CHRISTMAN FIELD OPTICAL MONITORING STUDY

William C. Malm, Bret A. Schichtel, Anthony J. Prenni, Derek Day, Elisabeth Andrews, Russel Perkins, Amy Sullivan, Mark Tigges

Interpretation and Use of

Purple Air Measurements

Integrating Nephelometer Measurements

Photo of NGN integrating nephelometer

PurpleAir – Inexpensive Air Quality Sensor

PROBLEM

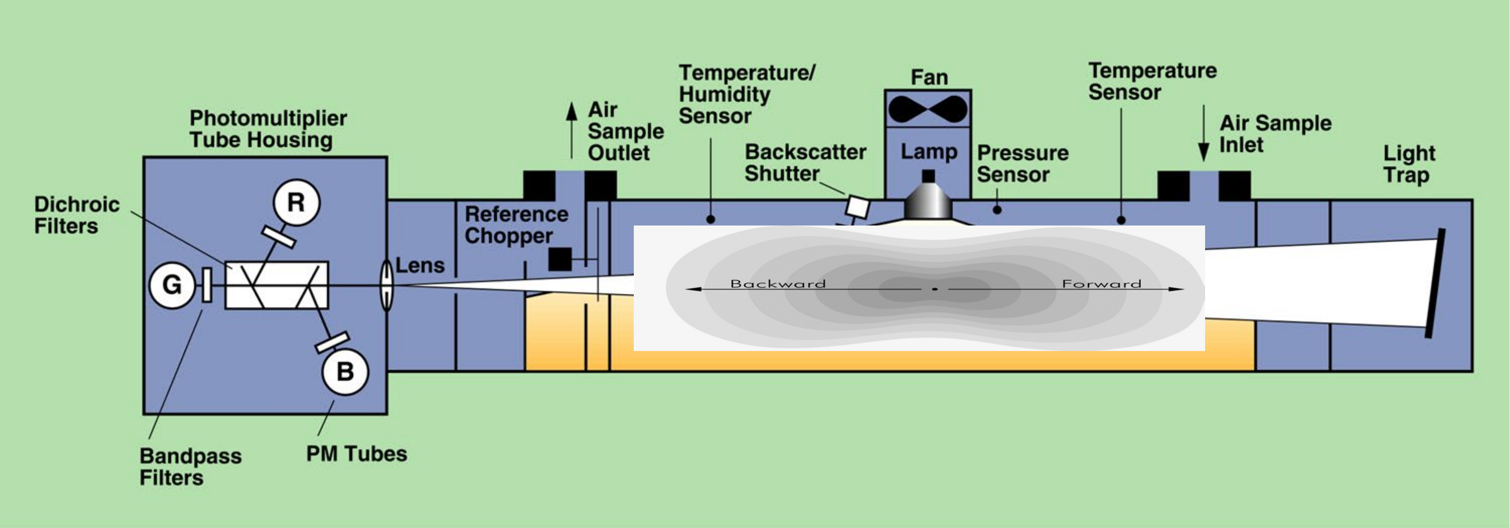
The NGN open air nephelometer was designed in early 90's and is no longer manufactured and spare parts are no longer available for repair. Question is: What type of instrument to replace the NGN with?

What is best way to cost effectively estimate PM levels in National Park Units? Purple Air?

Implemented a small measurement program to resolve nephelometer differences

- Operated five nephelometers under different environmental conditions
- IMPROVE particle monitors
- PILS one-hour inorganic aerosol concentrations
- Particle size distributions (three instruments)
- Operated a number of Purple Air monitors to better understand their limitations and operating characteristics

Schematic Diagram of an Integrating Nephelometer



TSI 3 wavelength Neph

2WIN 2 wavelength Neph

Open Air Optec 1 wavelength Neph

Question is: What type of instrument to replace NGN with?

Design issues

1. Electronic noise
2. Uncertain calibration numbers
3. Not Lambertian light source
4. Truncation error
5. Wavelength uncertainty
6. Inlet uncertainty
7. Temp and pressure variability
8. Inadvertent heating and modification of sample

Issue 1 – 7

- **Well characterized for TSI (Considered Gold Standard)**
- **Partially characterized for NGN and 2WIN**

Issue 8

- **Really not addressed for TSI and 2WIN – very important for NPS**

Objectives of nephelometer measurements

- Track changes in bsp (visibility) over time and space
- Verify optical models relating bsp to atmospheric particle concentrations
- Track changes in $f(RH) = b_{sp}(RH)/b_{sp}(dry)$ (climate forcing and visibility) over time and space

Problem and Design criteria

- Verify optical models:
  - Don't know the chemical and physical properties of aerosol – **primarily chamber RH issue**
  - Volatilization of particles from heating.
- Track bsp:
  - If goal is to link bsp changes to atmospheric aerosol concentration, then RH in chamber should be near one. RH variability confounds relationship.
  - If goal is to link bsp changes to visibility RH in chamber should be ambient.
  - At very least RH should be held at some predetermined level (RH<40%)
- Track f(RH): Reference bsp should be at RH near 1 and no inadvertent heating.

Nephelometer Issues from NPS perspective

- NPS and IMPROVE primarily use the nephelometer to verify the link between measured speciated particle concentrations and bsp (visibility)

OLD:

$$b_{ext} \approx 3 \times f(RH) \times [(NH_4)_2SO_4] + 3 \times f(RH) \times [NH_4NO_3] + 4 \times [POM] + 10 \times [LAC] + 1 \times [Soil] + 0.6 \times [CM] + 0.01.$$

Current:

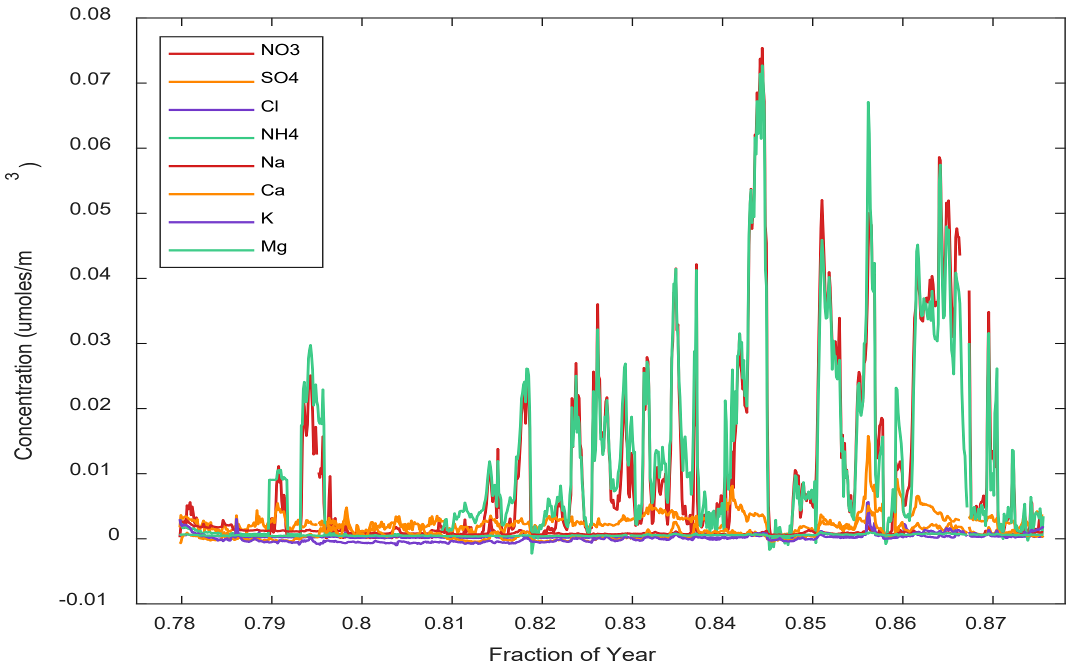
$$b_{ext} \approx 2.2 \times f_S(RH) \times [\text{small sulfate}] + 4.8 \times f_L(RH) \times [\text{large sulfate}] + 2.4 \times f_S(RH) \times [\text{small nitrate}] + 5.1 \times f_L(RH) \times [\text{large nitrate}] + 2.8 \times [\text{small POM}] + 6.1 \times [\text{large POM}] + 10 \times [LAC] + 1 \times [\text{soil}] + 1.7 \times f_{SS}(RH) \times [\text{sea salt}] + 0.6 \times [CM] + \text{Ray} + 0.33 \times [NO_2\ (\text{ppb})$$

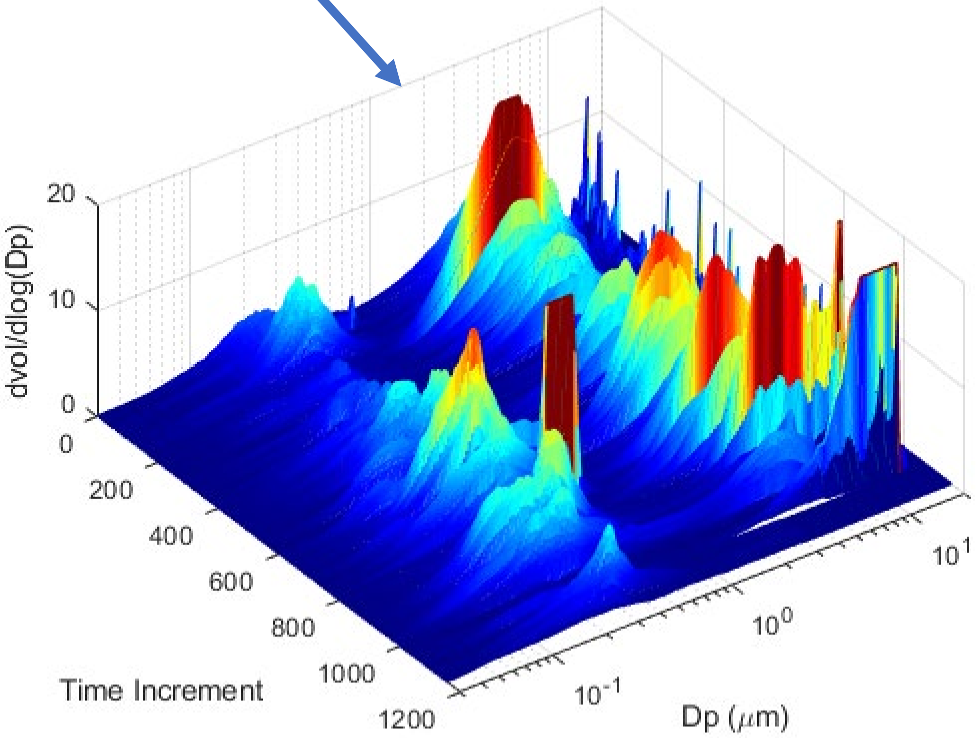
f(RH) terms

- Need to make bsp measurements at near ambient RH which requires precise measurement of scattering chamber RH
- Tracking trends using nephelometer measurements is a secondary objective.

For a one-month period

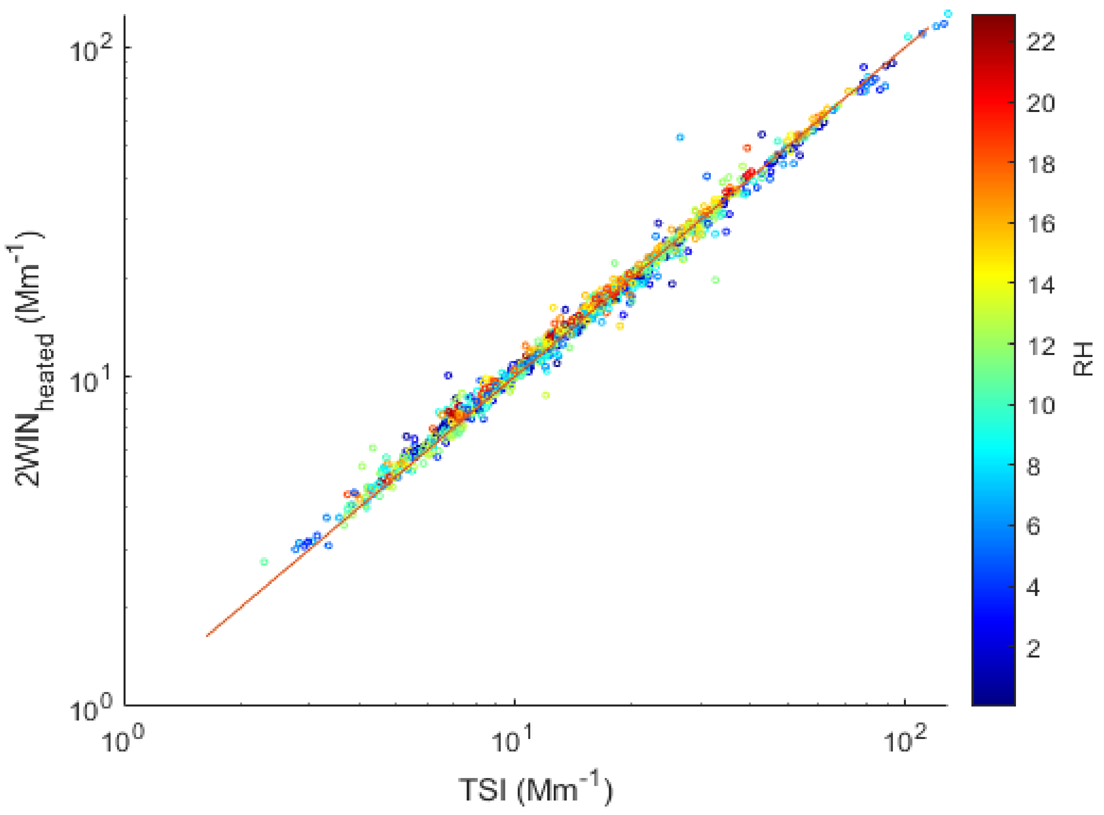
- PILs one hour ion measurements
- Particle number size distribution measurements

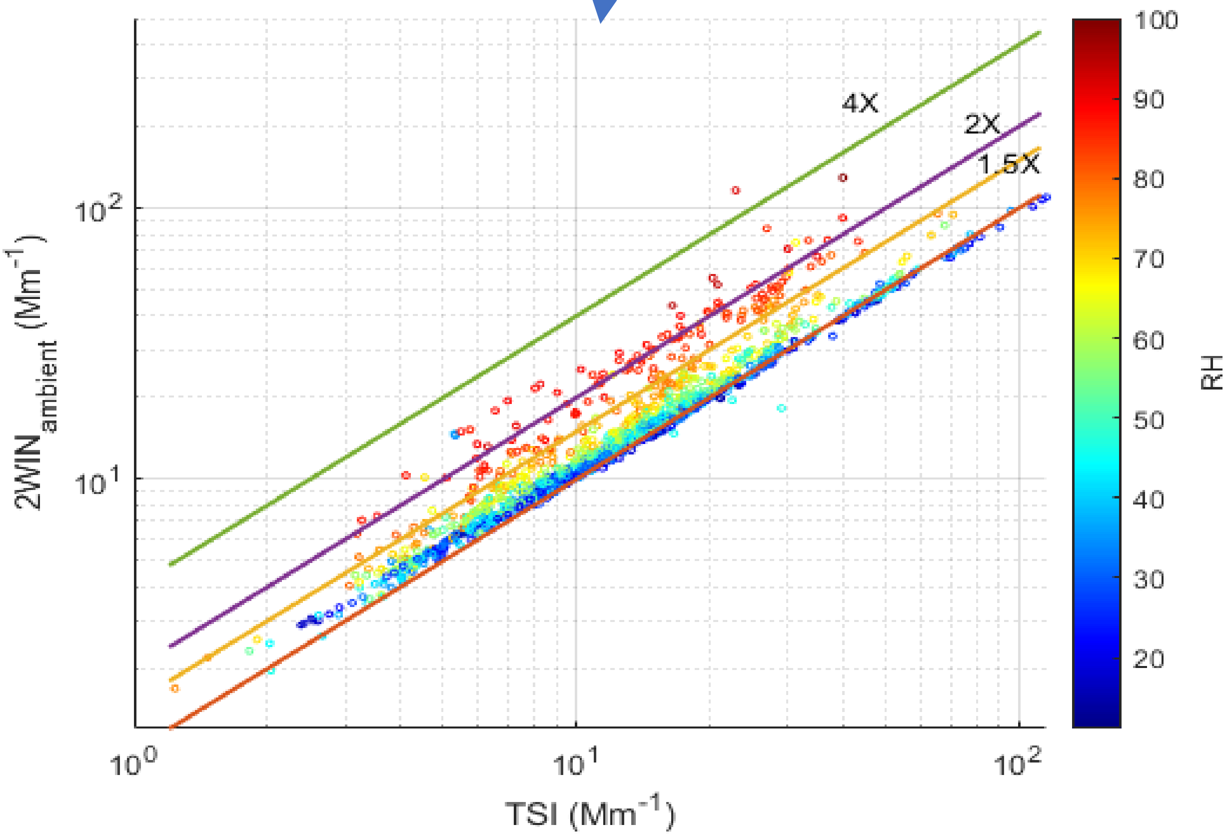




Operated 5 nephelometers

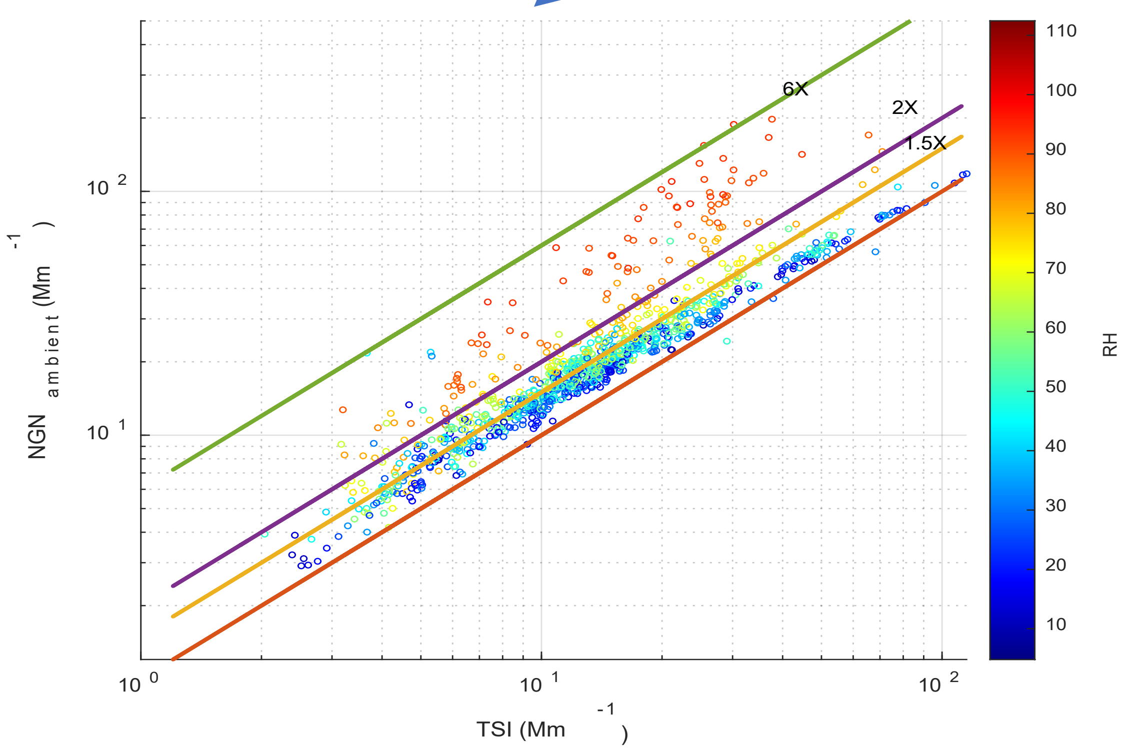
- TSI – inadvertent heating RH<35% - 2.5 um inlet
- 2WIN dry - RH<40% - 2.5 um inlet
- 2WIN ambient – Some heating – 2.5 um inlet
- NGN dry - heating to reduce RH – 2.5 um inlet
- NGN open

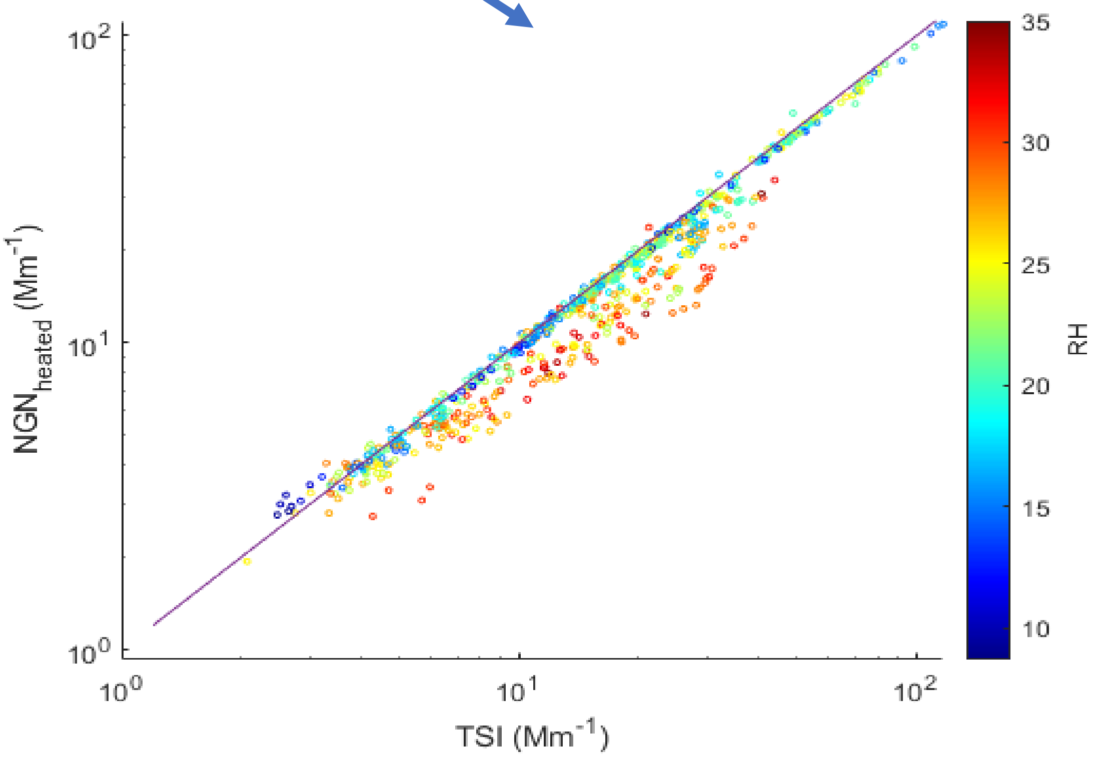




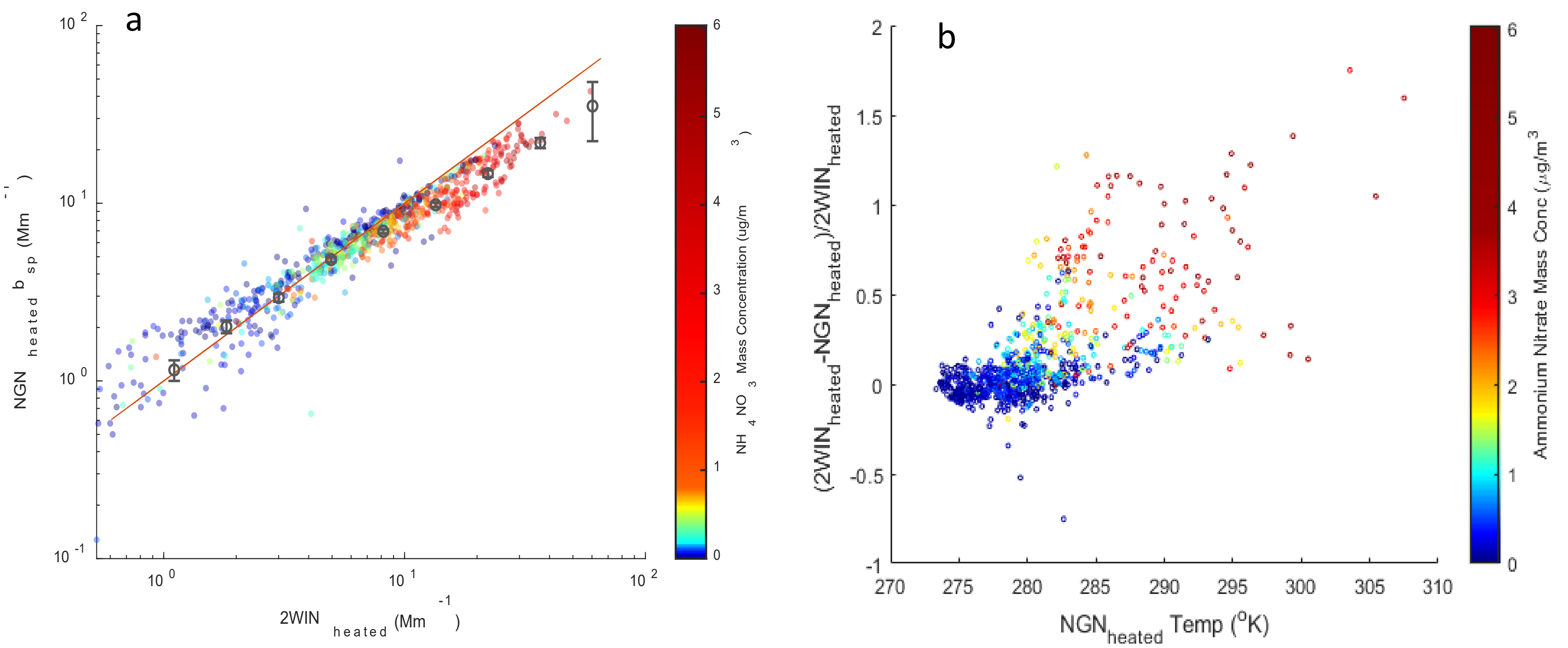
Operated 5 nephelometers

- TSI – inadvertent heating RH<35% - 2.5 um inlet
- 2WIN dry – Heated to reduce RH<40% - 2.5 um inlet
- 2WIN ambient – Some heating – 2.5 um inlet
- NGN dry - heating to reduce RH < 20% – 2.5 um inlet
- NGN open



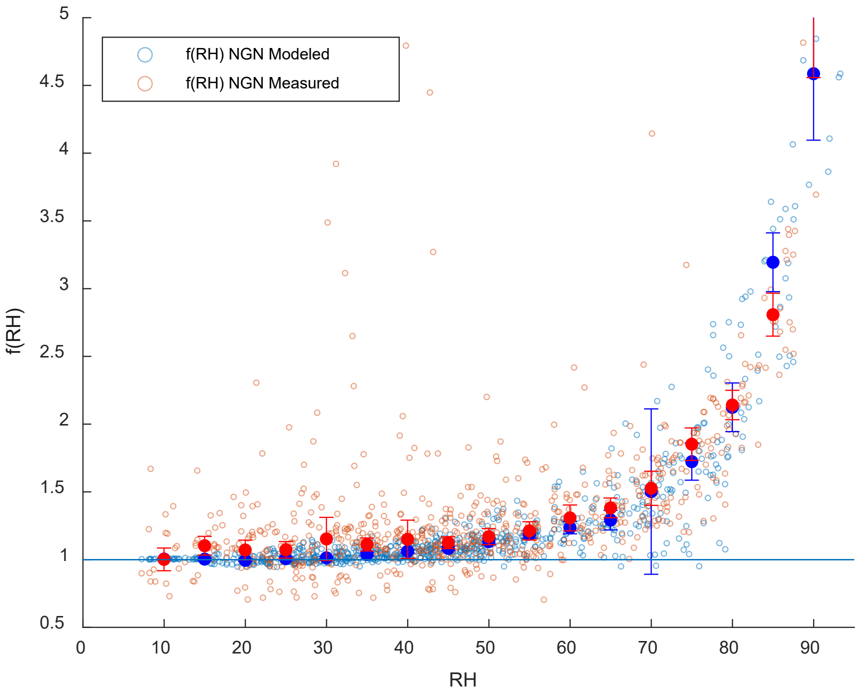


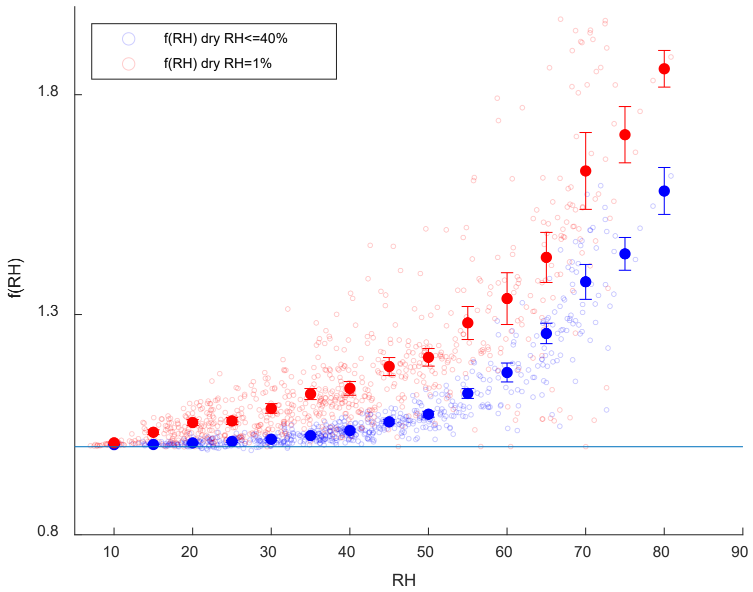
For the time period that particle size and composition were measured it appears that the NGN_{heated} nephelometer which was heated to reduce RH to less than 20% volatilized significant fraction of ammonium nitrate.



We were able to resolve all differences between integrating nephelometers based on varying chemical and physical properties in neph scattering chamber

Differences in bsp from nephelometer measurements made at the same time but varying chemical and physical characteristics of the aerosol.





What did we learn?

- Confidence in all nephelometers to accurately measure bsp of aerosol in chamber but with varying precision and MDL (Can model if you know the chemical and physical properties of the aerosol in the chamber)
- Nephelometers to measure truly ambient air are not manufactured
- All commercially available nephelometers heat (reduce humidity) to some extent
- All commercially available nephelometers will require an inlet (2.5 um)
- 2WIN instrument is accurate and precise with a very low MDL

Decision

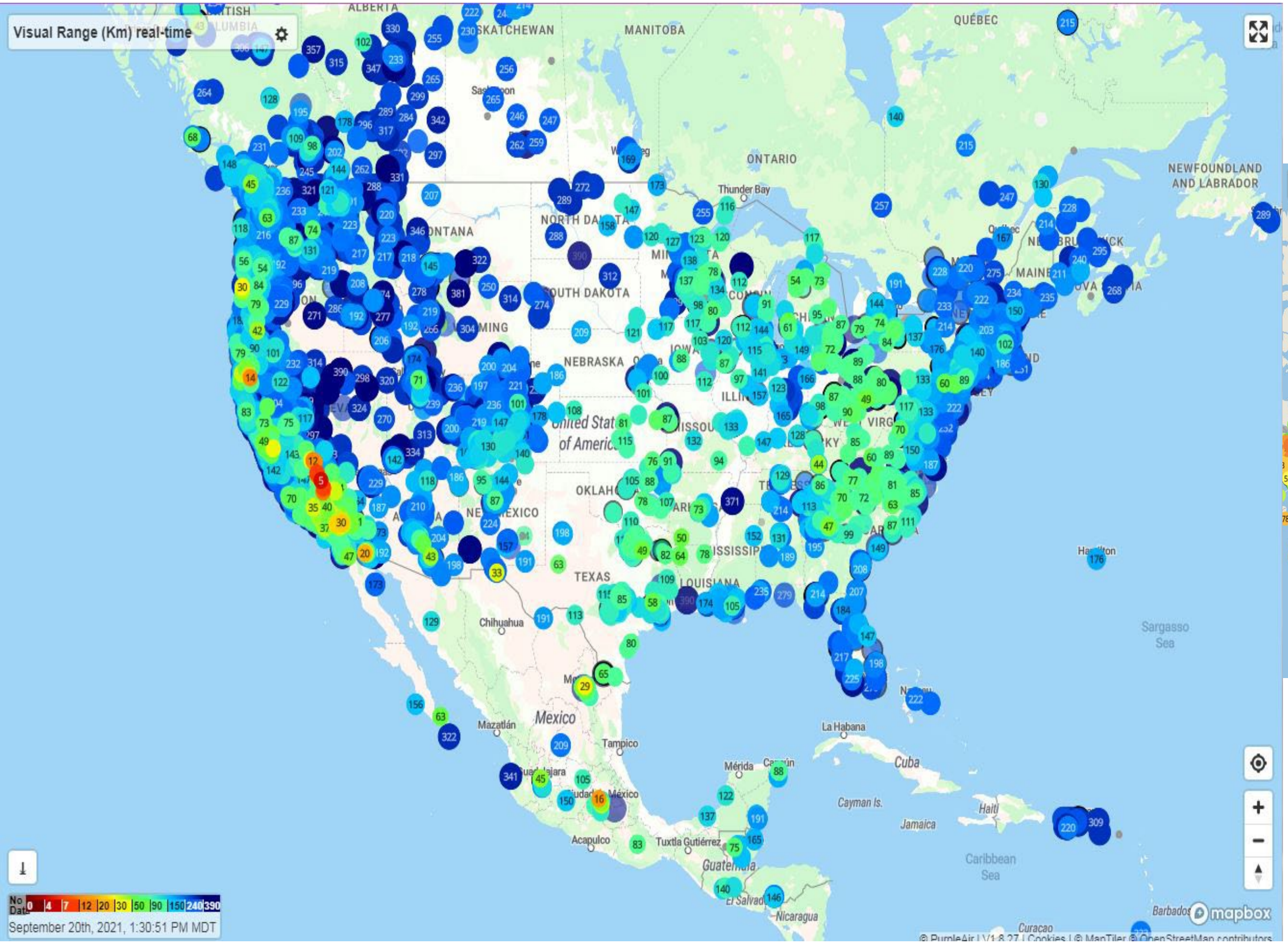
- Run 2WIN with 2.5 um inlet at near ambient conditions as possible
- Measure temperature and RH in or near the sampling chamber with high degree of accuracy

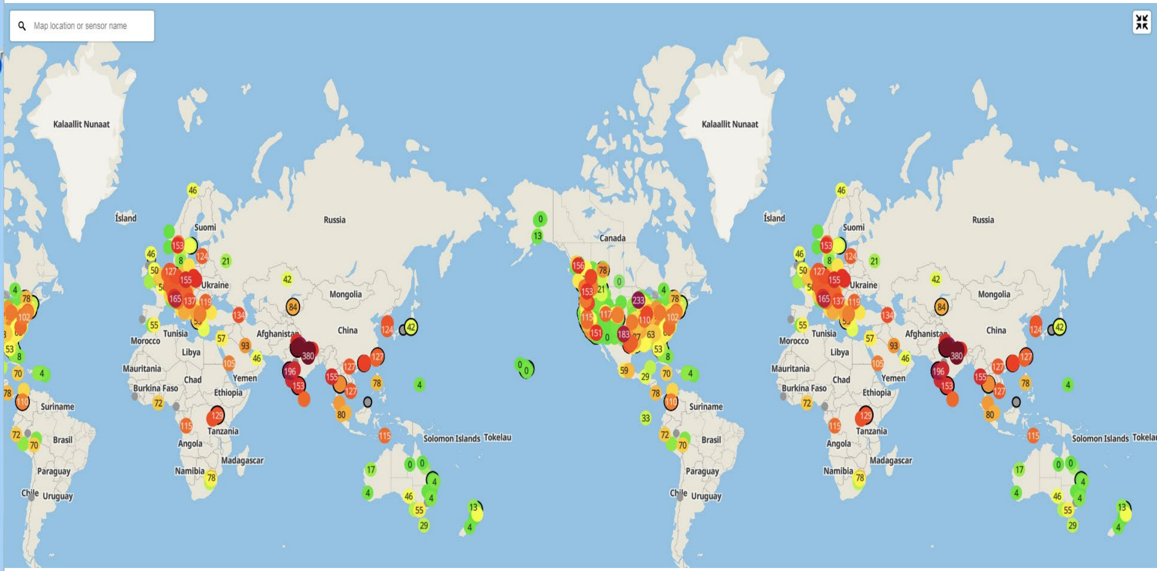
PurpleAir

PurpleAir – Inexpensive Air Quality Sensor

- PurpleAir (https://www2.purpleair.com/)
  - "A proven air quality monitoring solution for home enthusiasts and air quality professionals alike"
  - "Using a new generation of laser photometers to provide real-time measurement.
- The PurpleAir sensor consists of
  - Two Plantower PMS5003 "laser ~~particle counters~~"
  - RH and temperature sensor
  - Data logger – wifi and sd card enabled

Purple Air monitors are deployed around the globe!





Issues to be addressed

- Standard Operating Procedure
  - Deployment protocol
  - How long between servicing
  - Calibration
  - Routine Maintenance
- Acceptance testing – do all PA's report same value
  - How much divergence between instruments is acceptable
  - What is the inherent uncertainty (precision…)
- Accuracy of reported parameters (PM2.5, AQI ……)
  - What can we do to improve accuracy
- How to use PA readings – Important to NPS

What have we learned?

What does the PA purport to measure?

- **For each plantower sensor (A&B) the following parameters are reported (from the measurement of ONE photodiode voltage)**

- **AQI (3 of them)**
- **PM1.0 ug/m3**
- **PM2.5 ug/m3**
- **PM10 ug/m3**
- **>=0.3um#/dl (CH1A)**
- **>=0.5um#/dl (CH2A)**
- **>=1.0um#/dl (CH3A)**
- **>=2.5um#/dl (CH4A)**
- **>=5.0um#/dl (CH5A)**
- **>=10.0um#/dl (CH6A)**

Fine particulate light scattering (Mm^{-1})

$b_{sp1} = 0.015 * >0.3um$

Deciview (DV)

$DV = 10*\ln((10+1.3*b_{sp1}) / 10)$

Standard Visual Range (km)

$VR = 3900 / (10 + 1.3\ b_{sp1})$

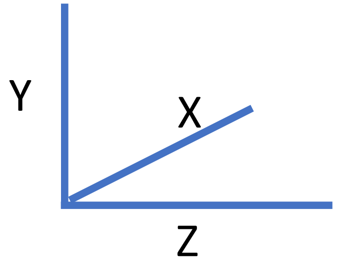
Note, the maximum visual range is 390 km, which occurs at bsp1 = 0, i.e.

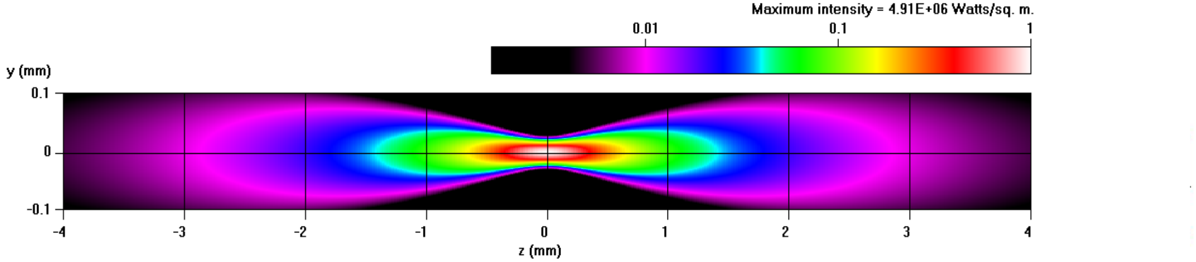
VR = 3900 / (10+0) = 390 km

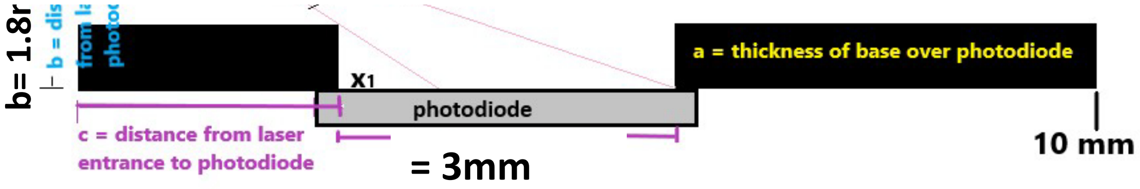
AND with separate sensor

- **Temperature**
- **Humidity**
- **Pressure**

Plantower Scattering Geometry

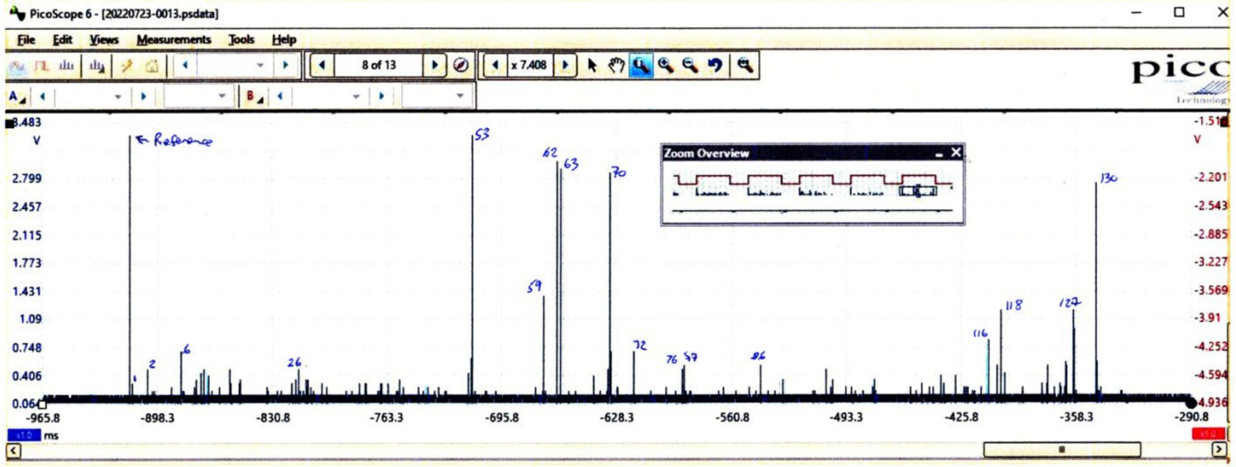






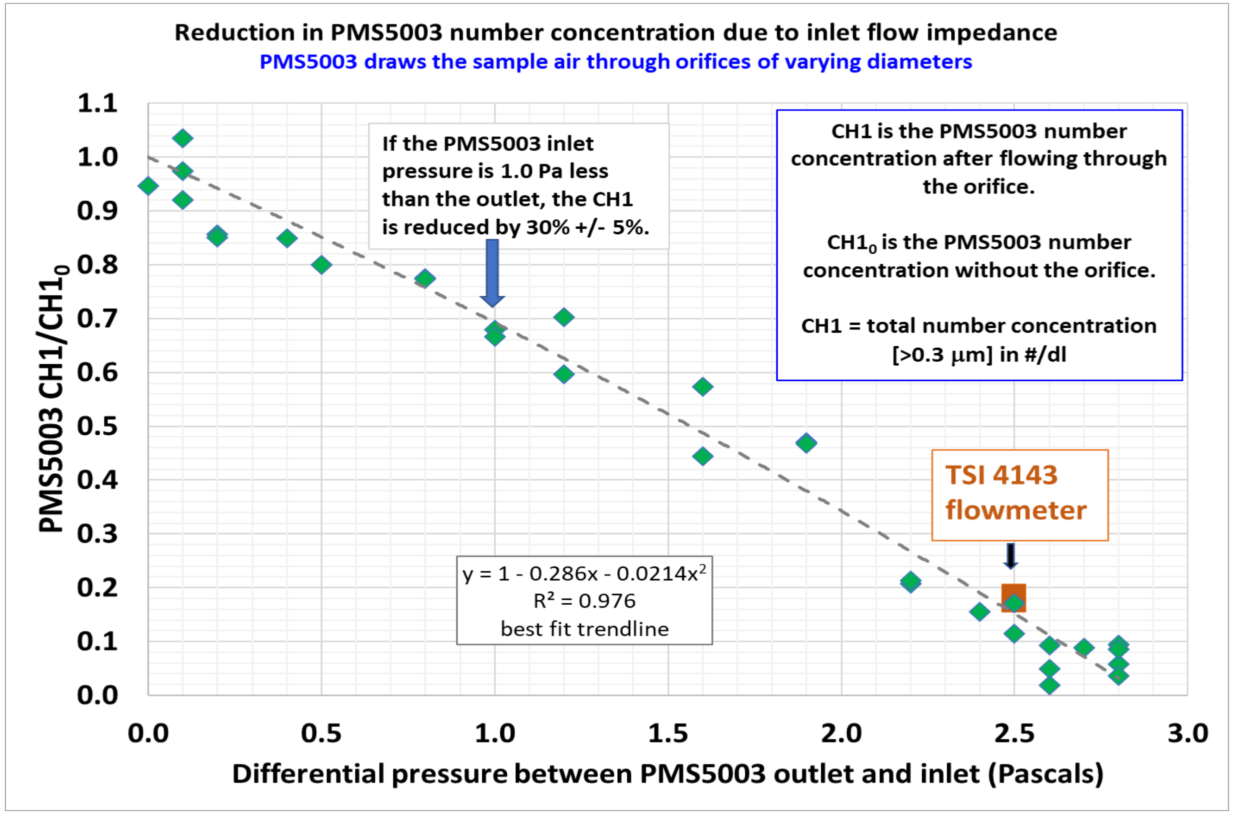
- Laser is focused and polarized perpendicular to plane of incidence
  - At z=0, x=0, y=0, Int=100
  - At z=1mm, x=0, y=0, Int=0.60
  - At z=0, x=0.1, y=0, Int=10^{-23}

Detected pulses associated with particles passing through the laser

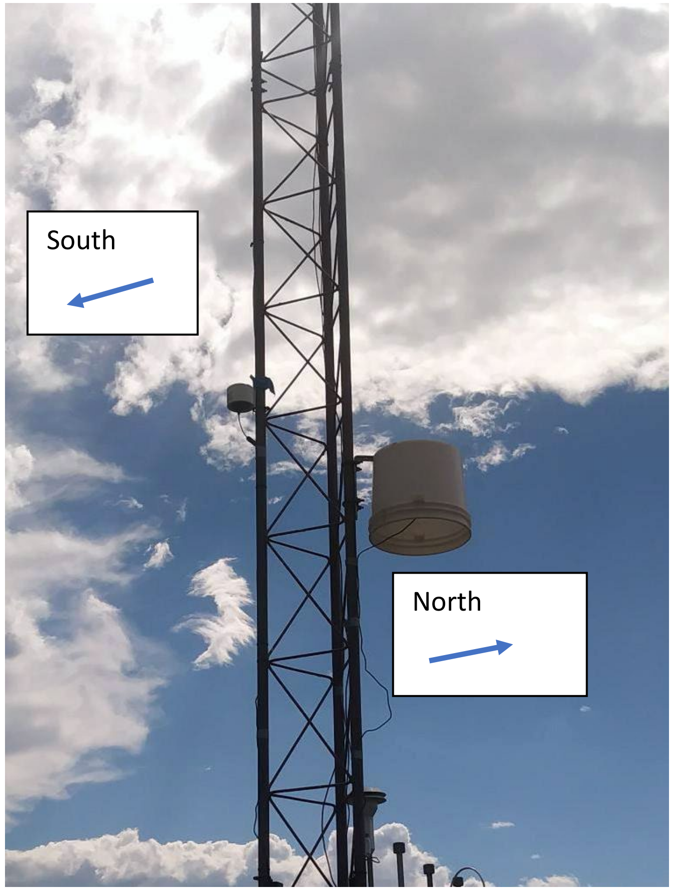


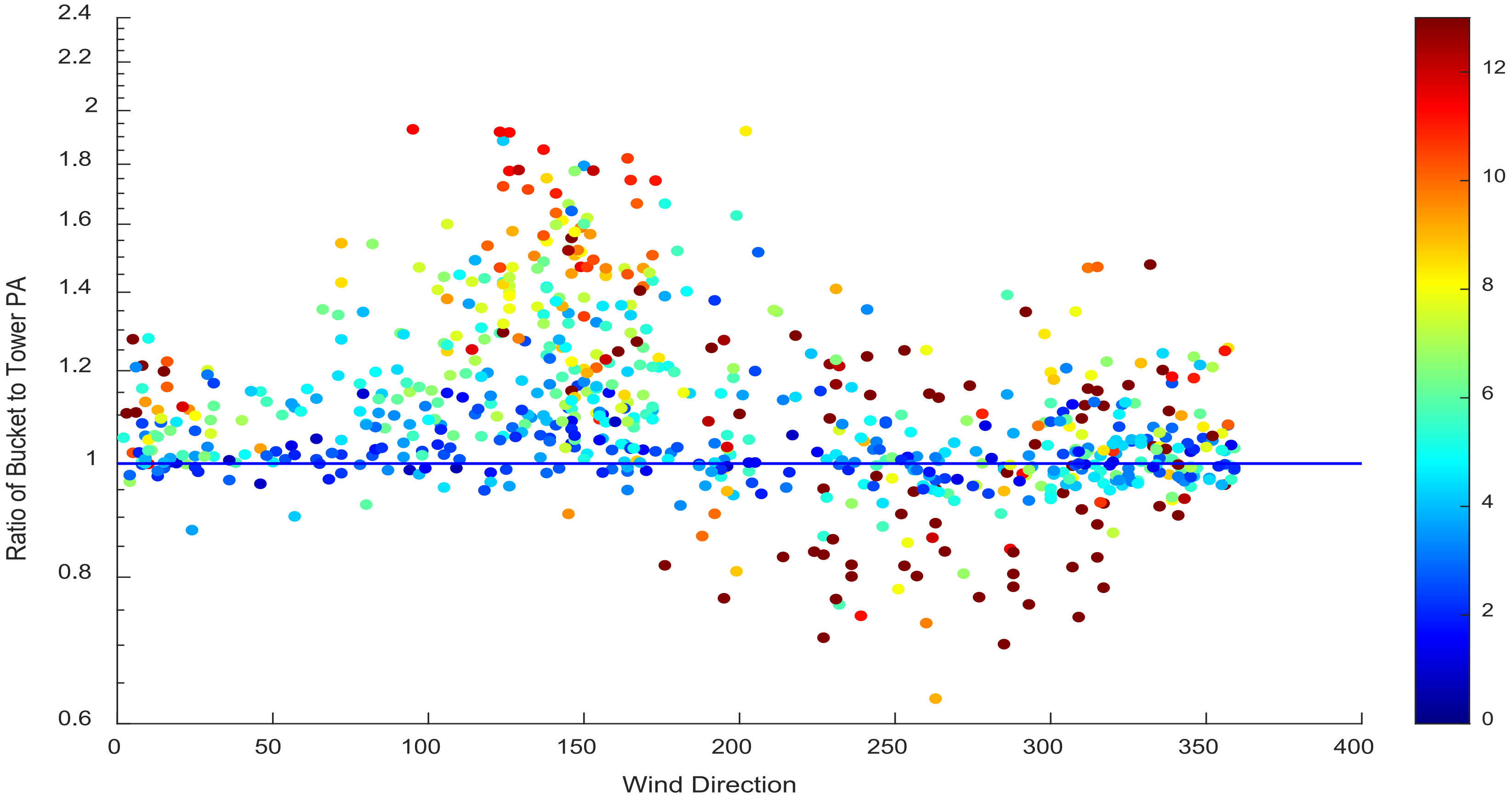
- Only pulse heights detected at x, y and z = 0 and associated with particles 0.3 um or greater are counted.
- Larger particles detected at x, y, z ≥ 0 generate pulse heights equal to or greater than a 0.3 um particle and consequently are over-counted.

PMS output as a function of difference in outlet and inlet pressure (flow rate)



Purple Air Wind Shield Measurements

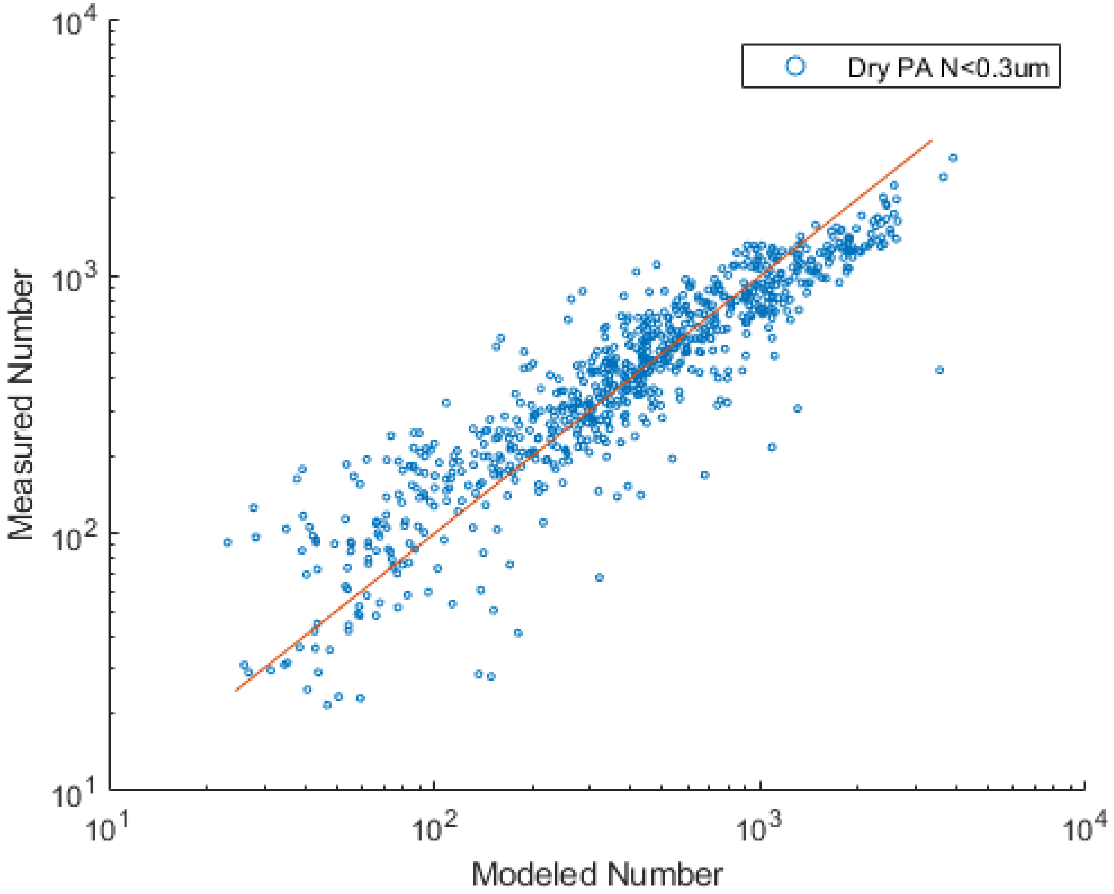


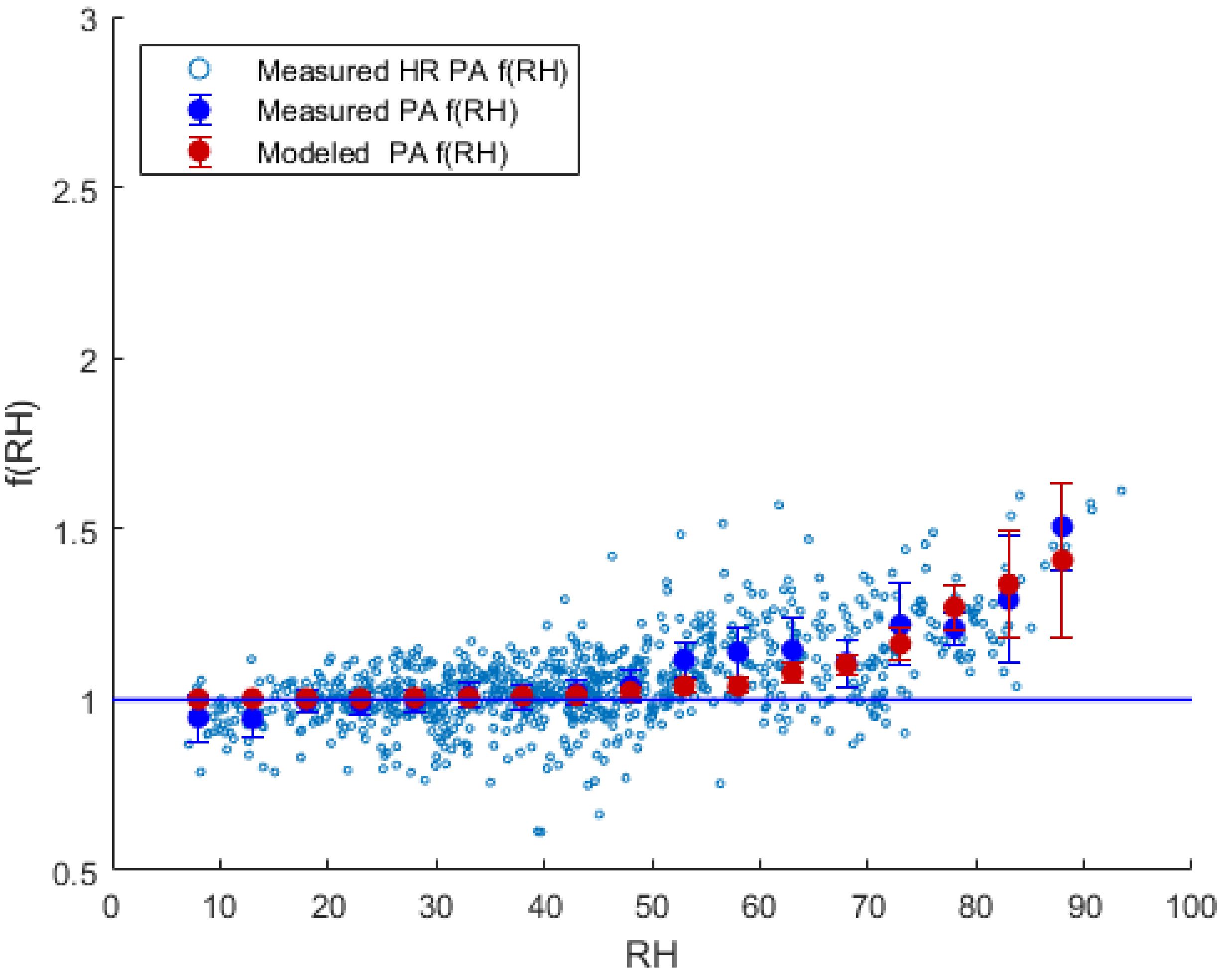


Cannot Calibrate in the classic sense

- Introduction of calibration gases PA resets to zero
- Alternatives
  - bsp lab reference to standard aerosol
  - bsp field reference
  - Other…………

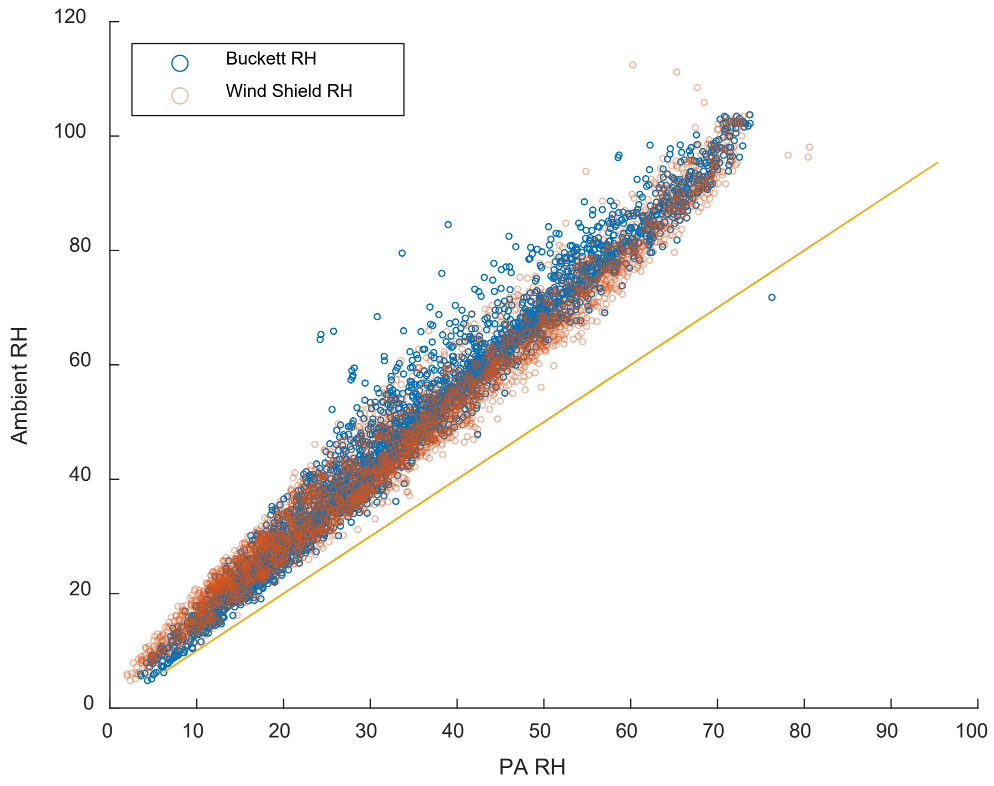
Modeled and measured Number and f(RH) for time period of PILs and size distribution measurements.

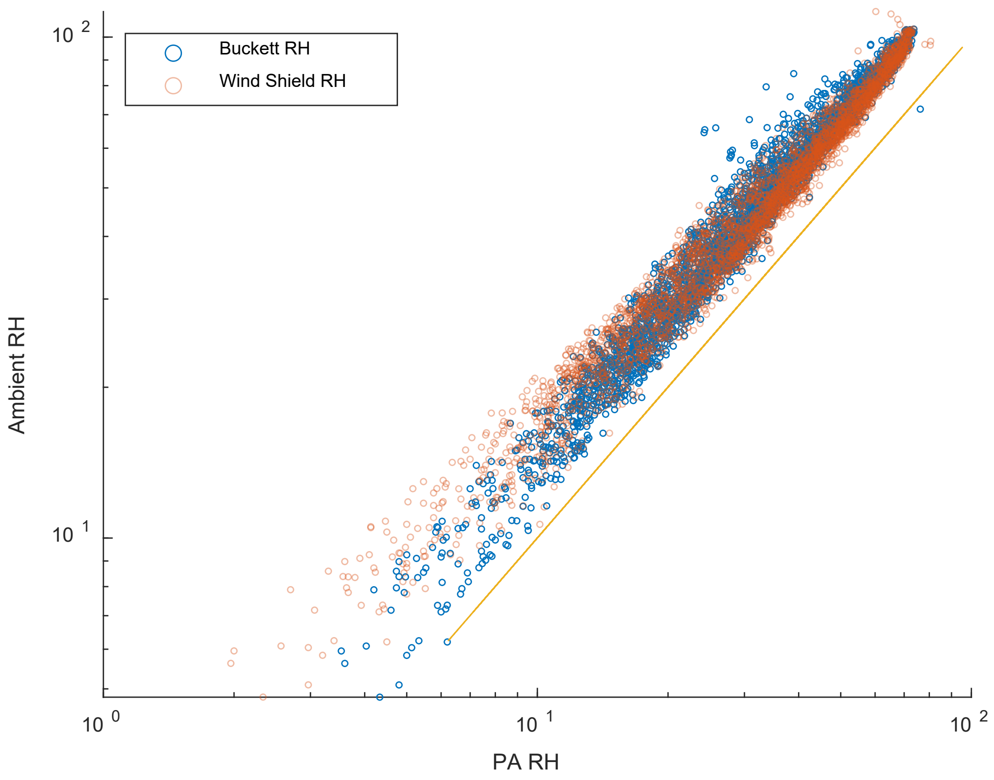




RH reported by all PA's are systematically low by about 20%-30%

AmbientRH≈1.3*PARH+offset





Back to “What have we learned?”

- PA reported RH is systematically 20%-30% low across all sensors
- Very sensitive to meteorological conditions (wind speed and direction)
- All variables are derived from a single sensor output – does not count particles
- High level of precision
- Measures primarily fine particles
- PA relationship to bsp and PM vary by factors of 3 to 4 (300% to400% uncertainty)
- Uncertainty in estimating bsp and PM varies with particle size which may be a function of mass concentration (Is this true for all areas of US and ambient conditions?)
- f(RH) from PA very close to Nephelometer f(RH)

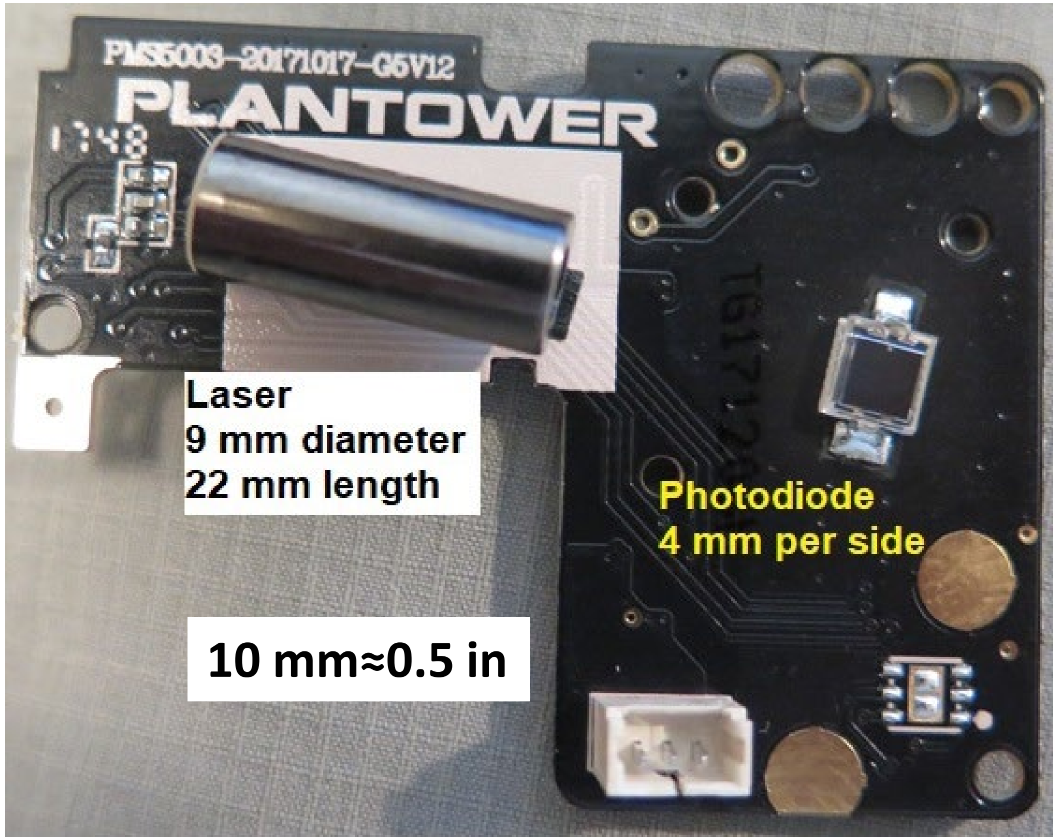
Recommendations

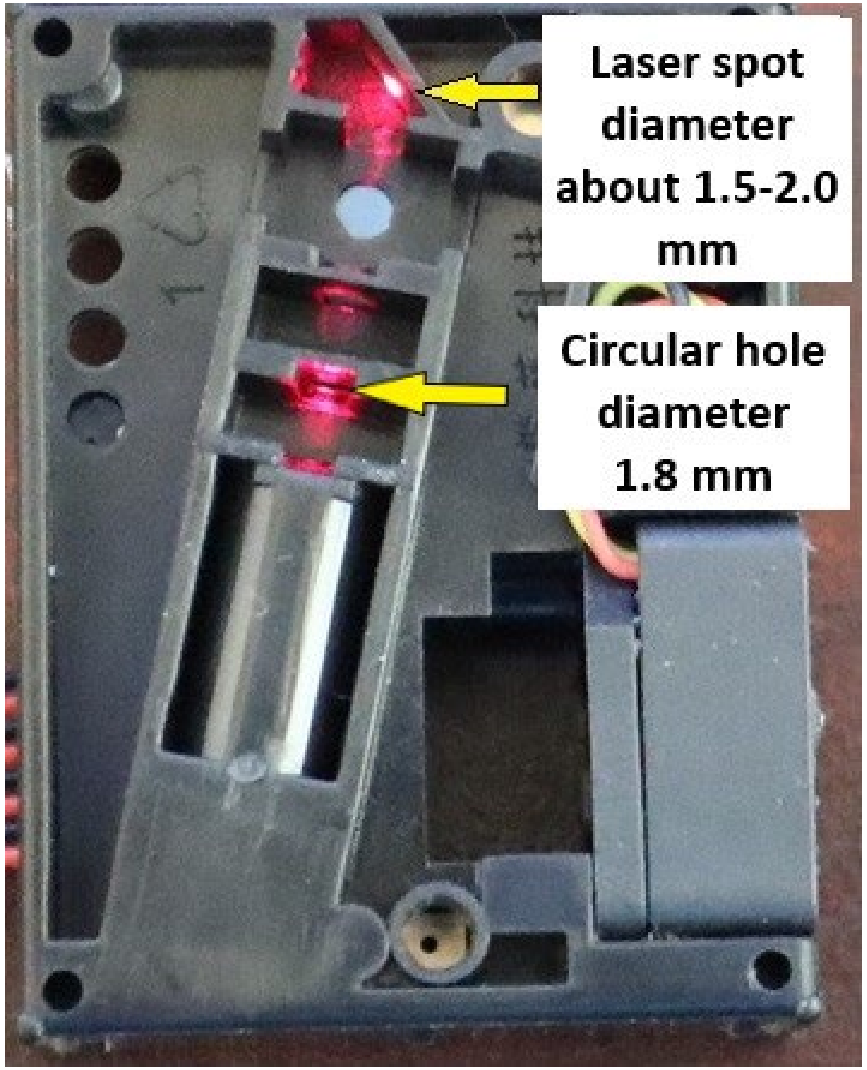
- Calibrate RH sensors before deployment
- Establish acceptable variability for “routine” monitoring
- Deploy only with wind shield (inverted bucket)
- Establish pre deployment calibration protocol
- Develop procedure for measuring “dry” scattering with known accuracy and precision

- **Develop recommendations to NPS users as to how to interpret PA data**
  - **Recommendations to park visitors**
    - For example: We are 90% sure the air is unhealth and there is a 5% chance the air is hazardous. Consider staying indoors and/or wearing masks.
  - **Closure of NPS unit**
    - For example: We are 60% sure that the air is very unhealthy and have closed park entry for x hours or days.

END

Plantower laser-photodiode detector configuration (Laser is polarized perpendicular to the plane of incidence)

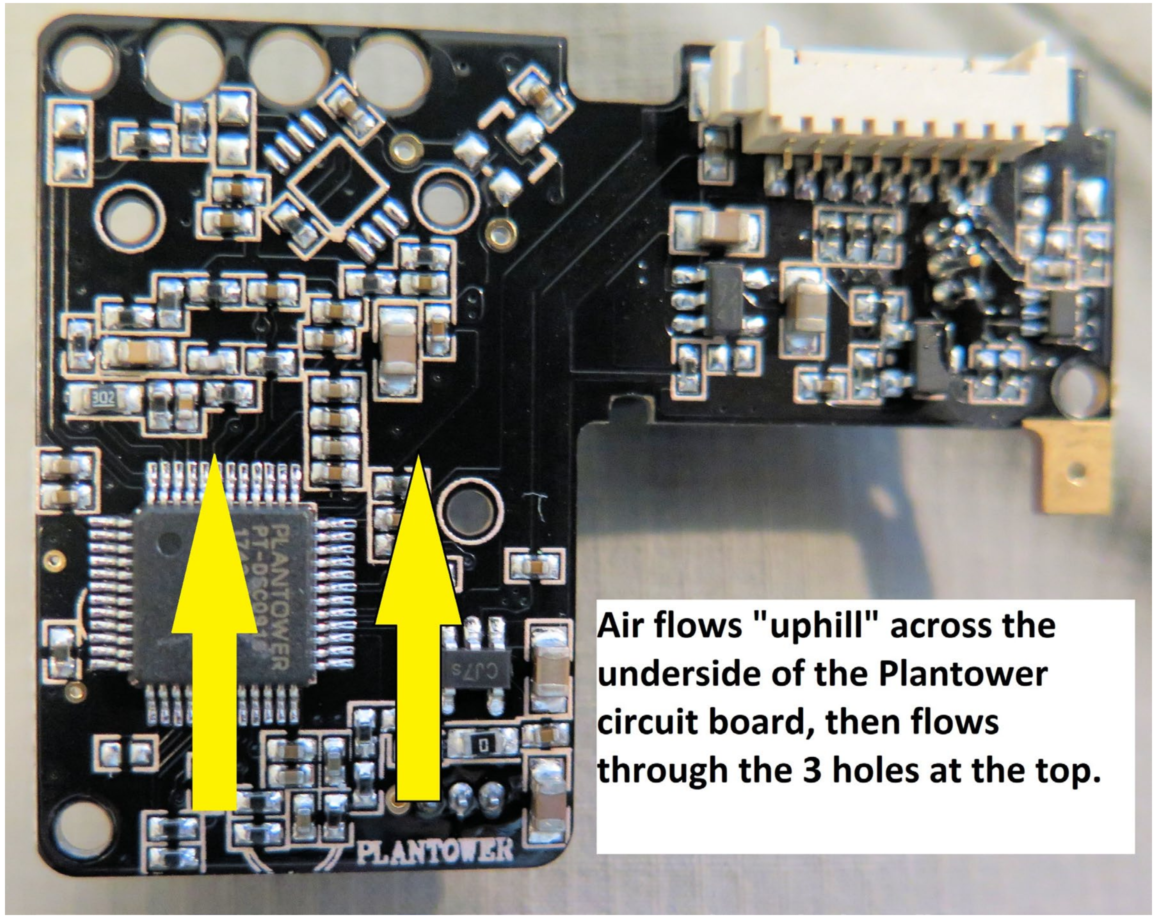


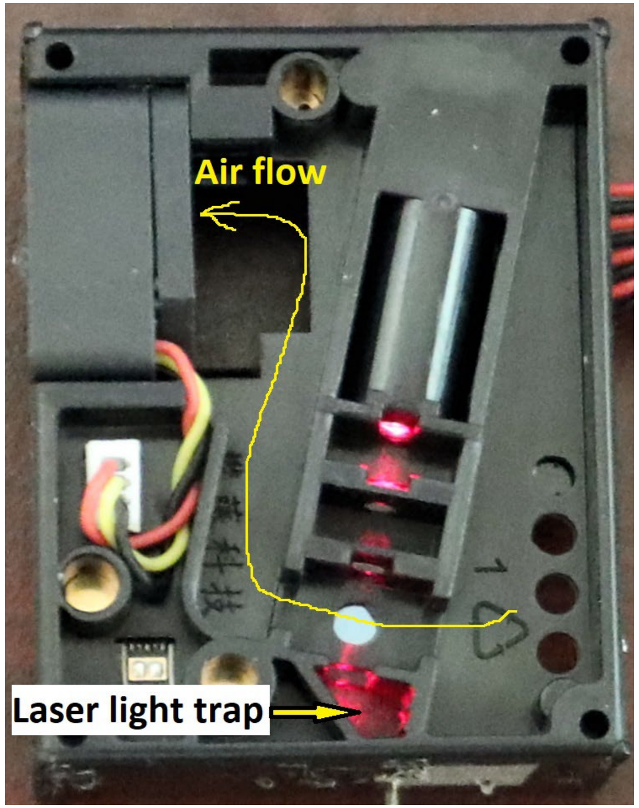


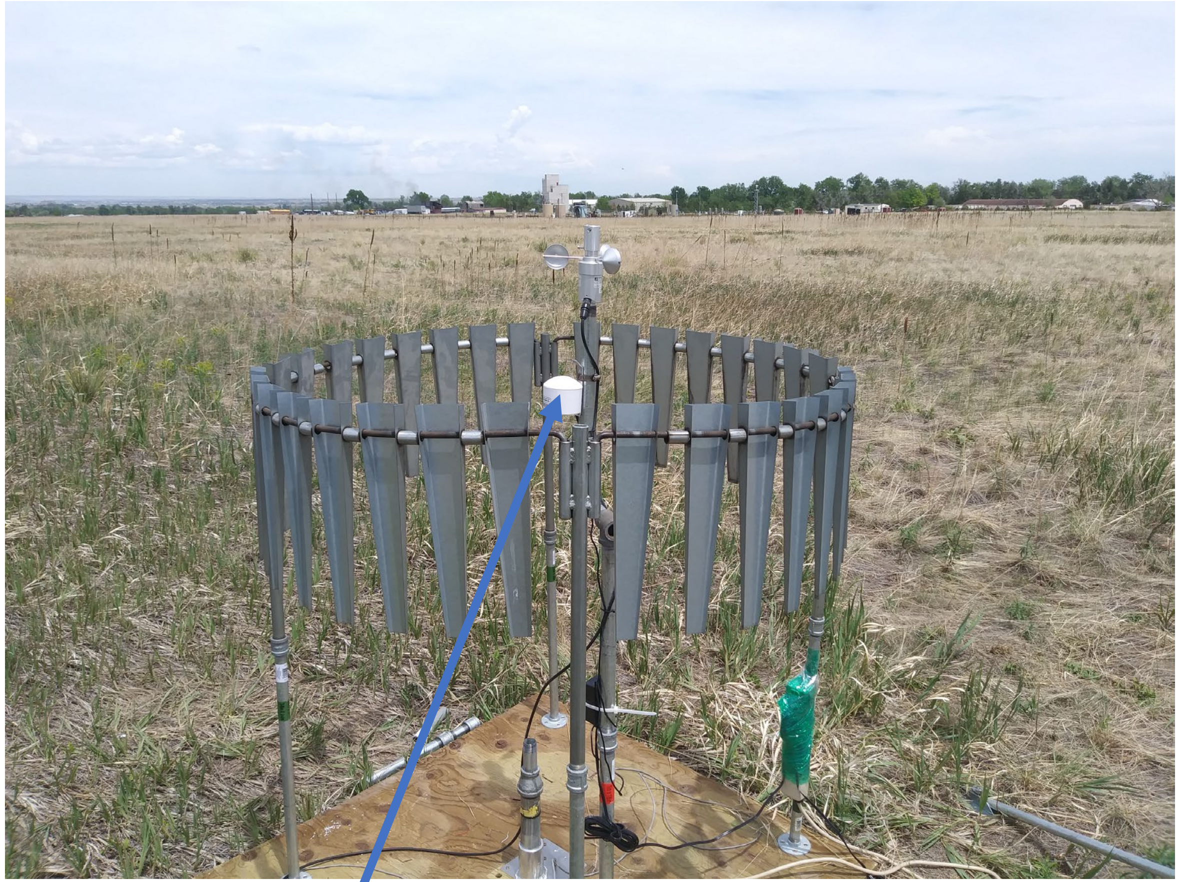
Affordable Small Polarized imperfect Reciprocal Integrating Nephelometer (The ASPRIN)

- The PMS sensor configuration inside the PA monitor (PA-PMS) appears to behave as an imperfect, reciprocal integrating nephelometer.
  - Yearlong field data at Mauna Loa and Table Mountain sites show that the 1 hr average of the PA-PMS CH1 is highly correlated with a nephelometer-measured fine aerosol scattering coefficient at 550 nm, b_{sp1}, over a wide scattering coefficient range **of 0.4 Mm^{-1} to 500 Mm^{-1} (4 orders of magnitude)**
  - The relationship between CH1 and at 550 nm was found to be $b_{sp1} = 0.015 \pm 5.72 \times 10^{-5} \times$ CH1 when both quantities are adjusted to the same temperature and pressure.
  - The CH1 and b_{sp1} relationship is highly dependent on the particle size distribution.
  - Defining the MDL as the 99% confidence interval of Un_{add} the CH1avg MDLs are shown to be as low as 14 which is approximately **0.4 Mm^{-1}!**
- As a scattering sensor, the PMS cannot directly count nor size particles in the air stream.
  - near constant normalized number distribution from which PM concentrations are estimated.
- The PMS uses an unknown algorithm to convert the scattering signal to reported variables.
  - The PMS was unresponsive to 100% CO_2 and Suva (can’t calibrate conventionally).

Plantower air flow direction







Purple Air mounted in a wind shield

Two Purple Airs mounted

- Open to meteorology
- Shielded by an inverted bucket

NPS use of Purple Air Monitor

- Recommend and/or limit visitor activity as a result of elevated PM2.5 or AQI.
- Secondary use of PA
  - Can PA output be used to track visibility (bsp) in space and time?
  - Could PA's be used to estimate f(RH)

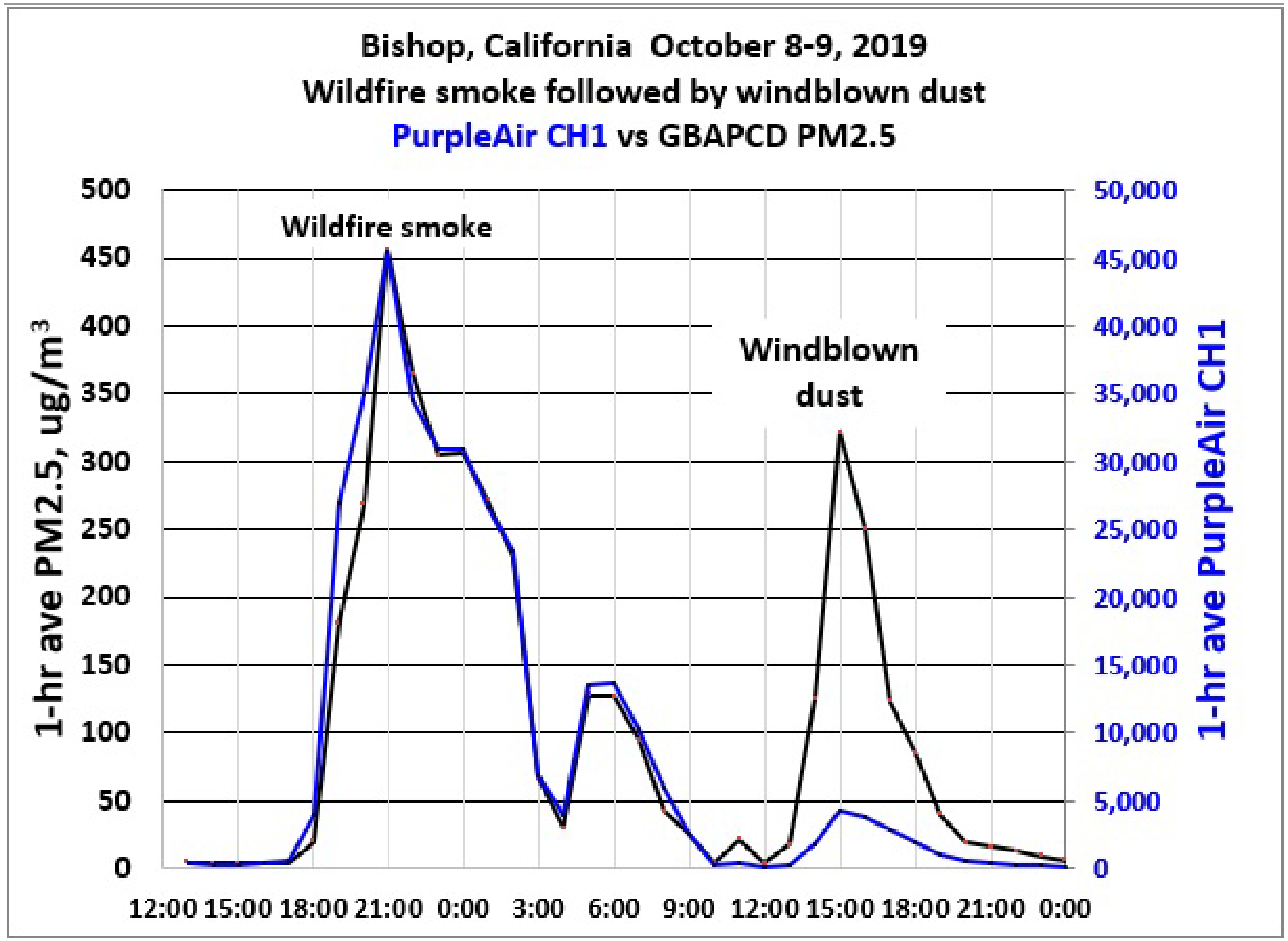
Air Quality Index Category	$PM_{2.5}$ or PM_{10} Levels (µg/m^3, 1- to 3-hr avg.)	$PM_{2.5}$ or PM_{10} Levels (µg/m^3, 8-hr avg.)	$PM_{2.5}$ or PM_{10} Levels (µg/m^3, 24-hr avg.)
Good	0 – 38	0 – 22	0 – 12
Moderate	39 – 88	23 – 50	12.1 – 35.4
Sensitive Groups	89 – 138	51 – 79	35.5 – 55.4
Unhealthy	139 – 351	80 – 200	55.5 – 150.4
Very Unhealthy	352 – 526	201 – 300	150.5 – 250.4
Hazardous	≥ 526	> 300	> 250.5 - 500

Air Quality Index	Who Needs to be Concerned?	What Should I Do?
Good (0-50)	It's a great day to be active outside.	
Moderate (51-100)	Some people who may be unusually sensitive to particle pollution.	**Unusually sensitive people:** Consider making outdoor activities shorter and less intense. Watch for symptoms such as coughing or shortness of breath. These are signs to take it easier. **Everyone else:** It's a good day to be active outside.
Unhealthy for Sensitive Groups (101-150)	Sensitive groups include **people with heart or lung disease, older adults, children and teenagers, minority populations, and outdoor workers.**	**Sensitive groups:** Make outdoor activities shorter and less intense. It's OK to be active outdoors, but take more breaks. Watch for symptoms such as coughing or shortness of breath. **People with asthma:** Follow your asthma action plan and keep quick relief medicine handy. **People with heart disease:** Symptoms such as palpitations, shortness of breath, or unusual fatigue may indicate a serious problem. If you have any of these, contact your health care provider.
Unhealthy (151-200)	**Everyone**	**Sensitive groups:** Avoid long or intense outdoor activities. Consider rescheduling or moving activities indoors.* **Everyone else:** Reduce long or intense activities. Take more breaks during outdoor activities.
Very Unhealthy (201-300)	**Everyone**	**Sensitive groups:** Avoid all physical activity outdoors. Reschedule to a time when air quality is better or move activities indoors.* **Everyone else:** Avoid long or intense activities. Consider rescheduling or moving activities indoors.*
Hazardous (301-500)	**Everyone**	**Everyone:** Avoid all physical activity outdoors. **Sensitive groups:** Remain indoors and keep activity levels low. Follow tips for keeping particle levels low indoors.*

The Plantower laser brand and model are unknown, but is probably like the ones sold on Alibaba.com

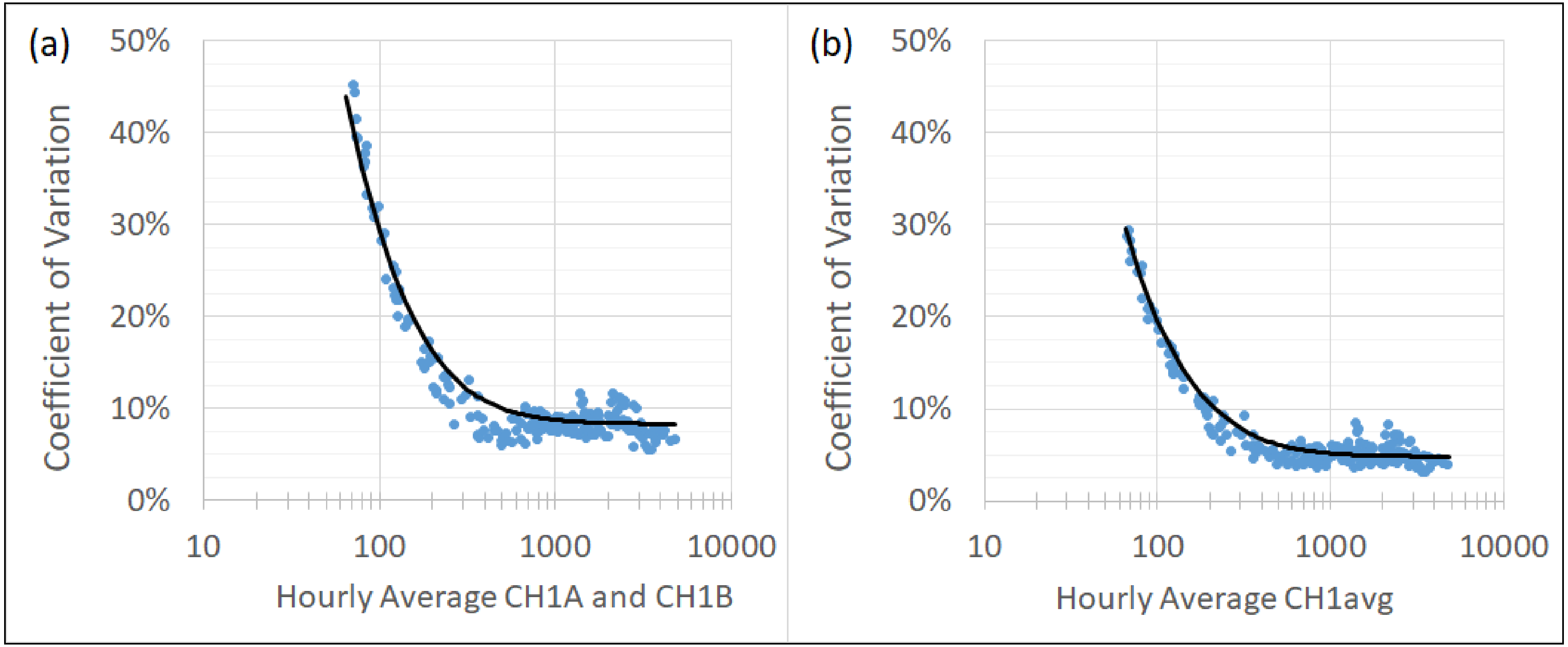
- **Laser is polarized – perpendicular to plain of incidence**
- **The Plantower laser power is probably rated at 5 mW. Pat Arnott measured 3.2 mW.**
- **The most common laser wavelength is 650 nm, not 680 nm. Pat Arnott measured 657 nm.**
- **Laser costs $0.10 to $1.00, depending on number**
- **Pat Arnott noticed it’s focused over the photodiode**

Coarse Particles do make it into the PA (GOOD)

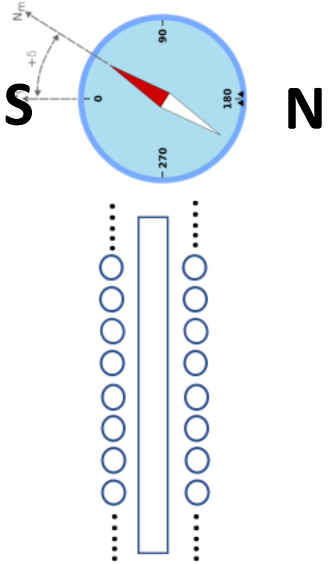


- The physical-optical model predicts that Plantower response to coarse aerosol is poor. Field data are consistent with this prediction.

Uncertainty between PA's very good (Precision)



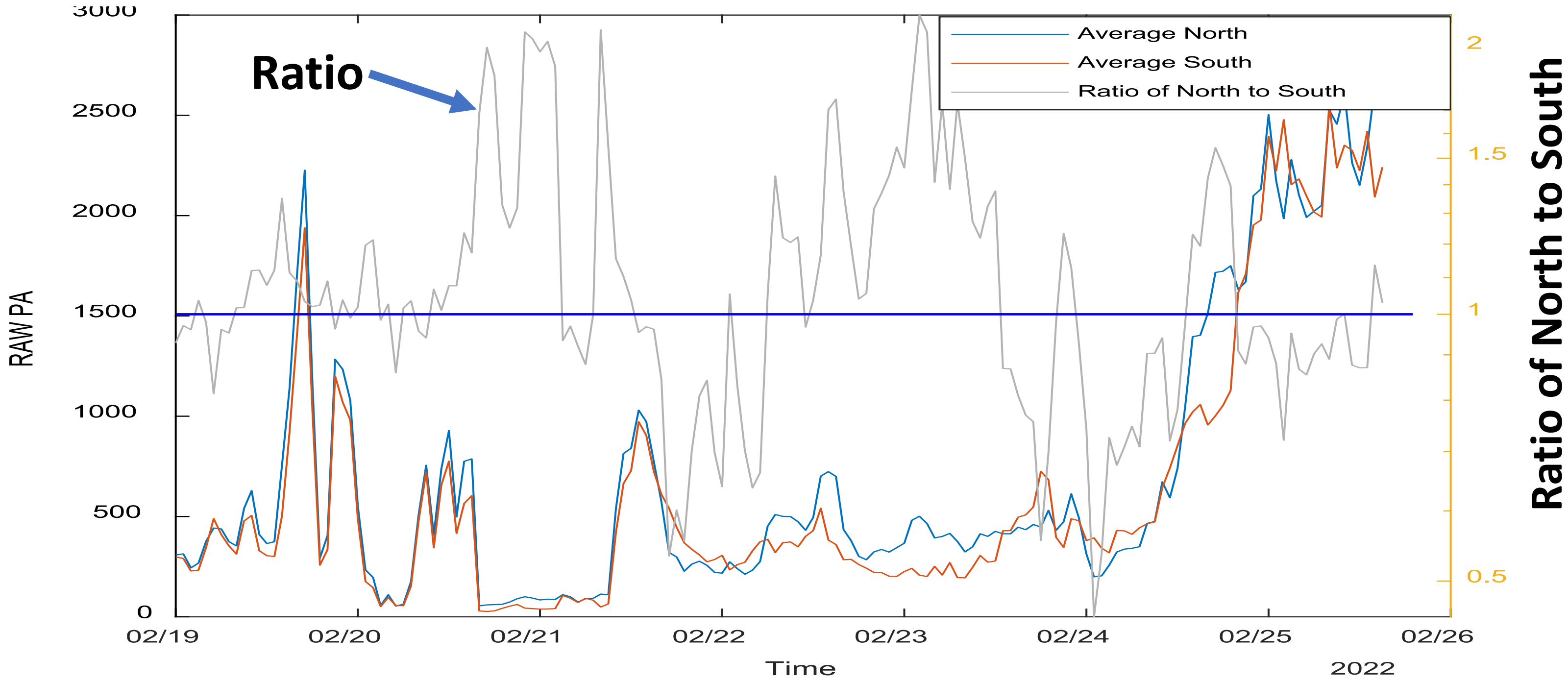
Purple Air Acceptance Testing



North side PA’s all same within uncertainty

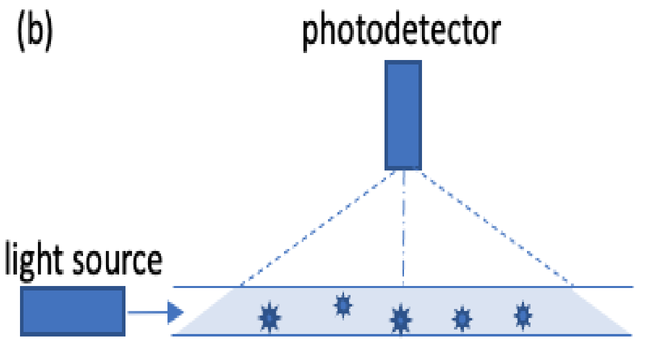
South side PA’s same within uncertainty

Plot of the ratio of average North/South PA

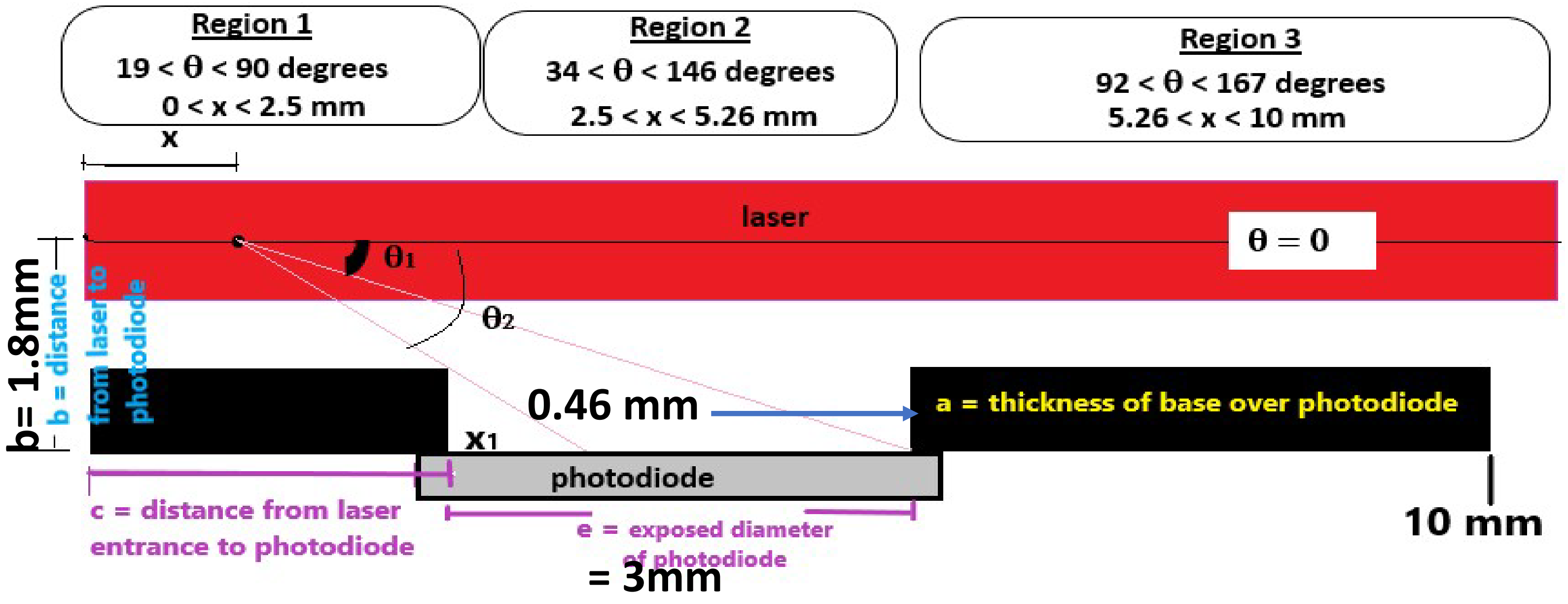


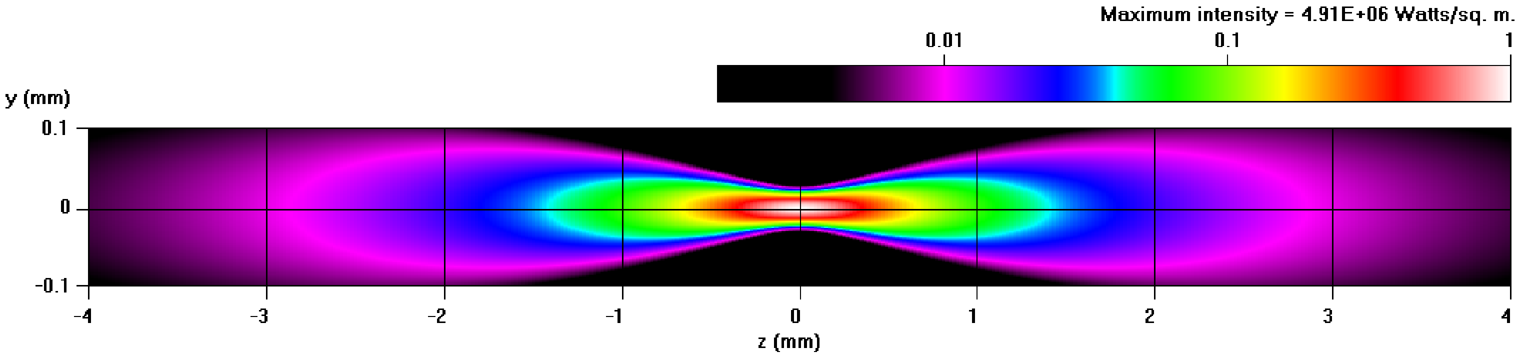
What about accuracy of PM2.5 and other physical variable estimates?

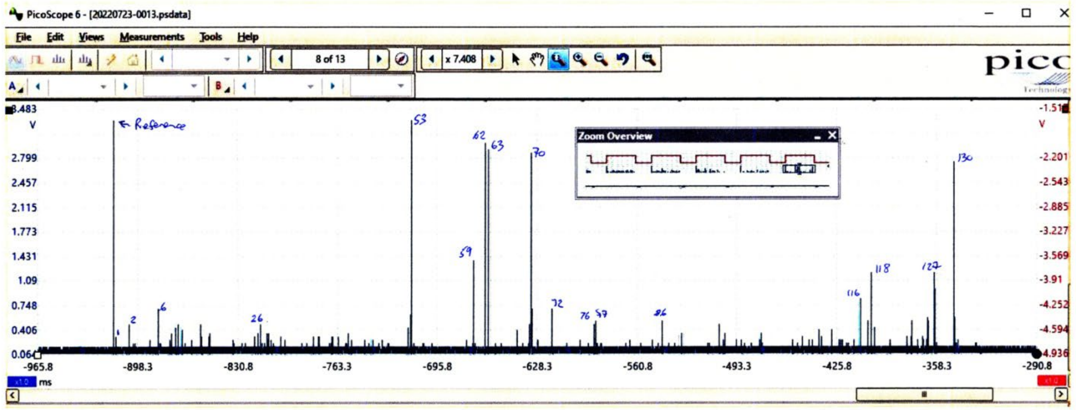
Plantower Scattering Geometry

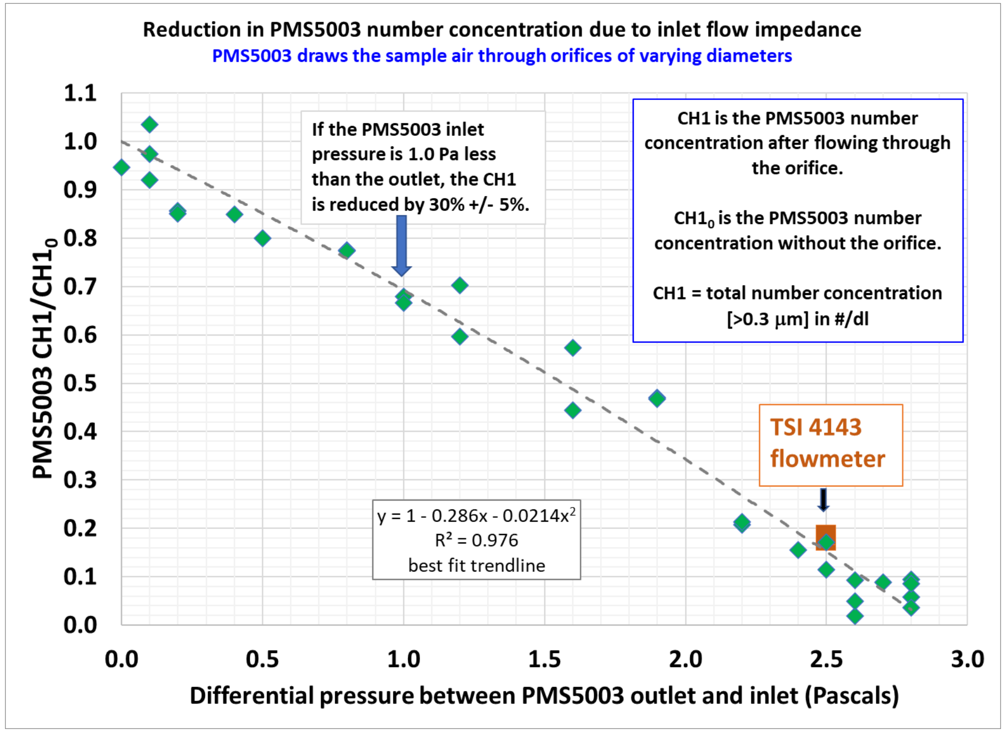


Reciprocal Integrating Nephelometer

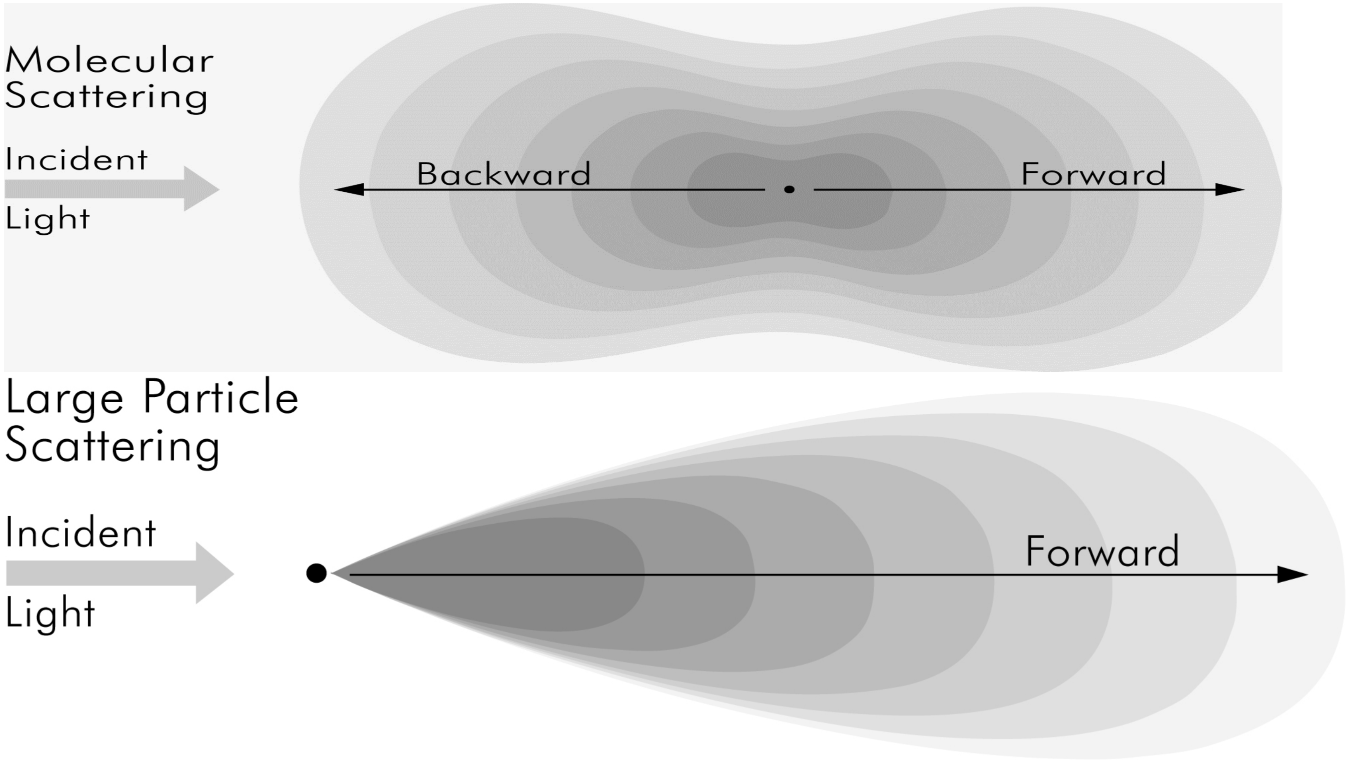





PicoScope 6 - [20220723-0013.psdata]
File Edit Views Measurements Tools Help
8 of 13
x 7.408
Zoom Overview
← Reference
-965.8
-898.3
-830.8
-763.3
-695.8
-628.3
-560.8
-493.3
-425.8
-358.3
-290.8
ms


Reduction in PMS5003 number concentration due to inlet flow impedance
PMS5003 draws the sample air through orifices of varying diameters
If the PMS5003 inlet pressure is 1.0 Pa less than the outlet, the CH1 is reduced by 30% +/- 5%.
CH1 is the PMS5003 number concentration after flowing through the orifice.
$CH1_0$ is the PMS5003 number concentration without the orifice.
CH1 = total number concentration [>0.3 µm] in #/dl
TSI 4143 flowmeter
$y = 1 - 0.286x - 0.0214x^2$
$R^2 = 0.976$
best fit trendline
PMS5003 CH1/$CH1_0$
Differential pressure between PMS5003 outlet and inlet (Pascals)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0

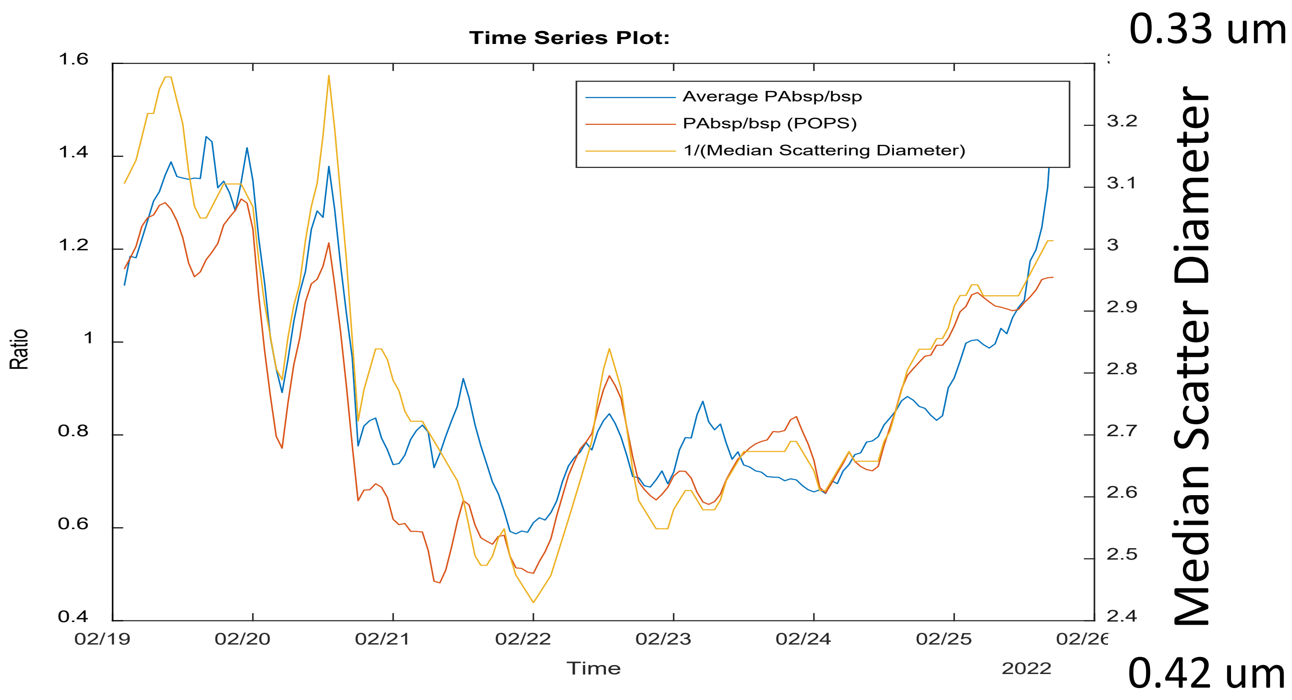
To understanding the Plantower response to atmospheric particle number size distributions
A 2-D light scattering model was created



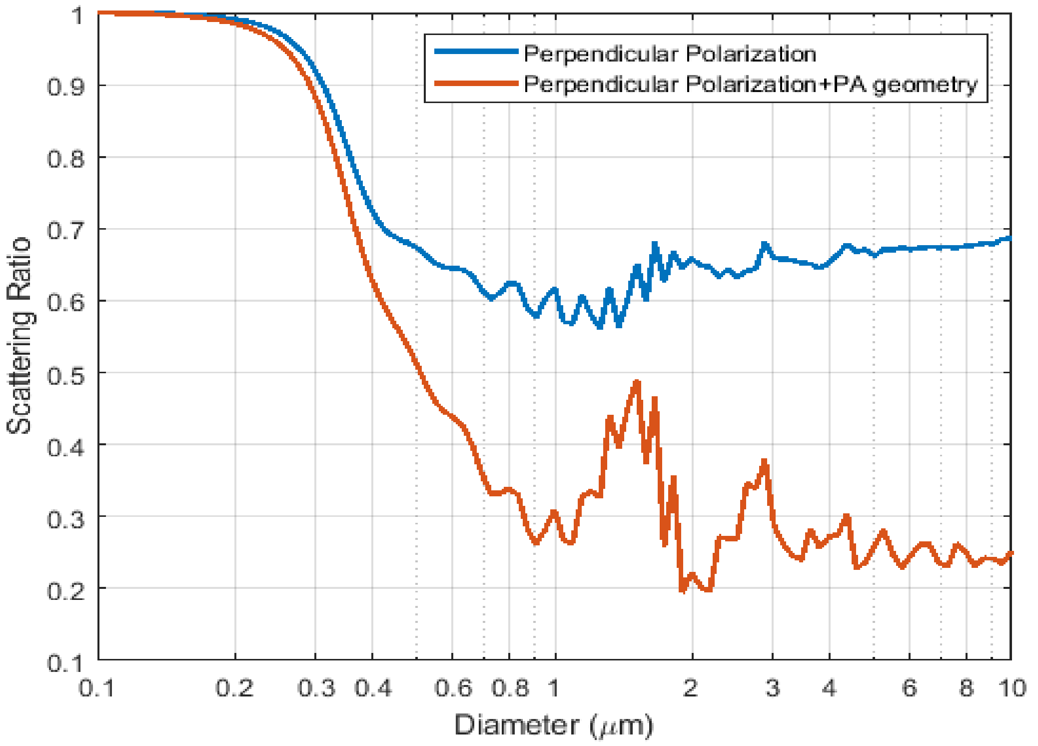
$$P = K \int_{Dp} \int_{x=0}^{x=10mm} \int_{\theta_1(x)}^{\theta_2(x)} \left(|S_1(m,\theta,D_p)|^2 + \cancel{|S_2(m,\theta,D_p)|^2}\right) \sin(\theta)\, N(D_p, m)\, d\theta\, dx\, dD_p.$$

Ratio of PA to bsp varies as a function of median scattering particle diameter – as size increases the ratio decreases.

Observed

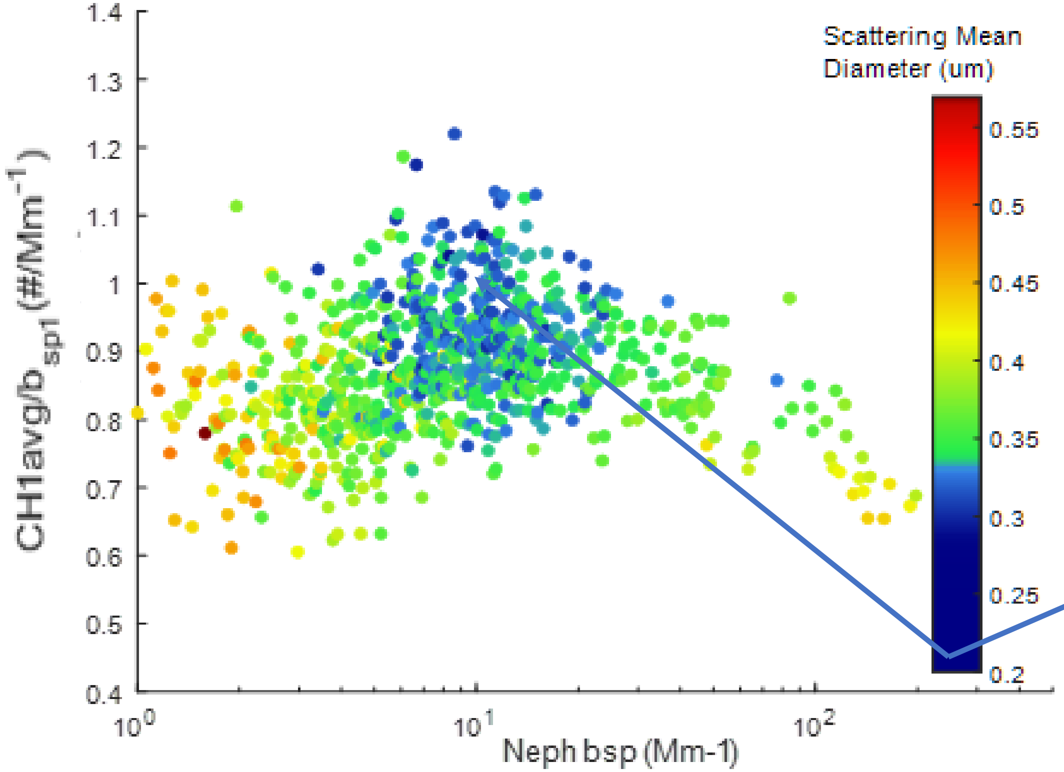


Modeled

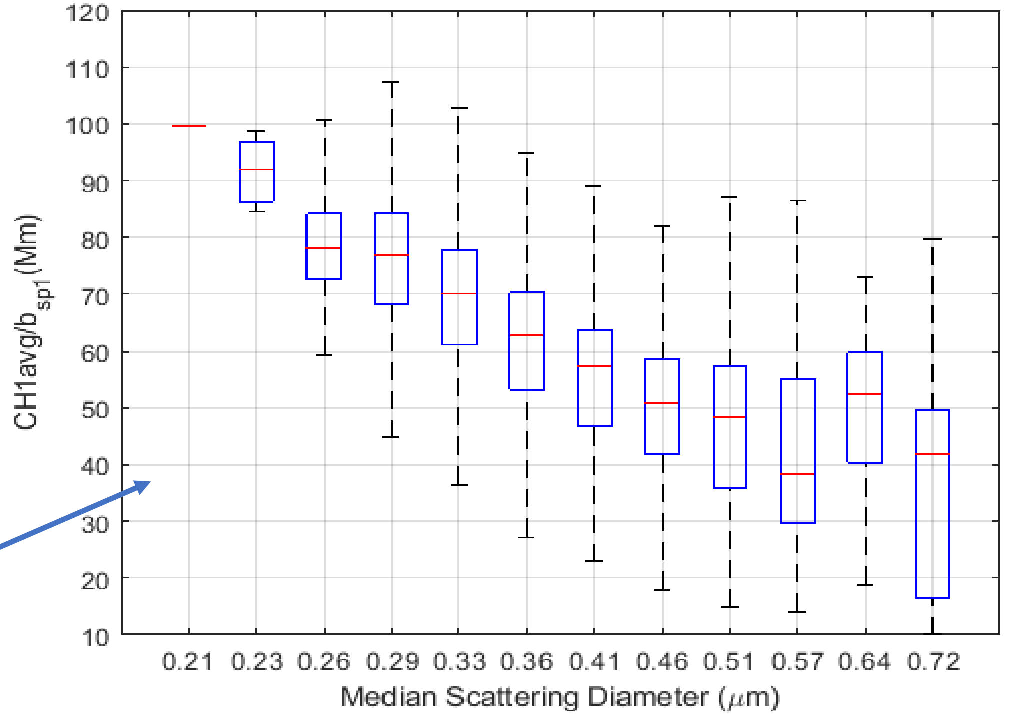


Ratio of scattering of a “perfect” nephelometer to a nephelometer with a light source that is perpendicularly polarized (blue) and to a perpendicularly polarized nephelometer with PMS geometry (red) as a function of particle diameter.

More observations – hundreds of data points

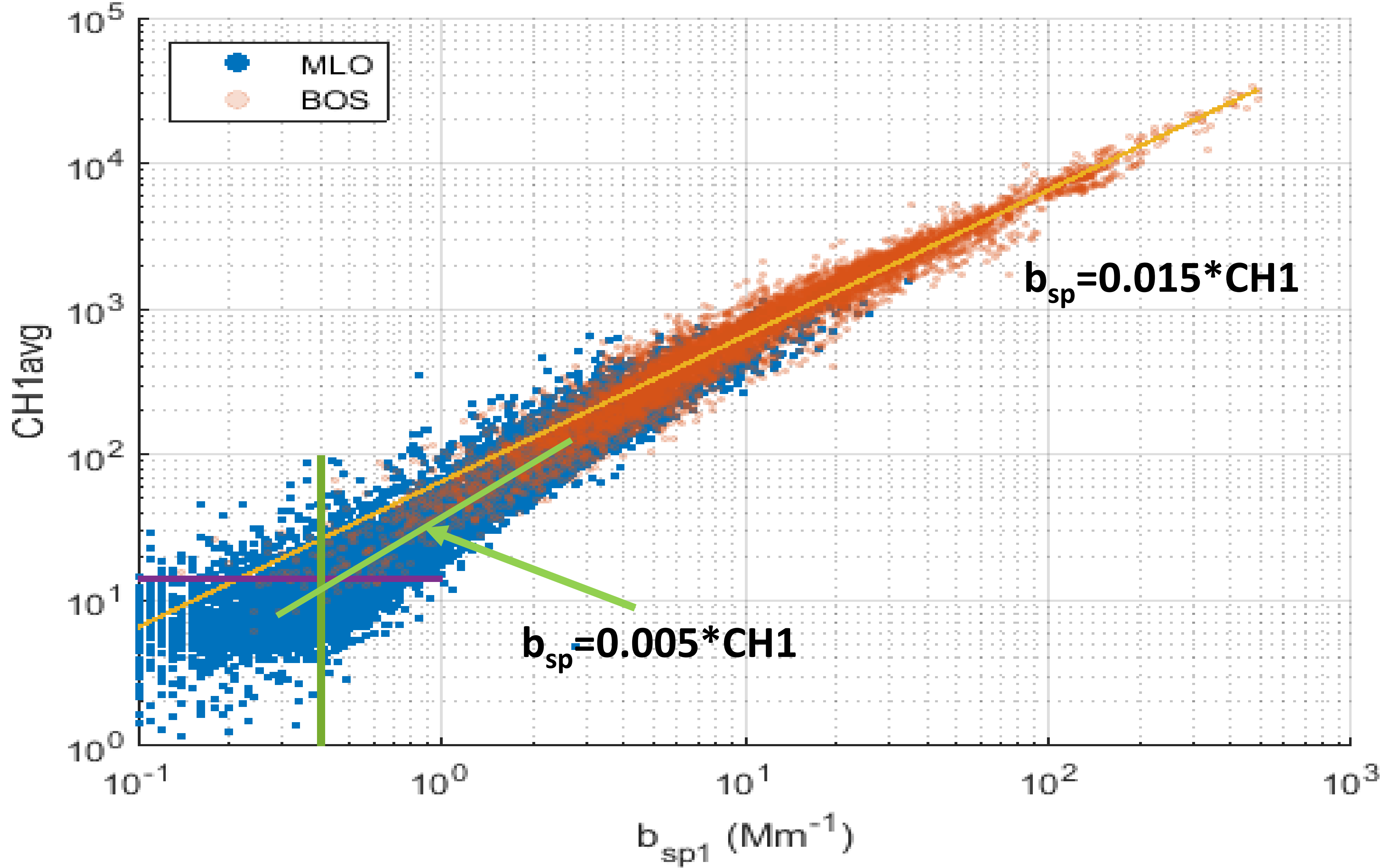


Plot of bsp vs $CH1/b_{sp}$. Color of filled circles represent the scattering median diameter (SMD) which corresponds to half of the total scattering being above the SMD and half below.



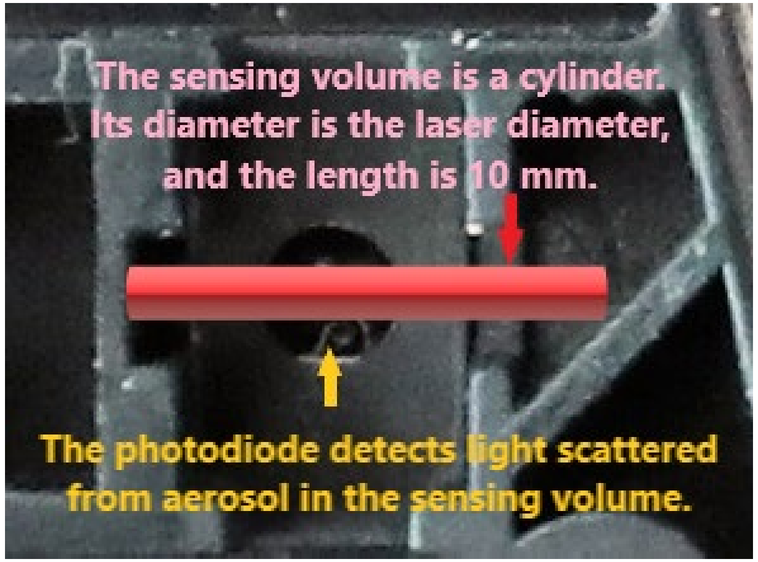
"Box" plot of scattering median diameter vs PA/bsp. On each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers.

Relationship between PA and bsp varies by about a factor of 3



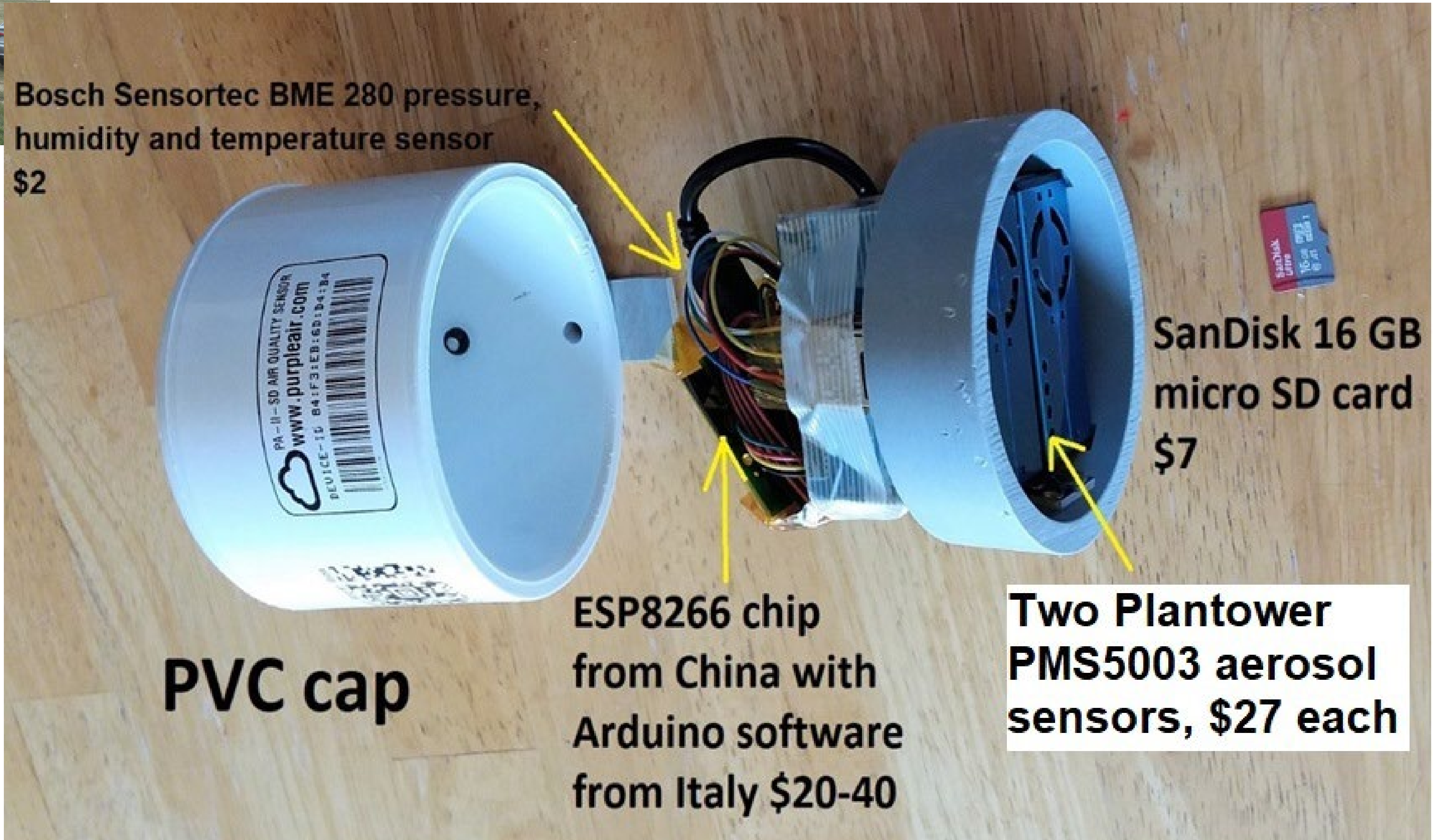
Why the Plantower cannot function as an optical particle counter

- **OPC's rely on at least two things:**
  - **a unique relationship between particle diameter and voltage output from the detector**
  - **Only one particle in the sensing volume at a time**
- **The Plantower fails both of these**
  - **The photodiode voltage output is higher for particles of size Dp near the laser exit (x < 4 mm) than for the same size particles far from the laser exit (x > 7 mm)**
  - **The Plantower sensing volume is much larger than an OPC, allowing more than one particle in the sensing volume at a time**



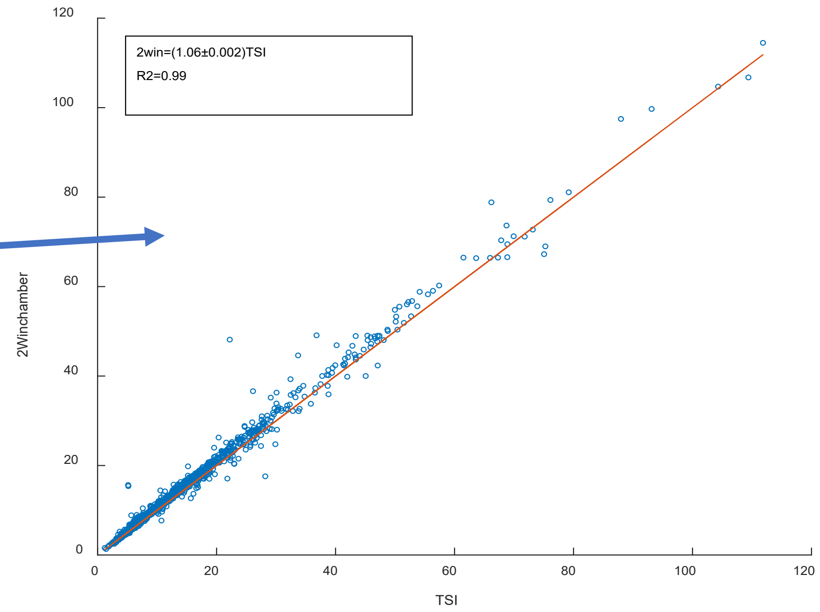
Plantower PMS 5003 sensors inside PurpleAir

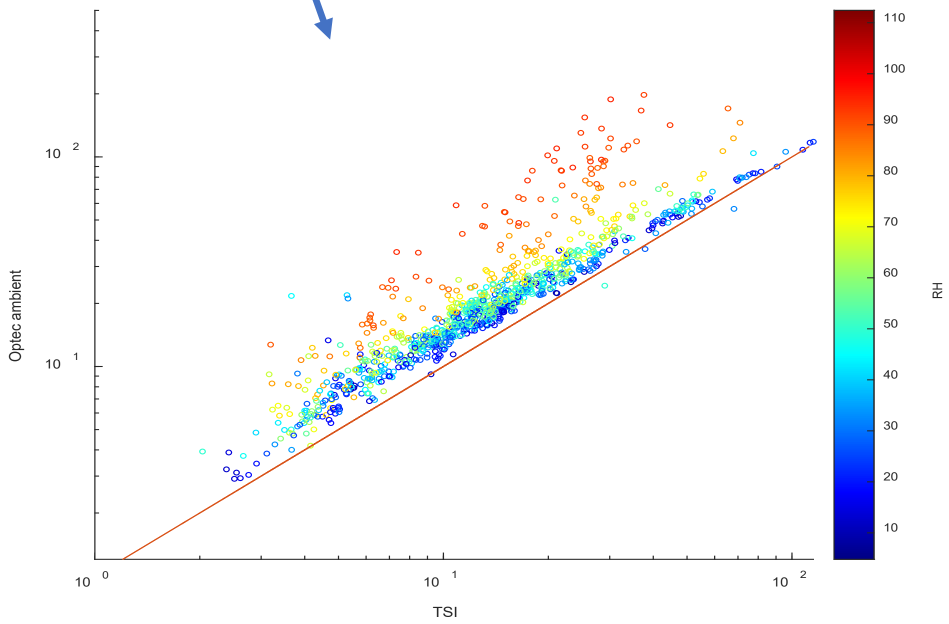
Two Typically Mounted Purple Air Monitors

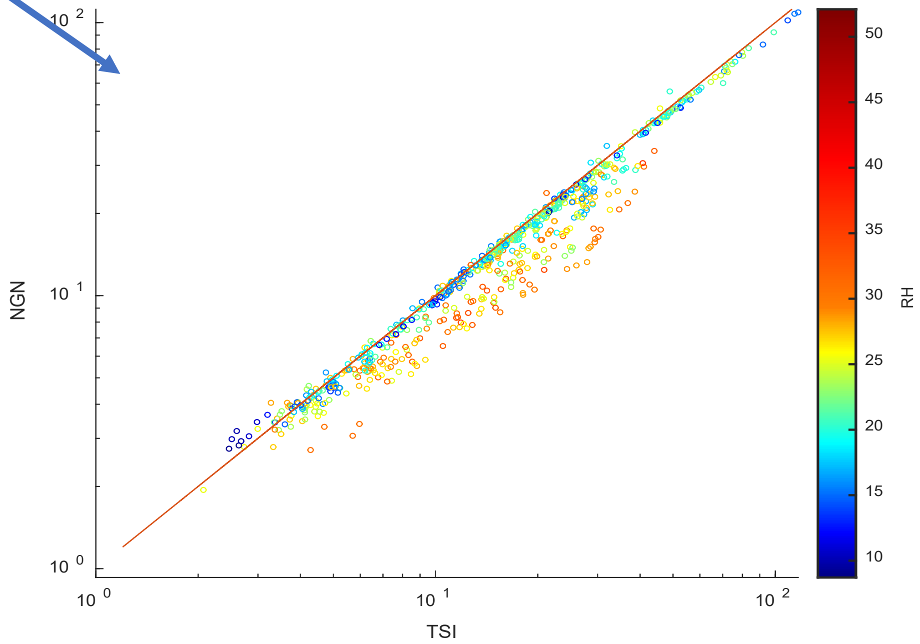


Operated 5 nephelometers

- TSI – inadvertent heating - 2.5 um inlet
- 2WIN dry - RH<40% - 2.5 um inlet
- 2WIN amb – Some heating – 2.5 um inlet
- NGN dry - heating to reduce RH – 2.5 um inlet
- NGN open







Some Photos of the Test Site

IMPROVE Particle Samplers

Side View – Open air Nephelometer

Constant Humidity Chamber

30 Collocated PA’s

Two typically mounted Purple Air instruments