Determination of hygroscopic aerosol growth based on the OPC—N3 counter

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Presentation plan

1. **Theory**
    a. Text Book: Köhler theory
    b. κ — parameter
    c. How a particle can behave exposed to different Rh?
    d. What is affected by Rh?
2. **Apparatus**
    a. OPC—N3
    b. ACS1000
3. **Results**
    a. κ
        i. Growth factors
        ii. Curve fitting & κ values
        iii. κ values for two seasons
    b. correction of PM data
        i. Rh from OPC—N3
        ii. applying the correction
4. **Conclusions**

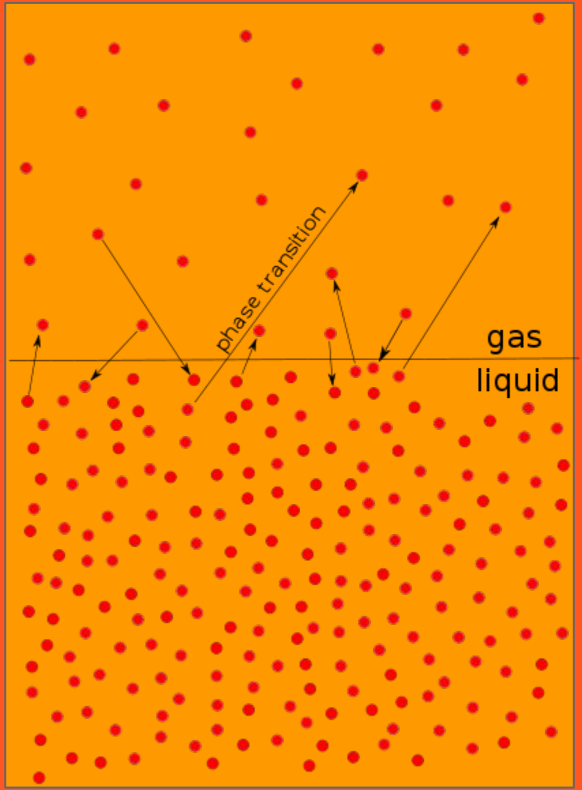
Theory

Hygroscopicity
water up-take

How to grow a particle?

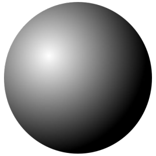
How to grow a particle?

equilibrium vapor pressure over a flat surface of pure water



HellTchi via Wikimedia Commons

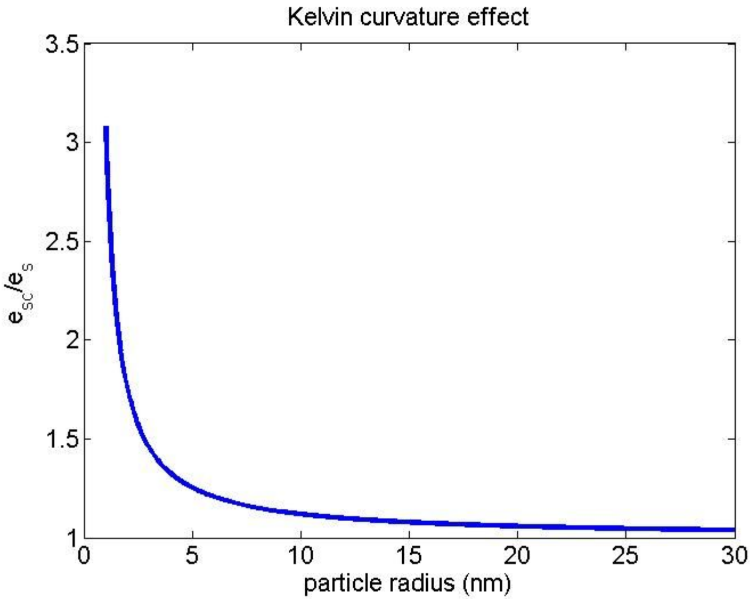
Kelvin equation



$$S = \frac{e_{sc}(D,T)}{e_s(T)} = exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D}\right) \quad (1)$$

Formation of droplet in pure air when relative humidity Rh~400%

S — Saturation ratio
e_{sc} — equilibrium vapor pressure over a curved surface of pure water
e_s — equilibrium vapor pressure over a flat surface of pure water
ϱ_w — density of water
M_w — molecular weight of water
$\sigma_{s/a}$ — surface tension of the solution/air interface
R — universal gas constant
T — temperature
D — diameter of droplet



Dependence of the ratio of the saturation vapor pressure over a curved surface to the saturation vapor pressure over a flat surface on the drop radius. Credit: W. Brune, Fundamentals of Atmospheric Science, PennState Collage

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Raoult's Law

$$S = \frac{e_{sol}(N_s)}{e_s(T)} = a_w = (1-\chi_s) \qquad (3)$$

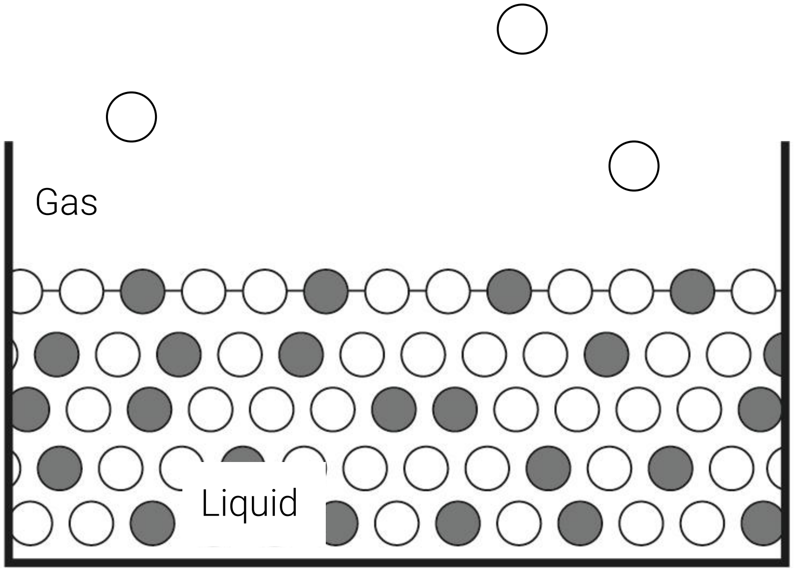
○ Solvent (in what we dissolve)

● Solute (the substance dissolved in solvent)

$$\chi_s = \frac{n_s}{n_w + n_s} \qquad (4)$$

Van't Hoff factor

$$for\ n_w > n_s \quad \chi_s \cong \frac{n_s}{n_w} = i\,B\,\frac{N_s}{r_d^3} \qquad B = \frac{3}{4\pi n_L} \qquad (5)$$



n_w – number of moles of **water** per unit volume of **solution**

n_s – number of moles of **solute** per unit volume of **solution**

n_L – number of moles of **water** per unit volume of **pure water**

N_s – total moles of solute

r_d – radius of droplet

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Köhler theory

[Petters and Kreidenweis, 2007]

$$S = \frac{e_{sc}(N_s, D, T)}{e_s(T)} = \underbrace{a_w}_{\text{Rault Law}} \underbrace{exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D}\right)}_{\text{Kelvin Equation}} \quad (2)$$

S – Saturation ratio

e_{sc} – equilibrium vapor pressure over a curved surface of water with solute

e_s – equilibrium vapor pressure over a flat surface of pure water

a_w – activity of water in solution

ϱ_w – density of water

M_w – molecular weight of water

$\sigma_{s/a}$ – surface tension of the solution/air interface

R – universal gas constant

T – temperature

D – diameter of droplet

N_s - number of moles of solute

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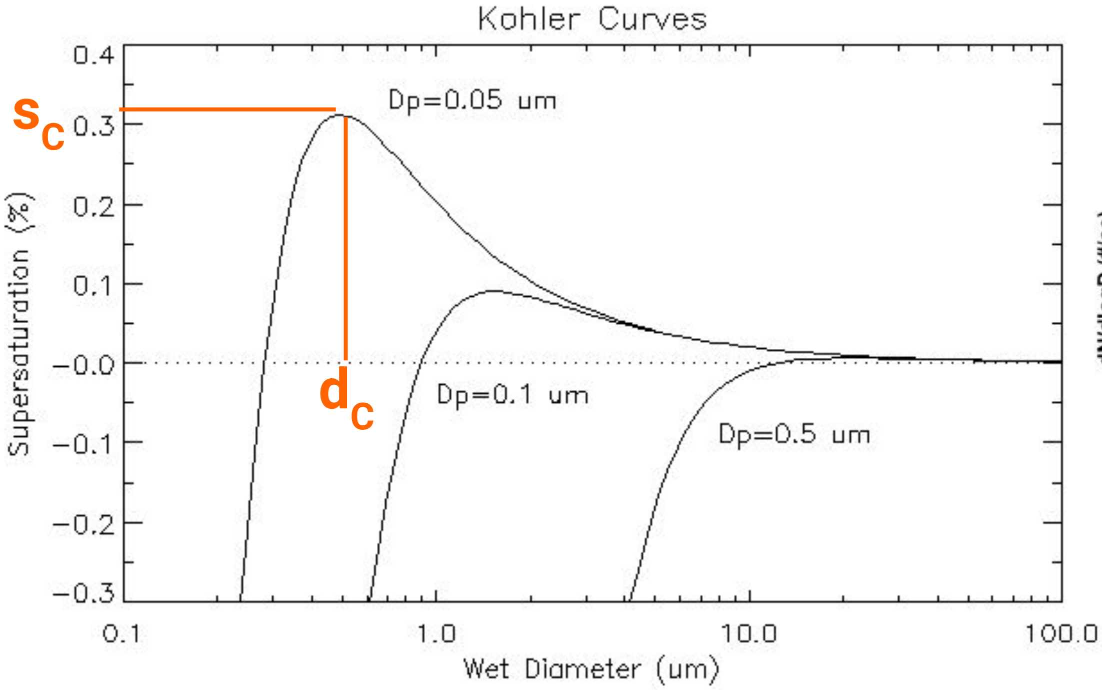

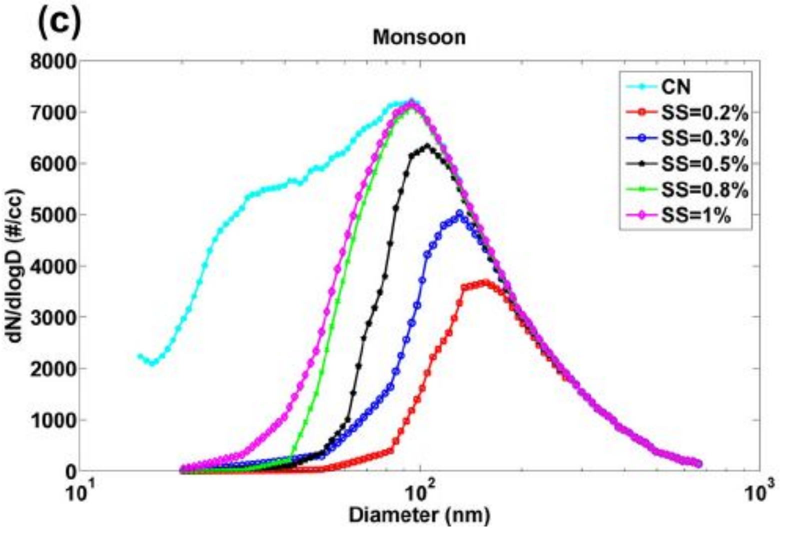

Number size distribution of CN and CCN at SS 0.2 - 1.0 averaged over Monsoon. [Bhattu & Tripathi, 2014]

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○ Solvent (in what we dissolve)

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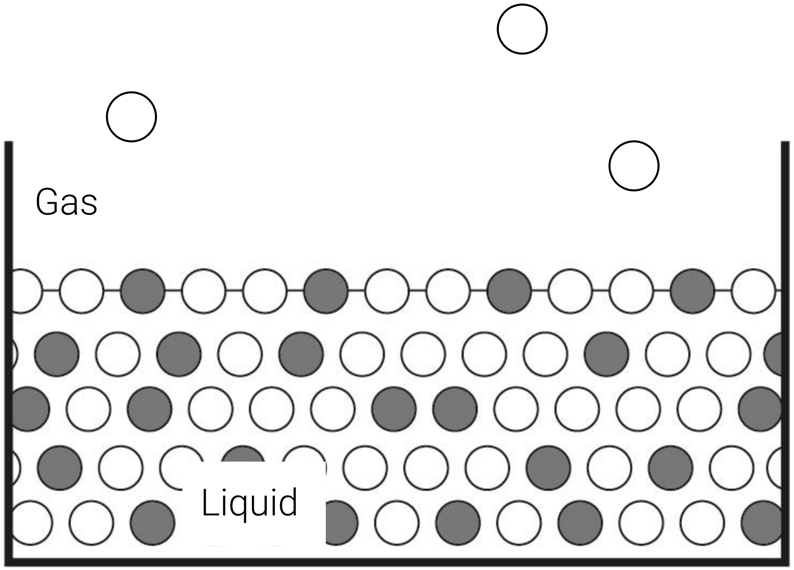

n_w – number of moles of **water** per unit volume of **solution**

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n_L – number of moles of **water** per unit volume of **pure water**

N_s – total moles of solute

r_d – radius of droplet

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Proposed parametrisation κ

[Petters and Kreidenweis, 2007]

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \quad (6)$$

κ – hygroscopicity parameter

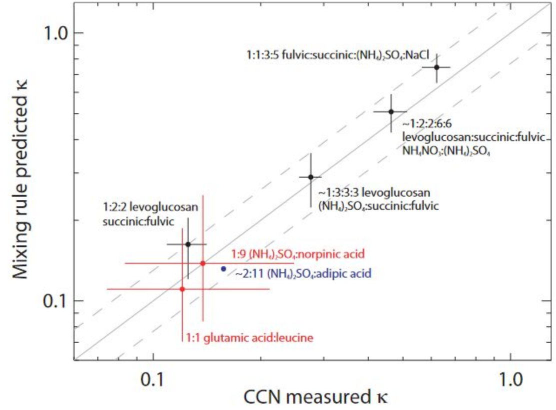
$$S(D) = a_w \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right)$$

V_s – volume of the dry particulate matter

V_w – volume of the water

D_d – dry diameter

D – diameter of the system (water + solute)



[Petters and Kreidenweis, 2007]

Fig. 3. Values of κ for multicomponent particles, predicted from the linear mixing rule (Eq. 7, ordinate) and estimated from CCN activity measurements (abscissa). Measurement-derived κ values were fit using $\sigma_{s/a}$=0.072 J m^{-2} and T=298.15 K. Black points: Svenningson et al. (2006); red points: Raymond and Pandis (2003); blue point: Broekhuizen et al. (2004). Indicated component ratios are mass ratios. The value and origin of each individual-component κ applied in the mixing rule is given in Table 1. Vertical and horizontal bars show an estimate of the uncertainty in measured and predicted κ. Dashed lines indicate ±30% deviation from the 1:1 line. Densities of the pure substances used for the conversion from mass to volume fraction were those reported in the original studies.

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right) \quad (7)$$

$$\kappa = \sum_i \varepsilon_i \kappa_i \quad (8)$$

ε_i – volume fraction of *i*-th solute in volume of all solute

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Computing κ

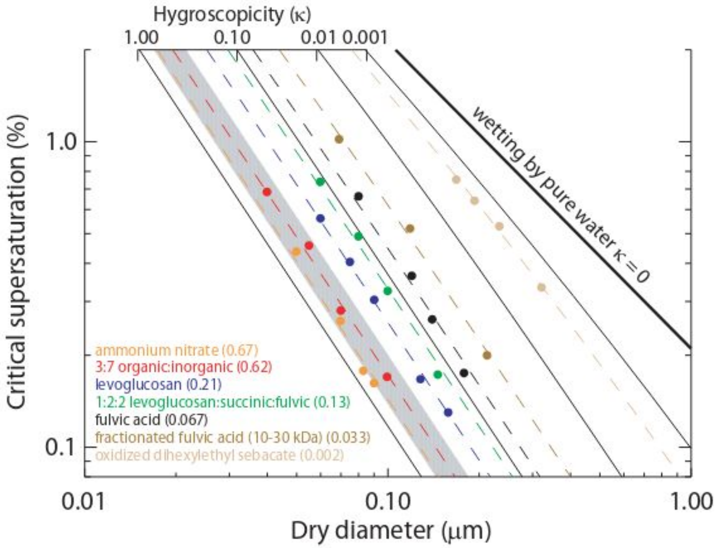
$s_c - D_d$ best fit of eq. 7

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right)$$

$$s = 1 + \frac{A}{D} - B\frac{D_d^3}{D^3},$$

HTDMA - humidified tandem differential mobility analyzer.

$$\frac{\mathrm{RH}}{\exp\left(\frac{A}{D_d gf}\right)} = \frac{gf^3 - 1}{gf^3 - (1-\kappa)} \qquad (9)$$



[Petters and Kreidenweis, 2007]

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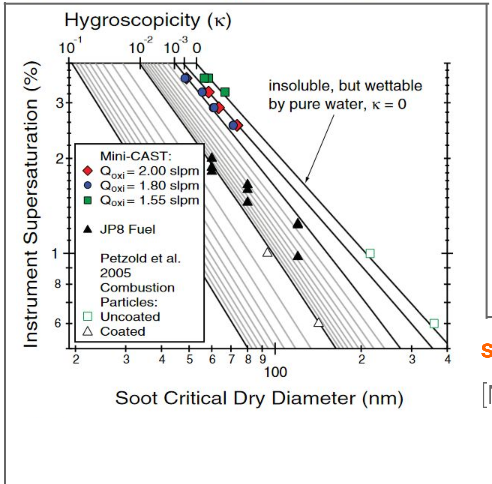
Typical κ values in the atmosphere

Compound	Growth factor derived κ			CCN derived κ		
	κ low	κ mean	κ up	κ low	κ mean	κ up
$(NH_4)_2SO_4$	$0.33^{(6)}$	0.53	$0.72^{(6)}$	N/A	$0.61^{(13)}$	N/A
NH_4NO_3	N/A	N/A	N/A	0.577	$0.67^{(10)}$	0.753
NaCl	$0.91^{(6)}$	$1.12^{(13)}$	$1.33^{(6)}$	N/A	$1.28^{(13)}$	N/A
H_2SO_4	N/A	$1.19^{(13)}$	N/A	N/A	$0.90^{(13)}$	N/A
$NaNO_3$	N/A	$0.80^{(13)}$	N/A	N/A	$0.88^{(13)}$	N/A
$NaHSO_4$	N/A	$1.01^{(13)}$	N/A	N/A	$0.91^{(13)}$	N/A
Na_2SO_4	N/A	$0.68^{(13)}$	N/A	N/A	$0.80^{(13)}$	N/A
$(NH_4)_3H(SO_4)_2$	N/A	$0.51^{(13)}$	N/A	N/A	$0.65^{(13)}$	N/A
malonic acid				0.199	$0.227^{(11)}$	0.255
glutaric acid				0.054 0.113	$0.088^{(5)}$ $0.195^{(8)}$	0.016 0.376
glutamic acid				0.113 0.158	$0.182^{(5)}$ $0.248^{(9)}$	0.319 0.418
succinic acid				0.166	$0.231^{(4)}$	0.295
adipic acid				N/A	$0.096^{(1)}$	N/A
levoglucosan				0.193	$0.208^{(10)}$	0.223
phthalic acid						
homophthalic acid						
leucine						

[Petters and Kreidenweis, 2007]



soot κ=0 to10^{-3}

[Moore, Ziemba, et al., 2014]

Atmospheric particulate matter is typically characterized by **0.1<κ<0.9**

no-hygroscopic	0
slightly	0.01
very hygroscopic	0.5
sea salt	**1.1**
sodium chloride	**1.5**

[Zieger, Väisänen, Corbin, 2017]

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How a particle can behave exposed to different Rh?

A) non — hygroscopic

soot

mineral dust

[Weingartner 1997, Sjogren 2007]

aged particles
insoluble particles with hygroscopic inorganic species

[Petters et al., 2006]

B) soluble & hygroscopic

sulfuric acid (H_2S0_4)

organic compounds

[Titos, 2016]

C) transition point & hygroscopic

sodium chloride (NaCl),

ammonium sulphate $(NH_4)_2SO_4$

[Titos, 2016]

deliquescence point (DRH)

efflorescence point (ERH)

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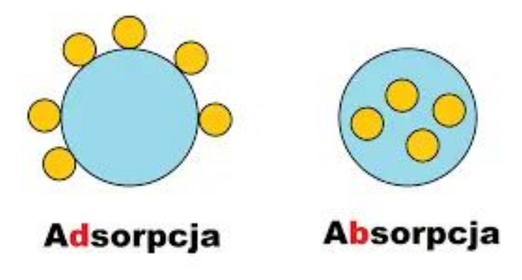
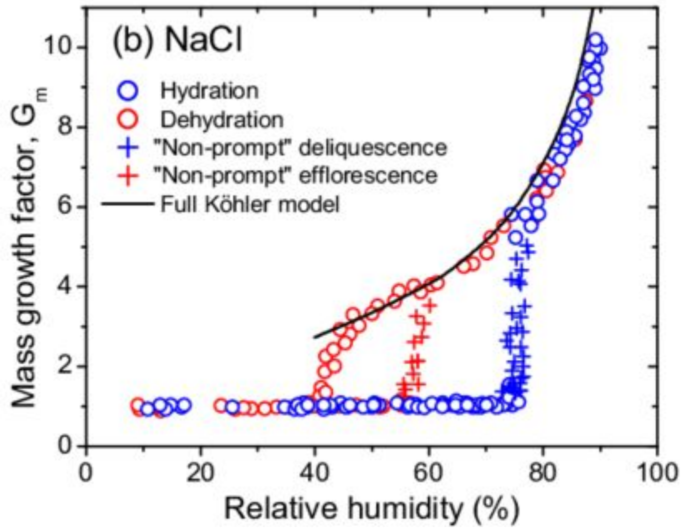
Absorption and Adsorption

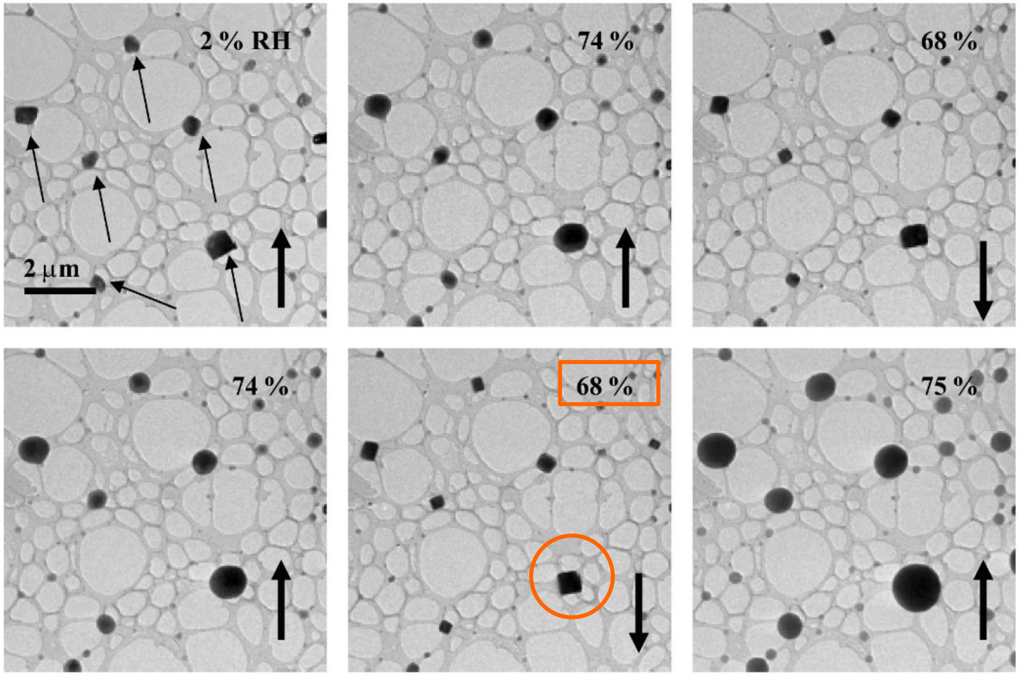


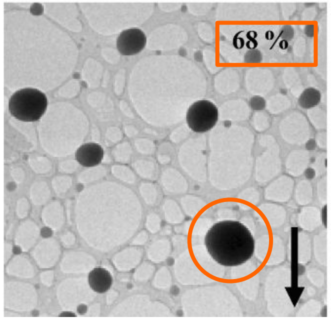
How a particle behave exposed to different Rh?



[Vlasenko S. et. al, 2017]

“The mass growth factor (G_m) of ammonium sulfate (a) and sodium chloride (b) aerosol particles observed as a function of relative humidity (Rh) compared to the full Köhler model: blue and red crosses represent apparent non—prompt deliquescence and efflorescence thresholds.”





DRH 75%± 2%

ETEM - environmental transmission electron microscope

The history of a particle is extremely important

[Wise, Martin et. al., 2008]

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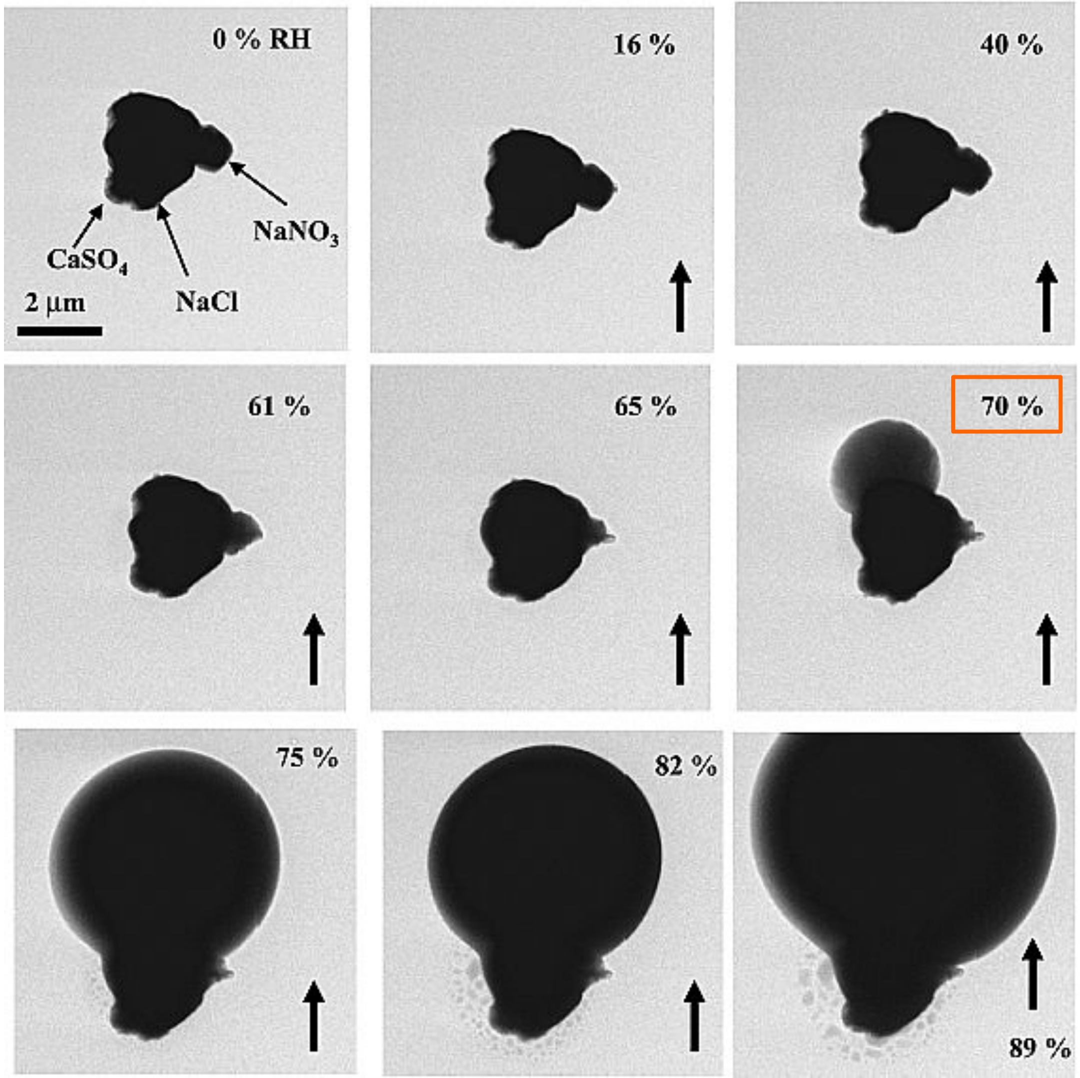


[Wise, Semeniuk et. al., 2008]

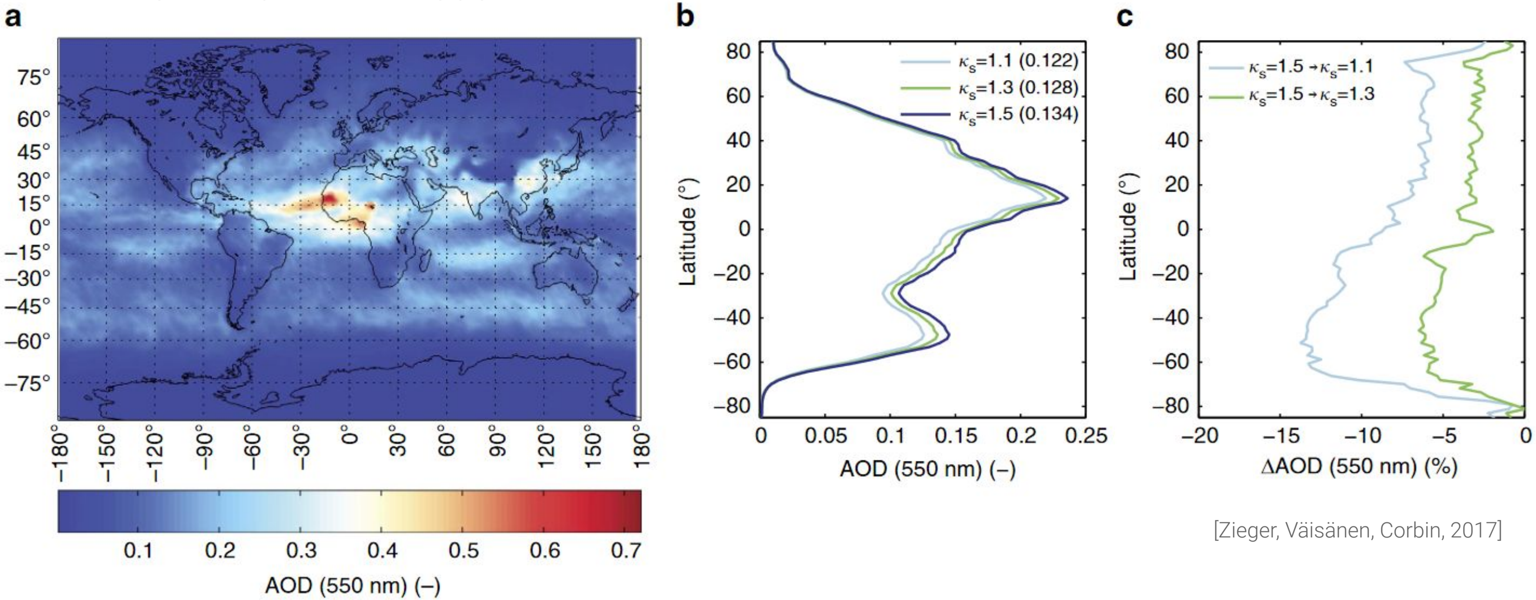
AOD

ϰ

sea salt	**1.1**
sodium chloride	**1.5**

[Zieger, Väisänen, Corbin, 2017]

ECHAM6-HAM2 model



[Zieger, Väisänen, Corbin, 2017]

Figure 4 | Impact of reduced inorganic sea salt hygroscopicity within a general circulation model. (**a**) Global map of the aerosol optical depth (AOD) at $\lambda = 550$ nm with the hygroscopicity of the inorganic sea salt component set to $\kappa_s = 1.5$ (NaCl). (**b**) Latitudinal mean of the AOD(550 nm) for $\kappa_s = 1.5$, 1.3 and 1.1. Global mean values of AOD for each model run are given in parenthesis in the legend. (**c**) Percental change in AOD when decreasing the hygroscopicity of the inorganic sea salt component from 1.5 to 1.3 and 1.1, respectively. Results are shown using the sea spray source function of Gong *et al.*[34].

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Arctic

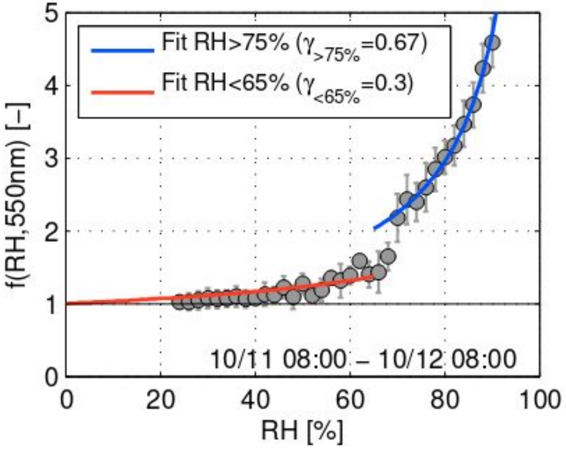
$$f(\mathrm{RH},\lambda)=\frac{\sigma_{\mathrm{sp}}(\mathrm{RH},\lambda)}{\sigma_{\mathrm{sp}}(\mathrm{RH}_{\mathrm{dry}},\lambda)}$$

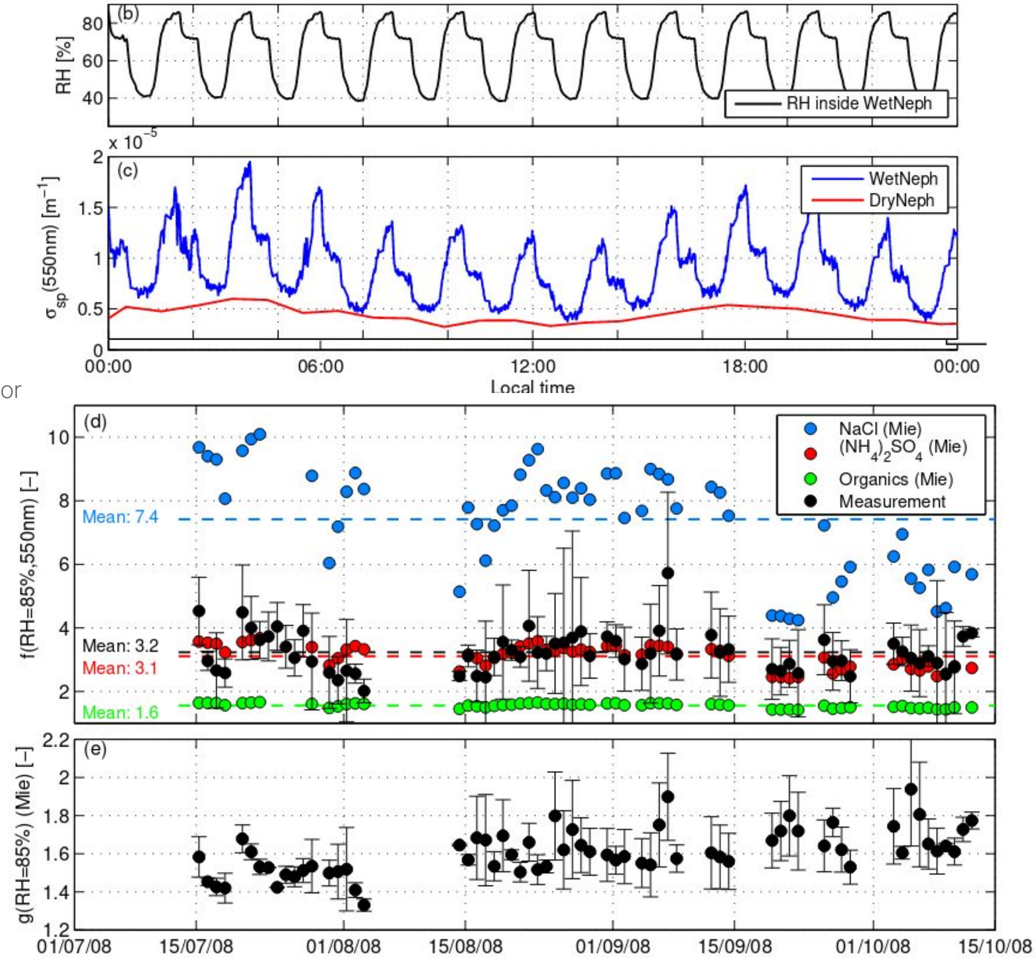
scattering coefficient

$$f(\mathrm{RH})=(1-\mathrm{RH})^{-\gamma}$$

scattering enhancement factor

γ – parameter describing magnitude of scattering enhancement





[Zieger, Fierz-Schmidhauser et al. 2010]

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What is affected by the humidification of aerosol

1. influences the direct aerosol radiative forcing - scattering, AOD
2. affects the particle’s efficiency to act as cloud condensation nuclei (CCN)
3. kinematics of particle deposition fluxes
4. increases the water volume available for absorption of gases and heterogeneous chemical reactions
5. models parametrisation

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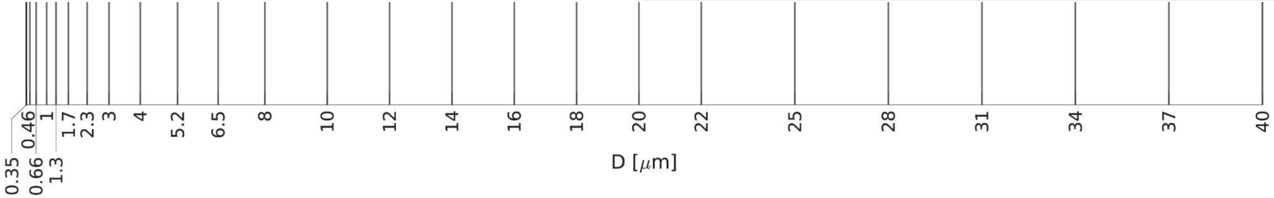
Apparatus

OPC—N3

Particle range spherical equivalent size 0.35 — 40 [µm]

- Sample flow rate (typical) 280 [mL/min]
- Laser: 658 [nm]
- Humidity range 0 — 95 [%] (non—condensing)
- Measures PM1 PM2.5 PM10
- Particle density 1.65 [g/ml]
- RI (refractive index) 1.5 + 0i
- Temperature range —10 — 50 [°C]



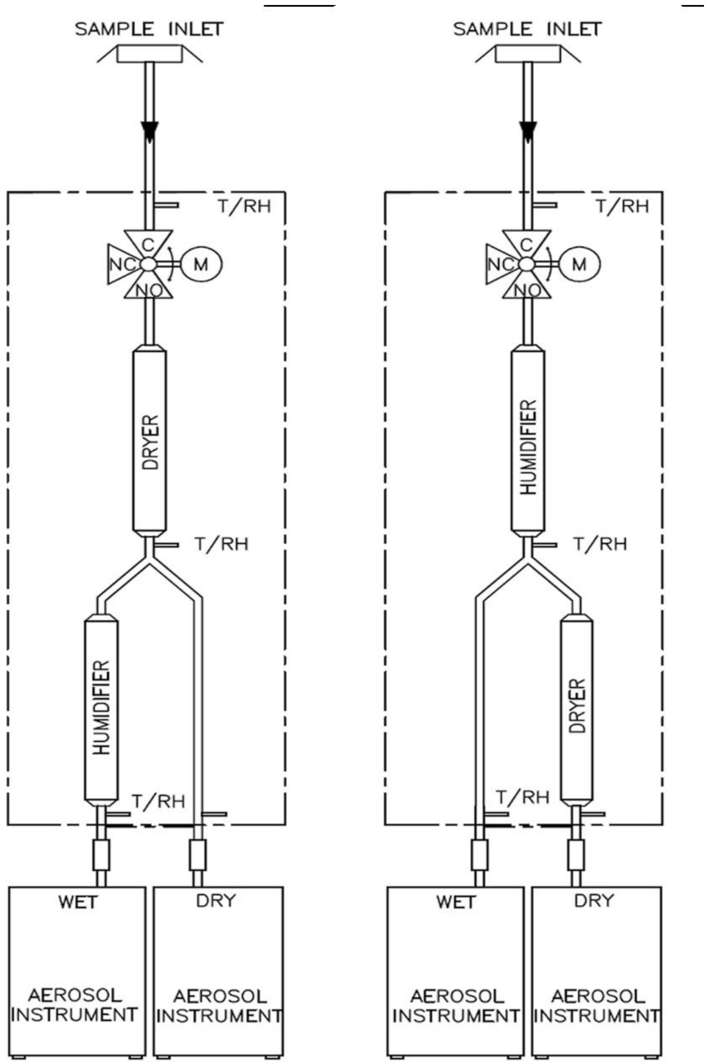
ACS1000

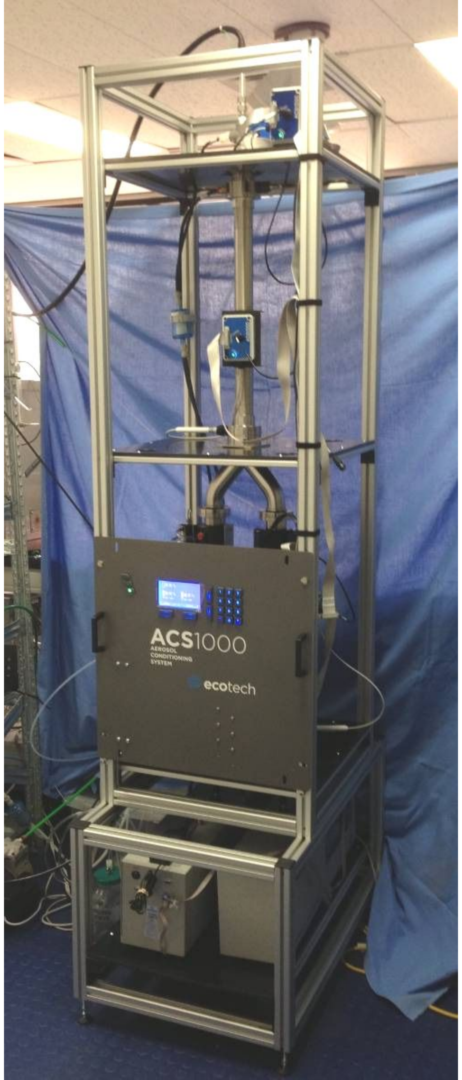
10% above ambient. 40% – 90%. (Dependant on flow)

Rise and Fall Time < 20 minutes

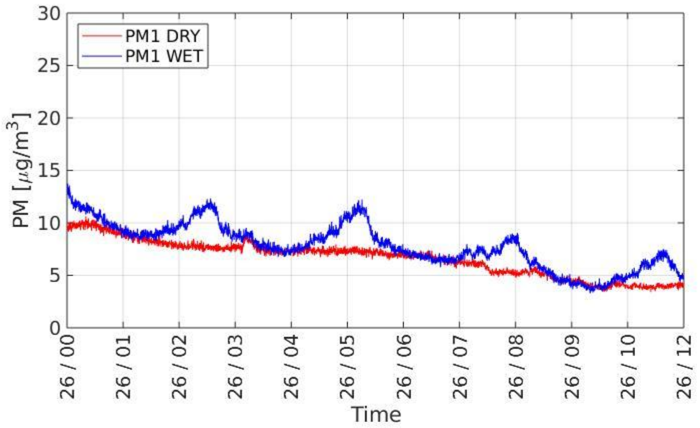
Flow Rate: 1 to 10 l/min

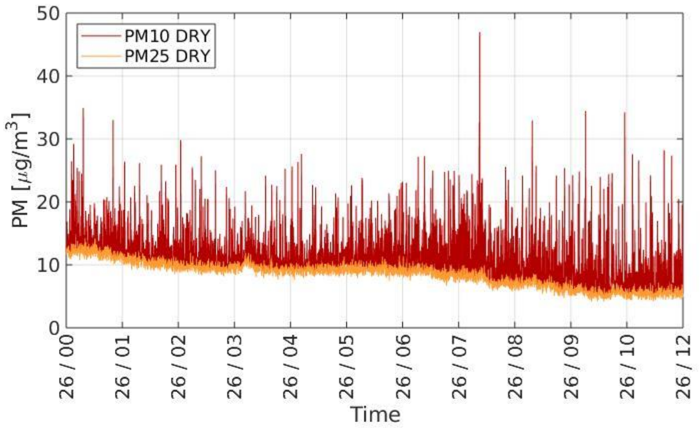
Sequence —> Points (sequence can have 4 subsequences)





OPC-N3





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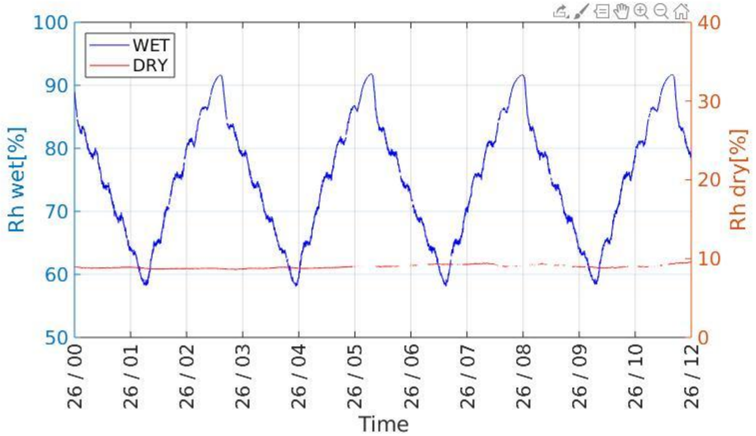
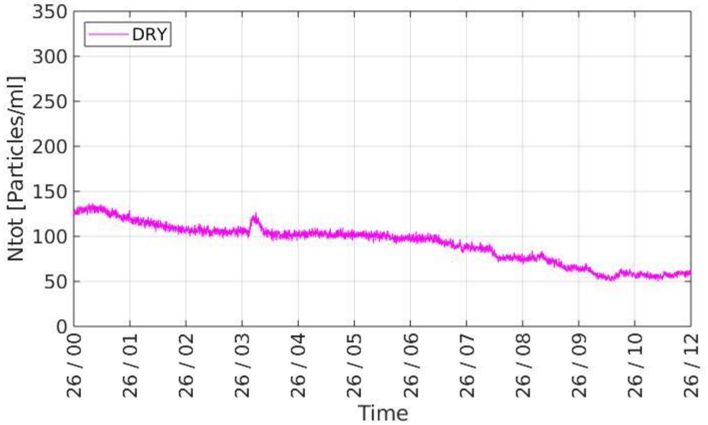




Results

Two seasons

Spring 2020

26—28.03.2020

5 6 8 .04.2020

29—30.04.2020

04.05.2020

16—23.05.2020

17 days

139 cycles

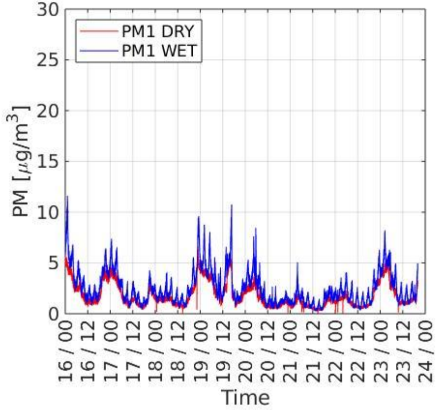
December 2020

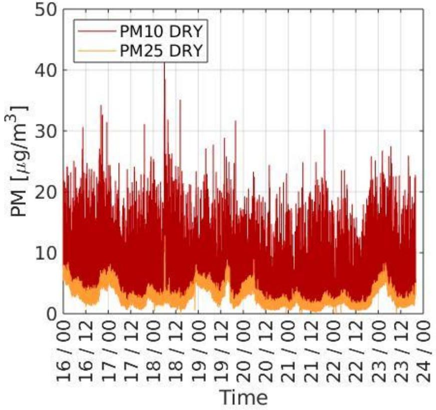
17—31.12.2020

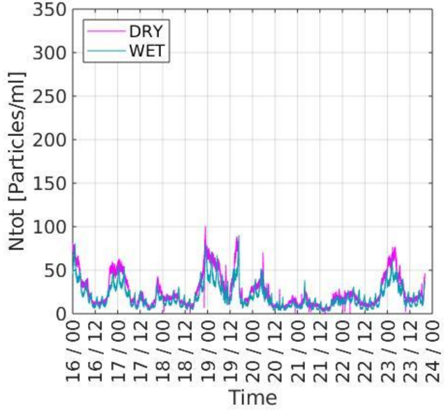
15 days

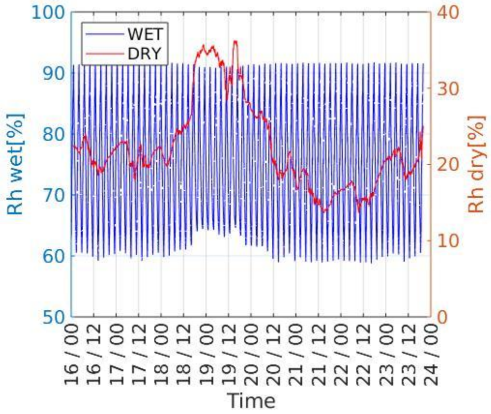
172 cycles

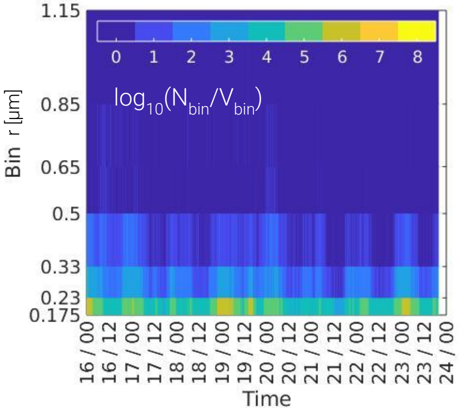
16—23.05.2020

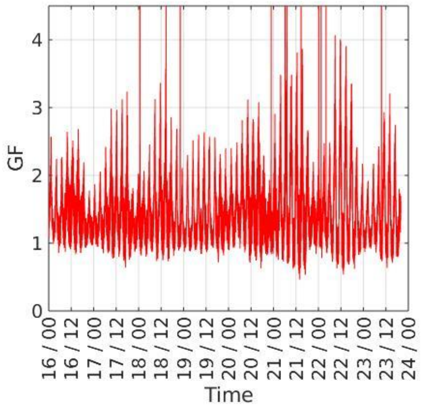












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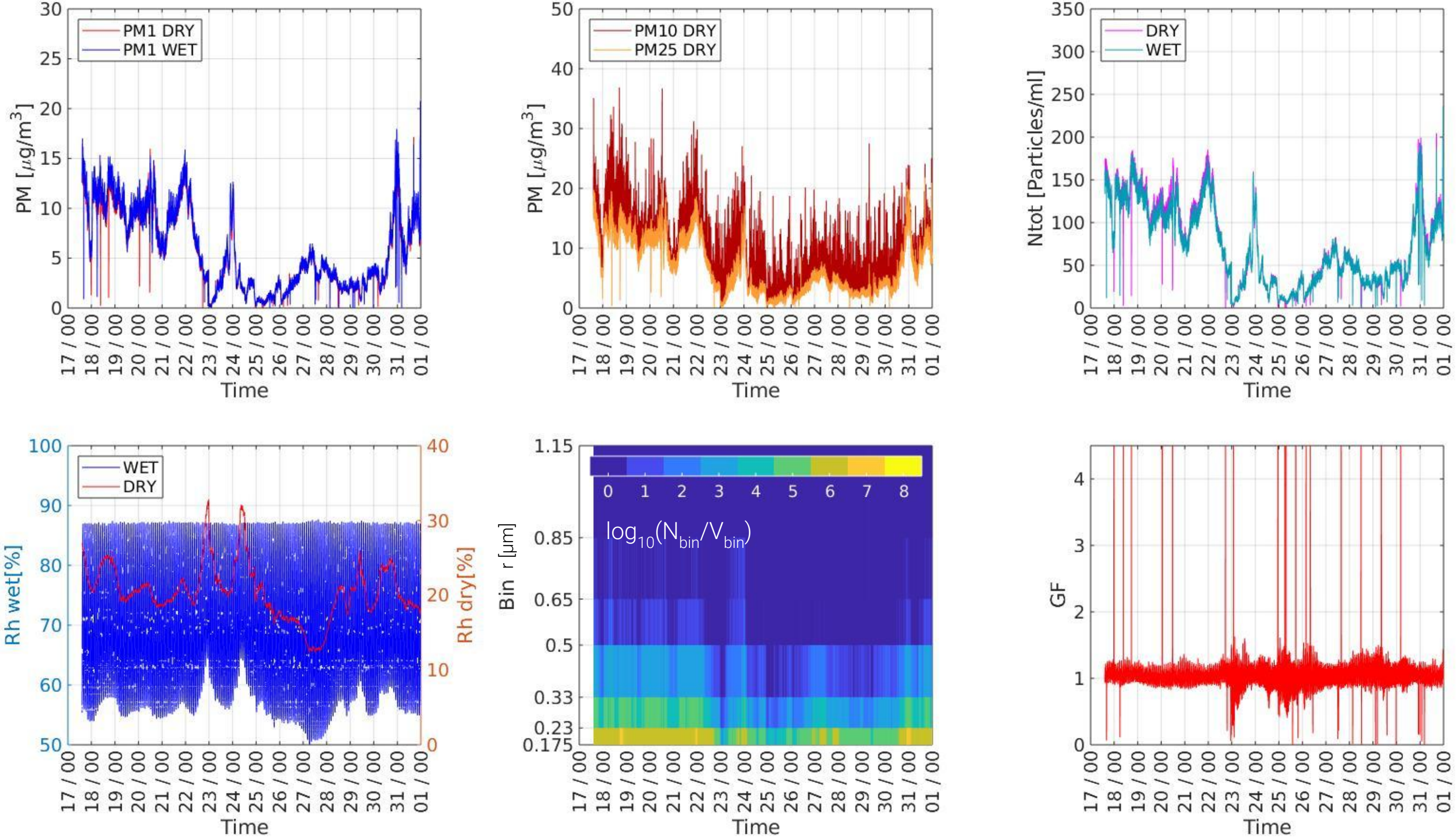
17—31.12.2020



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κ—Köhler theory

[Pope F. D., 2010]

$$S = a_w exp \underbrace{\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D} \right)}_{\text{assumed 1 for aerosol > 100 nm}}$$

Growth factor and κ

[Pope F. D., 2010]

$$GF = \frac{m}{m_0} = 1 + \frac{\frac{\rho_w}{\rho_p}\kappa}{-1 + \frac{1}{a_w}}$$

Saturation ratio (~Relative humidity) can be assumed as water activity

$$\boldsymbol{a_w = Rh}$$

ϱ_w — density of water
ϱ_p — density of aerosol particle
Rh — relative humidity
m — the wet aerosol mass (Rh > 0%)
m_0 — the dry aerosol mass (Rh = 0%)

κ—Köhler theory

[Crilley, 2018]

$$GF = \frac{m}{m_0} = 1 + \frac{\frac{\rho_w}{\rho_p}\kappa}{-1 + \frac{1}{a_w}}$$

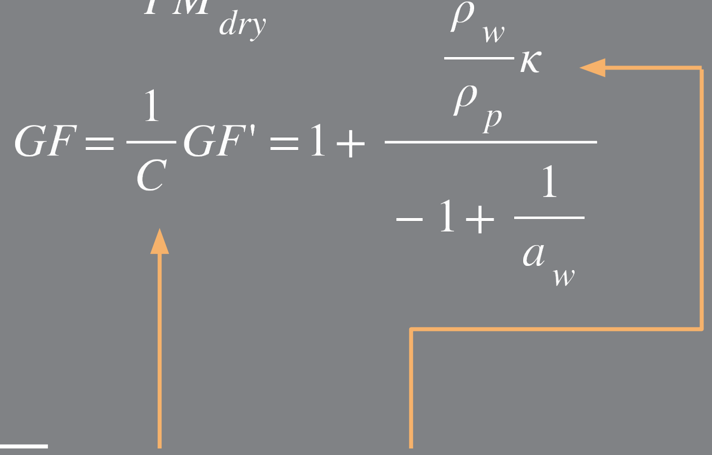
ϱ_w — the density of water is 1 [g/cm^3],
ϱ_p — bulk dry particle density is **1.65 [g/cm^3]**.

The value for κ can be found by a **non—linear curve fitting** of a humidogram (m/m_o vs. a_w)

PM_{wet} — particulate matter from OPC—N3 from wet pipe (changing humidity)

PM_{dry} — particulate matter from dry pipe

$$GF' = \frac{PM_{wet}}{PM_{dry}}$$

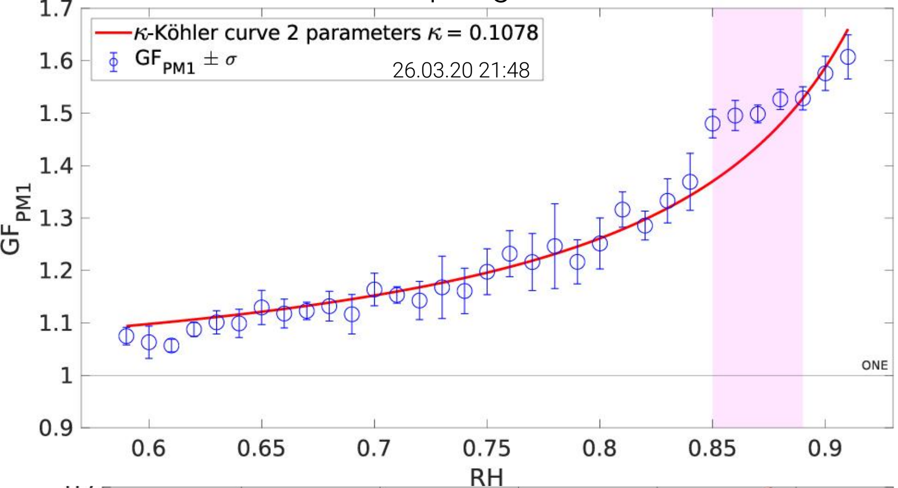


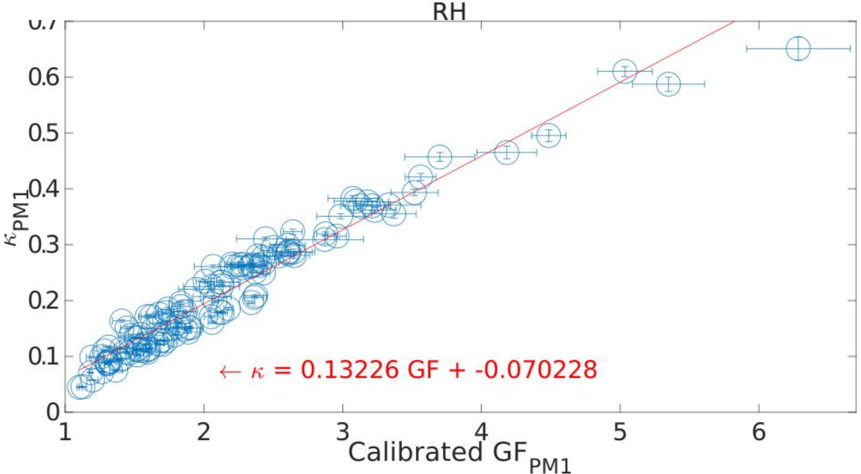
$$GF = \frac{1}{C} GF' = 1 + \frac{\frac{\rho_w}{\rho_p}\kappa}{-1 + \frac{1}{a_w}}$$

non—linear curve fitting with 2 parametres

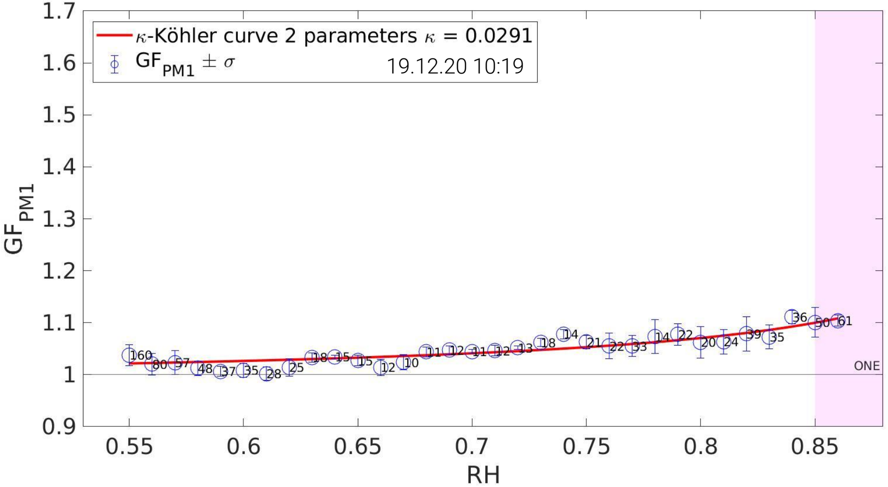
Example of curve fitting

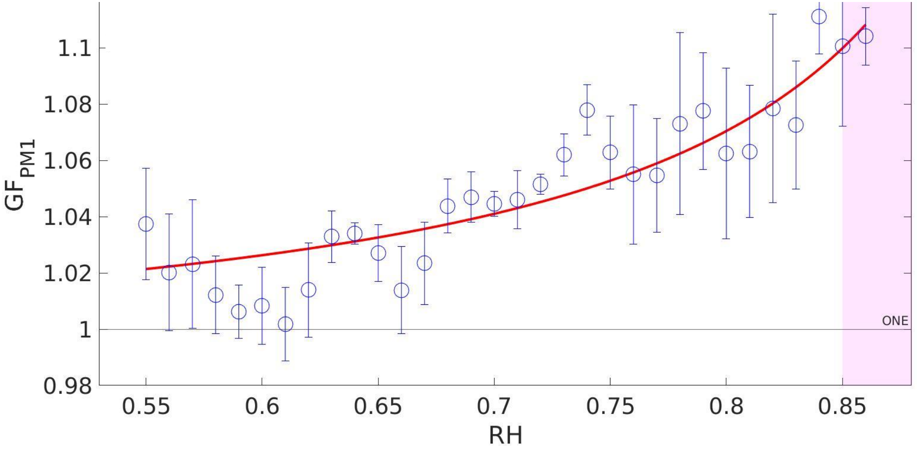
Spring 2020

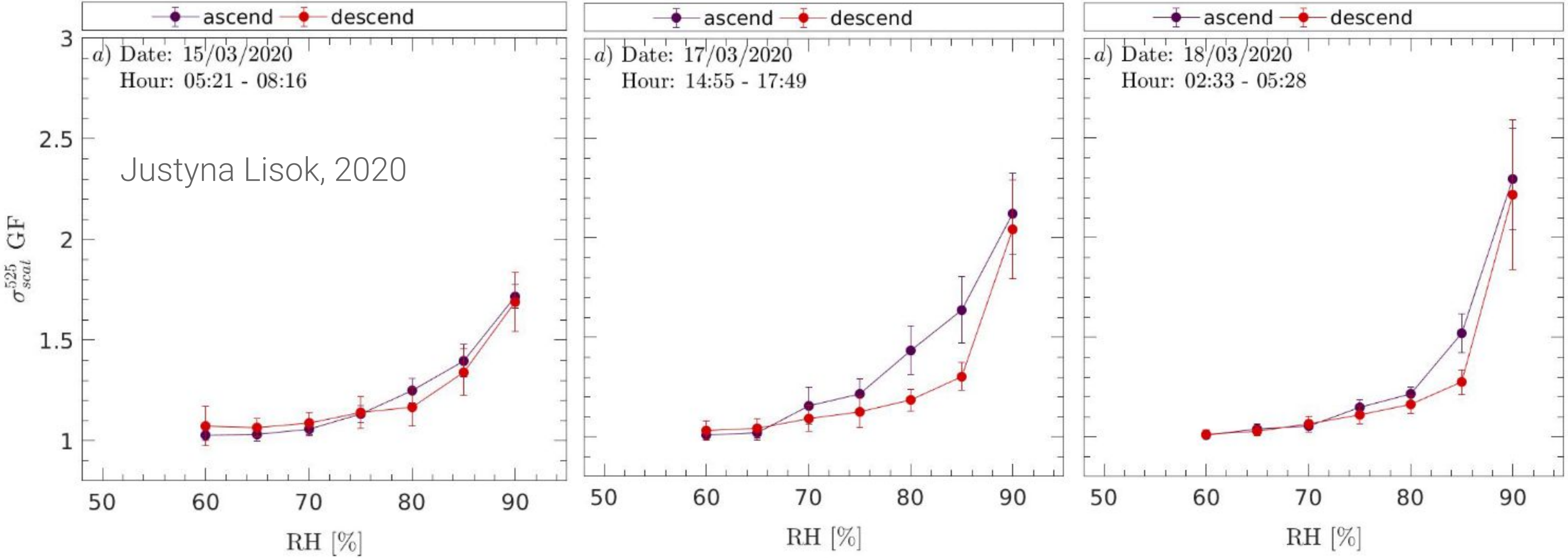




December 2020





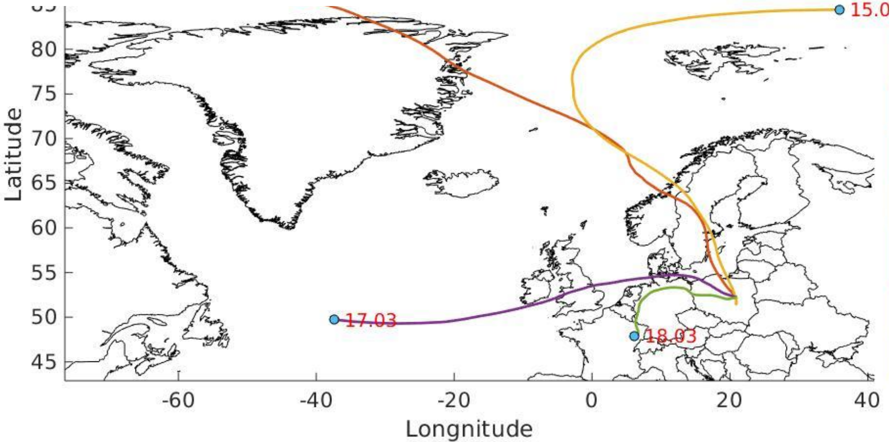


Justyna Lisok, 2020

Aurora 4000
Spring 2020

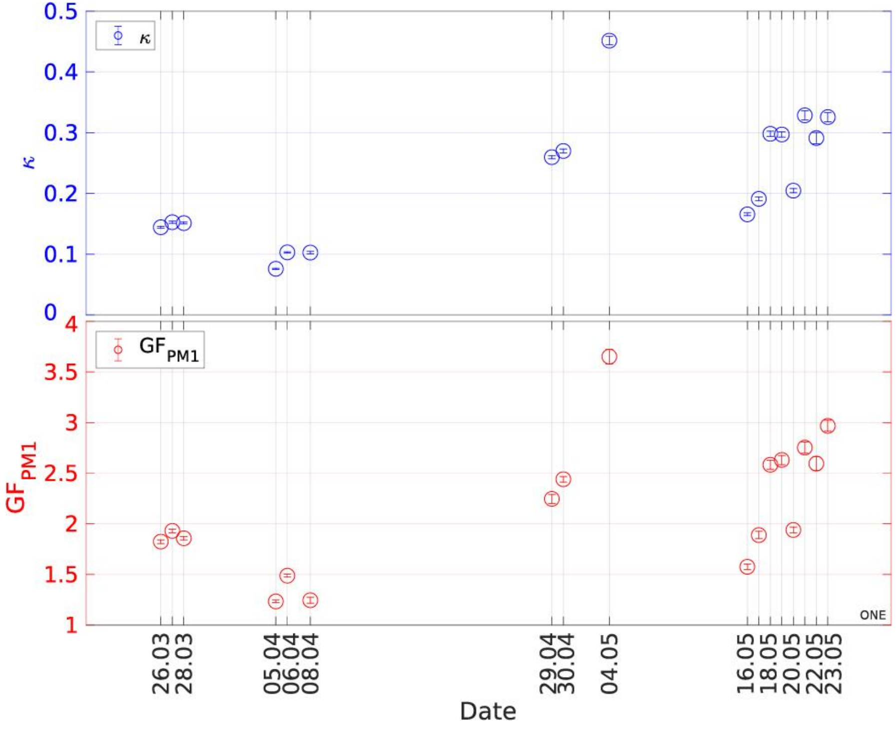
$$f(\mathrm{RH},\lambda) = \frac{\sigma_{\mathrm{sp}}(\mathrm{RH},\lambda)}{\sigma_{\mathrm{sp}}(\mathrm{RH}_{\mathrm{dry}},\lambda)}$$

scattering enhancement factor



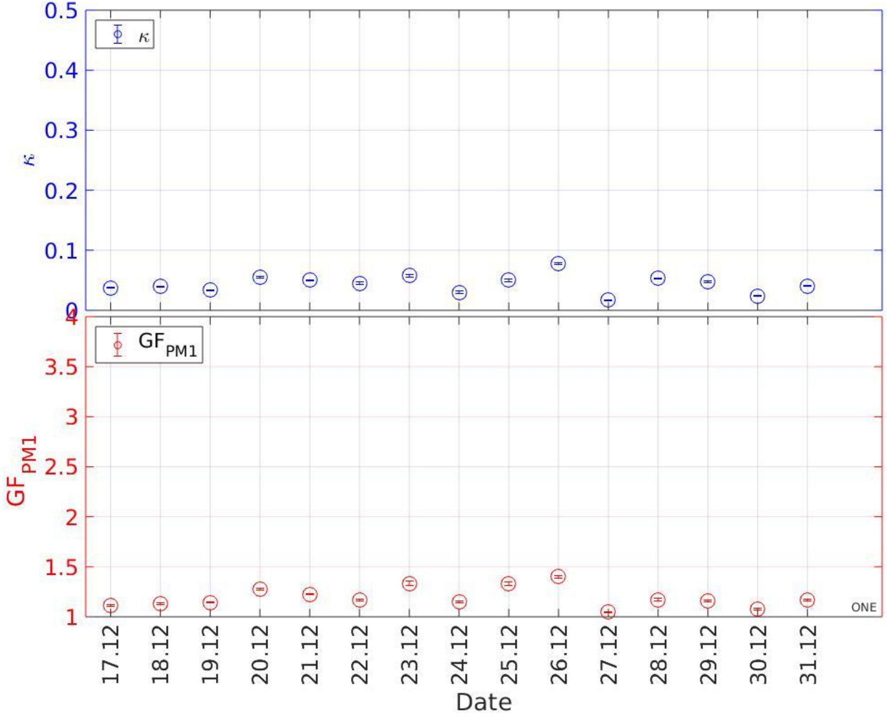
κ and *GF*(RH= 85%)

Spring 2020



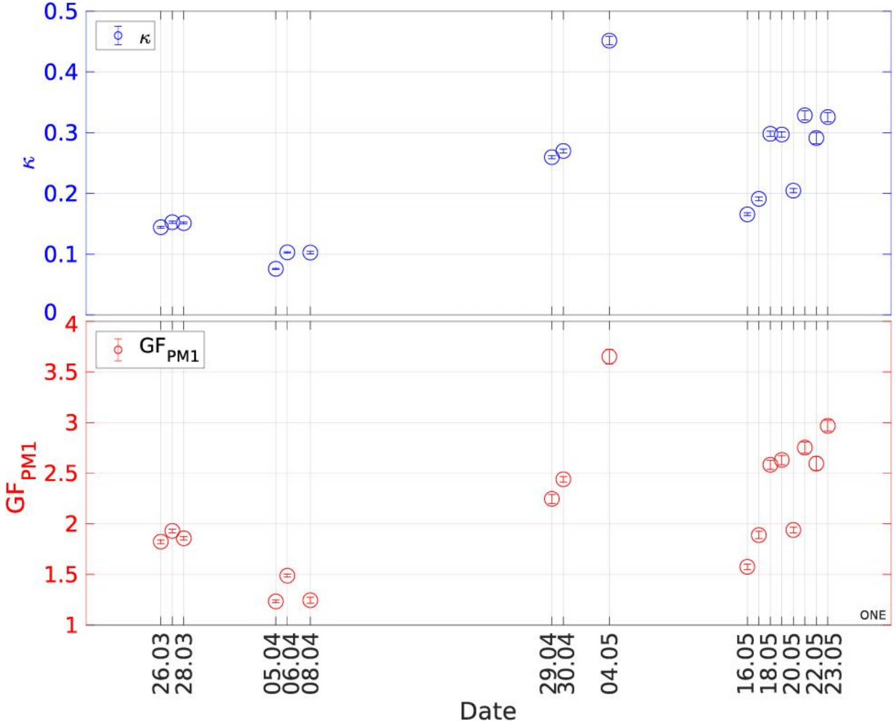
$\langle\kappa_{Spring}\rangle$= **0.21**51±0.0041

December 2020

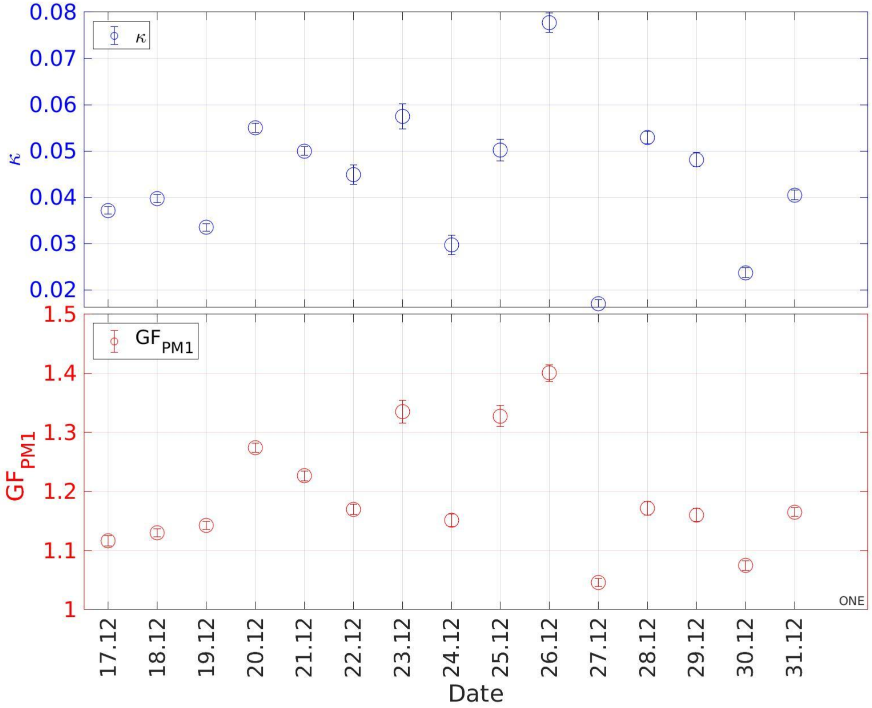


$\langle\kappa_{Winter}\rangle$= **0.04**40±0.0016

κ and *GF*(RH= 85%)

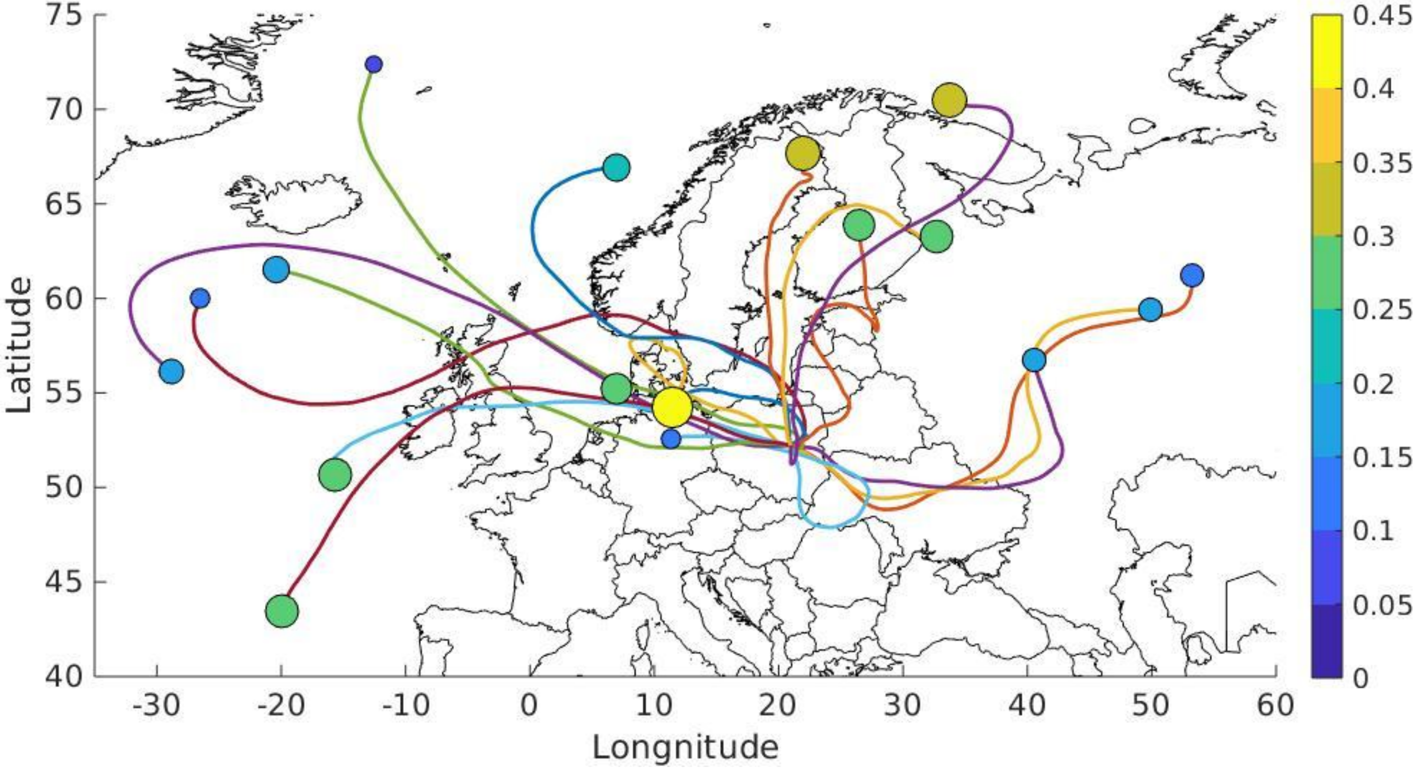


$<\kappa_{Spring}>= 0.2151\pm0.0041$

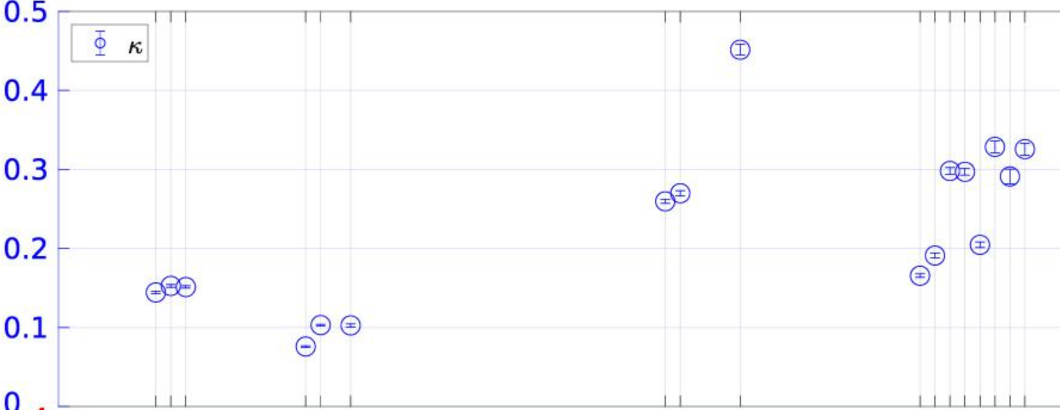


$<\kappa_{Winter}>= 0.0440\pm0.0016$

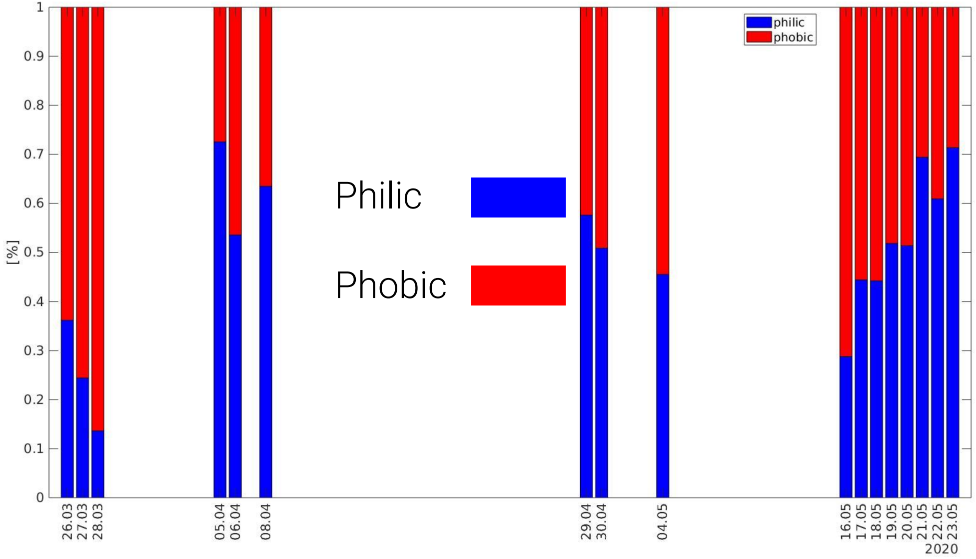
κ and air mass trajectories Spring 2020



κ



MERA II

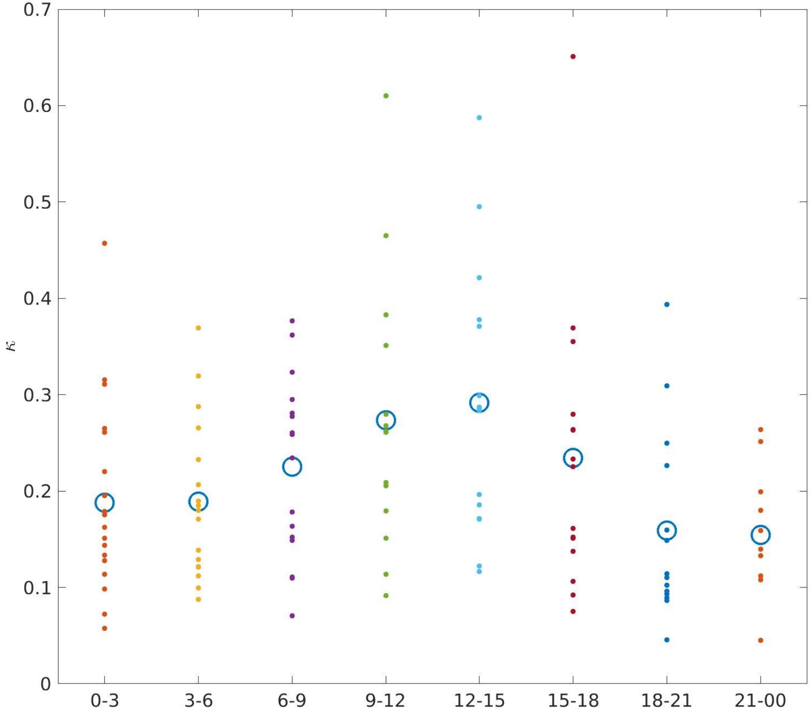


Philic 🟦

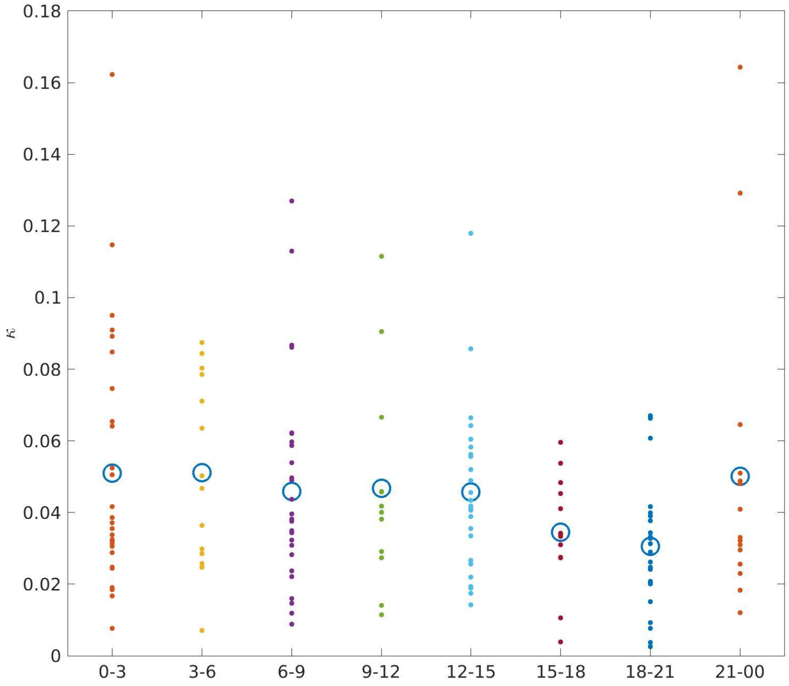
Phobic 🟥

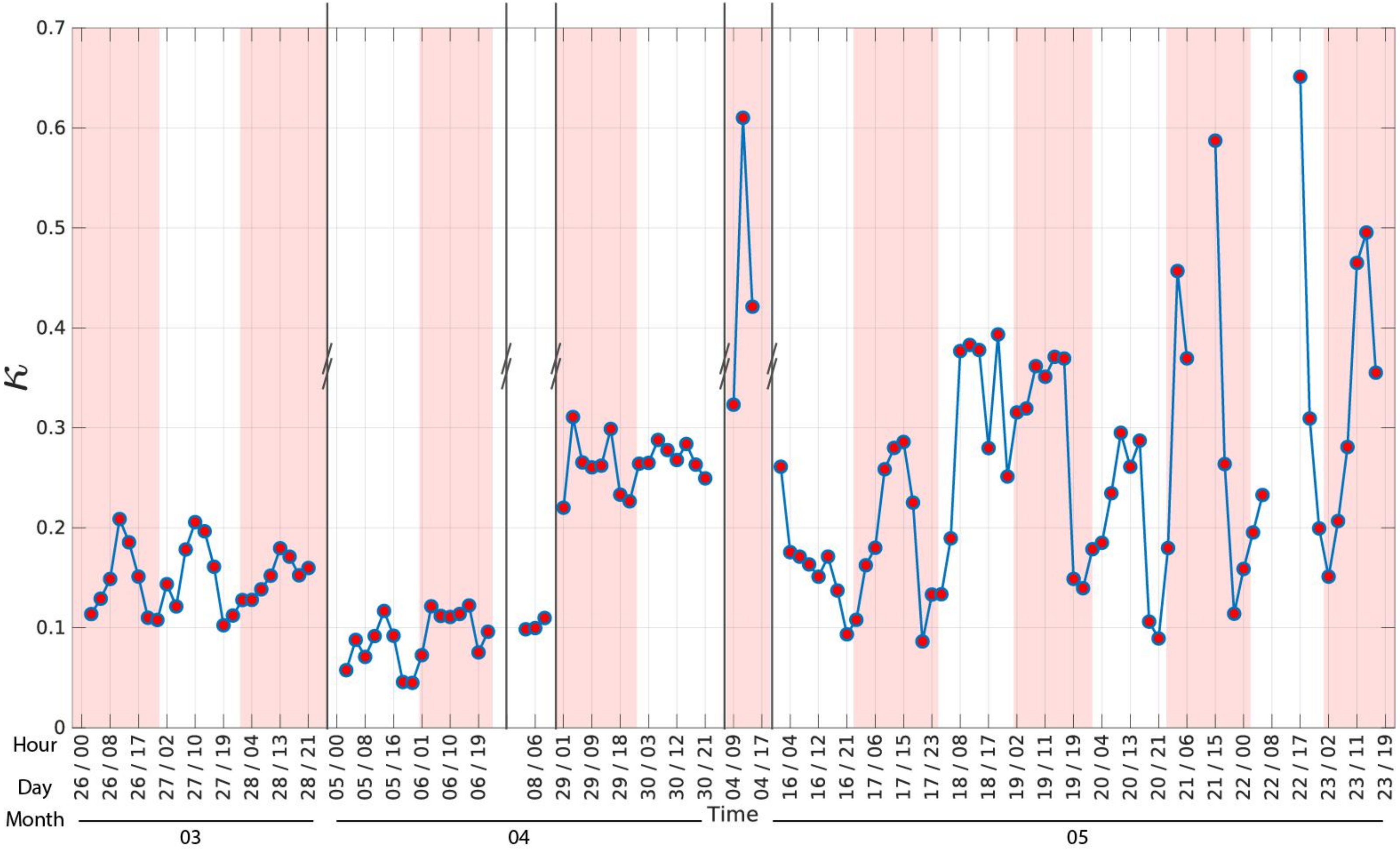
Diurnal variation of κ

Spring 2020



December 2020





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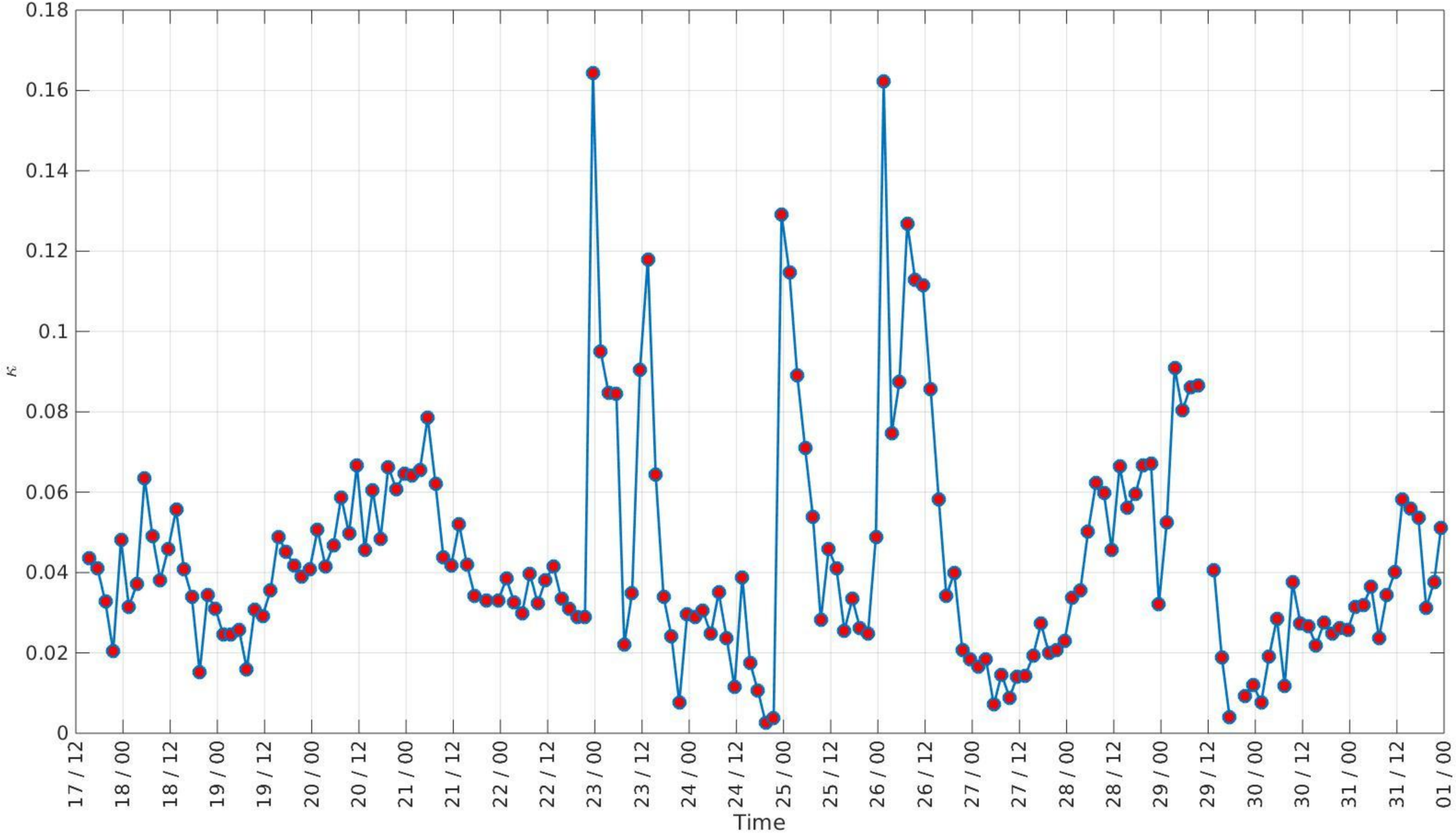
0.18
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Time

Correction of PM data from OPC—N3

Rh from OPC—N3 and from ACS1000

Spring 2020

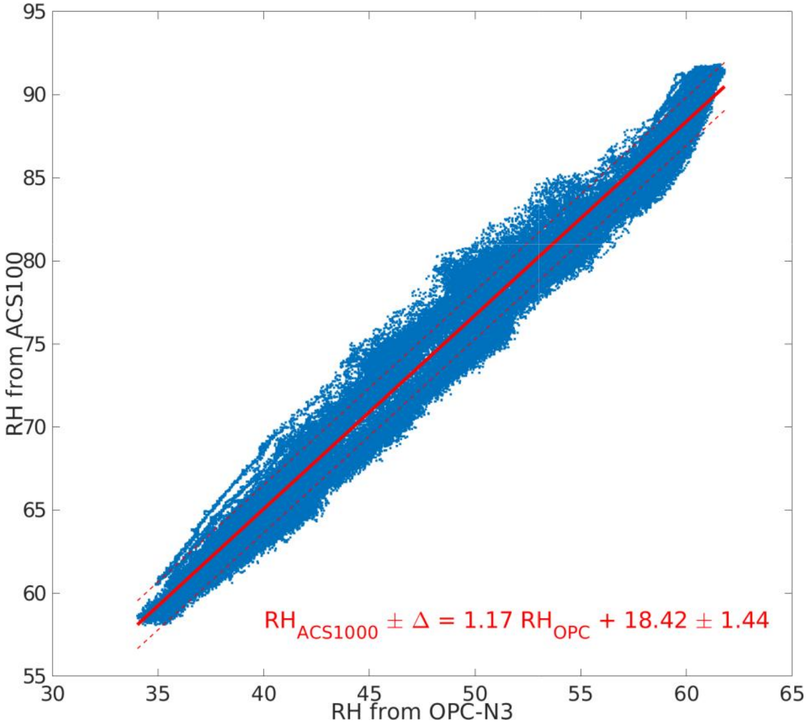
Maximum Rh at OPC—N3: 61.8%

Maximum Rh of ACS1000: 91.83%

time depending response

$$RH_{ACS1000} \pm \Delta = a \cdot RH_{OPC} + b \pm \Delta$$

$$= 1.17 \cdot RH_{OPC} + 18.42 \pm 1.44$$



Correction equation

$$RH_{ACS1000} \pm \Delta = a \cdot RH_{OPC} + b \pm \Delta$$

$$= 1.17 \cdot RH_{OPC} + 18.42 \pm 1.44$$

$$GF = \frac{m}{m_0} = 1 + \frac{\frac{\rho_w}{\rho_p}\kappa}{-1 + \frac{1}{a_w}}$$

$$\boxed{PM_{RH=0} = \frac{\left(1 - a \cdot RH_{OPC} + b\right) \cdot PM_{wet}}{1 + \left(\frac{\rho_w}{\rho_{opc}}\kappa - 1\right) \cdot \left(a \cdot RH_{OPC} + b\right)}}$$

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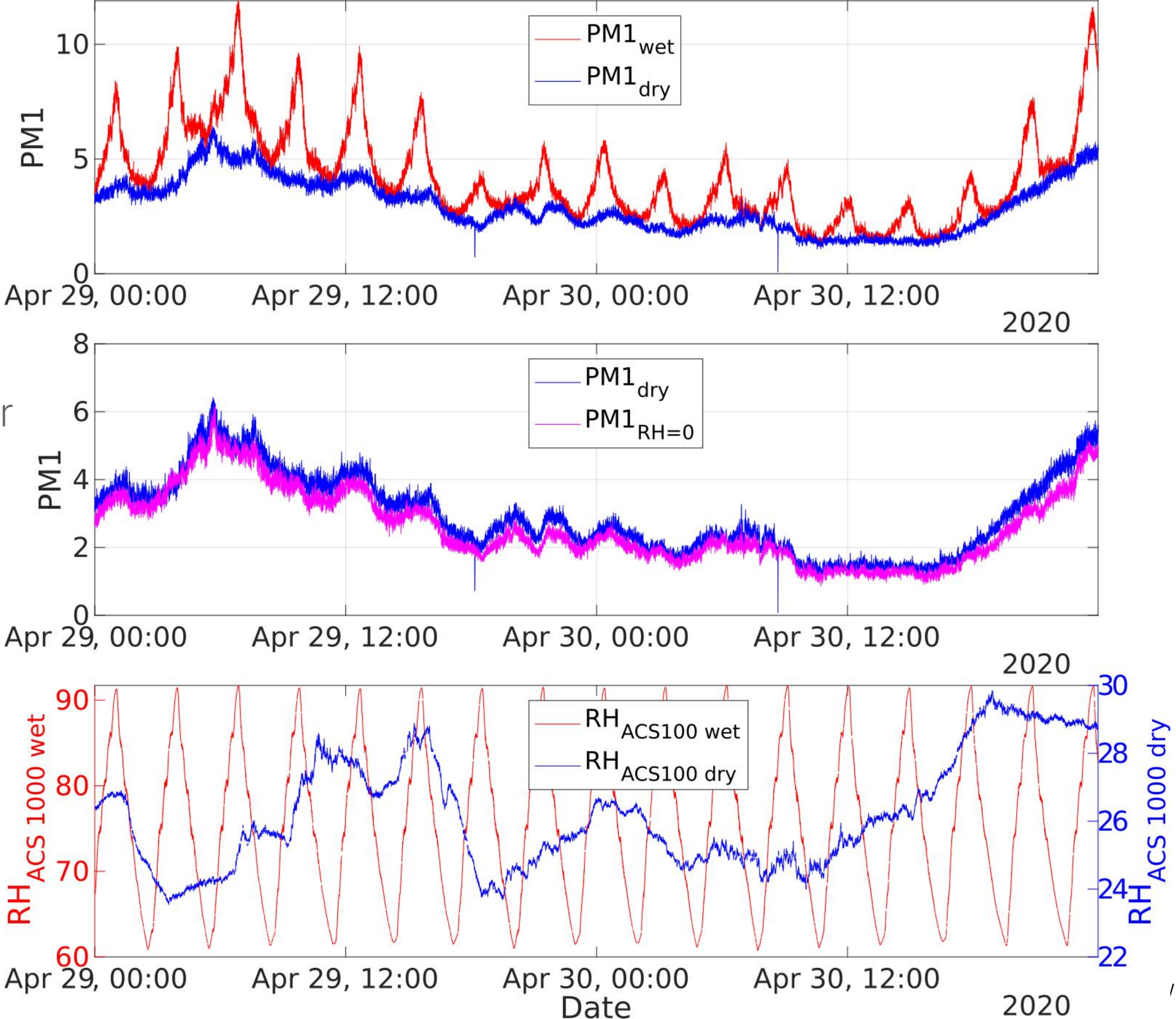
mean κ value for the period 29-30 April 2020

κ= 0.2647



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Conclusions

OPC-N3:

1. **Dependence of relative humidity** can be:
    - advantage —> measurement of hygroscopic properties
    - disadvantage —> needed correction for PM measurements
2. The single parameter κ can be used to **correct the PM data**
3. Rh given by OPC—N3 is biased and not reliable

κ

4. The κ variates with day time during Spring measurements.
5. The κ change between seasons drastically **$<\kappa_{Spring}>= 0.22$** **$<\kappa_{Winter}>= 0.04$**

Acknowledgments

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Thank you for your attention

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