3+NO_3+org): aged aerosol

Can hygroscopic growth be accurately predicted from chemistry?



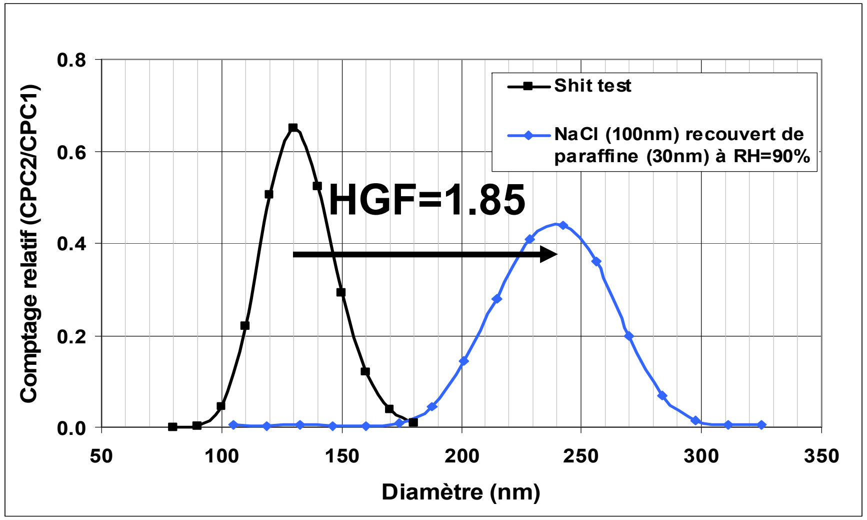
Freney et al. in prep

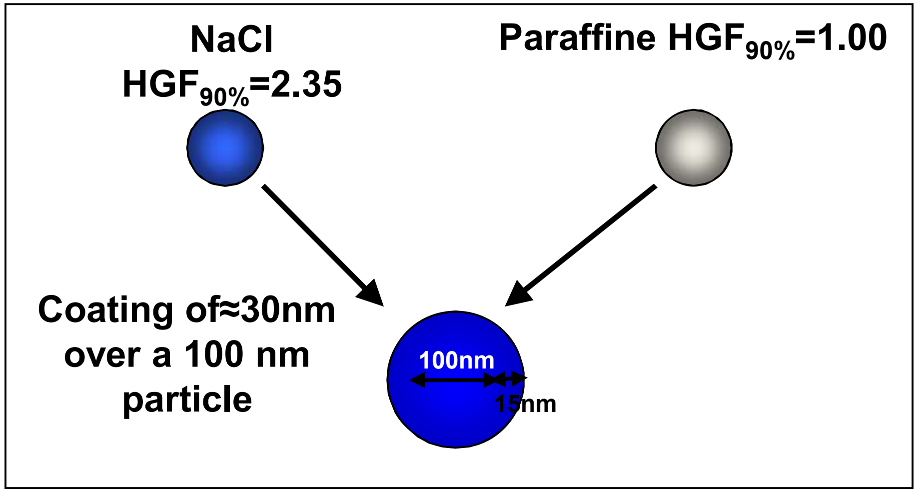


Are there any surface or kinetic effects?

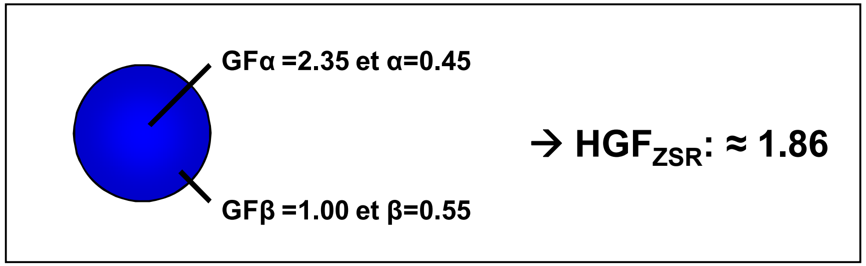
How does aerosol surface impact water uptake?

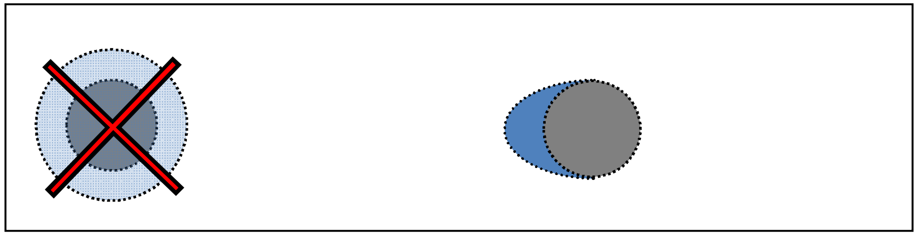
Simulation of the ageing of sea salt with an hydrophobic substance (organic)





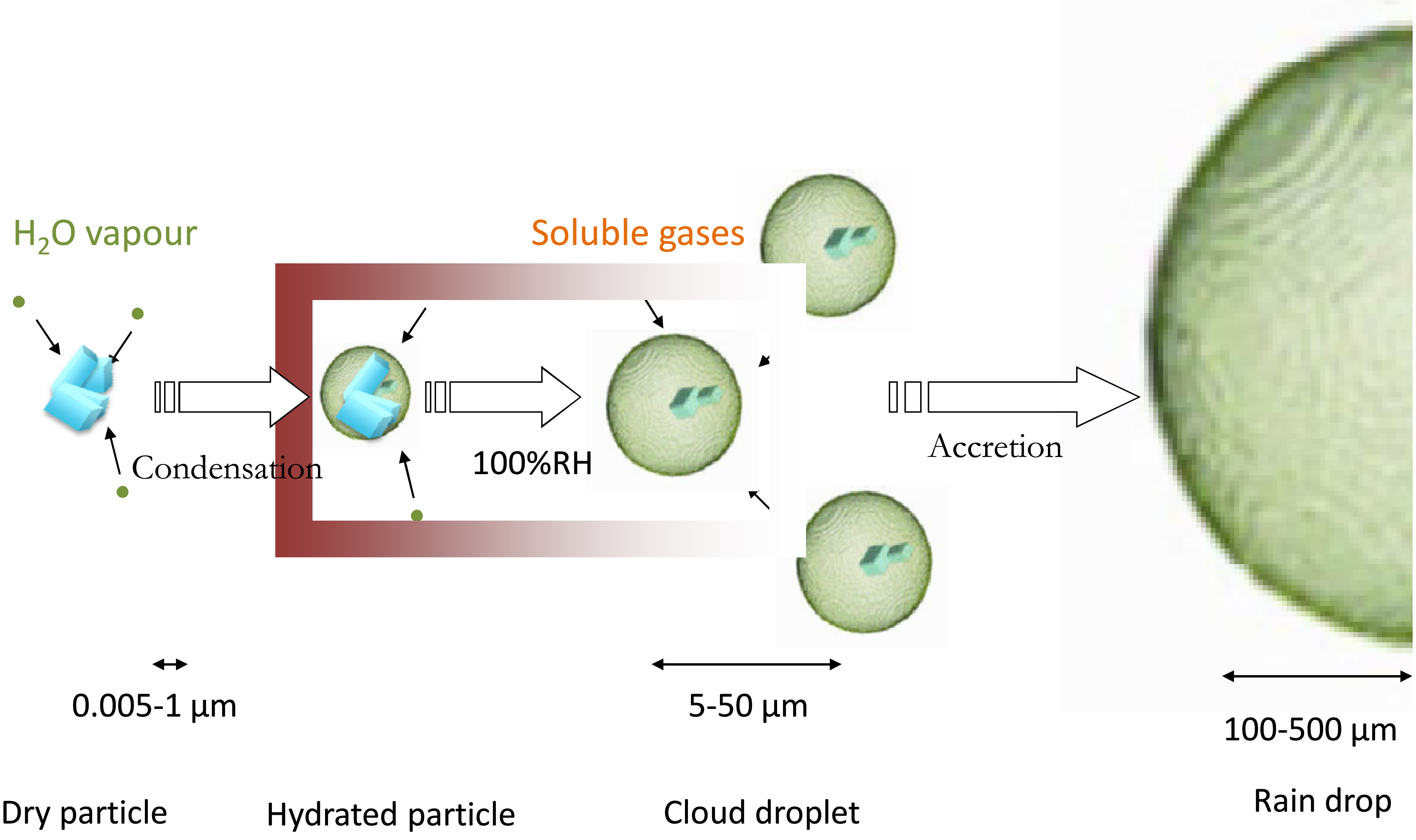
HGF ≠ HGF paraffine ➔ non homogeneous coating



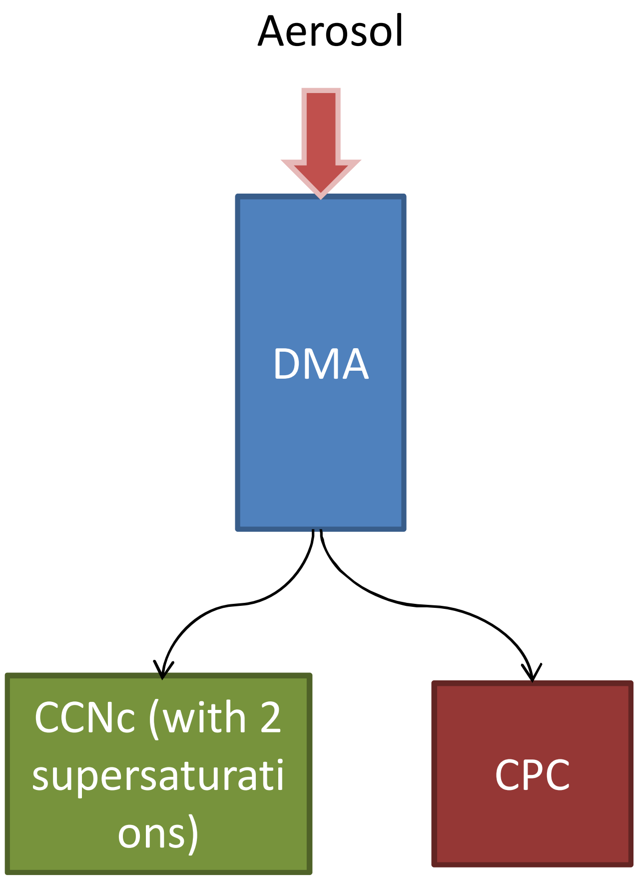


Surface propertie does not seem to impact significantly water uptake on an aerosol particle at subsaturation . Does this apply at sursaturation?

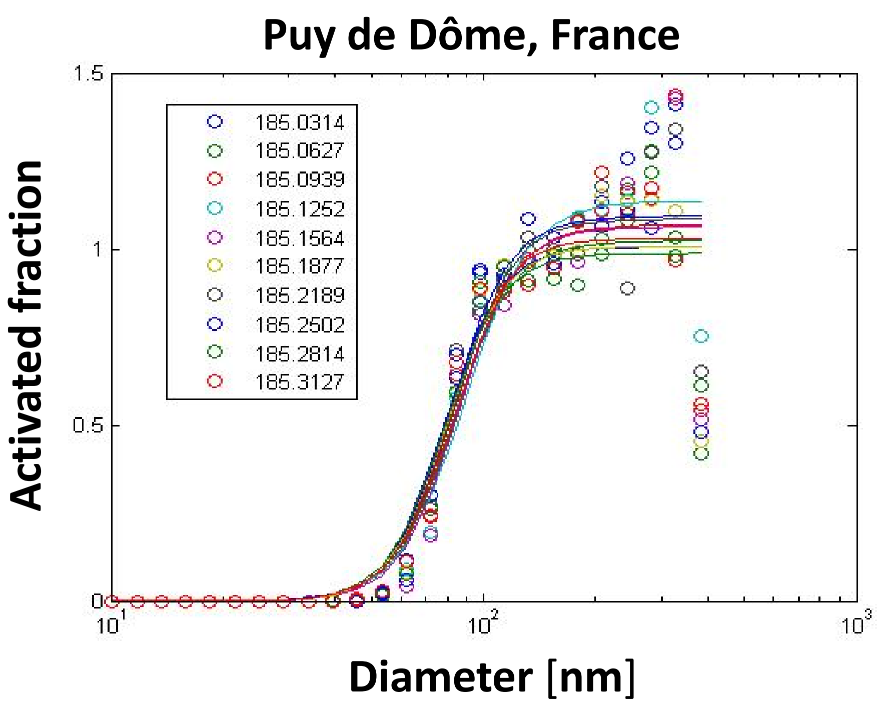
Processes in the sursaturation regime



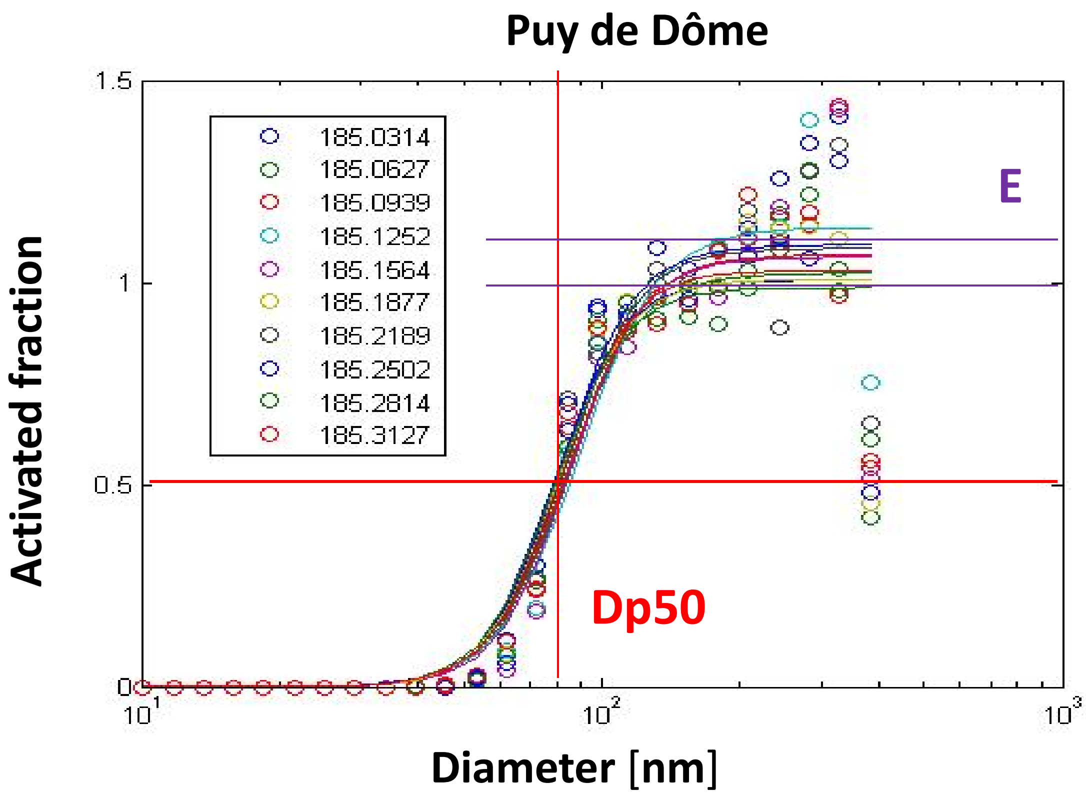
Aerosol-water vapour interactions using controlled humidification systems



Size resolved CCN properties



Activation parameters

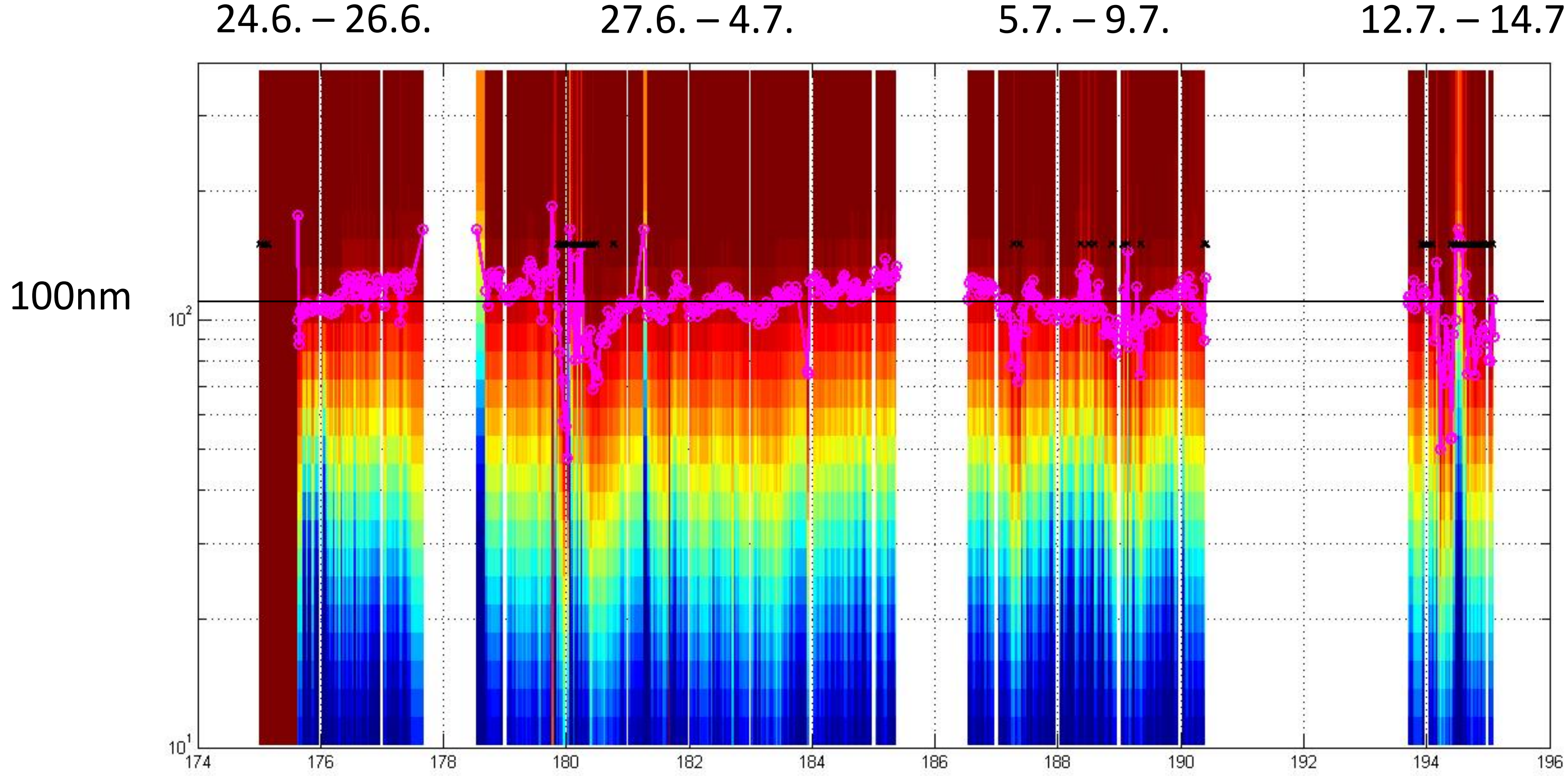


Fitting:

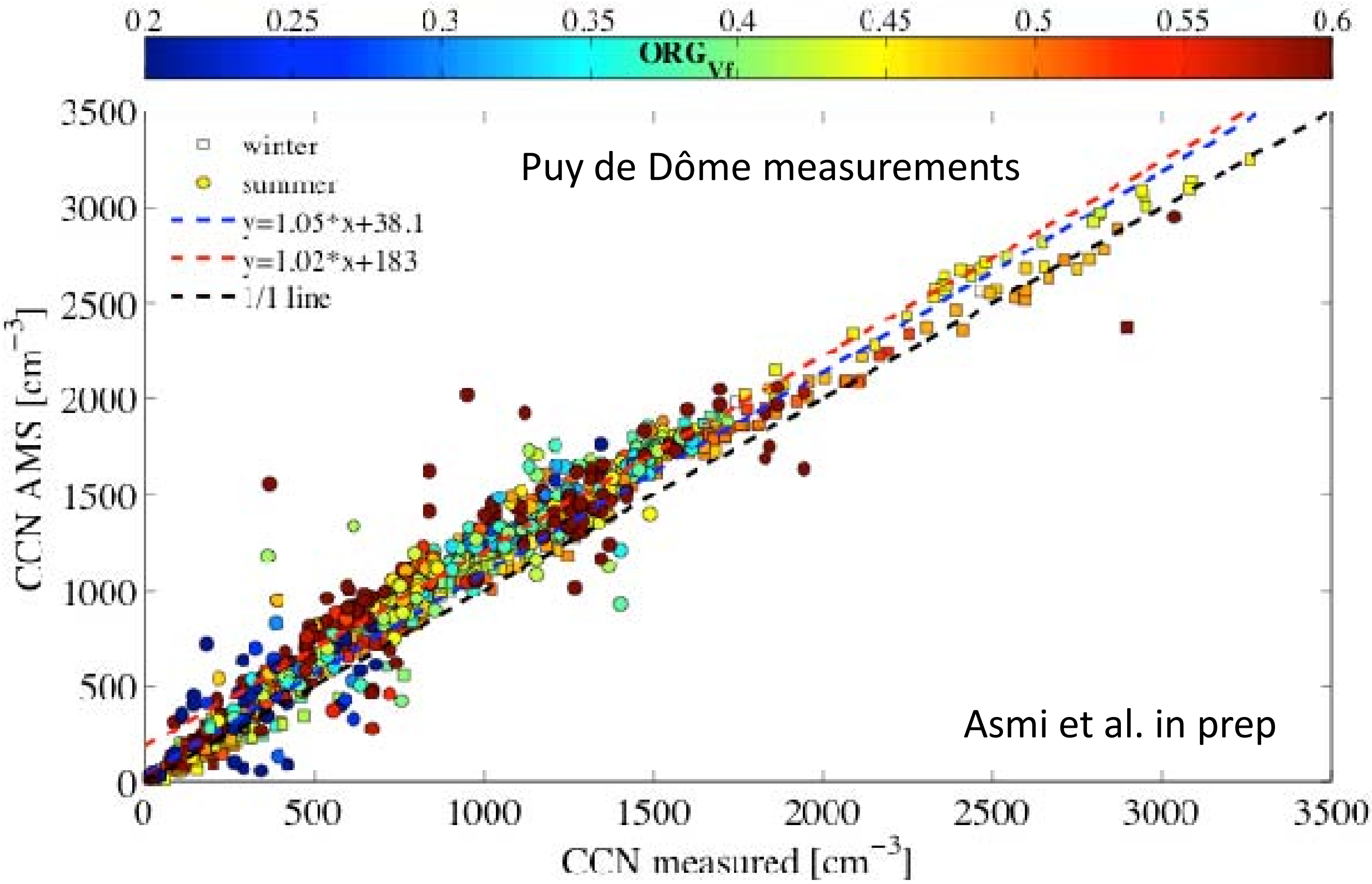
$$\frac{CCN(Dp)}{CN(Dp)} = \frac{E}{1 + \left(\frac{Dp50}{Dp}\right)^{c}}$$

Time series of aerosol activated fraction

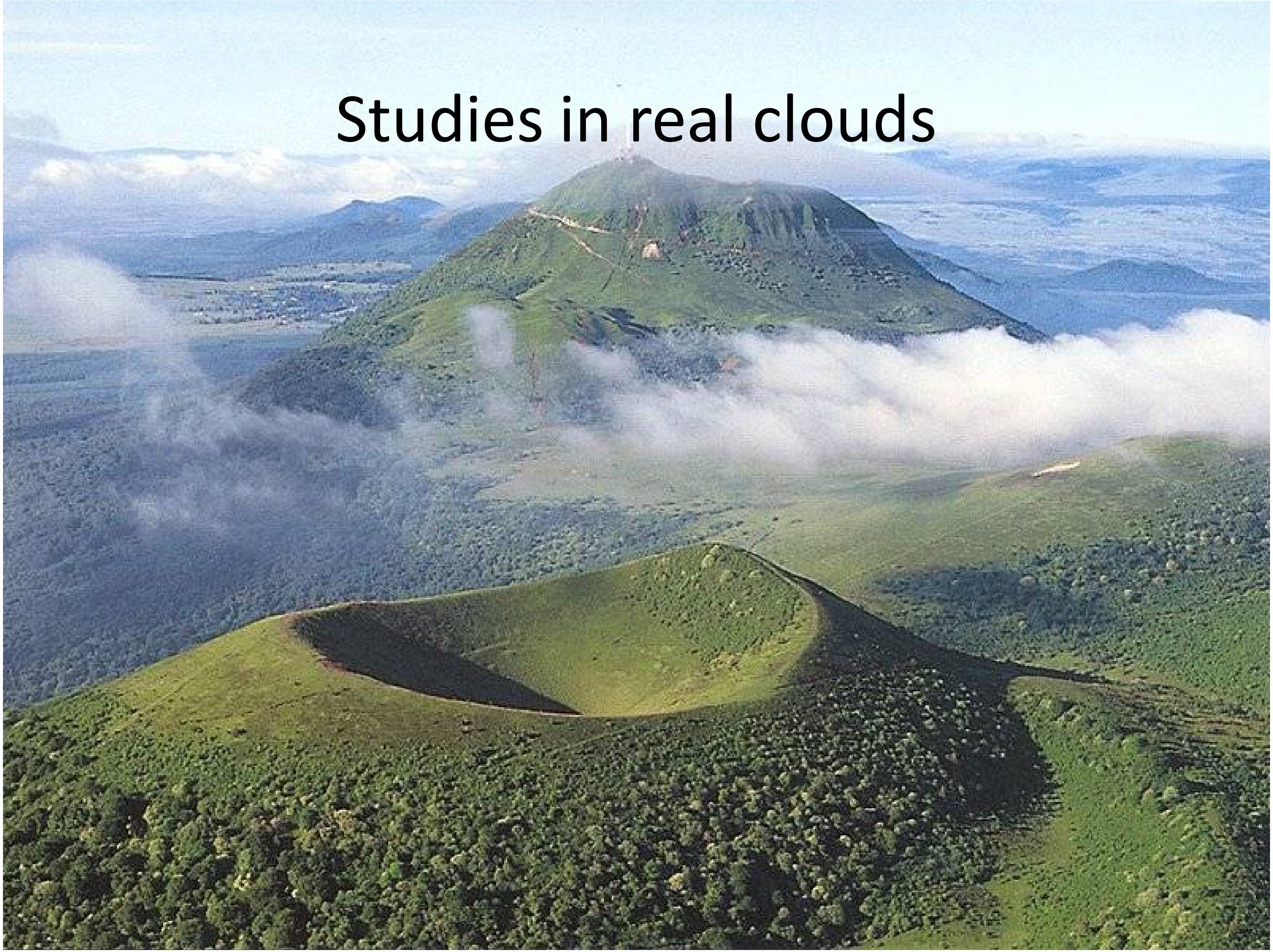
Fitted CCNc activation at SS=0.25%, puy de Dôme, France



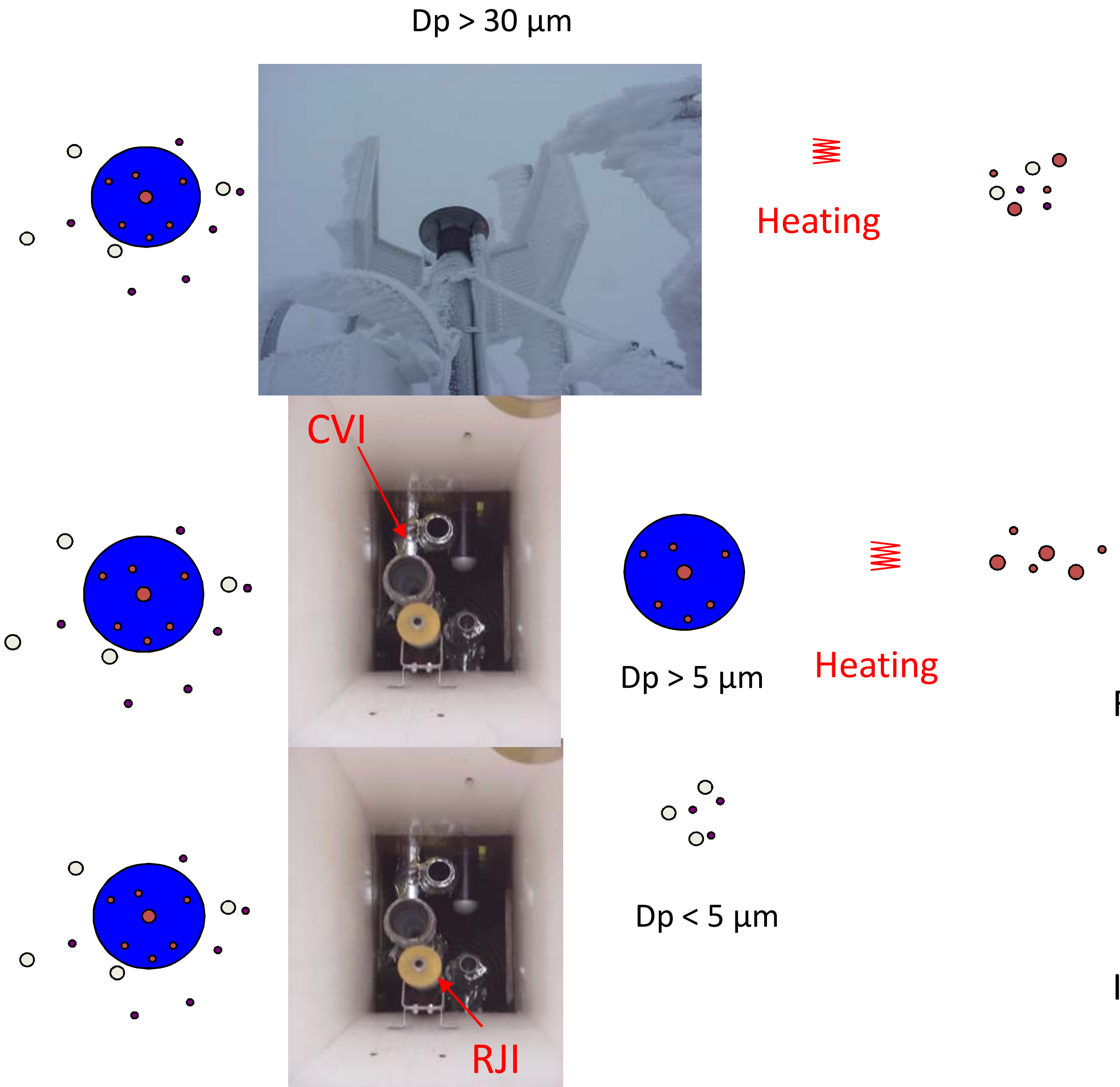
Ability to predict CCN number under controlled conditions



Studies in real clouds



Inlets: Separating activated aerosol from non activated aerosols



Whole Air Inlet (WAI)

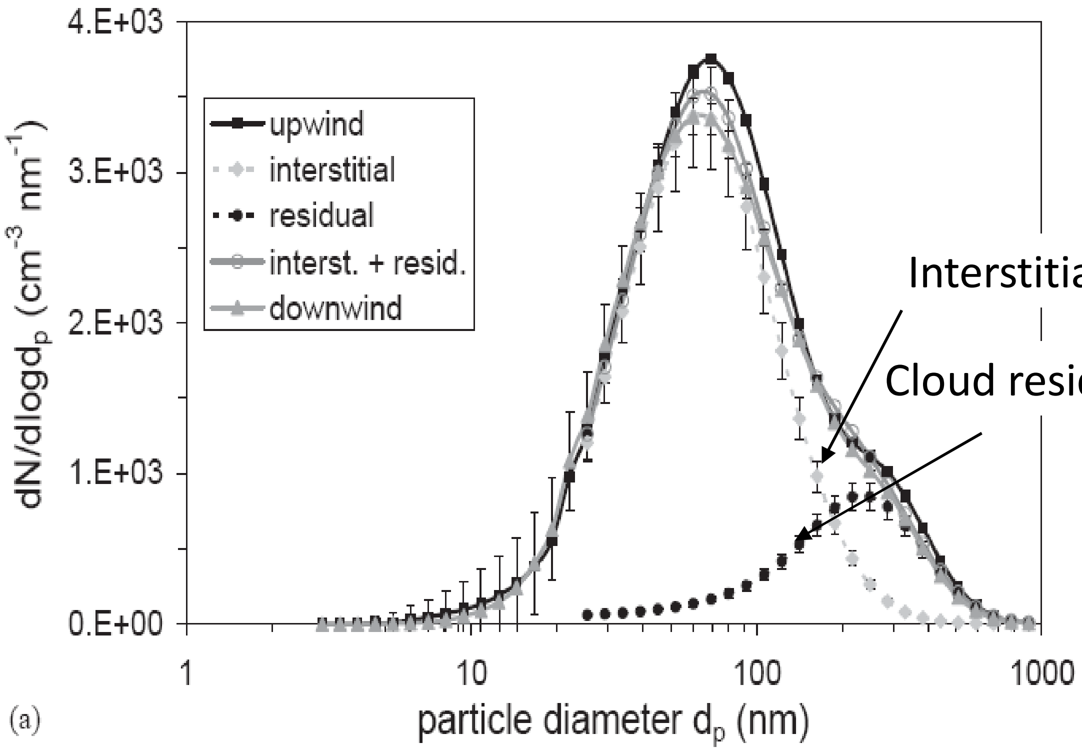
Cloud droplets (Cloud Droplet Impactor *CVI)*

Residual particles and gazes

Interstital inlet (Round Jet Impactor RJI)

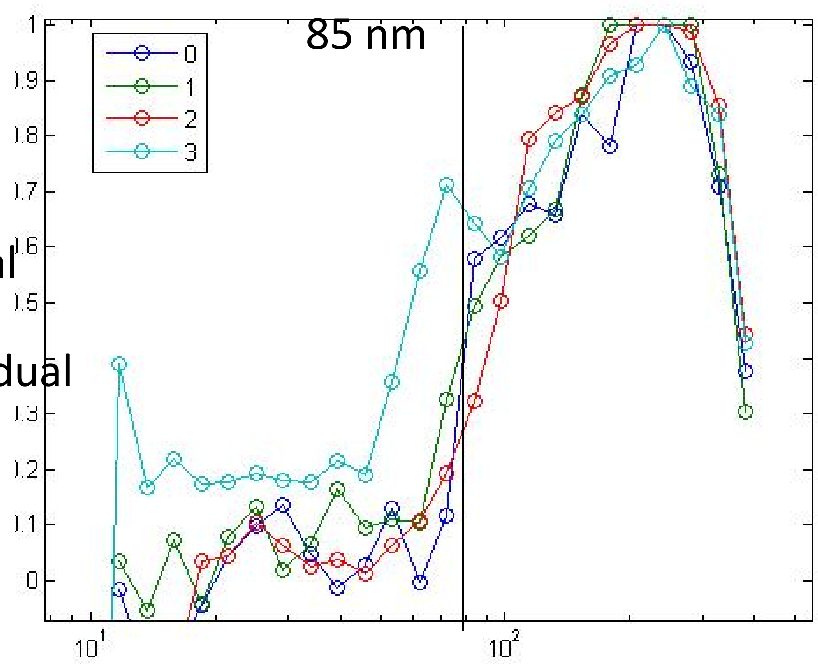
Interstitial particles and gazes

Activated size distribution



Mertes et al. (2005). Atmos. Env. 39, 4233- 4245

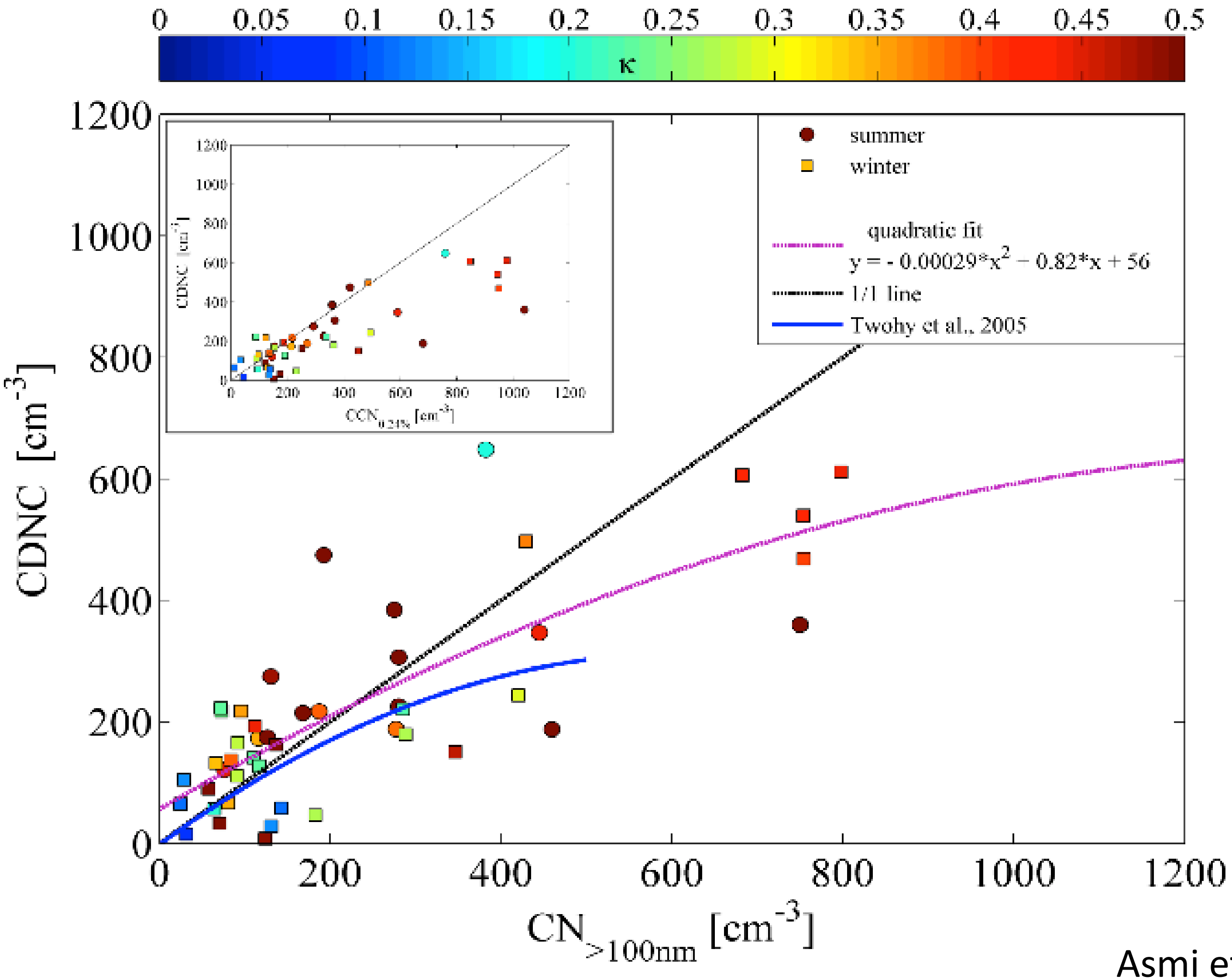
Activated fraction at Puy de Dôme



- Aerosol particle larger than 100 nm form cloud droplets
- The are found are residual particles from evaporated cloud droplets

- The ratio activated/total gives the activation diameter

Droplet number prediction

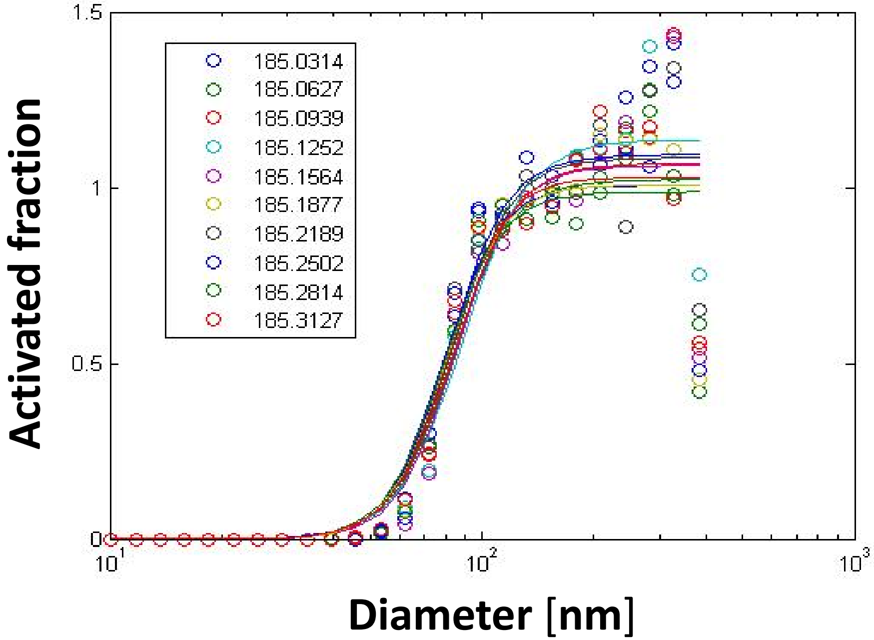


Asmi et al. in prep.

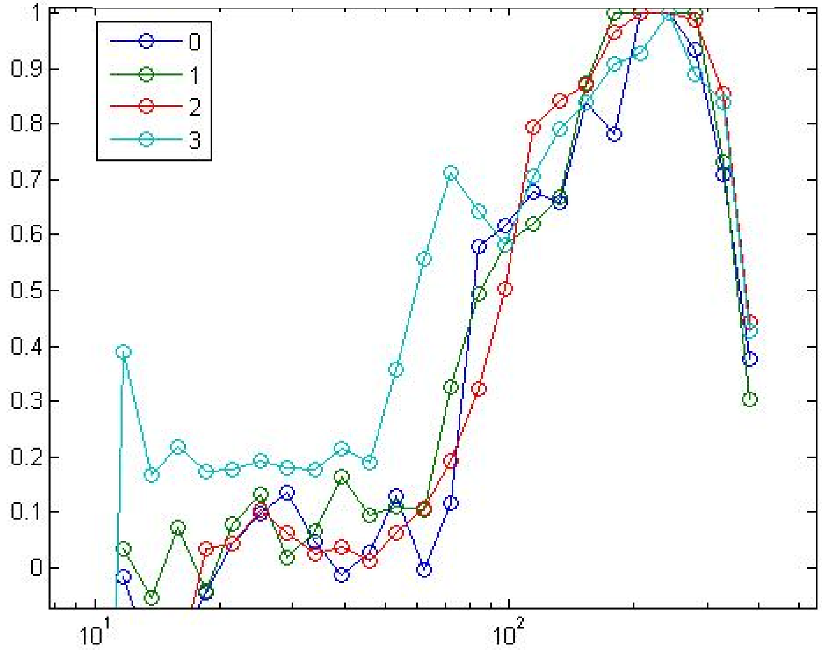
Activated fraction at Puy de Dôme

Some large aerosols not activated

CCN Chamber



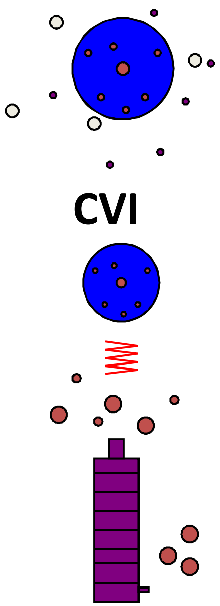
Real cloud

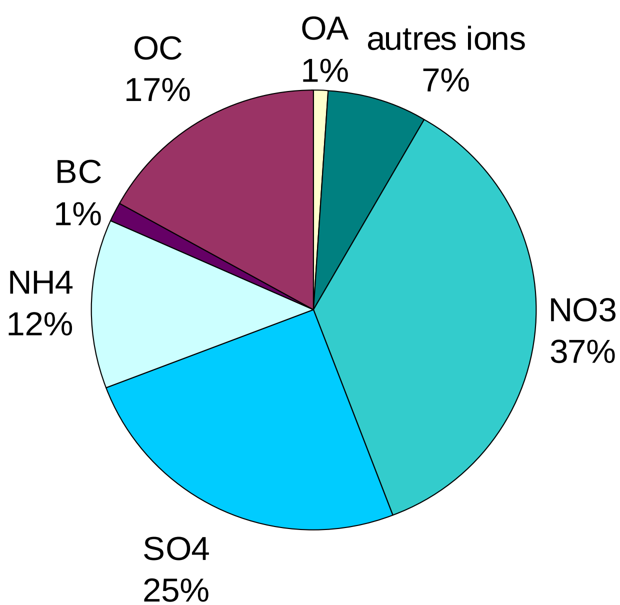


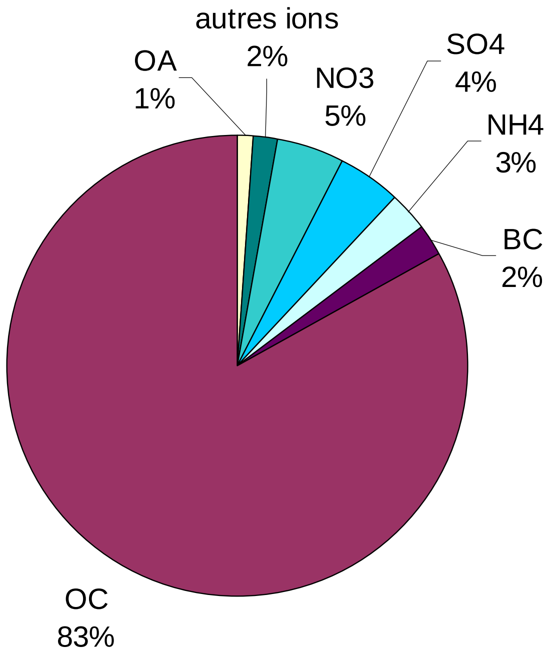
Some mall aerosols activated

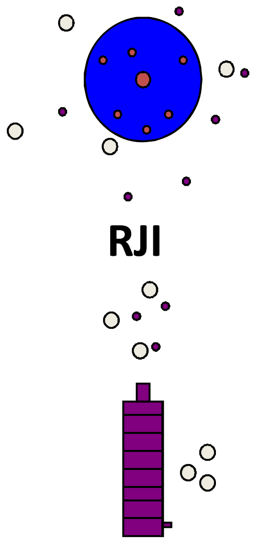
Chemistry of activated aerosols

Activated aerosols | Interstitial aerosols

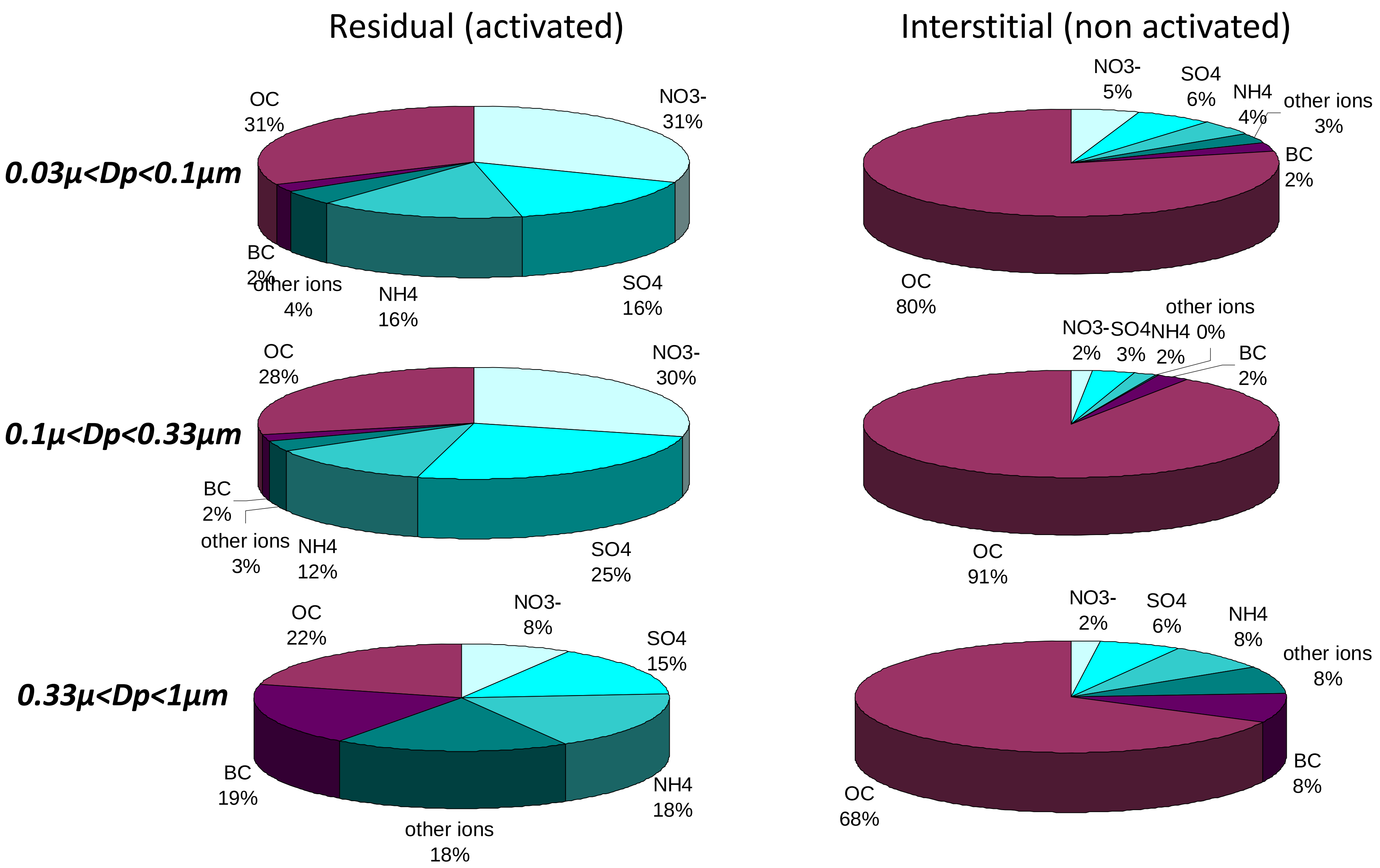






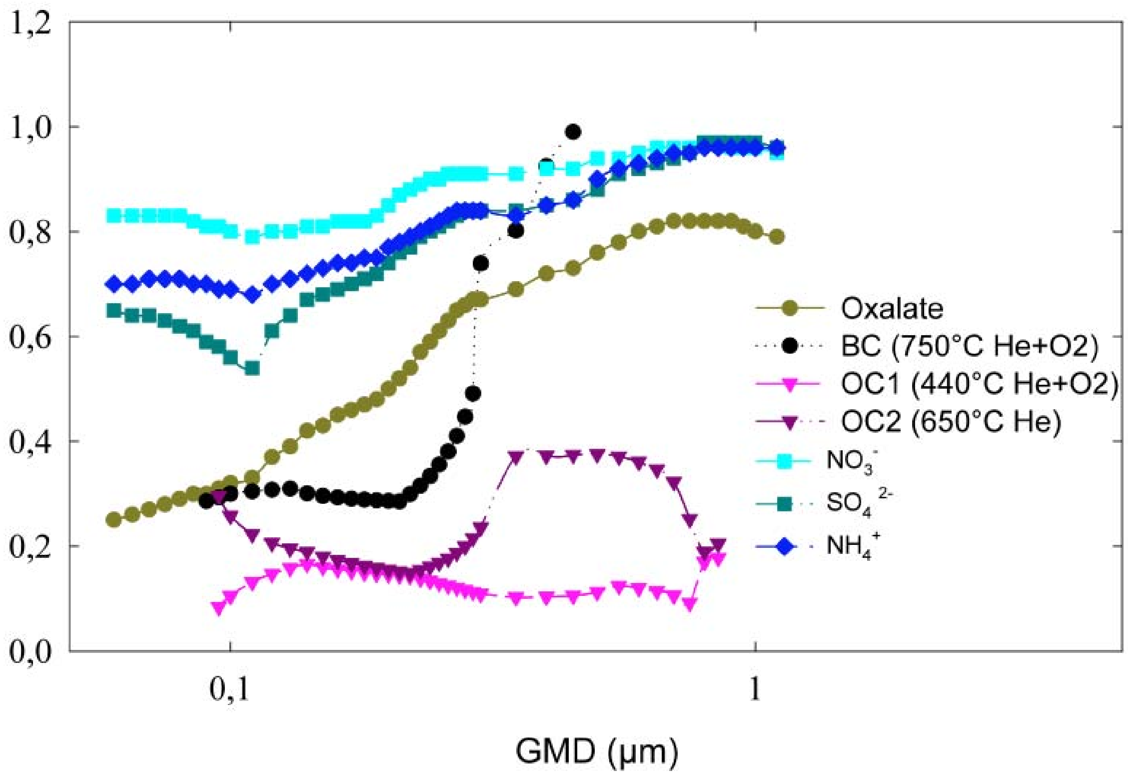


Chemistry of activated aerosols



Evidence of complex mixture/role of chemistry

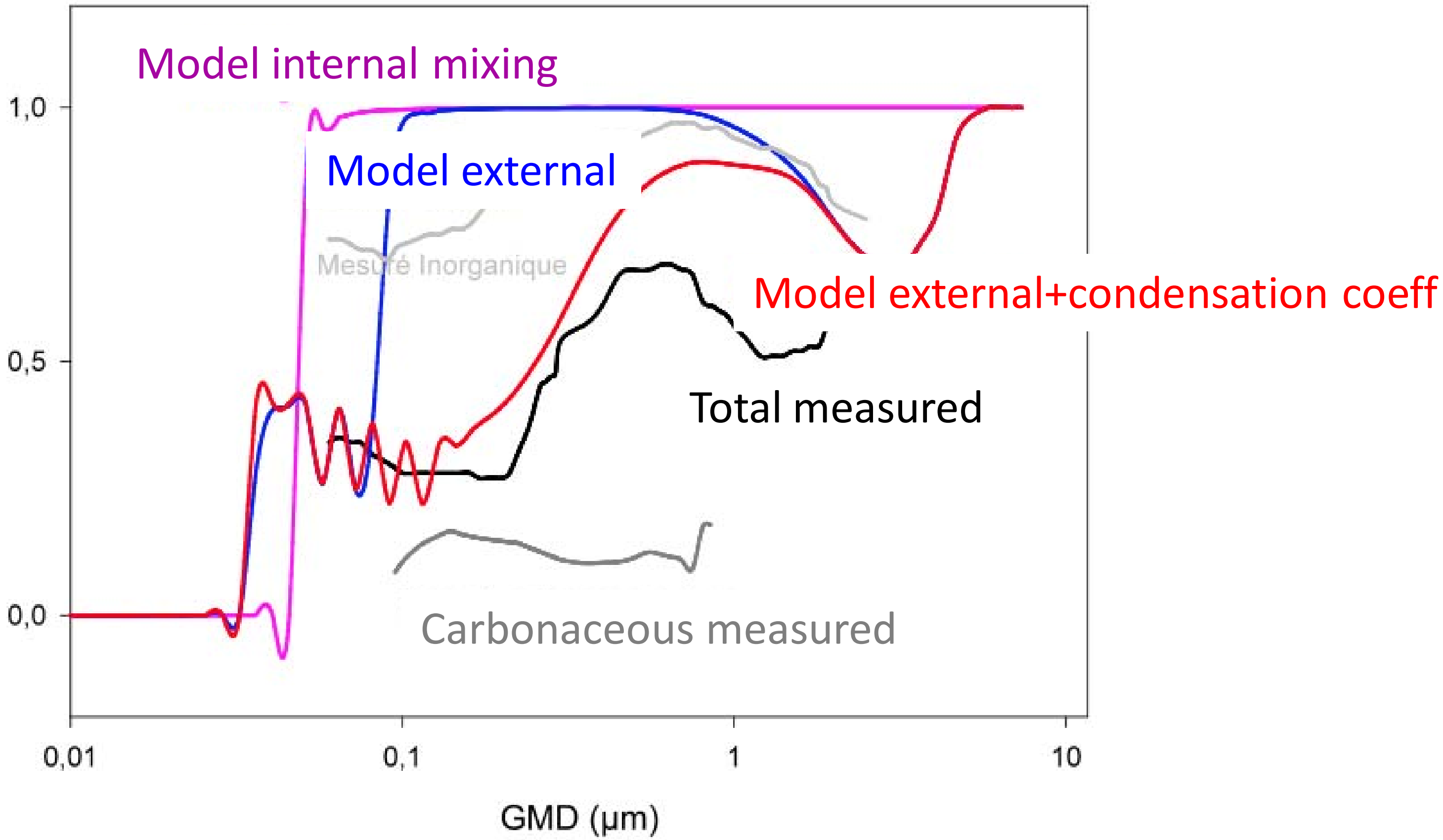
Activated aerosol fraction



Sellegri et al. JGR, 2003

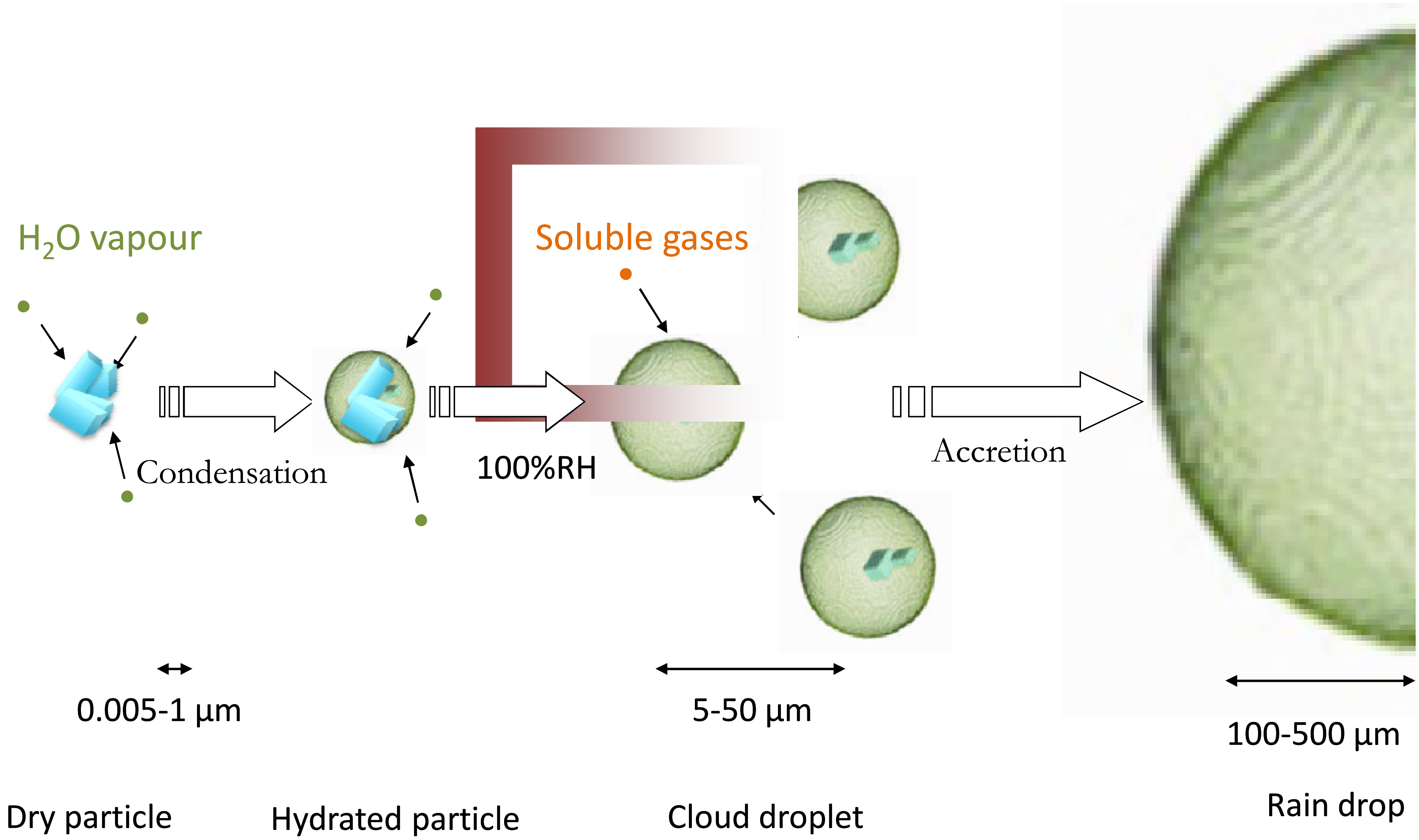
Aerosol activation modeling

Activated aerosol fraction modelled using EXMIX/measured

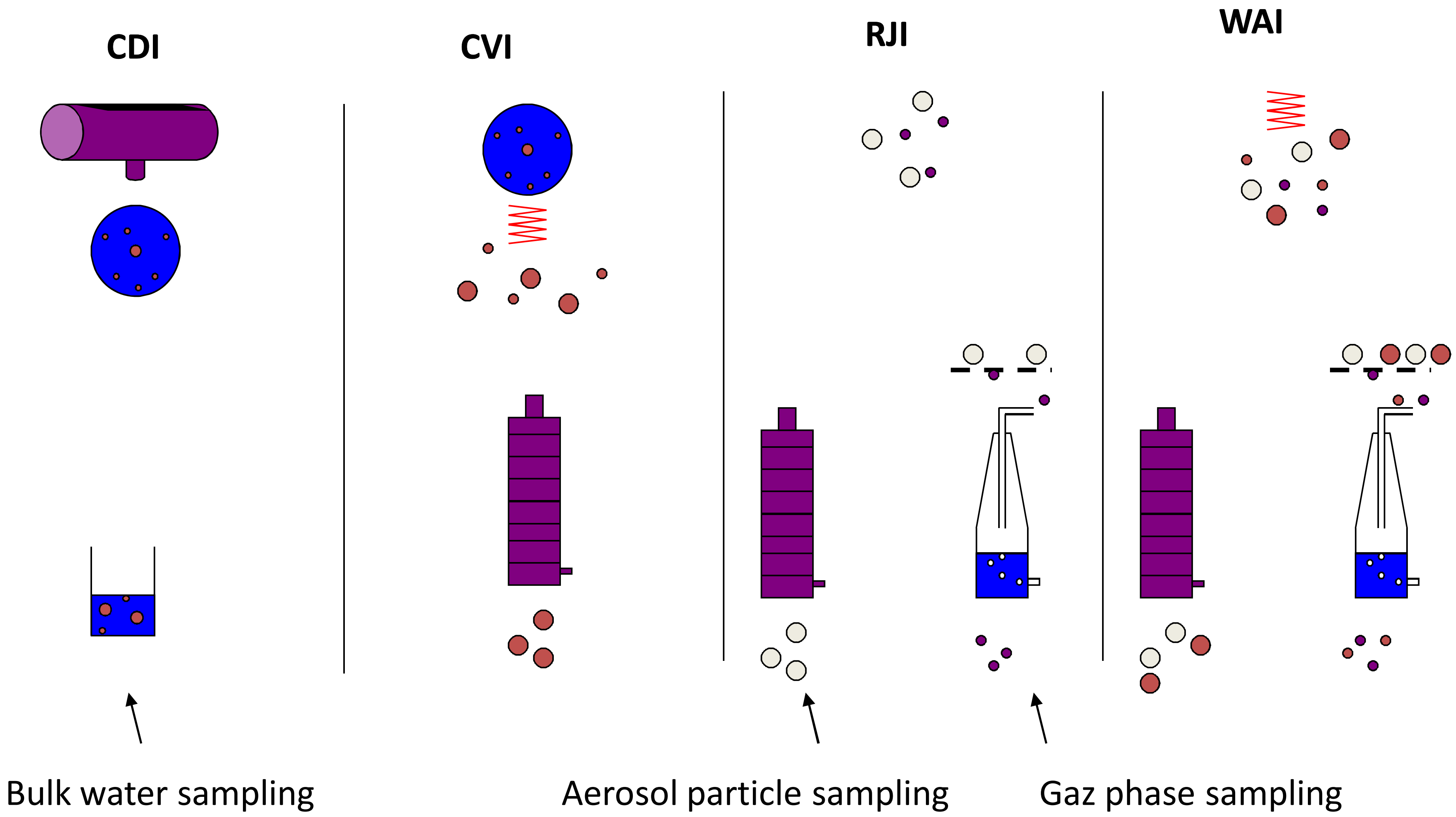


Taking into account chemical associations (external mixing) and kinetics of water vapour diffusion is necessary to model the real cloud mass transfer

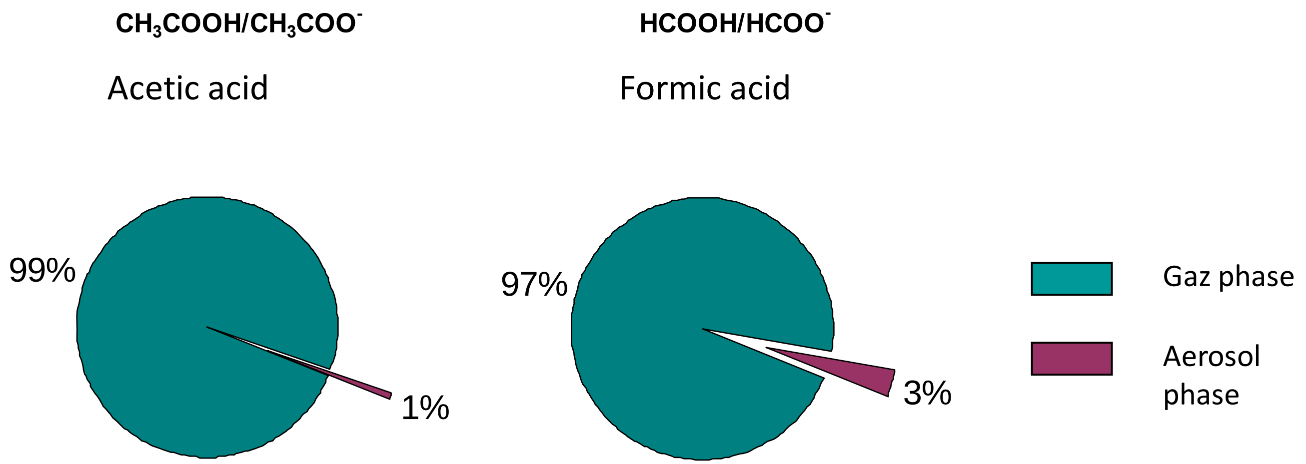
Uptake of other gaz phase pecies

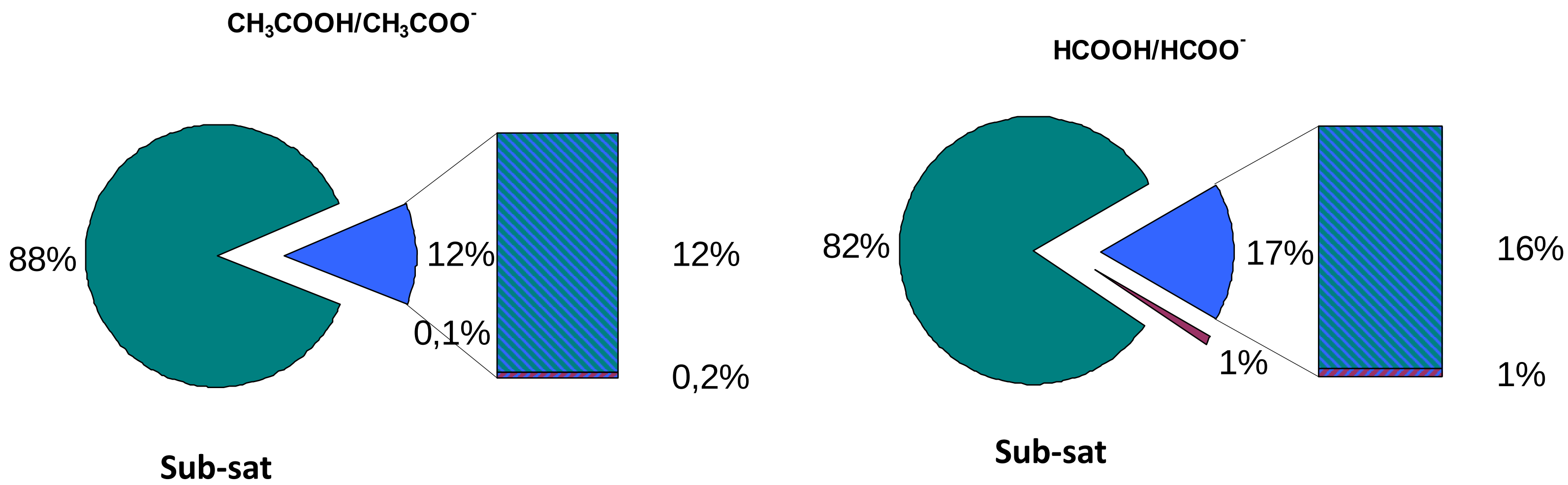


Instrumental strategy

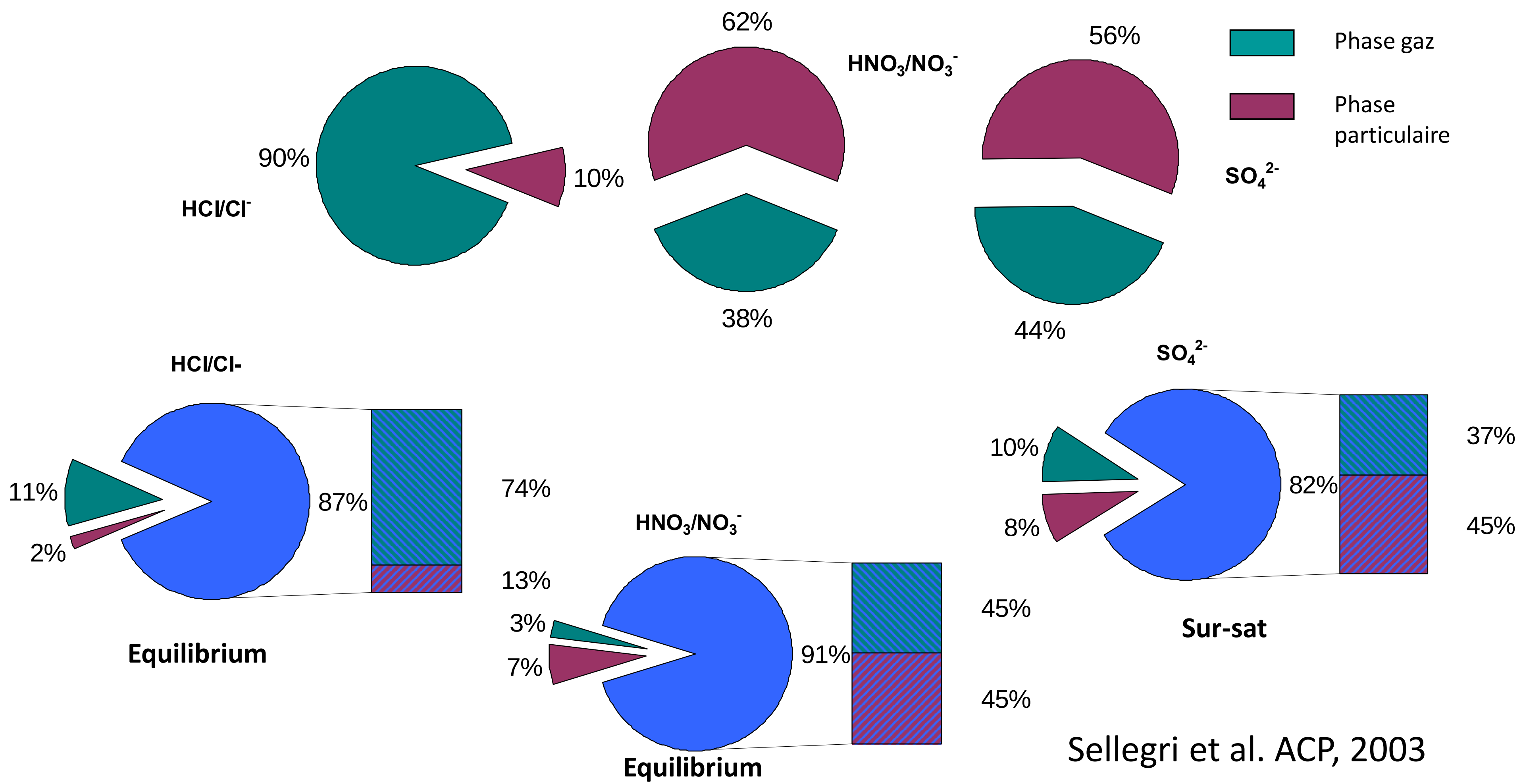


Gazeous contribution to droplet chemical composition





Gazeous contribution to droplet chemical composition



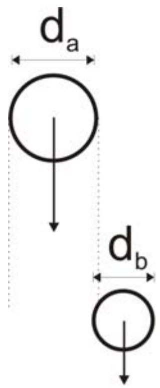
Sellegri et al. ACP, 2003

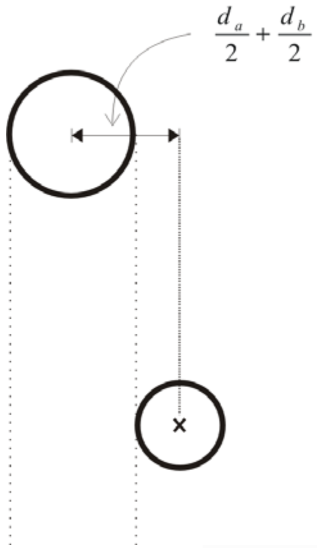
Below-cloud impaction scavenging

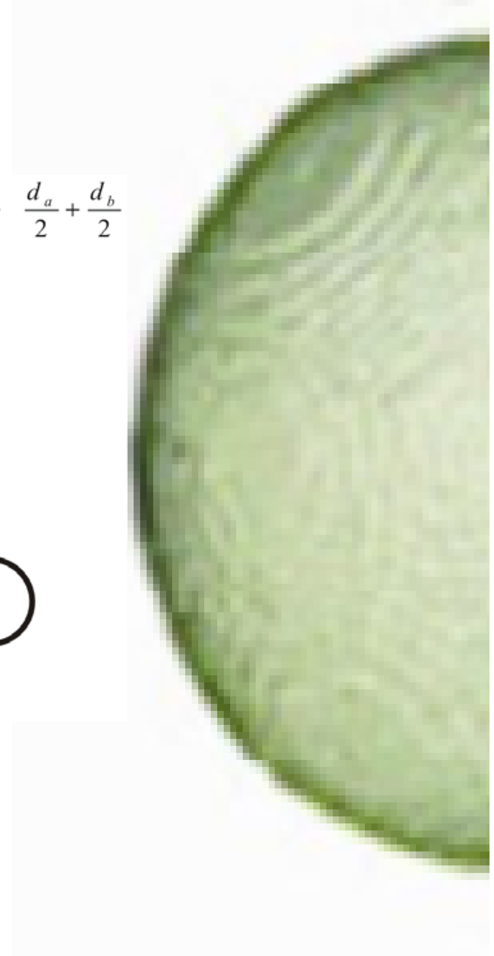
$$v_t = \frac{\rho_p dp^2 g Cc(dp)}{18\mu};$$

$$\lambda = 0.066$$

$$Cc = 1 + \frac{2\lambda}{dp}[1.257 + 0.4e^{-\frac{1.1dp}{\lambda}}]$$







Droplet d_a, particle d_b
Sedimentation velocities v_a, v_b
Num Conc. N_a, N_b
Volume before colision:

$$= \pi\left(\frac{d_a}{2} + \frac{d_b}{2}\right)^2 (v_a - v_b)\Delta t$$

Number of particles impacted $= \pi\left(\frac{d_a}{2} + \frac{d_b}{2}\right)^2 (v_a - v_b)\Delta t \cdot N_a$

Below-cloud scavenging experiments

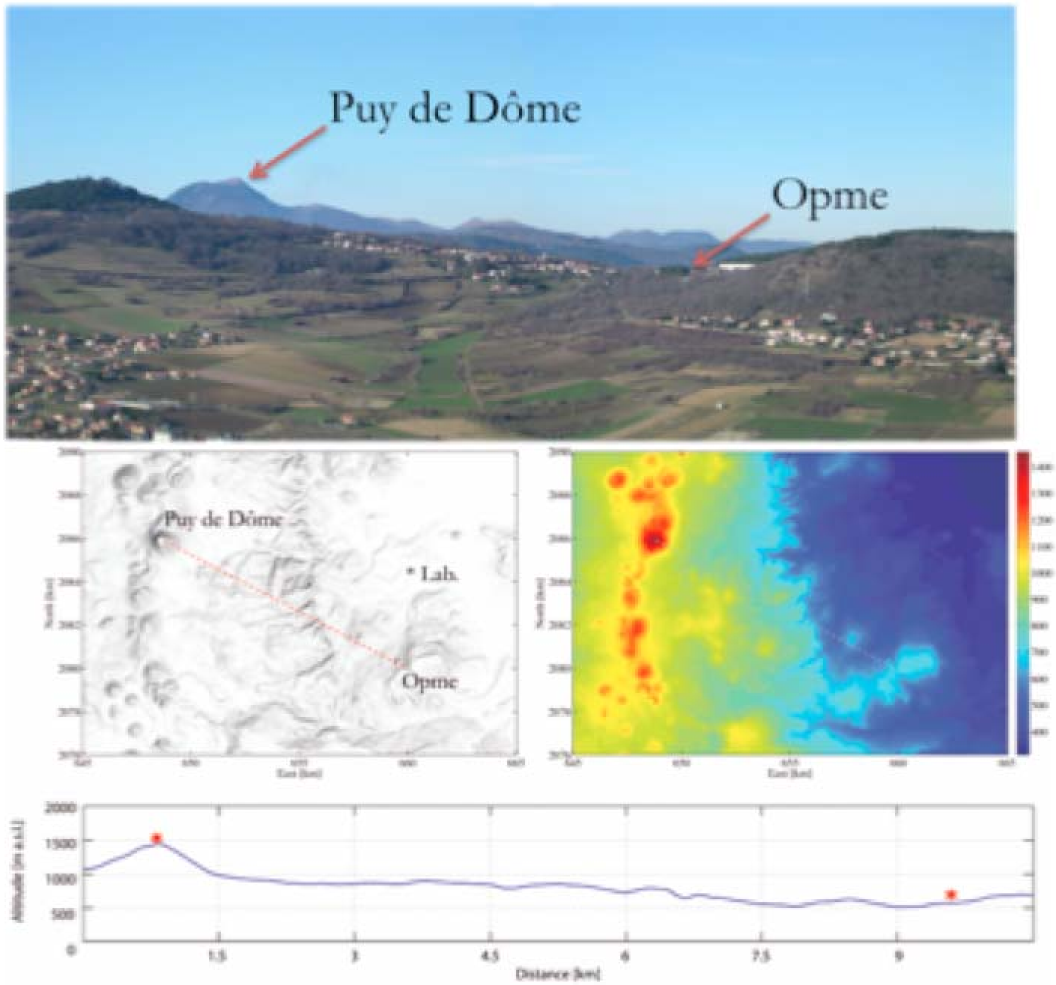
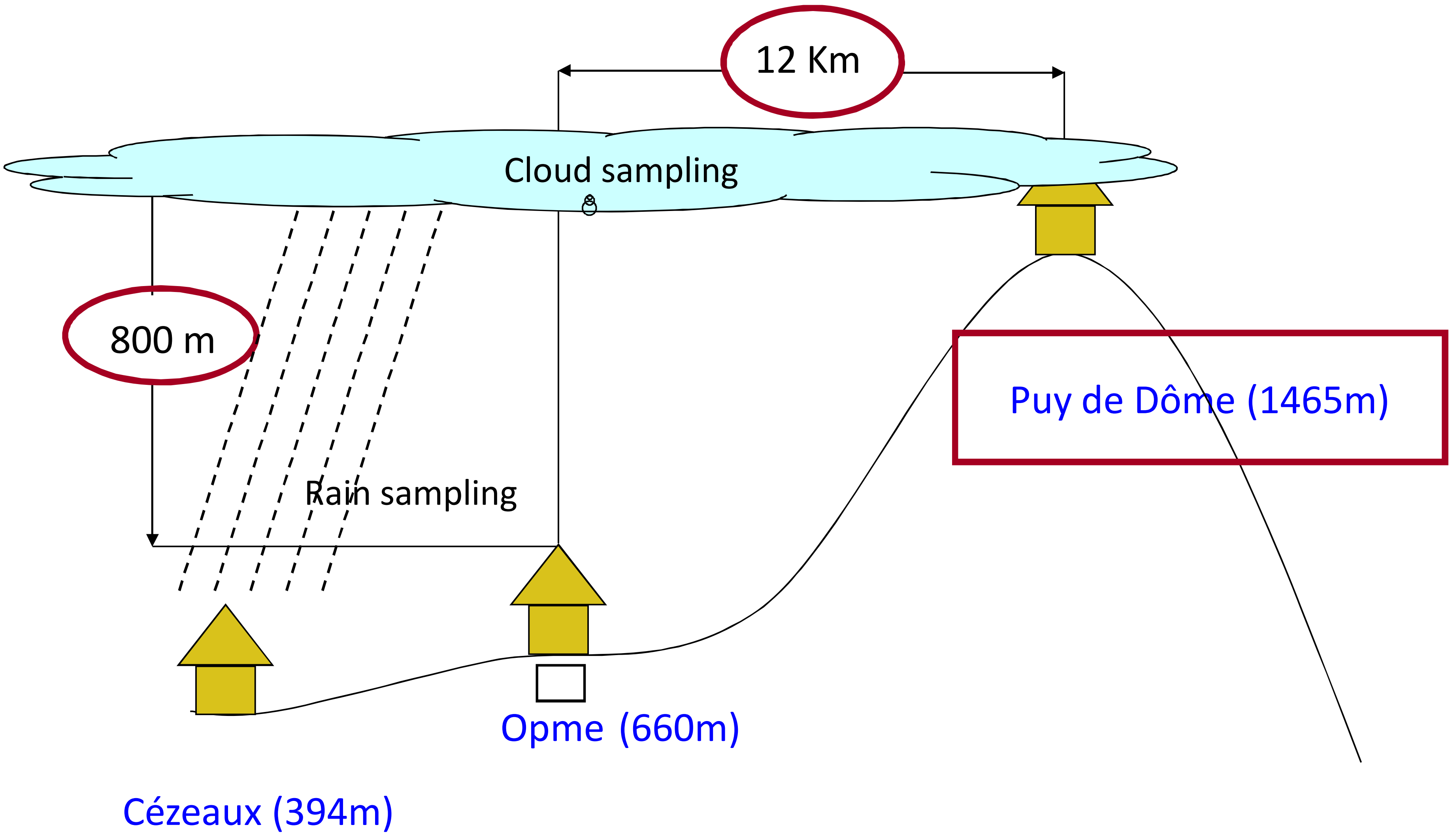


Fig. 1. Topographical view of the two measurement sites.
figure

Sampling Methodology



Washout ratio

$$W_r = \frac{\rho \cdot C_{rain}(X)}{C_{aerosol}(X)}$$

(McNeary and Baskaran, 2003

Jaffrezo and Colin, 1988)

With ρ, air volumic mass (1.2 kg/m$^{3)}$

C_{rain} (X), concentration in rain (µg/kg)

$C_{aerosol}$ (X), concentration in aerosol, (µg/m$^{3)}$

- sampling the rain water/aerosol: can not separate below-cloud scavenging from in-cloud scavenging (activation)
- Which aerosol?

Rain and aerosol concentrations seasonal variation

Rain : max summer

min winter

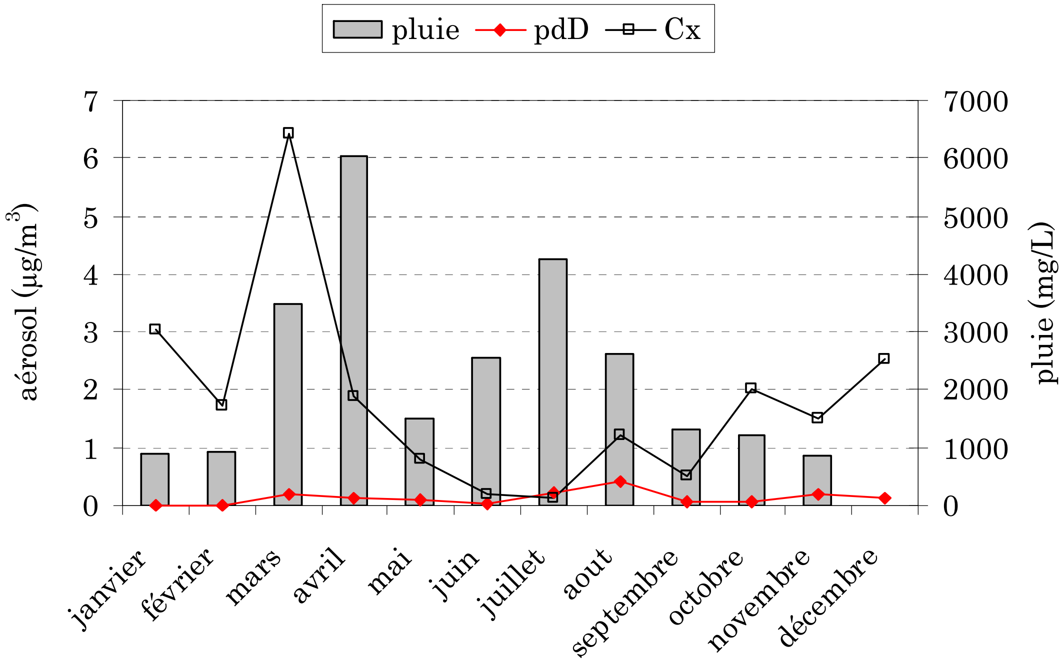
Aerosol: Same at pdD

Opposite at surface site (Cx)

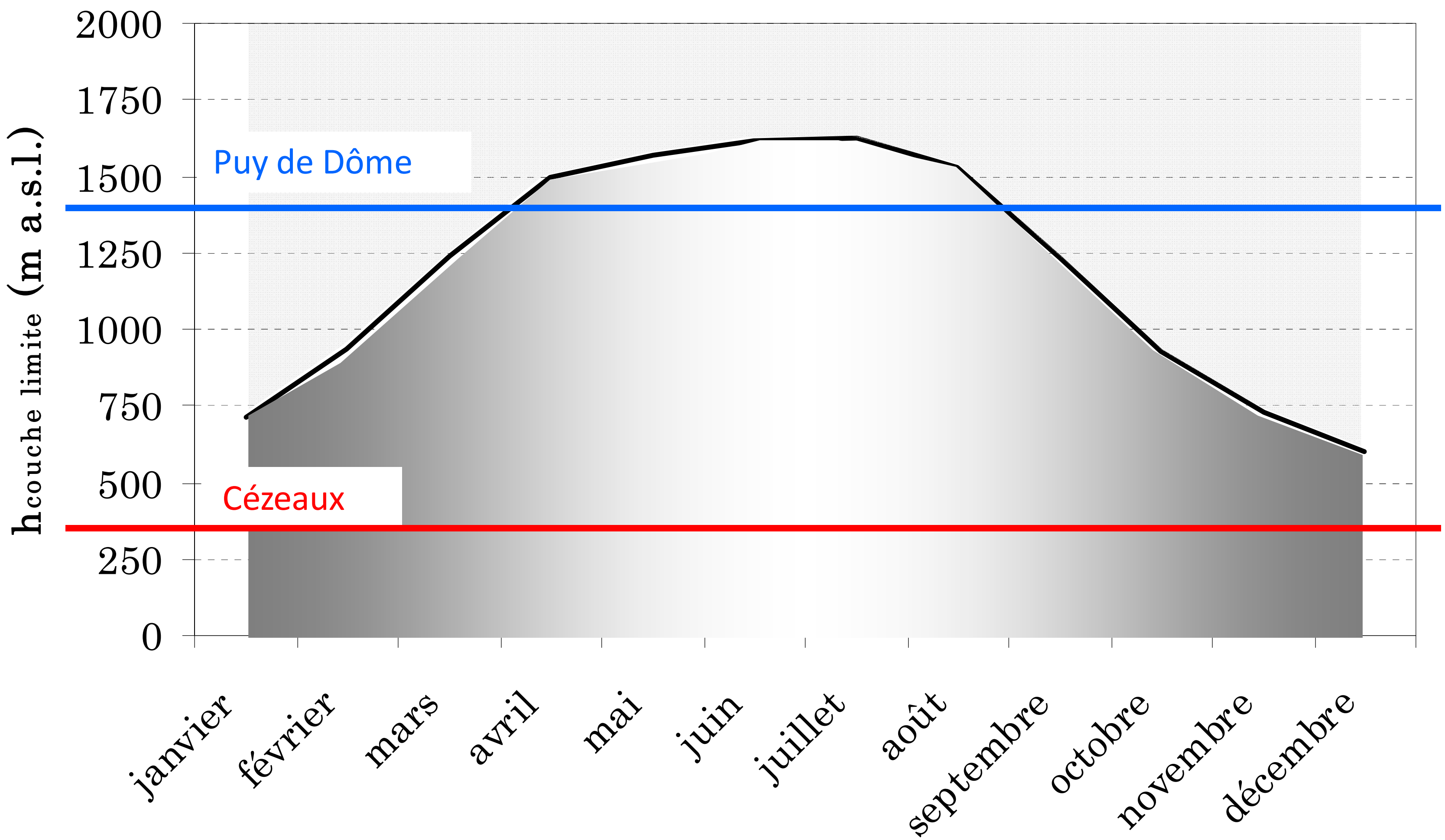
Using aerosol concentration at cloud level more adapted?

But using the Puy de Dôme aerosols, the ratio summer/winter higher in the rain (11.6) than in aerosol (1.4)

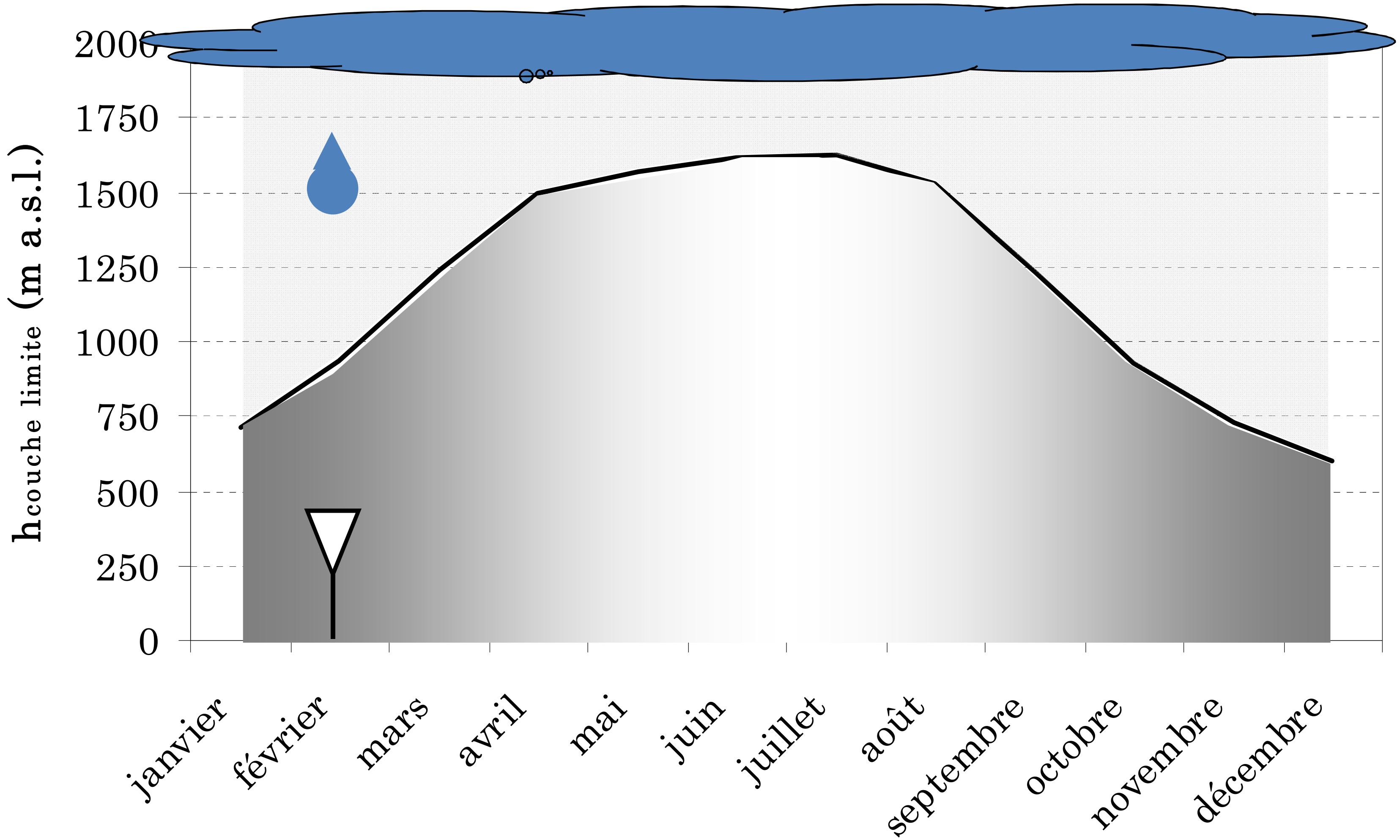
Other factors influence rain composition



Effect of Boundary layer dynamics



Effect of Boundary layer dynamics



Taking the Boundary layer height in the washout ratio calculation

$$Wr = \frac{V_{rain}}{h_{BL}} \times \frac{C_{rain}(X)}{C_{aerosol}(X)}$$

	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$	NH_4^+	K^+	^{7}Be	^{210}Pb	^{137}Cs
Average	5.1	1.2	0.8	1.3	2.4	7	8.7	37.3
	4703	1921	1639	1893	2629	782	415	3083
variability	137%	75%	87%	100%	79%	164%	460%	460%
	82%	*222%*	*212%*	*179%*	*116%*	*87%*	*122%*	*109%*

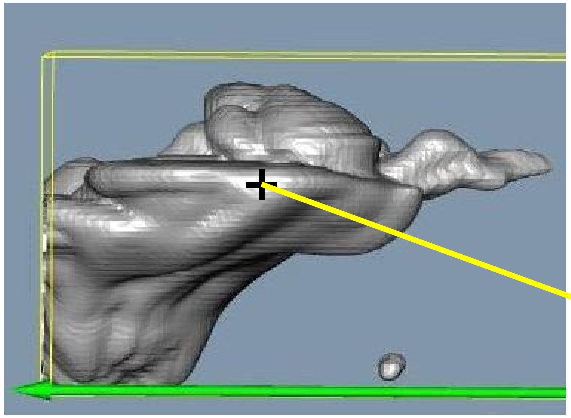
Taking into account the BLH increases reliability of Wr

Bourcier et al. 2012

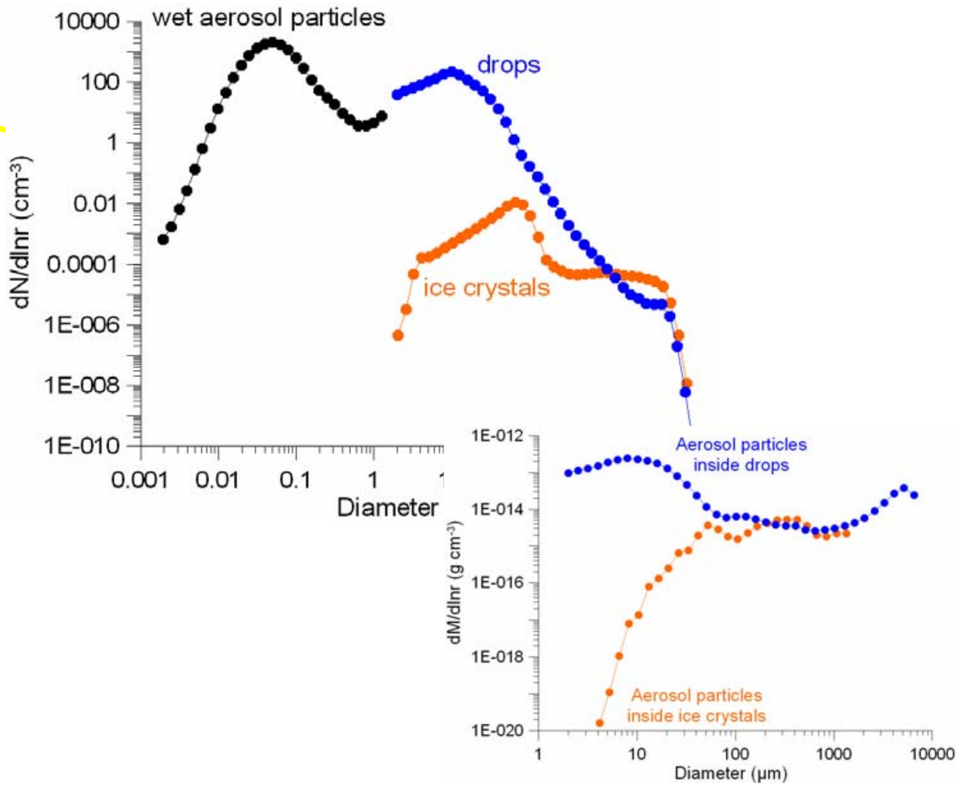
Integrating all processes using modelling tools

DESCAM 3D: a 3D cloud model with detailed microphysics

Example: a cumulonimbus cloud



Dynamics: NCAR *Clark-Hall* cloud scale model (Clark and Hall, 1991)
Microphysics: *DE*tailed *SCA*venging *M*odel (Flossmann and Wobrock, 2010)



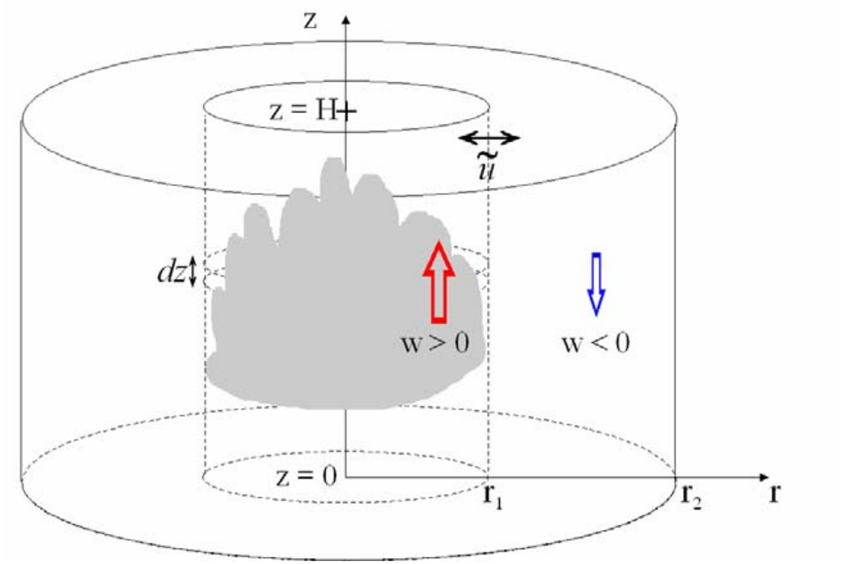
We follow the spectra of :

- ♦ **wet aerosol particles,**
- ♦ **drops,**
- ♦ **ice crystals**
- ❖ **aerosol mass in drops**
- ❖ **aerosol mass in ice crystals**

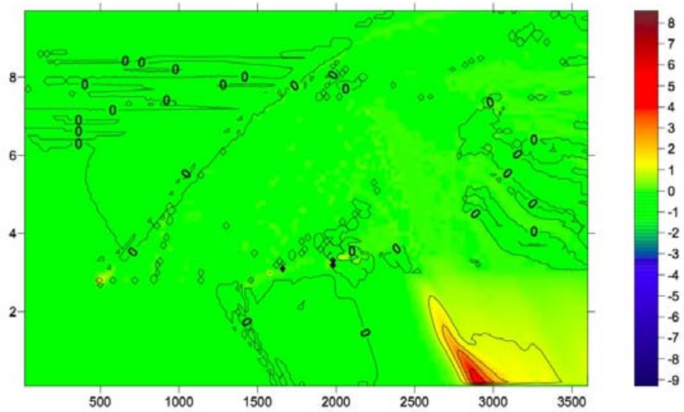
⇒ 5 x 39 size bins = 195 variables

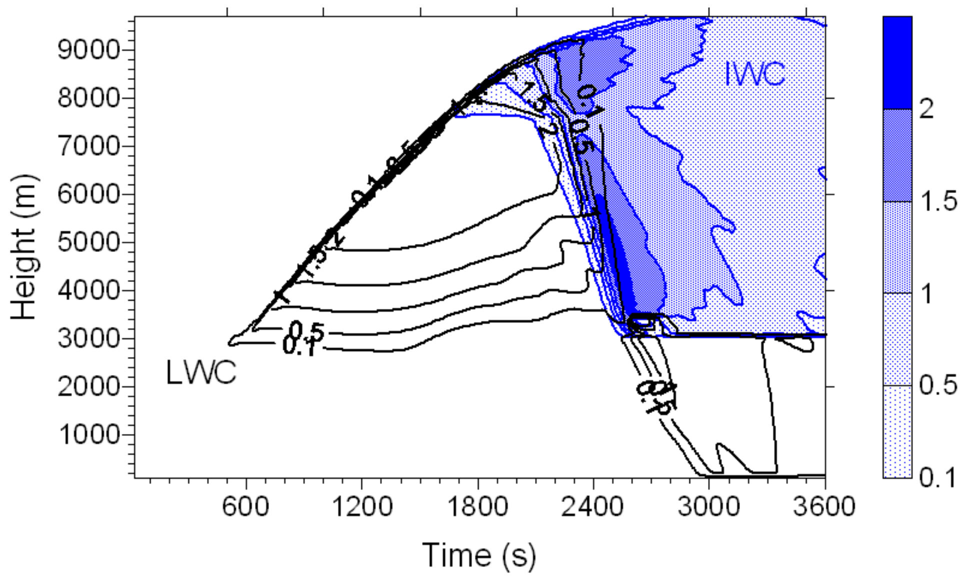
(Leroy et al. 2009, Atm. Res.)

Influence of the impaction scavenging



DESCAM 1.5 D model





Difference with/without impaction scavenging:
Factor 2 in the aerosol mass deposited

Summary

- A large percentage of aerosol mass deposited by rain originates from aerosol in-cloud activation
- One can accurately predict the hygroscopic growth (RH<100%) of aerosol at a given RH from its size and chemical composition
- Surface effects does not influence the hygroscopic growth of aerosols at RH<100
- At RH>100% aerosols are activated at sizes ranging from 50 to 150 nm for internally mixed pollutations
- N100nm is a good proxy of cloud droplet numbers for clouds studied at puy de Dôme
- However, chemistry play a major role when aerosol is externally mixed and some species will preferentially be incorporated in cloud droplets
- Gases also significantly contribute to the cloud droplet concentrations
- Below cloud scavenging contribution is difficult to separate from in-cloud activation and scavenging when studying rain water composition experimentally but modelling tools indicate a factor 2 in the aerosol mass deposited
- The boundary layer mixing height should be taked into account when calculating wash-out ratios but simplifactions/parametrizations are difficult and 3D modelling tools necessary