Optical Properties of Moderately Absorbing Organic and Mixed Organic/Inorganic Aerosols at Relative Humidities up to 95%

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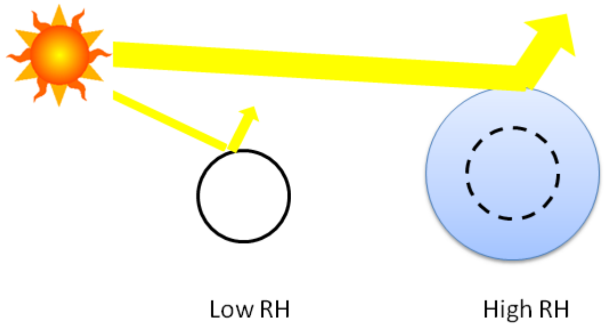
Relative Humidity Effects on Aerosol Optical Properties

- Aerosol water uptake and aerosol size = function of aerosol chemistry and relative humidity (RH)
- Water uptake alters light scattering and light absorption



- RH effects on scattering previously characterized (RH < 90%)
- **Limited understanding of RH effects on absorption**

Primary Light Absorbing Organic Carbon (LAOC) Aerosols

- Emission Sources of Primary OC:
  - 91% from open and residential biomass burning (Bond *et al*., 2004)
- Chemical Characteristics:
  - Complex mixture of polycyclic aromatic hydrocarbons (PAHs), humic-like substances and biopolymers (Pöschl , 2003*)*
  - Up to 70% water soluble by mass *(*Chen and Bond, 2010*)*
- Optical Properties:
  - Weakly absorbing at visible wavelengths
  - Wavelength dependent absorption with strongest absorption towards blue\ ultraviolet
  - Few *in situ* measurements at multiple wavelengths and variable RH

LAOC on Filter

Research Motivations & Objectives

Instrumentation challenges limit light absorption measurement as a function of RH

- Objective 1: Build and benchmark equipment to measure aerosol absorption and scattering as a function of RH up to 95% in a laboratory setting (presented at previous ASR meetings)

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- Objective 2: Measure absorption and scattering of LAOC as a function of RH and evaluate optical closure (main focus of this presentation)

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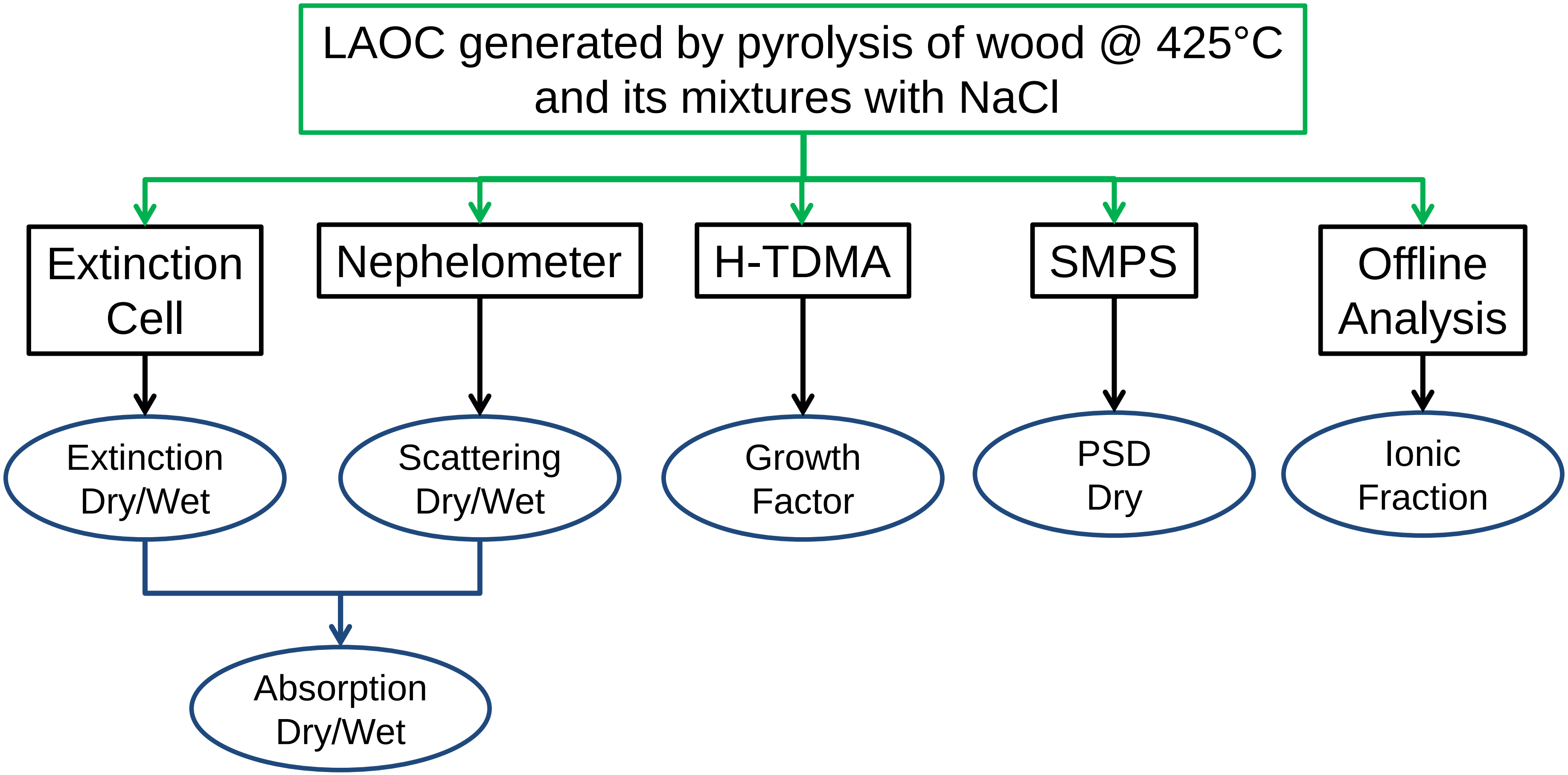
- Objective 2: Measure absorption and scattering of LAOC as a function of RH and evaluate optical closure (main focus of this presentation)

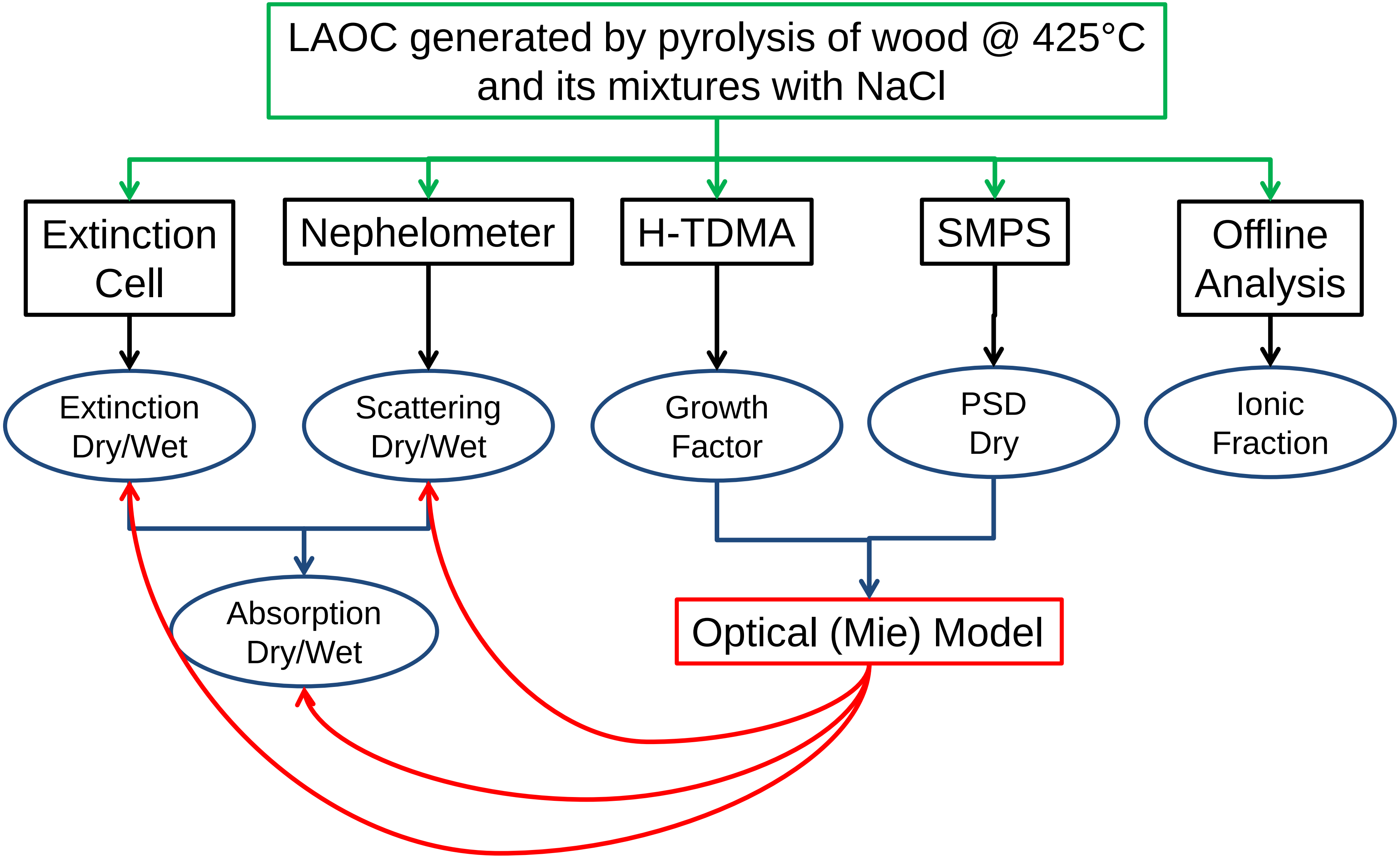
Limited understanding of optical properties as a function of RH for internal LAOC/ inorganic solute mixtures

- Objective 3: Perform closure study for LAOC mixed with inorganic solute as a function of RH (in the works)

Approach Overview



Approach Overview

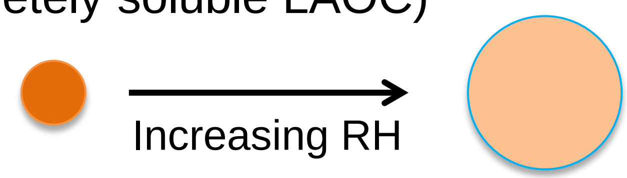


Optical (Mie) Modeling Inputs

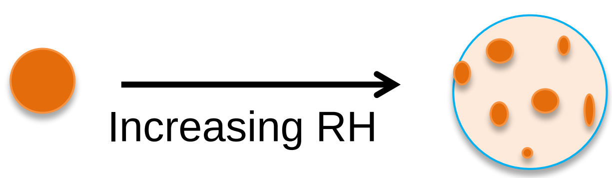
- Dry size distribution & hygroscopic size growth factors → humidified size distribution and aerosol water content

- Dry LAOC refractive index:
  - 1.57+0.017*i* (467nm), 1.57+0.01*i* (530nm), 1.57+0.002*i* (660nm)
    n from literature, k*i* from spectroscopy from filter extracts

- Humidified refractive index mixing models:
  - **Linear Volume Average (LVA)** : commonly used for OC, infers uniform mixture (completely soluble LAOC)



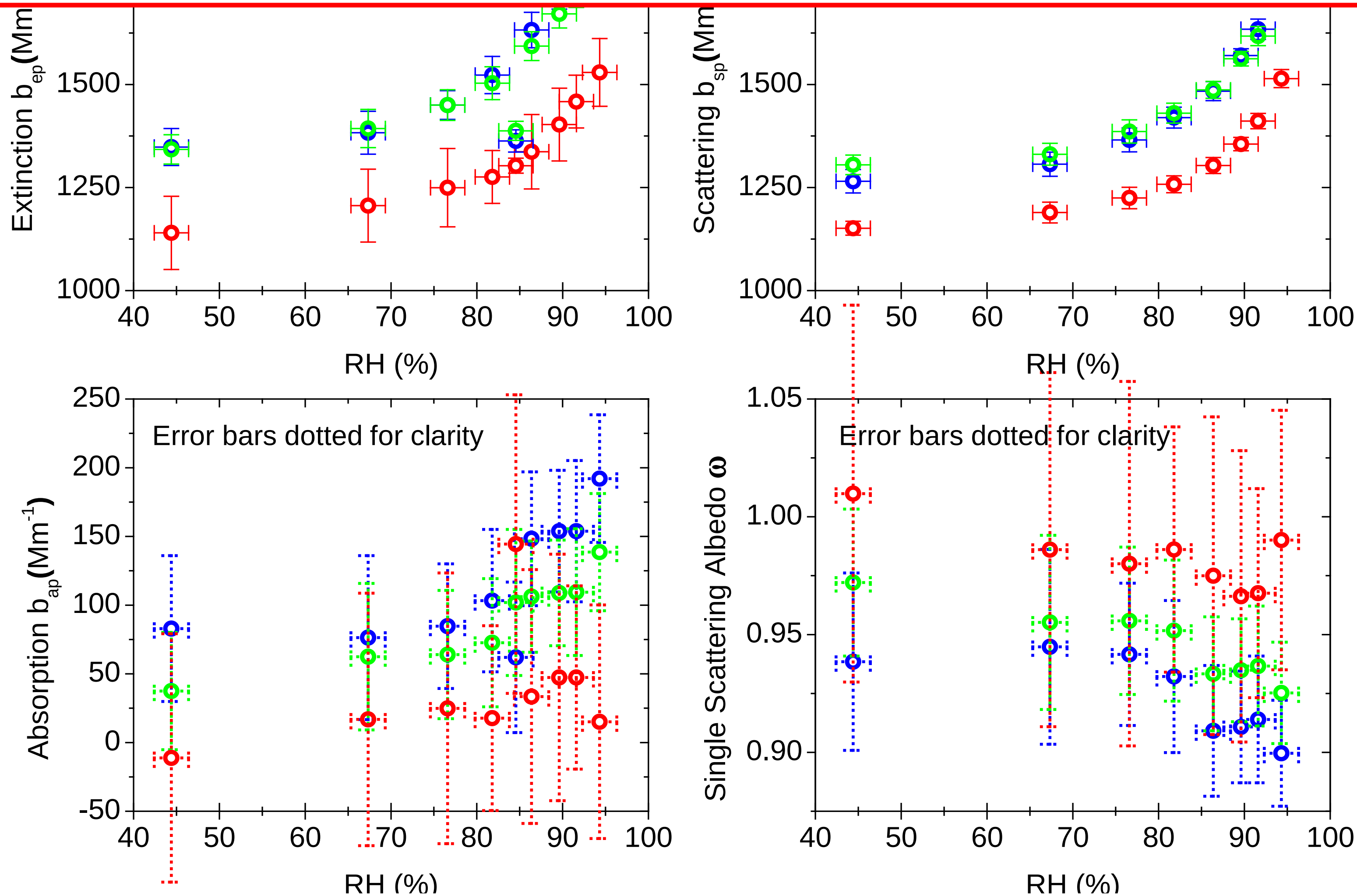
  - **Dynamic Effective Medium Approximation (DEMA)**
    Infers non-uniform, composite media with randomly distributed insoluble inclusions of absorbing material (Chylek, 1984)



Measured LAOC Optical Properties

FINDINGS:

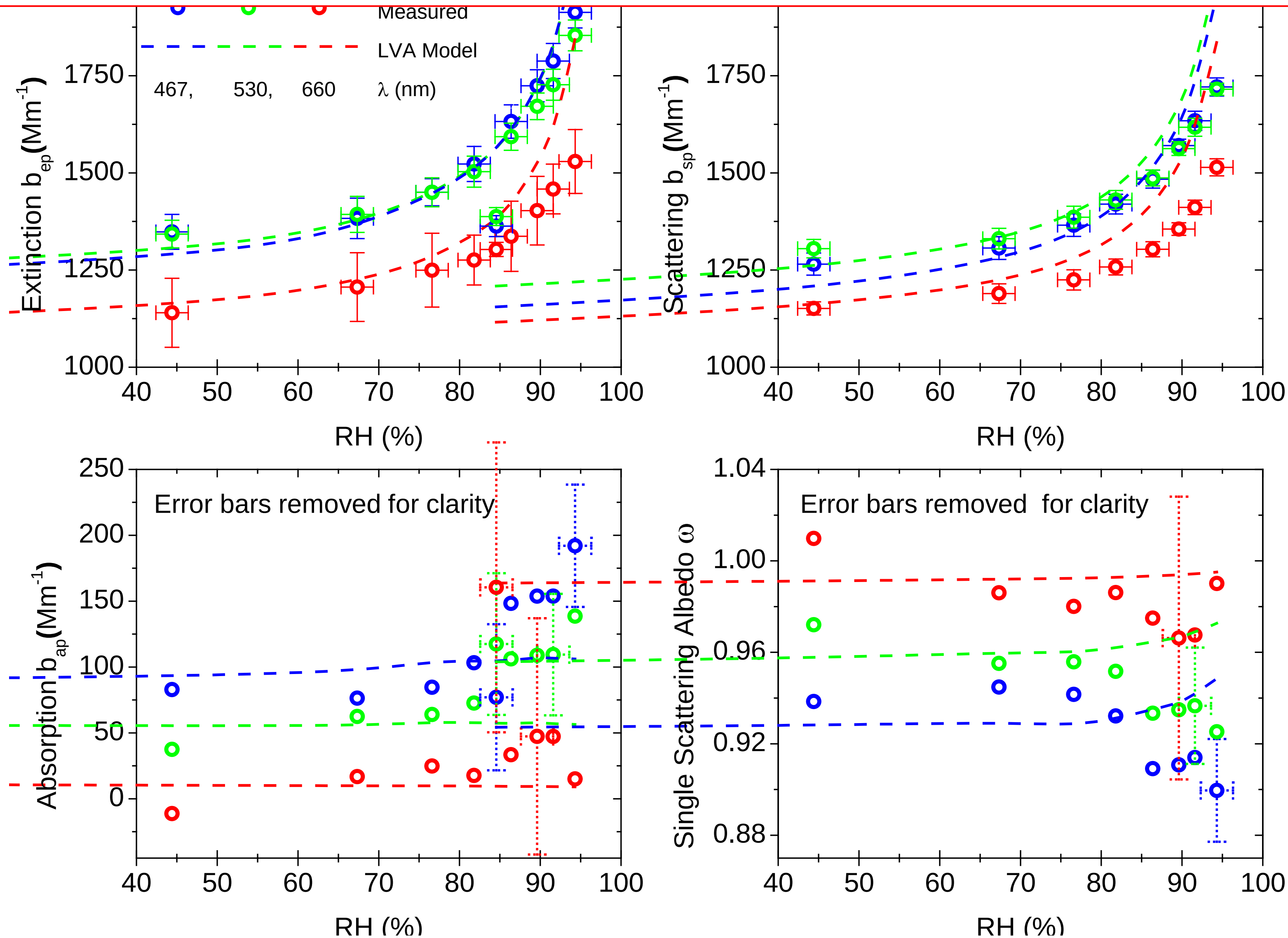
- *Absorption increases by a factor of 2 at High RH (λ = 467 and 530 nm)*
- *Absorption at λ = 660 nm is below detection limit of instrumentation*



Optical Closure Results (1):

Linear Volume Average (LVA) RI Mixing

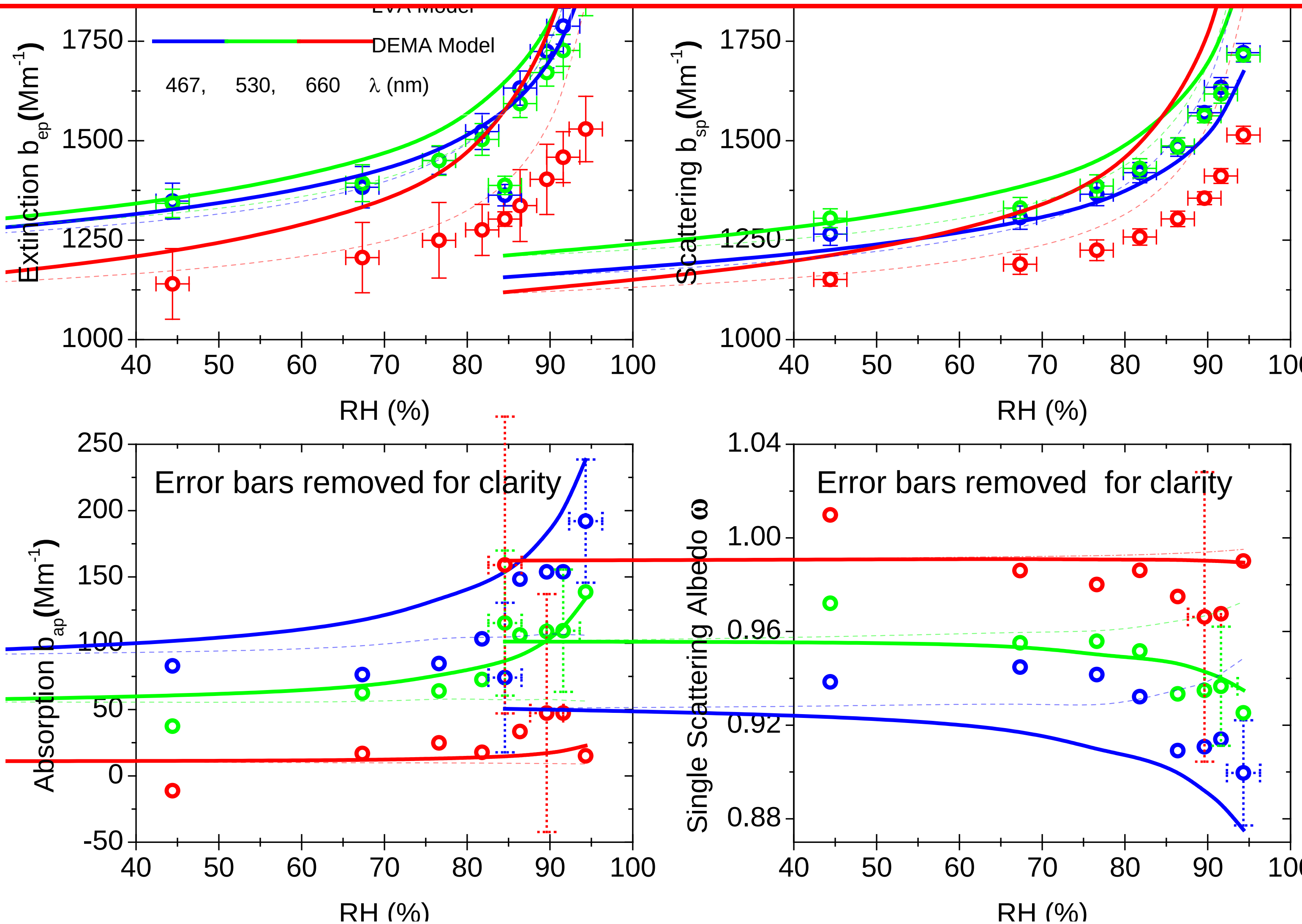
FINDING: LVA predicts extinction and scattering, but not absorption



Optical Closure Results (2) :

Dynamic Effective Medium Approximation (DEMA) RI Mixing

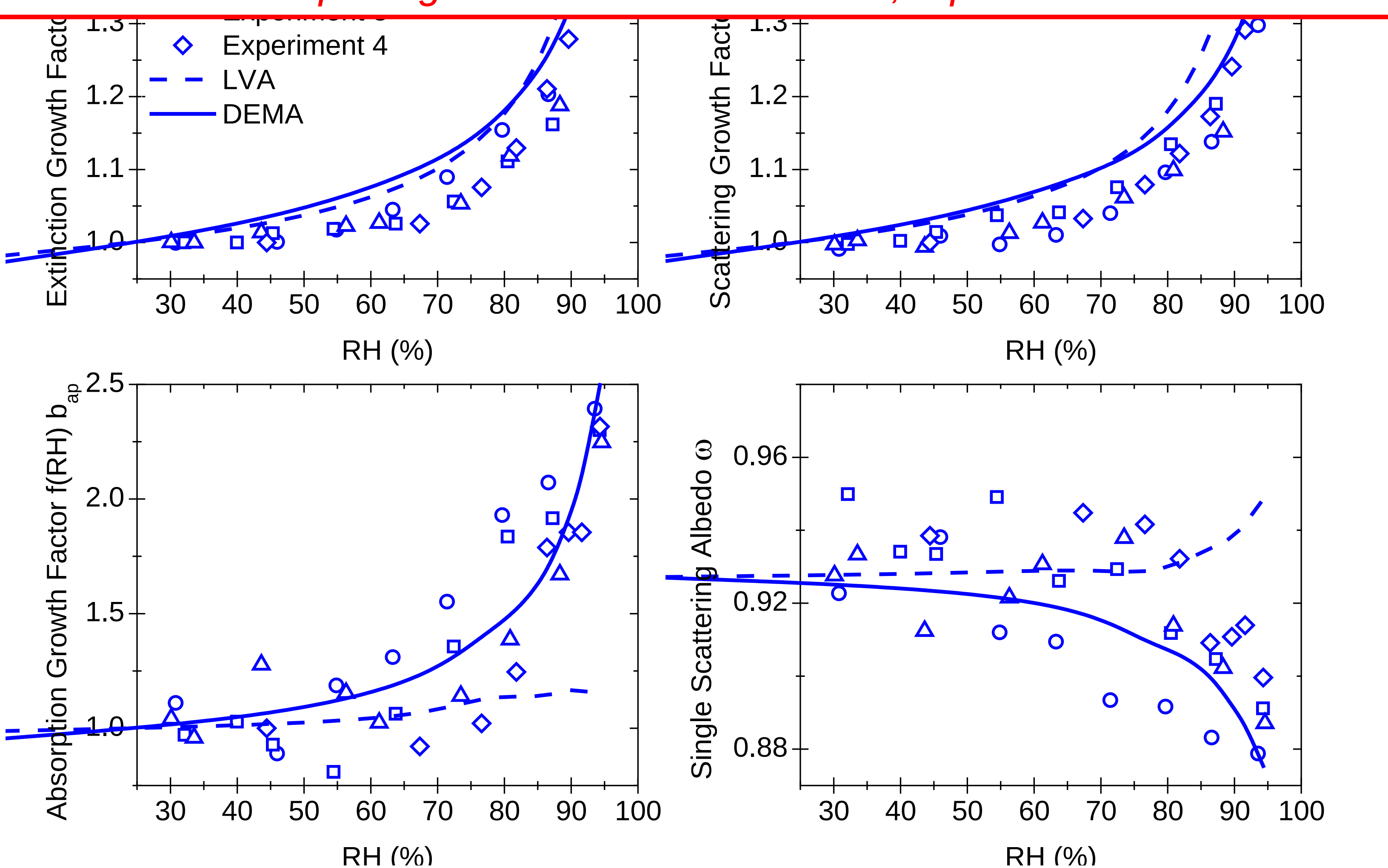
FINDING: DEMA captures trends in absorption and SSA indicating that configuration of insoluble absorbing material might be responsible for absorption enhancement



Normalized LAOC Optical Properties for Multiple Experiments (λ = 467nm)

FINDINGS:

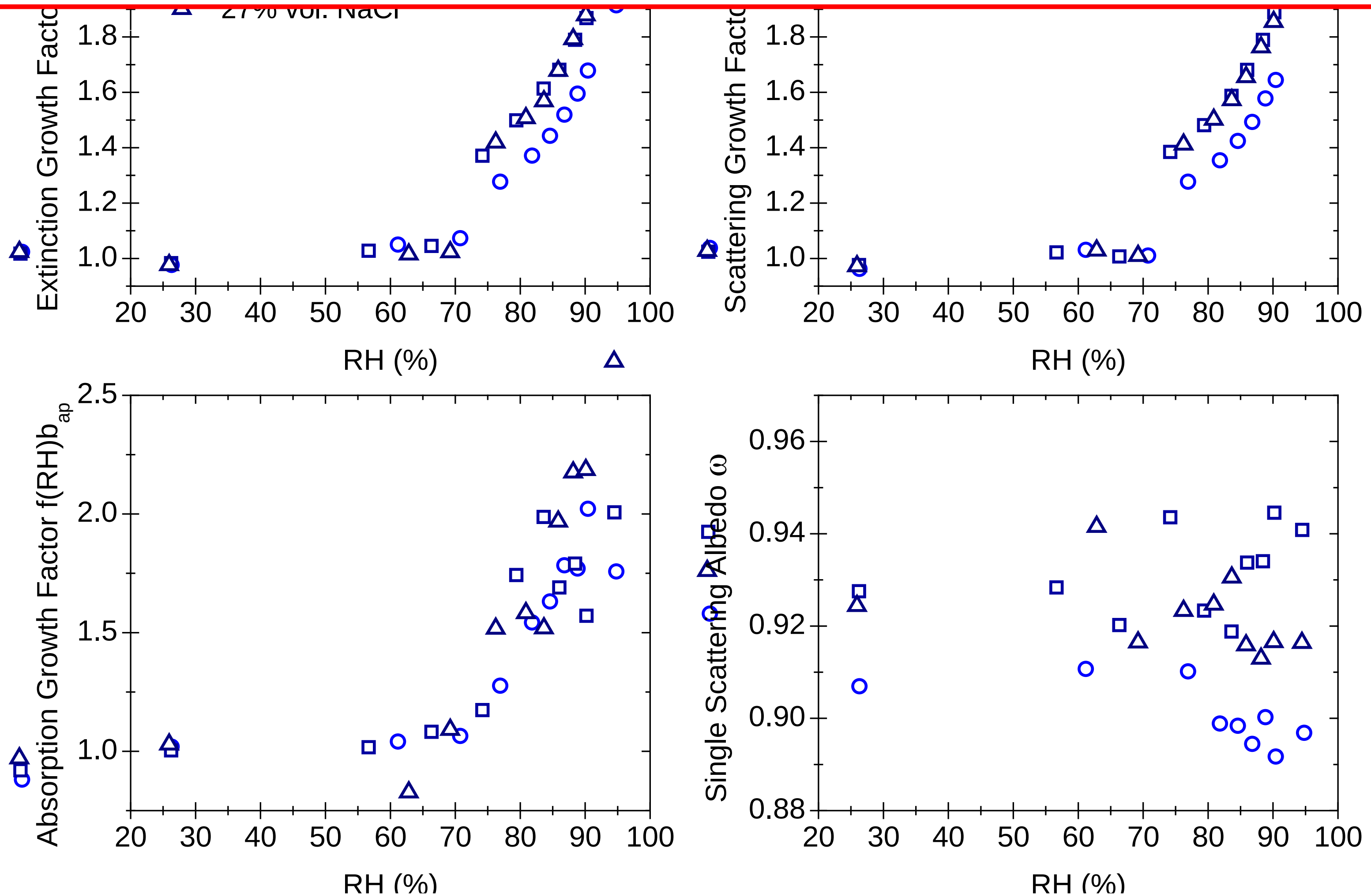
- *Low Variability in f(RH) ext. and scat. → particles have same hygroscopicity*
- *Same trend in absorption growth and SSA reduction, represented best with DEMA*



Normalized LAOC Optical Properties for LAOC- NaCl Mixtures (λ = 467nm)

FINDINGS

- *Observable deliquescence ~ 76% RH*
- *Absorption increase is in the same range as for pure LAOC*



Summary & Outlook

- LAOC absorption↑ and SSA↓ with RH↑ at the 467 and 530 nm wavelengths. (660 nm below detection limit)
- Change in LAOC absorption and SSA is currently not implemented in models
- Widely used LVA RI mixing rule is unable to catch trends in absorption and SSA with RH
- DEMA captures trends in absorption and SSA indicating that configuration of insoluble absorbing material might be responsible for absorption enhancement
- Addition of NaCl affects scattering but no specific trend (in comparison to pure LAOC) was observed for absorption

Thank you for your attention

QUESTIONS?

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Acknowledgements

- Bond / Rood Research Groups
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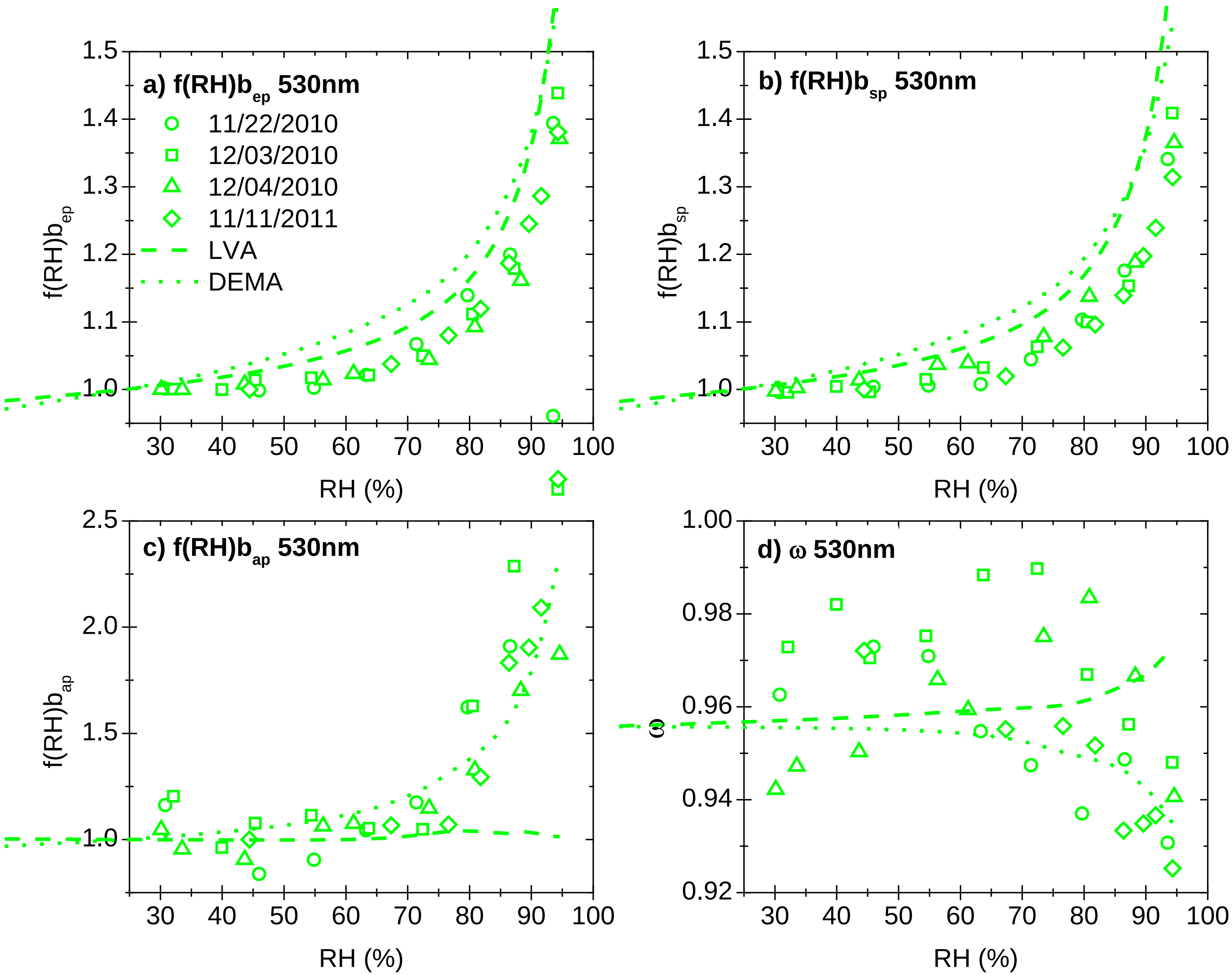
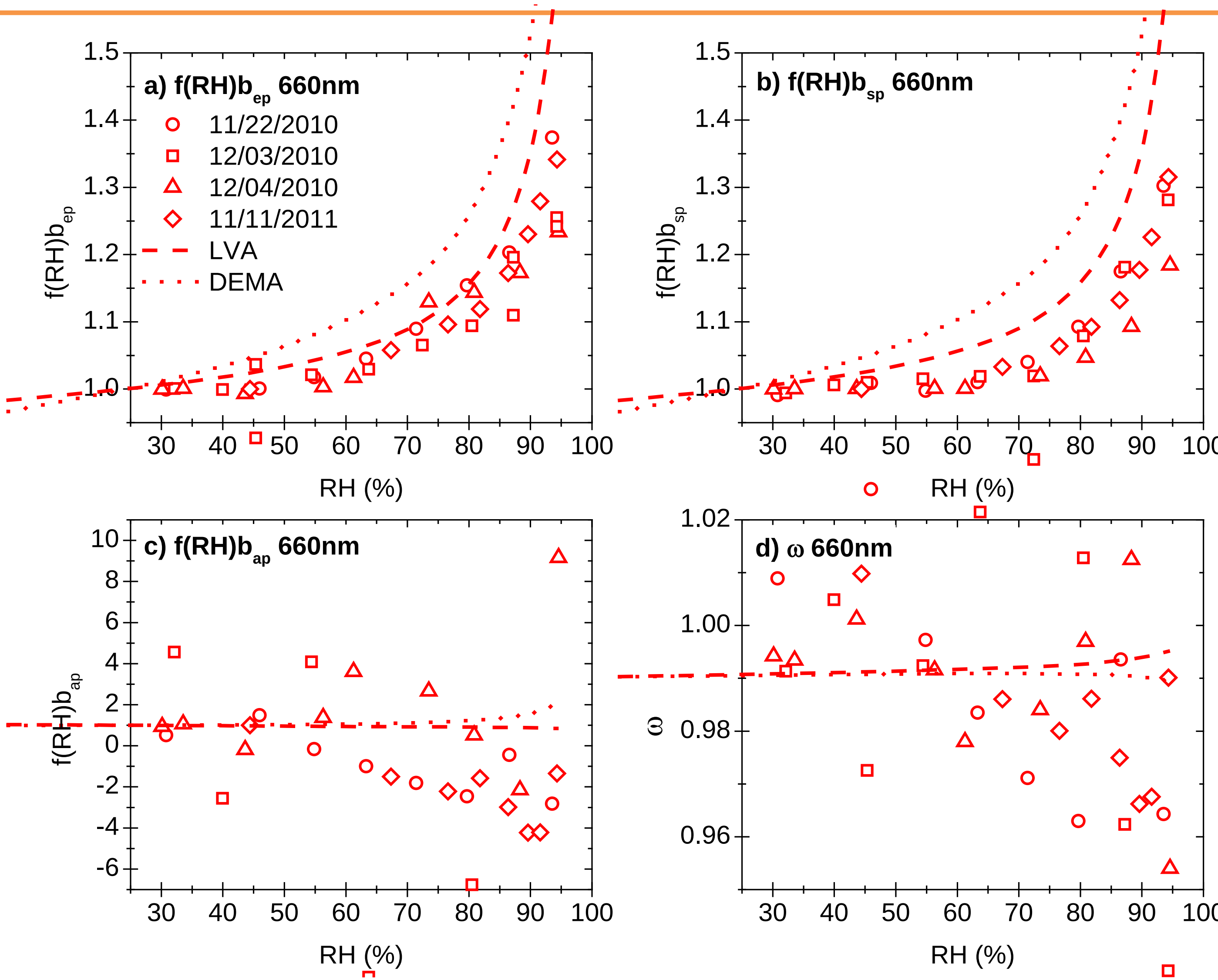
- DoE-ASR Grant No. DE-SC0006689 (current ASR support)

Appendix: Normalized LAOC Optical Properties for Multiple Experiments (λ = 530nm)



Appendix: Normalized LAOC Optical Properties for Multiple Experiments (λ = 660nm)



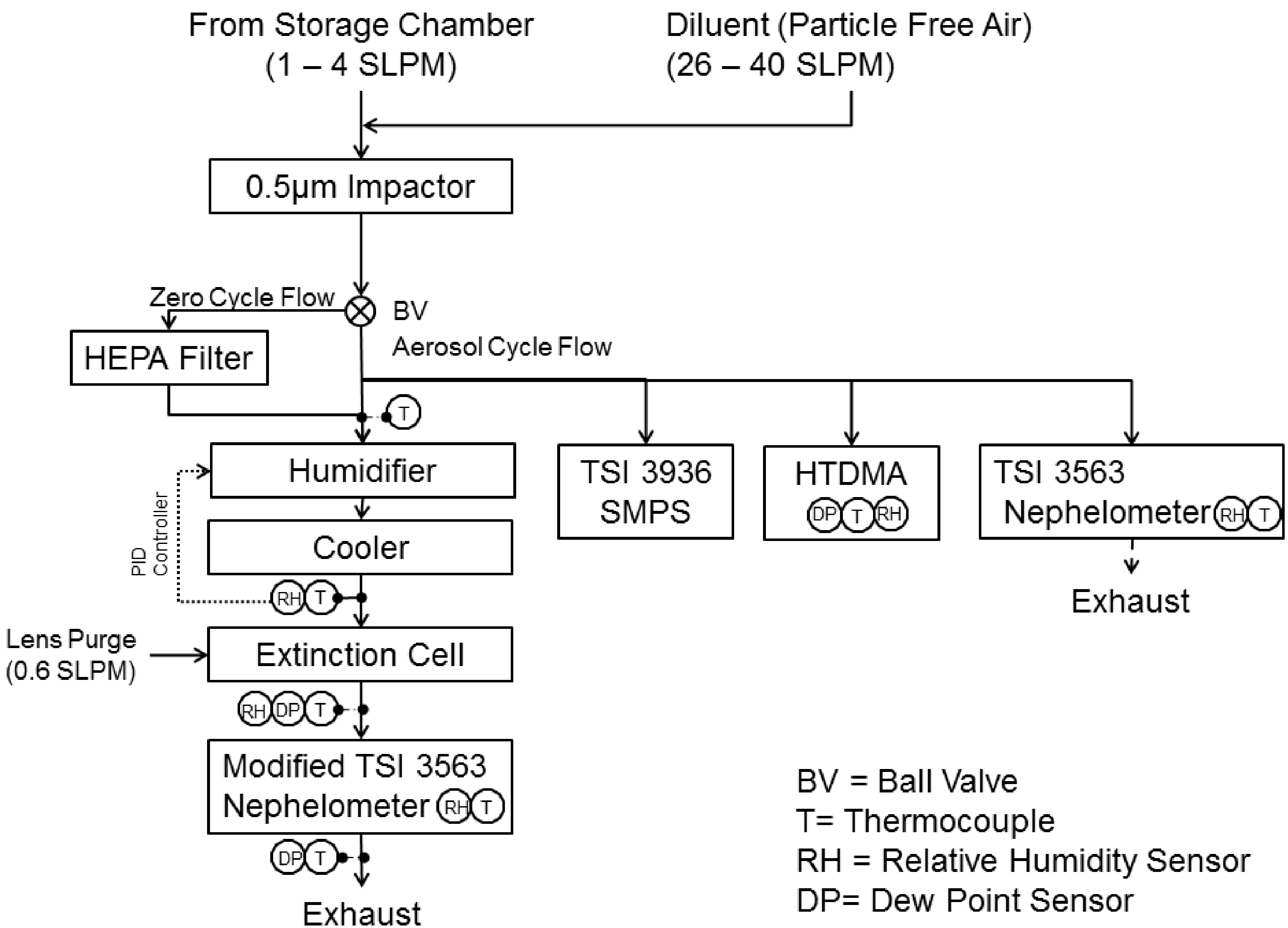
Appendix: Methods: Aerosol Generation and Treatment

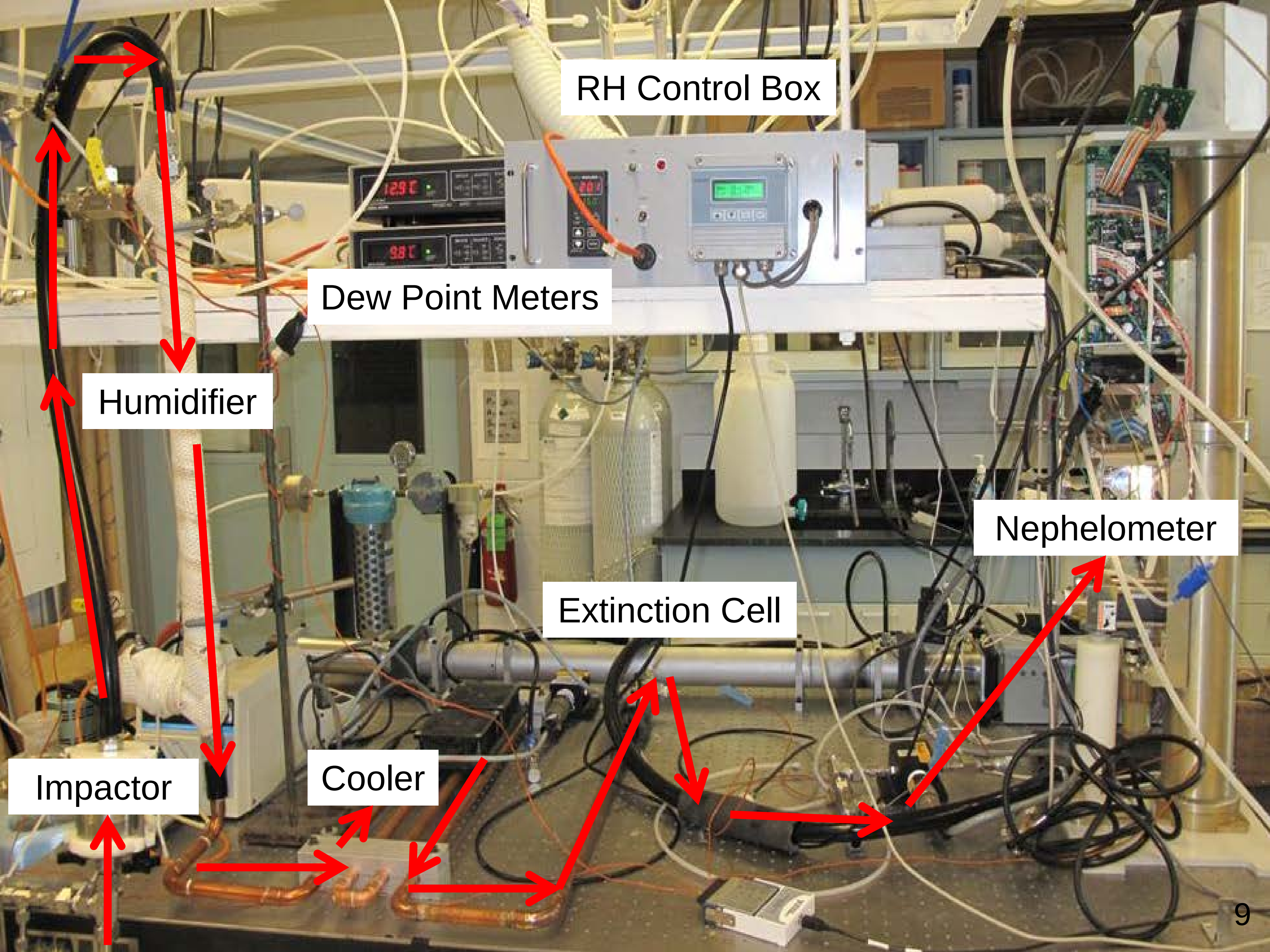
- LAOC aerosol was generated by pyrolyzing wood in an electrically-heated combustor at 425 ± 10 ºC
- Flaming (formation of BC) was avoided by using nitrogen sheath flow
- Aerosol was sampled at a 10:1 dilution into a 220 L storage chamber
- After pyrolysis event (~4-6 min), chamber was disconnected from sampling system and connected to optical instrumentation
- For mixing experiments inorganic solute was atomize into diluent

Appendix: Instrumentation

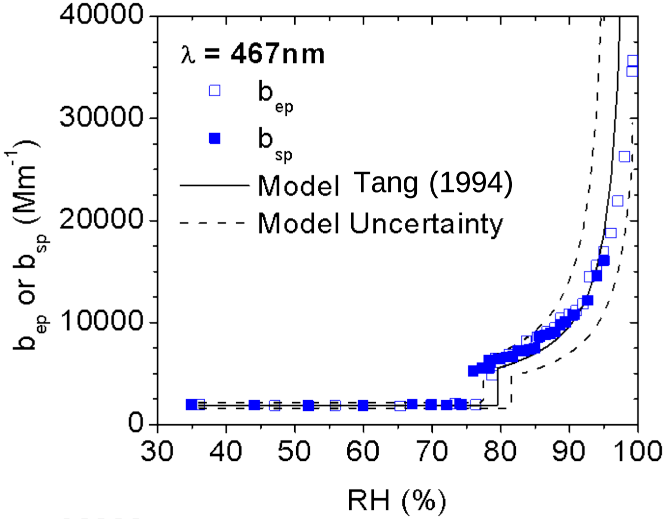
- Optical Properties:
  - b_{ep} → Short path extinction cell (SPEC) λ= 467, 530 and 660 nm
  - b_{sp} → λ and temperature modified nephelometer
  - b_{ap} → Difference between b_{ep} and b_{sp}
- Physical Properties:
  - D_p → SMPS (TSI)
  - $G_f(D_p)$ → H-TDMA
- Environmental Variables
  - RH / dew point temperature → 2 RH (Vaisala), 2 Dew point (GE)
  - Temperature → 4 Thermocouples
- Offline Filter Measurements (Chemical Properties)
  - OC/EC, Ions, OC functional groups ^{1}H and ^{13}C NMR

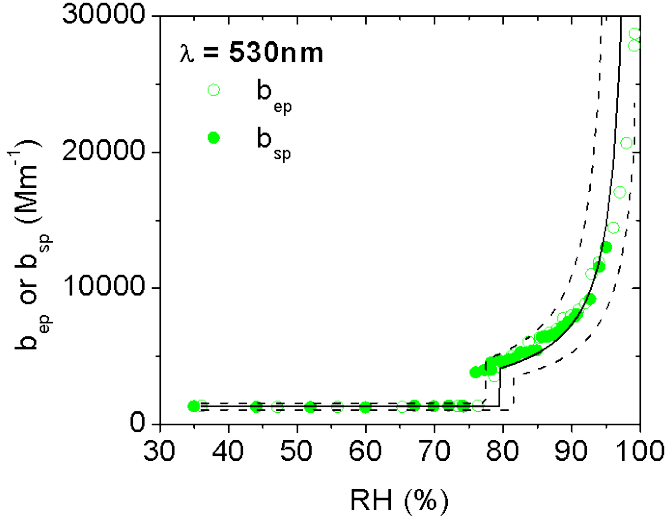
Appendix: Instrumentation

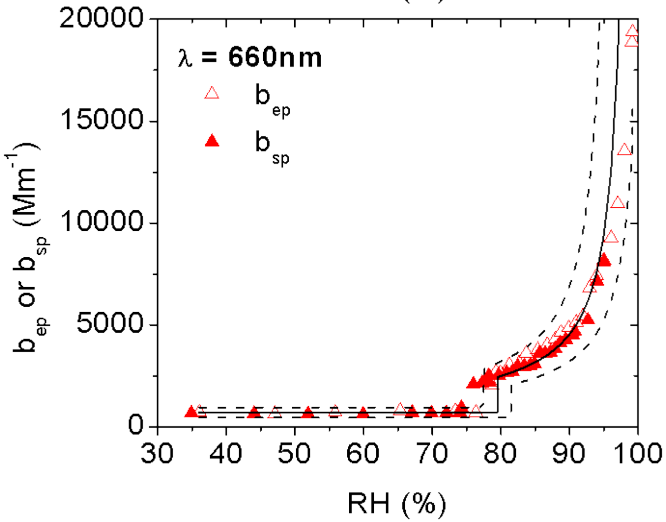



RH Control Box
Dew Point Meters
Humidifier
Nephelometer
Extinction Cell
Impactor
Cooler

Appendix: Benchmarking Ammonium Sulfate → System Performance under purely Light Scattering Conditions

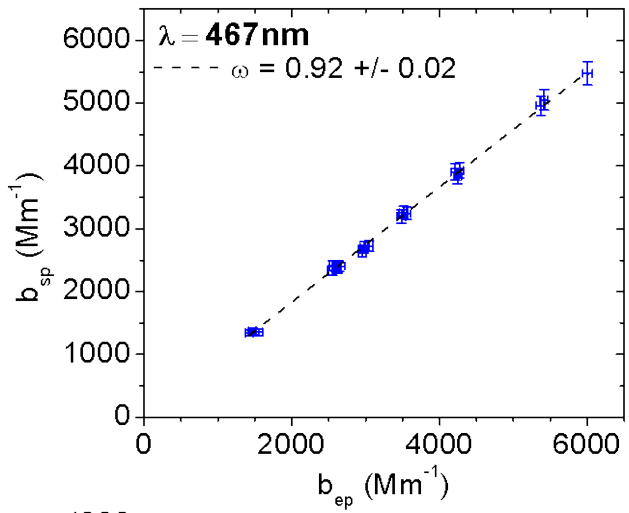


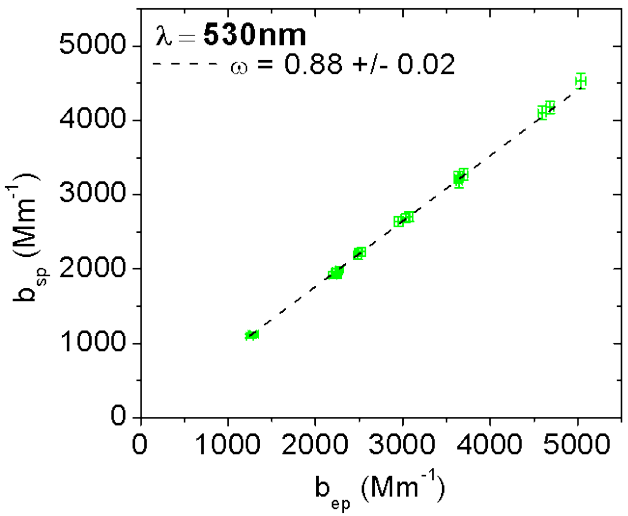


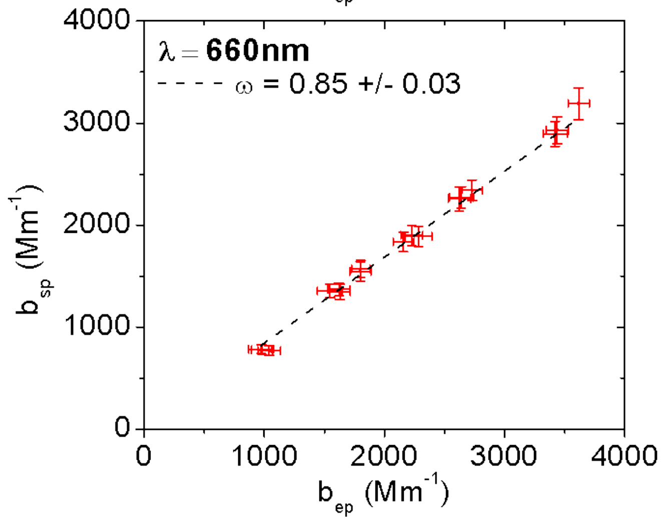


- Instrumentation capable of measuring optical properties up to 95% RH
- Measured data lie within uncertainty of model
- Shift in b_{sp} deliquescence due to nephelometer heating of 0.5°C

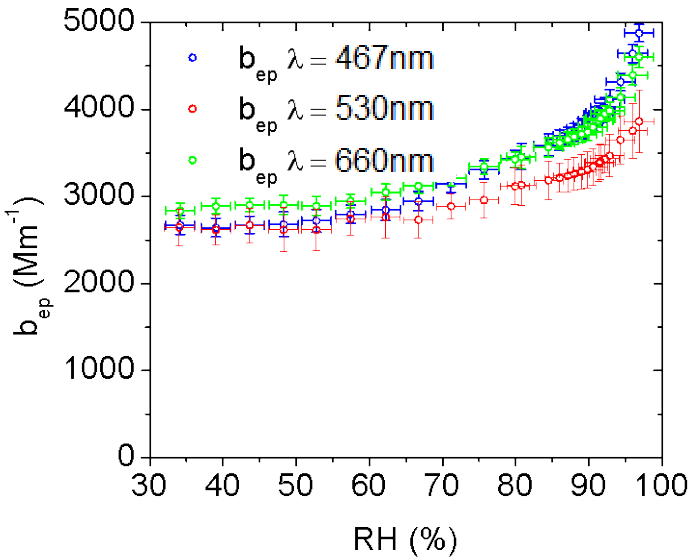
Appendix PSL Results

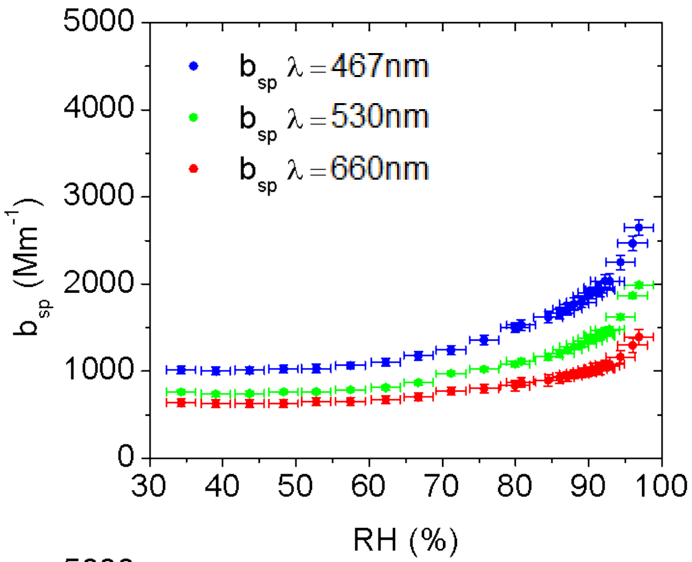




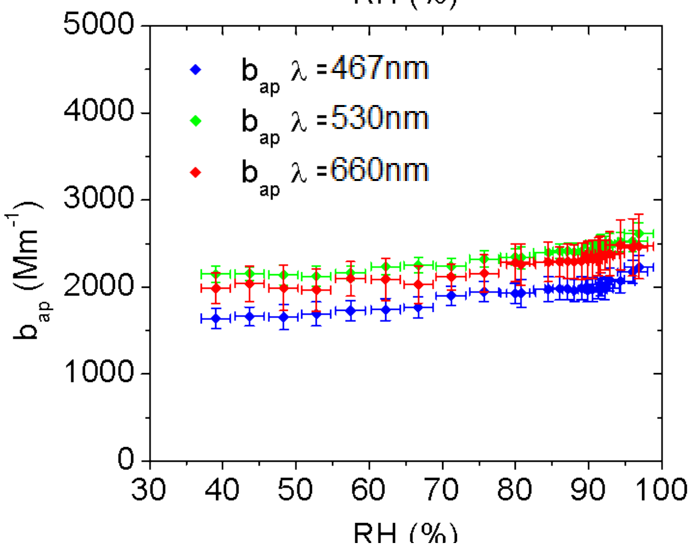


Benchmarking with Nigrosin → System Capable of Measuring Absorption as a Function of RH

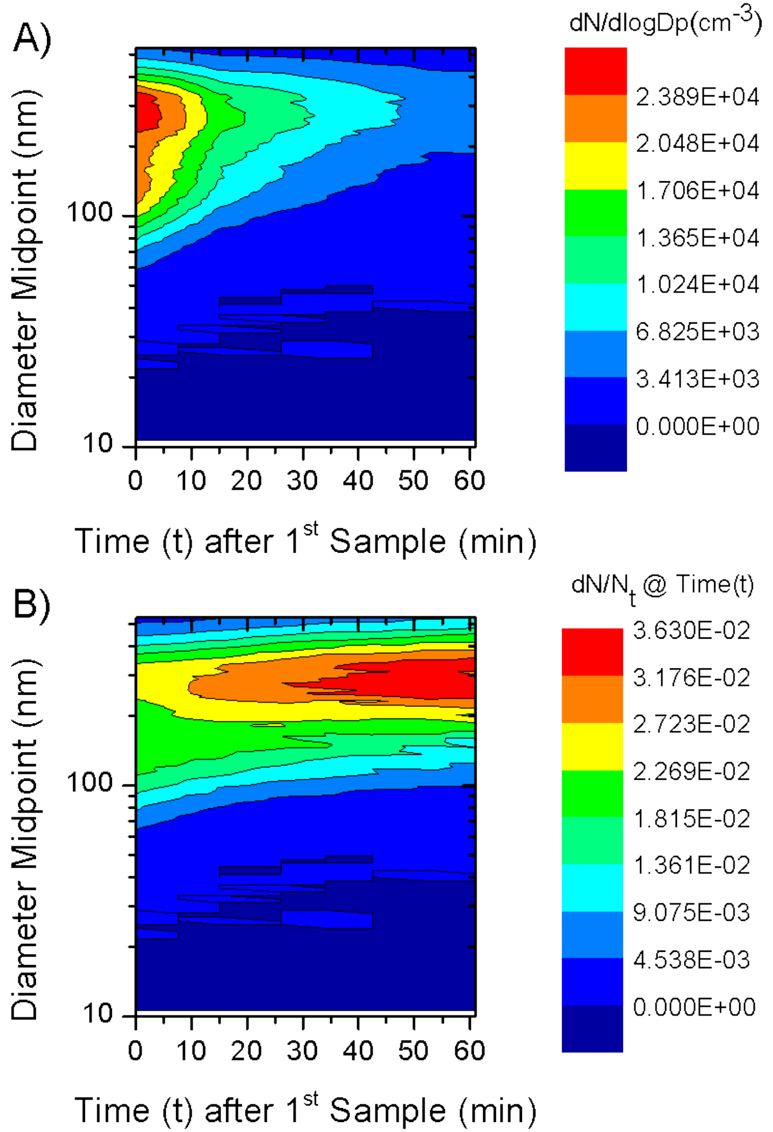




- b_{ap} enhanced by a factor of 1.2 between 35 and 95% RH
- b_{ap} λ dependence similar to bulk measurements
- Closure modeling → Poster Mena et al. Number: 2E8



Appendix LAOC PSD



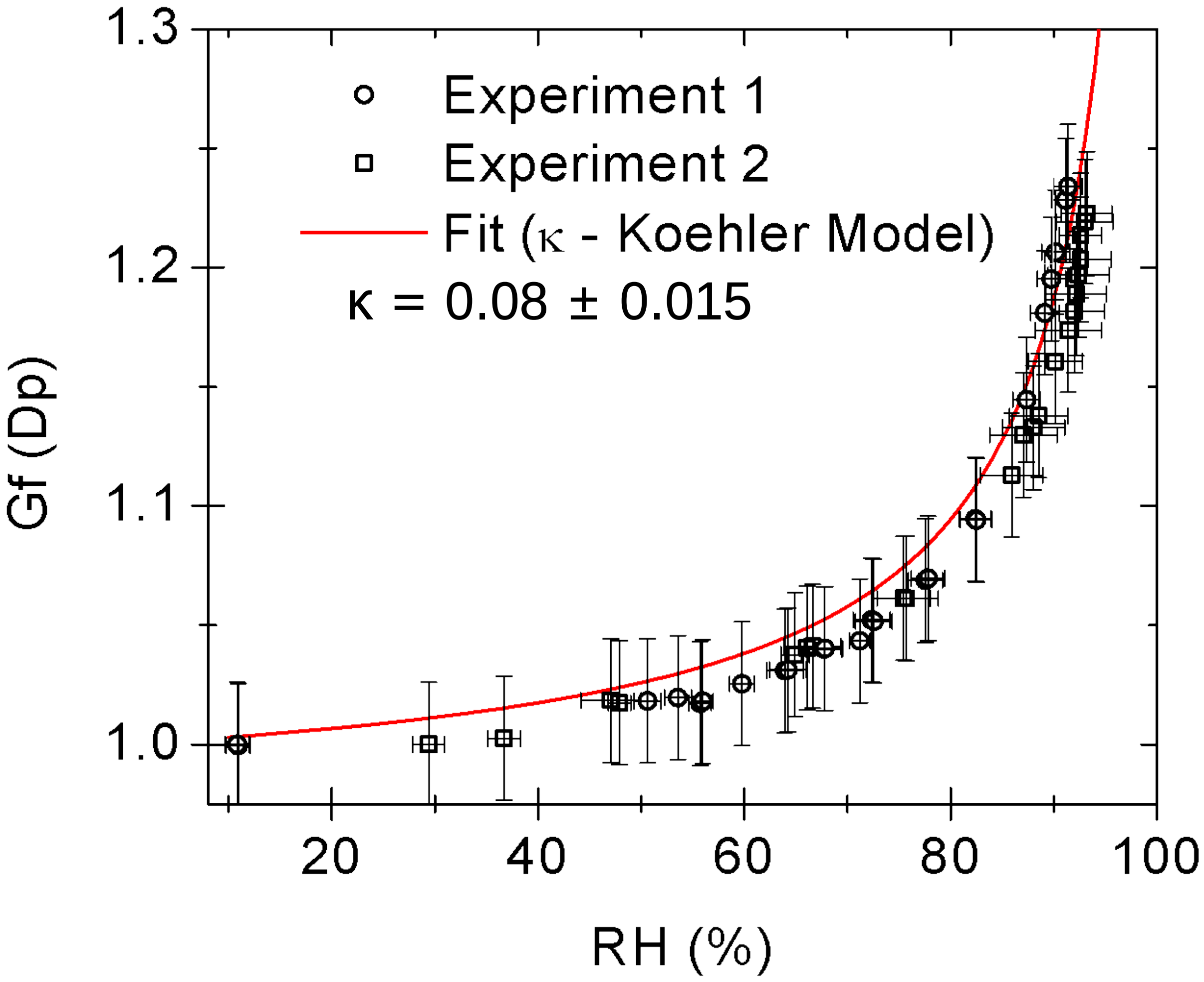
Appendix LAOC Composition

Table 1 Composition analysis of OC aerosol generated by the pyrolysis of oak wood at 425°C. Elemental carbon (EC) and the ions of Br^-, PO_4^{3-} and Mg^{2+} were also determined but the results were below the detection limit of the analysis

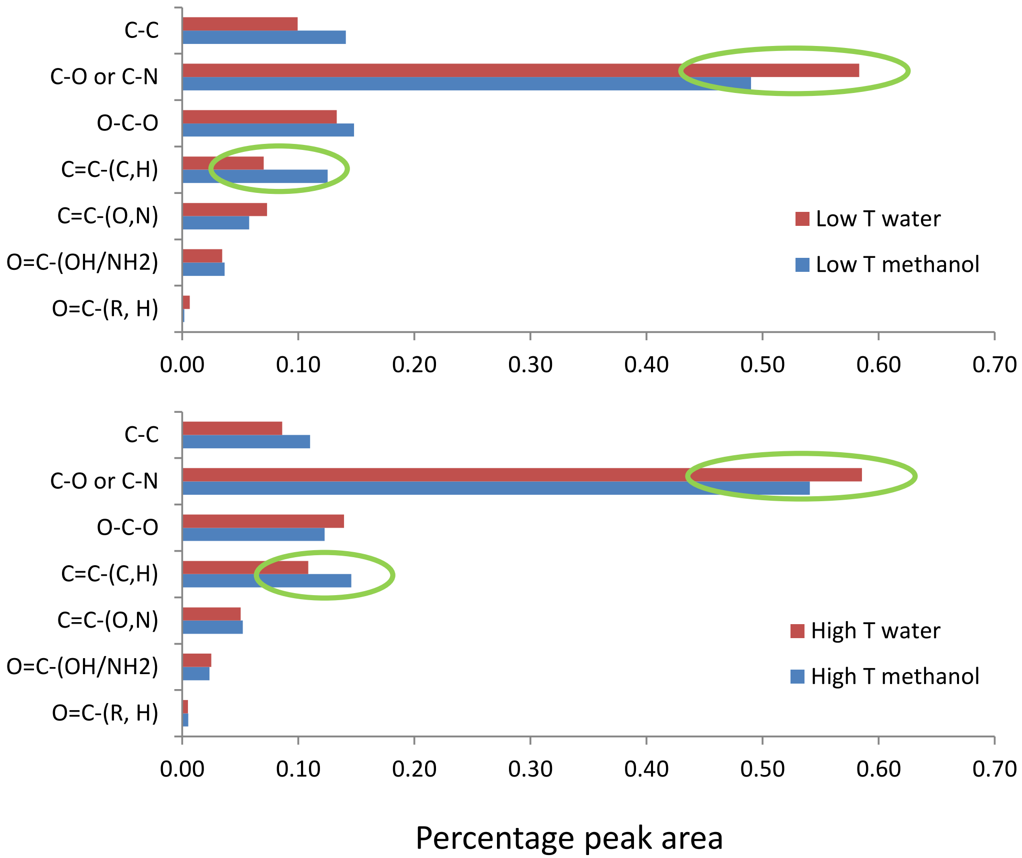
	OM*	OM*/ OC	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	K^+	Na^+
Mean	97.25	1.68	0.74	0.28	0.21	0.07	0.21	0.87	0.17
Std.	1.13	0.06	0.23	0.04	0.20	0.08	0.15	0.25	0.06

*Corrected by forcing closure with mass analyzed by gravimetric analysis (OM/ OC describes the correction factor).

LAOC HTDMA Results

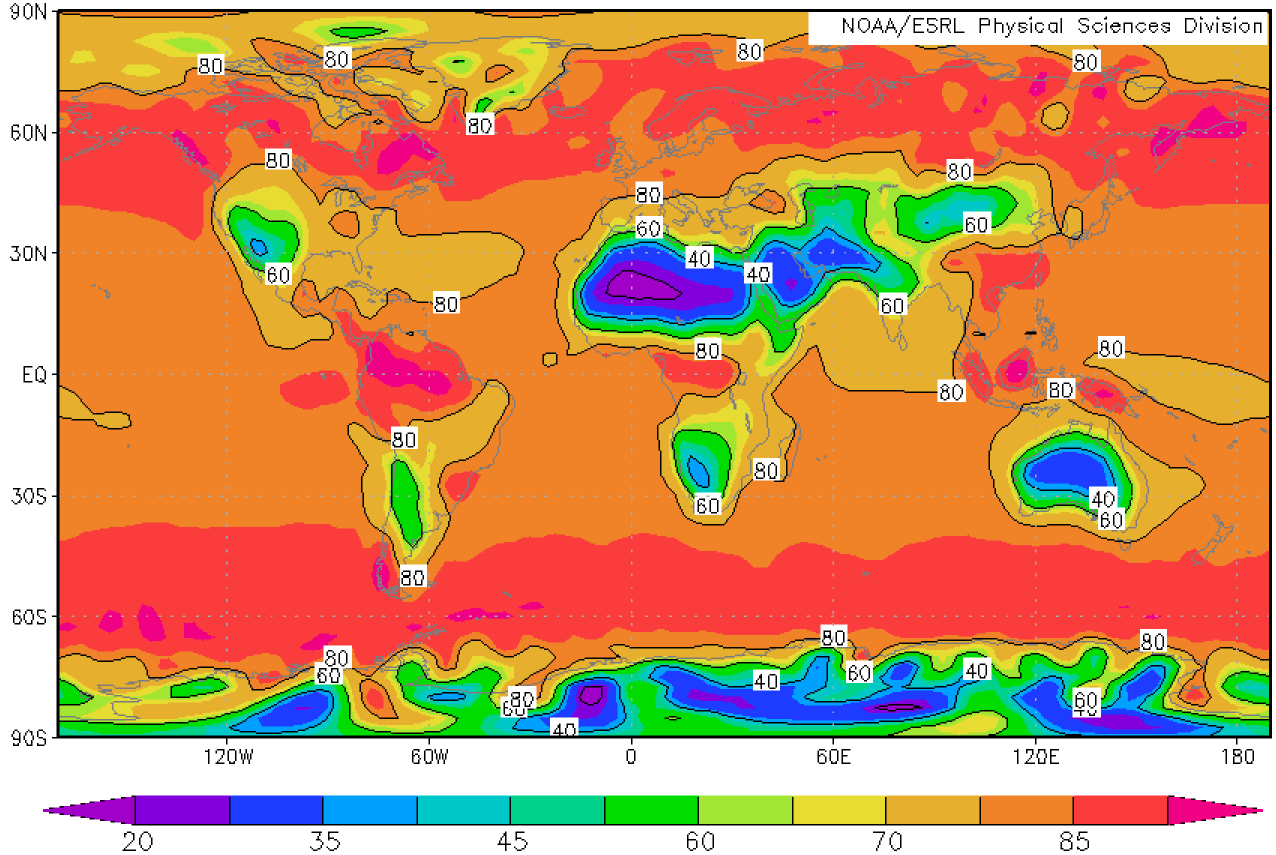


Appendix: LAOC NMR Results



Percentage of total ^{13}C NMR peak area under each spectral region for methanol and water extracts of OC generated at two 300 and 425C. Difference of contribution from two major functional groups is highlighted with green circles.

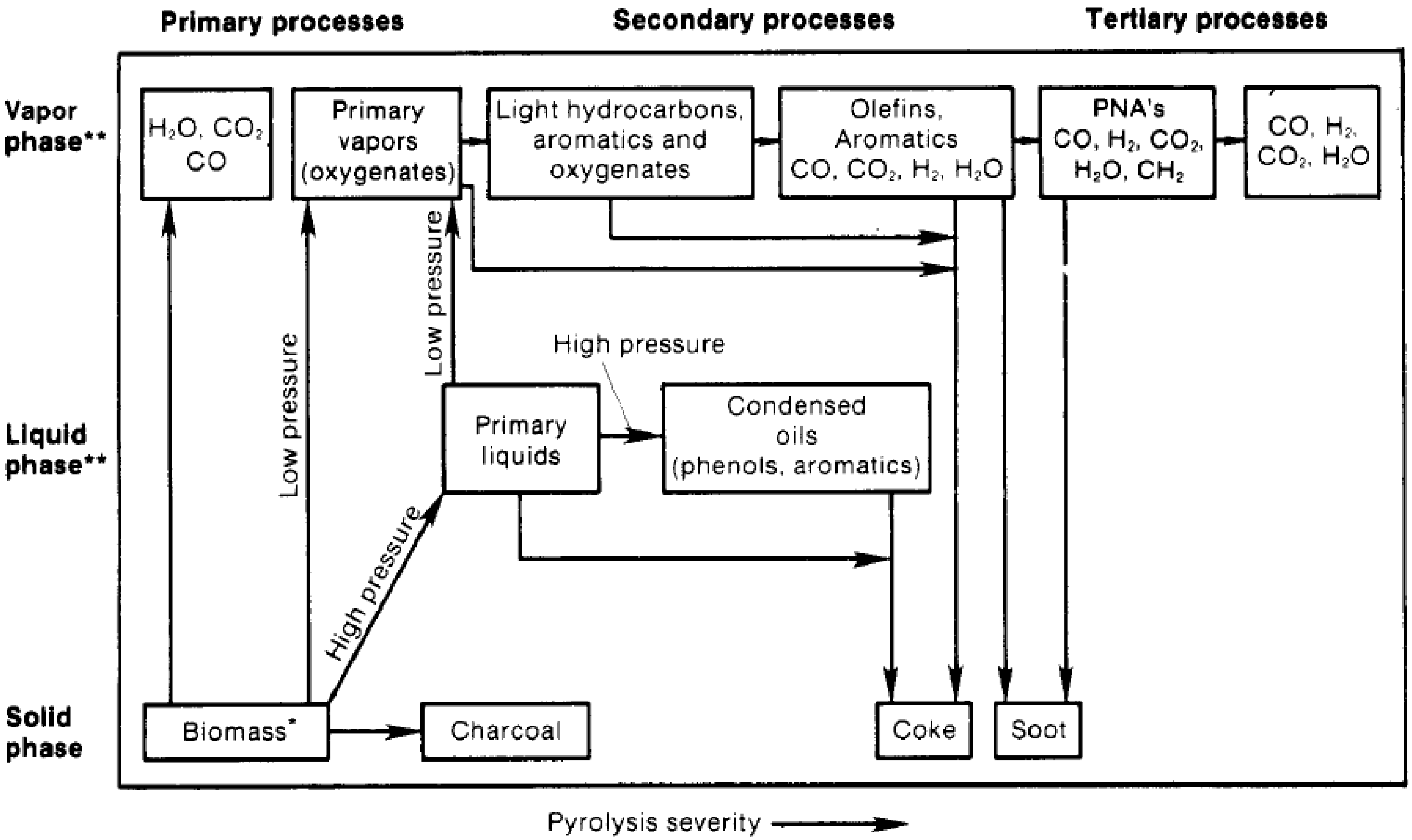
Appendix Global Relative Humidity (RH) Conditions



Observation-derived average global surface RH for the years between January 1960 and January 2011.

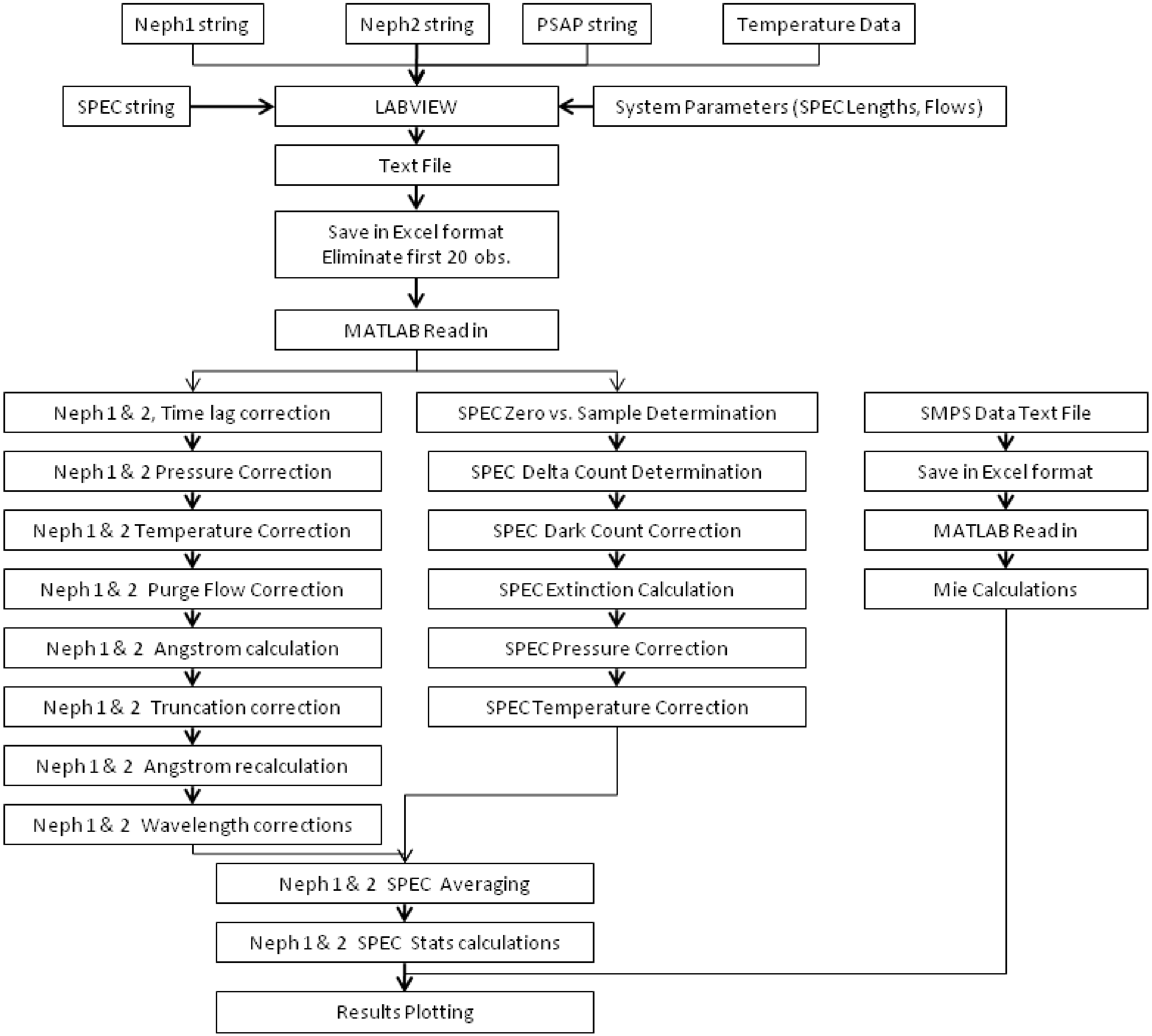
Image provided by NOAA-ESRL, Boulder, Colorado

Appendix: Wood combustion process

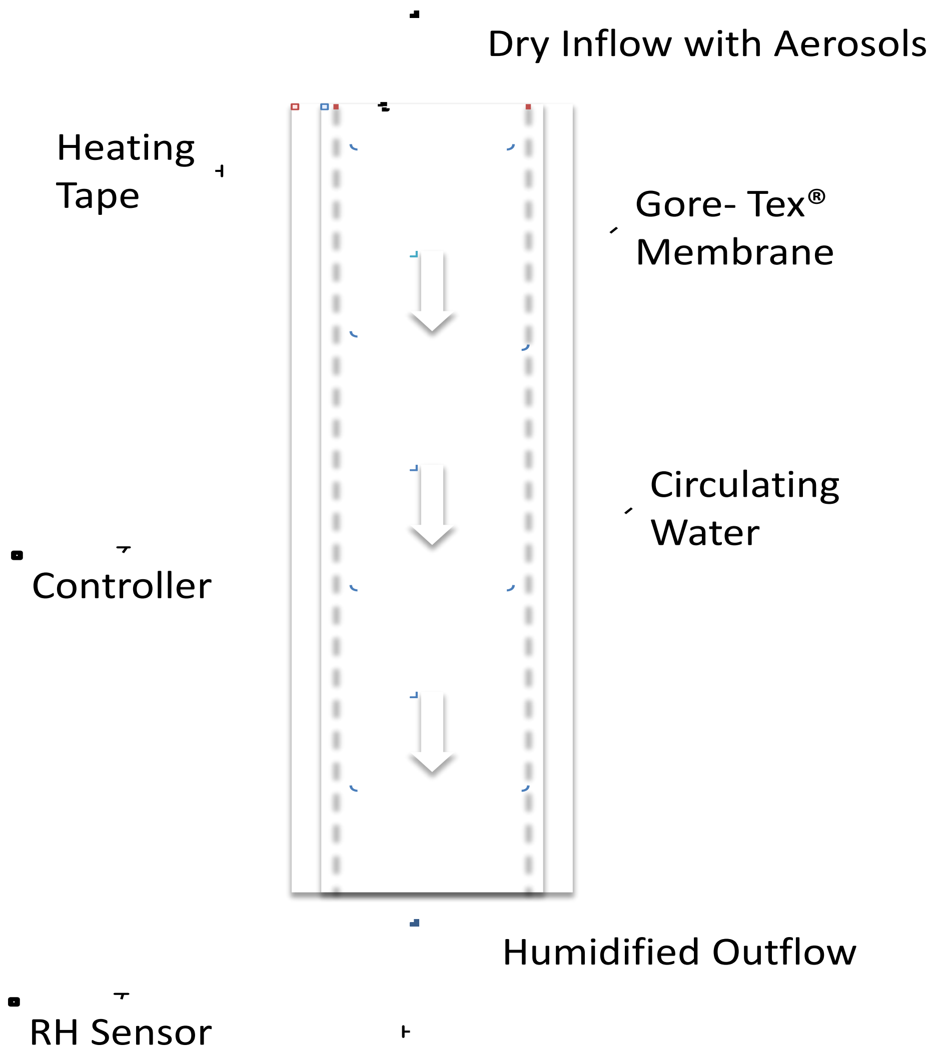


Evans and Milne, 1986

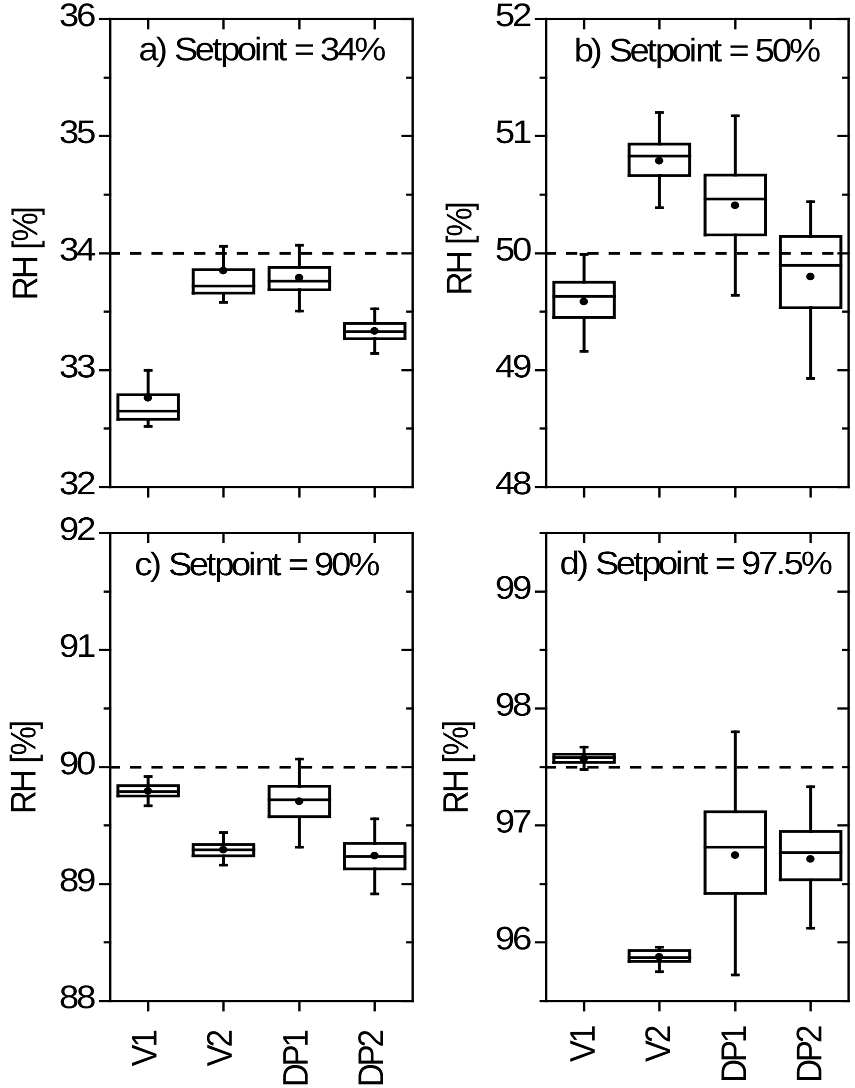
Appendix Dry Data Processing



Appendix: Humidification System Details & Function



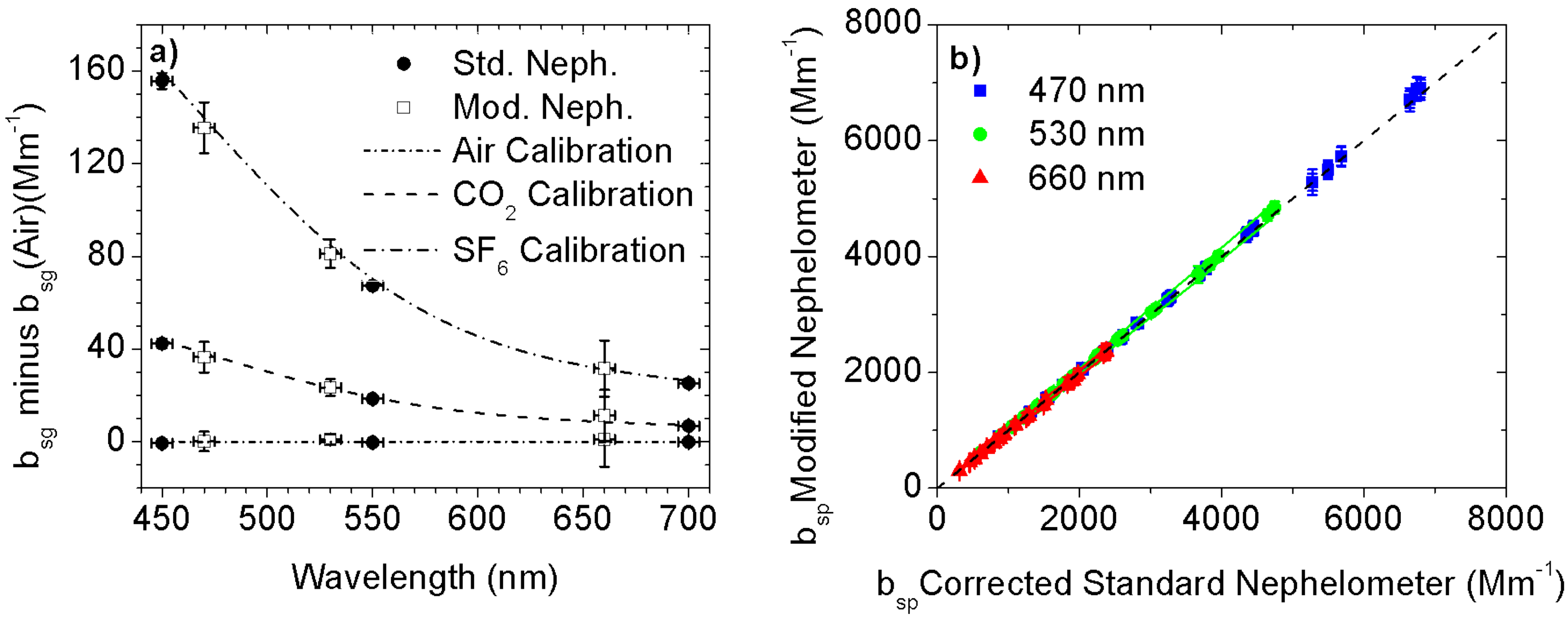
Appendix: RH Sensor Performance



V1, V2 = Capacitance based Vaisala Sensors

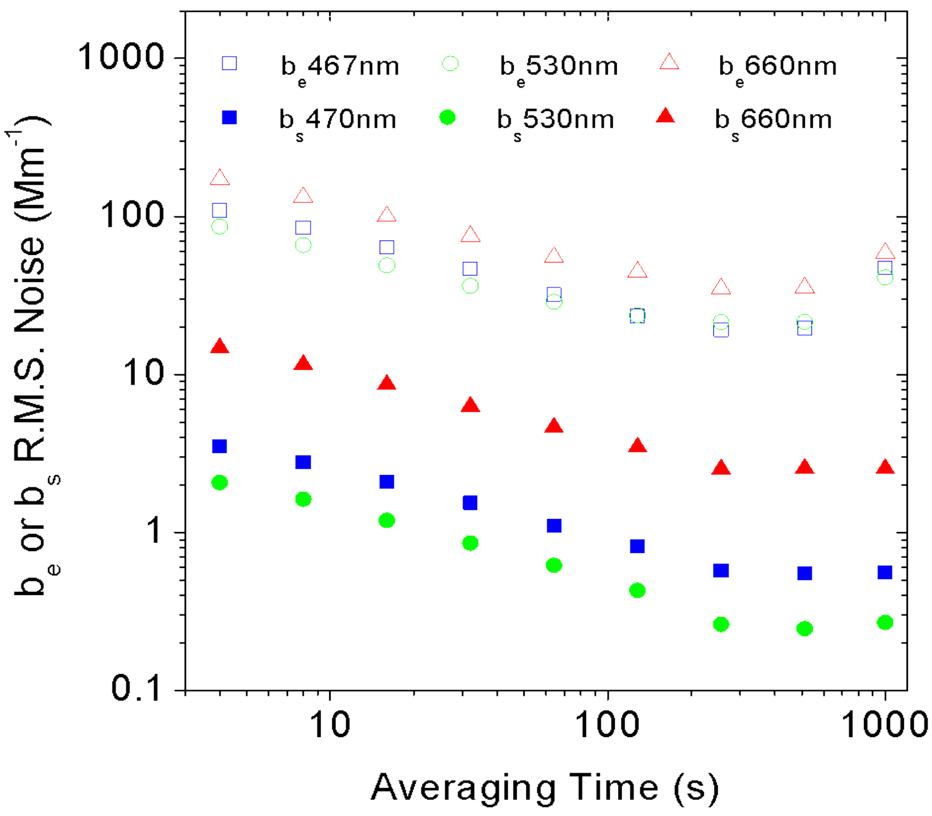
DP1, DP2 = General Eastern Dew Point Meters (RH calculated with dry bulb temperatures)

Appendix: Modified Nephelometer Performance



- For all three wavelengths, the instruments differ less than 1.5%

Appendix: Extinction Cell and Nephelometer Sensitivity and Detection Limit



- Function of integration time
- Best sensitivity is btw. 100 and 300s integration time
- Corresponding absorption detection limits: 57.3 Mm^{-1} (467 nm), 54.5 Mm^{-1} (530 nm) and 105 Mm^{-1} (660 nm) with a signal to noise ratio is assumed to be 3

Appendix POA Sources