



Influence of particle-bound water on aerosol mass measurements

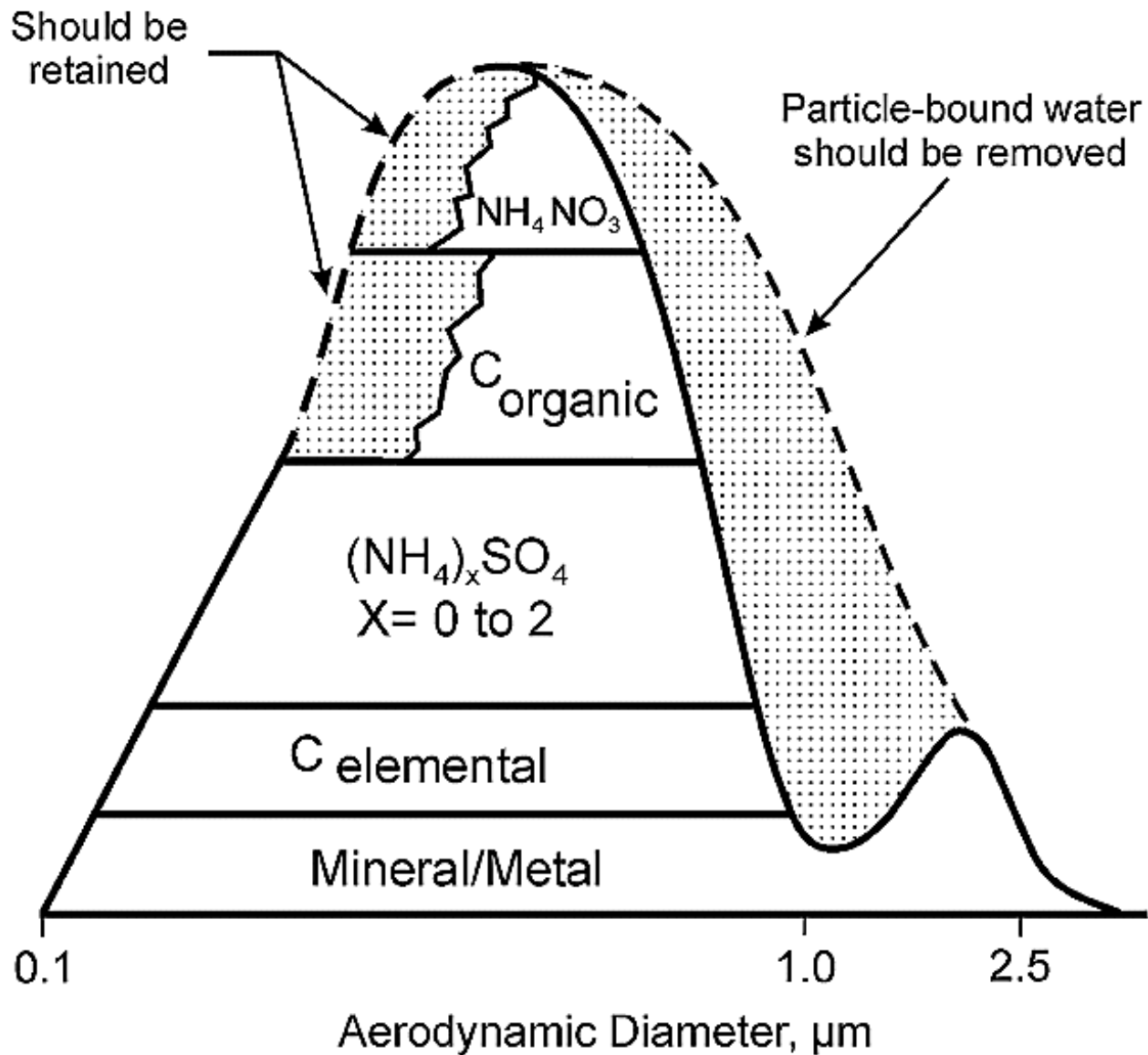



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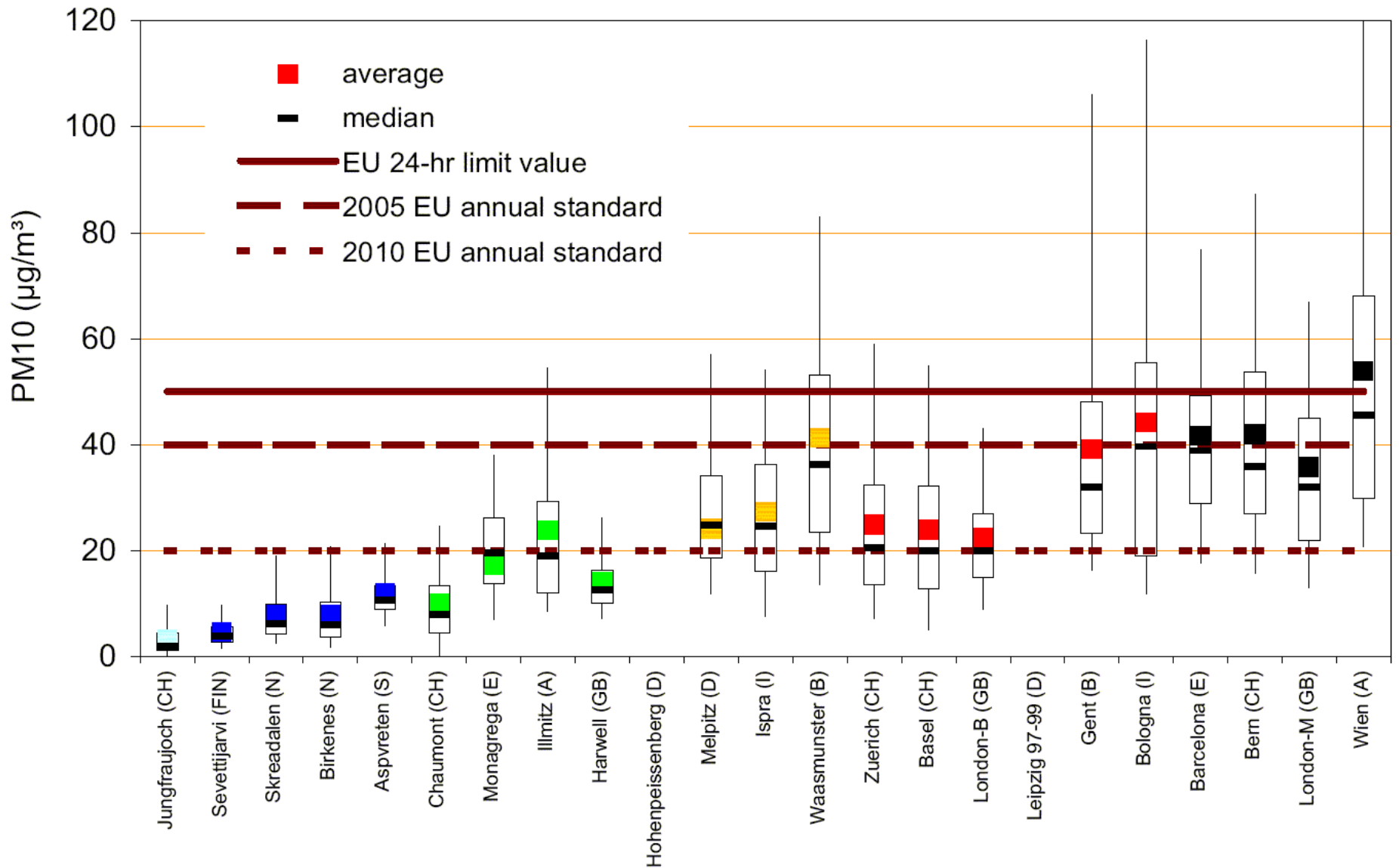


 Semivolatile components subject to evaporation during or after sampling

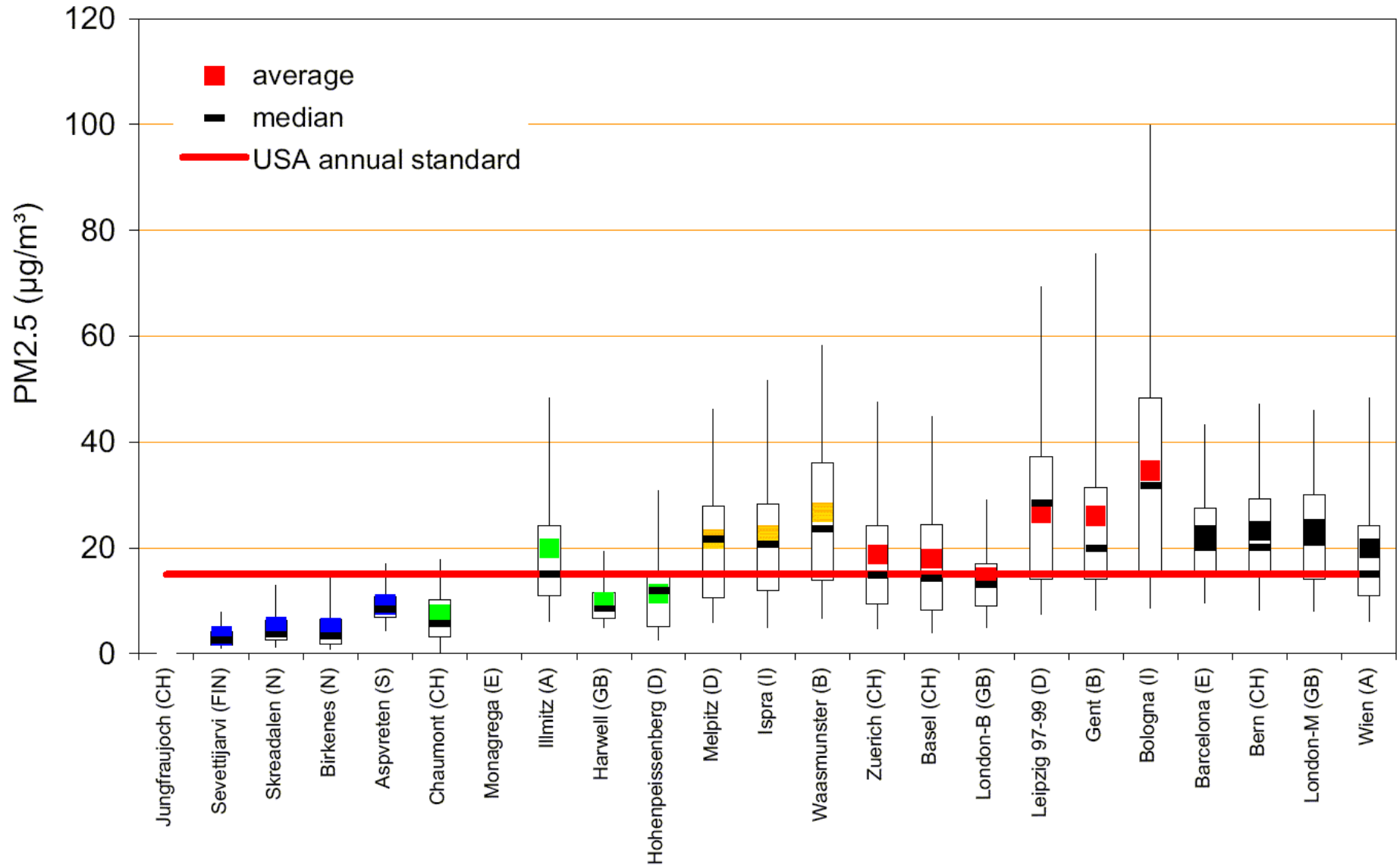
Effect of hygroscopic particles on PM measurements

- Water mass added to PM mass.
Regulating water?
- Particles might grow in size past the cut-off of the PM₁₀/PM_{2.5} inlet.
Loose PM mass at high RH?

European PM10 Concentrations



European PM2.5 Concentrations



Water vapour – liquid equilibrium

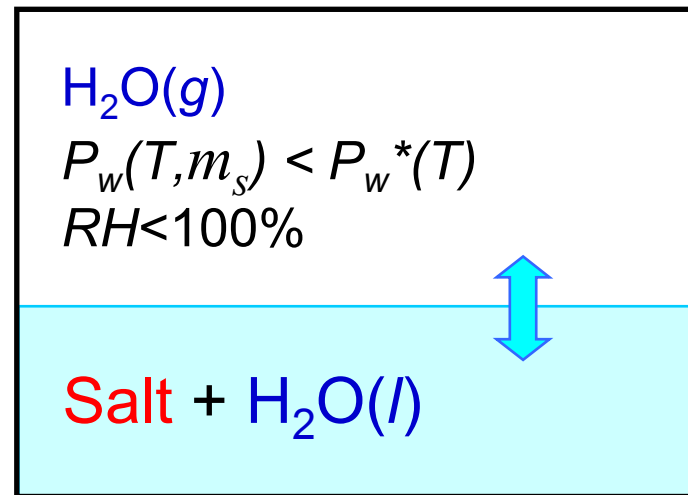
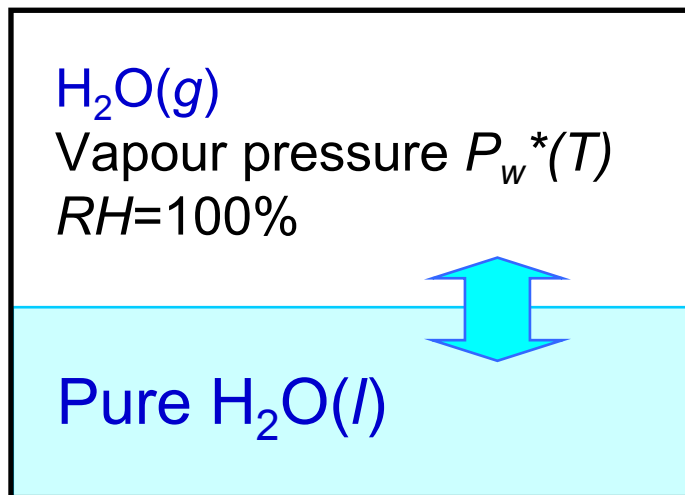
Raoult's law (ideal solutions) states that the equilibrium water vapour pressure is reduced over a salt solution:

$$RH = \frac{P_w}{P_w^*} = \frac{n_w}{n_s + n_w} = a_w$$

Water activity:

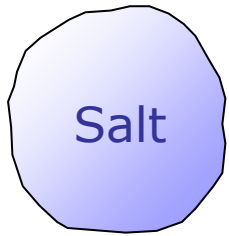
$$a_w = \frac{1}{1 + iM_w m_s}$$

RH relative humidity; n_w moles of water; n_s moles of salt ions in solution

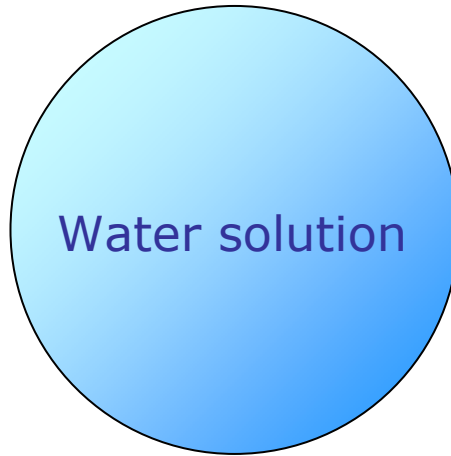


Molality of salt in solution: m_s mol / kg water

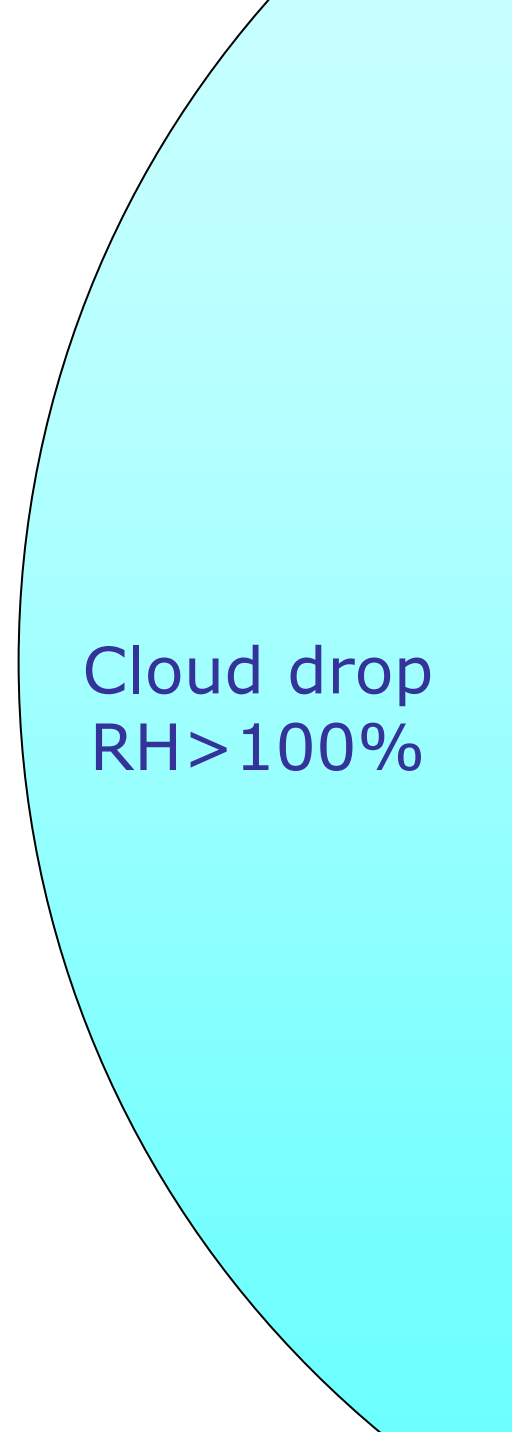
Dry particle



Humidified particle
RH=90%

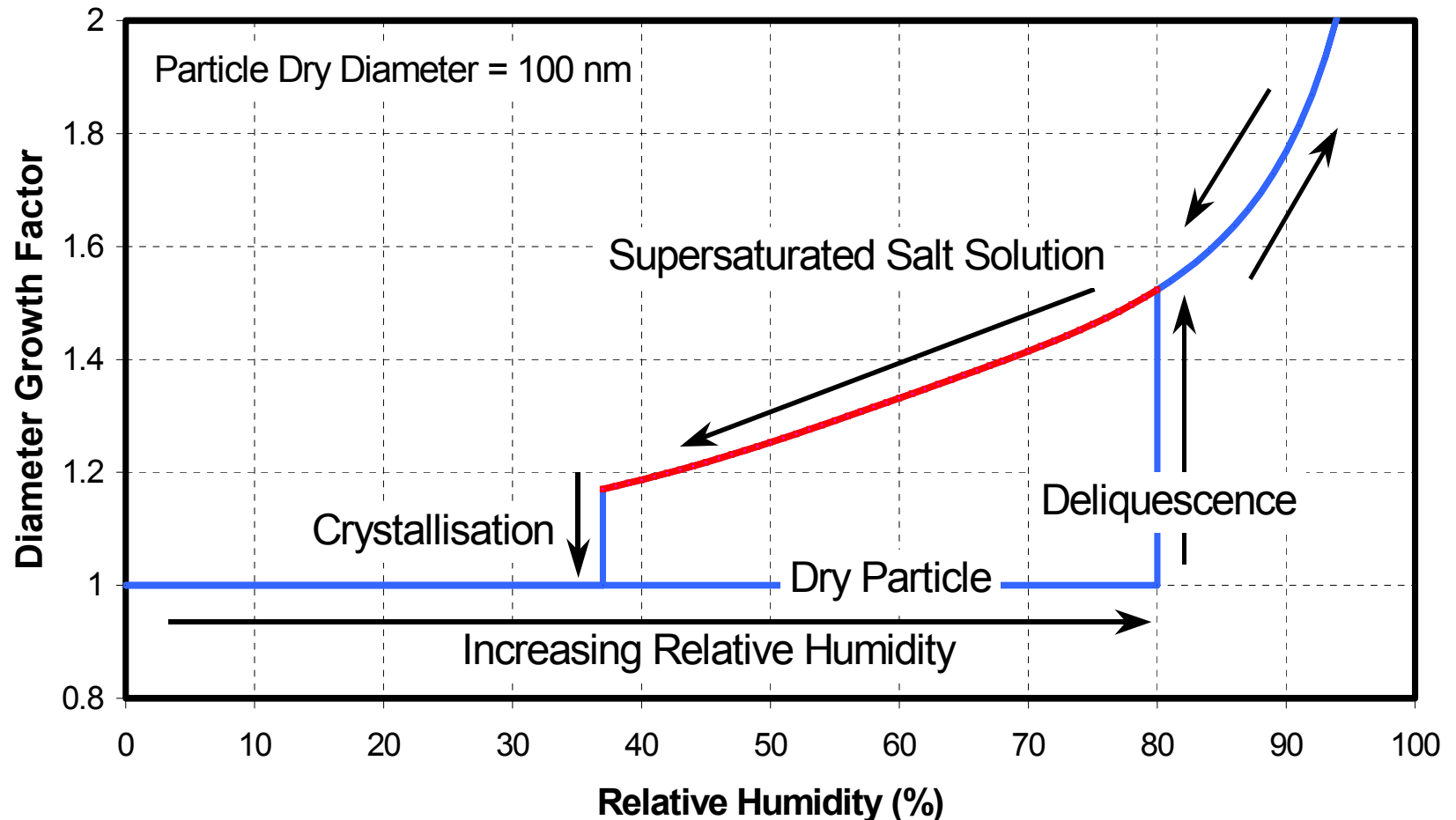


Cloud drop
RH > 100%

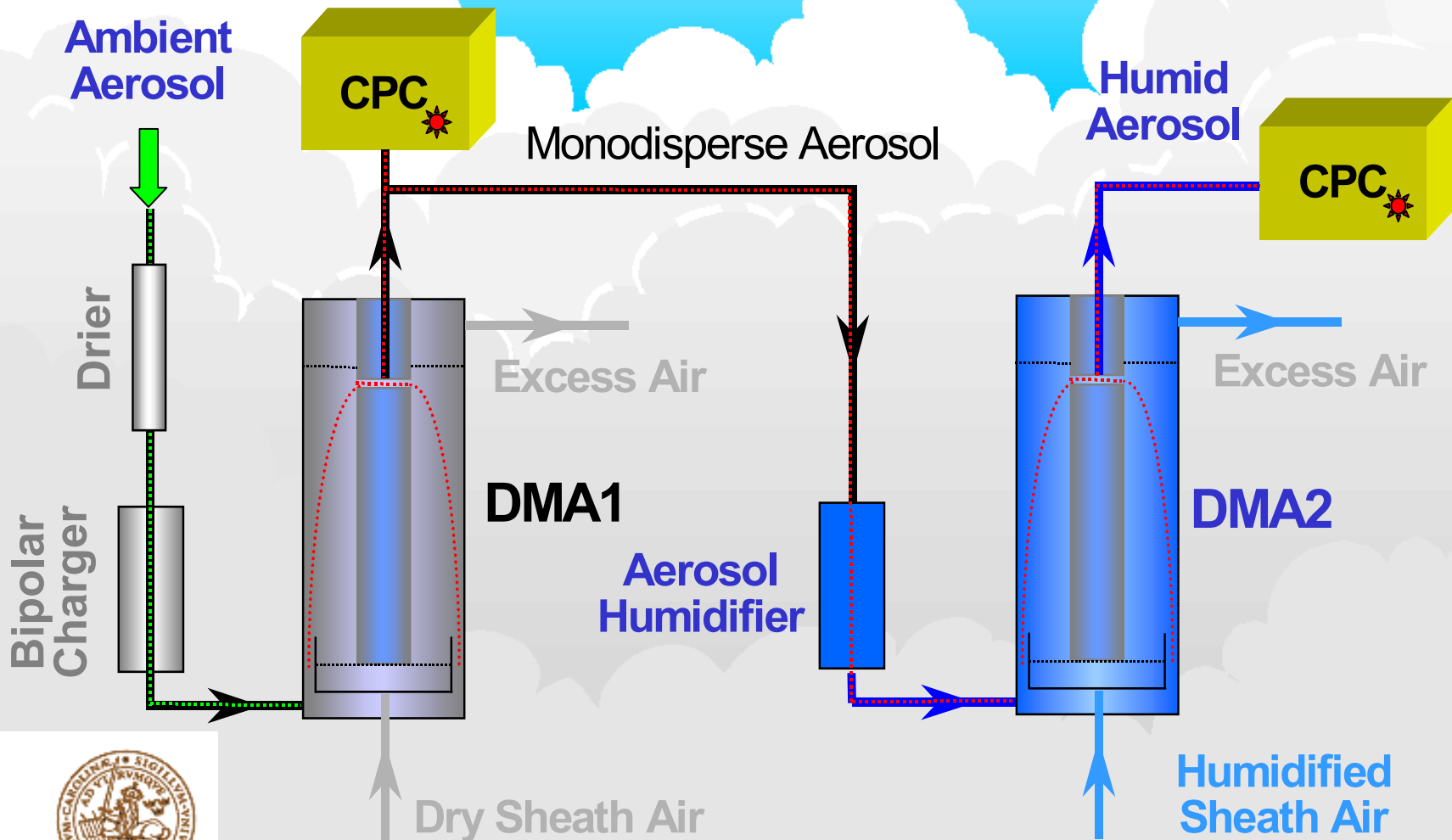


RH Hysteresis Effect

Ammonium Sulphate RH Hysteresis

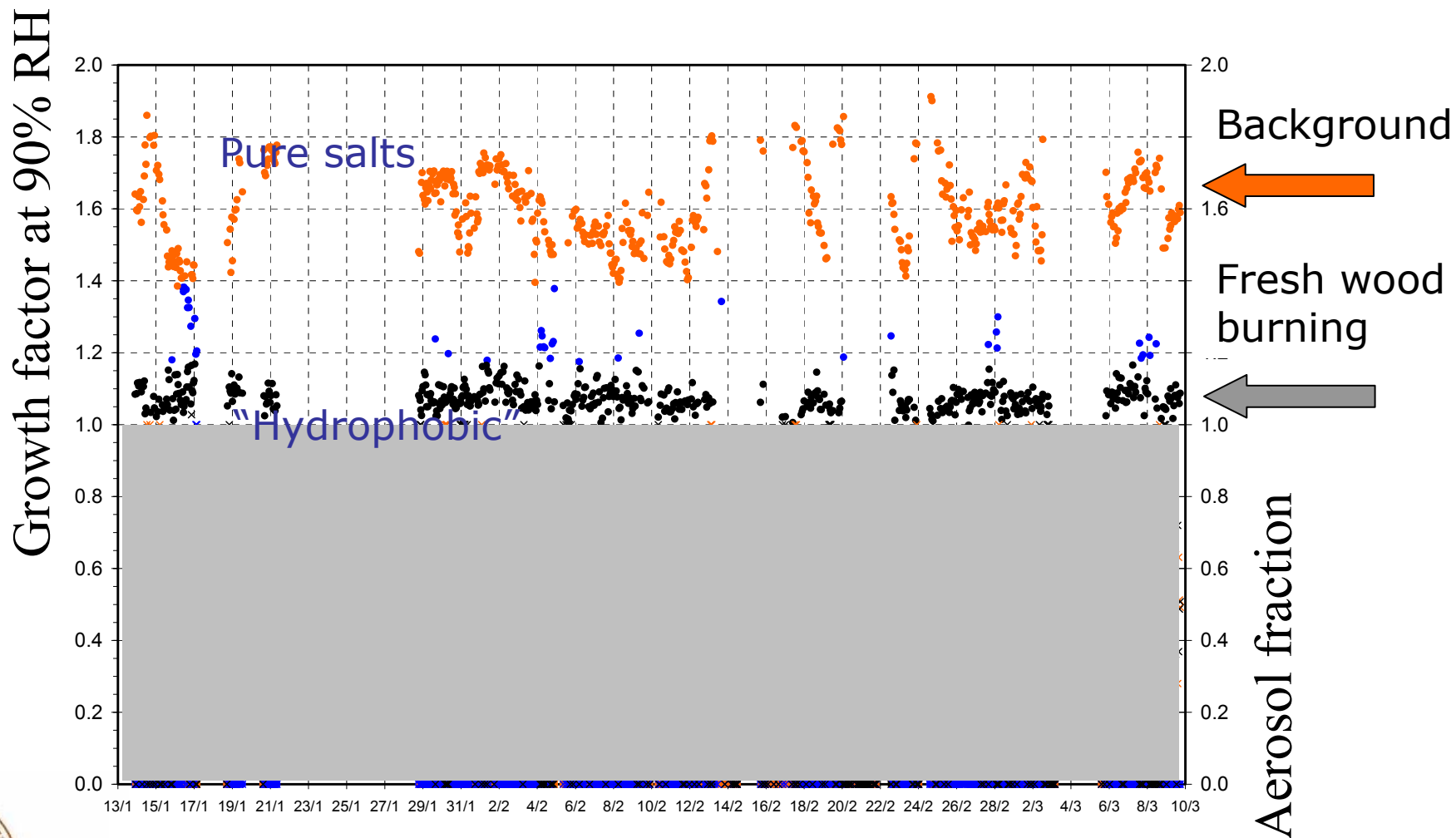


Hygroscopic Tandem Differential Mobility Analyser H-TDMA





Hygroscopic properties (H-TDMA) *Energimyndigheten* 265 nm (Forsdala)

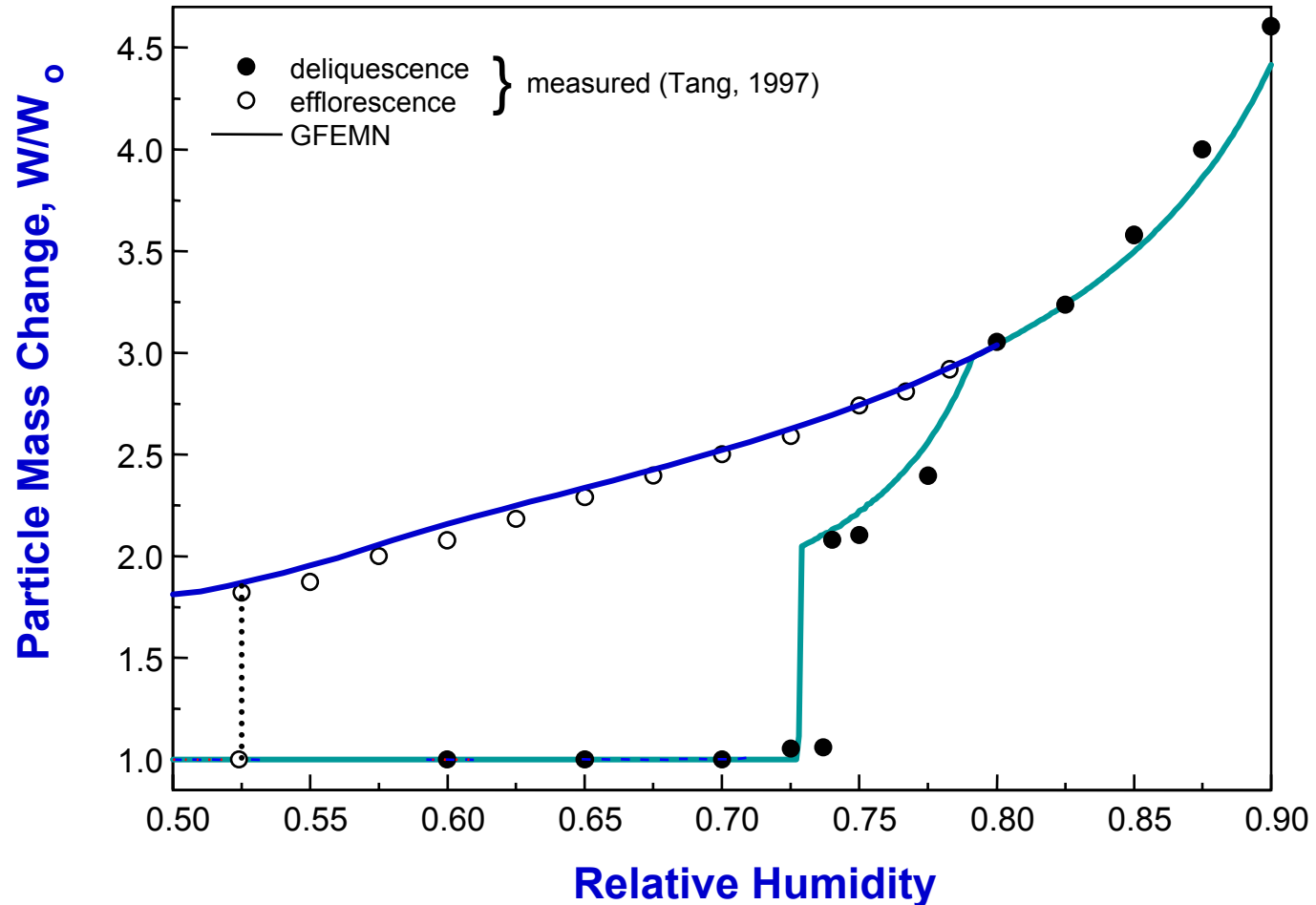


• hygroscopic, • intermediate, • hydrophobic



GFEMN Model Predictions for NaCl/Na₂SO₄

(Ansari and Pandis, Atmos. Environ., 1999)

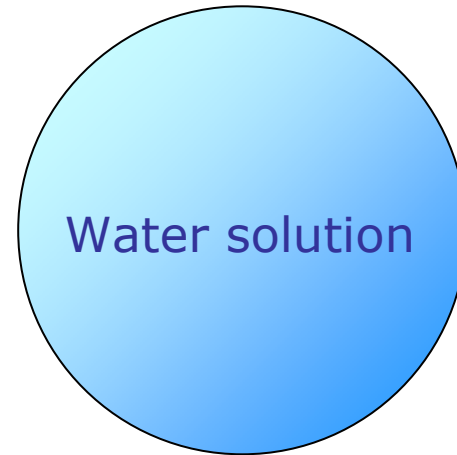
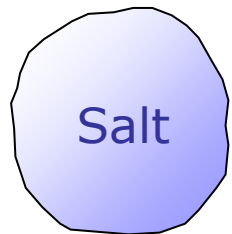


Effect of Soluble Fraction

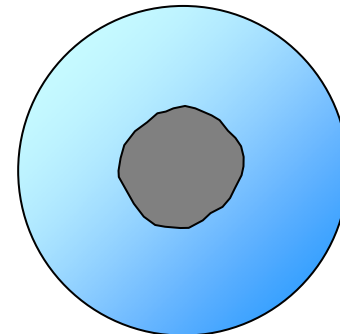
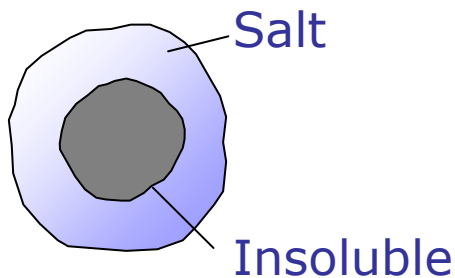
Dry particle

Humidified particle

Fully
soluble



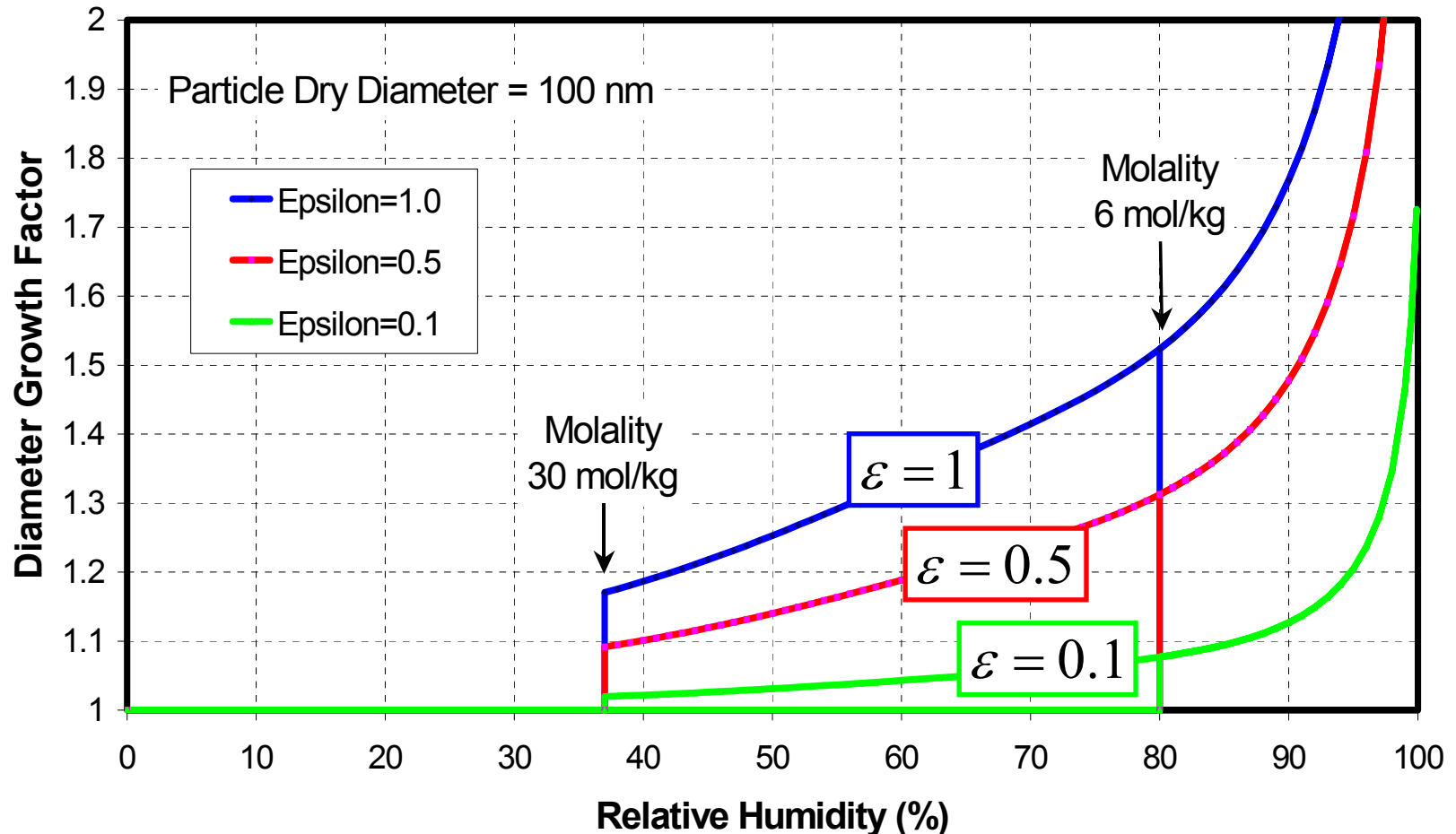
Only
partly
soluble



Effect of Solubility

Ammonium Sulphate

Diameter Growth Factors at various Soluble Volume Fractions



ZSR Model for Water Uptake of Mixtures

ZSR mixing rule to estimate the water activity of a mixture, based on the water activity of the pure compounds:

$$1 = \sum_s \frac{m_s(a_w)}{m_{o,s}(a_w)}$$

m_s is the molality of compound s in the mixture,

$m_{o,s}$ is the molality of the single electrolyte solution of component s for which the water activity equals that of the solution mixture.

The ZSR method can also be expressed as

$$mass_{water_tot} = \sum_s mass_{water_s}$$

$mass_{water_tot}$ is the mass of water in the mixture at the given water activity,

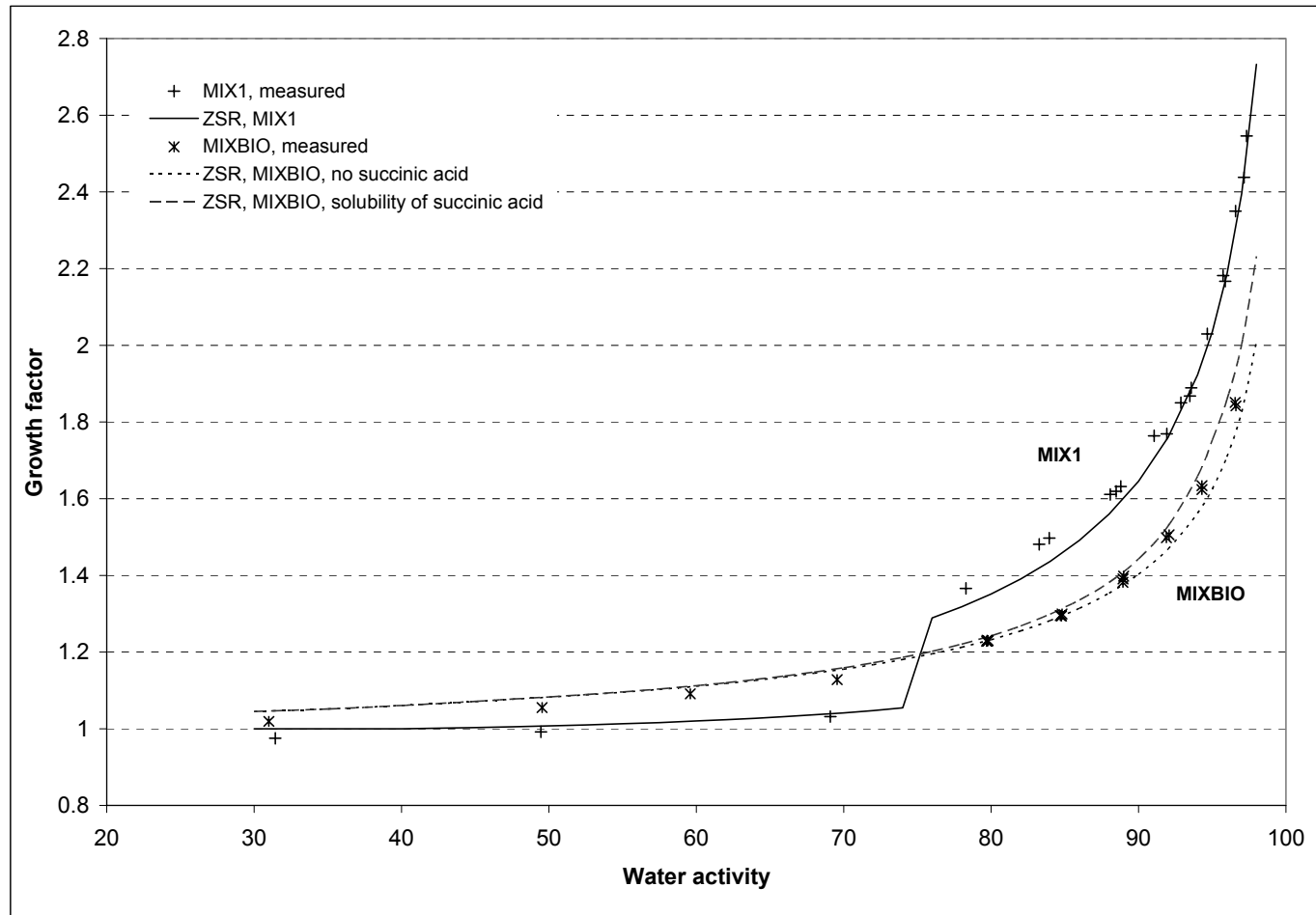
$mass_{water_s}$ is the mass of water that would have been associated with the amount of the single electrolyte present in the mixed particle at the given water activity.

H-TDMA Hygroscopic Diameter Growth Factors

Organic-Inorganic Mixtures

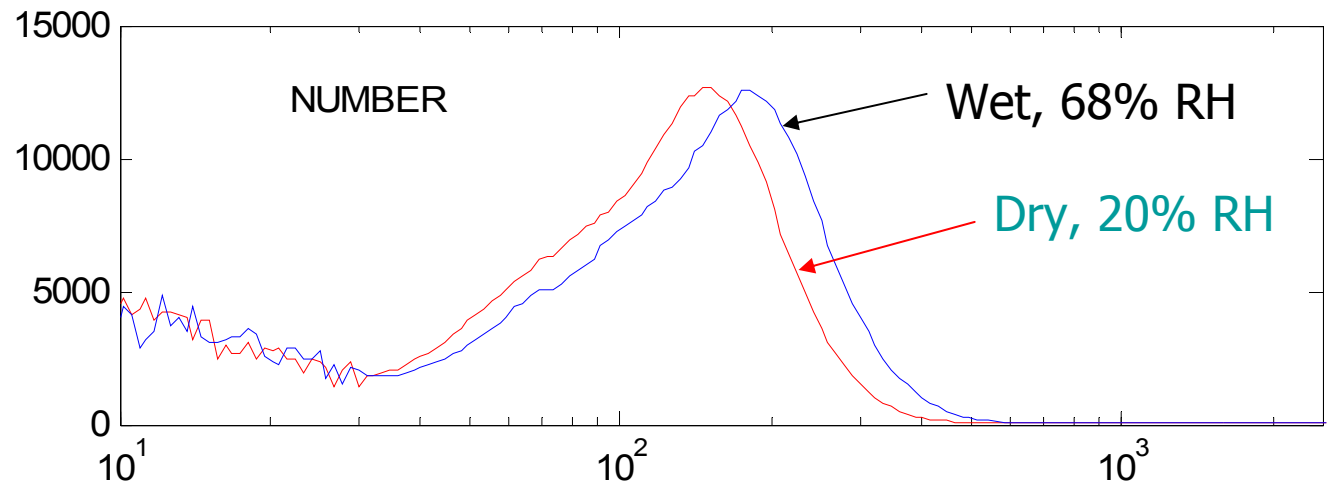
ZSR Model for Water Uptake of Mixtures

ZSR model shows good agreement for MIX1 and MIXBIO.



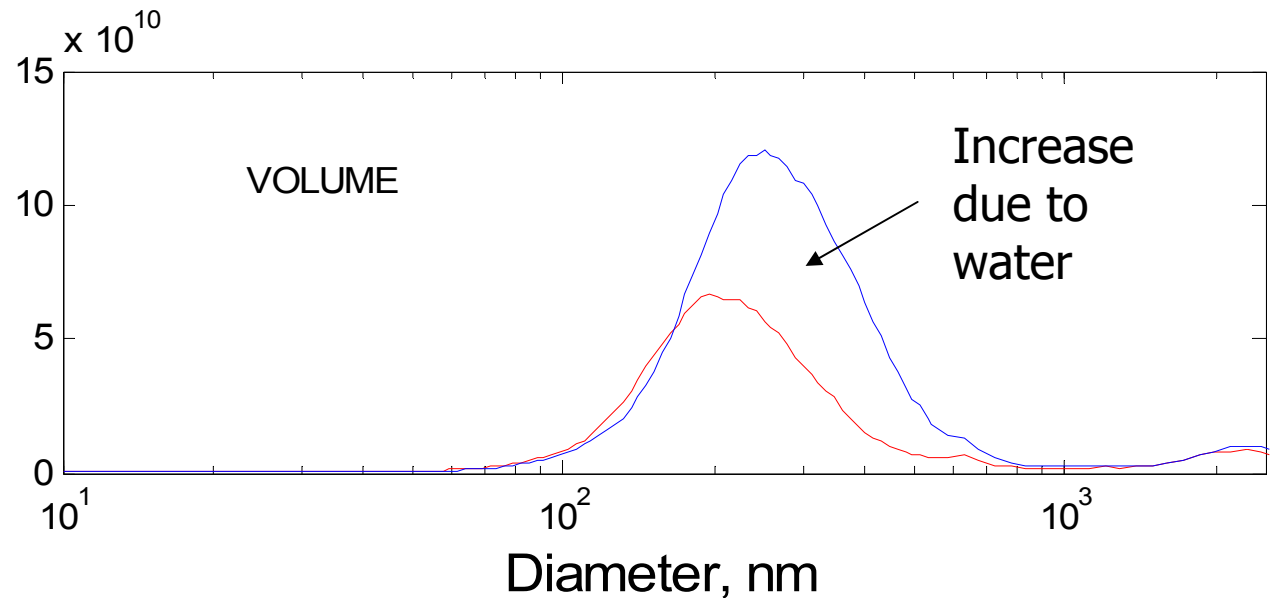
Wet and Dry PM Size Distributions

(Pittsburgh Air Quality Study, PAQS, Pandis et al.)

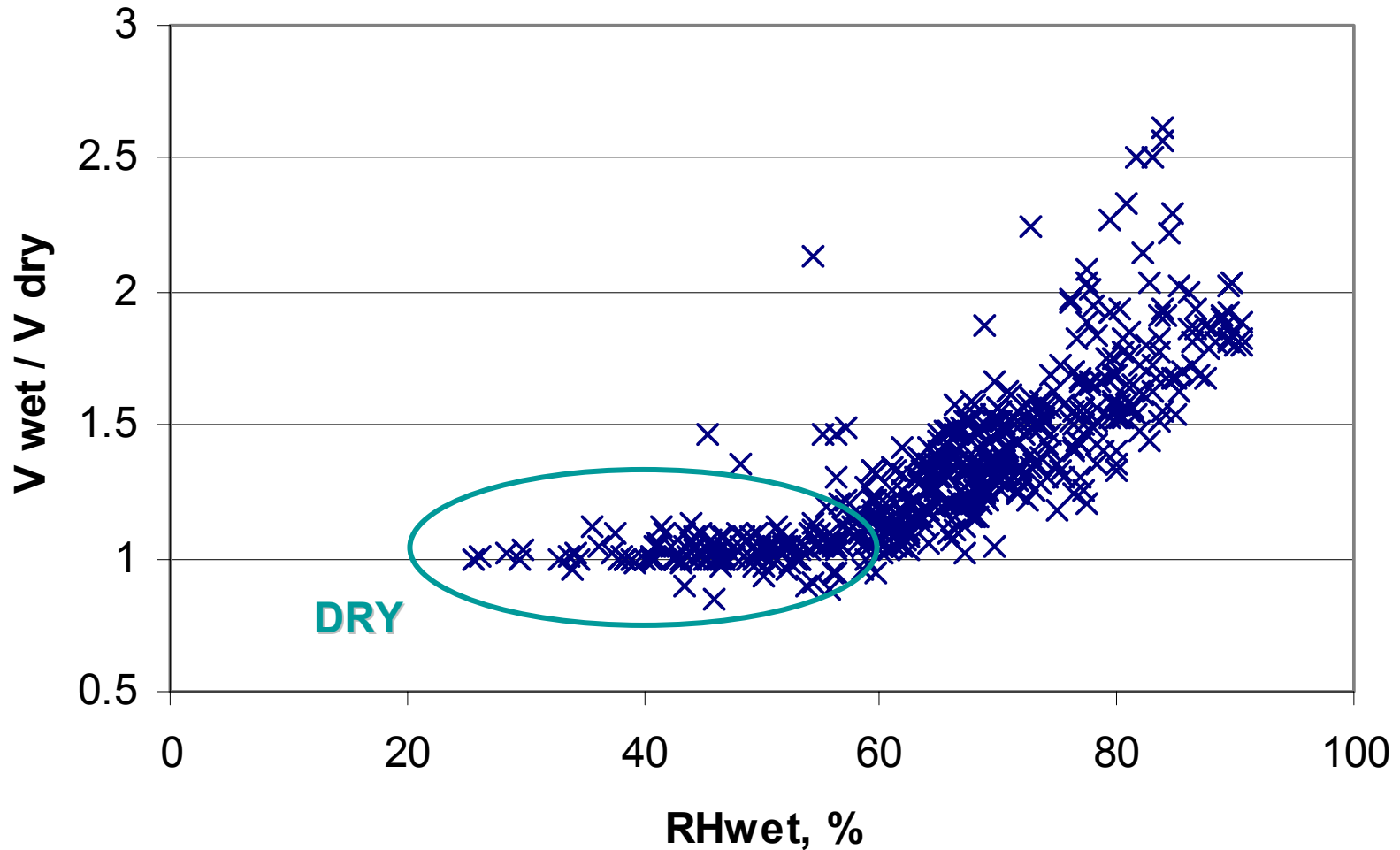


Aerosol water =

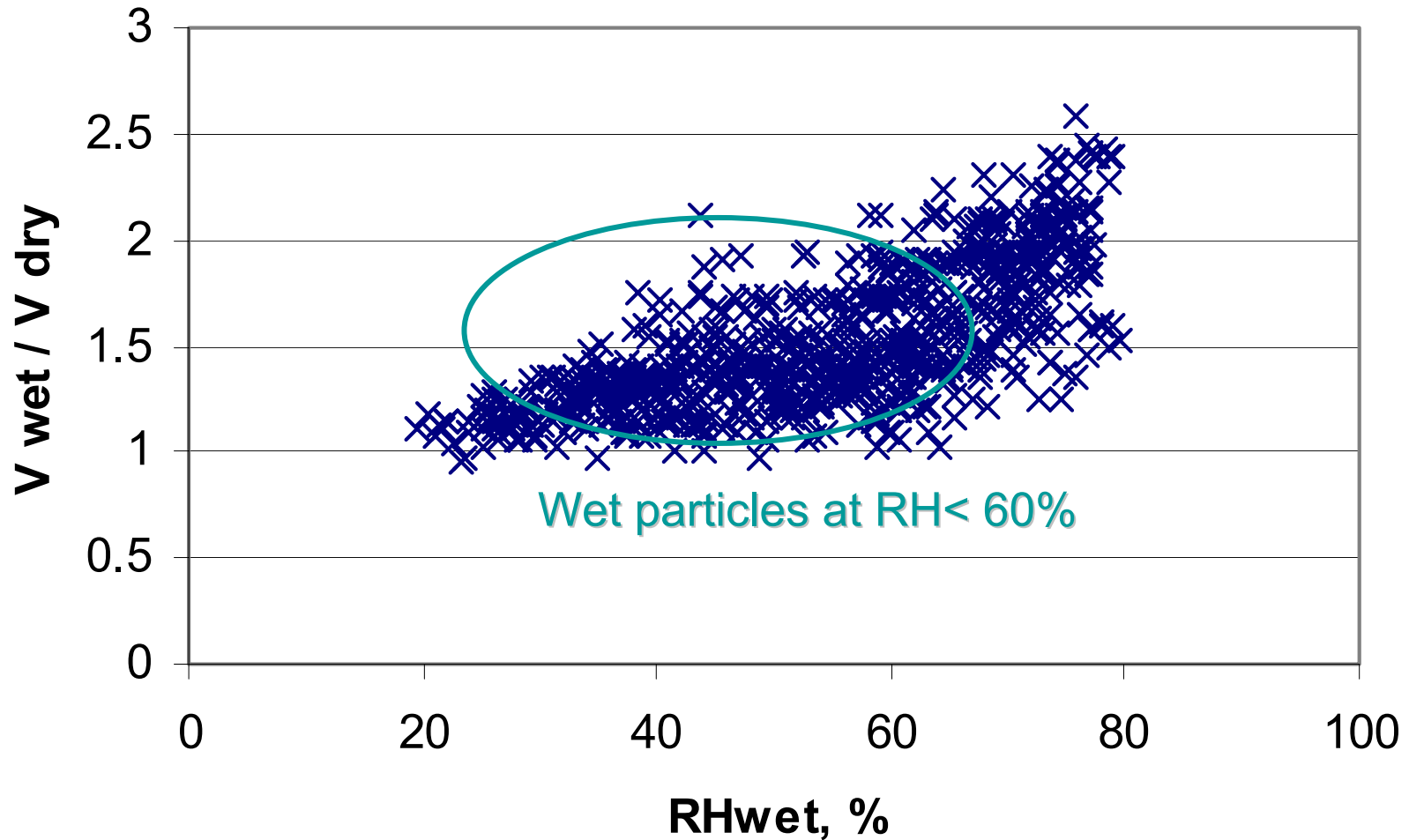
$$\rho_w(V_{\text{wet}} - V_{\text{dry}})$$



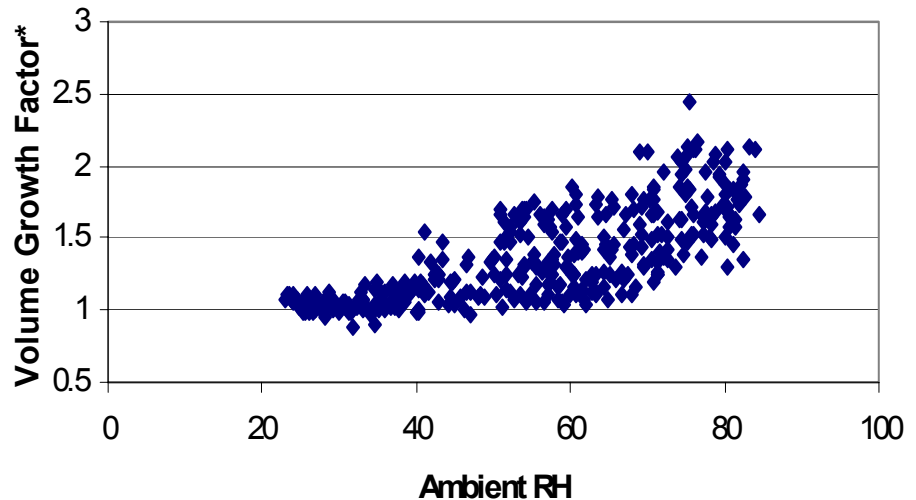
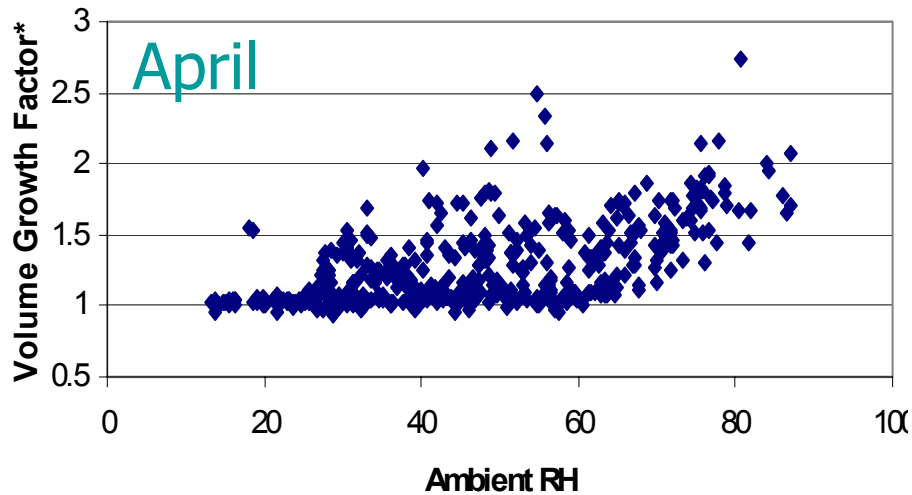
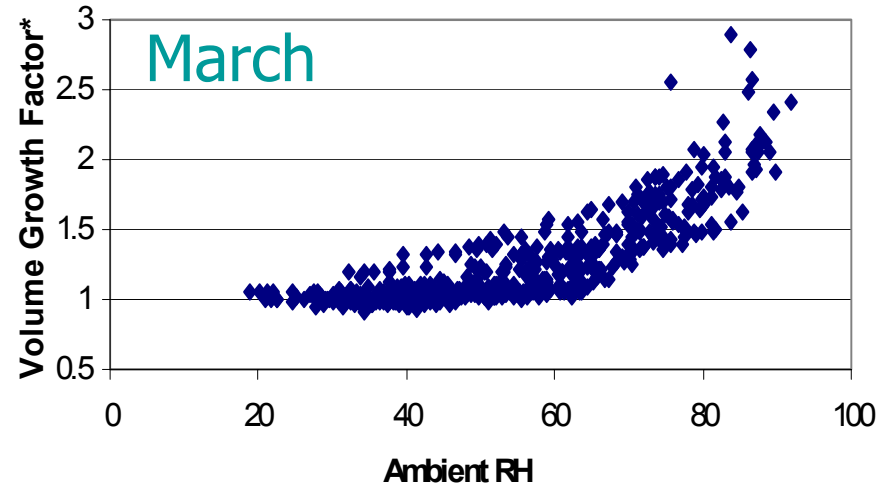
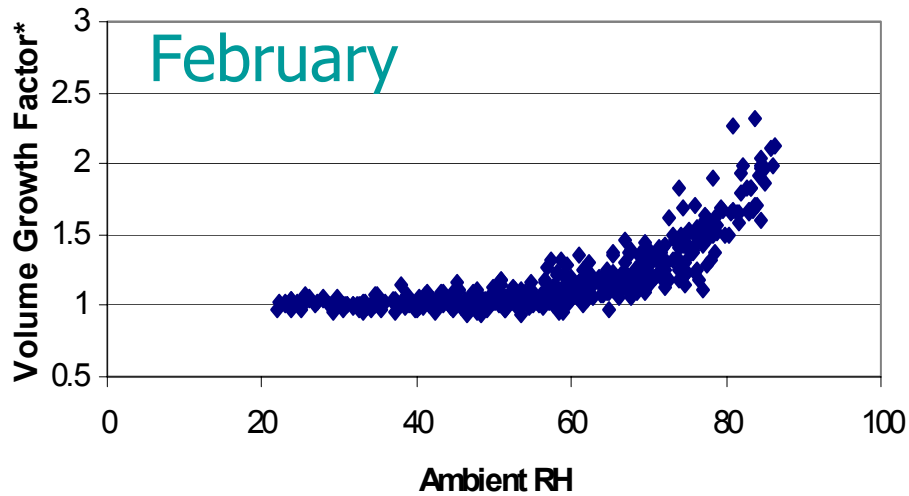
Aerosol Water During January 2002



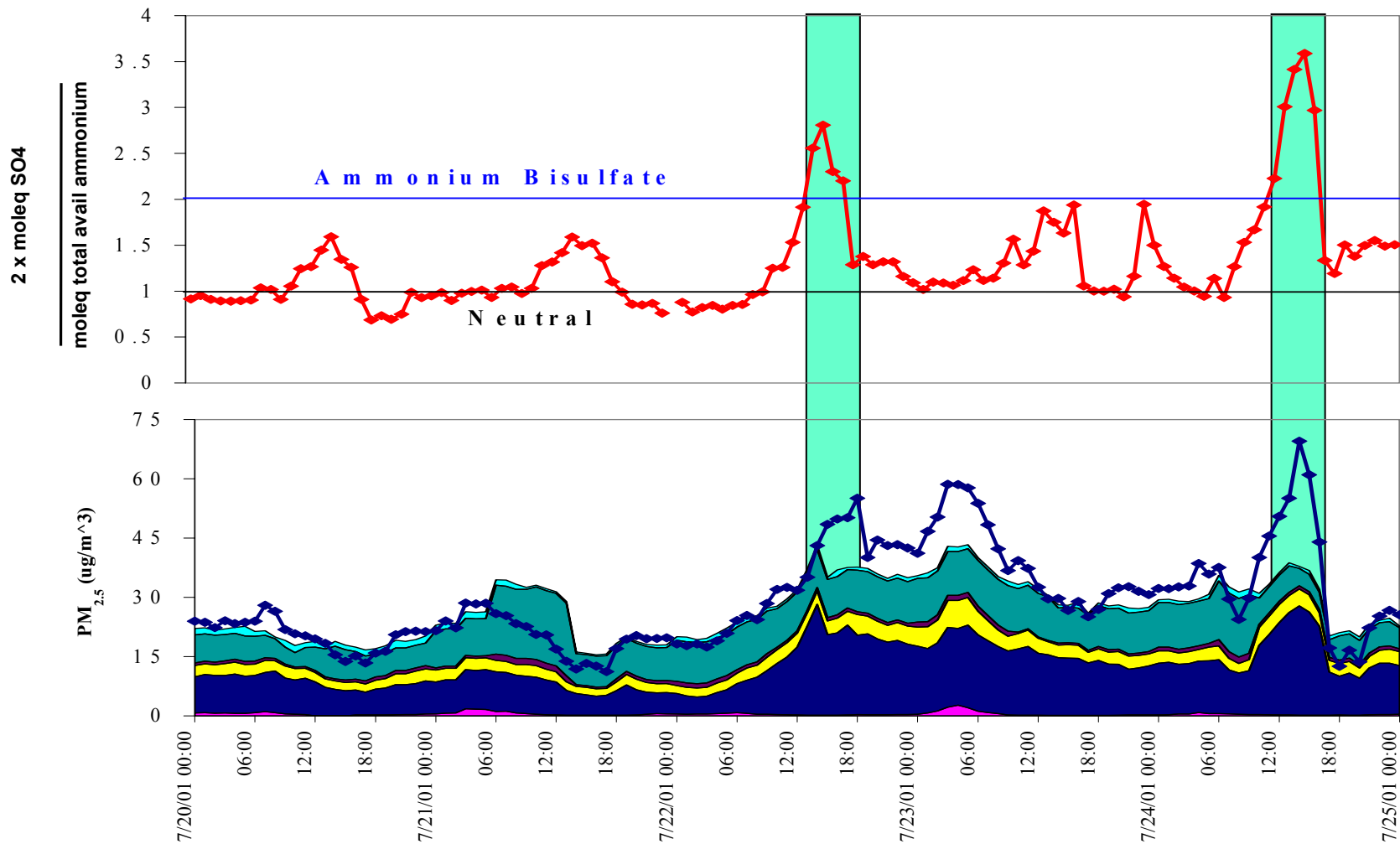
Aerosol Water During July 2001



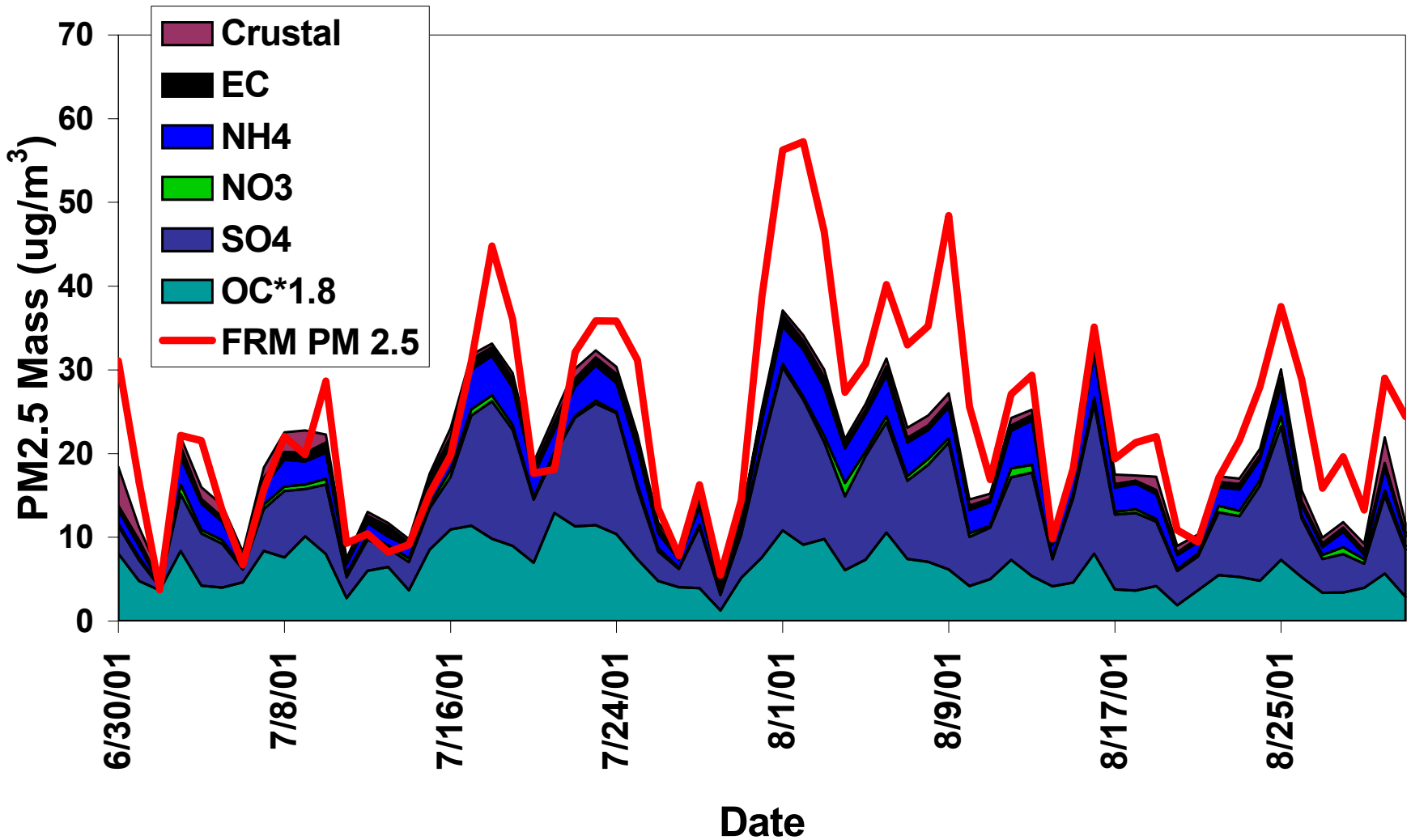
Aerosol Water During Spring 2002



Mass Discrepancy and Atmospheric Acidity



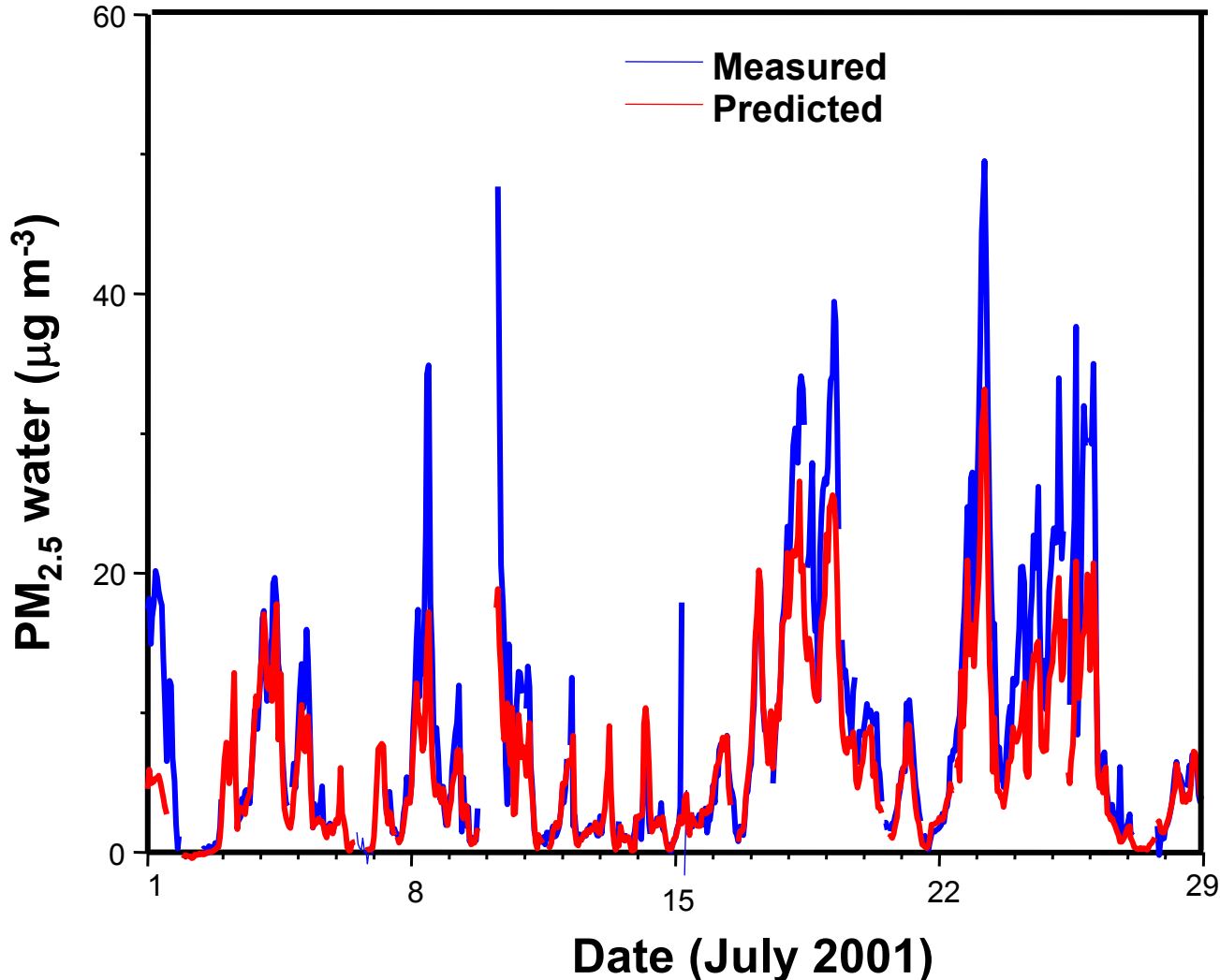
Fine PM Composition



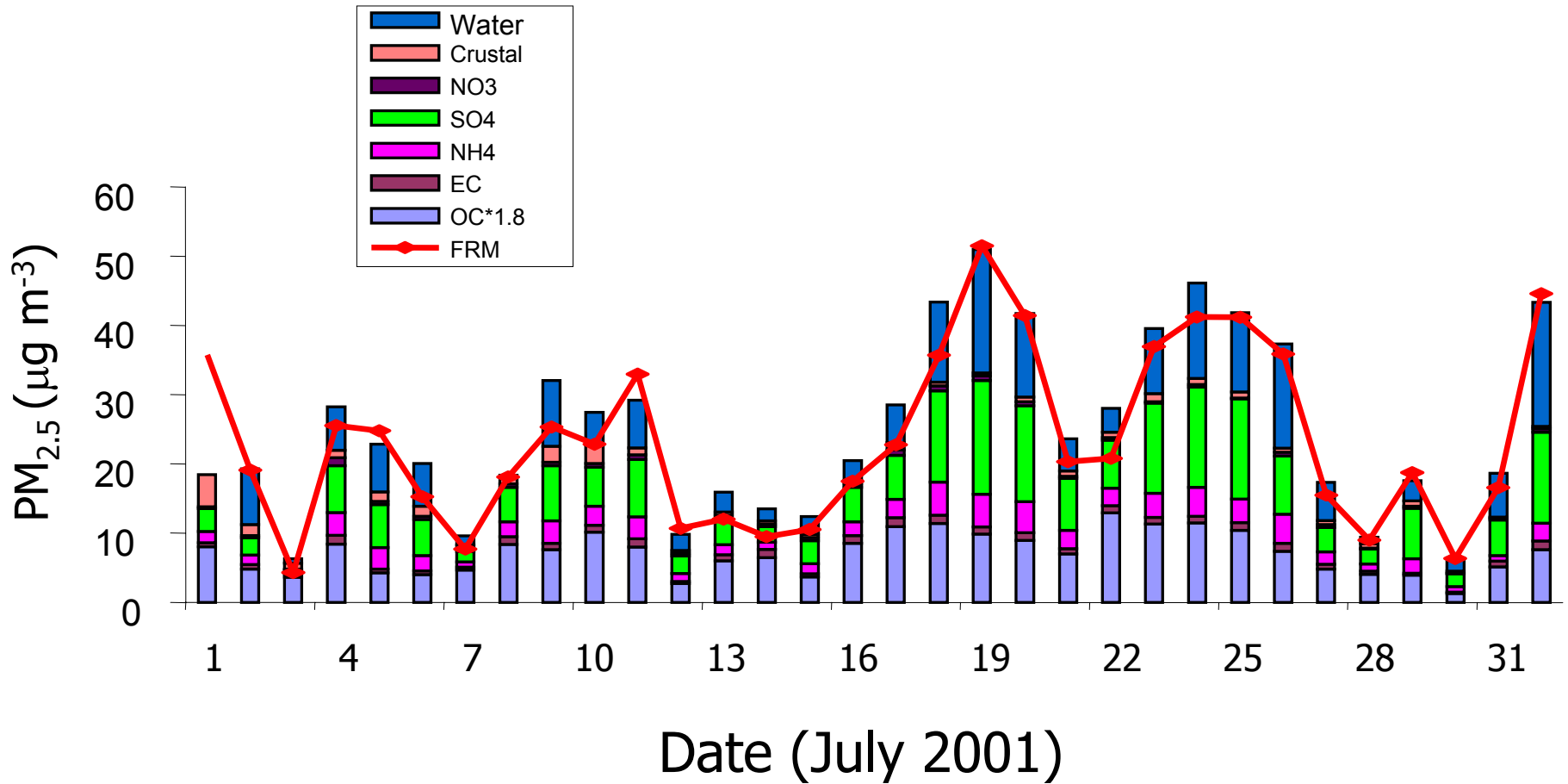
Comparison with theory

- GFEMN (Ansari and Pandis, 1999)
- Input :
 - hourly data of inorganic species:
 - Sulfate
 - Total nitrate, ammonium, chloride, sodium, etc. from the steam sampler
 - OC and EC from 4 hour filter measurements
 - OC contribution to aerosol water is neglected
- Calculates equilibrium PM volume at the RH of dry and ambient measurements

Predicted and Measured Water

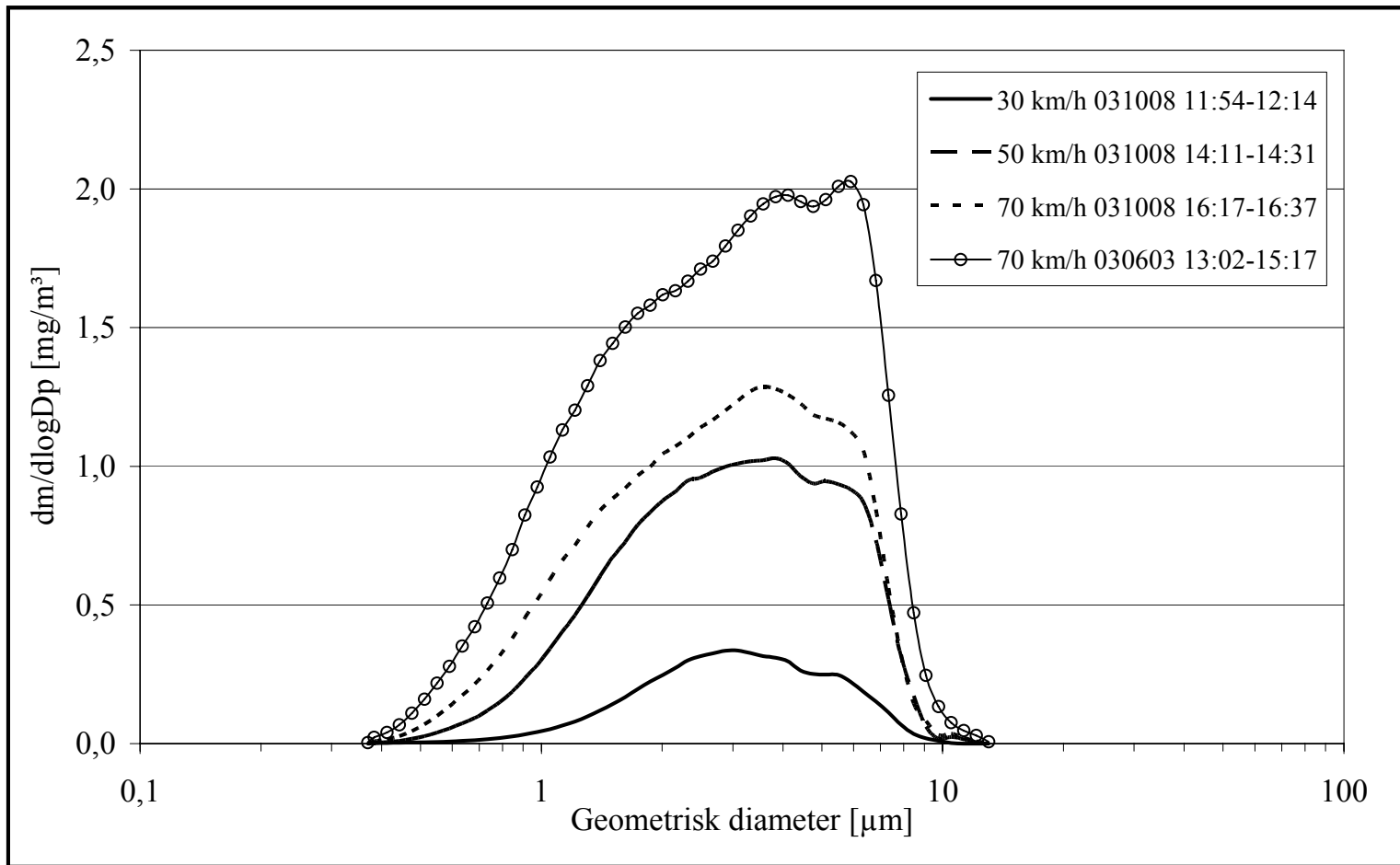


Mass Balance Closure – July 2001

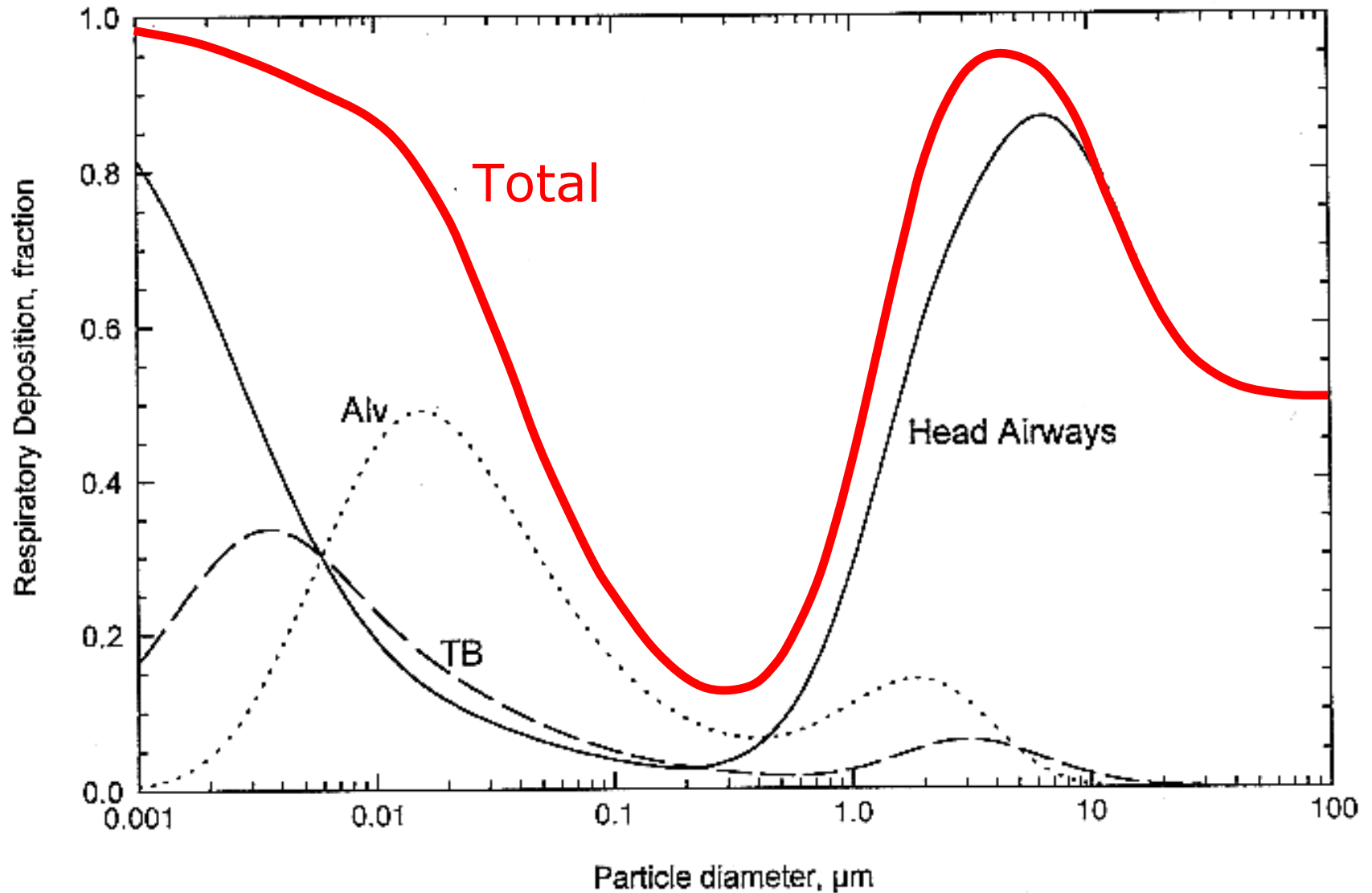


Good mass balance was achieved for the winter months

Hygroscopic particles might grow past the cut-off of the PM10 Inlet



Lung Deposition av particles - ICRP

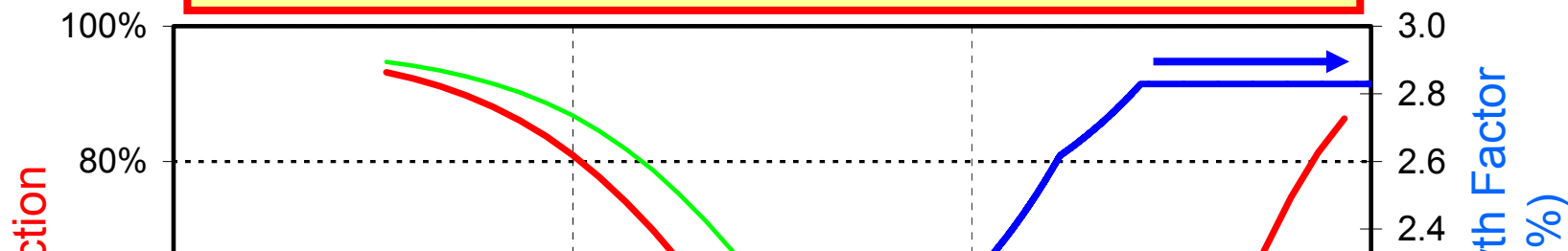




Particle hygroscopic properties

Importance for deposition in the lungs

Hygroscopic particles shift the minimum in the deposition curve to smaller sizes.



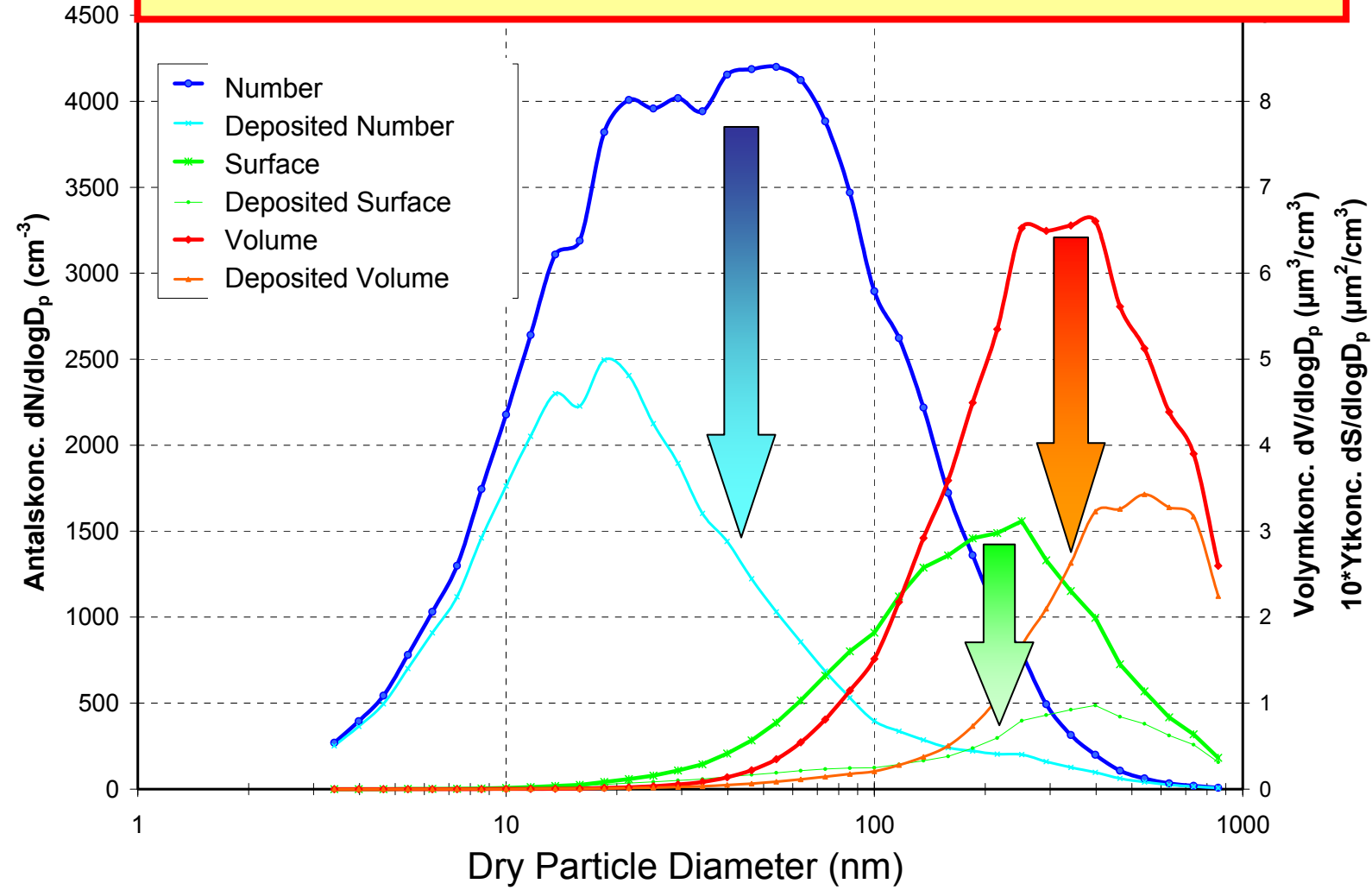
Hygroscopic particles affect deposition:

- More particle mass (>200 nm) is deposited in the upper airways.
- Fewer very small (<100 nm) particles are deposited in the lower airways (number).

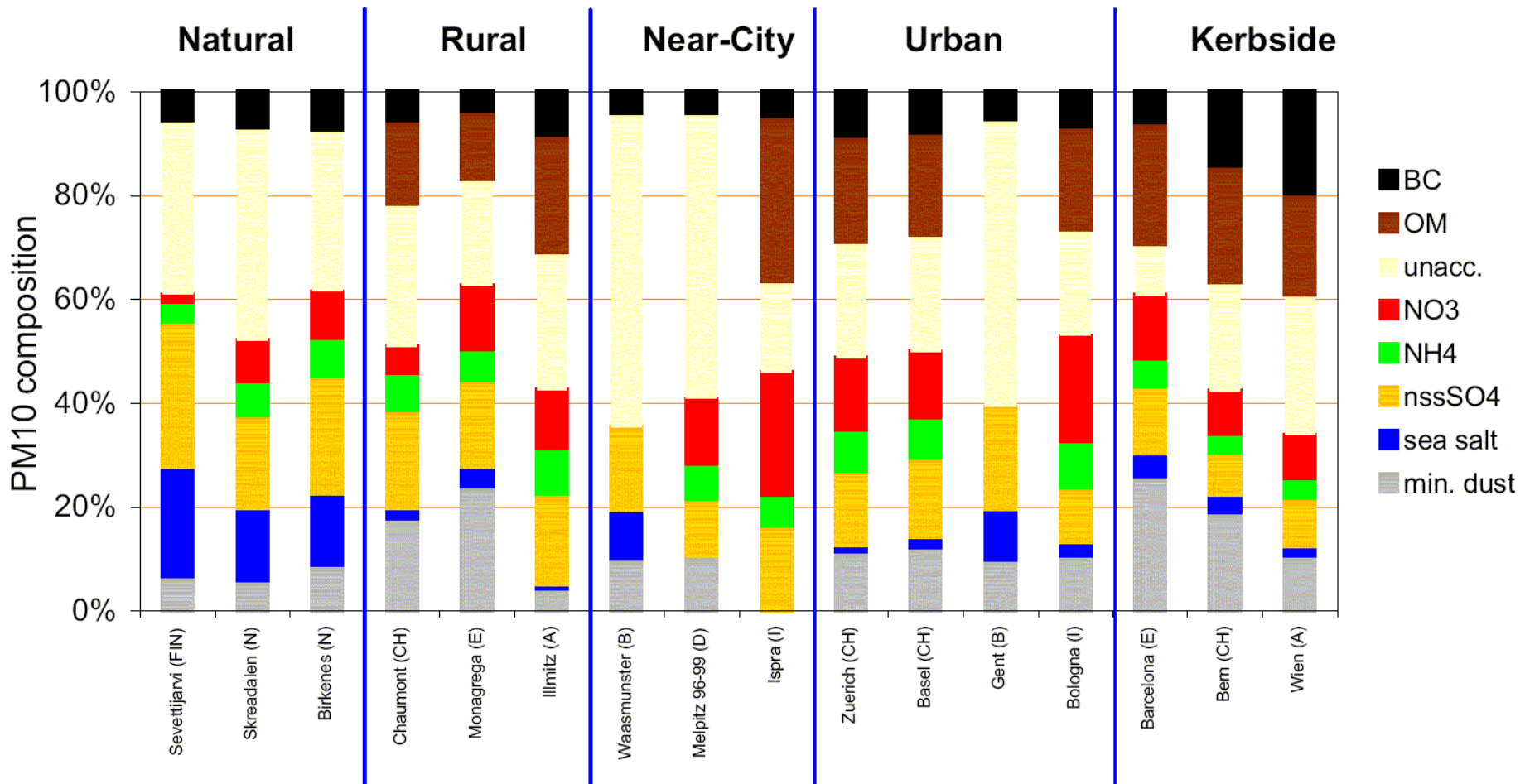


Particle hygroscopic properties

Particle lung deposition (number, surface area, volume) can be calculated with a time resolution of 10 minutes.

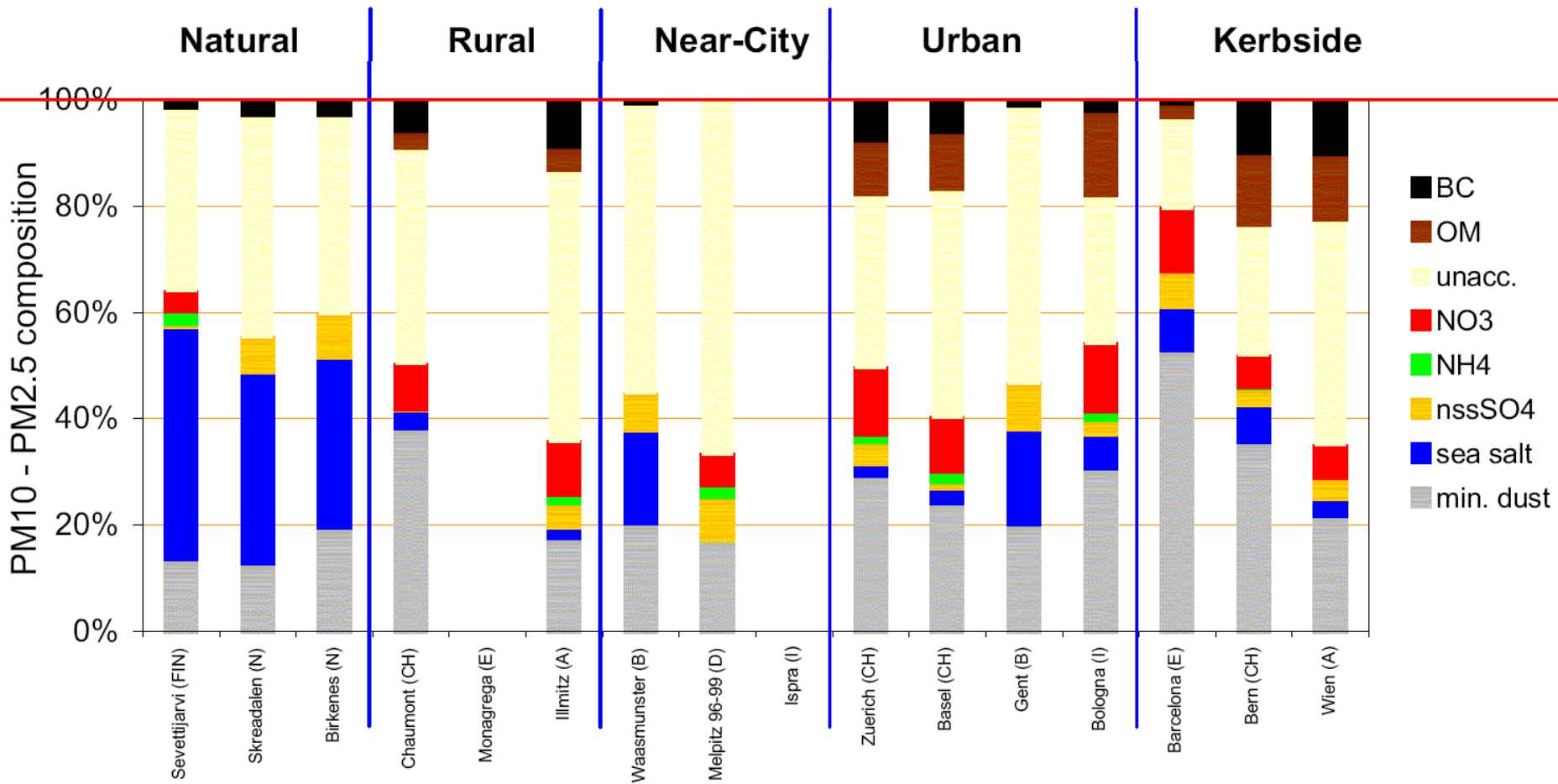


European PM10 Composition

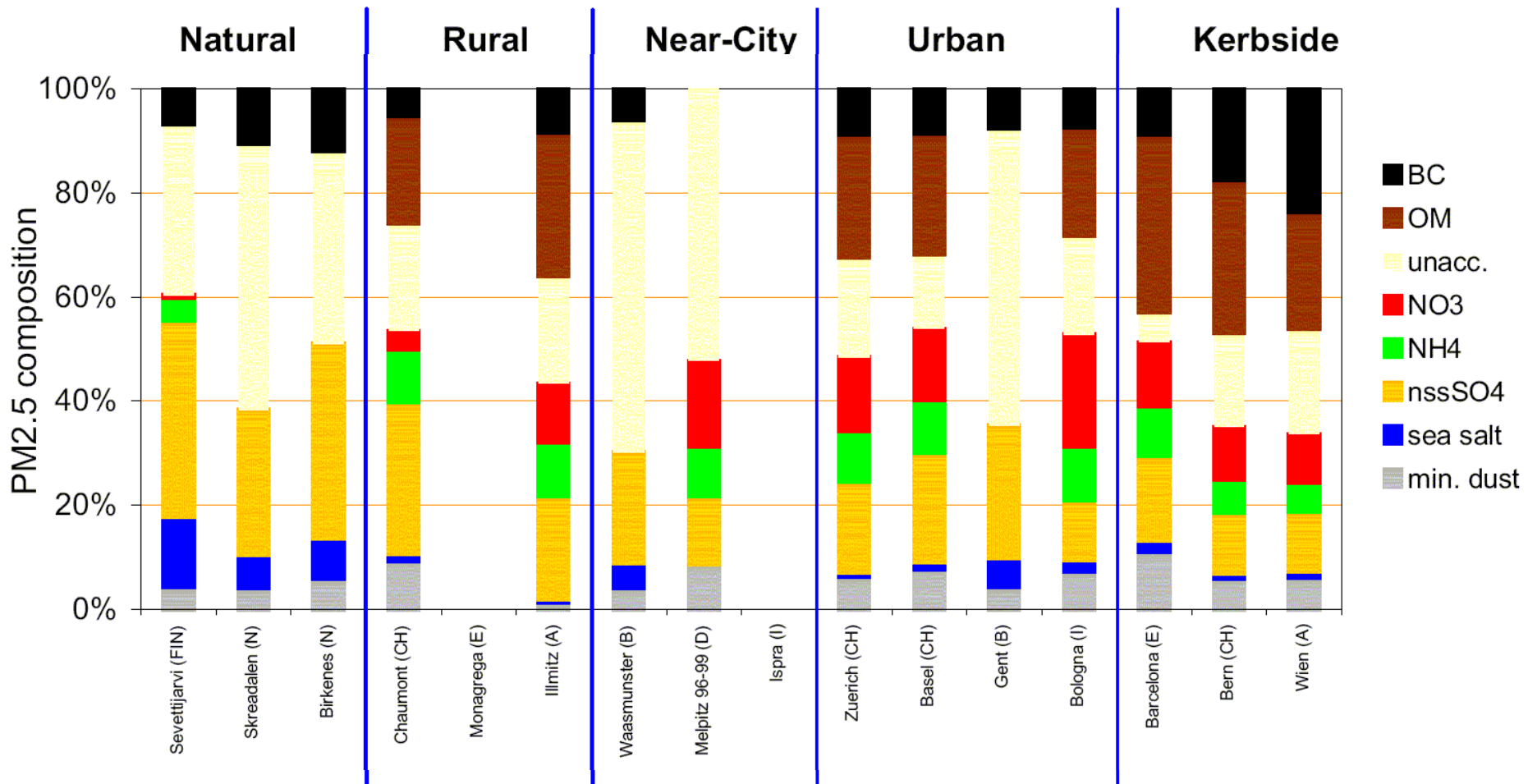


European Coarse Mode Composition

PM10-PM2.5



European PM2.5 Composition



A European Aerosol Phenomenology

Physical and chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe.

Jean-P. Putaud et al. EU-JRC 2003 (EUR 20411 EN)

Conclusion 10:

“When all main chemical components of the aerosol are measured, they **account for about 70% or more of the PM10 and PM2.5 mass**. The rest is thought to be due to the presence of **water** or to the underestimation of the molecular mass – to – carbon mass ratio when calculating organic matter concentrations.”

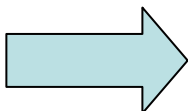
As much as 30% of the aerosol mass can be water!

“This may be an important source of inconsistency between the PM mass concentrations determined according to the EN 12341 norm and TEOMs.”

Table A5.1 Average concentration of PM₁₀ and PM_{2.5} and main chemical components in the city of Berlin and the regional background.

µg/m ³	Traffic [#] (Frankfurter Allee)	Urban back. [#] (Nansens- tr)	Regional back. [#] (Neuglo- sow)	Berlin+ Kerbside	Berlin+ Kerbside	Berlin+ Urban back	Berlin+ Urban back
	1998	1998	1998	2000	2001	2000	2001
PM ₁₀	51.5	37.7	18.6	37	42	28	29
OM	11.0	7.5	3.0				
EC	9.0	5.1	1.8				
OM+EC	20.0	12.6	4.8	11.2	12.7	7.1	8.1
SO ₄ ²⁻	5.7	6.1	3.9	5.4	4.6	4.9	4.9
NO ₃ ⁻	4.6	4.4	2.4	5.8	5.2	5.3	5.2
NH ₄ ⁺	3.3	3.4	2.0	3.0	2.7	2.9	3.0
Secondary inorg.	13.6	13.9	8.3	14.2	12.5	13.1	13.1
Cl ⁻	0.8	0.7	--				
Marine				2.3	2.2	2.1	2.0
Unaccounted *	17.9	11.2	5.5	9.3	14.7	5.8	5.8
PM _{2.5}	38.6	30.2	--	25	27	22	22.5
OM	9.4	7.0	--				
EC	7.7	4.7	--				
OM+EC	17.1	11.7		9.5	10.4	6.0	6.8
SO ₄ ²⁻	5.6	5.5	--	4.6	4.2	4.6	4.6
NO ₃ ⁻	4.3	3.7	--	4.6	4.1	4.6	4.0
NH ₄ ⁺	3.8	3.7	--	2.9	3.1	2.8	2.8
Secondary inorg.	13.7	12.9		12.1	11.4	12.0	11.4
Cl ⁻	0.7	0.5	--				
Marine				1.0	1.1	0.9	1.1
Unaccounted*	7.8	5.6	--	2.4	4.2	3.1	3.1

* Unaccounted, mainly metal oxides (soil) and water, # from Lenschow et al. (2001), + Abraham (2001) and Abraham H.J. (personal communication).



Effect of hygroscopic particles on PM measurements

- Water mass added to PM mass.
Regulating water?
- Particles might grow in size past the cut-off of the PM₁₀/PM_{2.5} inlet.
Loose PM mass at high RH?

Thank you for your attention!