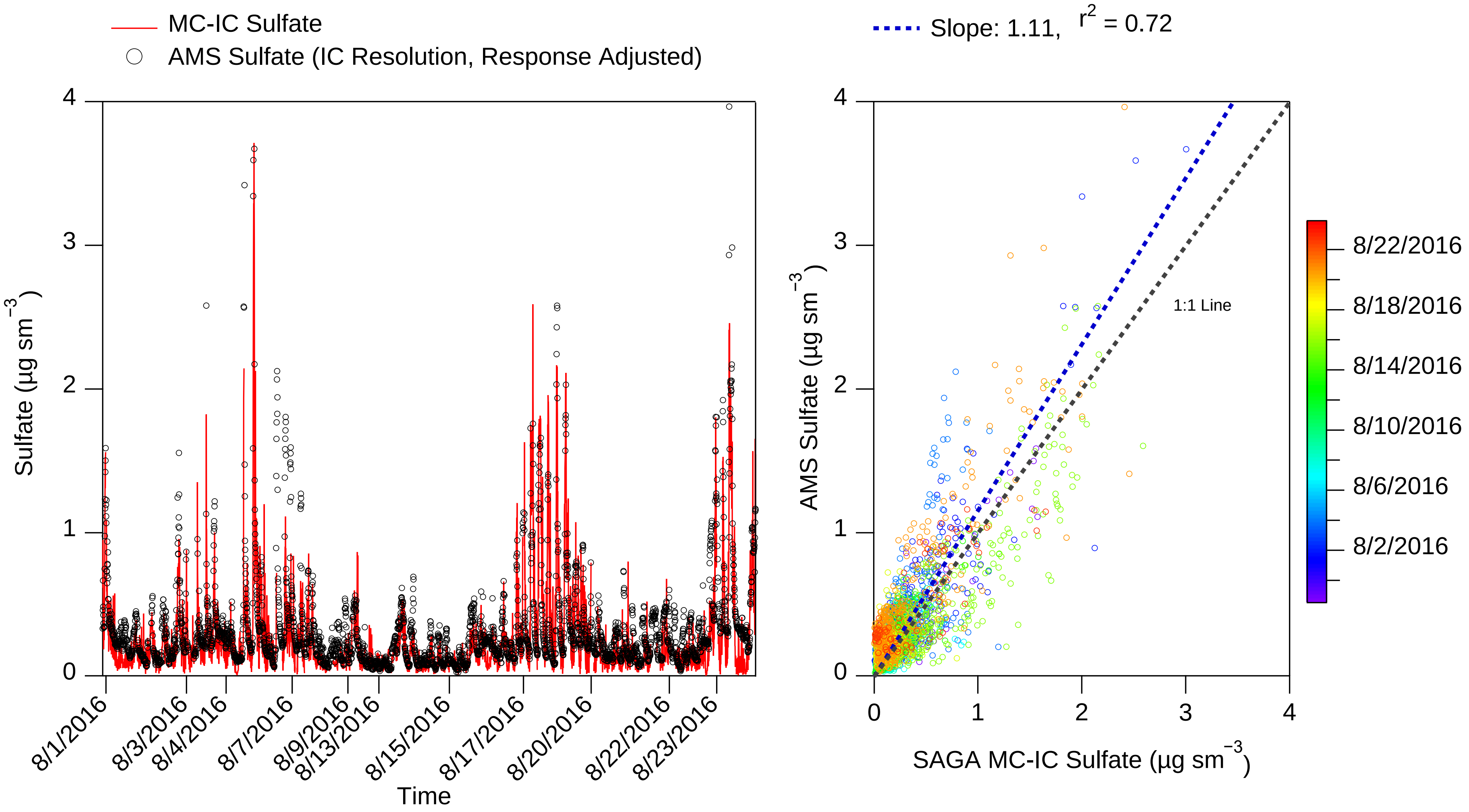
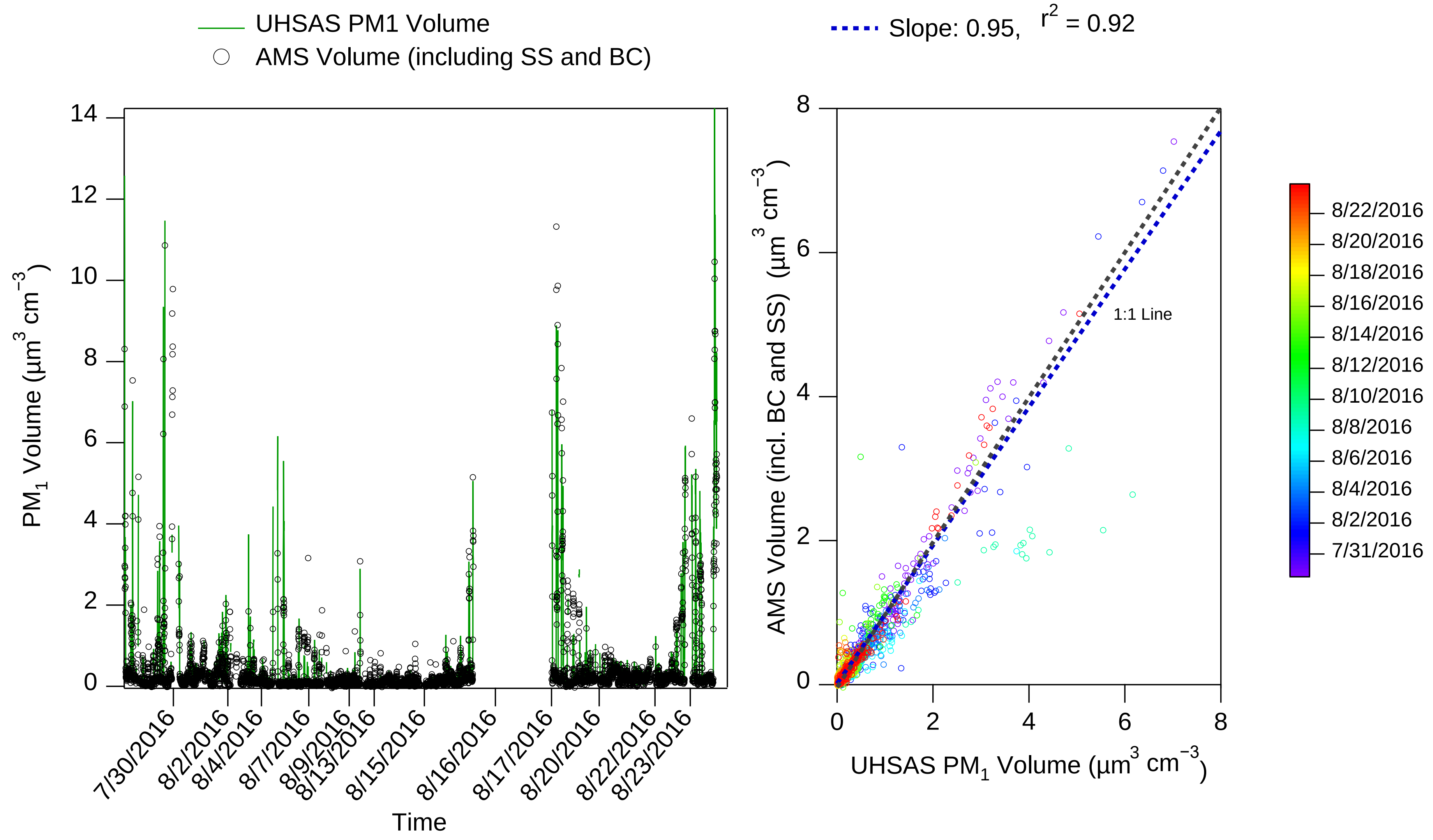
AMS Quantification—Calibrations and Comparisons from Recent Campaigns

Benjamin A. Nault, Pedro Campuzano-Jost, Doug A. Day, Hongyu Guo, Jason C. Schroder, Jose L. Jimenez, and the Science Teams from KORUS-AQ and ATom

When AMS is fully and carefully calibrated and characterized, the measurements are completely quantitative

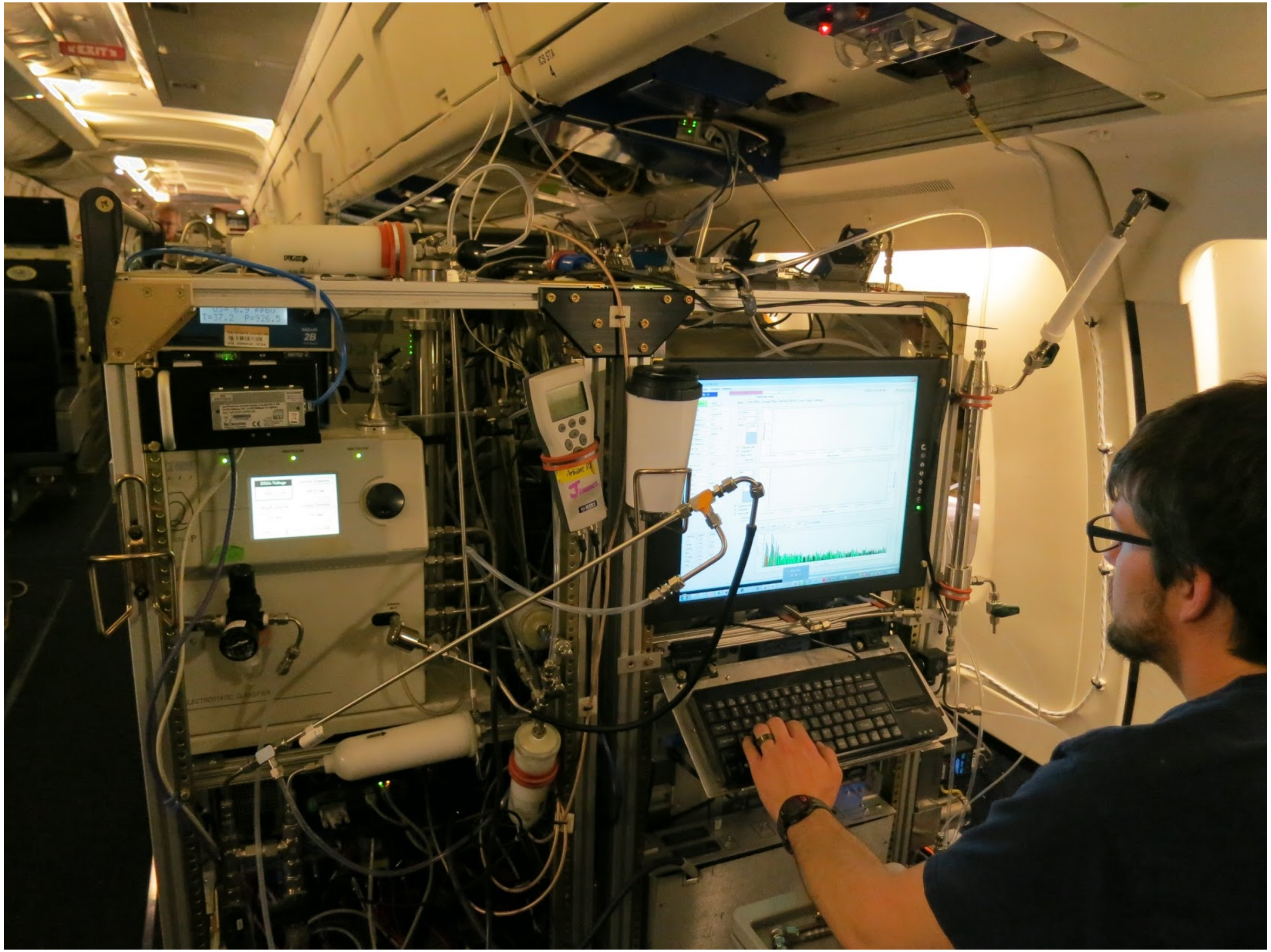


When AMS is fully and carefully calibrated and characterized, the measurements are completely quantitative



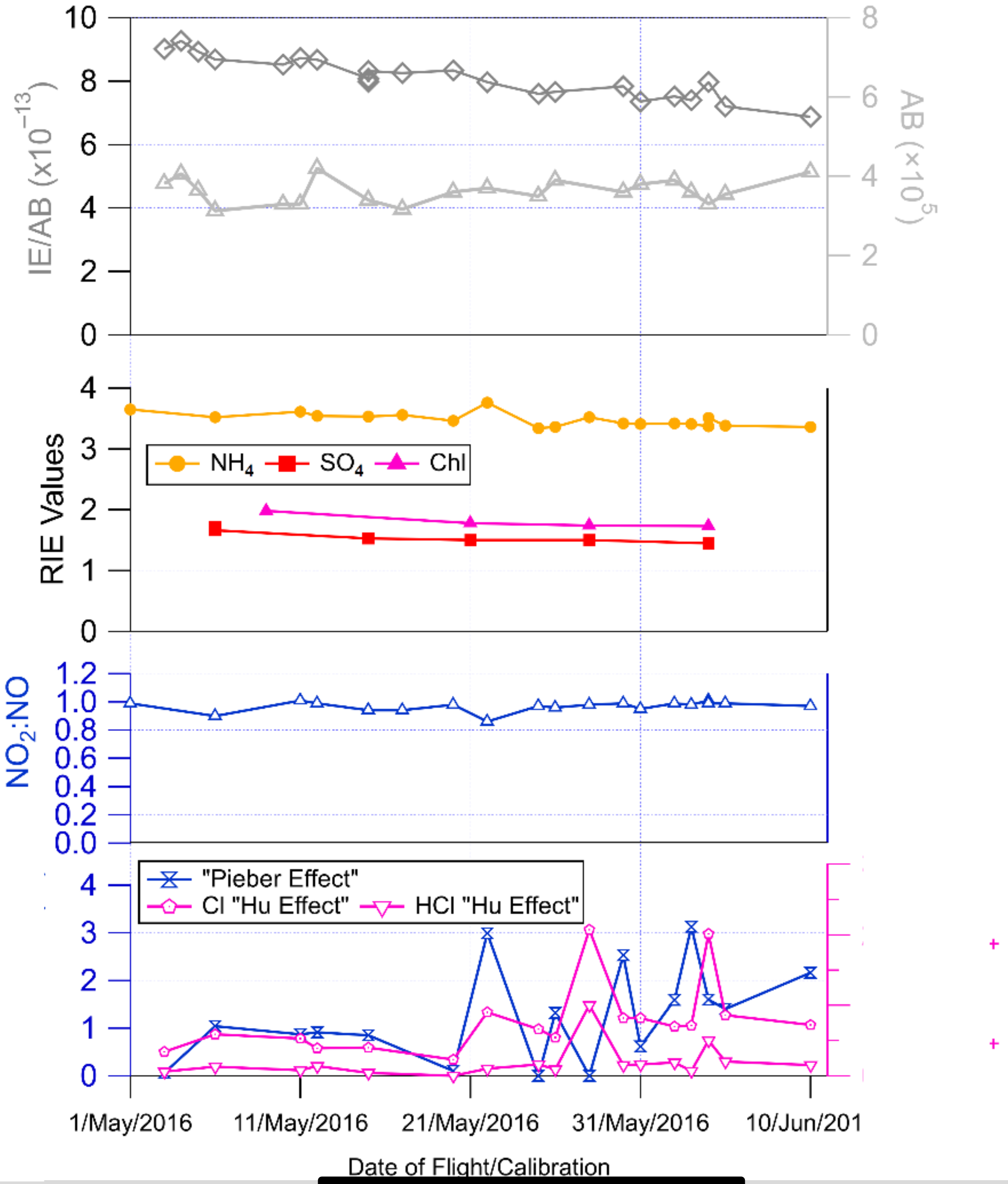
Calibrations
(not including exotic species)

Current CU-AMS Aircraft Configuration



General Calibrations

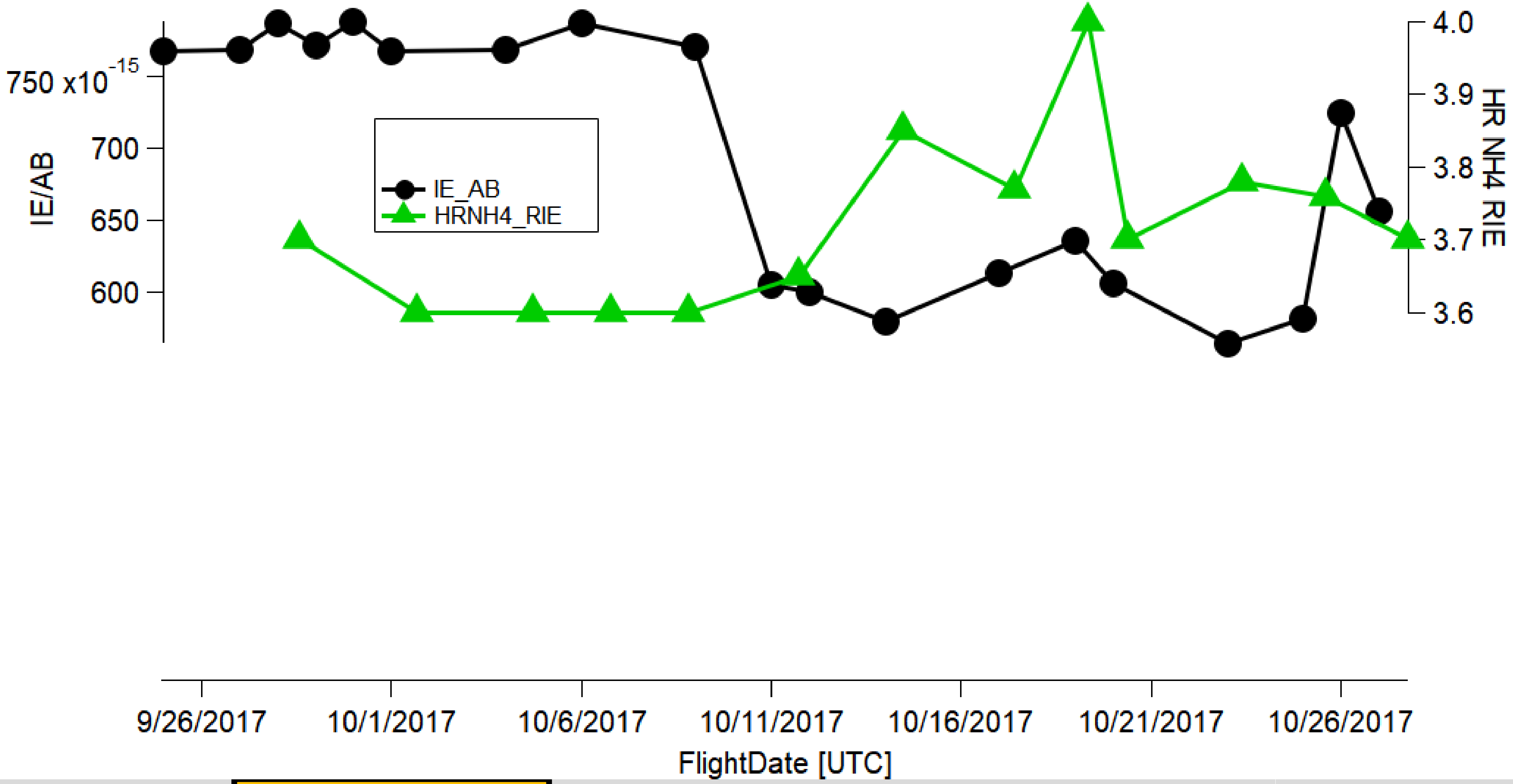
Calibrations of the Ammonium Salts for RIEs and Ion Ratios



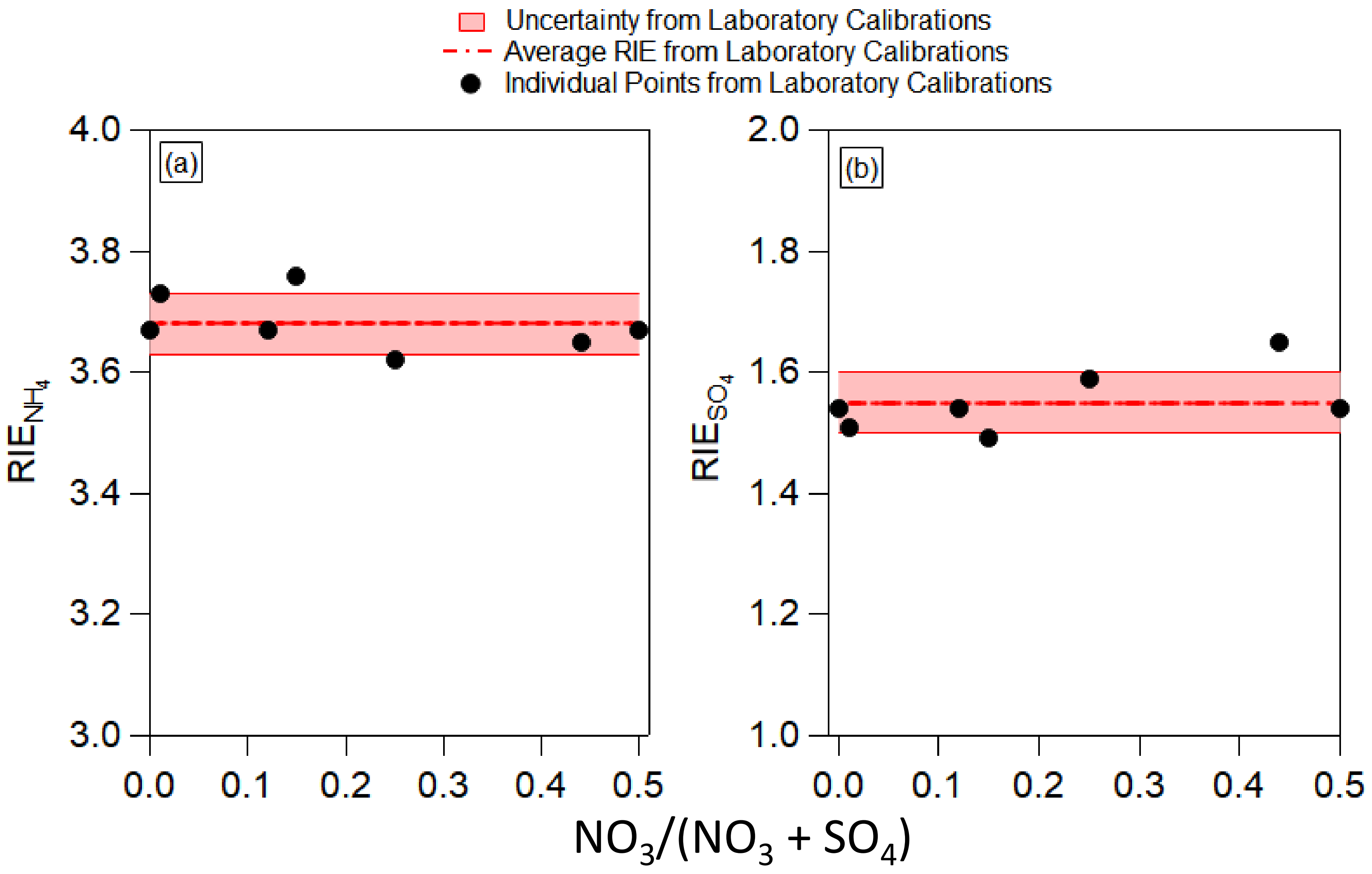
- See John Jayne's, Manjula Canagaratna's, and Phil Croteau's Talks
- Calibrate NO_3 IE as often as possible (for aircraft).
  - Look for changes in AB to help determine if you should calibrate for ground (40/28 for MCP)
  - For ground, calibrate as often as you feel comfortable (maybe 2 – 4 days)
- **Calibrate everything before and after a filament change**
- Calibrate SO_4 RIE
  - Average observed during one campaign 1.56
  - Typical value in Batch Table is 1.2
- The NO_2:NO ratio, NH_4 RIE, and CO_2^+/NO_3 Artifact
  - NO_2:NO ratio needed for particle organic nitrate values
  - NO_2:NO ratio can be used for instrument performance evaluation
- Ideally, calibrate Chl before and after campaign
  - Typically not much non-refractory Chl
  - Chl can linger on vaporizer, causing artifacts

Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/ (SI Fig. 3)

IE, RIE, and Comparisons NOT Always Stable



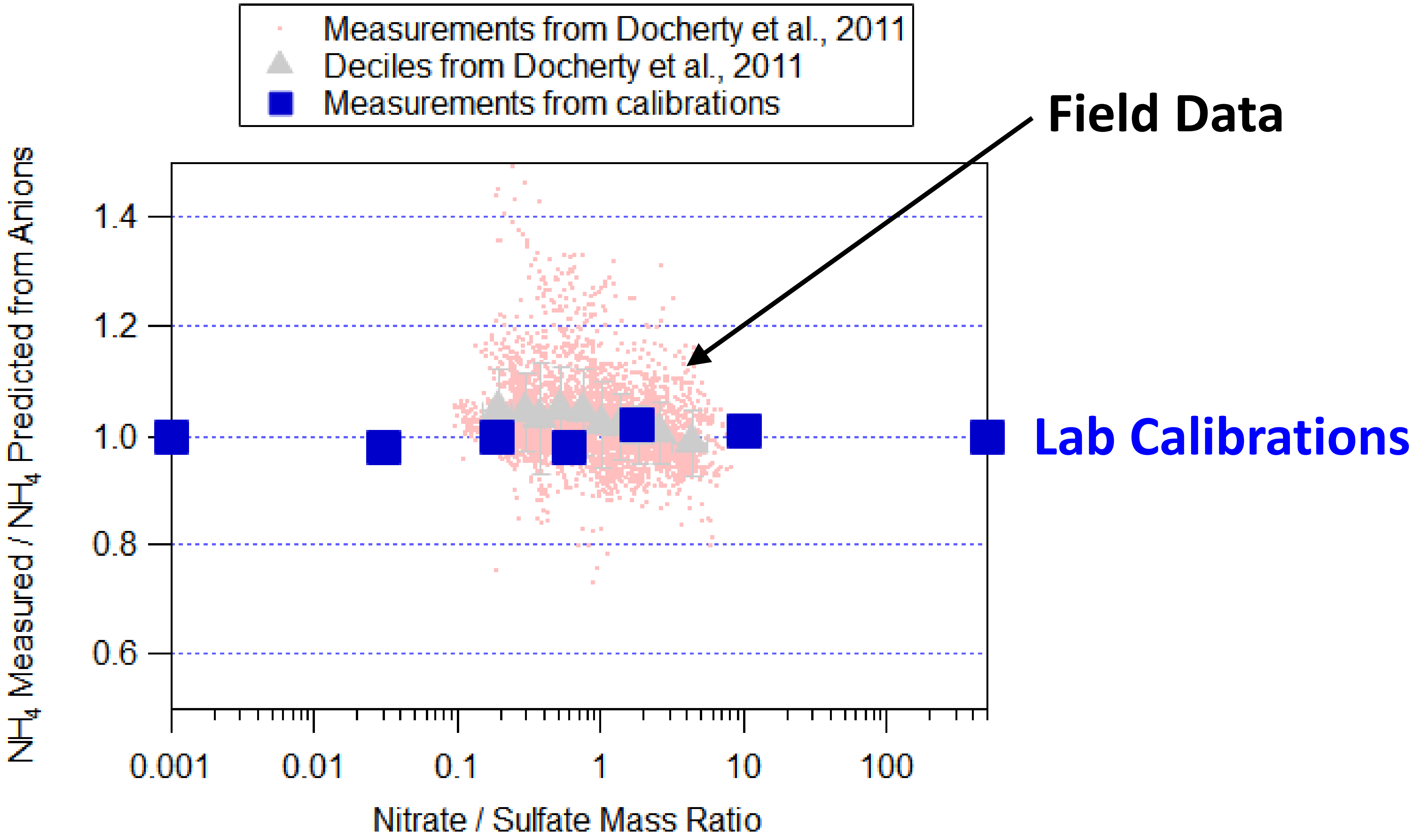
Impact of Mixtures vs Pure Ammonium Salts on the RIEs



- No variation of RIE from pure particles to mixtures of variable composition
- This implies that RIE should be constant for ambient particles as composition varies

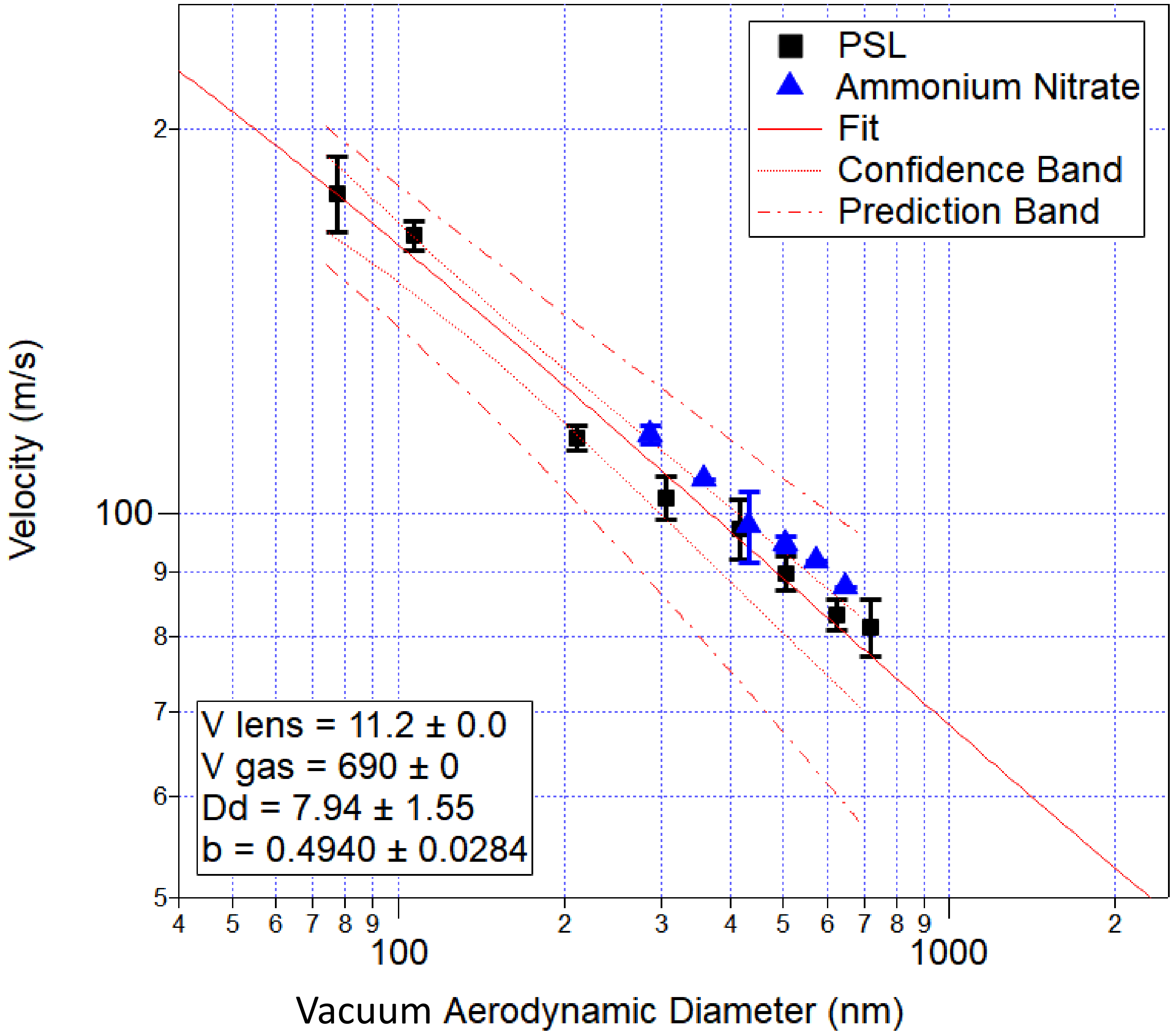
Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/ SI Fig. 7

Impact of Mixtures vs Pure Ammonium Salts on the RIEs



Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/, SI Fig 6

Calibrating (e)PToF

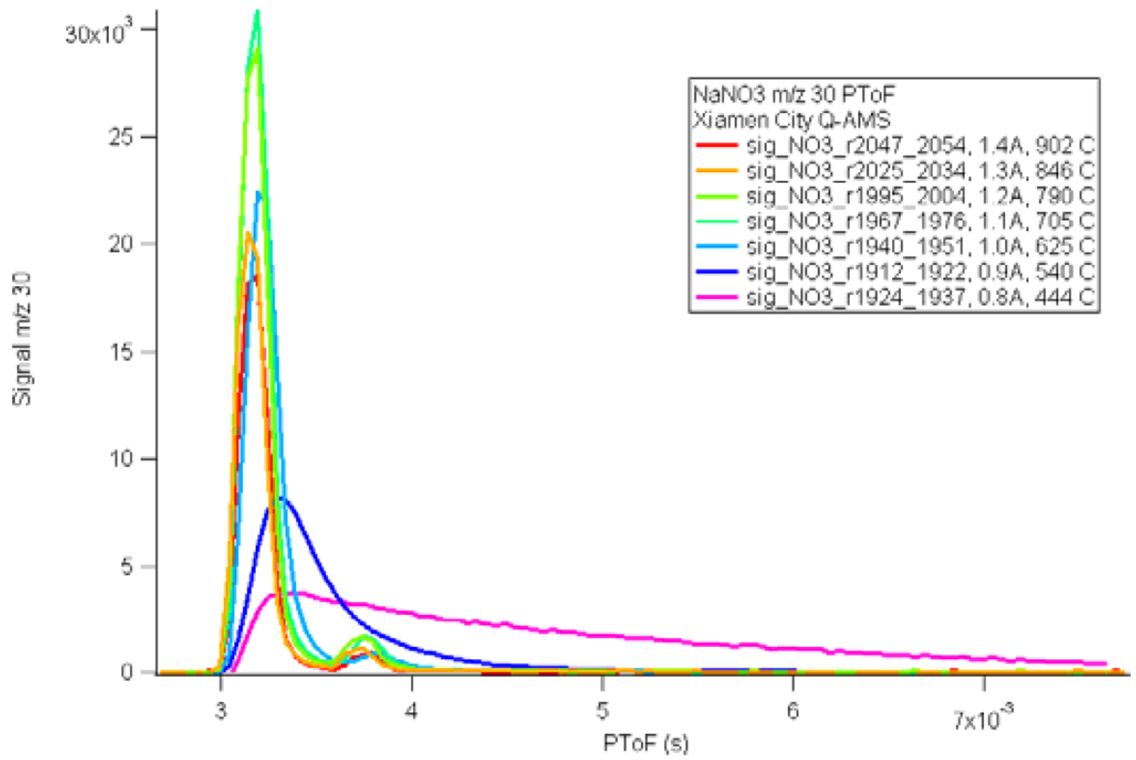


- PSLs provide calibration of (e)PToF, and a check of the sizing of the DMA calibration system as well
- Check the DMA sizing of NH_4NO_3 (and its lack of evaporation) by comparing with PSL cals
- Calibrate at beginning of intensive measurements
  - Calibration only works for a given pressure inside the lens
  - E.g. if flying in aircraft may experience some changes in lens pressure →calibrate (e)PToF at those pressures as well!

Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018 https://www.atmos-chem-phys-discuss.net/acp-2018-838/, SI Fig 5

Calibrating vaporizer temperature for non-refractory compounds and to minimize refractory compounds

Use of NaNO3 to "calibrate" Vaporizer Temperature in pTOF mode

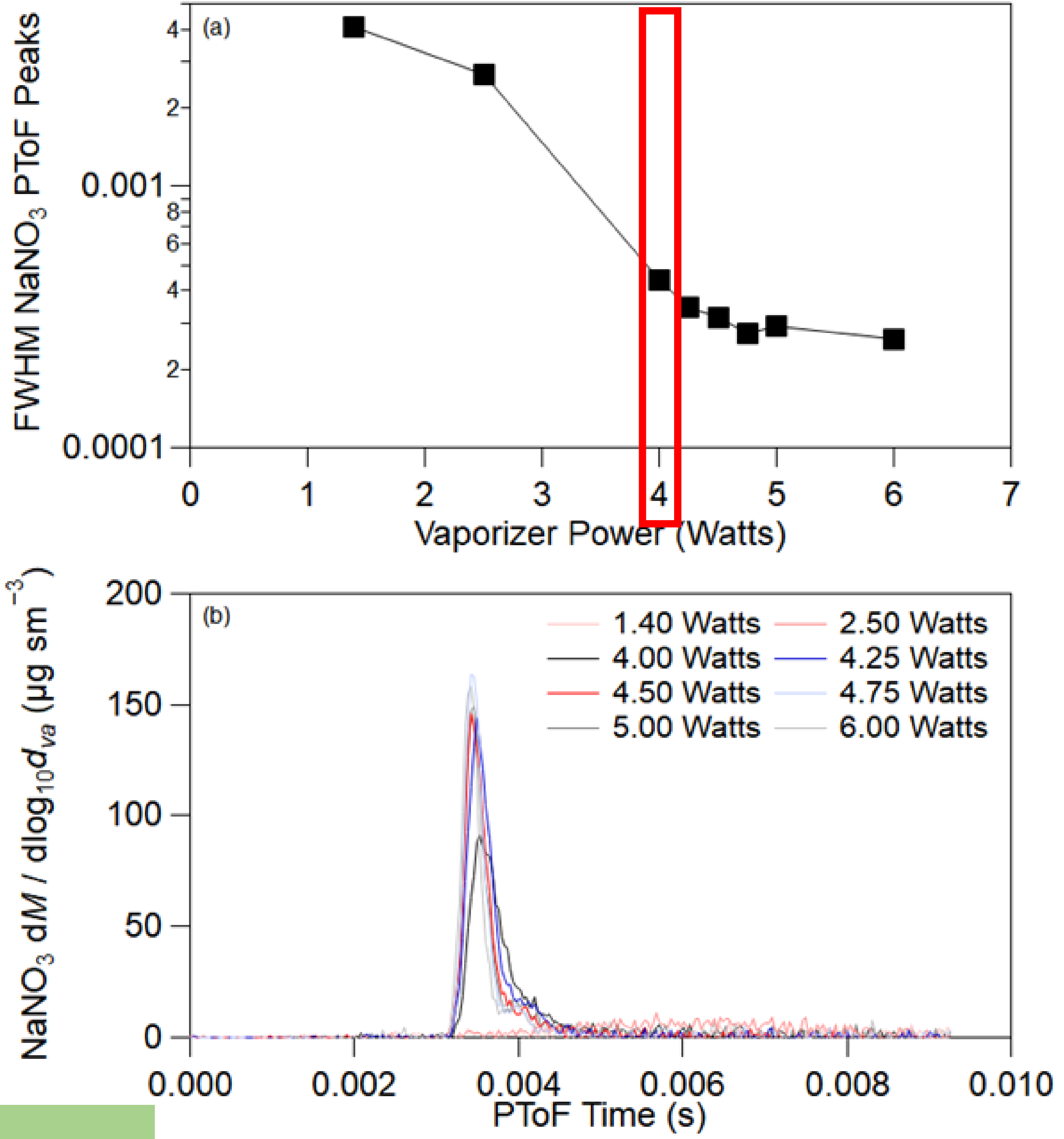


Approximately 750C (4.5W) gives good PToF traces for NaNO3 (m/z 30).

Leah Williams
http://cires1.colorado.edu/jimenez-group/UsrMtgs/UsersMtg11/WilliamsAMSUsersMtg_2010_VapT.pdf
http://cires1.colorado.edu/jimenez-group/UsrMtgs/UsersMtg12/Presentations/Williams_VapT.pdf
http://cires1.colorado.edu/jimenez-group/UsrMtgs/UsersMtg13/AMSUsersMtg_2012_VapT.pdf

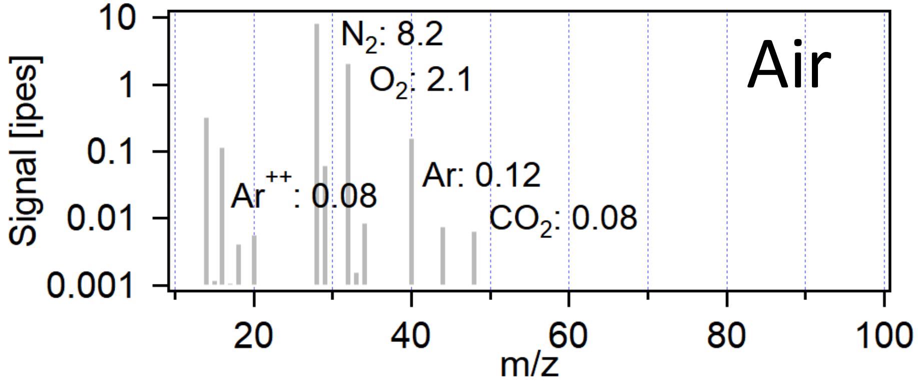
Select power setting prior to sharp $NaNO_3$ PToF peak

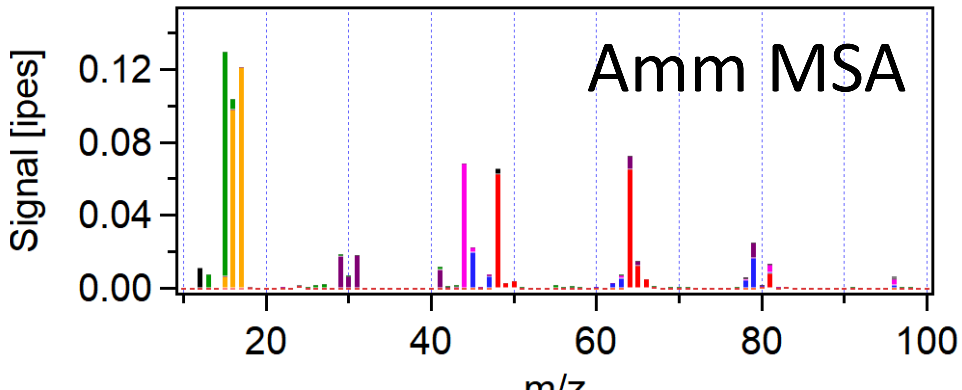
- INSTRUMENT DEPENDENT!
- Depends on boards and vaporizer
- Only needs to be calibrated at beginning of intensive measurements, UNLESS:
  - Any boards are changed
  - Vaporizer was changed
  - Wires were changed

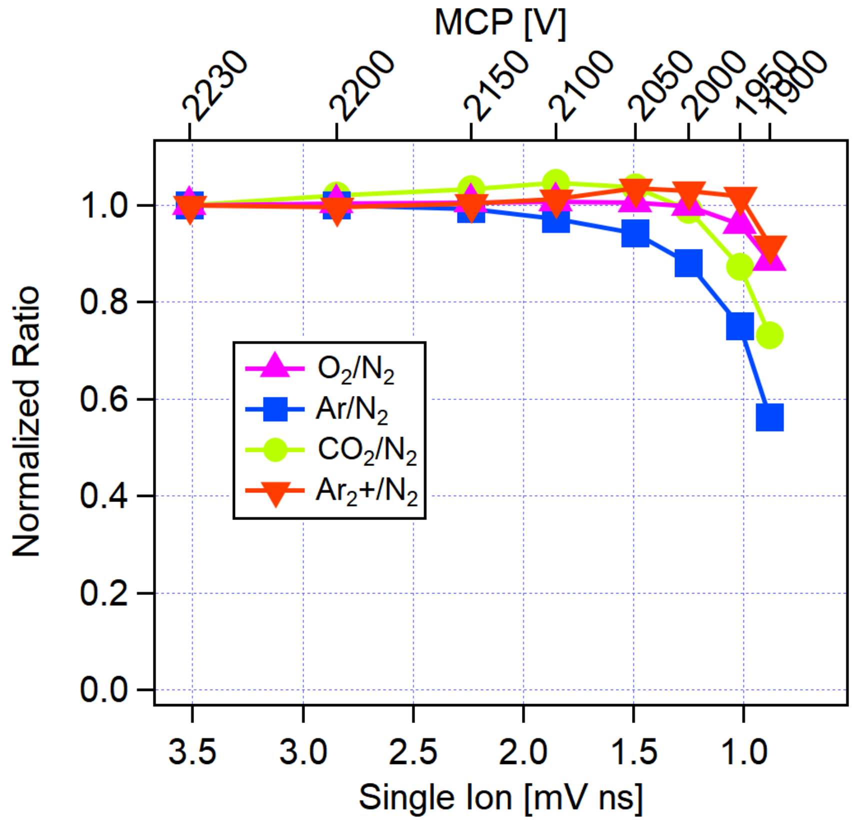


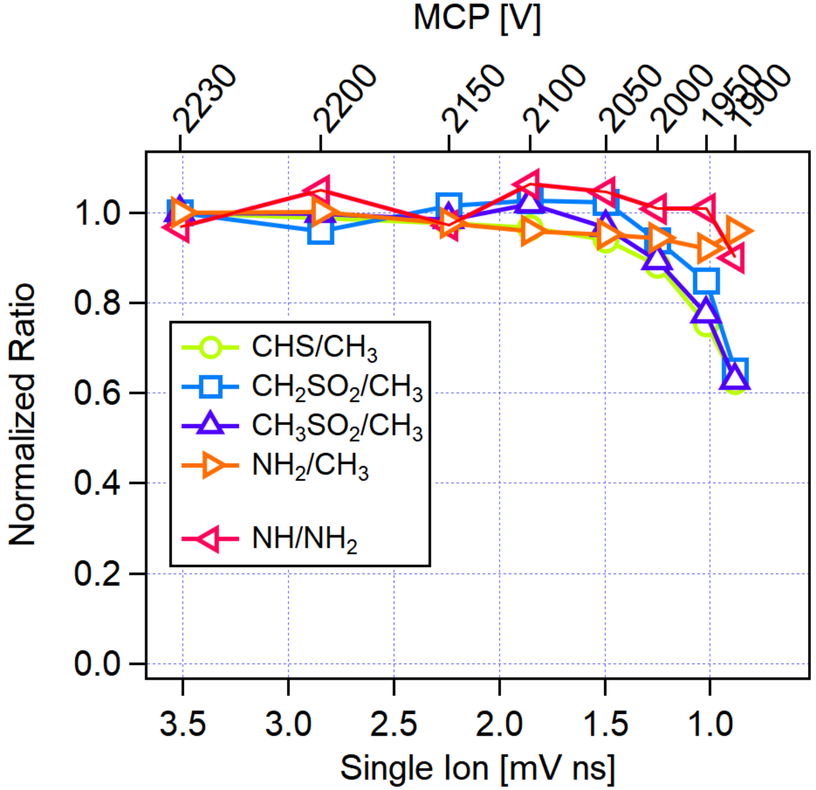
Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig 8

Check MCP voltage not too low & calibrating single ion - Instrument Specific









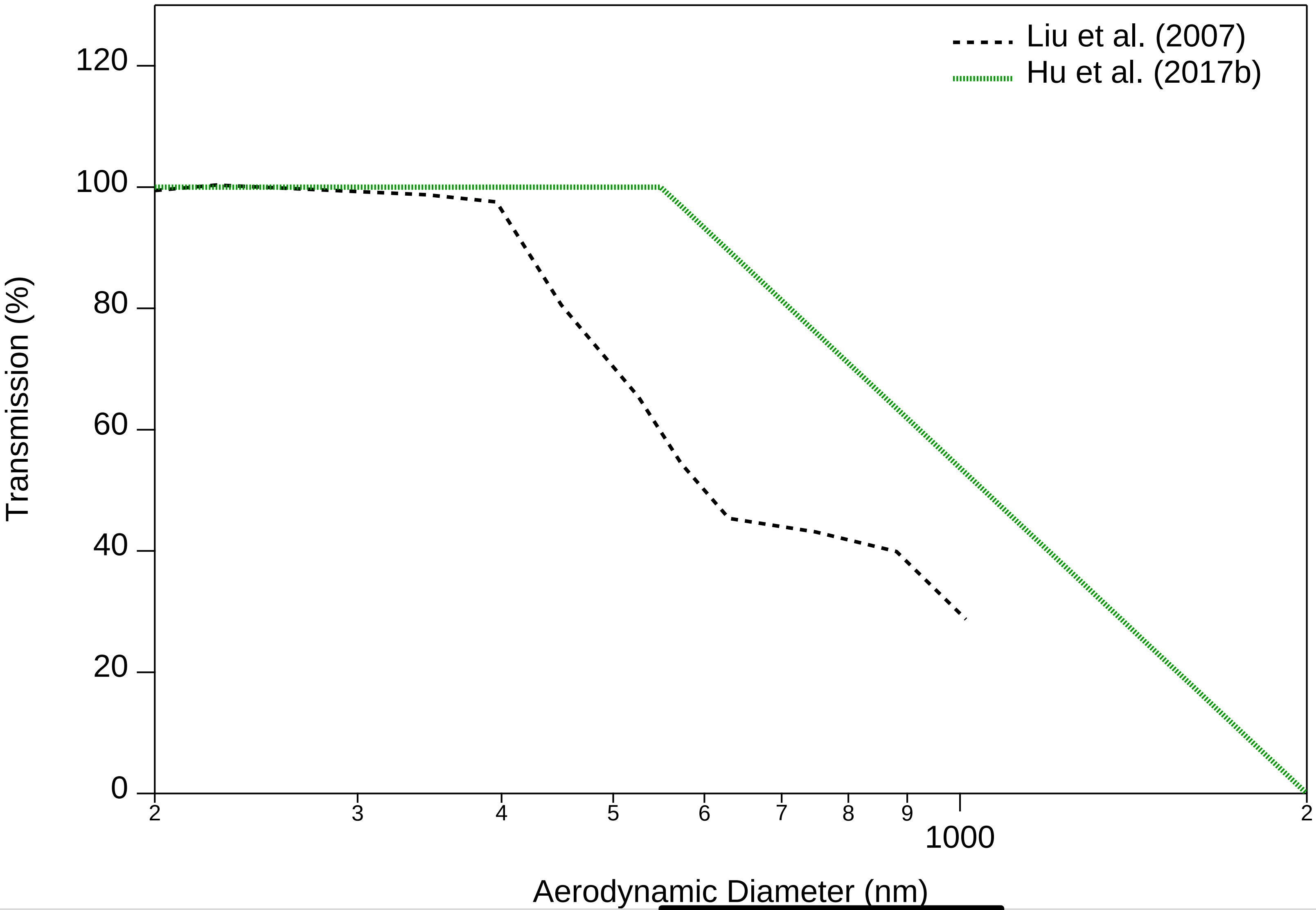
- Ratio of air ions shows that for big ions, the stable setting is ~1.8 mV ns, or ~2100 V
- Air ions show that for small ones, the stable setting is ~1.3 mV ns, or ~2000 V
- For aerosol, same trend
- **INSTRUMENT & MCP SPECIFIC, CHANGES IN TIME! NEED TO CALIBRATE**

Conclusion on Calibrations

- Calibrate NO_3 IE and NH_4^+ RIE frequently (for aircraft) and as often as you feel confident (for aircraft, laboratory, ground)
  - Provides insight into instrumental performance
  - Prevents headaches later if the instrument values drastically change
  - Provides insight into NO_2^+/NO^+ ratio
  - But… problems can be introduced when trying to calibrate (need a lot of practice)
- Calibrate SO_4^{2-} RIE frequently as well
  - Our group has consistently observed the calibrated RIE is not the same as the default value in Squirrel/PIKA
- Only calibrate halogens beginning and end of campaign
- RIEs not impacted by mixtures
- Calibrate (e)PToF sizing at beginning of measurements
- Calibrate vaporizer temperature once a campaign/intensive laboratory study (more often if parts or electronics are replaced)
- Check MCP voltage is appropriate before and during the campaign

Transmission Curve

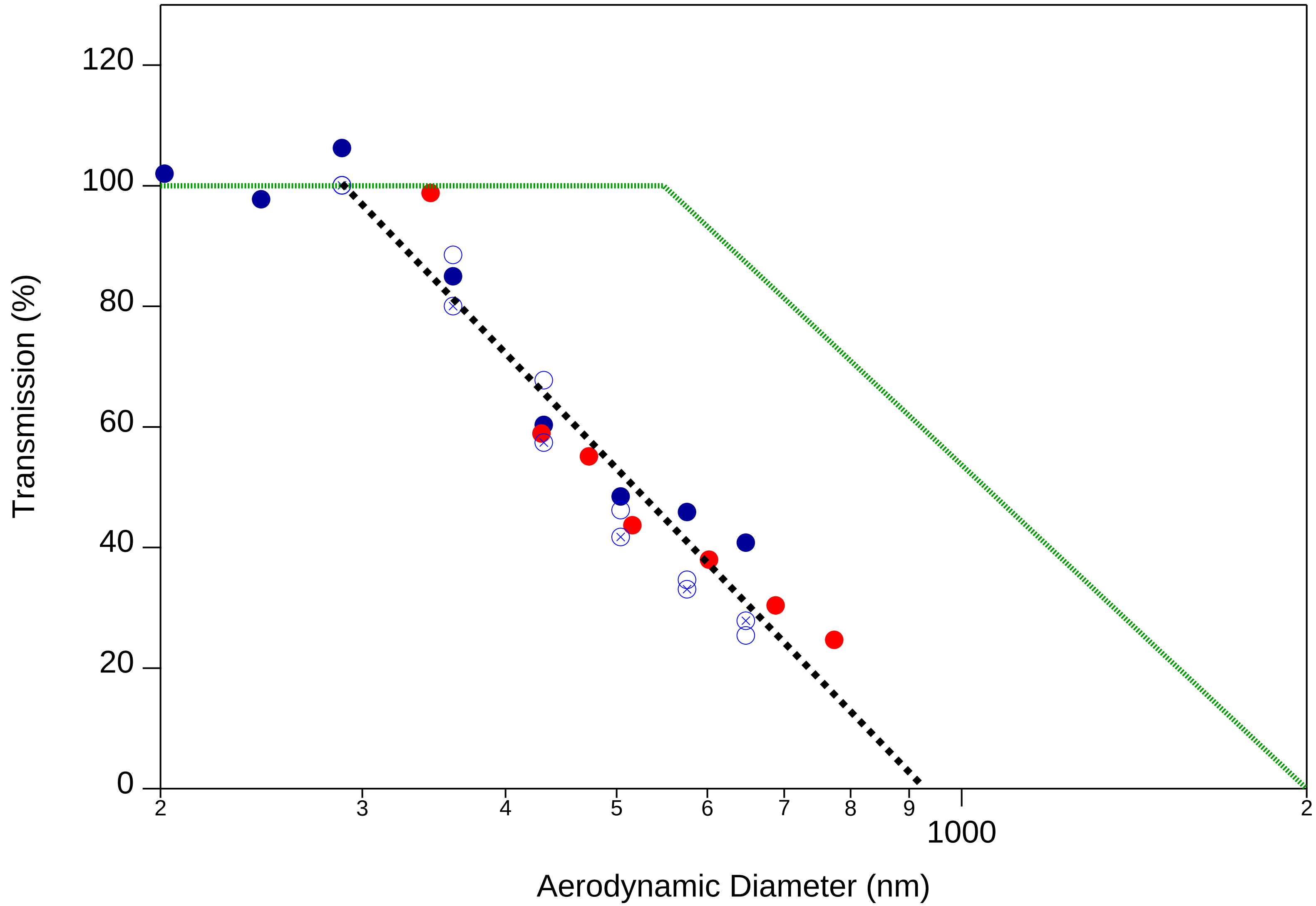
Differences in two different literature transmission curves



- Ideally, calibrate at least once prior to intensive measurements
- If in a moving environment (e.g., airplane, mobile lab), may need to calibrate more often during intensive measurements (it can change, although unusual)
- BE CAREFUL! Mass based transmission curves can be challenging due to doubly-charged particles at low concentrations. (ET cal can be found at this talk).
- Need to know the curve to do quantitative comparisons with other measurements *or with models*
- MAYBE instrument specific

CU AMS, beginning of one campaign

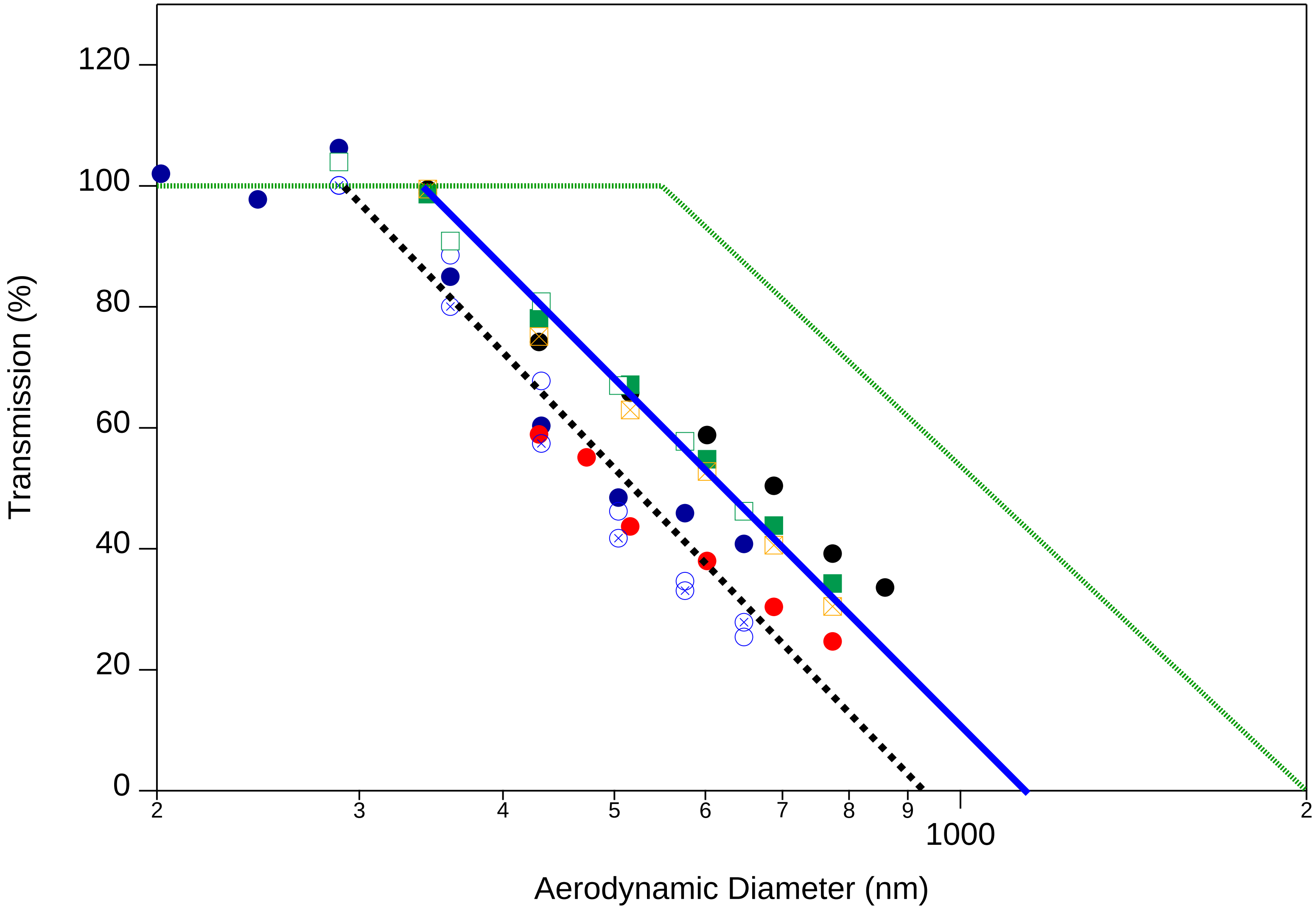
Campaign 1a



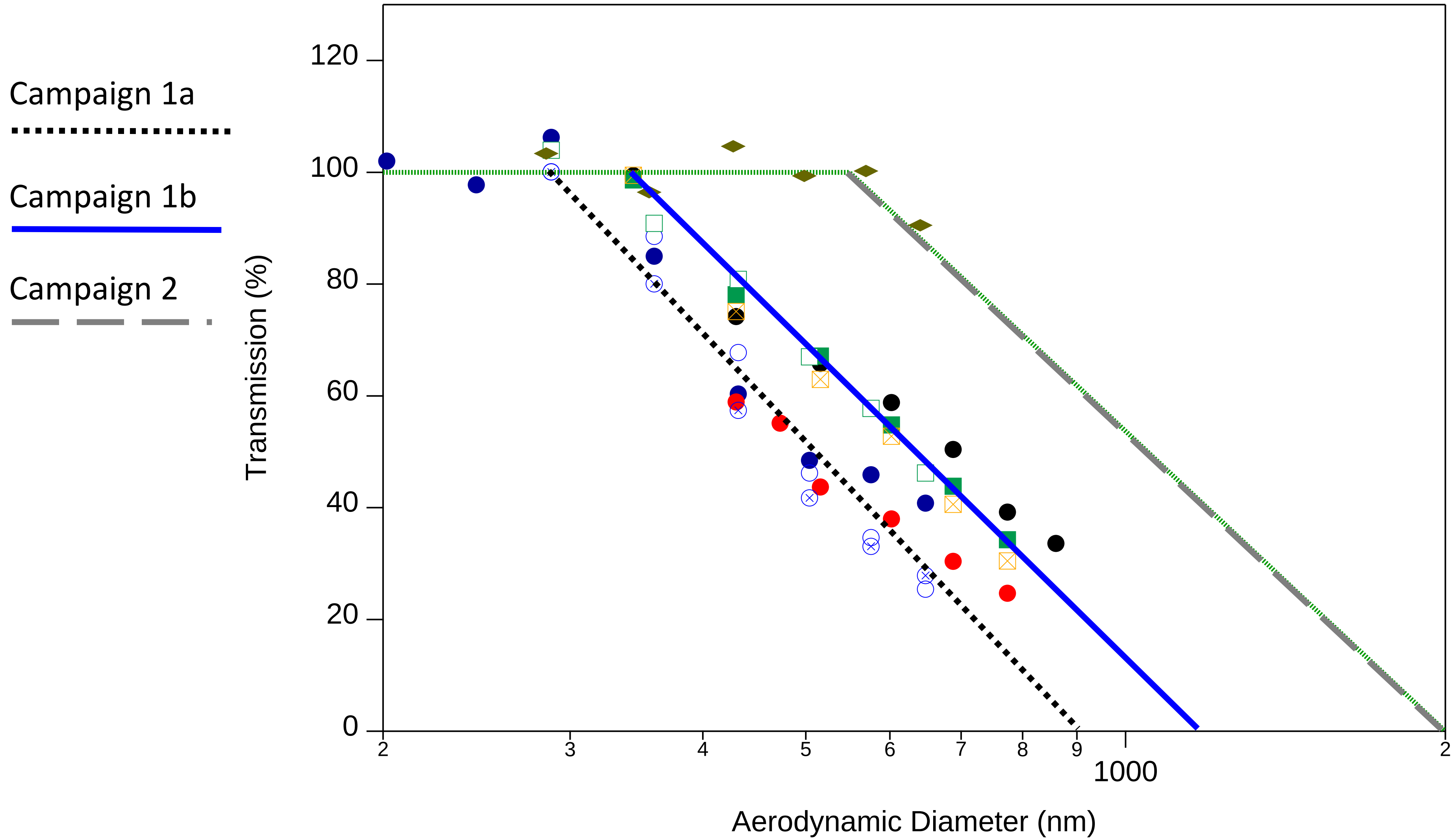
CU AMS, end of campaign

Campaign 1a

Campaign 1b



CU AMS, campaign 2 years later



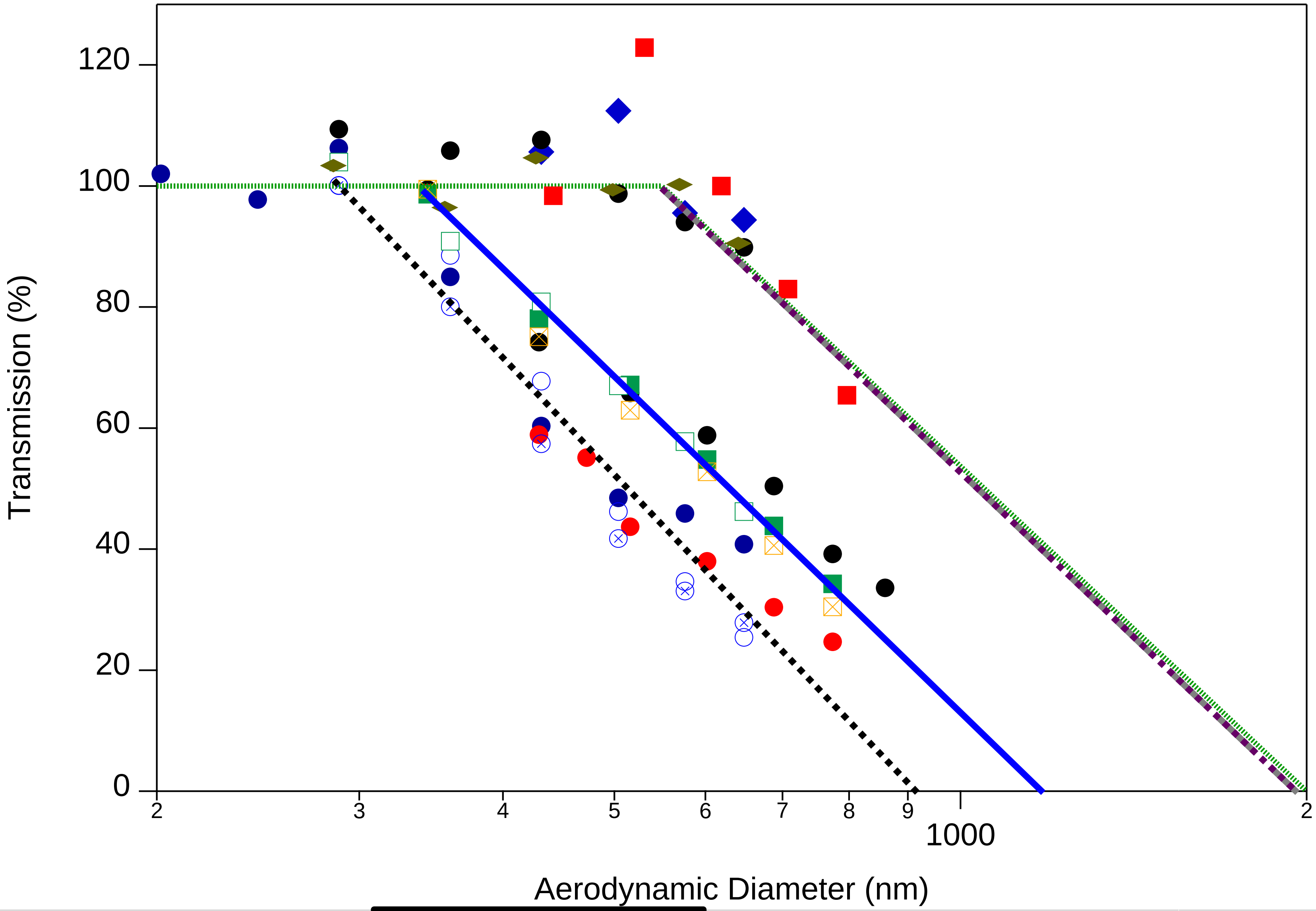
CU AMS, campaign 1 year later

Campaign 1a

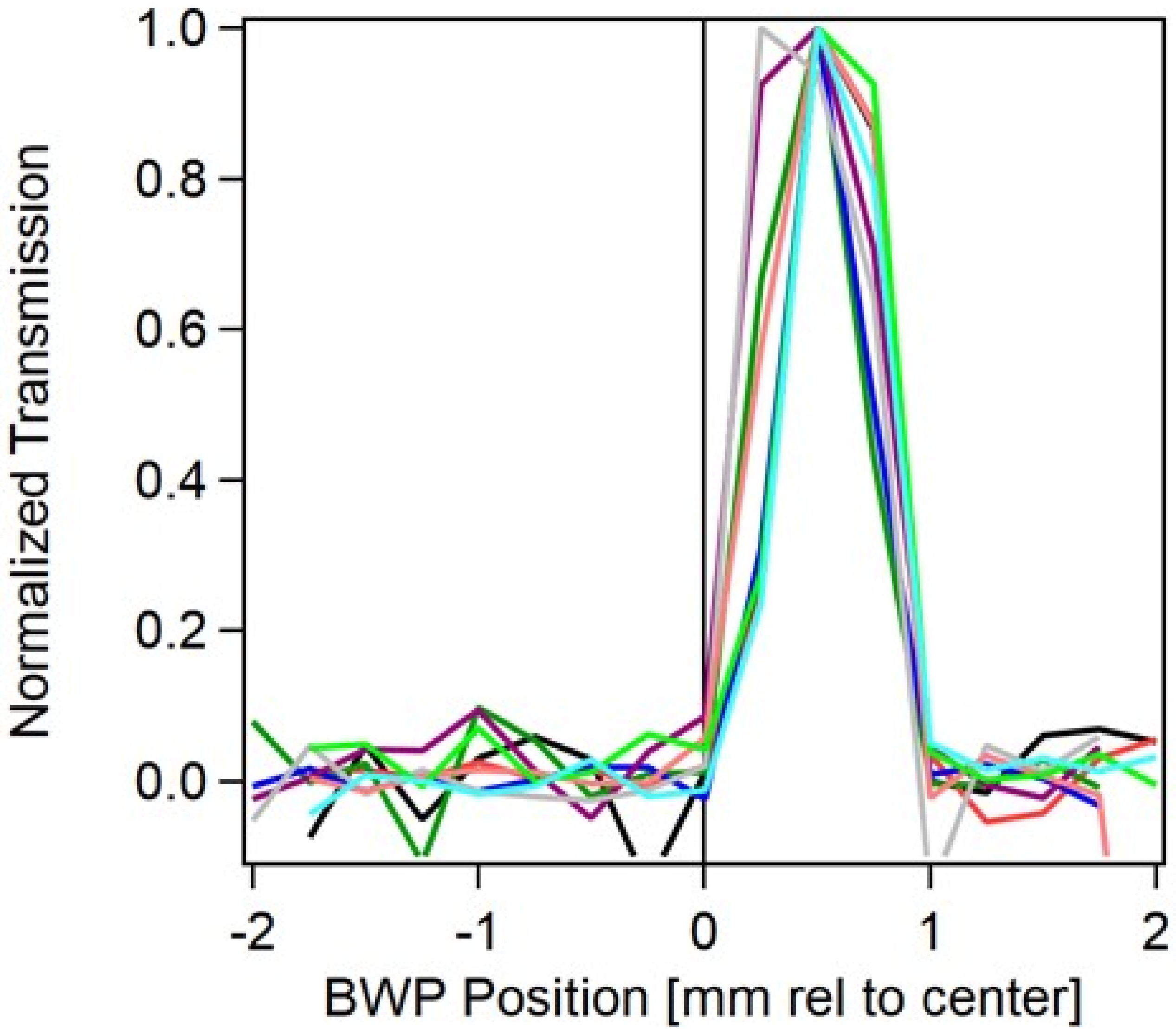
Campaign 1b

Campaign 2

Campaign 3

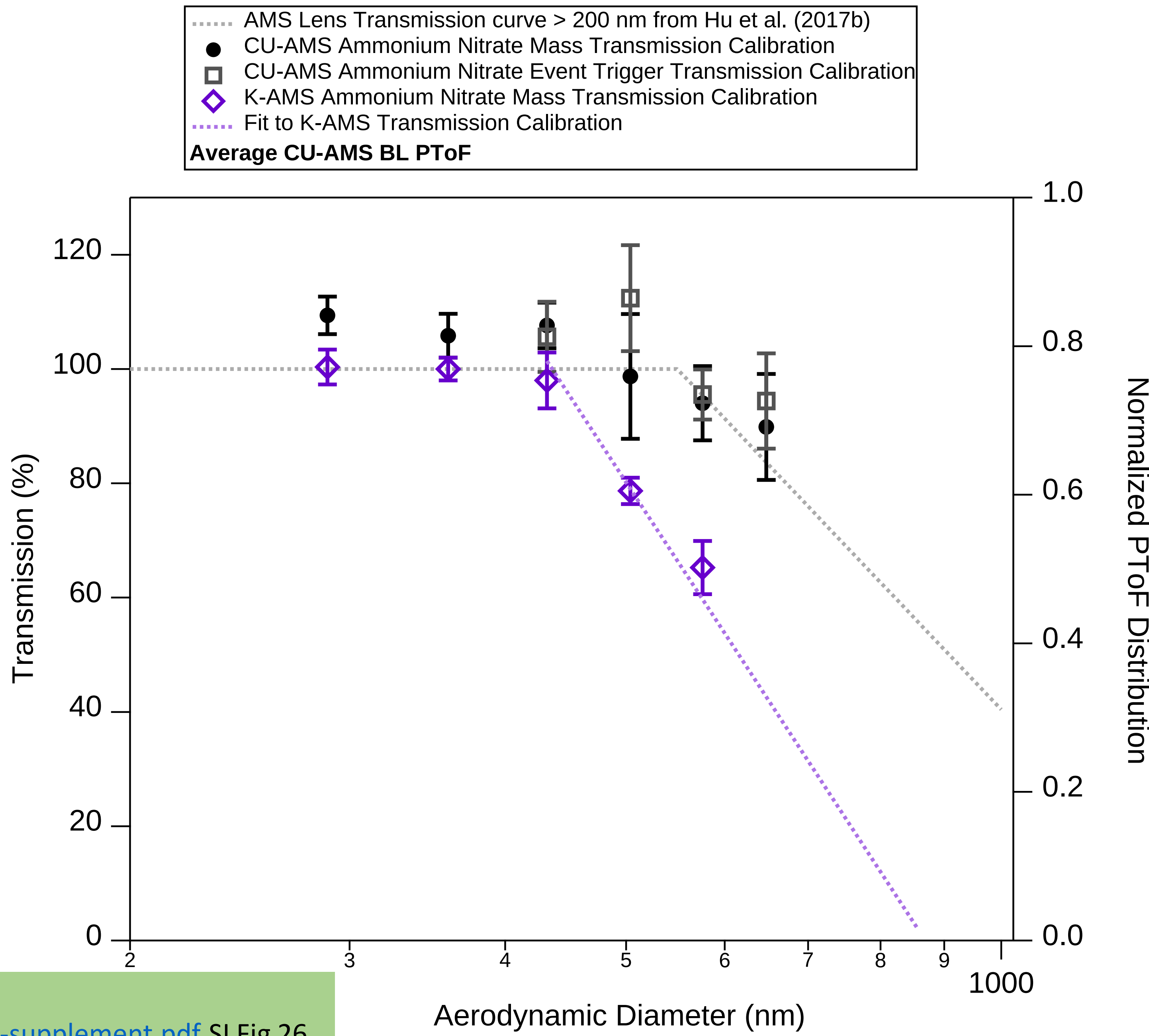


Using Beam Width Probes to “Probe” Transmission



- Use BWP to spot check center of air and particle beam every day (flight→calibrate every day)
- Changes in location of center of particle beam → full transmission curve calibration → realignment → full transmission curve
- For aircraft measurements, have not seen center of beam move after each flight (and some VERY rough landings)

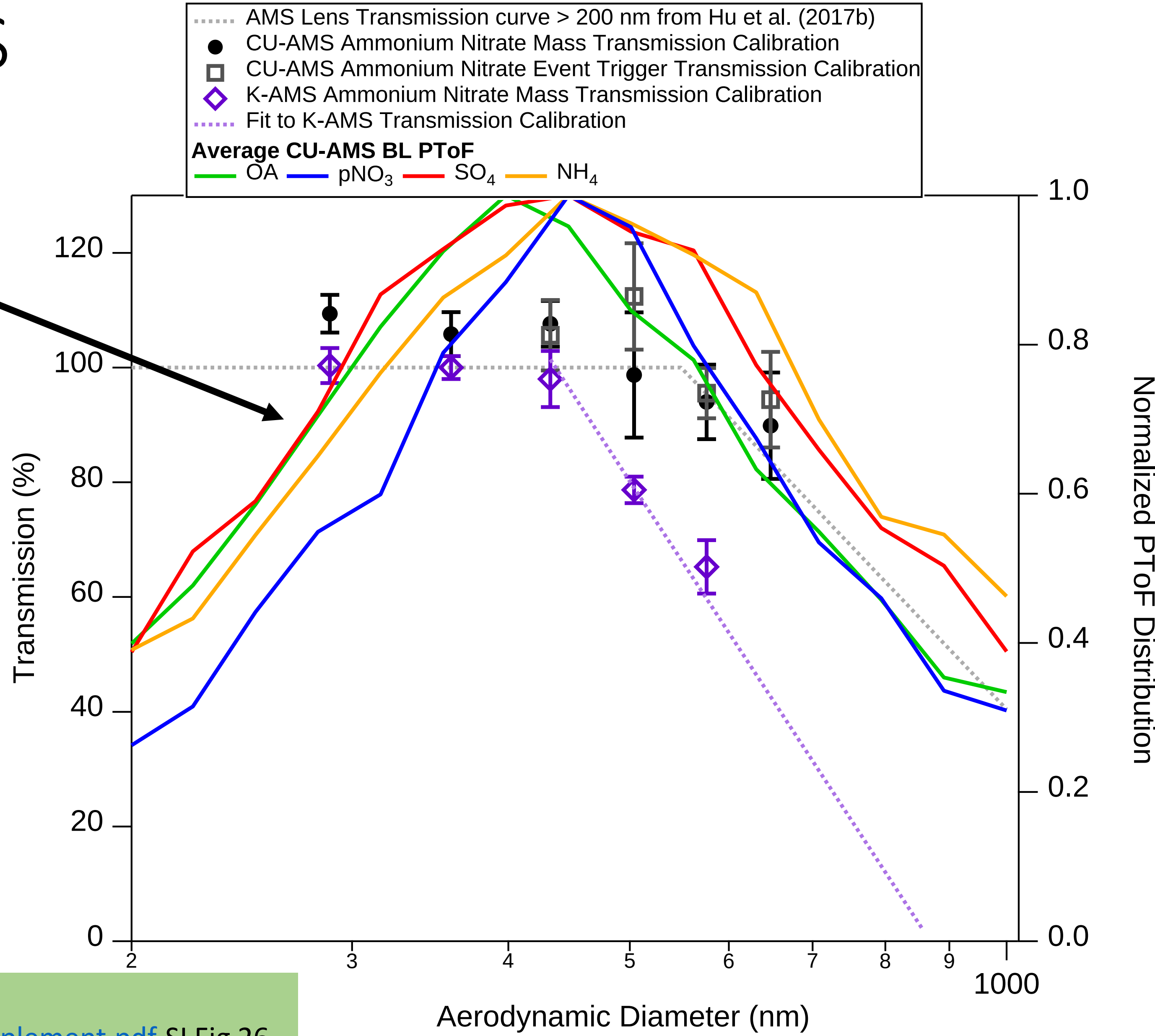
Comparison of two AMSs during 1 campaign



Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf SI Fig 26

Average size distribution of species peaked above size cut-off for one AMS

Ambient size distributions

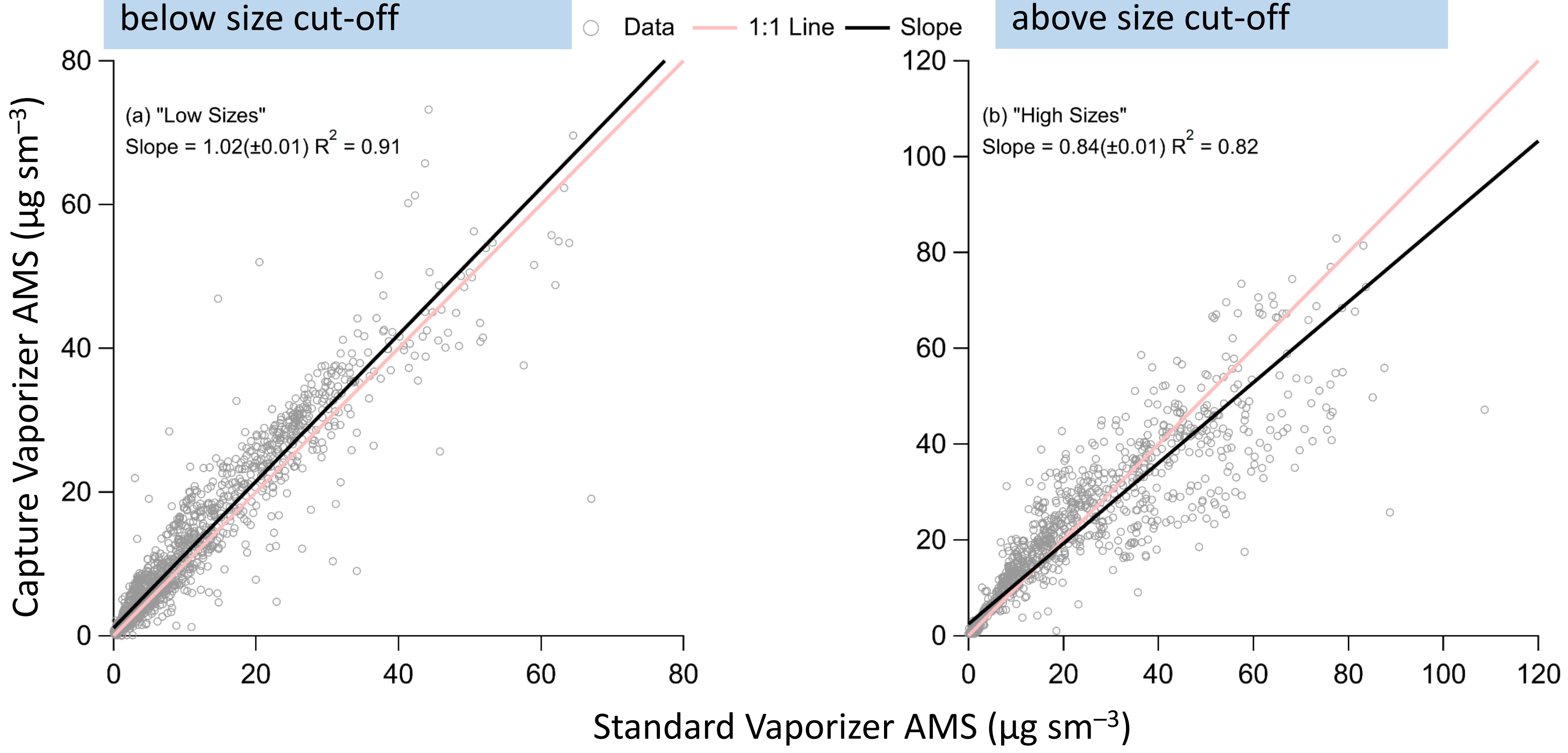


Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf SI Fig 26

Very different fits and R^2 between periods with high and low aerosol sizes

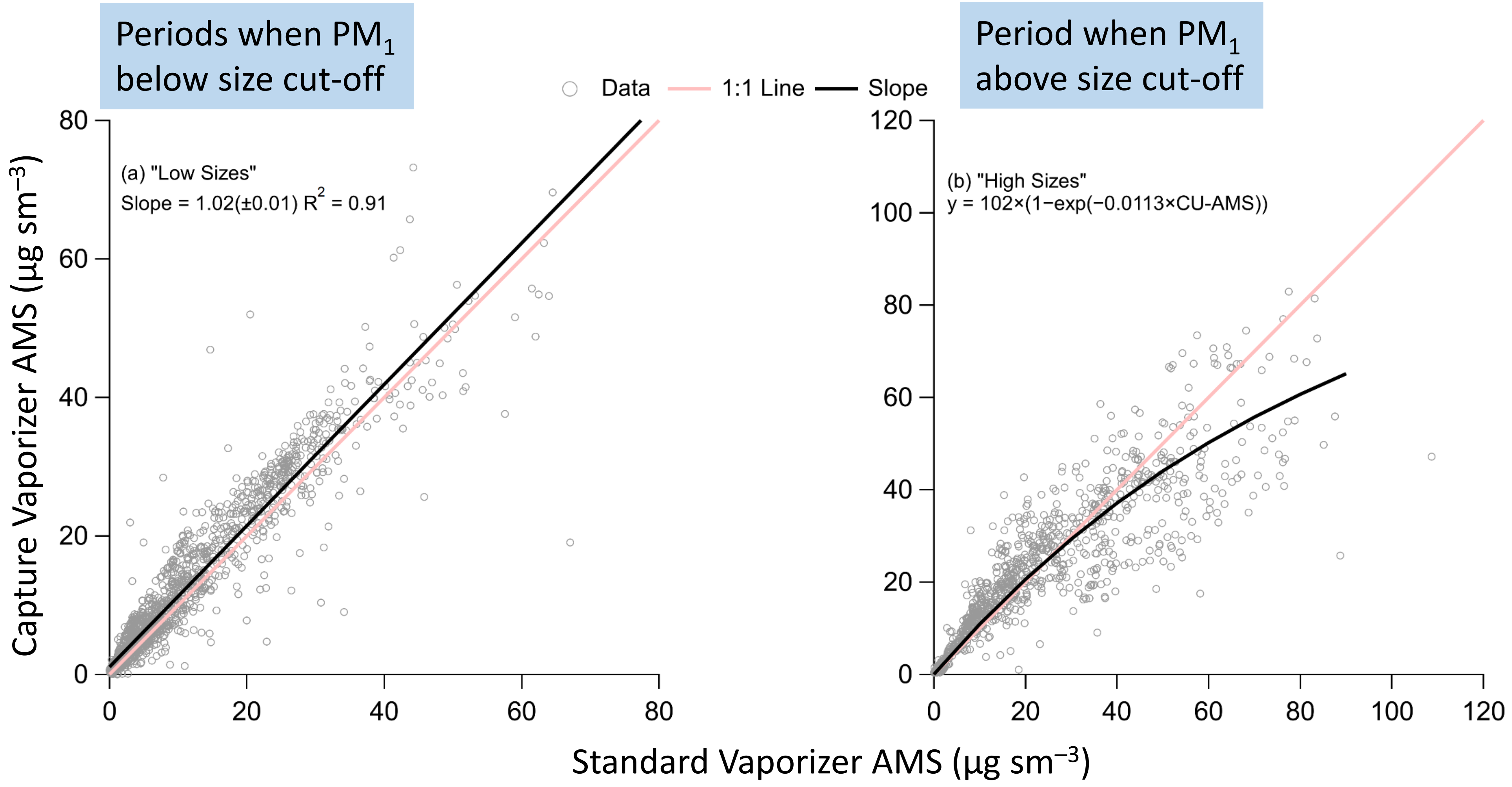
Periods when ambient PM_1 below size cut-off

Period when ambient PM_1 above size cut-off



Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig. 27

The fit is more exponential due to transmission curve



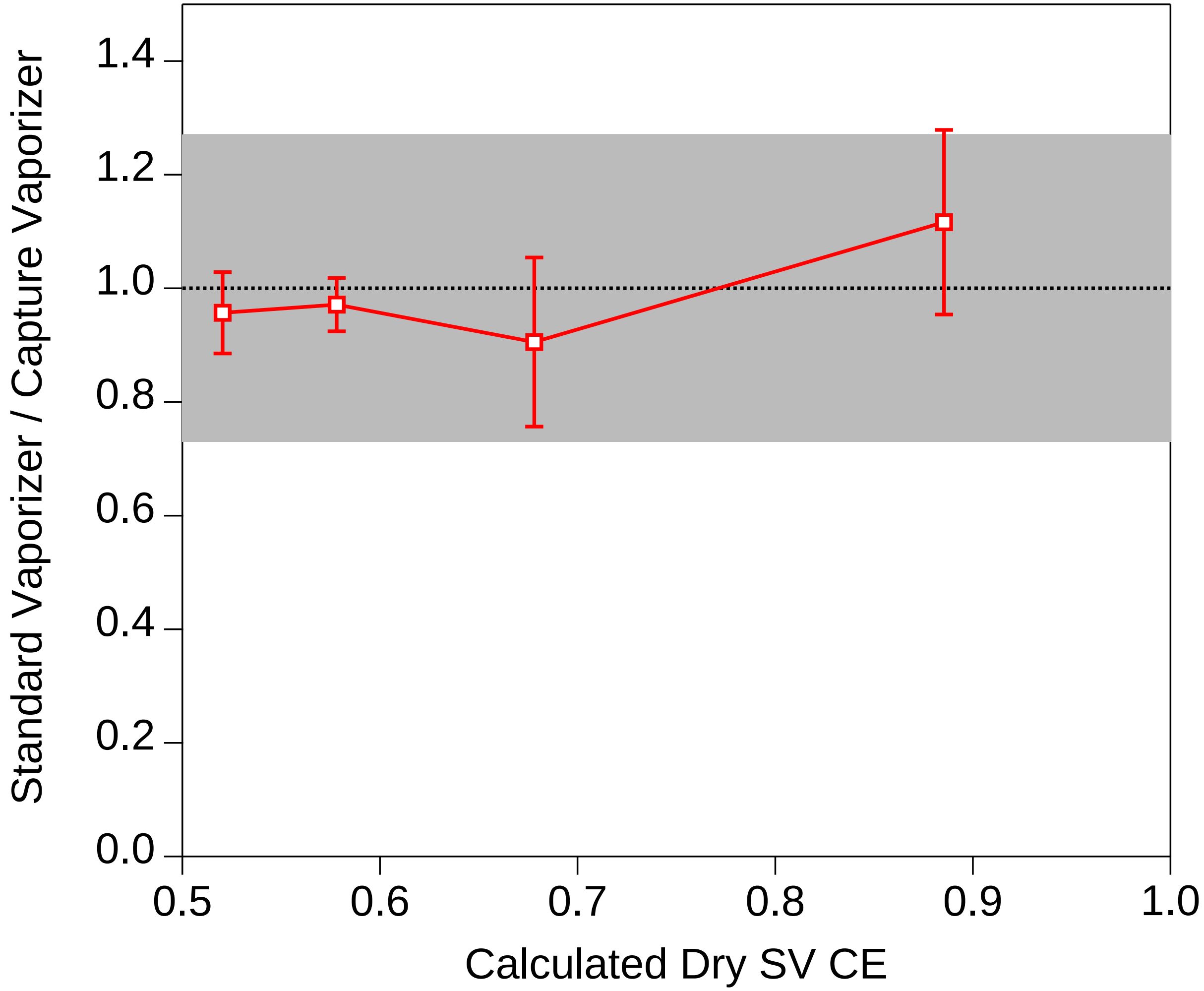
Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig. 27

Conclusions on transmission curve calibration

- This should be done prior to start campaign/laboratory study
- Spot checks throughout study maybe necessary, as alignment/performance may change
- Calibrated transmission curve is NECESSARY to compare against volume and other aerosol measurements
- Calibrated transmission curve is NECESSARY to know what is being measured and in order to be able to provide insight on the chemistry

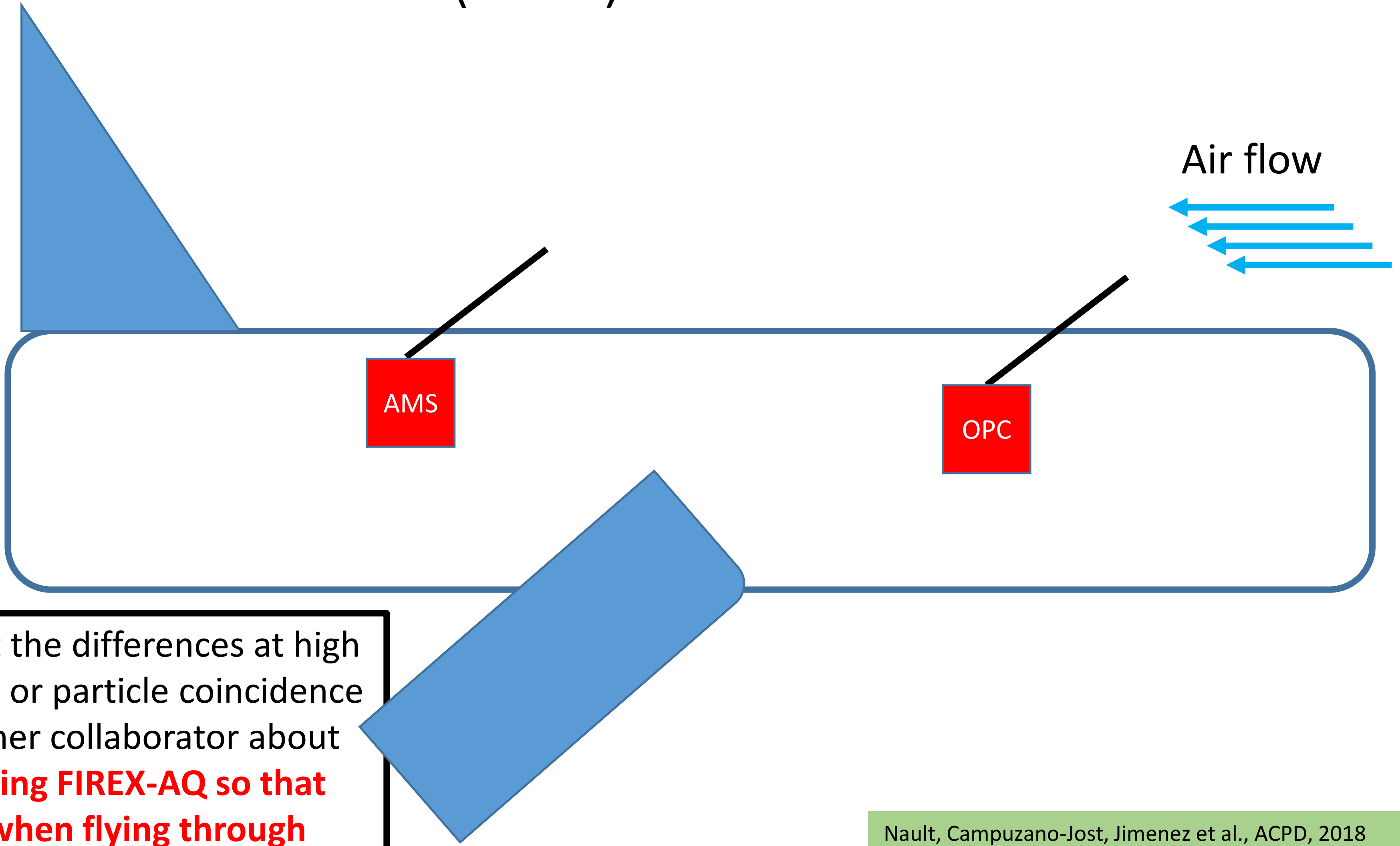
First order comparisons

Total nr-PM_1 measured by capture and standard vaporizer agreed across different collection efficiencies



Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig 28

Comparison of calculated PM_1 volume (AMS species + . . .) versus any optical particle counter (OPC)



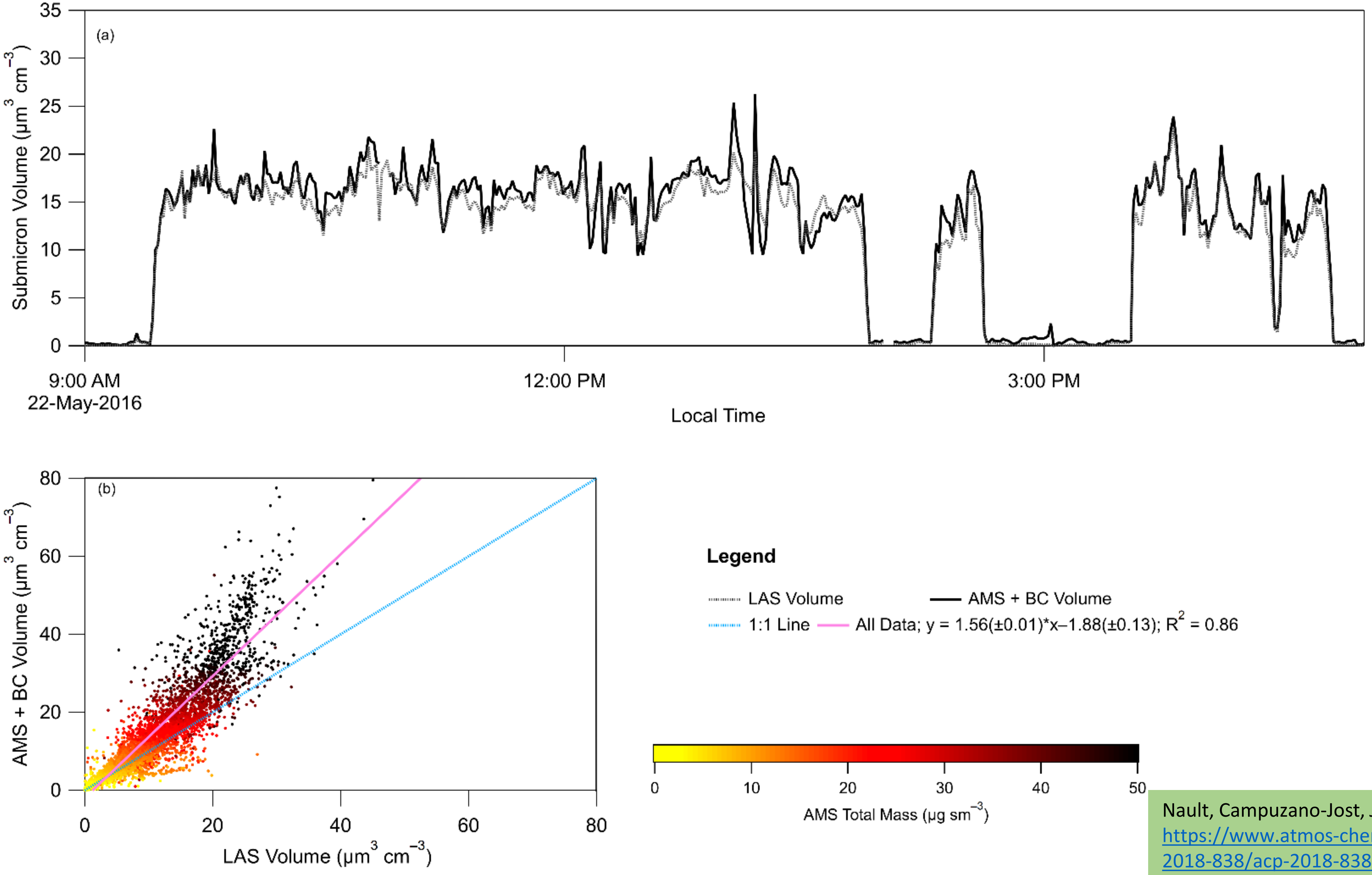
Settings for
<u>Laser Aerosol Spectrometer</u>

Particle Concentration Range
18,000 particles/cm³ at 10 cm³/min.
3,600 particles/cm³ at 50 cm³/min.
1,800 particles/cm³ at 95 cm³/min.

"I believe you're right in concluding that the differences at high concentrations are caused by saturation or particle coincidence in the LAS. We've been talking to another collaborator about **deploying a sample dilution system during FIREX-AQ so that we can avoid these types of problems when flying through fresh biomass burning plumes**." (PI of LAS OPC team)

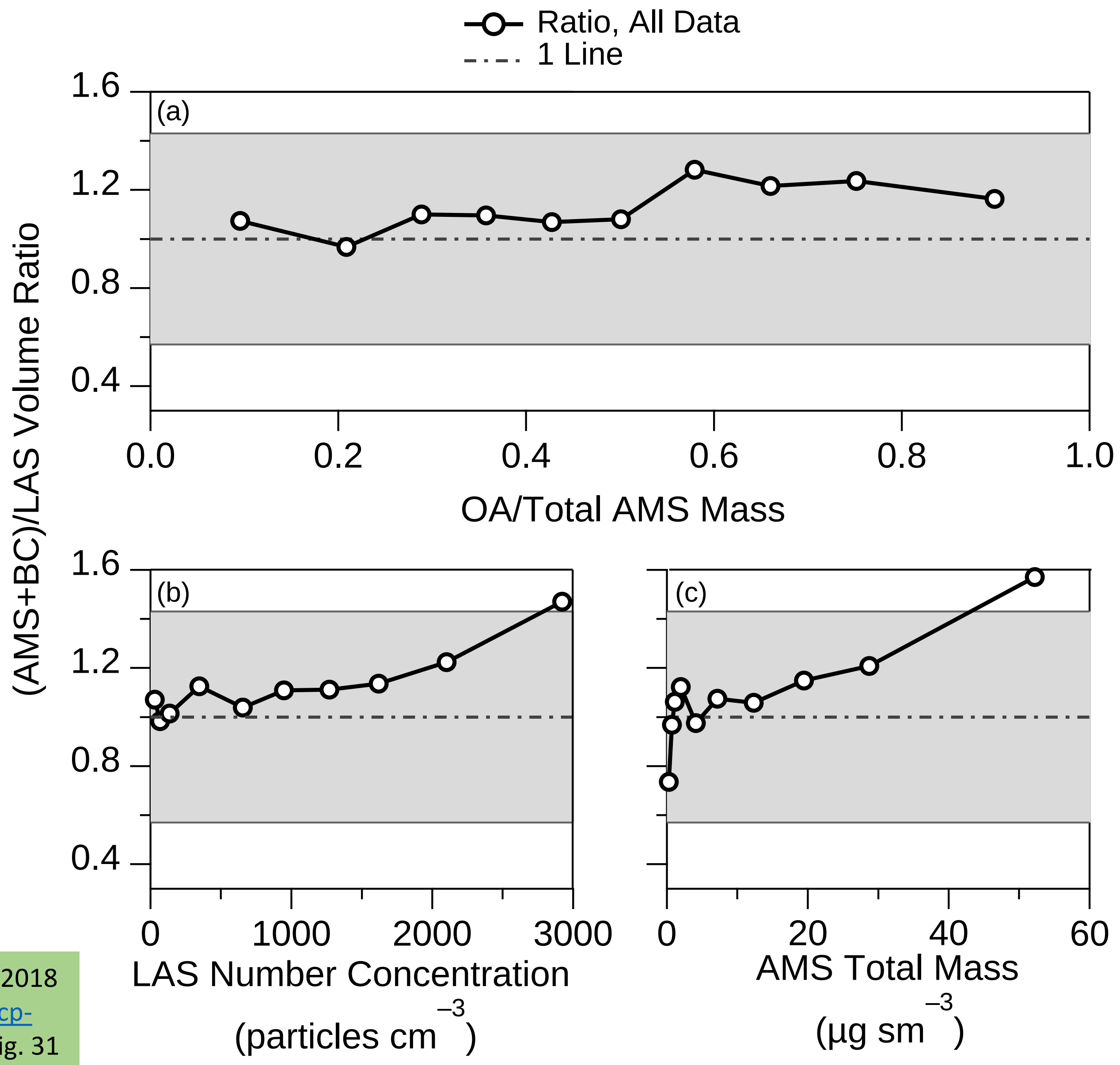
Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf

Comparison of total PM_1 versus optical volume measurement



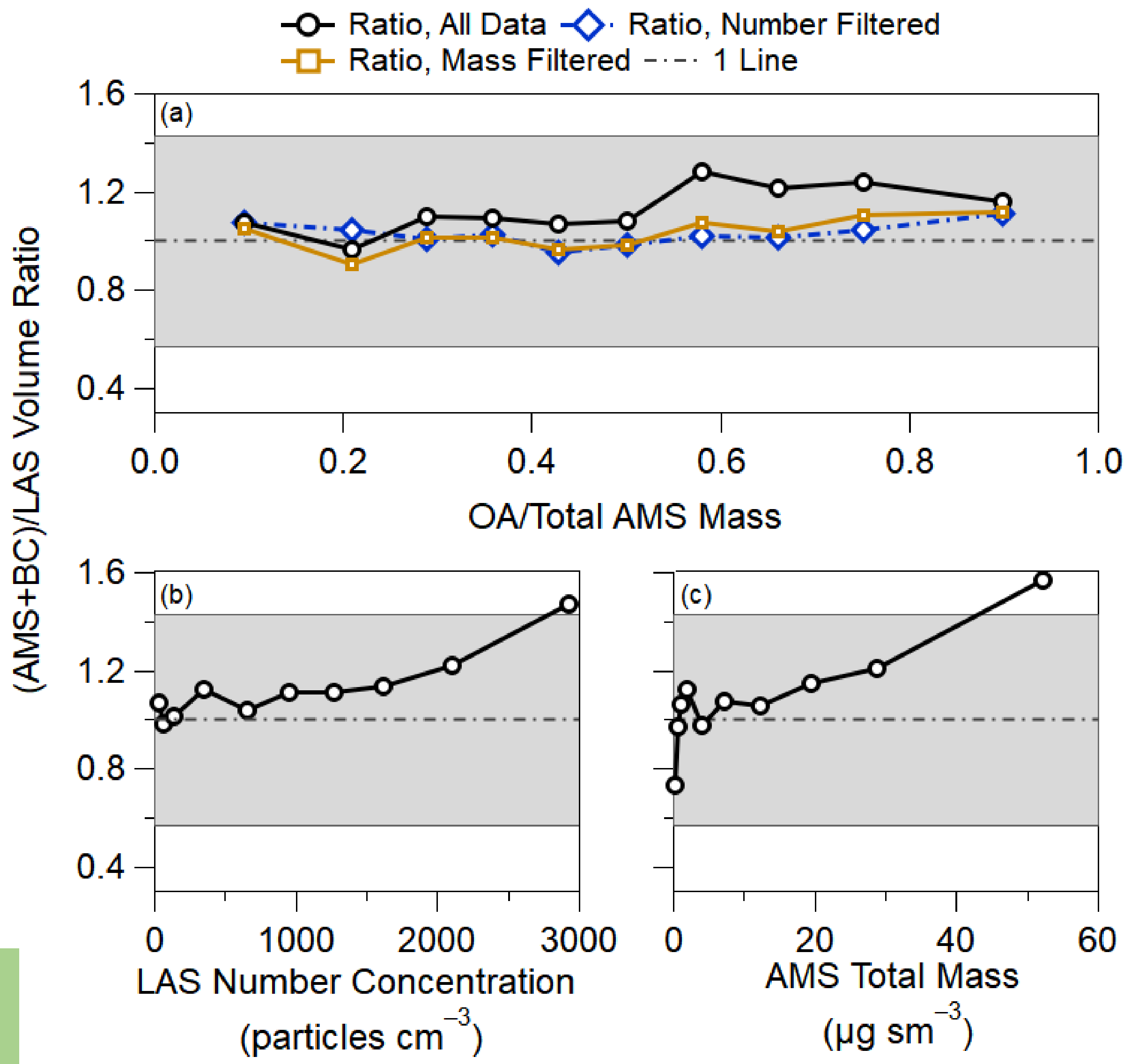
Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig 30

Investigating whether Organic RIE caused the discrepancy



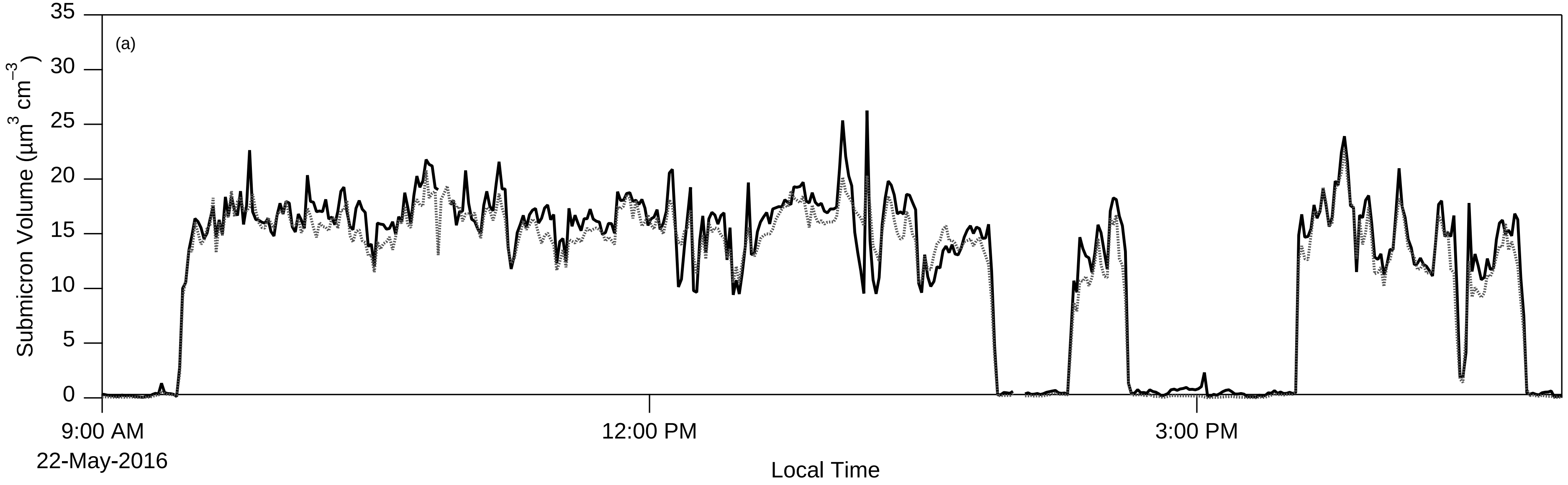
Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig. 31

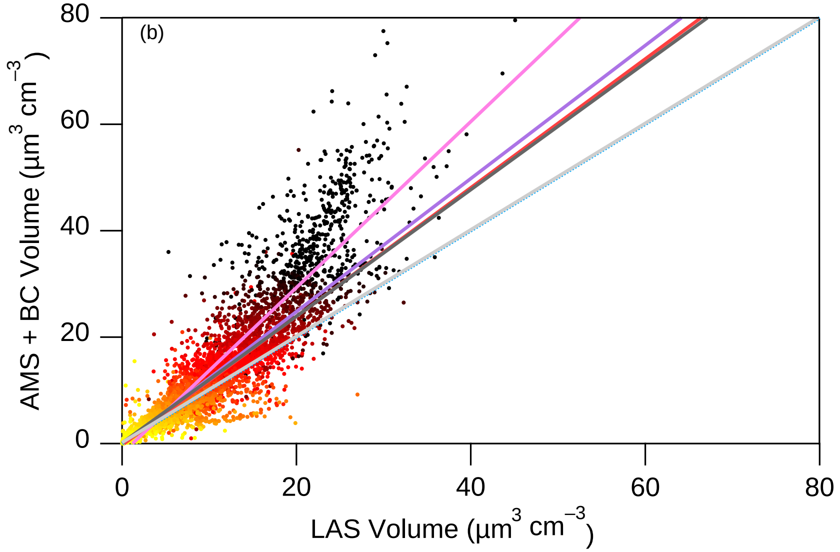
Instead, it appears that optical saturation of the LAS is causing the discrepancy



Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig. 31

Improved slopes when saturation is taken into account





Legend

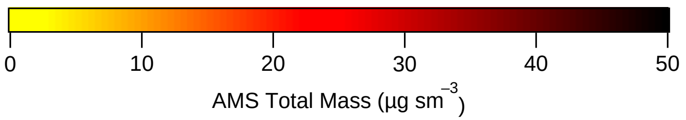
LAS Volume — AMS + BC Volume

1:1 Line — All Data: y = 1.56(±0.01)*x–1.88(±0.13); R^2 = 0.86

Filtered by #: Slope = 1.25, R^2 = 0.85

Filtered by Mass (40): Slope = 1.21, R^2 = 0.87

Filtered by Mass (20): Slope = 1.00, R^2 = 0.79



Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/acp-2018-838-supplement.pdf, SI Fig. 31

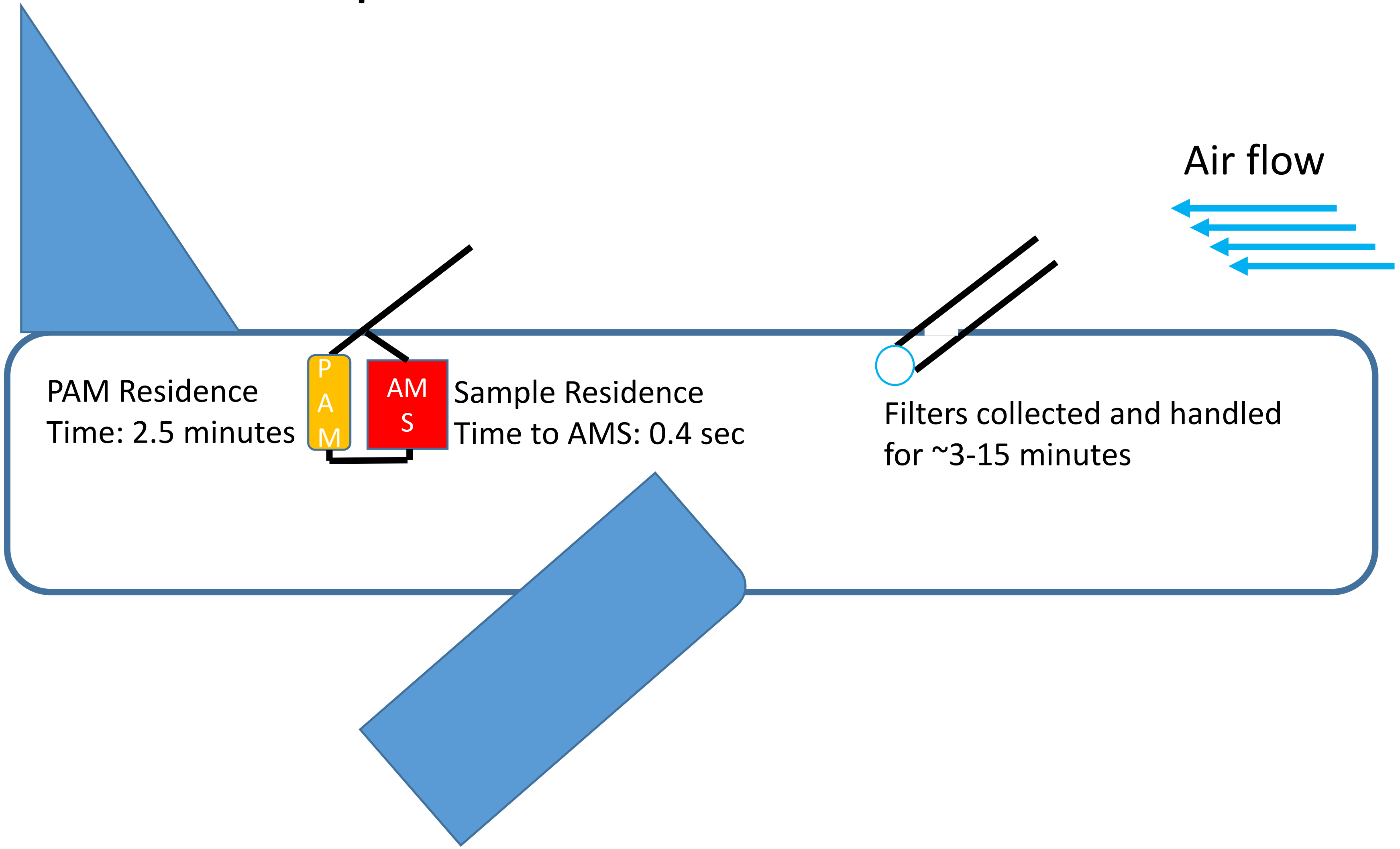
Conclusions for first order intercomparisons

- Be aware of size cut-offs prior to comparisons
  - E.g., optical particle counters have a lower size cut that's often larger than the small size cut for the AMS
  - OPCs measure particles above the AMS size range
- Be aware of other instrumental limitations
  - OPCs can easily saturate under moderately polluted conditions. OPC operators are not always aware of this, and it is easy to blame the AMS

Nault, Campuzano-Jost, Jimenez et al., ACPD, 2018
https://www.atmos-chem-phys-discuss.net/acp-2018-838/

Filters

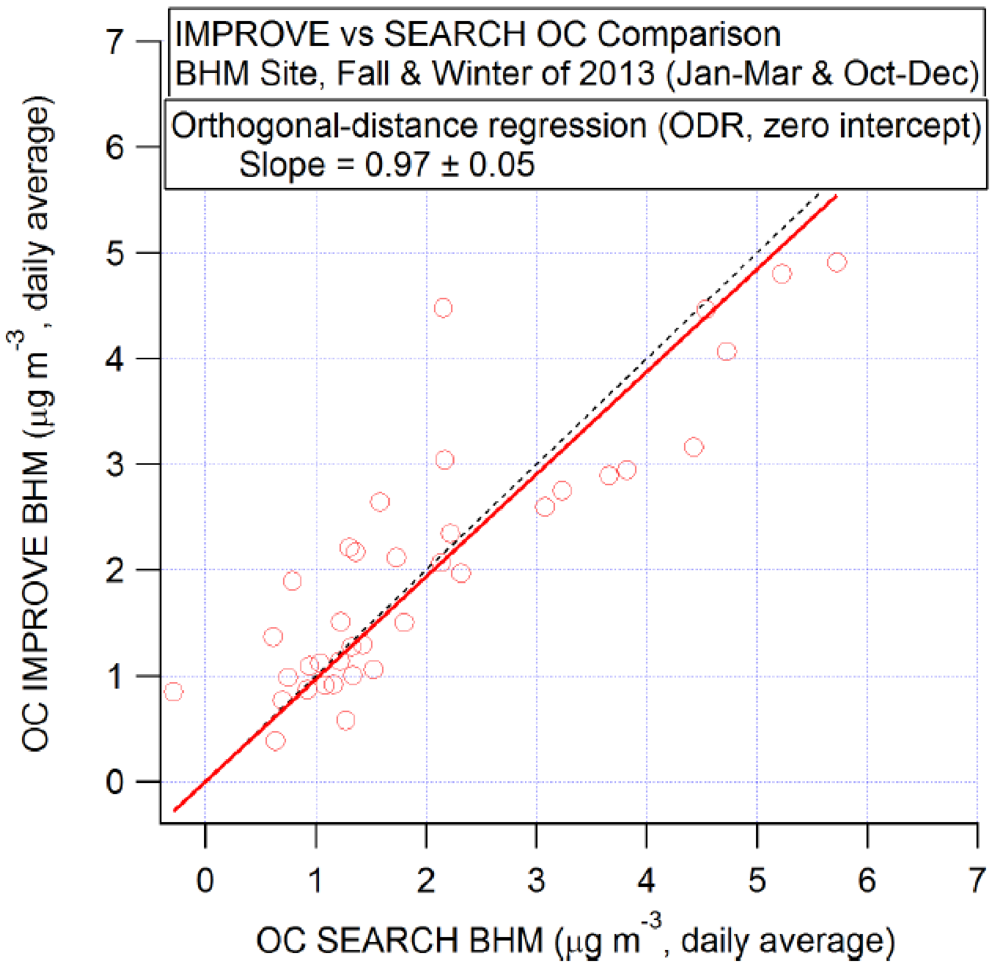
Aircraft OFR Operation



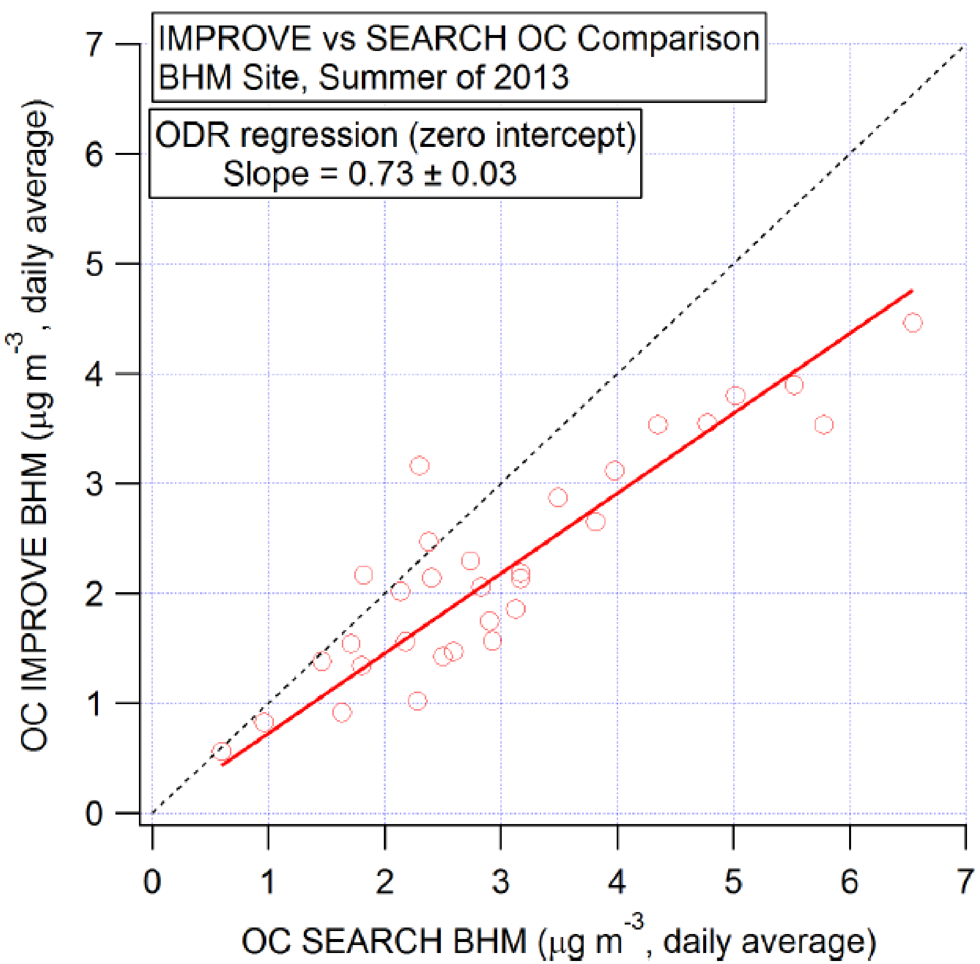
Losses of organic aerosol mass during hot periods due to evaporation

Sit in the field at ambient T for few days after sampling, shipped without refrigeration

FALL & WINTER 2013



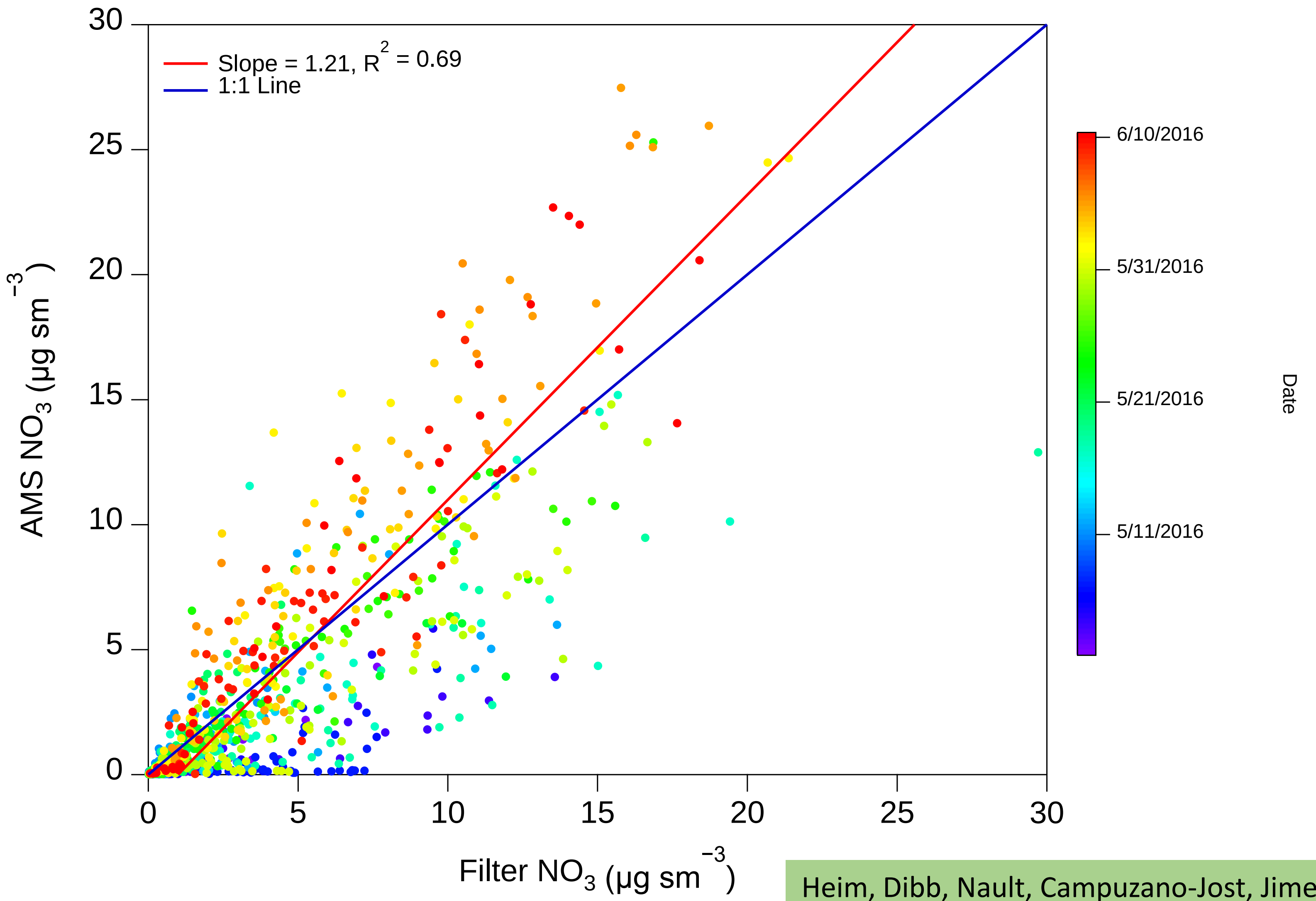
SUMMER 2013



Kim, Campuzano-Jost, Jimenez et al., ACP, 2015

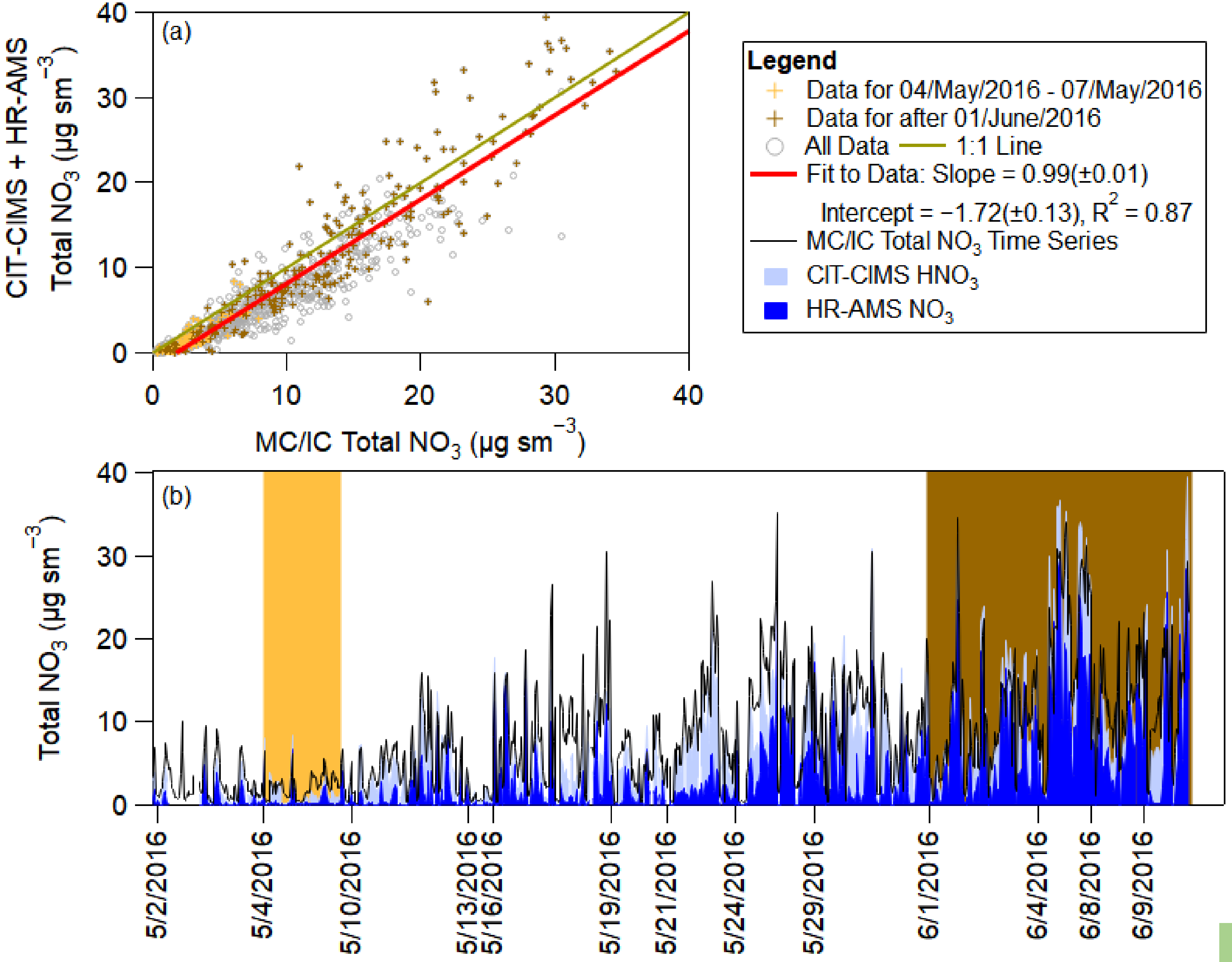
Measured in situ every 1 hr

Comparison of AMS and filter NO_3 measured on airplane changed with date



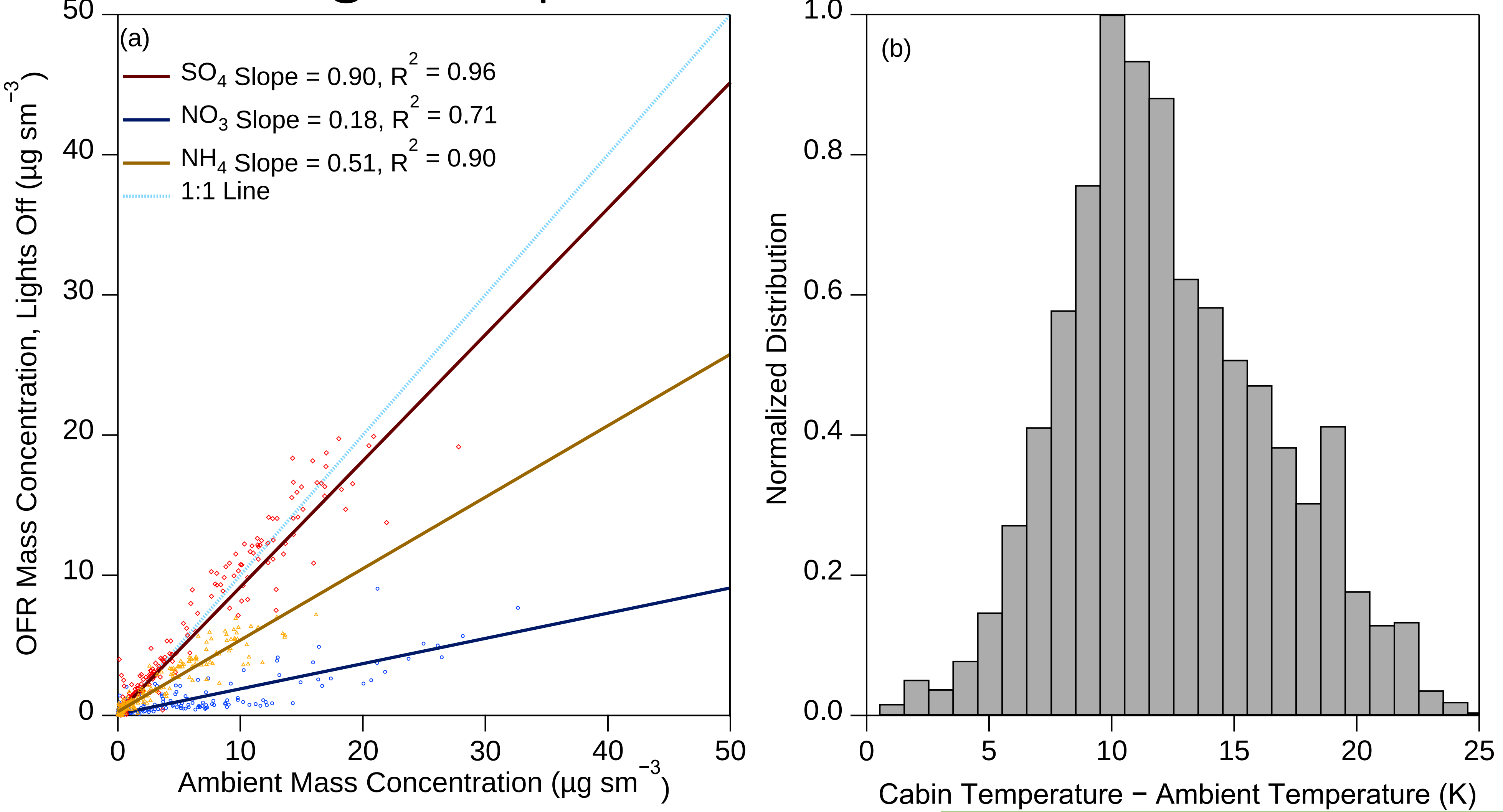
Heim, Dibb, Nault, Campuzano-Jost, Jimenez et al., JGR, in review

However, total nitrate (PM_1 NO_3 + HNO_3) agreed throughout campaign



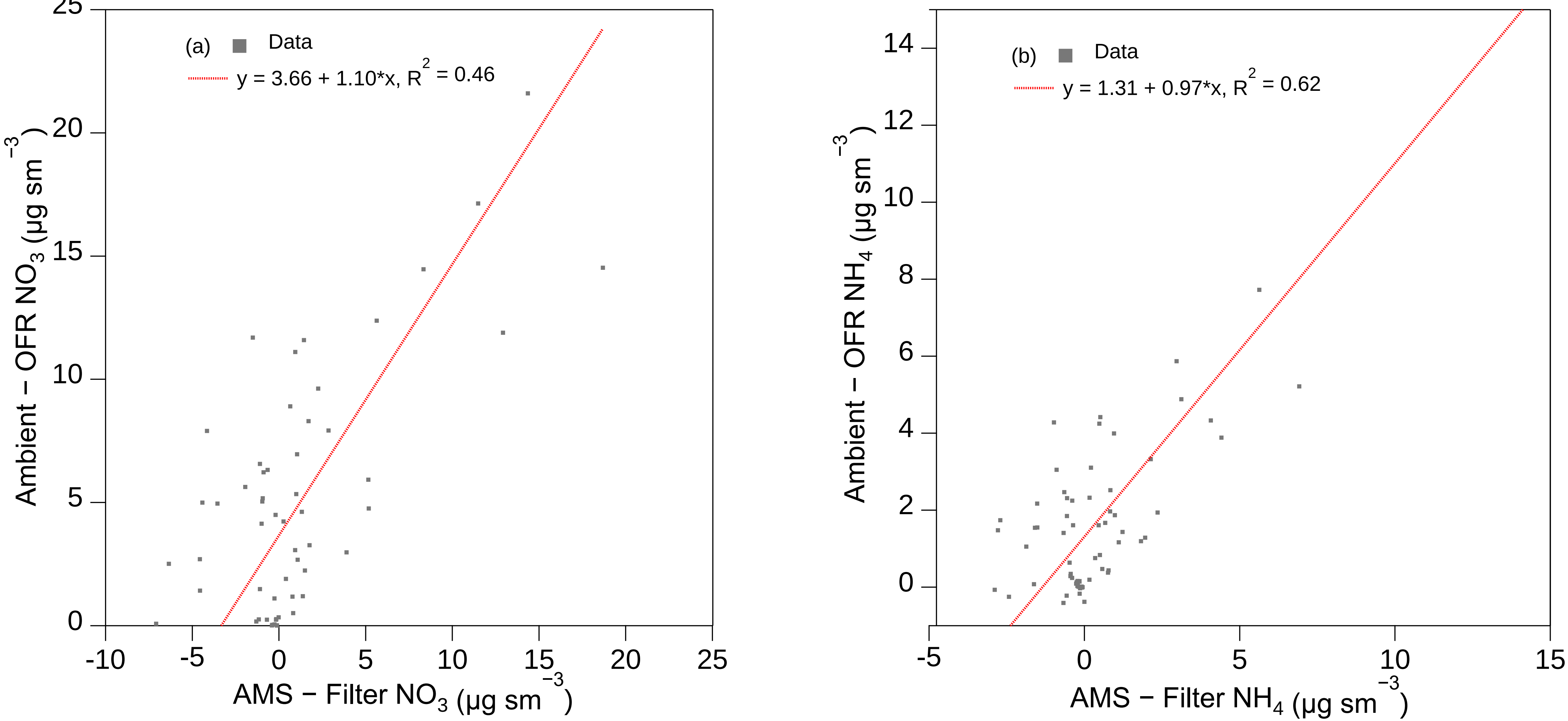
Heim, Dibb, Nault, Campuzano-Jost, Jimenez et al., JGR, in review

Ammonium nitrate shows large losses in non-chemistry OFR as there was a large temperature difference



Heim, Dibb, Nault, Campuzano-Jost, Jimenez et al., JGR, in review

Differences between OFR and Ambient are same as differences between Filter and Ambient



Heim, Dibb, Nault, Campuzano-Jost, Jimenez et al., JGR, in review

Conclusions for comparisons with filter measurements

- Though not shown here, be aware what size cut-off is for filters vs AMS
- BE CAREFUL:
  - Be aware sampling time and handling of filters. May cause evaporation of aerosol species.
  - Also, handling of filters may lead to other forms of biases (positive or negative)
    - E.g. if particles are very acidic, filters will pick up NH_3(g) from human breath etc., and show particles that are more neutralized than what the AMS sees