IE Calibration Bias from Hygroscopicity and DMA Multiple Charge

Reporter: Yan Zheng **Position:** Master Student

Institution: College of Environmental Science and Engineering, Peking University

Supervisor: Qi Chen **Contact:** yan_cese@pku.edu.cn

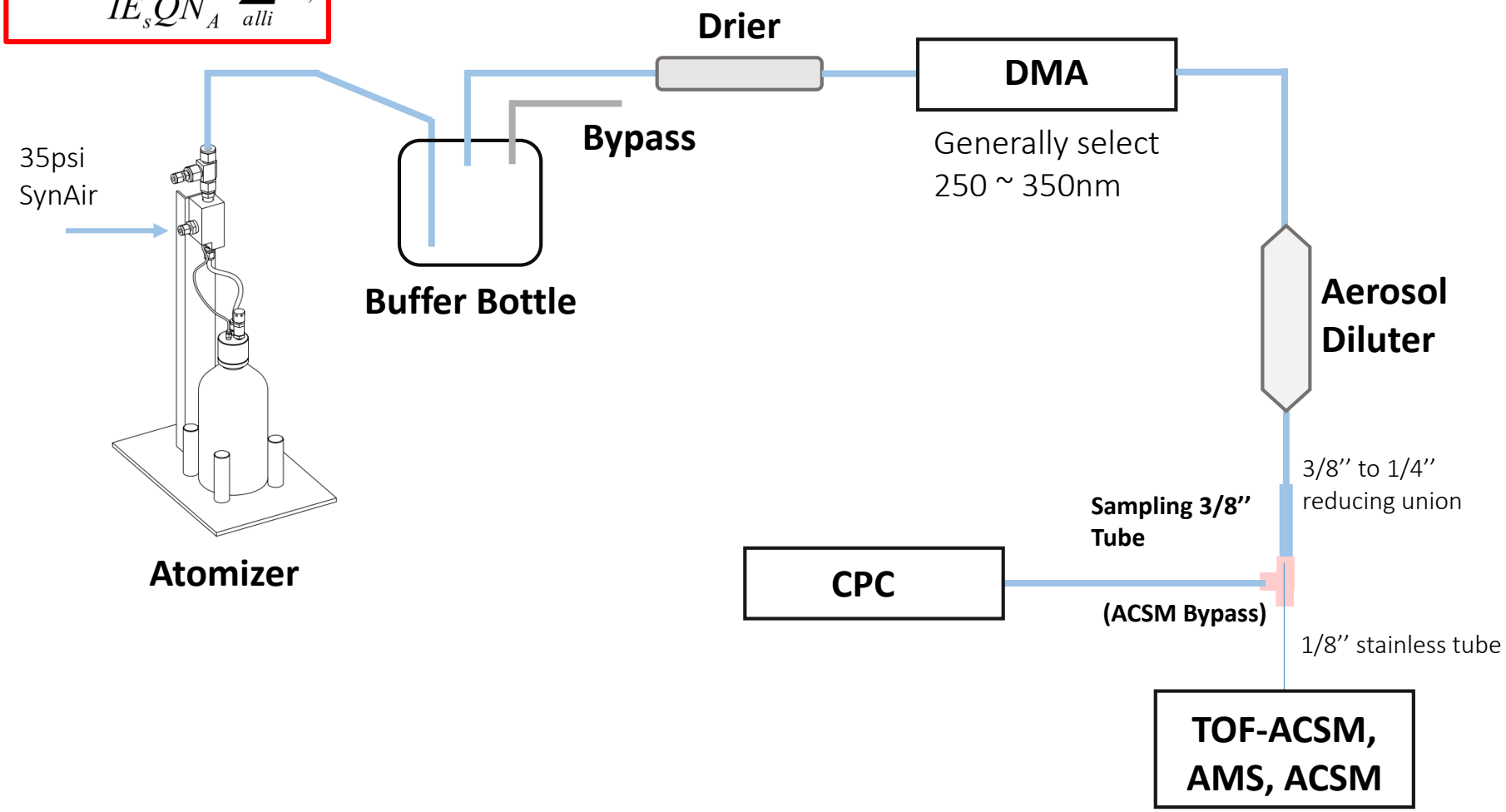
DMA – CPC
IE Calibration Setup

IE: Ionization Efficiency

$$C_s = \frac{10^{12} MW_s}{IE_s Q N_A} \sum_{alli} I_{s,i}$$

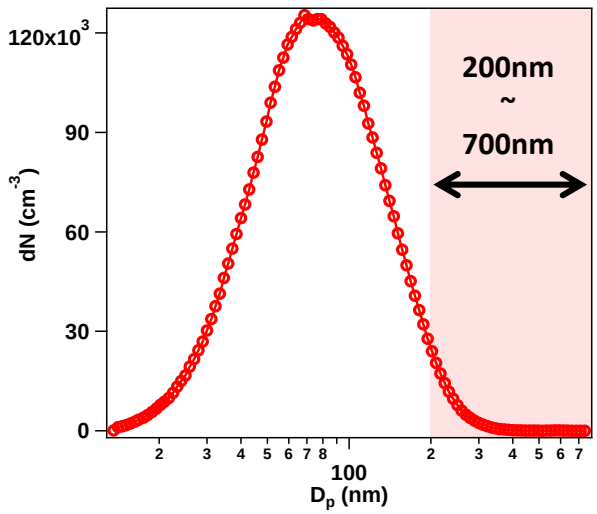
Important Settings:

- 0.015M NH_4NO_3 solution
- Dry efficiency: Depends on different driers
- DMA: 250nm ~ 350nm

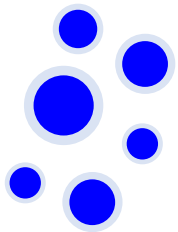


IE Calibration Setup Schematics

Atomizer Generated



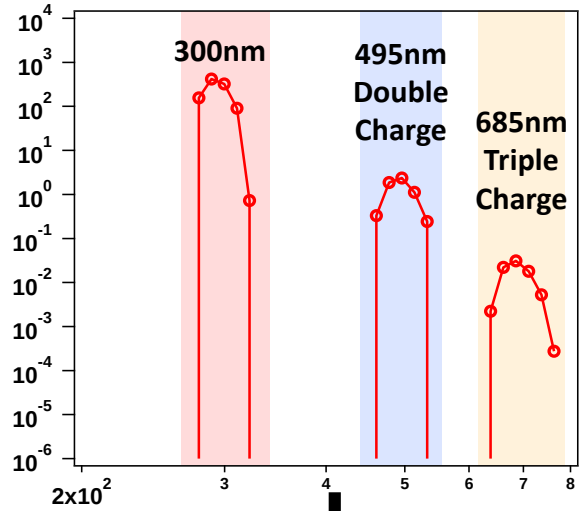
Drier



NOT completely dry
STILL contain water!

DMA Selection 300nm

DMA Multiple Charge



Assumptions:

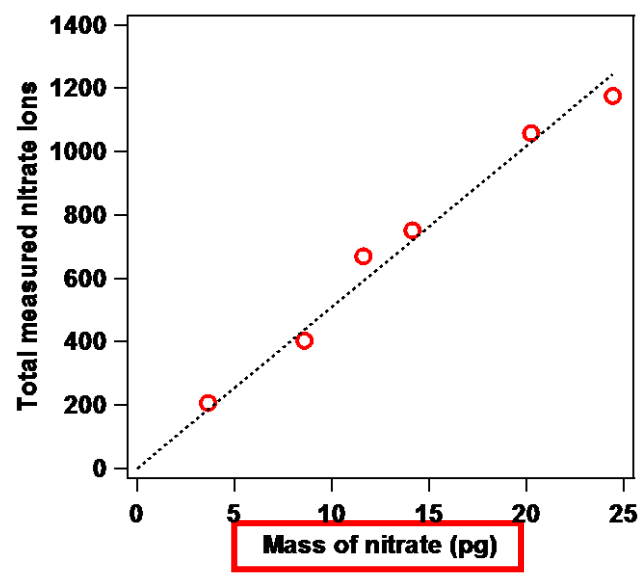
- Spherical particle → Shape Factor (~ 0.8 for NH_4NO_3)
- CPC and ACSM/AMS test the same NH_4NO_3 burden
- Dry particle
- Uniform distribution at mode diameter

$$RF = \frac{Nitrate\ Ions}{CPC\ Mass}$$

$$IE \propto RF$$

CPC **ACSM/AMS**

RF Fitting (ions/pg)



Reality:

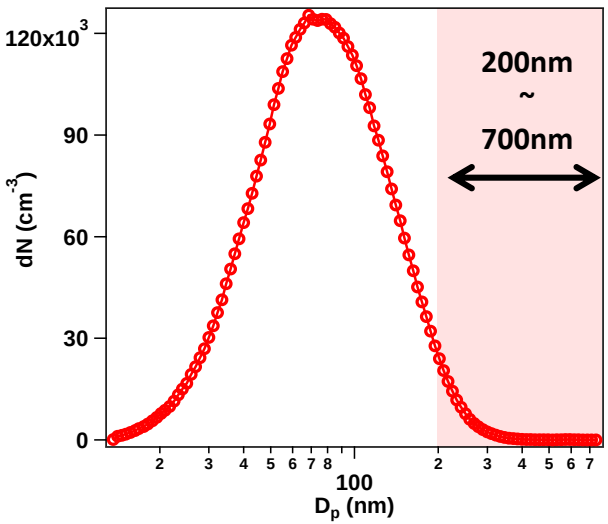
- Actual distribution has multiple charges (495nm, 685nm etc. while they are considered to be 300nm)
- Incompletely dry NH_4NO_3 particles

IE Bias

Drier Type	RH after drying
Silica Drier(tested here)	~ 35%
PD-Series Nafion Drier	~ 15%
MD-700 Nafion Drier	~ 10%

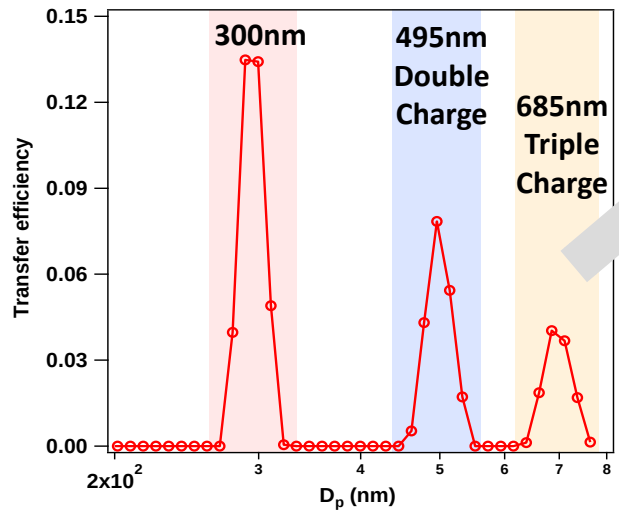
DMA Multiple Charge Determined by

Atomizer
size distribution

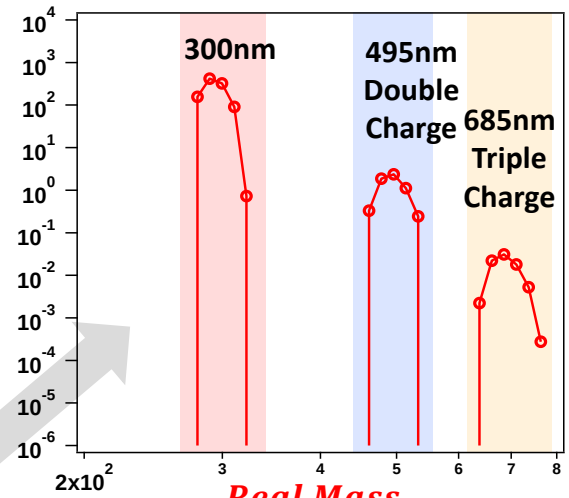


×

DMA
Transfer function (select 300nm)



Real mass tested in TOF-ACSM

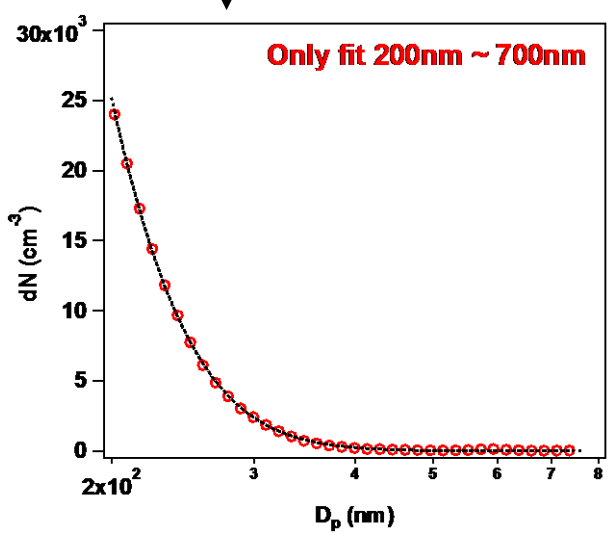


$$Bias = \frac{Real\ Mass}{Assumed\ Mass} - 1$$

Assume that they are all dry and spherical particles

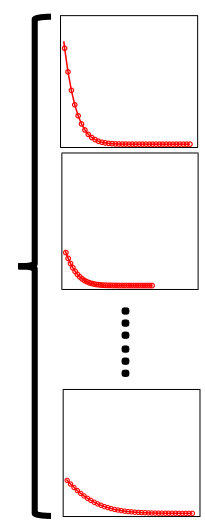
$$Assumed\ Mass = CPC\ Number\ Concentration * \frac{1}{6} * 300^3$$

Log-normal
Curve fitting

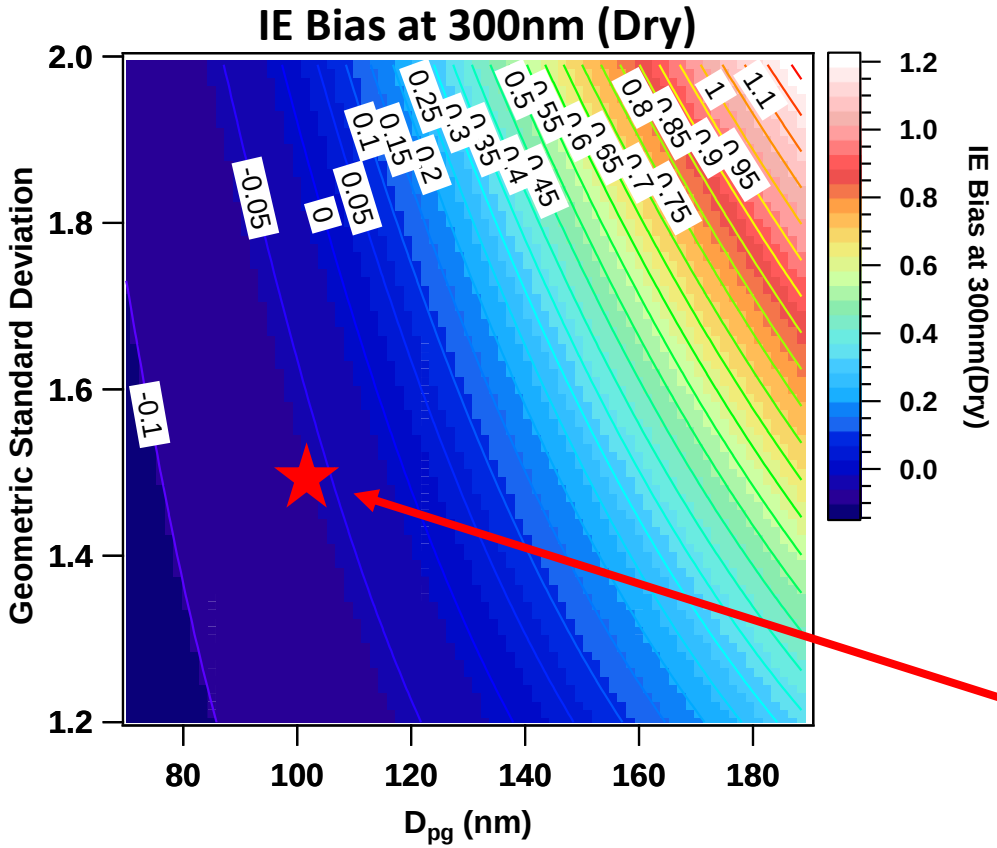


$$\frac{dN}{dlnD_p} = \frac{N_t}{\sqrt{2\pi} \cdot ln\sigma_g} \cdot \exp\left(-\frac{(lnD_p - ln\ \bar{D}_{pg})^2}{2ln^2\sigma_g}\right)$$

- Use N_t, σ_g, $\bar{D}_{pg}$ to describe a log-normal distribution
  - σ_g — *geometric standard deviation(gsd) of* D_p
  - N_t — *total particle number*
  - $\bar{D}_{pg}$ — *Median number of* D_p
- **Generate** a series of distributions



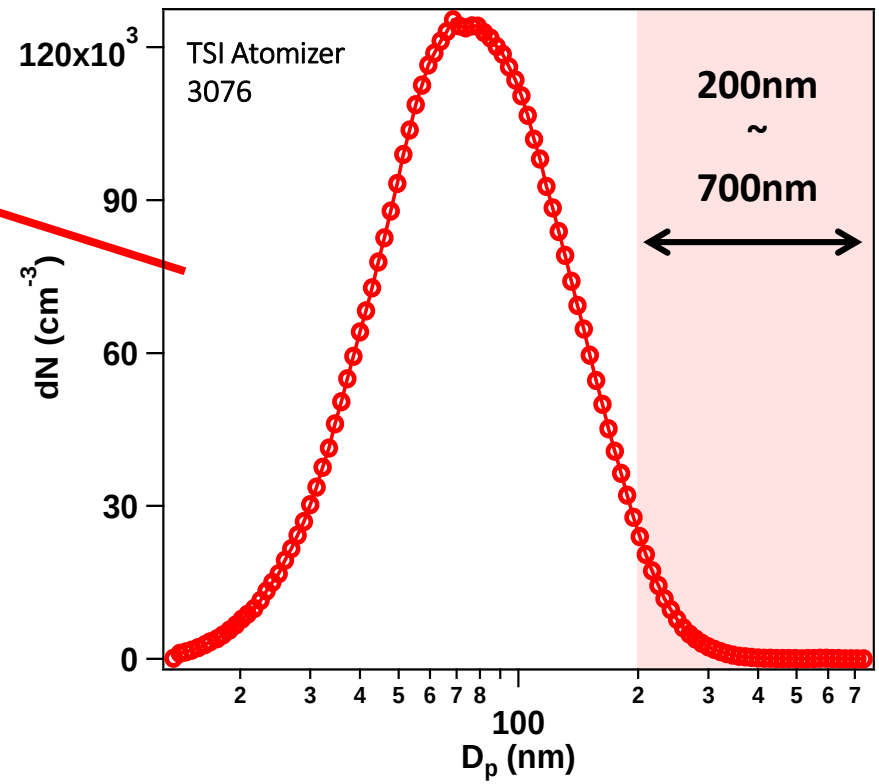
DMA Multiple Charge Bias on IE



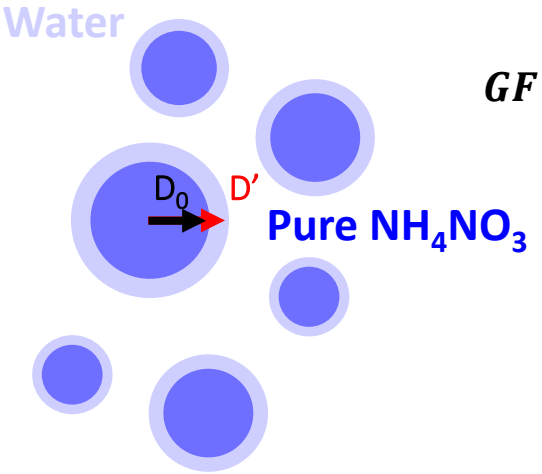
- If the size distribution generated by your atomizer has larger D_{pg} or σ_g, the bias might be high
- **While TSI 3076 atomizer is often used for AMS/ACSM calibration**, the bias from the assumption of uniform 300nm is small

TSI Atomizer 3076

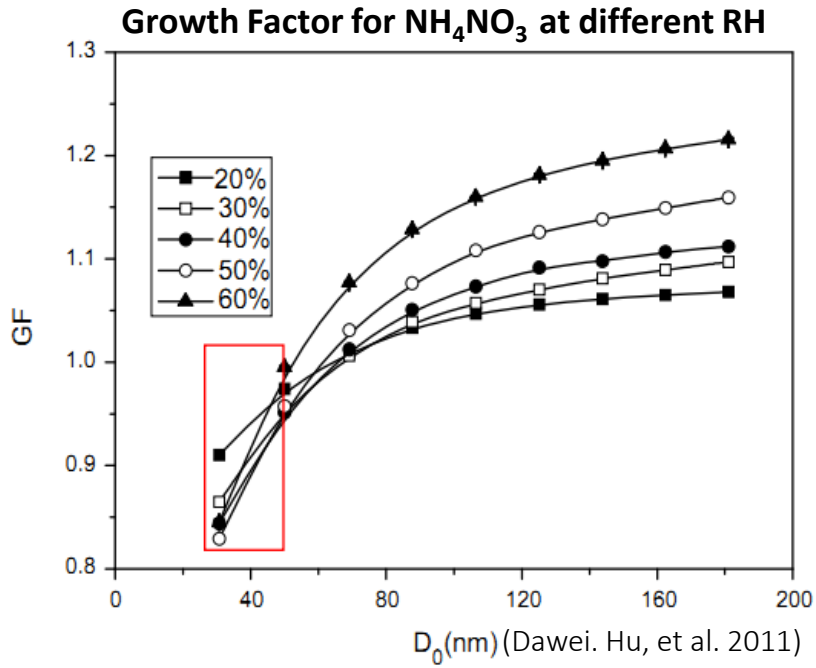
0.015mM NH_4NO_3
35 psi SynAir
D_{pg} = 98nm
σ_g = 1.49



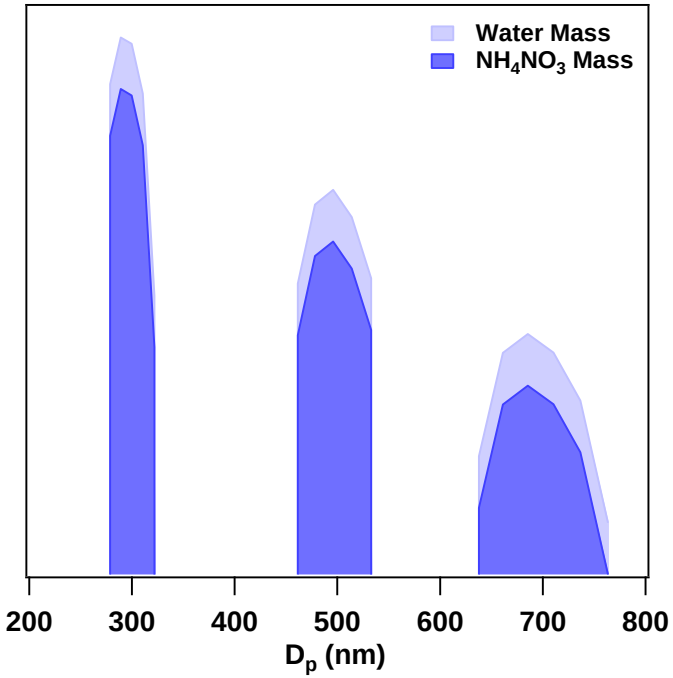
NH_4NO_3 Hygroscopicity



$$GF = \frac{D'}{D_0}$$



(Dawei. Hu, et al. 2011)



$$Bias = \frac{Real\ Mass}{Assumed\ Mass} - 1$$

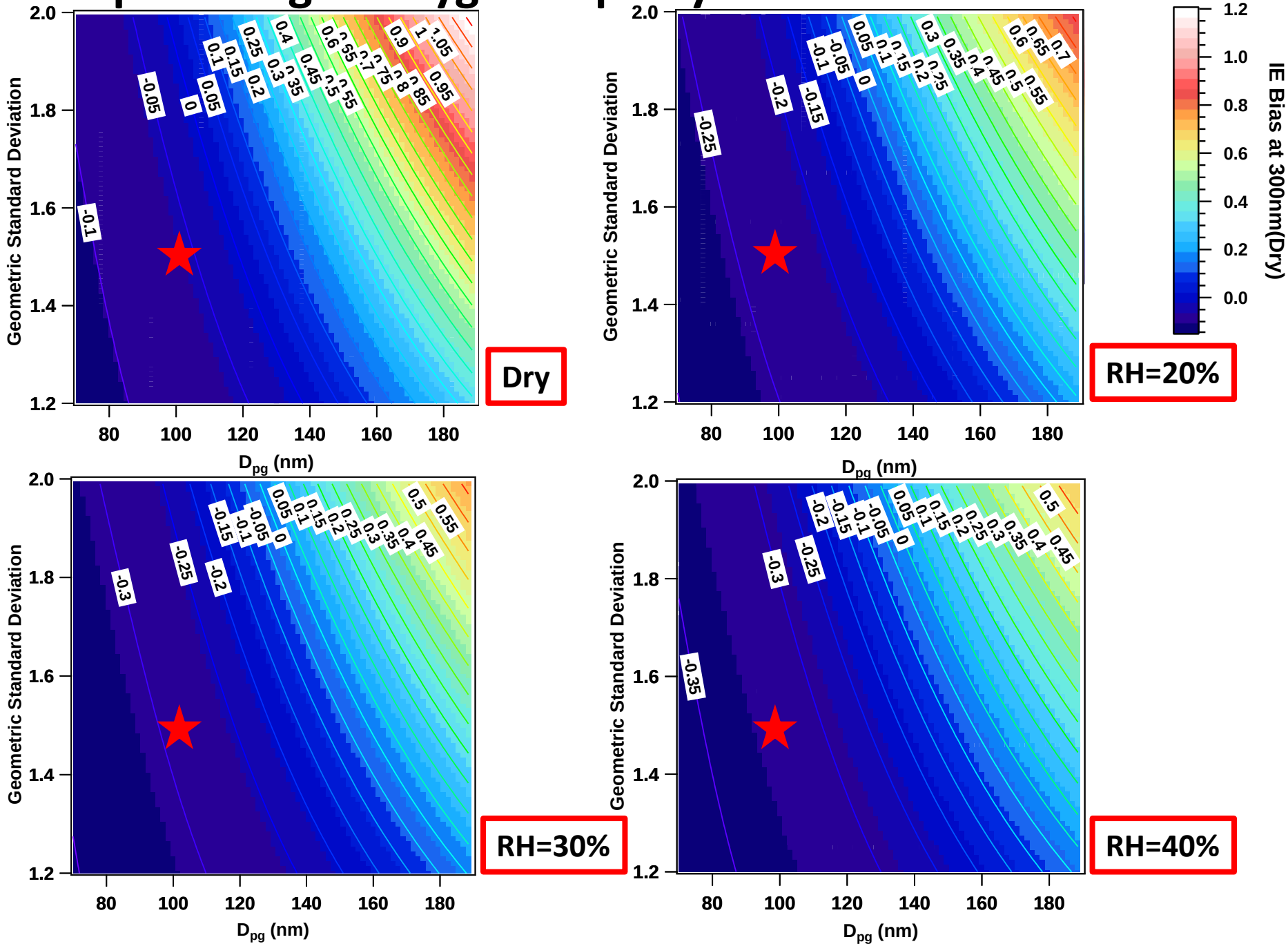
○ *There contains water in the NH_4NO_3 particle they are all dry and*

○ *Assume that they are spherical particles*

Assumed Mass

= CPC Number Concentration * 300^3

Multiple Charge & Hygroscopicity combined Bias on IE



A real example

- **IE Calibration Setup Parameters**
  - ✓ Atomizer 3076: NH_4NO_3 Concentration of 0.015 M
  - ✓ DMA Selected Diameter: 300nm
  - ✓ CPC Type: TSI 3775
  - ✓ SMPS Type: TSI 3080

- **Total Bias on IE**

RH (%)	0	20	30	40
IE Bias	-1.64%	-19.76%	-25.98%	-29.13%

Drier Type	RH after drying
Silica Drier(tested here)	~ 35%
PD-Series Nafion Drier	~ 15%
MD-700 Nafion Drier	~ 10%

- **Importance for Capture Vaporizer**
  - ✓ CE = 1
  - ✓ IE bias directly influence the quantification

$$C_s = \frac{10^{12} MW_s}{\boxed{IE_s} Q N_A} \sum_{all\,i} I_{s,i}$$

MWs: Molecular Weight
Q: Flowrate
NA: Avogadros number
I: Ions intensity

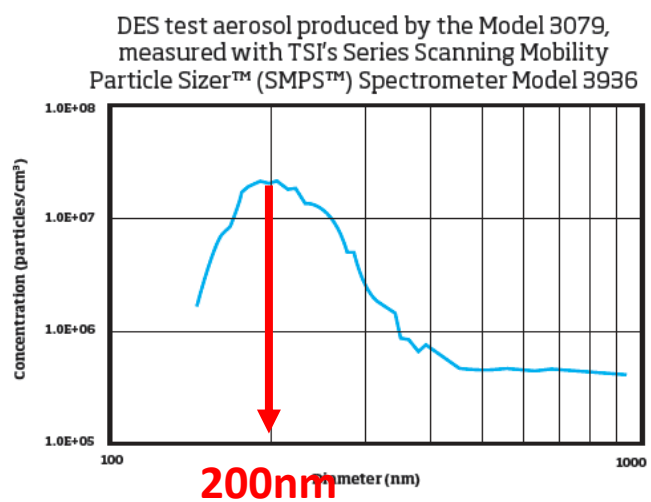
Conclusion

- **Bias factors of IE calibration**
  - ✓ Polydisperse distribution from Atomizer -- Size distribution
  - ✓ Drier efficiency – Hygroscopicity of NH_4NO_3

  The influences on IE by the actual size distribution and hygroscopic growth can be negative or positive, depending on these two factors.

  Be more careful when doing your IE calibration!
  Check the size distribution from the atomizer and check the RH after the drier!
- **May the bias of IE explain some of the discrepancies of the CE?**
  - ✓ For example, large CE at urban locations…

TSI Atomizer 3079



Thanks for your attention!

Q & A