

First Results from New *in situ* Aerosol Spectral Optical Measurements during KORUS-OC:

Exploring links among optical properties & aerosol chemistry

C. Jordan^{1,2}, R. Stauffer³, B. Lamb⁴, M. Novak³, A. Mannino³,
C. Hudgins², K. L. Thornhill^{2,5}, E. Crosbie^{2,5}, E. Winstead^{2,5},
G. Schuster², B. Anderson², R. Martin², M. Shook^{2,5},
L. Ziemba², A. Beyersdorf^{2,6}, C. Corr^{2,7}, & C. Robinson^{2,5}

¹National Institute of Aerospace, ²NASA – LaRC, ³NASA- GSFC, ⁴CUNY, ⁵SSAI,
⁶CSU-San Bernardino, ⁷Bennington College



Atmospheric & Planetary Sciences Seminar
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Ministry of Environment
National Institute of
Environmental Research



Overview

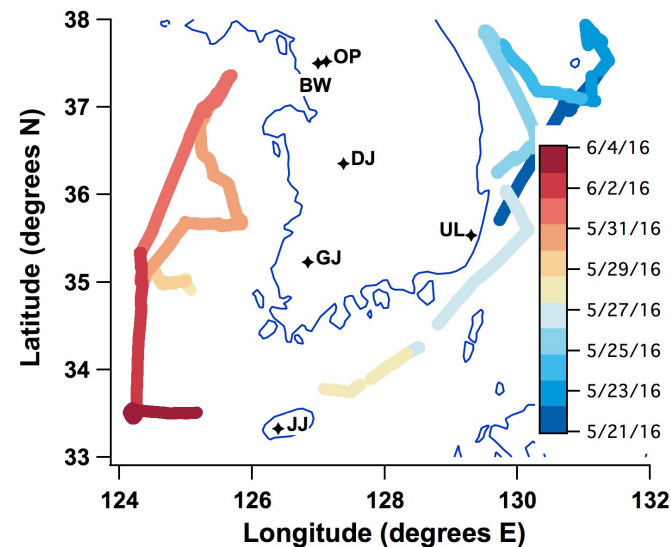
- **Part 1: KORUS – OC**
- **Part 2: Spectral Representation of Aerosols**
- **Part 3: In Situ Spectral Measurements**
 - Extinction with SpEx
 - Total Absorption with Integrating Sphere
 - Soluble Absorption with Liquid Waveguide Capillary Cell
- **Part 4: KORUS-OC Observations**
- **Part 5: What's Next**

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Korea U.S. – Ocean Color (KORUS-OC) Cruise

- Affiliated with airborne KORUS-AQ & KOCOIA cruise
 - joint missions to study S. Korean air quality (AQ) & OC
- Under view of S. Korean Geostationary Ocean Color Imager (GOCI)
 - providing hourly OC & AOD
- Cruises conducted from May 20 to June 4, 2016
- OC objectives for atmospheric measurements to
 - address atmospheric correction requirements
 - explore interdisciplinary science questions
- KIOST R/V Onnuri (KORUS-OC)

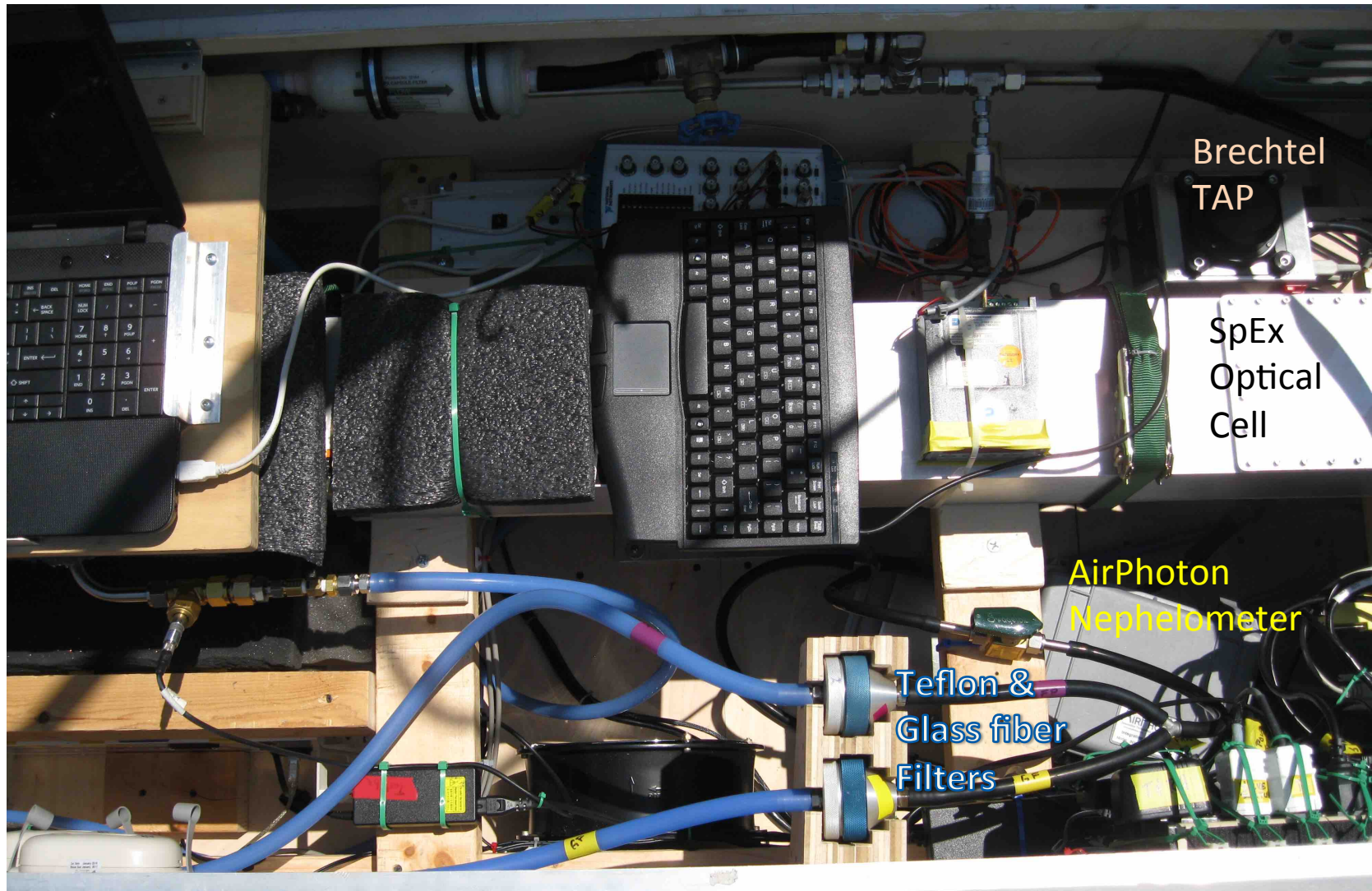


Korea U.S. – Ocean Color (KORUS-OC) Cruise

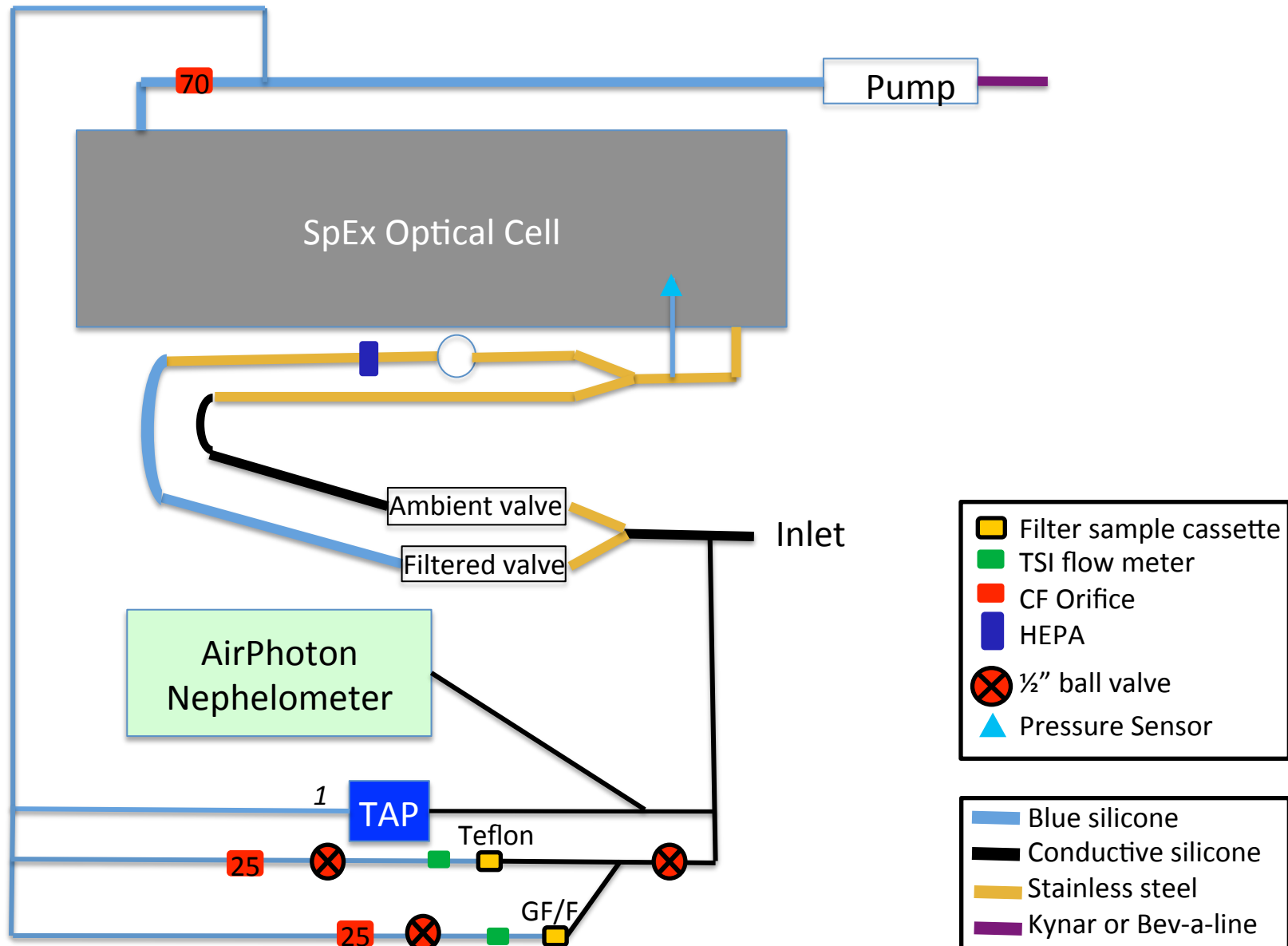
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In situ Aerosol Measurements – R/V Onnuri



In situ Aerosol Measurements – R/V Onnuri

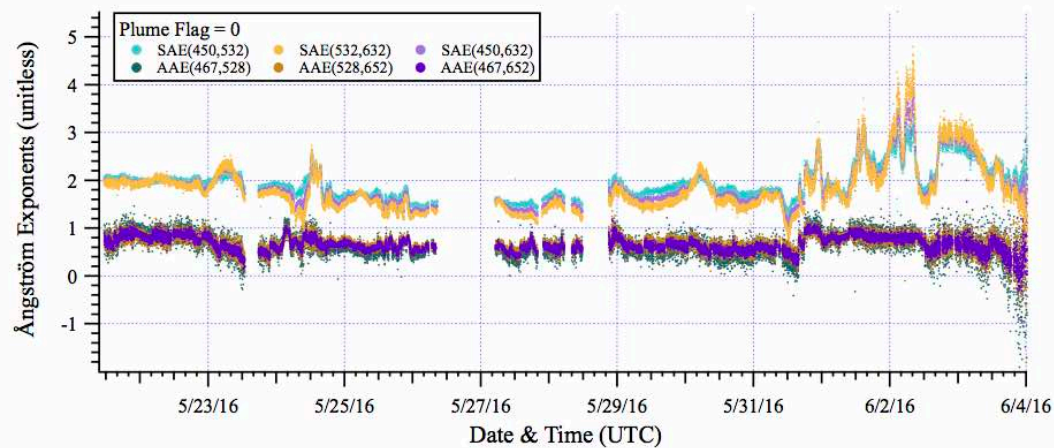
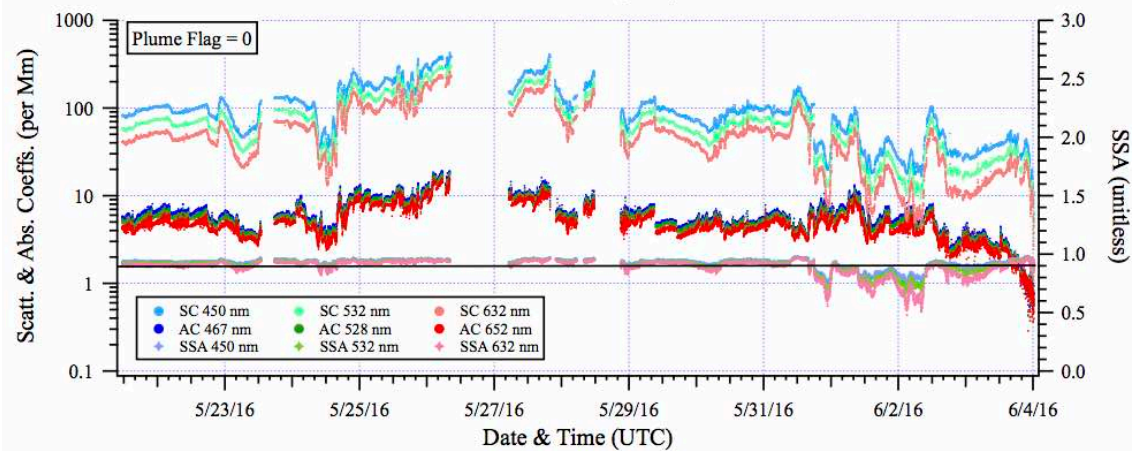
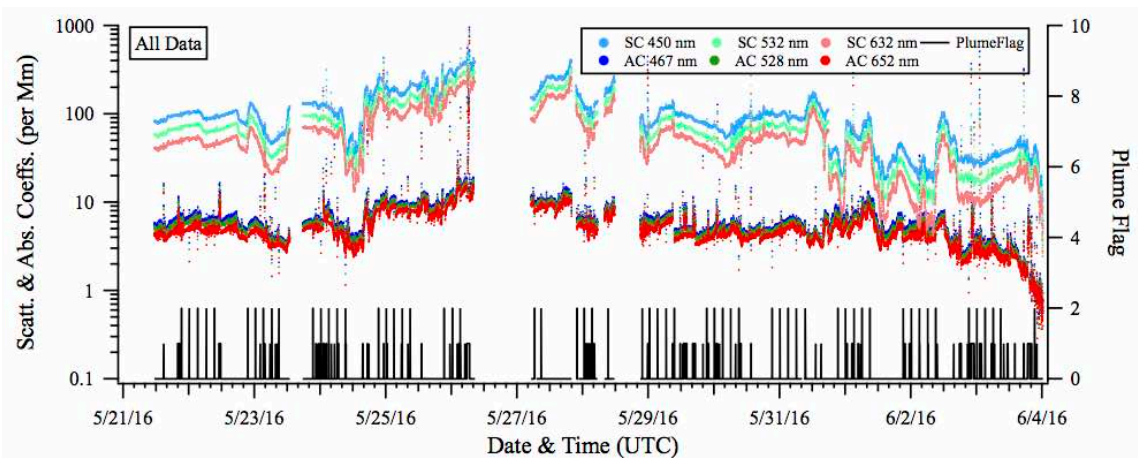


AirPhoton Nephelometer & TAP

- **1 minute Data Set**
 - Scattering (AirPhoton Nephelometer, ~14 s)
 - 450, 532, and 632 nm
 - Absorption (Brechtel Tricolor Absorption Photometer, TAP, 1 s)
 - 467, 528, and 652 nm



Images from the AirPhoton & Brechtel manuals.



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Key Atmospheric Aerosol Optical Properties

- Extinction = Scattering + Absorption
- Scattering is primarily a function of particle size distribution
- Absorption in organic compounds requires conjugated bonds in their molecular structure:
 - wavelength range of absorption depends on the number of such bonds
 - black carbon (BC):
 - graphitic sheets of carbon, many π -bonded carbon atoms
 - delocalized electrons readily absorb light over UV-IR range
 - largely wavelength-independent absorption
 - represented by wavelength-independent refractive index
 - brown carbon (BrC):
 - strong UV absorption with limited, if any, visible absorption
 - more π -bonds in organic molecular structures => absorption at longer wavelengths
 - aromatic rings, heteroatoms (e.g., N or O), other functional groups
 - strongly wavelength-dependent absorption
 - requires wavelength-dependent refractive index
- Absorption in dust particles is related to their iron oxide and clay content

Aerosol Optical Properties & Ångström Exponents

- Aerosol interaction with light is wavelength dependent
 - often characterized by a power law: $p(\lambda) = \lambda^{-\alpha}$
where, α is known as Ångström exponent
 - p can be any optical property described by a power law,
e.g., scattering, absorption, extinction, etc.
- Commercially available instruments often target a few λ s, such that Ångström exponents are calculated from these few wavelengths, e.g.,

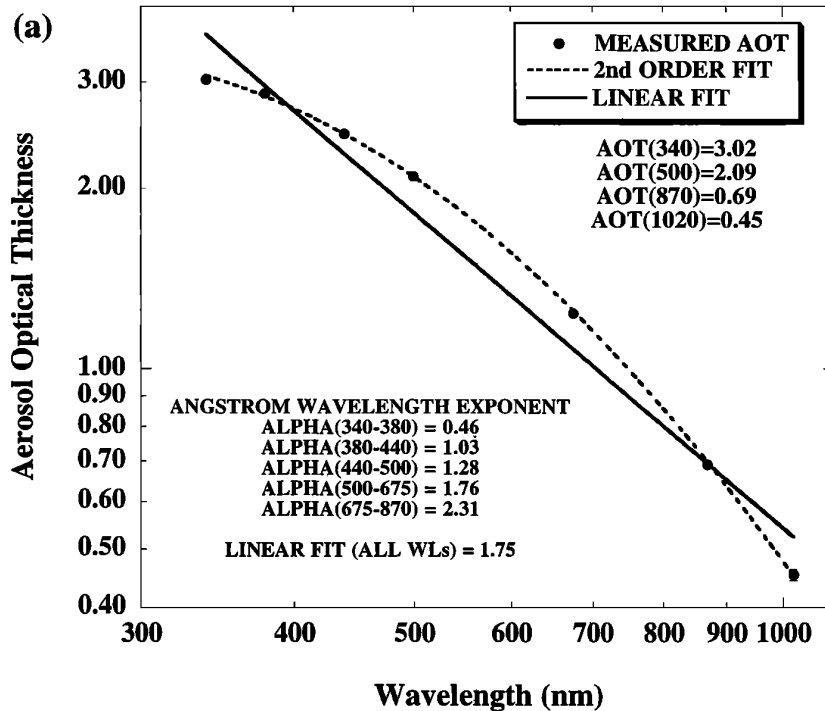
$$\alpha(\lambda_1, \lambda_2) = -\frac{\ln(p(\lambda_1)/p(\lambda_2))}{\ln(\lambda_1/\lambda_2)}$$

- Additional wavelength-dependent parameters include
 - refractive indices, $m(\lambda) = n(\lambda) + ik(\lambda)$
 - single scatter albedo, $\omega(\lambda) = b(\lambda) / g(\lambda)$
 $= b(\lambda) / (b(\lambda) + a(\lambda))$

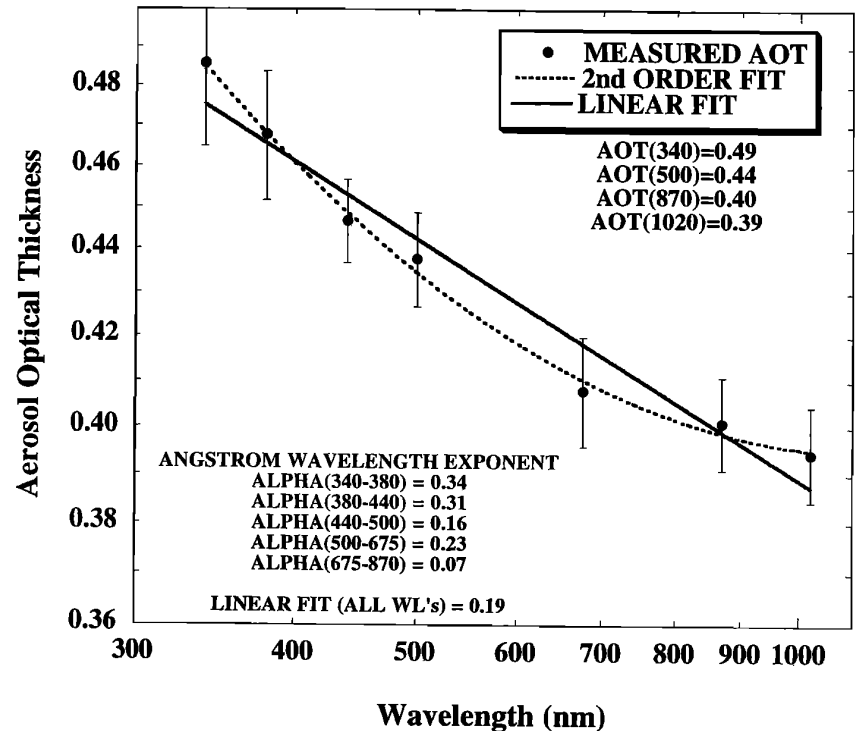
Atmospheric Importance of Spectral Aerosol Optical Properties

- Spectral dependence of optical properties important for studies of the Earth's radiation budget and photochemical processes, e.g.,
- climate sensitivity to absorbing aerosols rapidly increases with altitude
 - vertical aerosol distributions over continental US measured from aircraft from May-June 2012 [Zhang et al., 2017] show
 - 1) BrC prevalent in troposphere, transported to mid- and upper-troposphere altitudes by deep convection
 - 2) BrC absorbs more short-wavelength radiation than BC from 5-12 km
 - 3) ~2/3 of estimated BrC radiative forcing occurs above 5 km
 - 4) most BrC mass found below 5 km
 - 5) in-cloud heterogeneous processes may produce BrC
- strong wavelength dependence of BrC absorption, negligible in visible increasing with decreasing wavelength from 368 to 305 nm found using ground and satellite remote sensors to limit UV-B radiation reaching surface during biomass burning season (Sept.-Oct., 2007) in Bolivia [Mok et al., 2016]
 - 1) reduced UV-B decreases erythema, plant damage, and photolysis rates
 - 2) box model indicated BrC absorption reduced (beyond that of BC alone)
 - net rate of production of O_3 by up to 18%
 - radical concentrations of OH, HO_2 , and RO_2 by up to 17%, 15%, and 14%, respectively

1998 AERONET Observations

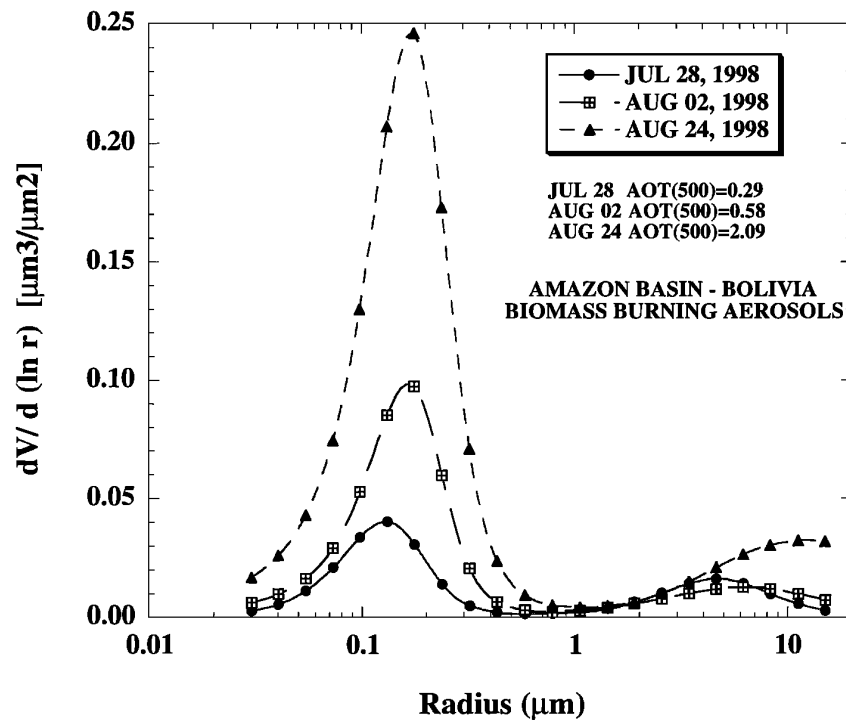


Biomass burning aerosols
 Concepcion, Bolivia, 24 Aug. 1998
 AOT (500 nm) = 2.09
 Error bars smaller than symbol size

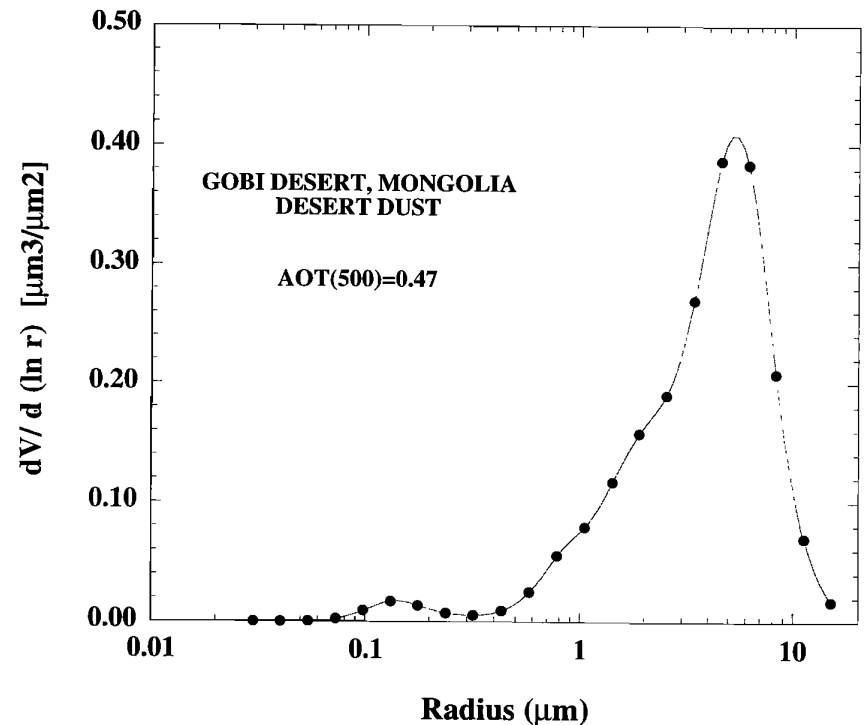


Desert dust aerosols
 Dalanzadgad, Mongolia, 18 April 1998
 AOT (500 nm) = 0.44

1998 AERONET Observations

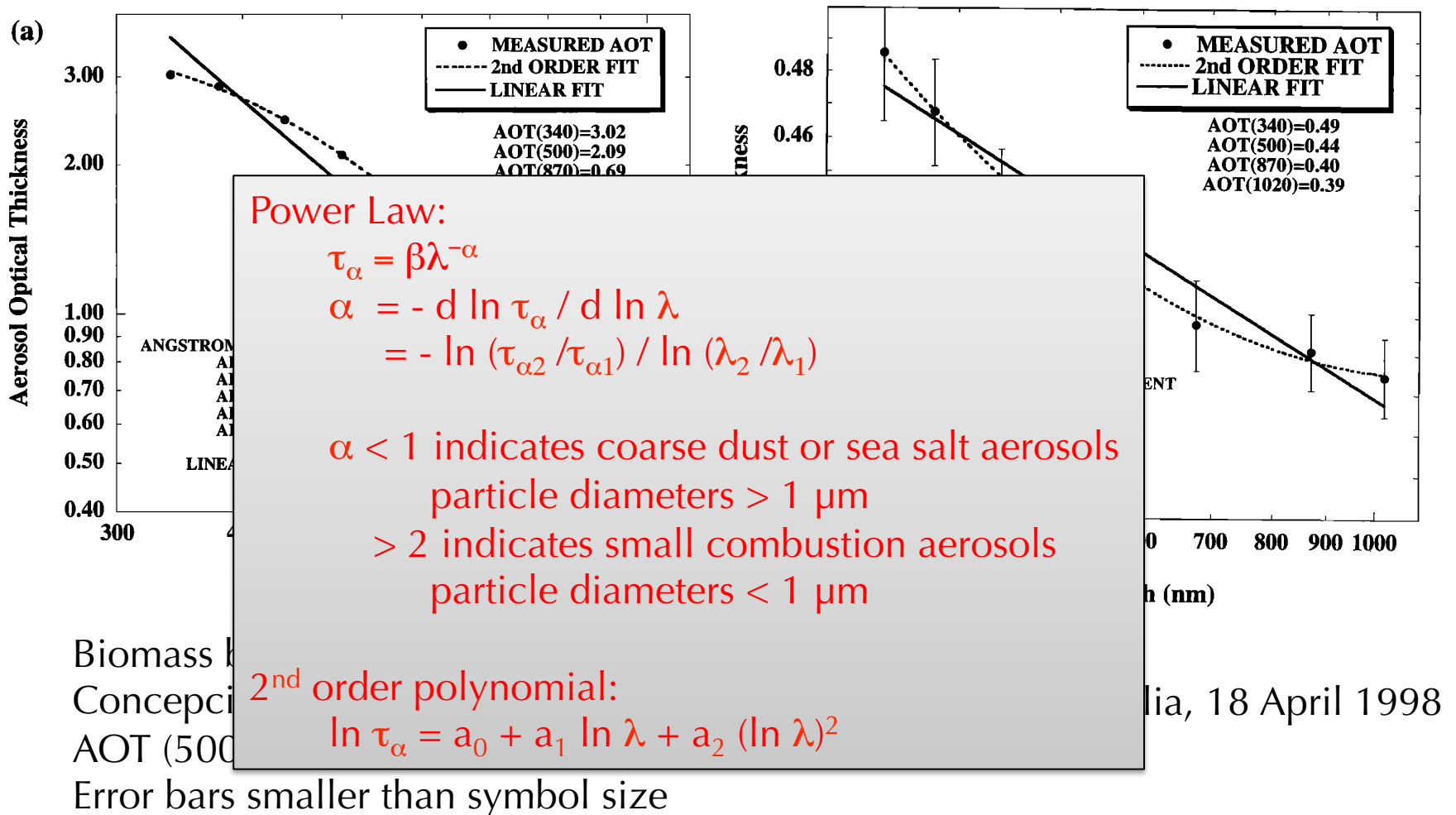


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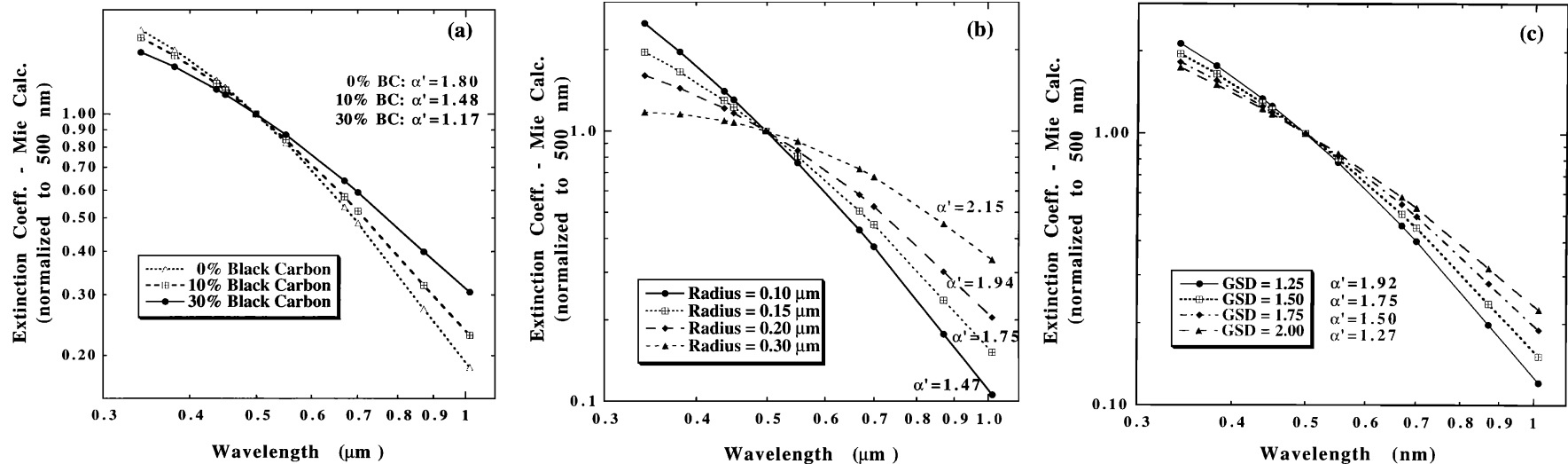


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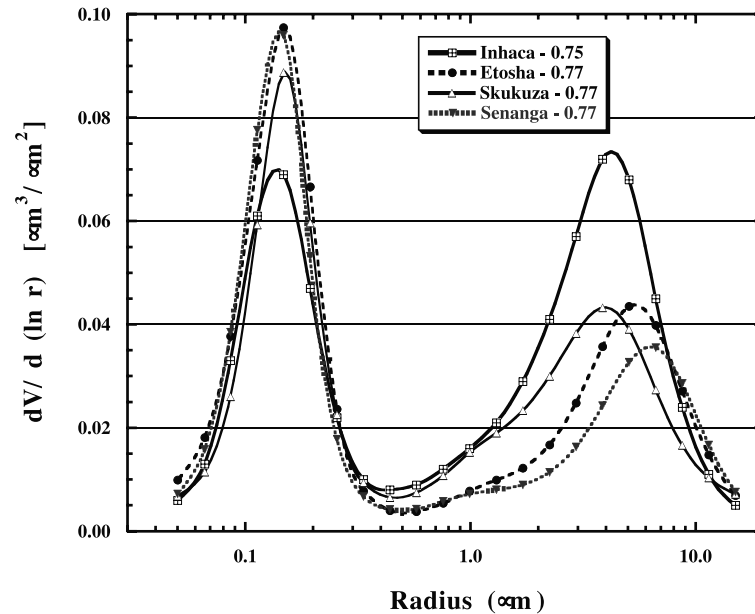
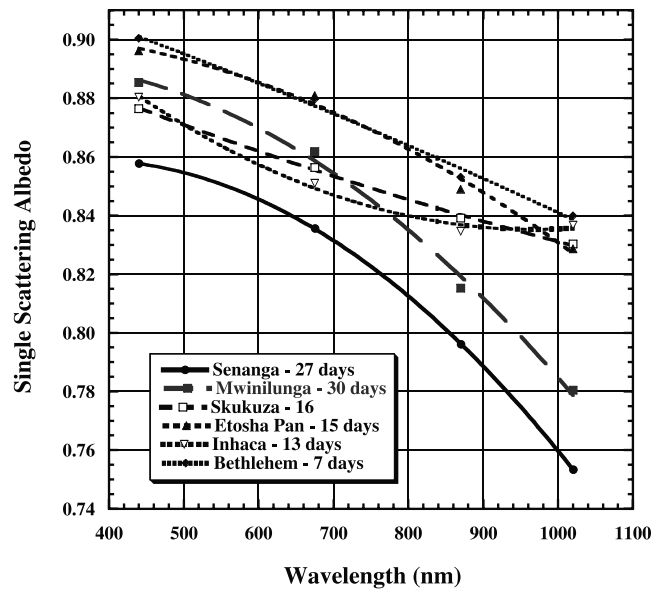


Sensitivity to Composition & Particle Size



- Tested sensitivity of spectral curvature to composition and particle size using Mie calculations of accumulation mode aerosols
 - As BC increased from 0-30%, curvature decreased
 - As radius increased from 0.10 to 0.30 μm, curvature increased
 - As lognormal size distribution narrowed, curvature increased
- Results suggest weakly absorbing, relatively large modal size accumulation mode aerosols will exhibit largest departures from linear relationship

2000 AERONET Single Scattering Albedo Retrievals



- Mean SSA from several AERONET sites across southern Africa from Aug.-Sept. 2000
- Relatively high SSA at long wavelengths attributed to larger proportion of coarse mode in ambient aerosols
- Presence of dust aerosols mixed with biomass burning aerosols tends to decrease spectral dependence of SSA

Spectral Curvature from Mie Theory & AERONET

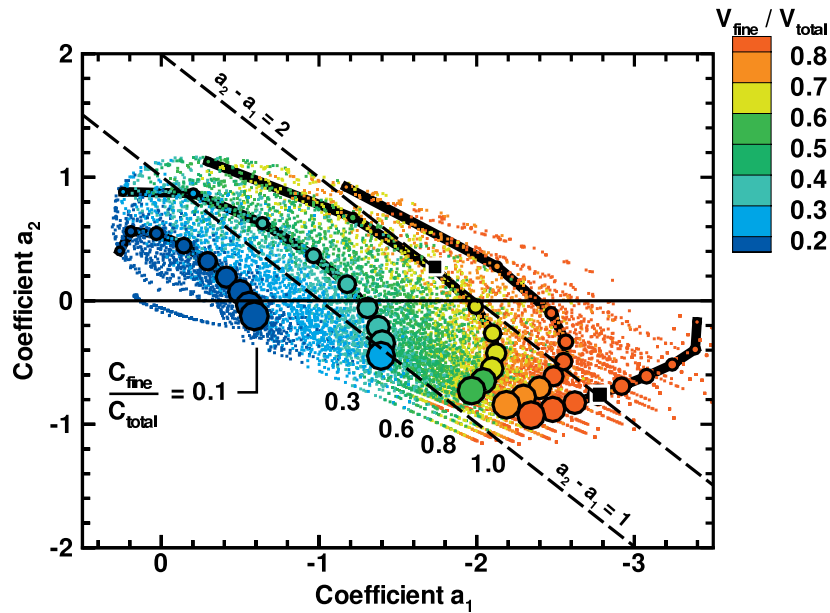
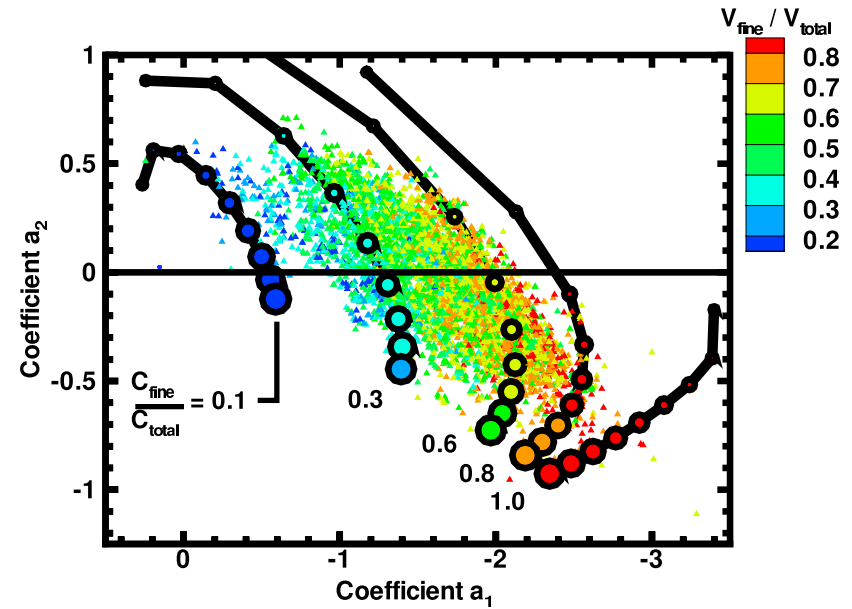


Table 1. Bimodal Lognormal Size Distribution Parameters Used to Calculate the Points in Figure 6^a

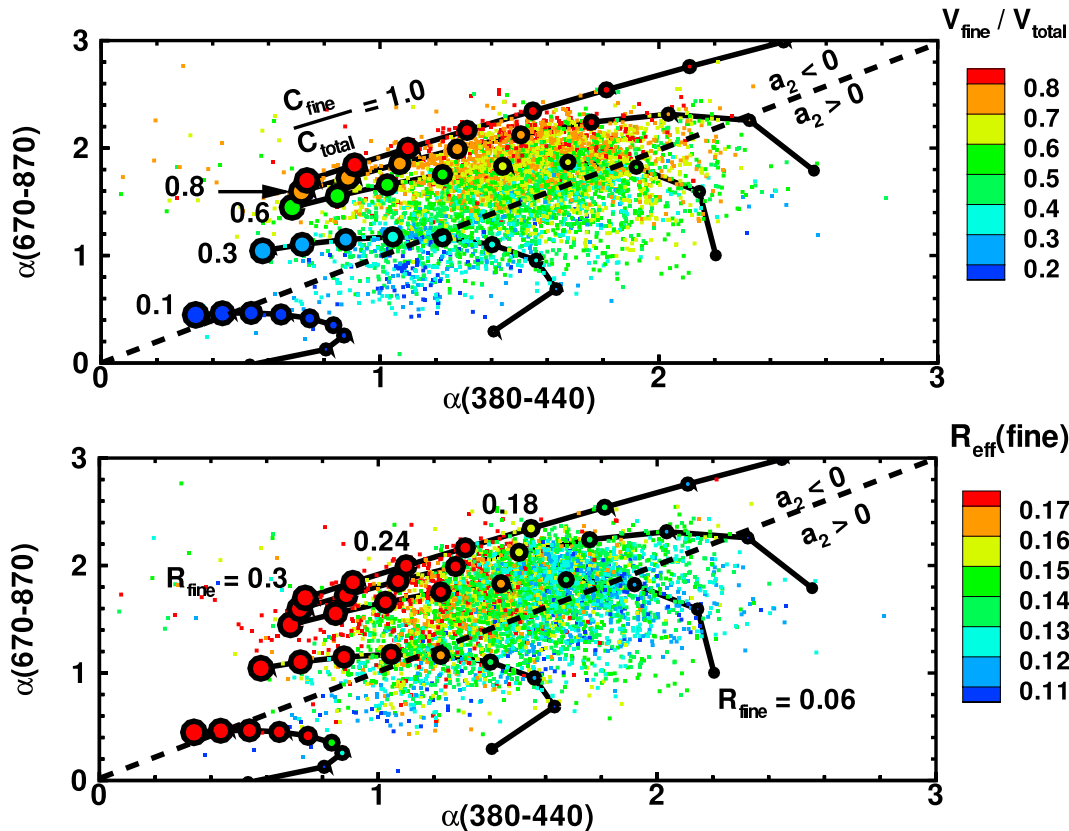
Parameter	Values
R_{fine} , μm	0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24, 0.27, 0.30
σ_{fine}	0.38, 0.5
R_{crs} , μm	1.9, 2.2, 2.7, 3.2 , 3.7
σ_{crs}	0.75, 1.0
m_r	1.34, 1.37 , 1.4, 1.43, 1.47, 1.5, 1.54
m_i	0.003
C_{fine}/C_{total}	0.0, 0.1 , 0.2, 0.3 , 0.4, 0.5, 0.6 , 0.7, 0.8 , 0.9, 1.0

^aValues in bold are also used to calculate the circles in Figures 5, 6, 7, 9, and 10.



- 13,860 bimodal size distributions parameterized with values in Table 1 used in Mie theory (left)
- AERONET retrievals (right)
- $\alpha \sim a_2 - a_1$
 - ≥ 2 , dominated by fine aerosols
 - ≤ 1 , dominated by coarse aerosols
 - intermediate values represent range of bimodal distributions

Spectral Curvature from Mie Theory & AERONET



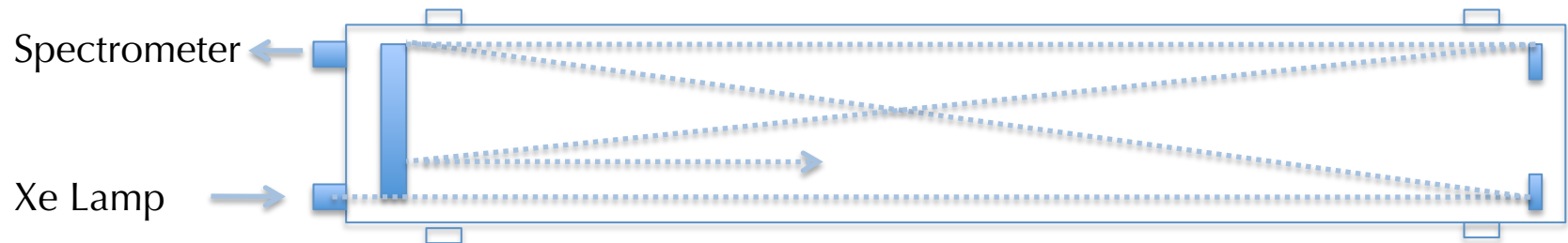
- Small points from 53 AERONET sites
- Circles from Table 1 parameters
- α from wavelength pairs rarely fall on 1:1 line
-i.e., spectral curvature is typical
- α from longer wavelength pairs more sensitive to fine mode volume fraction (top)
- α from shorter wavelength pairs more sensitive to fine mode effective radius (bottom)

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SpEx Aerosol Extinction Spectra, 300-700 nm

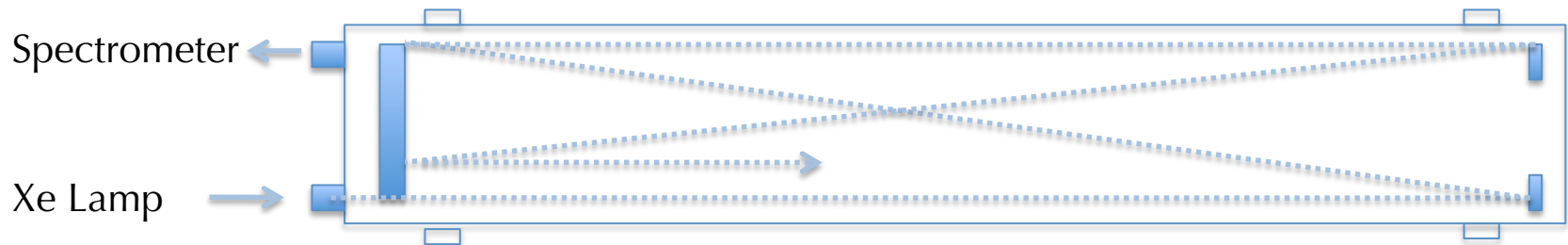
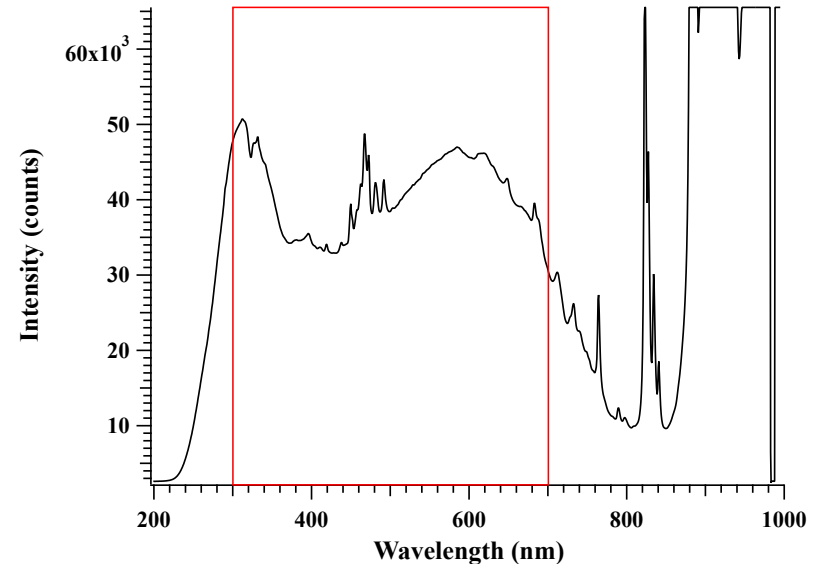
- Spectral Aerosol Extinction (SpEx) instrument
 - 39.4 m optical path
 - 17 l internal volume
 - Flow rate ~ 70 lpm
 - Flush time 90 s
 - Integration time ~20-50 ms
 - Sample time 30 s
 - Intensity spectra every 2 min
 - Extinction spectra every 4 min
 - $\text{Ext} = -\ln(I/I_0) / L$



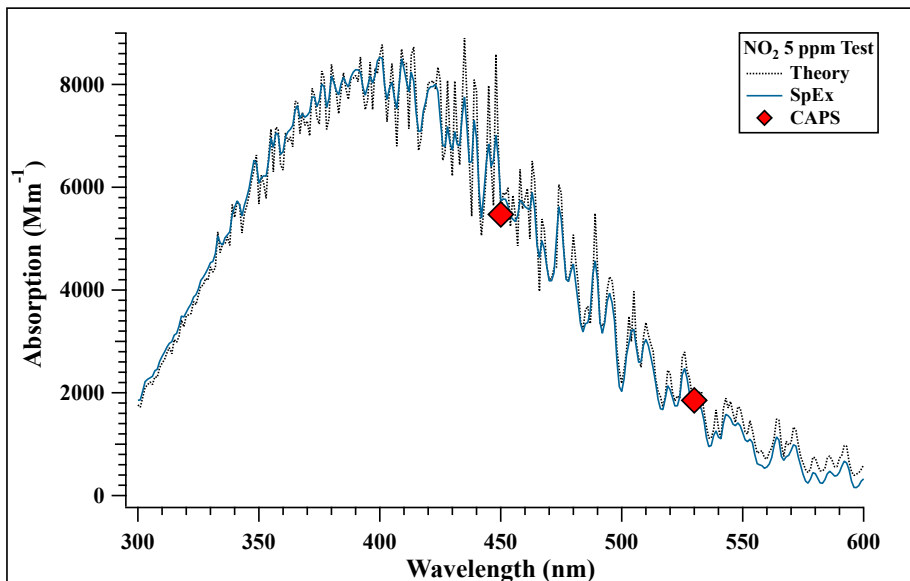
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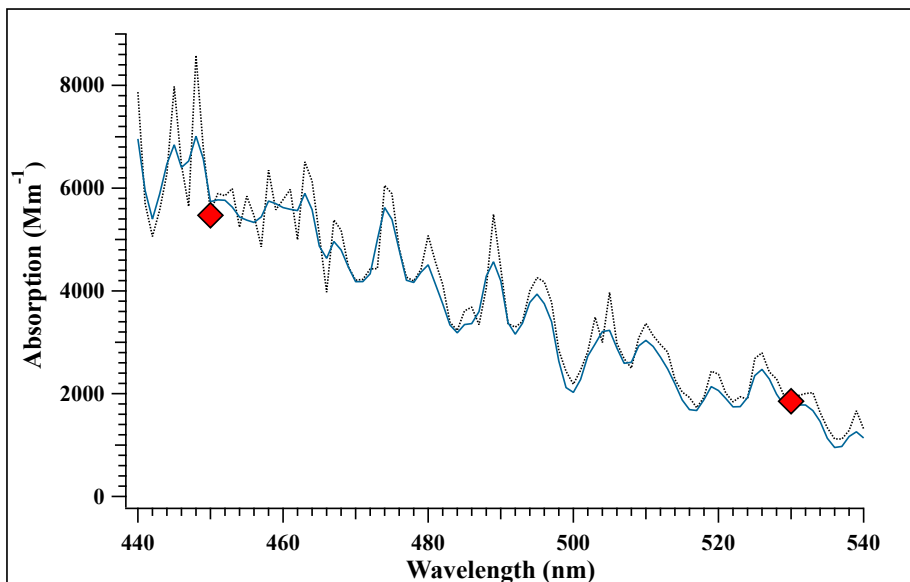
Gas-phase Laboratory Tests



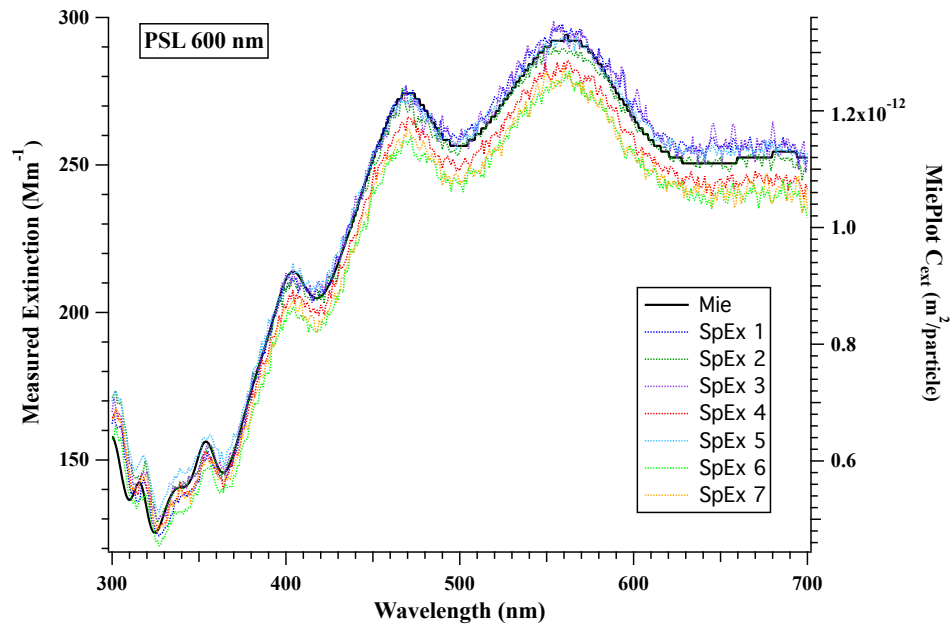
- No evidence of O₃ production nor NO₂ loss in light beam of optical cell with 80 lpm flow

- No loss of NO₂ through the filter in the reference inlet line

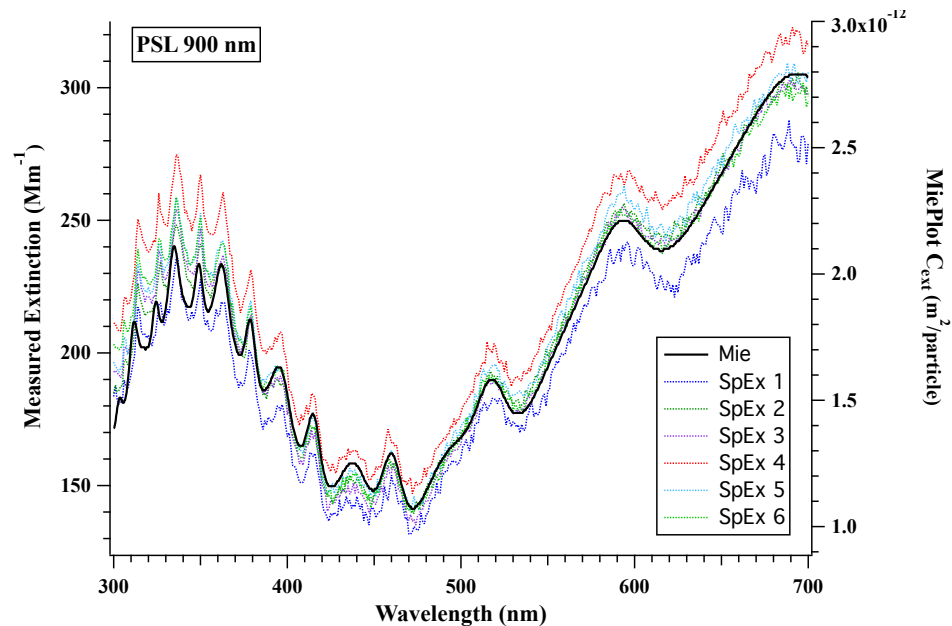
***SpEx MEASURED
NO₂ SPECTRUM
AGREES WELL WITH THEORY***



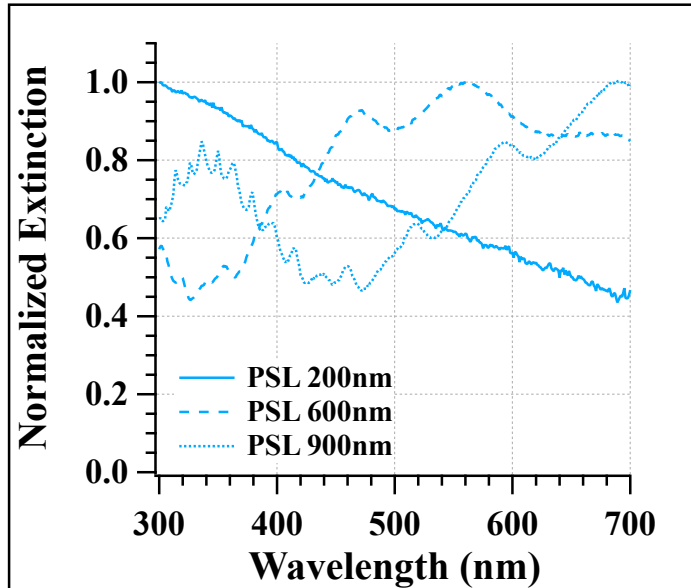
SpEx PSL Spectra & Mie Theory



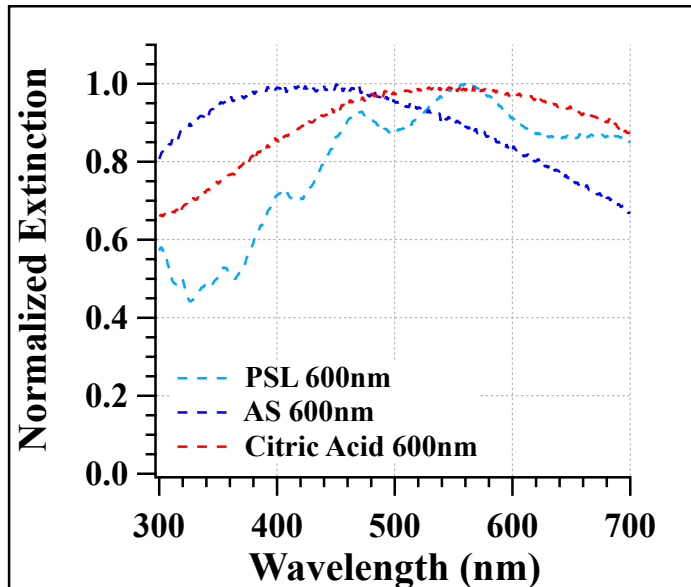
***SPEx MEASURED
AEROSOL SPECTRA
AGREE WELL WITH
MIE THEORY***



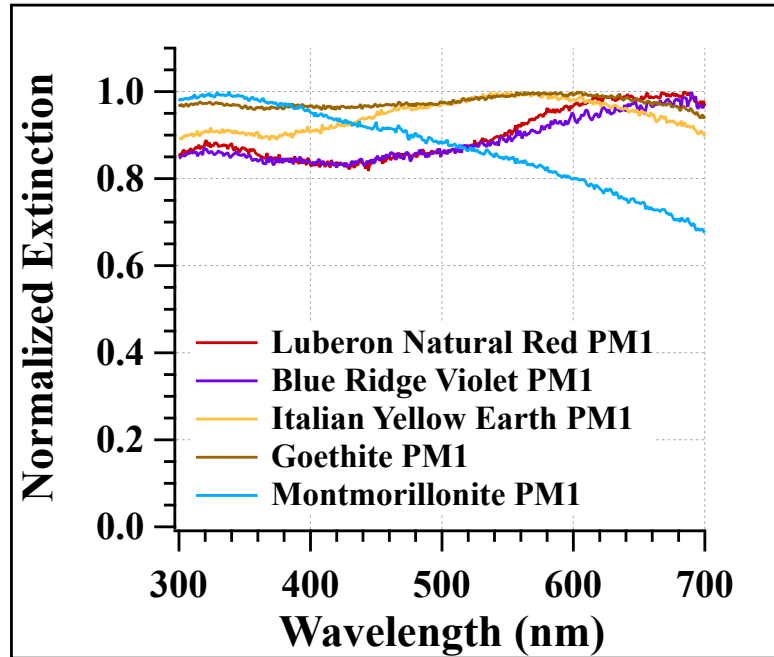
Normalized Mean Spectra



- Peak extinction decreases with particle size
- Spectral shape depends on particle composition, as well as, size

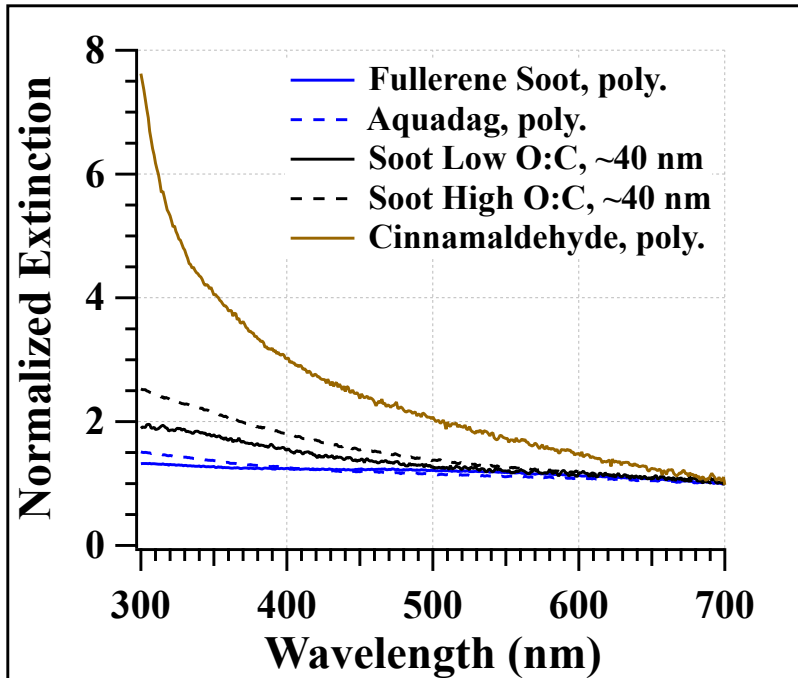


Normalized Mean Spectra: PM1 Dust

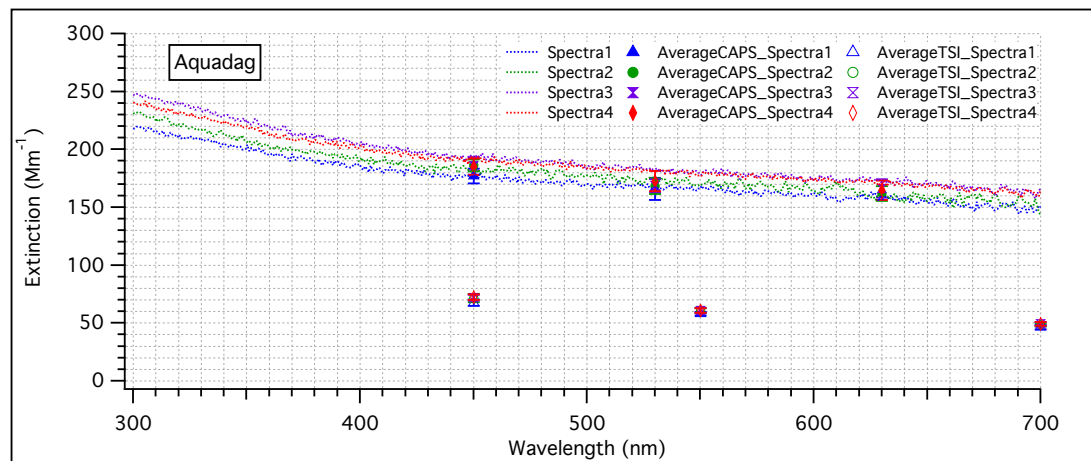
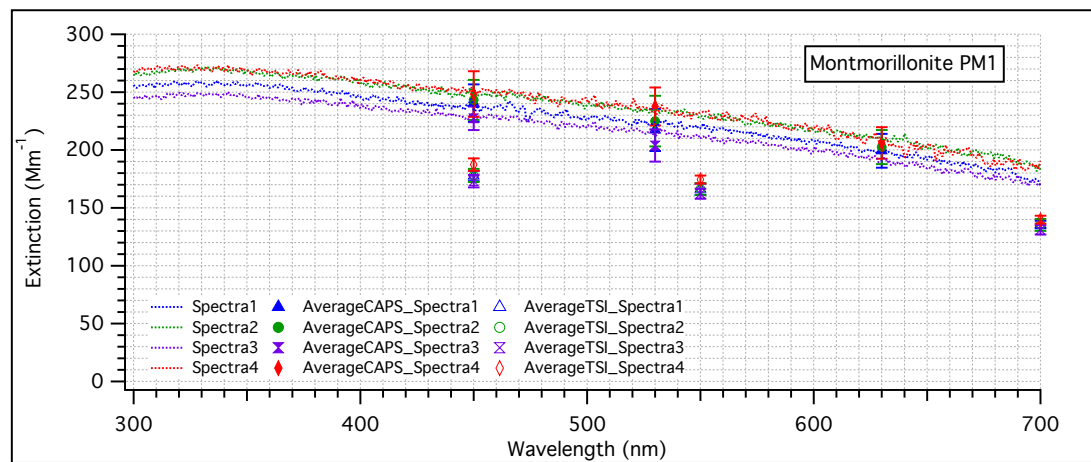
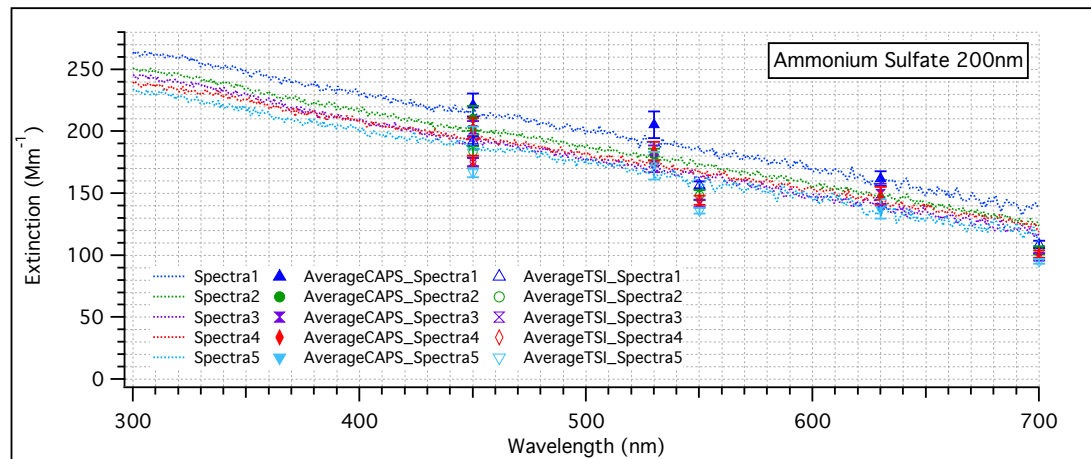


- PM1 Dust Spectra show little wavelength dependence
- Pigments influence spectral shape

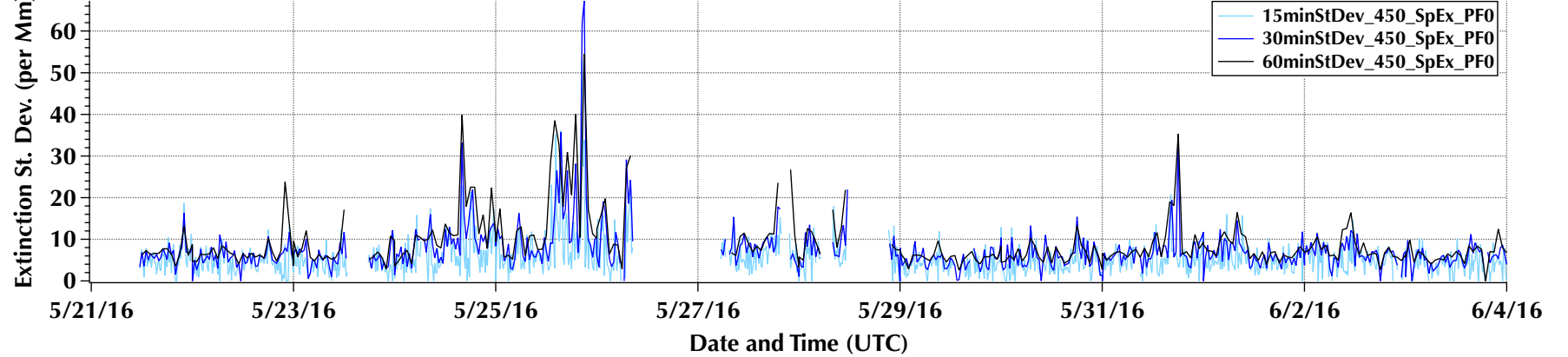
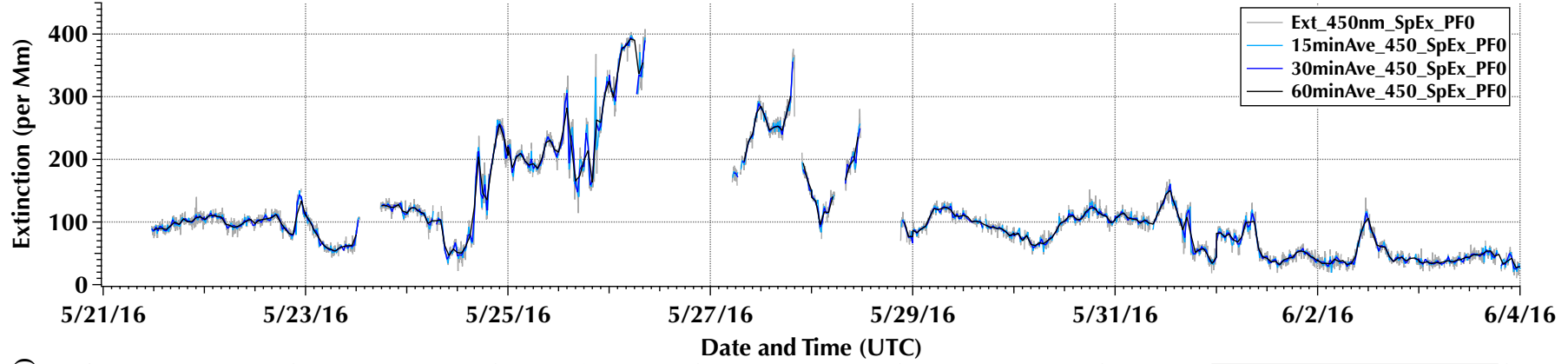
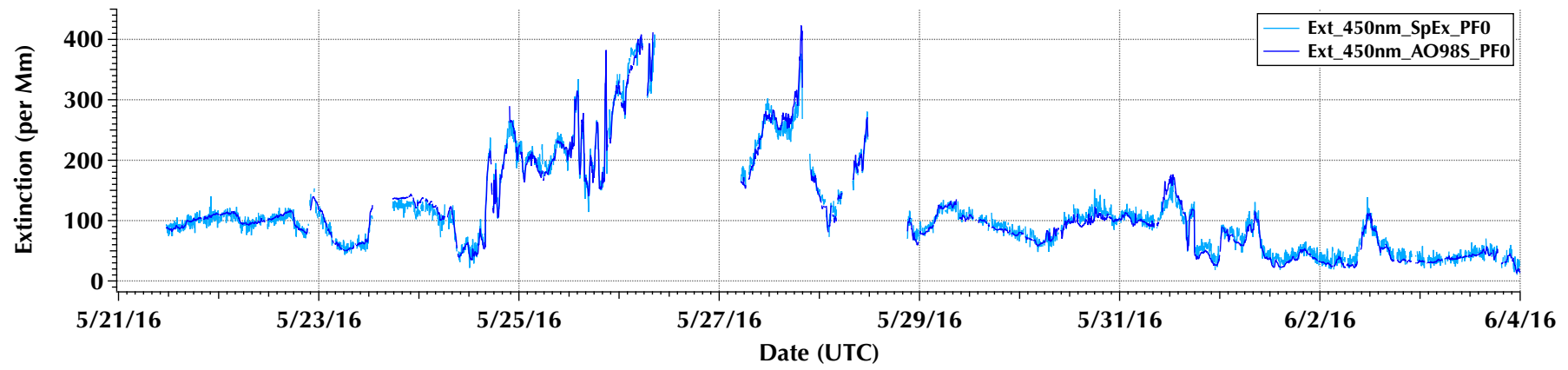
Normalized Mean Spectra: scaled to 700 nm



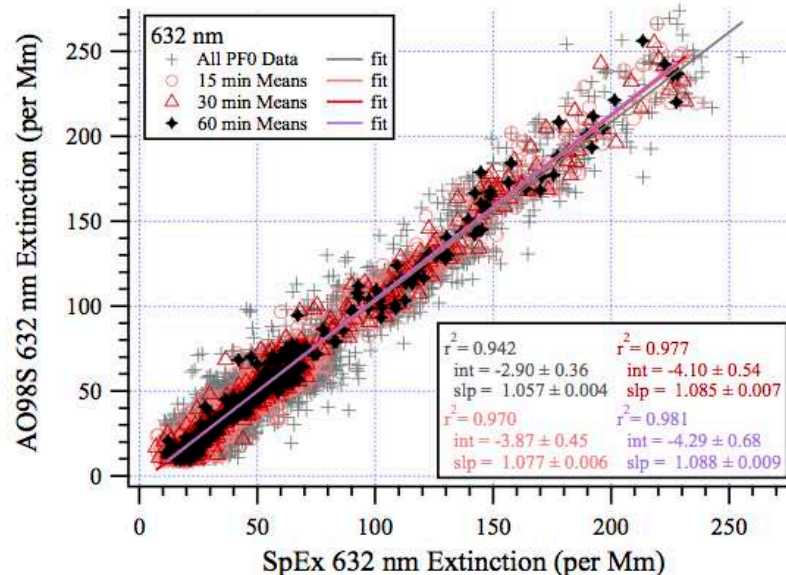
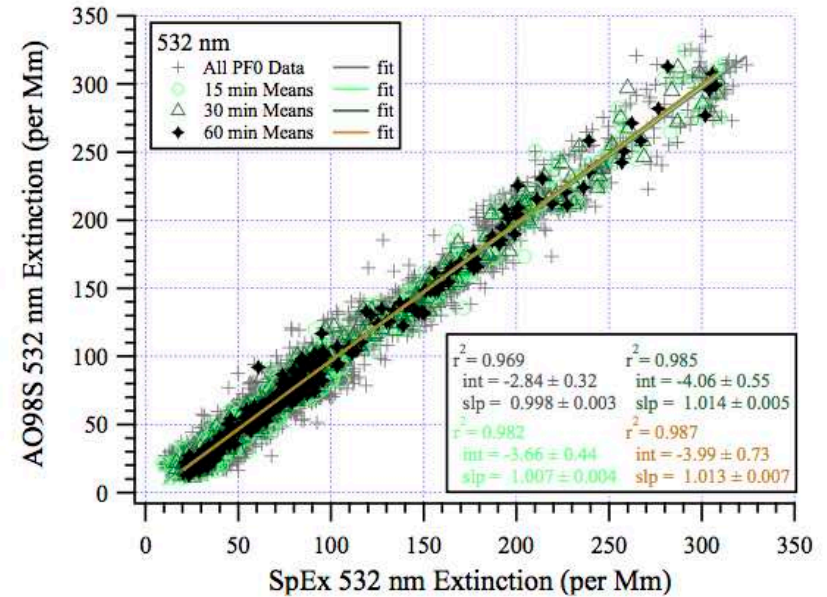
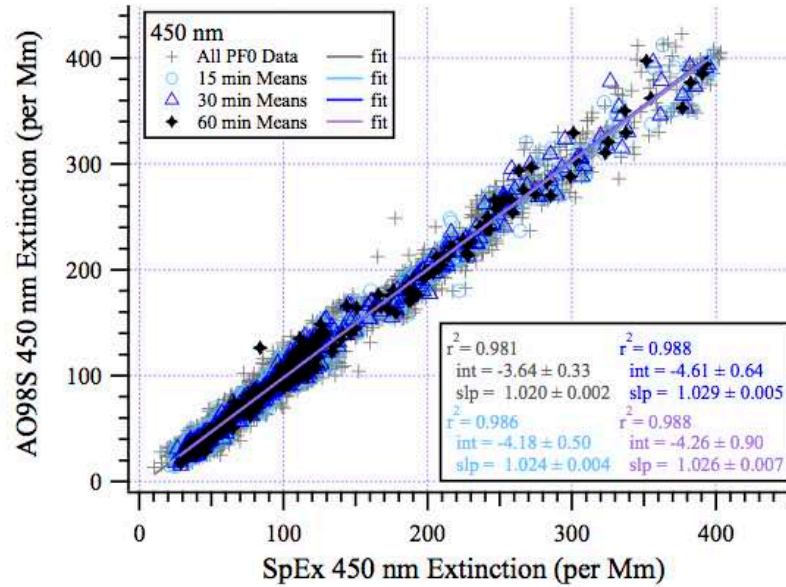
- Uncoated soot compared to:
BC surrogates:
 Fullerene soot
 Aquadag
BrC surrogate:
 Cinnamaldehyde
- UV extinction of uncoated soot found in range between BC & BrC
- Little variability among soot & BC samples from 500-700 nm



SpEx Comparison to Neph+TAP Extinction 450nm

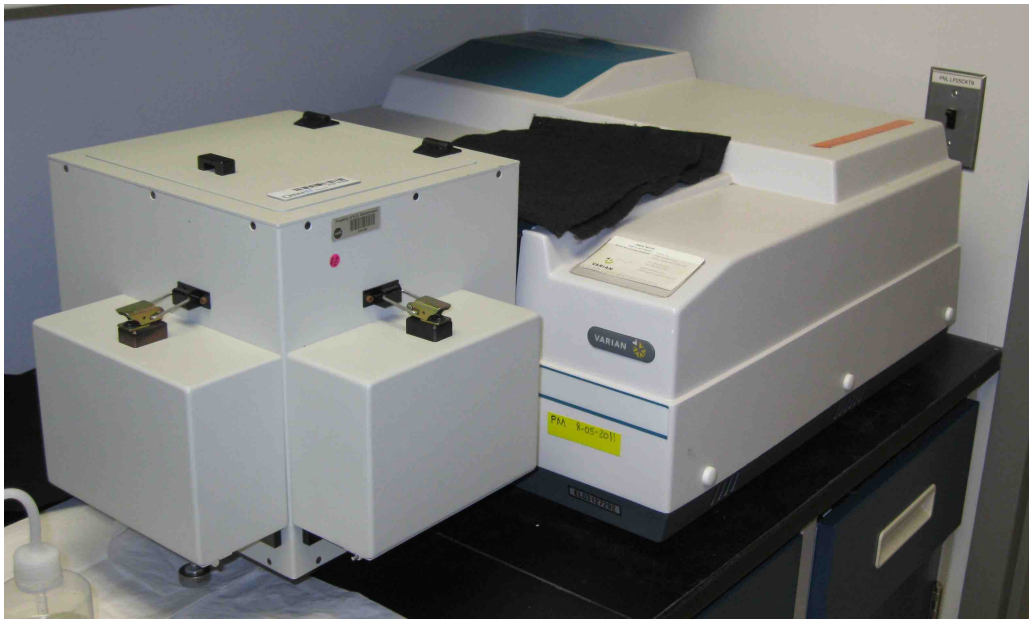


Neph+TAP Exts. fit to SpEx: 450, 532, & 632nm

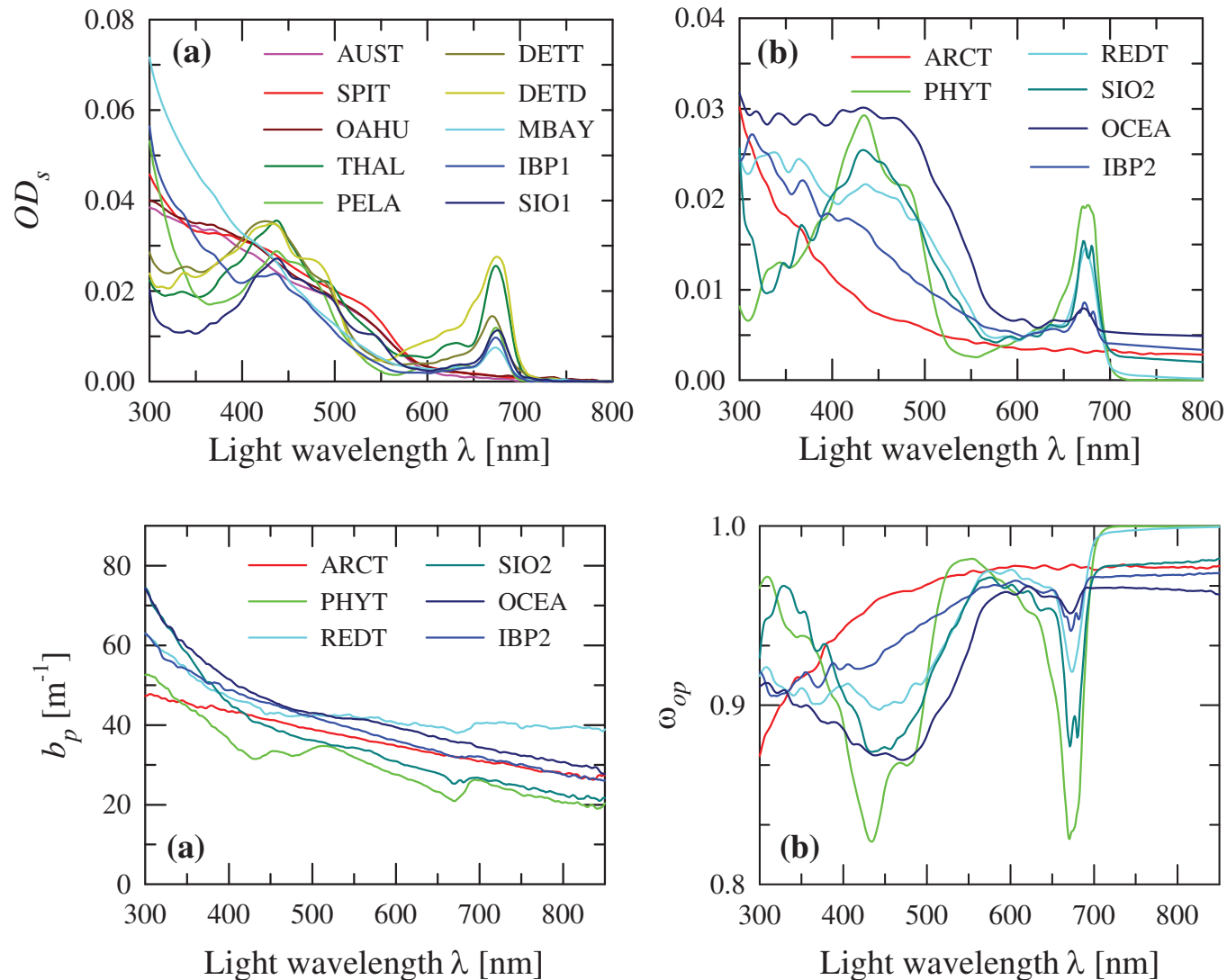


Total Aerosol Absorption Spectra 300-700 nm

- Glass fiber filters (GFF)
 - (3 hr daytime; 12 hr night)
- Placed in center of integrating sphere
 - (Labsphere DRA-CA-30)attached to dual beam spectrometer
(Cary 100 Bio UV-Visible Spectrophotometer)

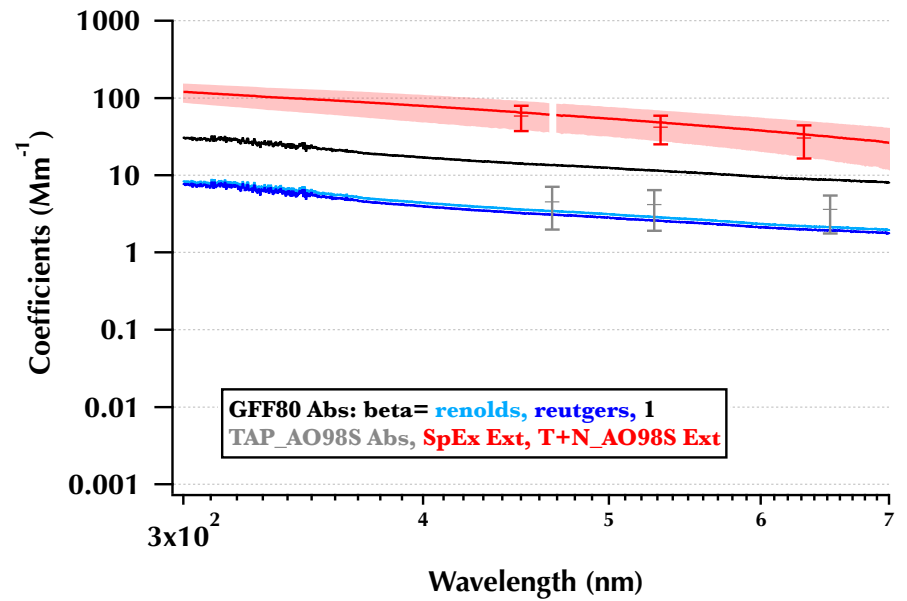
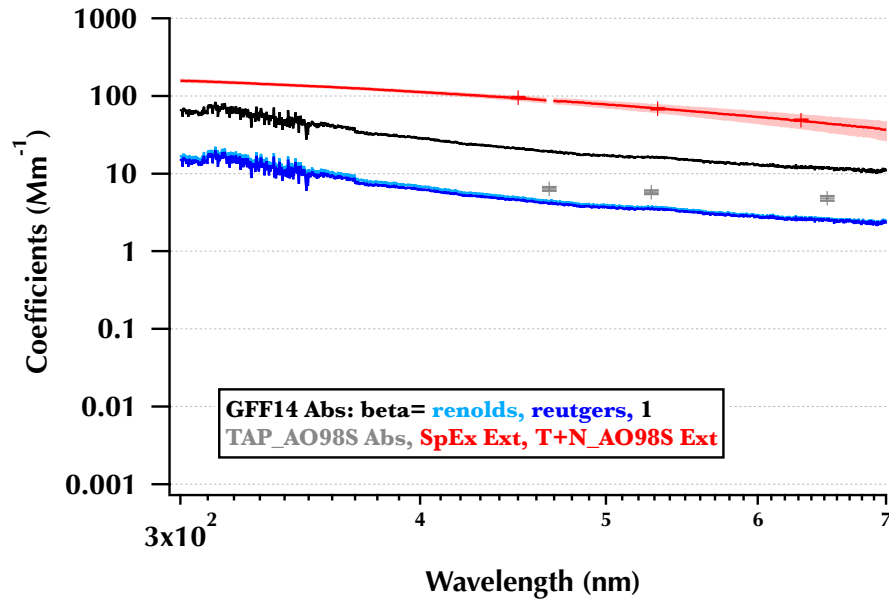


Seawater Particle Spectra

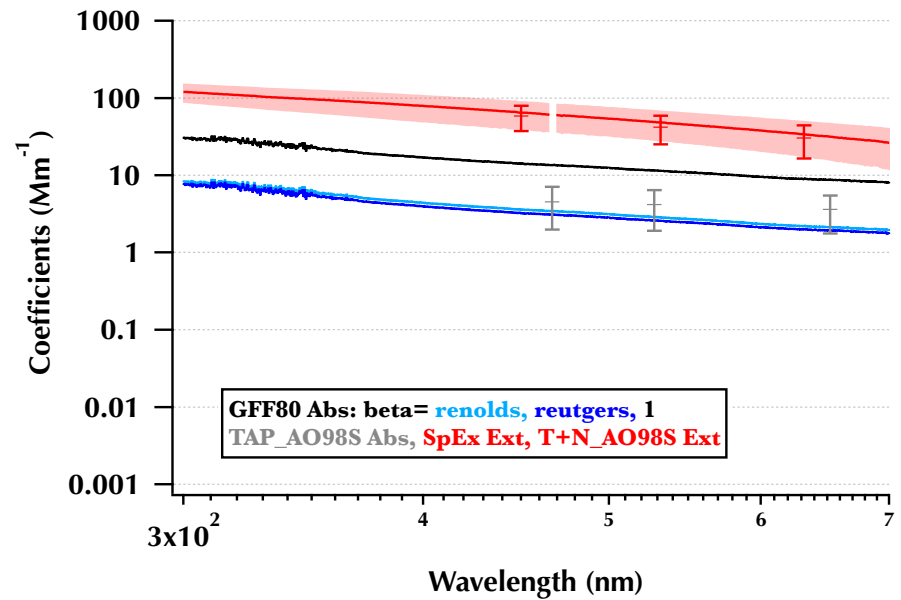
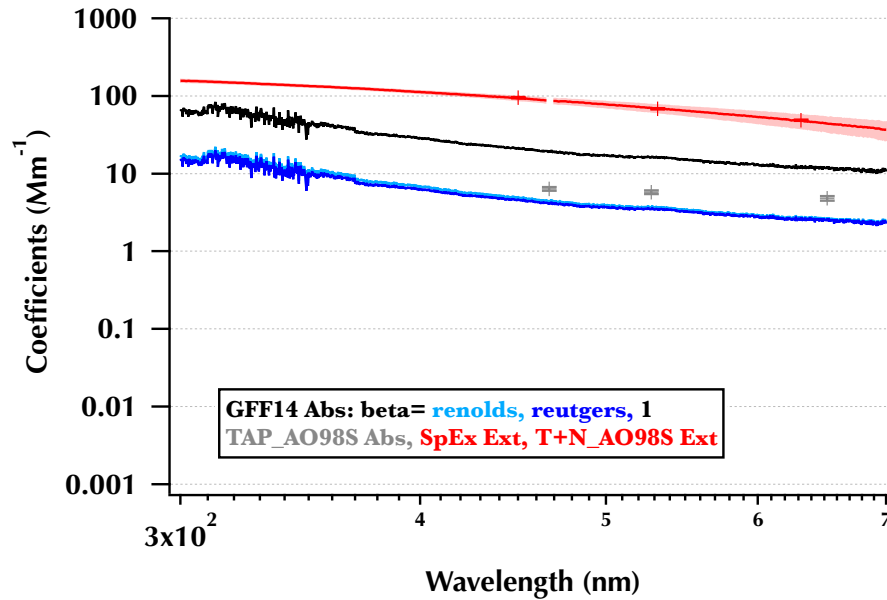


[Stramski et al., Applied Optics, 54(22), 6763-6782, 2015]

Total Absorption: GFF Comparison to TAP



Total Absorption: GFF Comparison to TAP



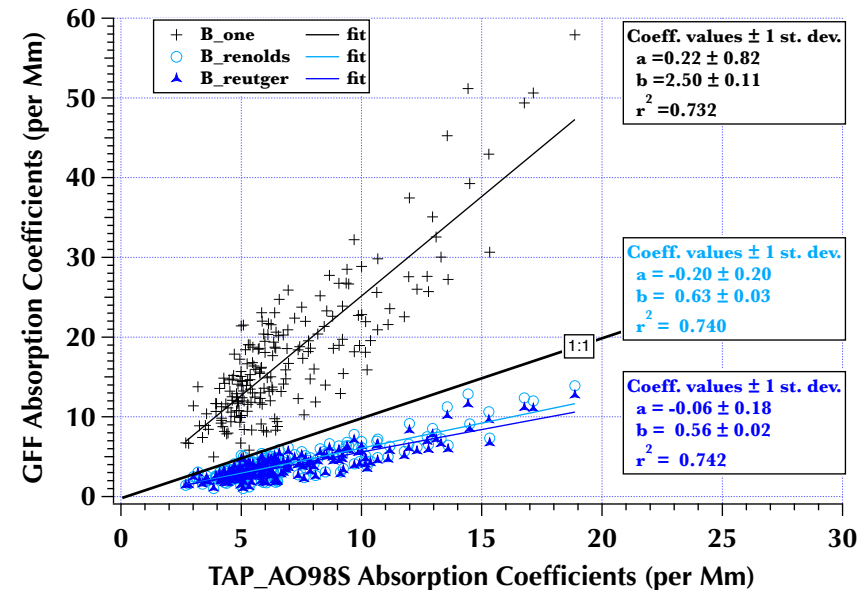
Absorption Coefficient calculated from measured Absorbance via:

$$a_p = (2.303 * (abs) * (\pi * r^2) / V) / \beta;$$

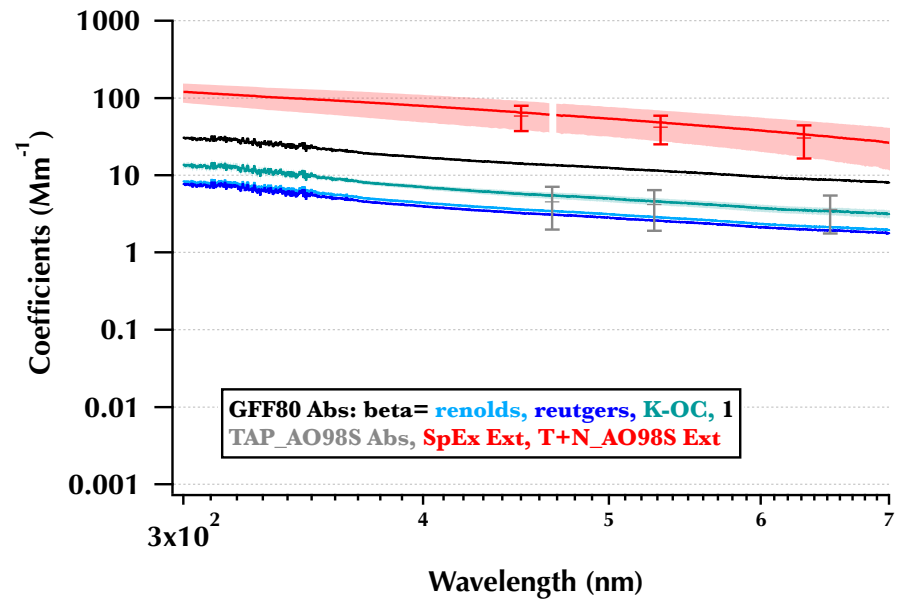
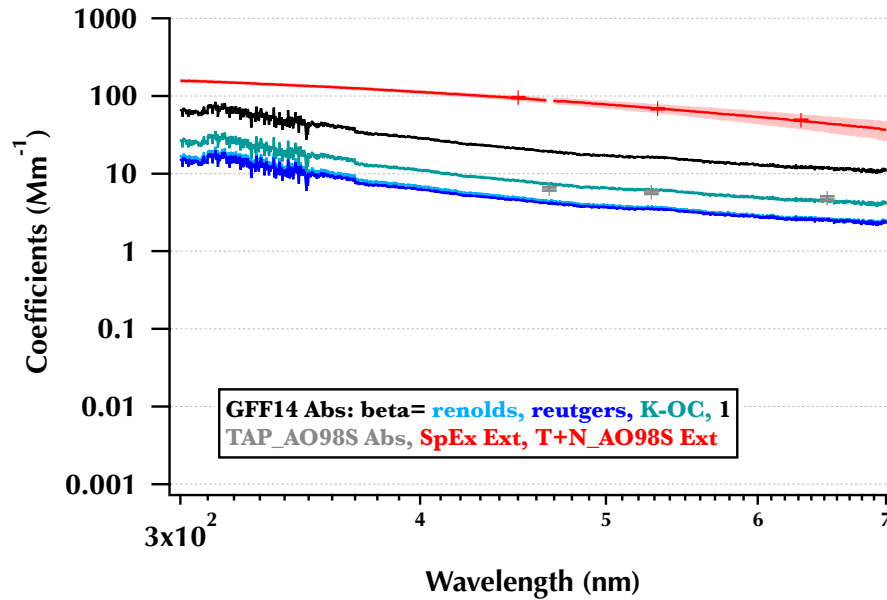
Empirical β correction factors:

$$\beta_{\text{Renolds}} = 3.0927 * abs^{-.0877}$$

$$\beta_{\text{Reutger}} = 6.475 * abs^2 - 6.474 * abs + 4.765$$



Total Absorption: GFF Comparison to TAP



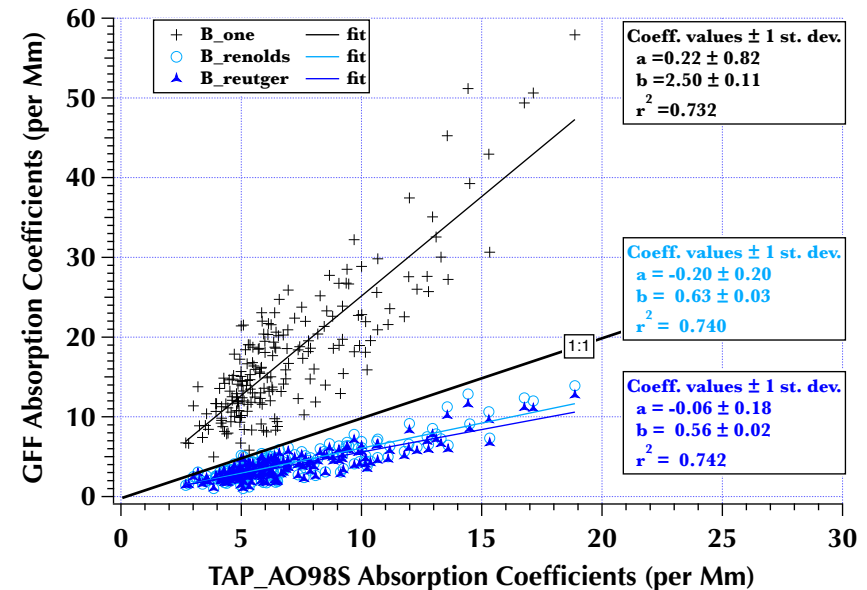
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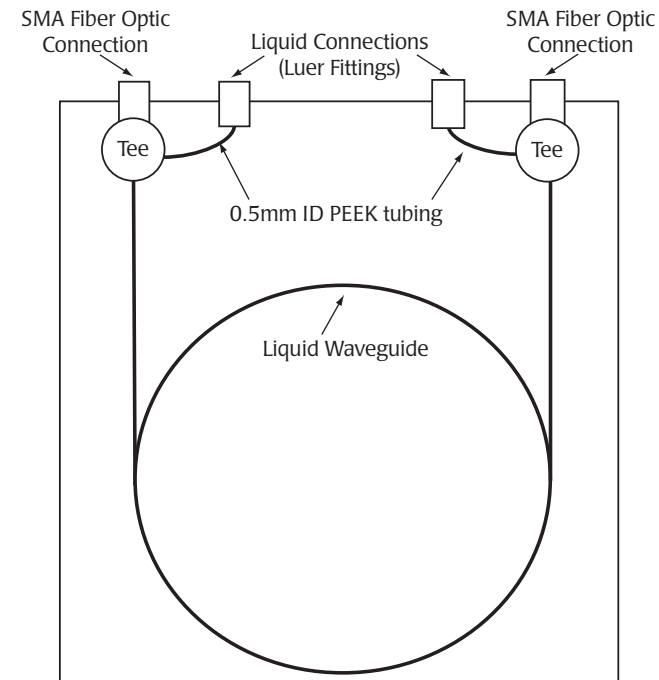


Water- & Methanol-soluble Aerosol Absorption Spectra 300-700 nm

- Telfon Fluoropore filters – cut in half
 - (3 hr daytime; 12 hr night)
- Filter halves extracted in
 - 18 M Ω deionized water (DIW) or
 - Spectrographic grade methanol (MeOH)
- Extracts filtered to remove particles, injected into Liquid Waveguide Capillary Cell (LWCC)
 - World Precision Instruments LWCC-3100
 - 100 cm path length
- DIW extracts also analyzed via
 - Dionex ICS-3000 Ion Chromatography System
 - Aerodyne High Resolution – Time Of Flight Aerosol Mass Spectrometer (HR-TOF AMS)



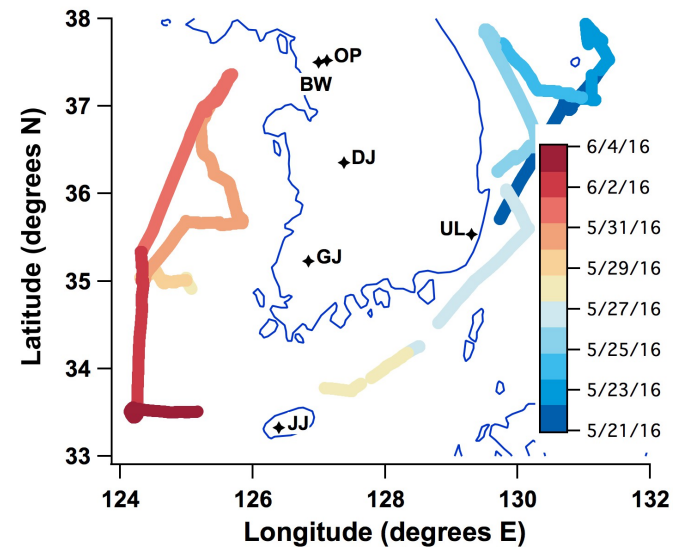
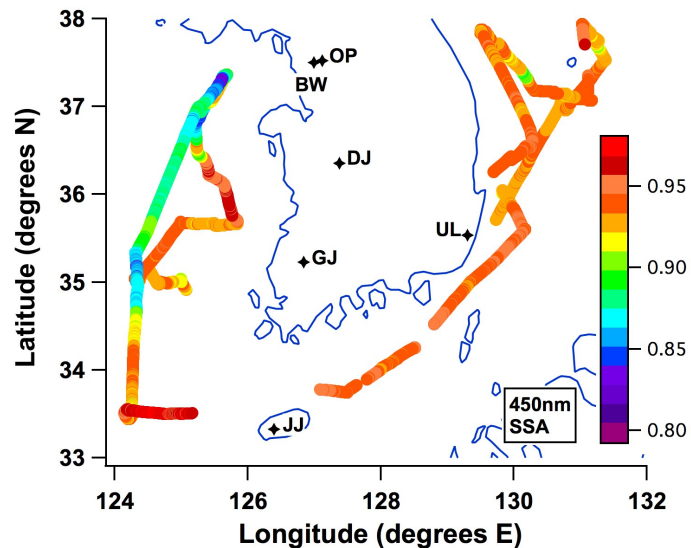
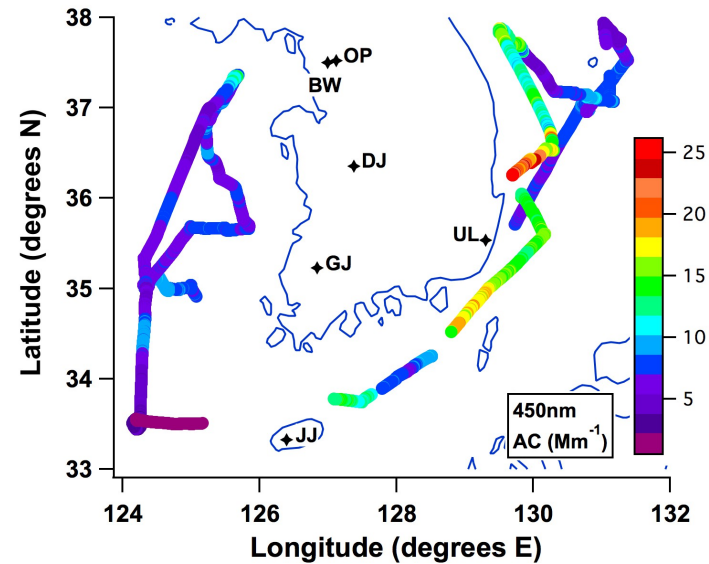
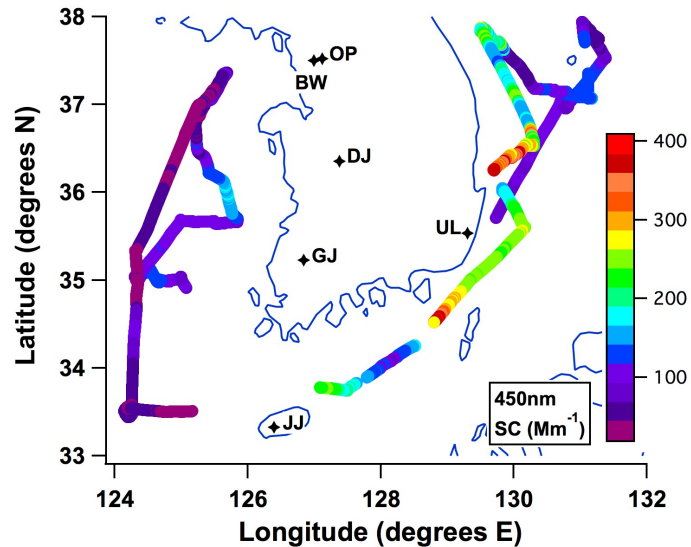
Images from World Precision Instruments LWCC-3100 manual.



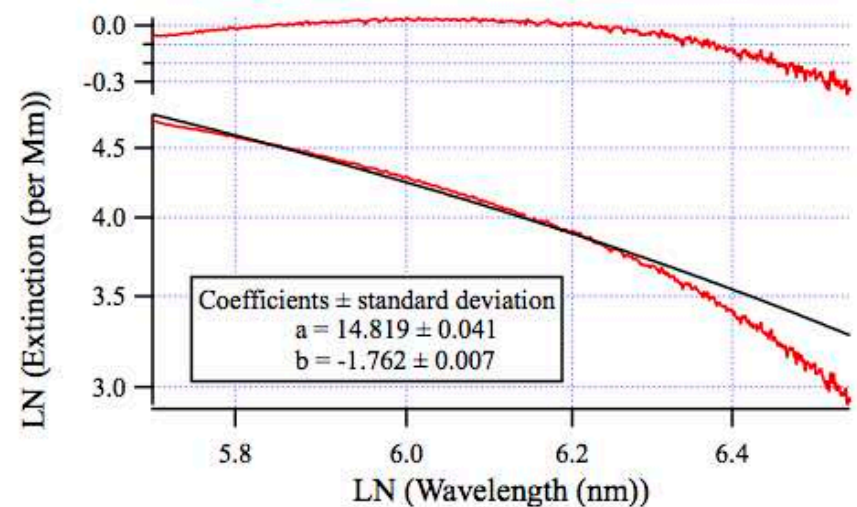
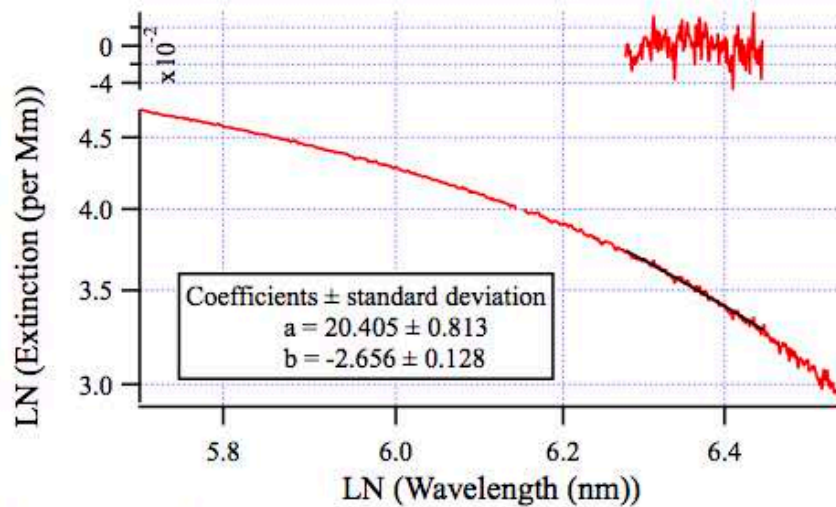
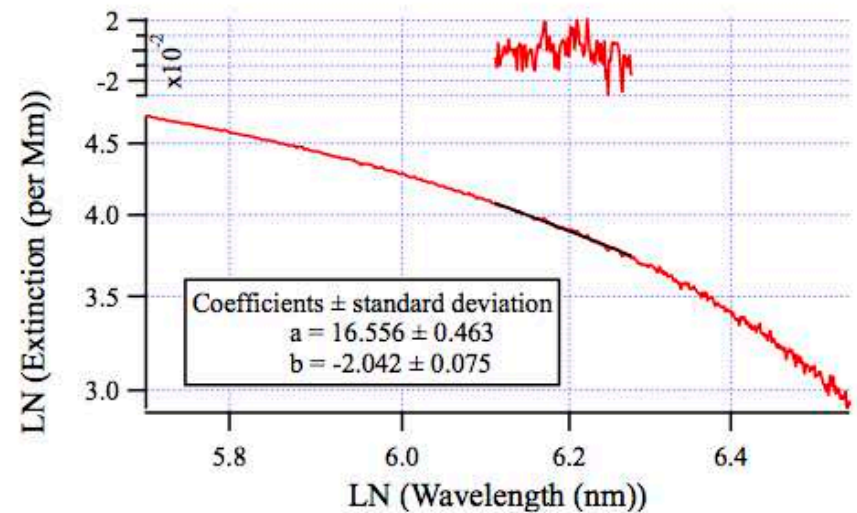
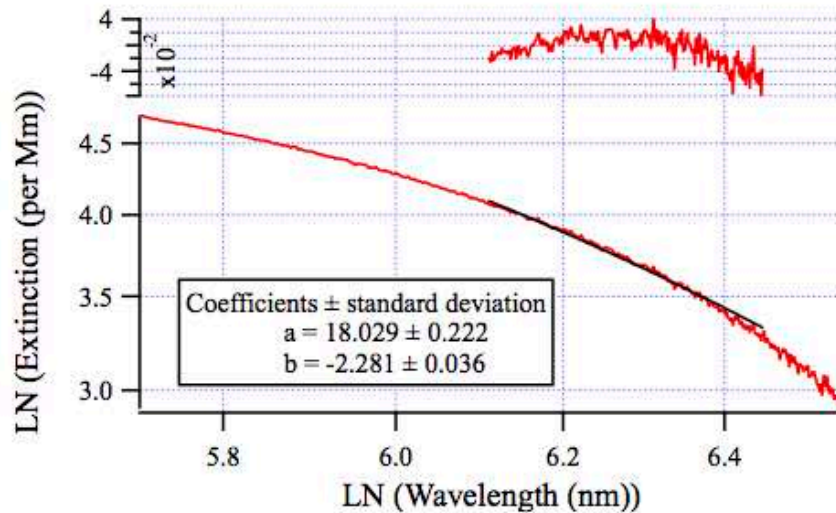
Overview

- Part 1: KORUS – OC
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- **Part 4: KORUS-OC Observations**
- Part 5: What's Next

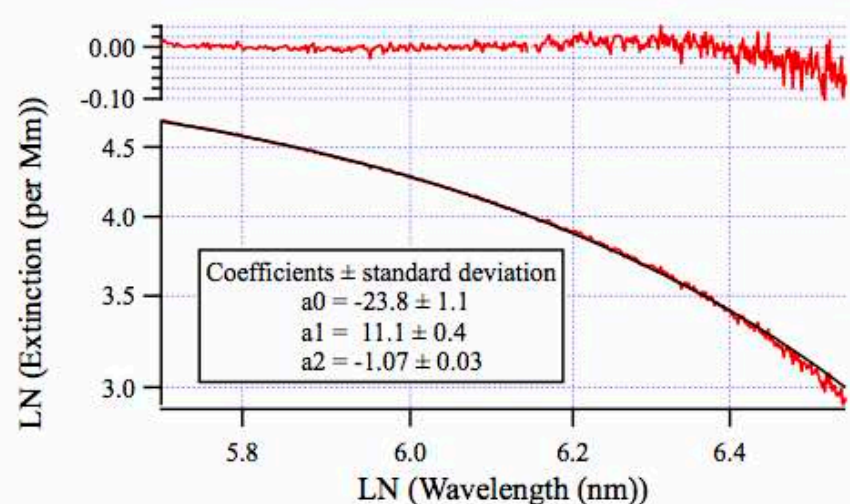
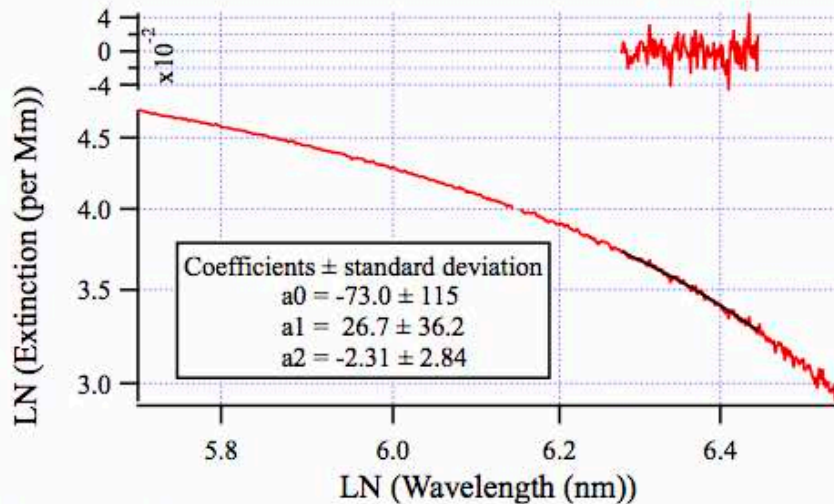
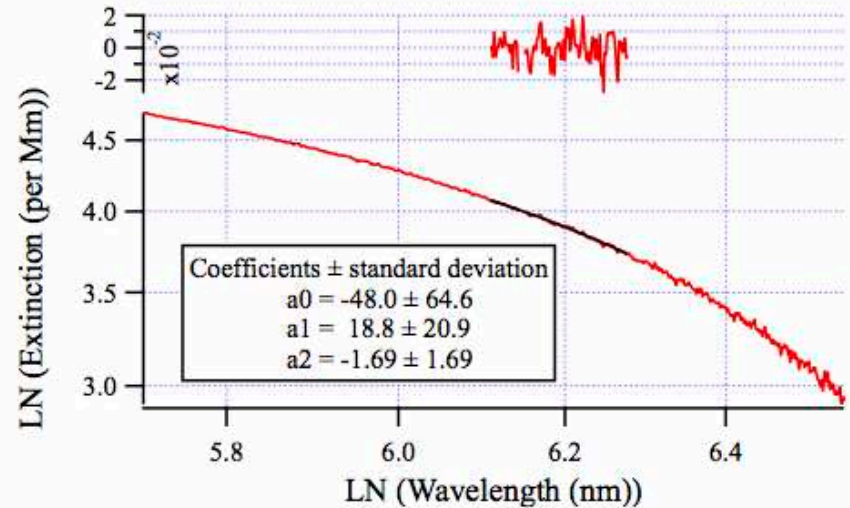
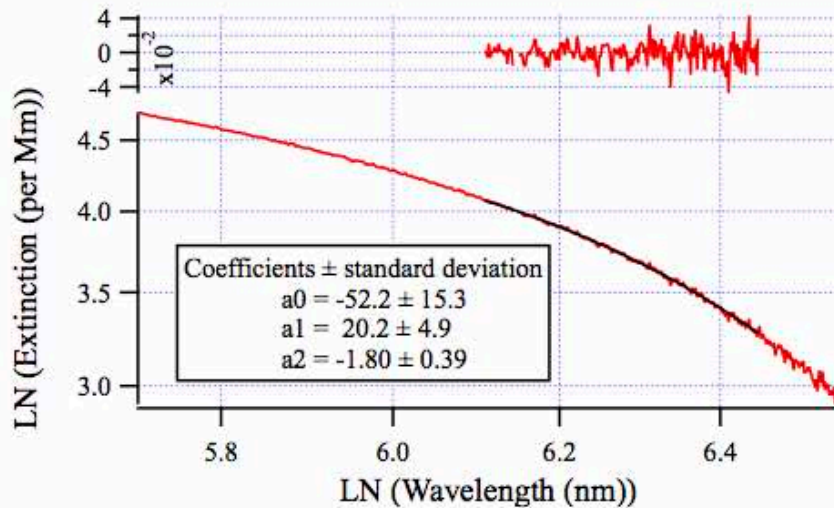
Maps of Scattering, Absorption & SSA



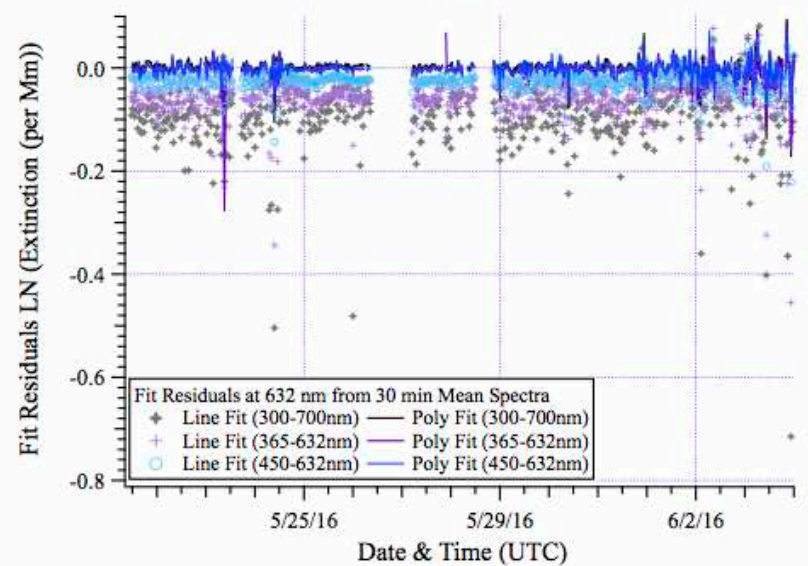
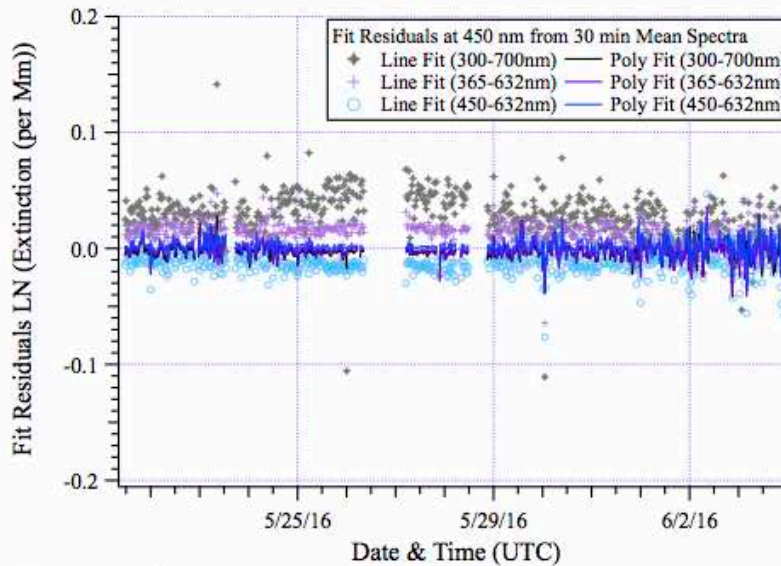
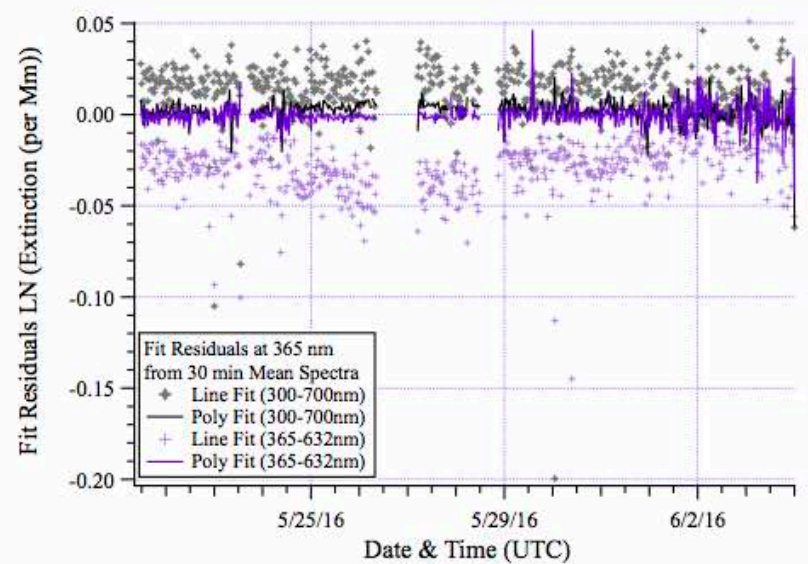
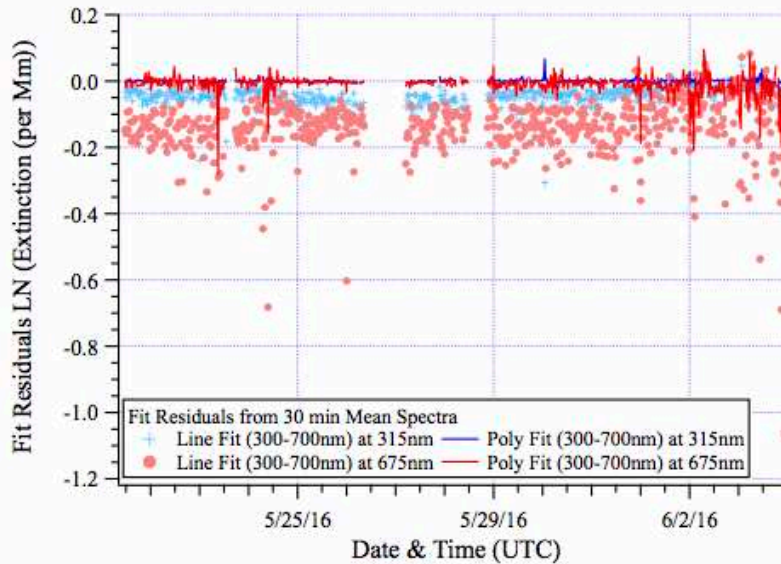
Linear Fit to SpEx Example



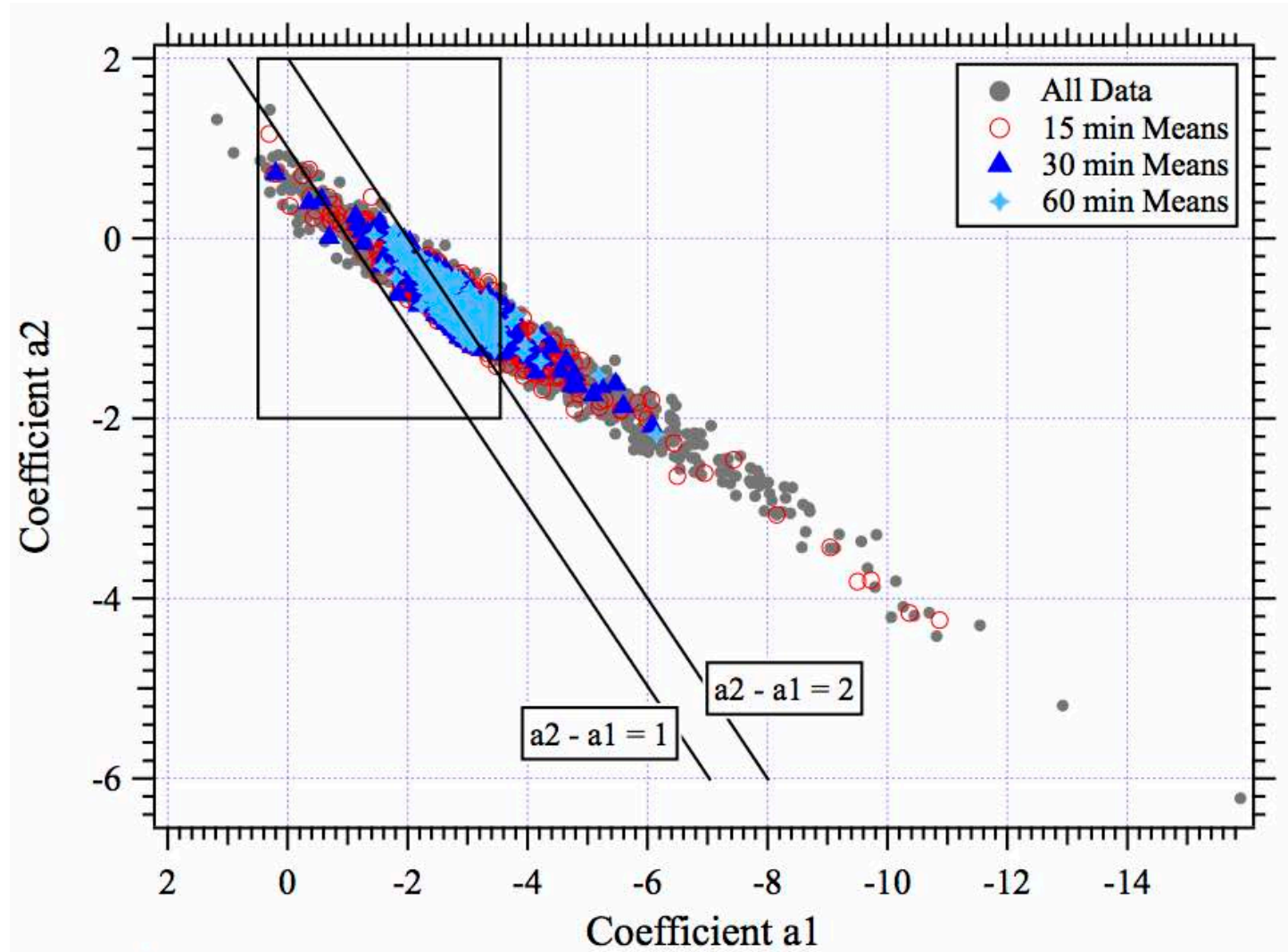
2nd Order Polynomial Fit to SpEx Example



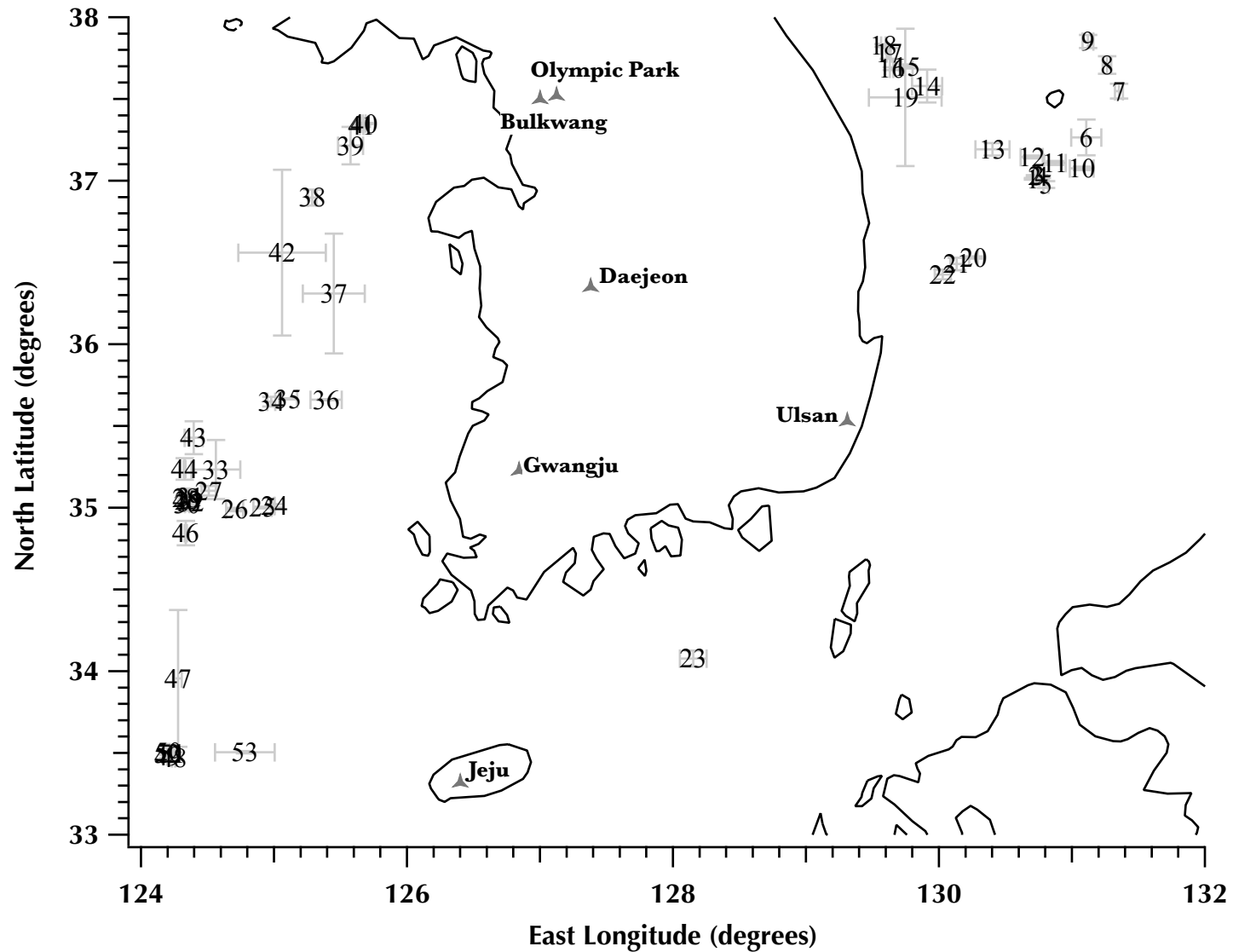
Fit Residuals Comparison



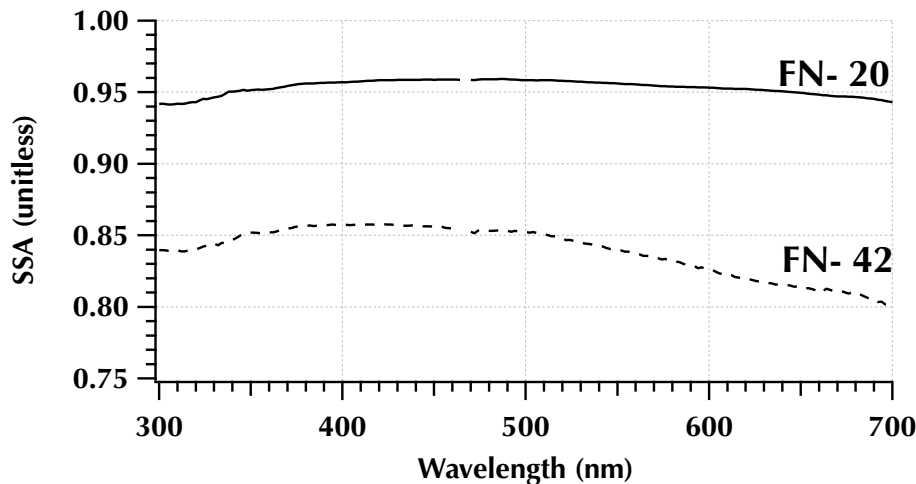
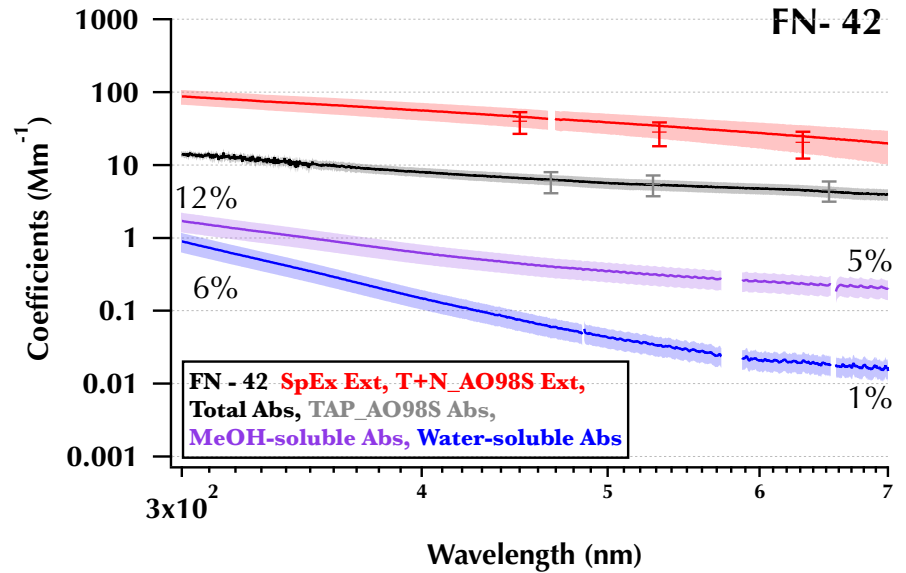
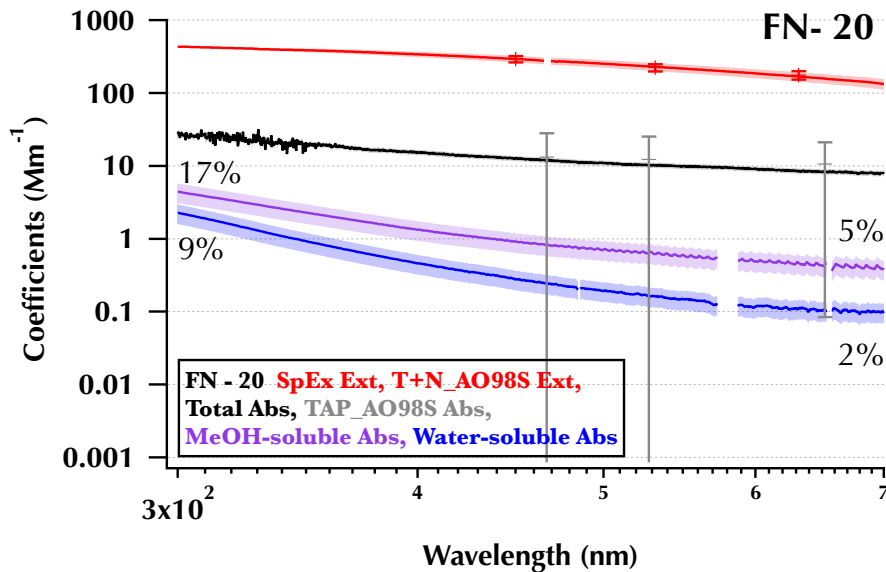
SpEx 2nd Order Polynomial Coefficients



Filter Sample Map



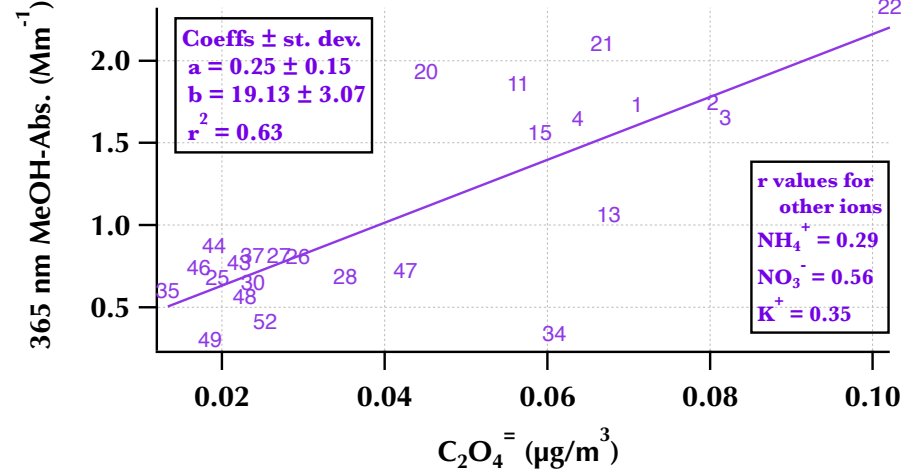
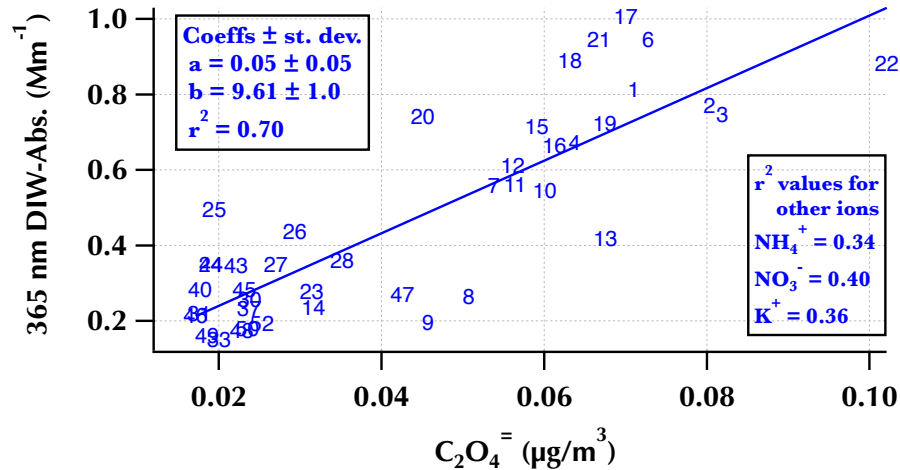
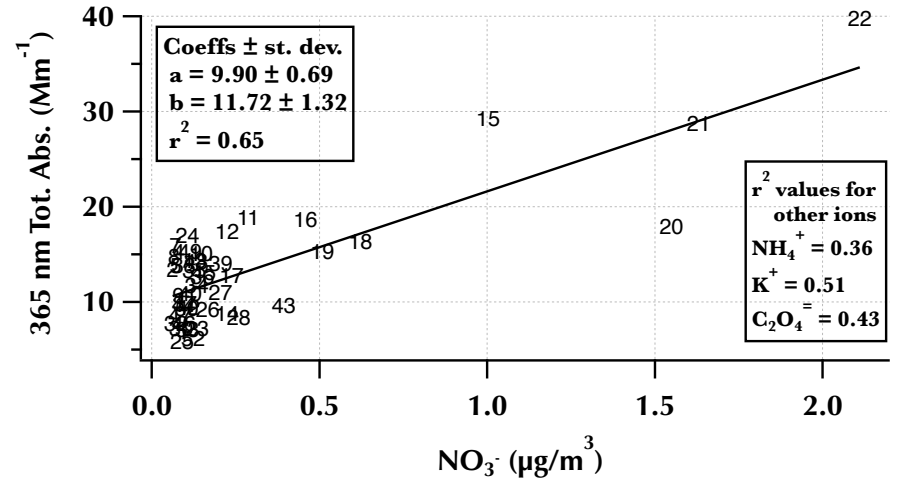
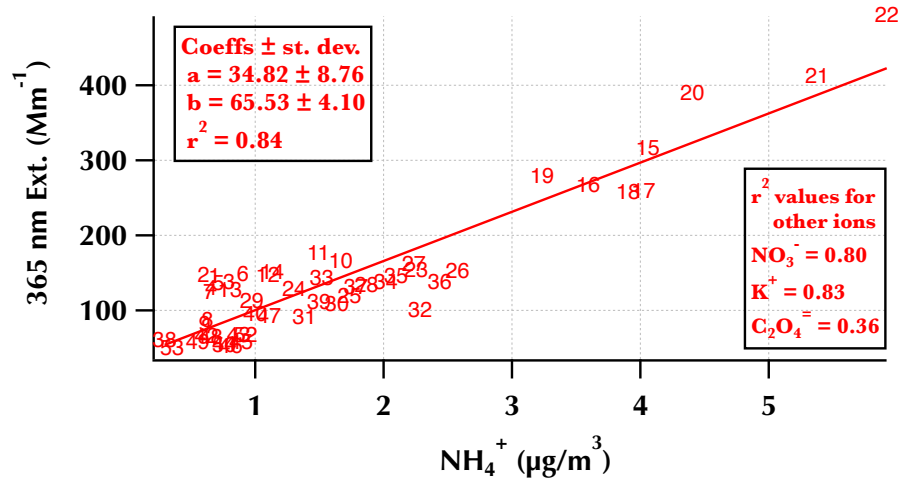
4 Sets of Measured Spectra



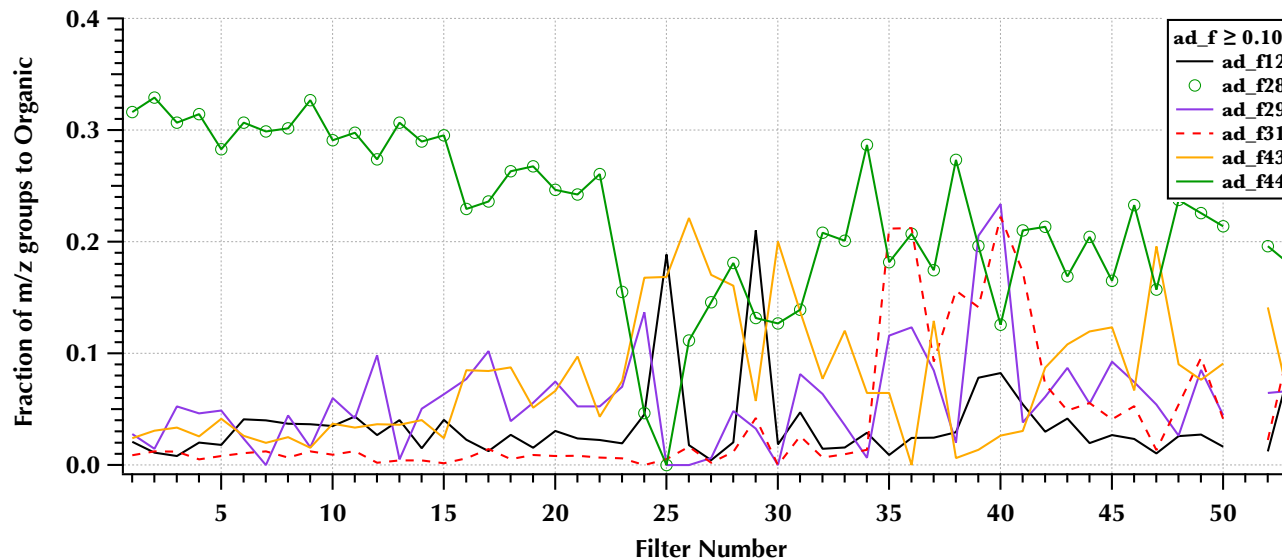
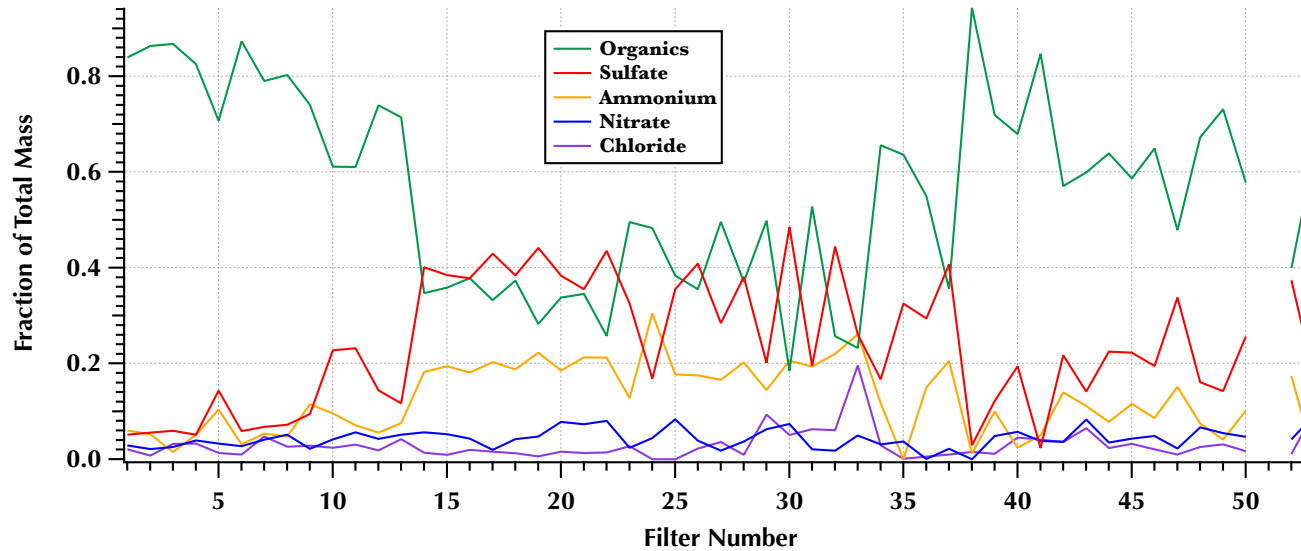
Measured spectra can be used to

- Compare measured wavelength-dependence to power law relationships
- Calculate spectra for other quantities, e.g., SSA
- Investigate relationships between total absorption and absorption of soluble chromophores

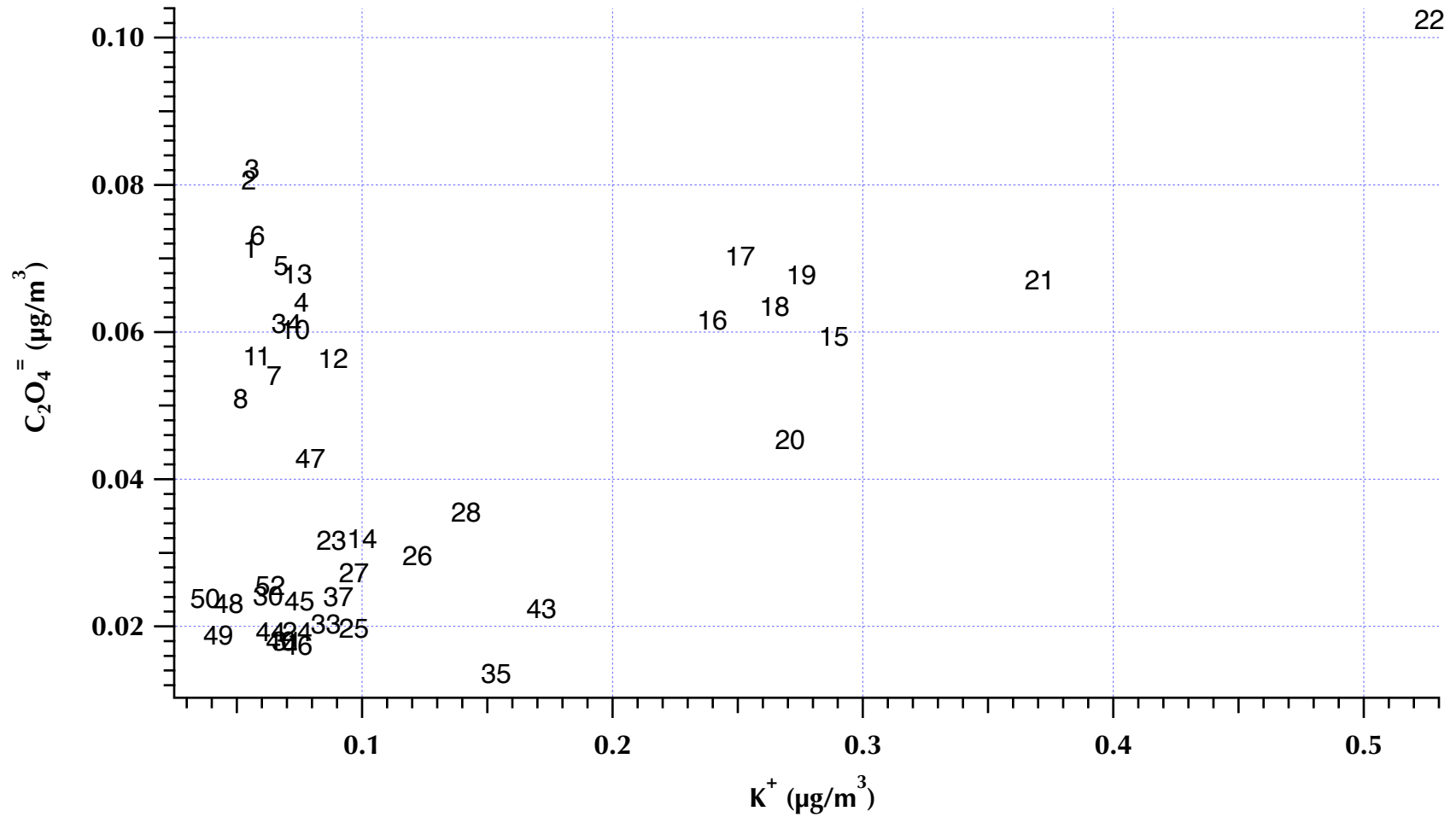
365nm Absorption and Extinction v. WSII



HR-TOF AMS Time Series

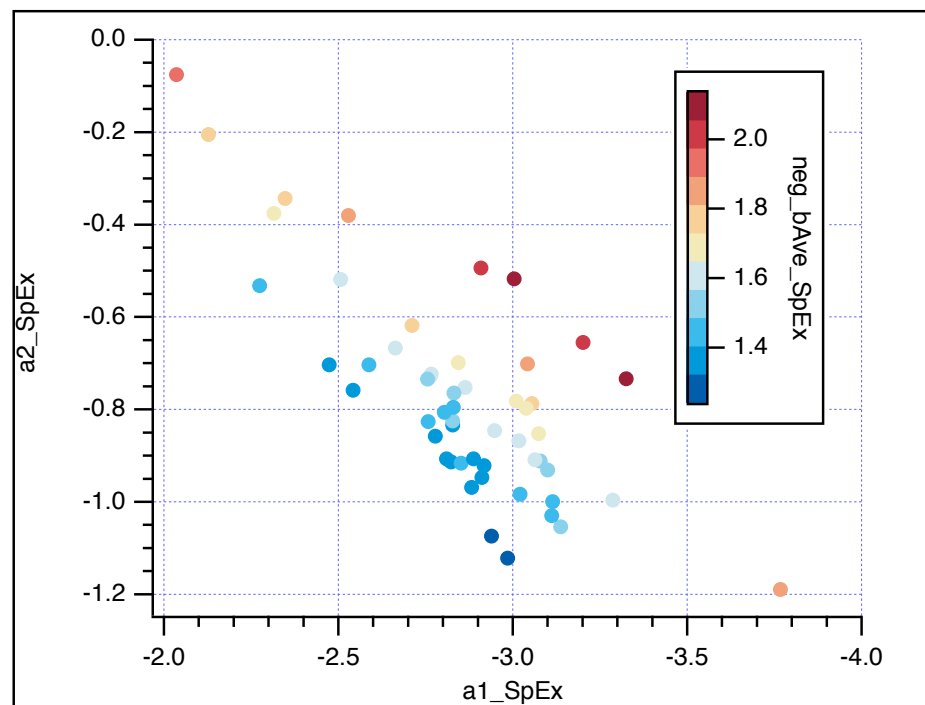
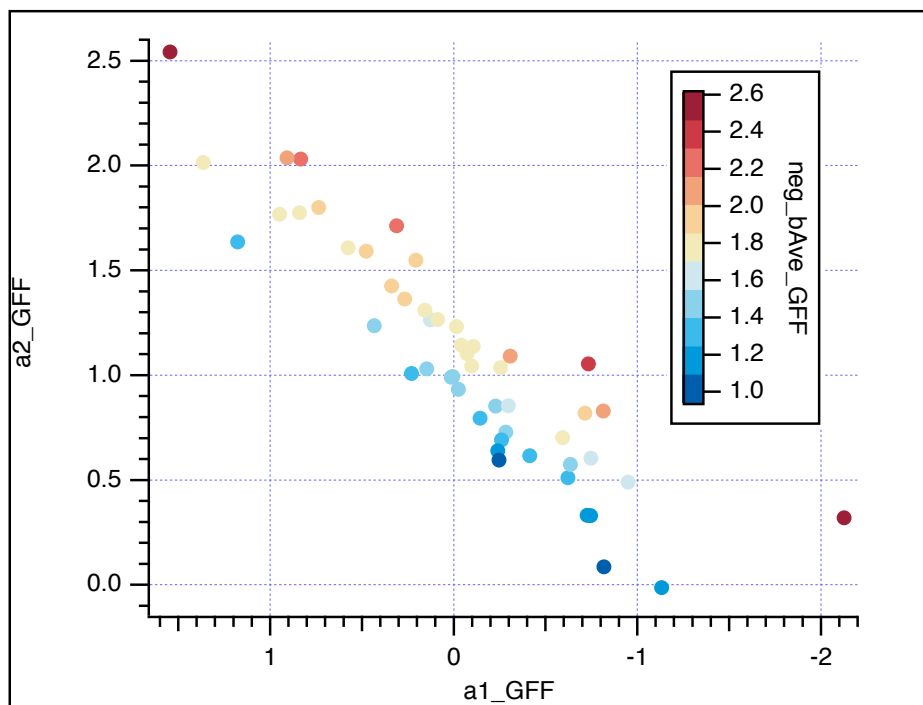
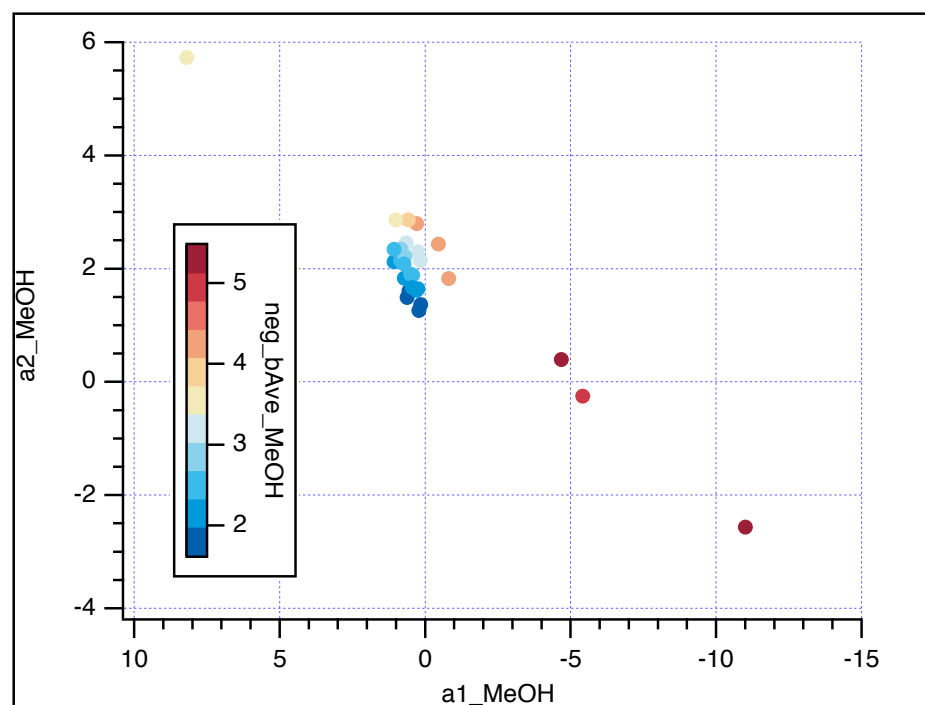
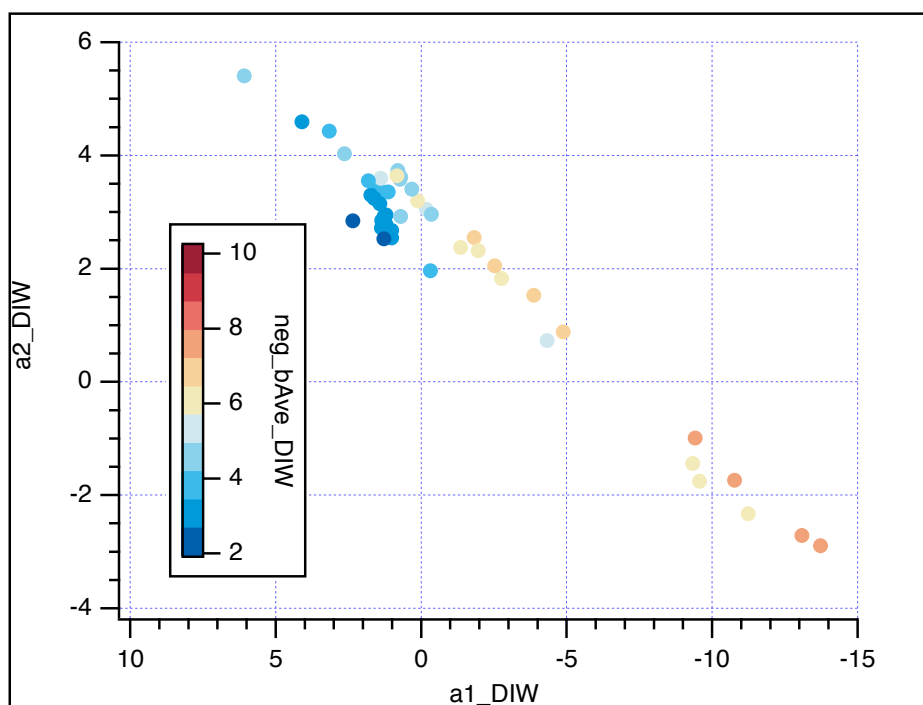


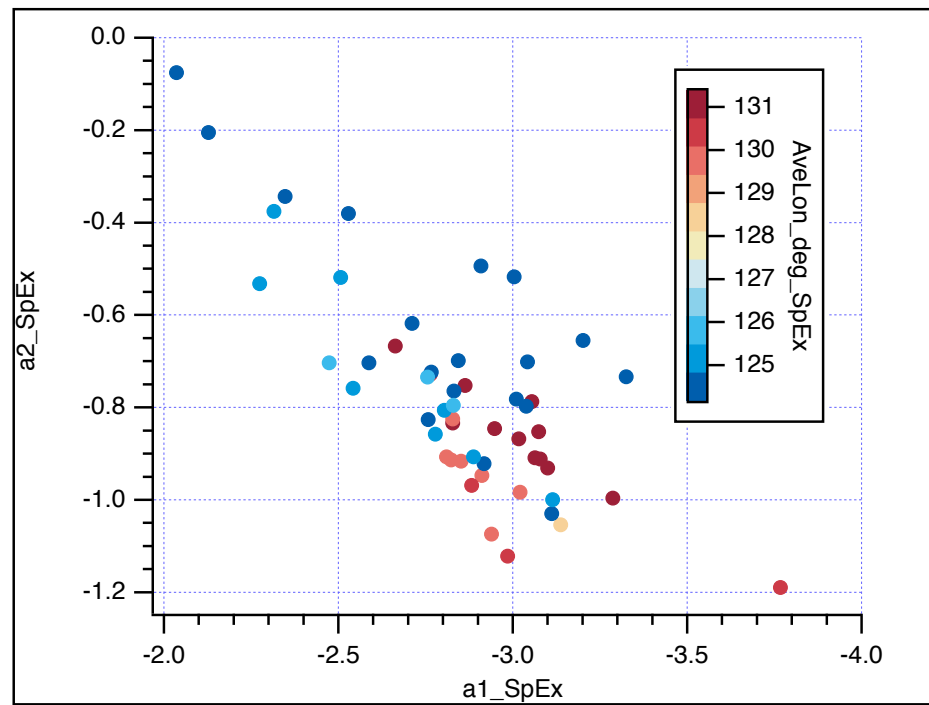
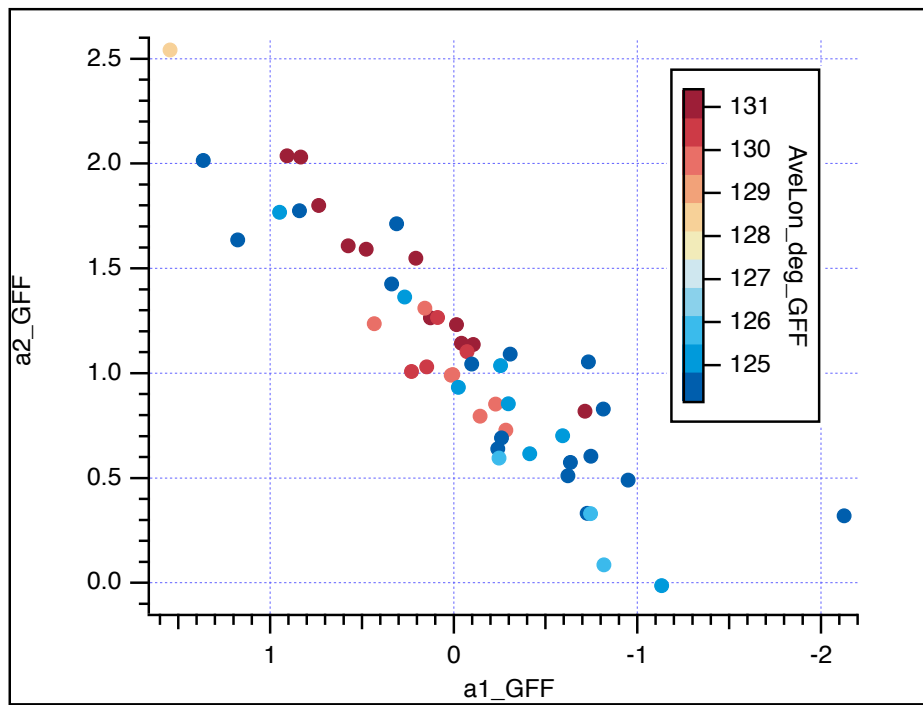
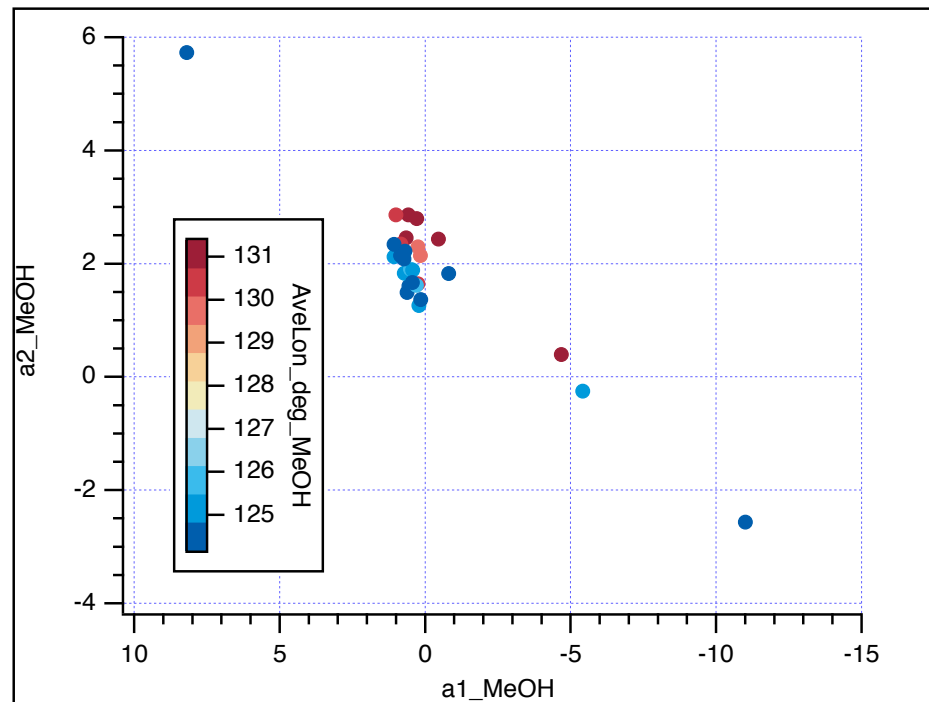
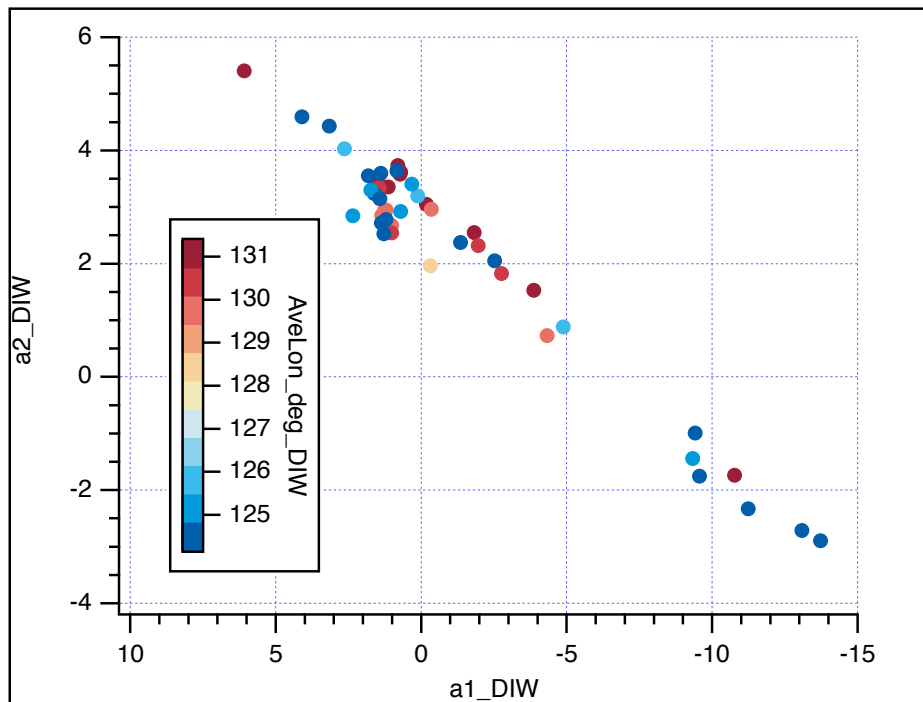
2 Subsets of Absorbing Oxalate

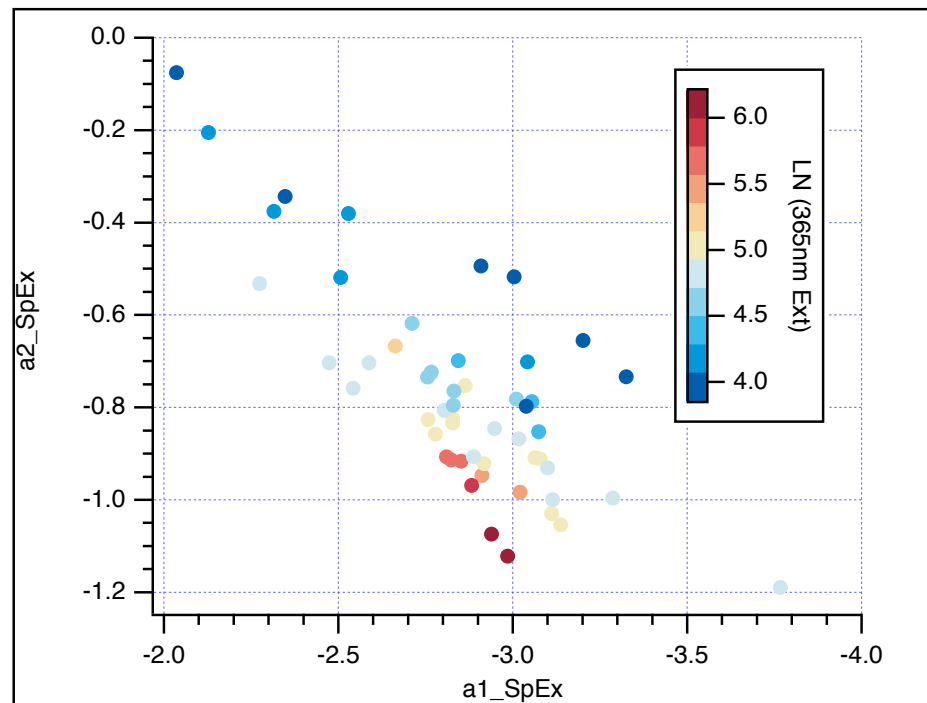
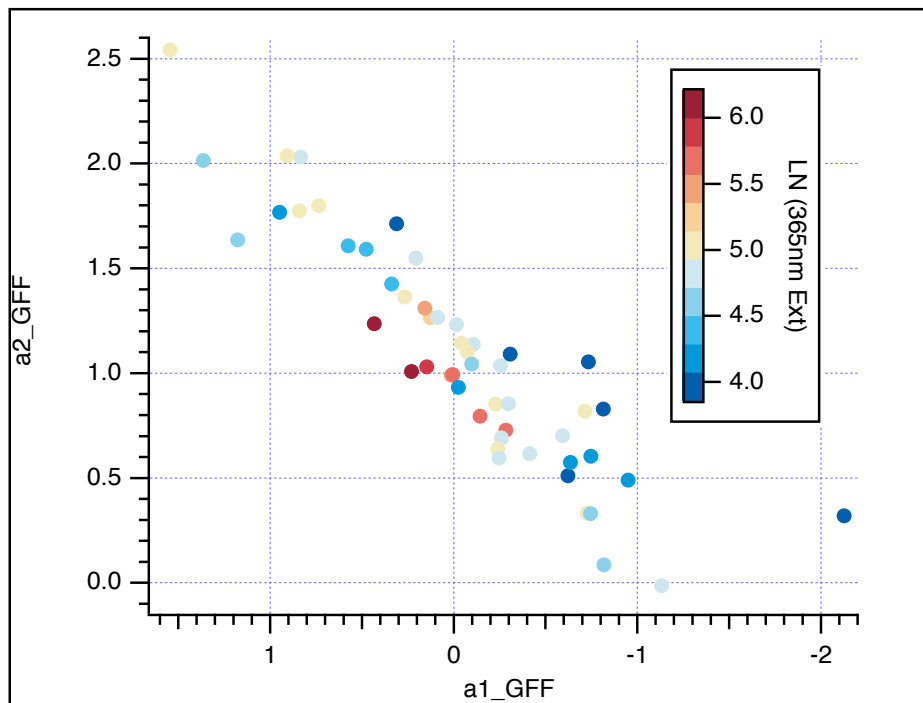
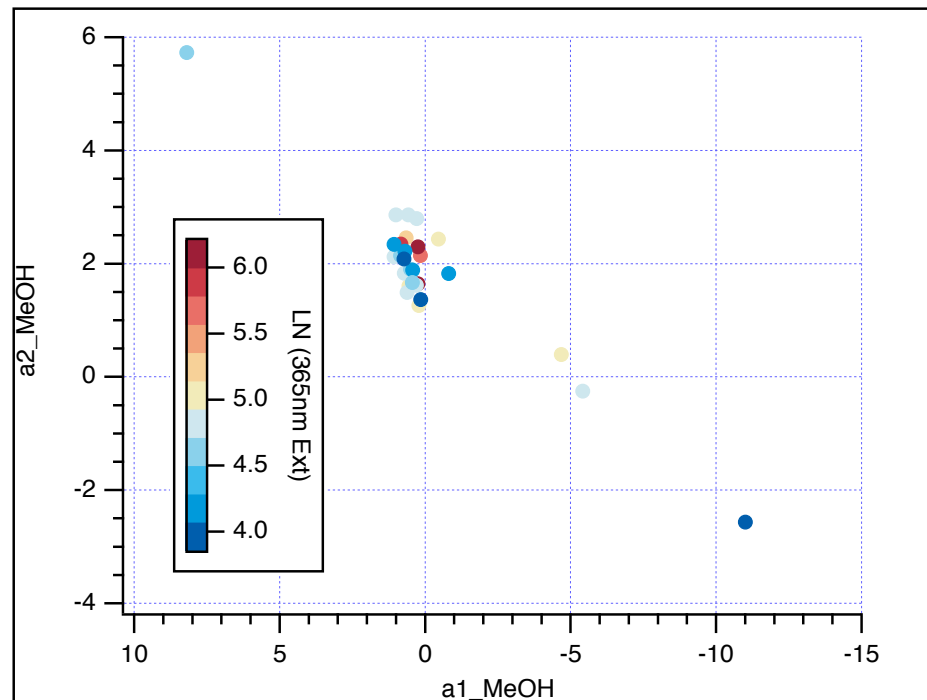
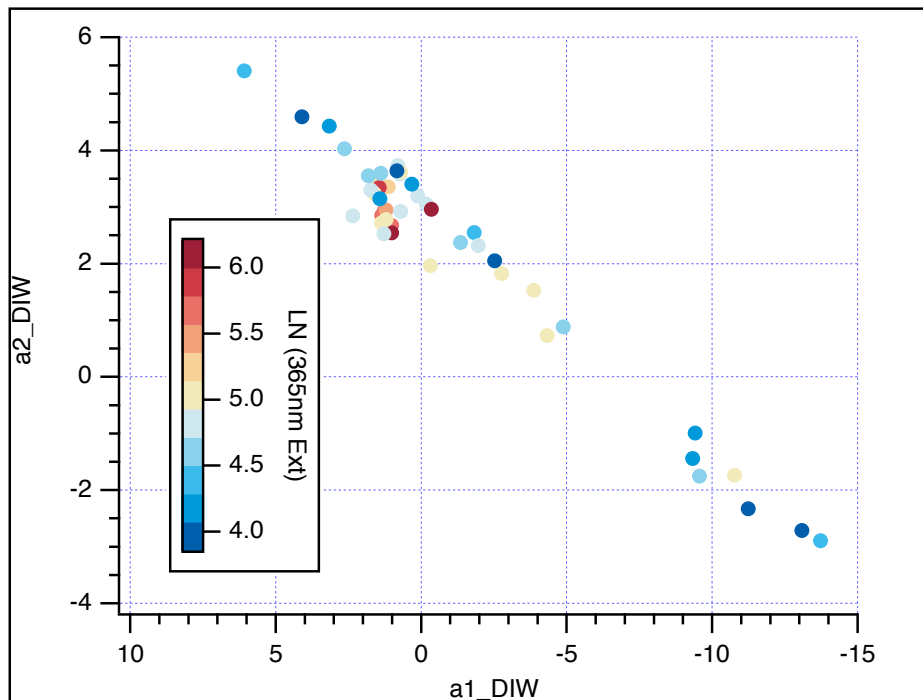


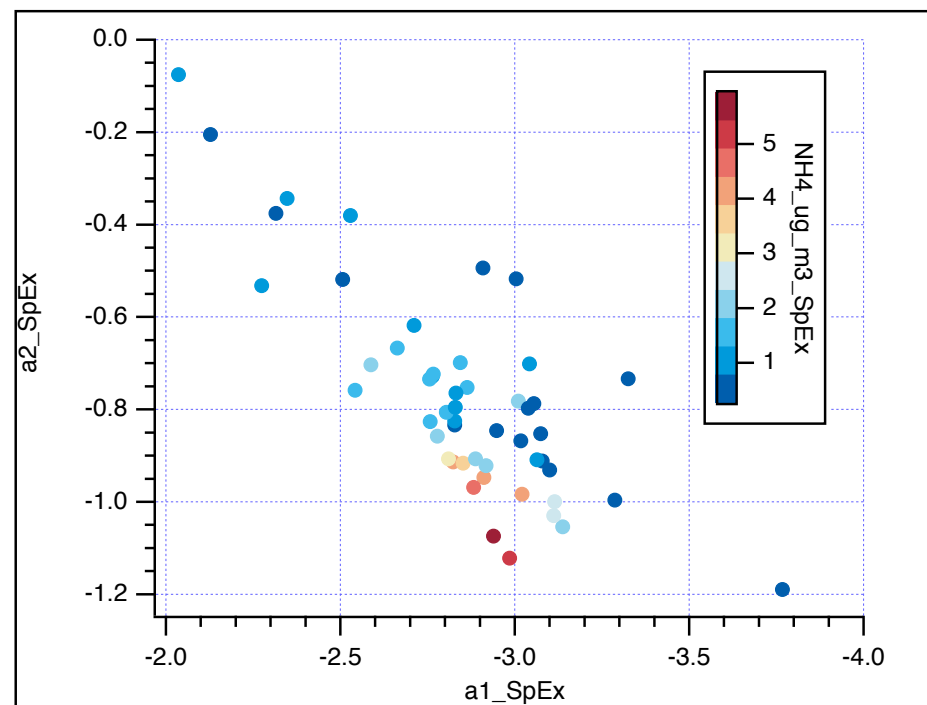
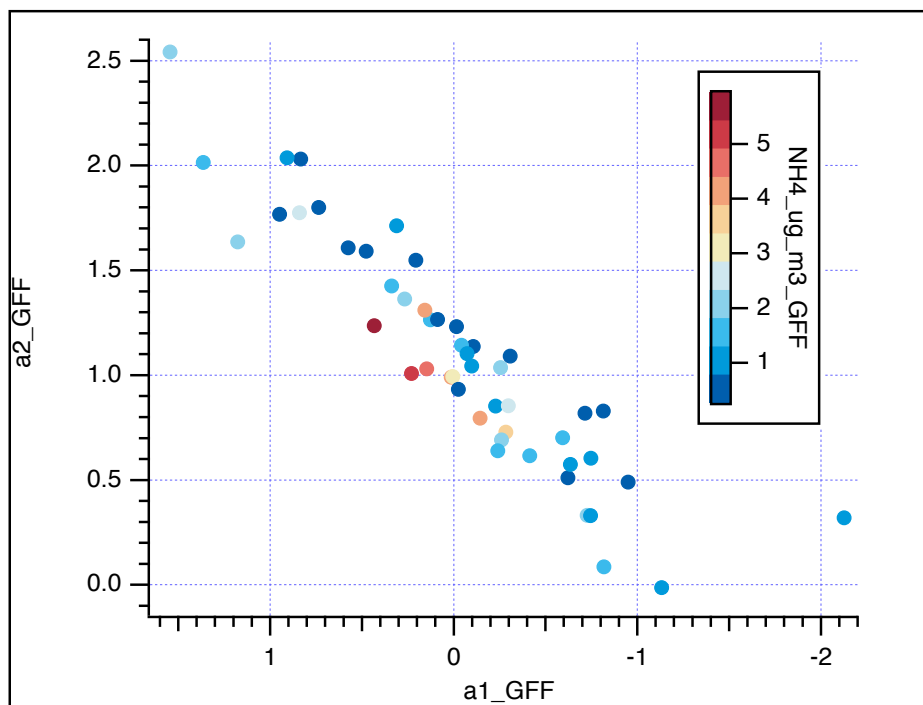
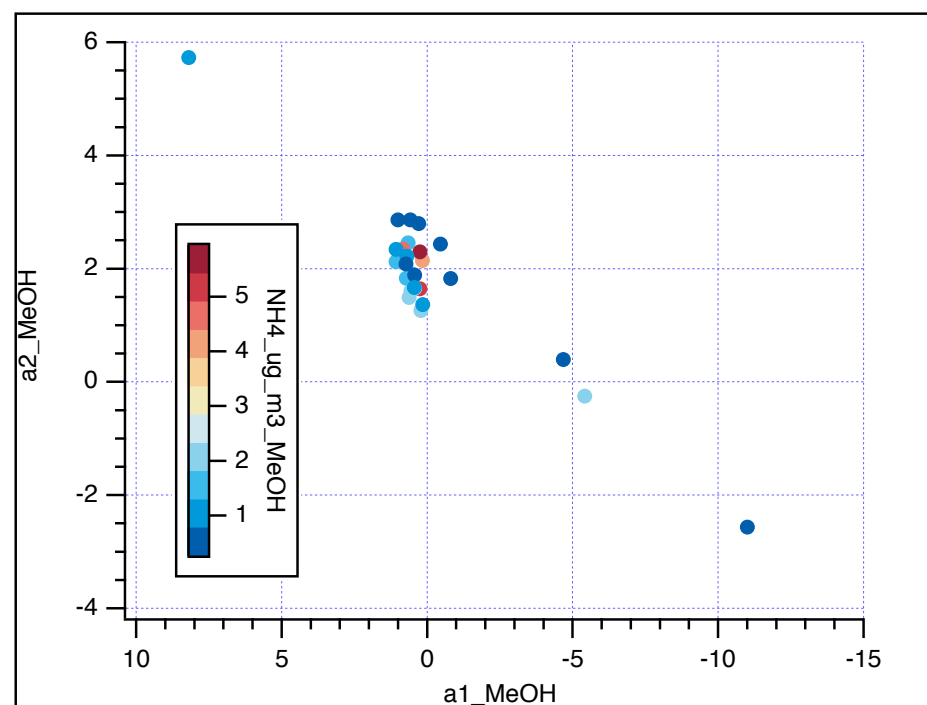
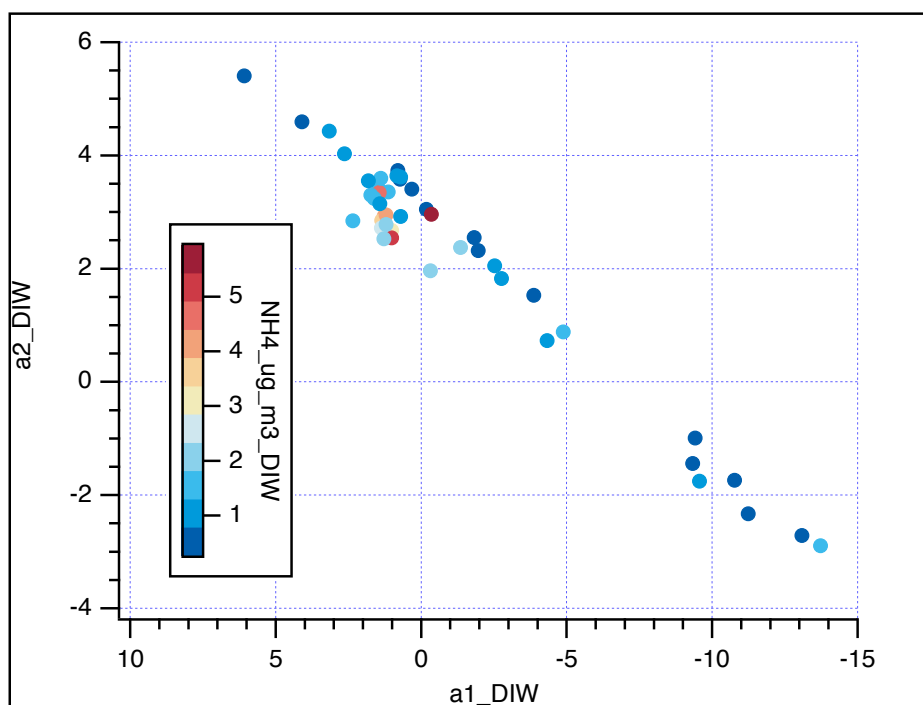
Overview

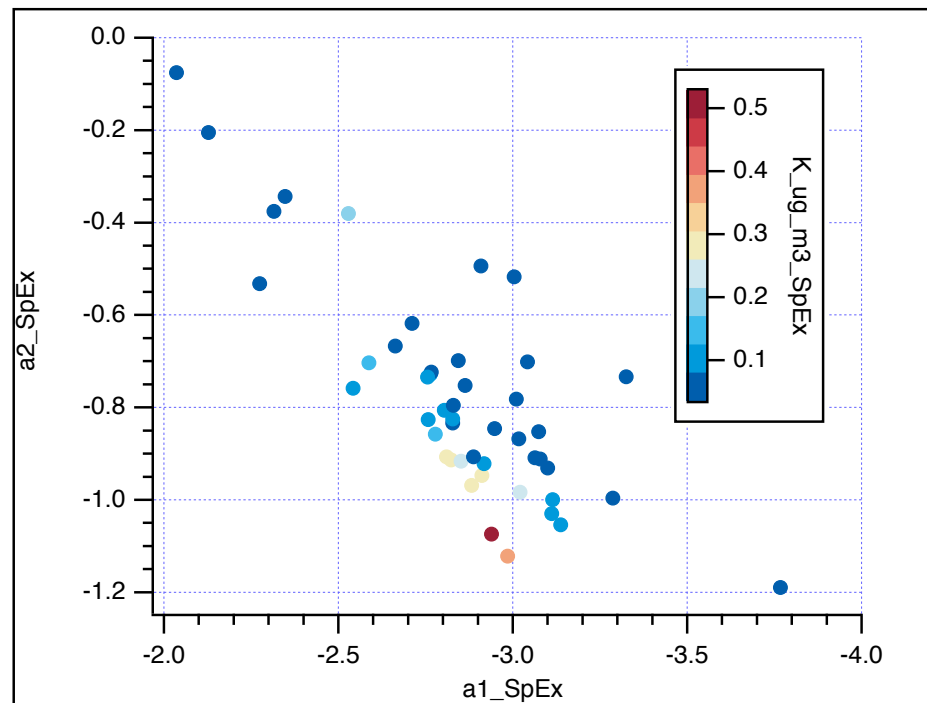
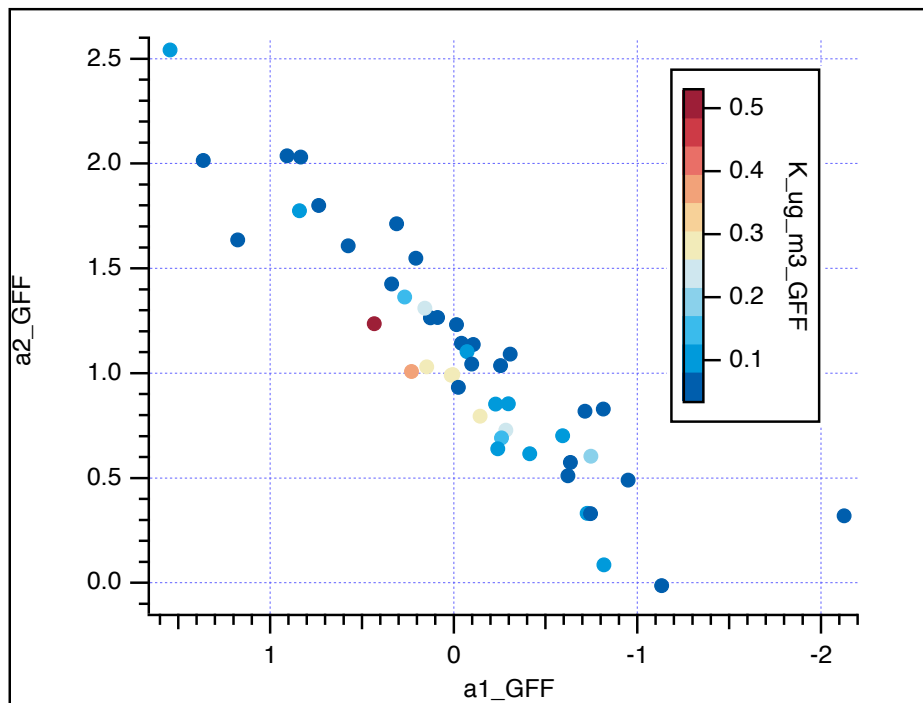
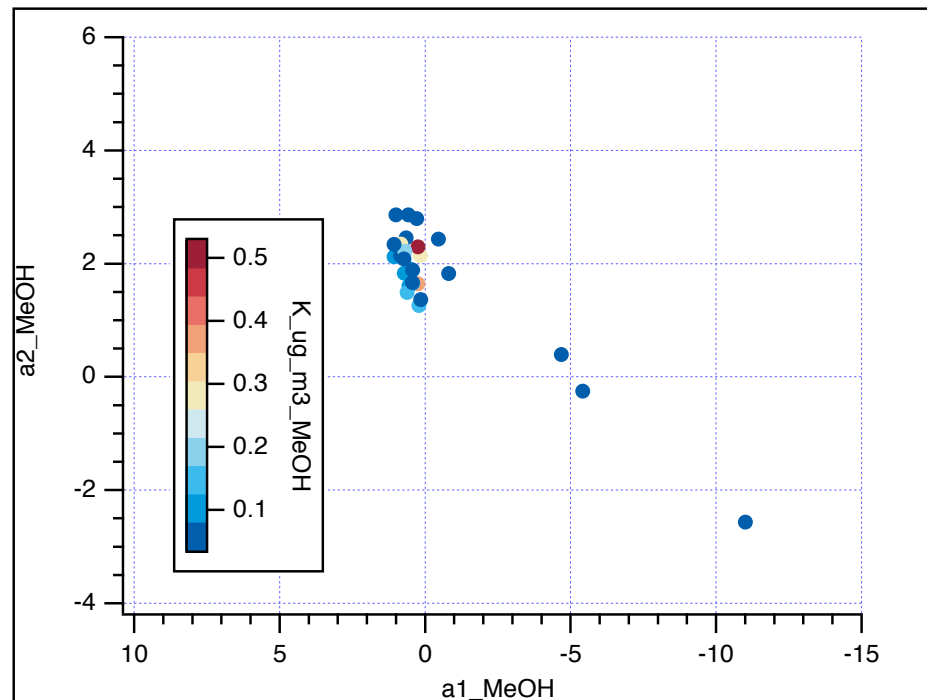
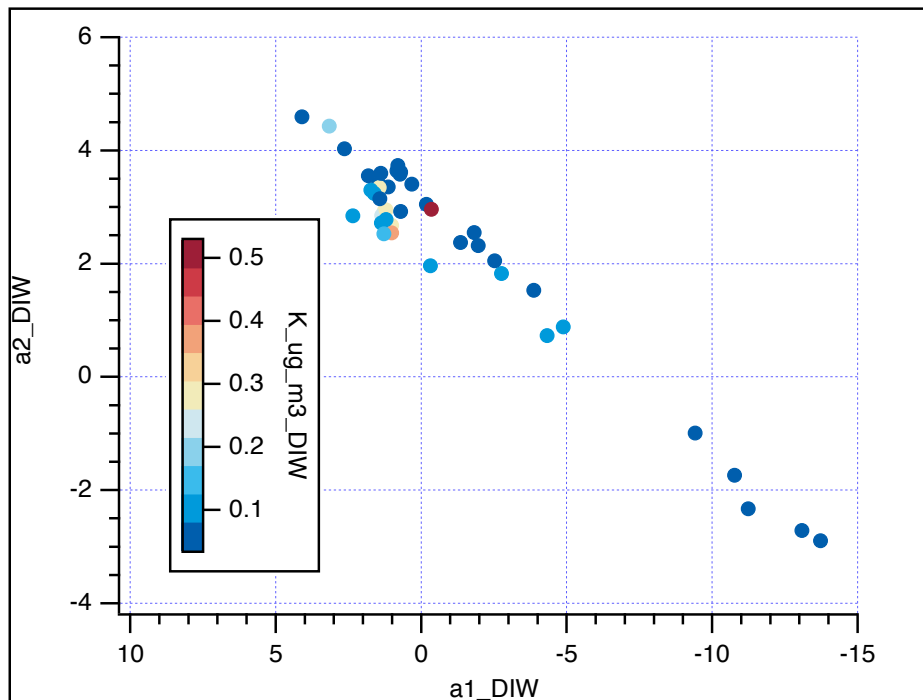
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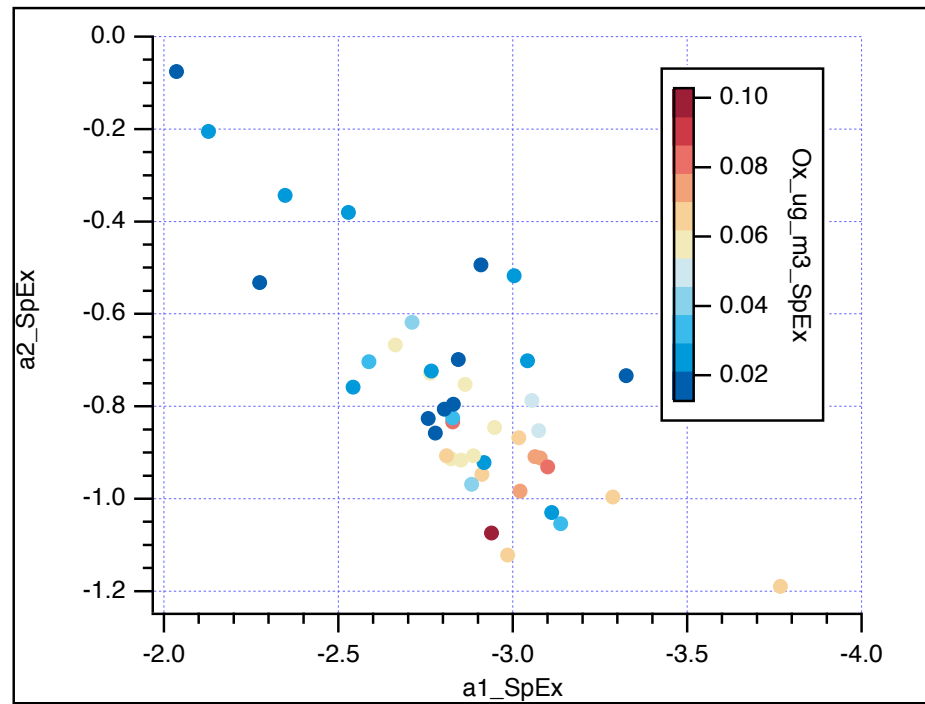
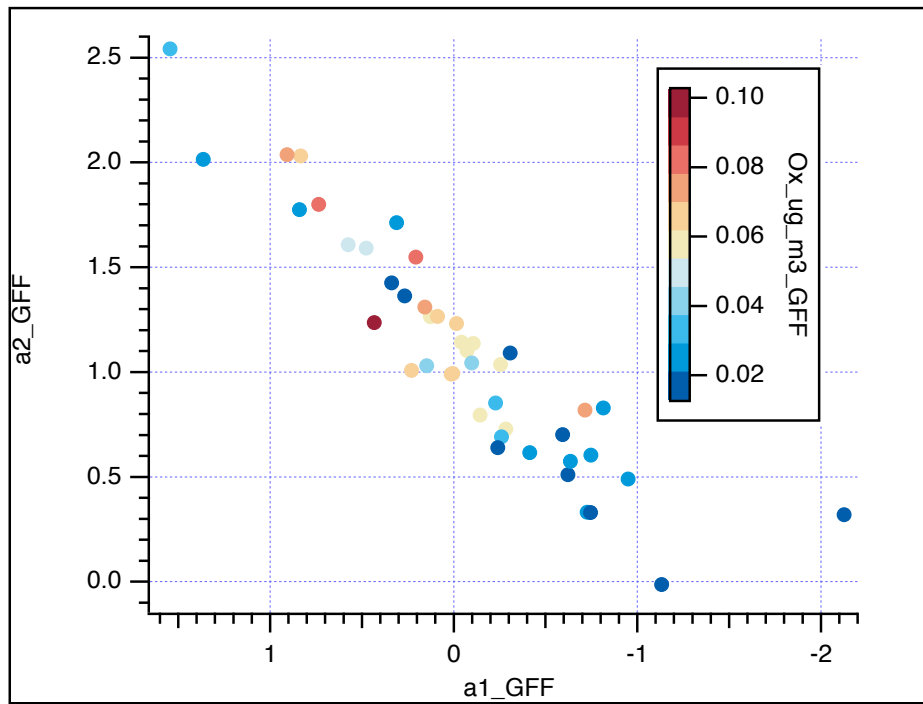
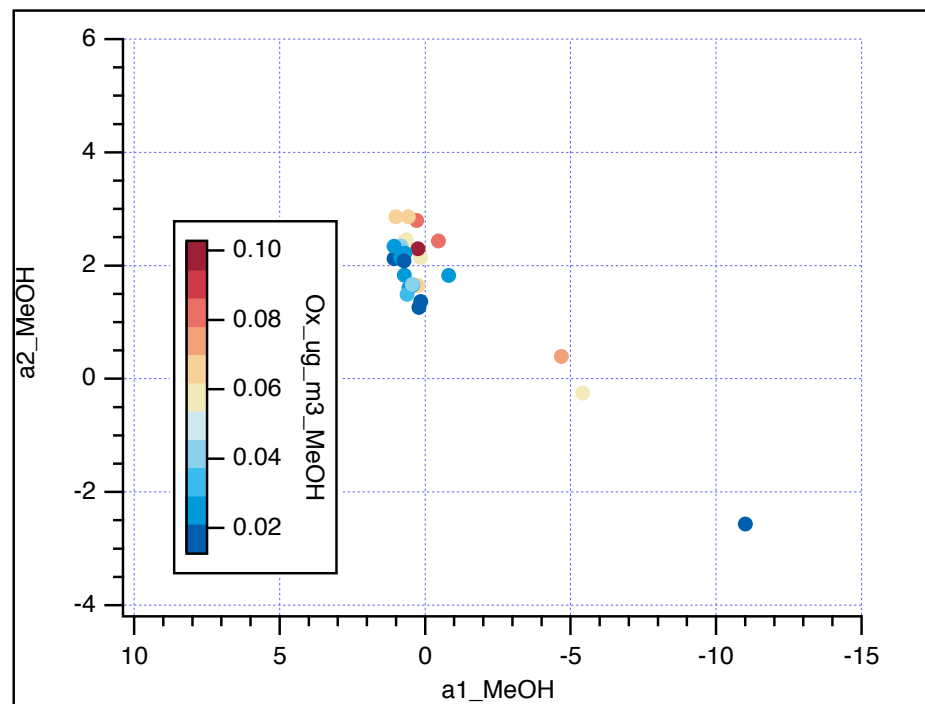
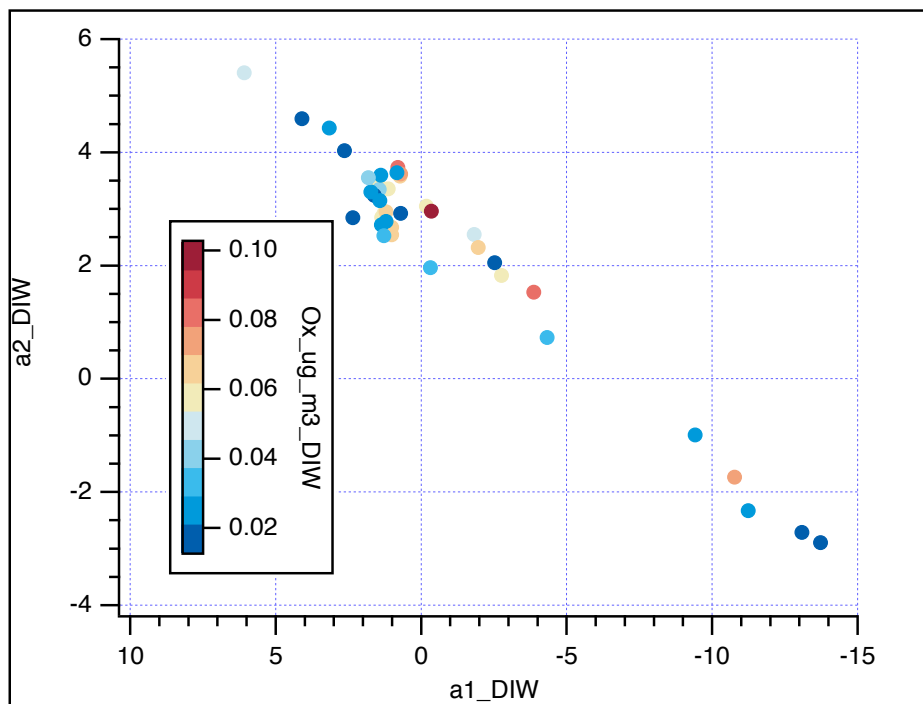




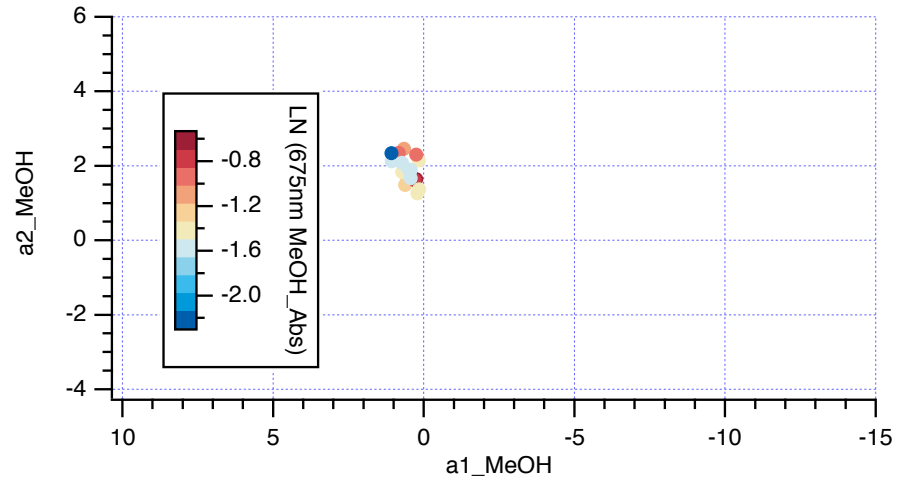
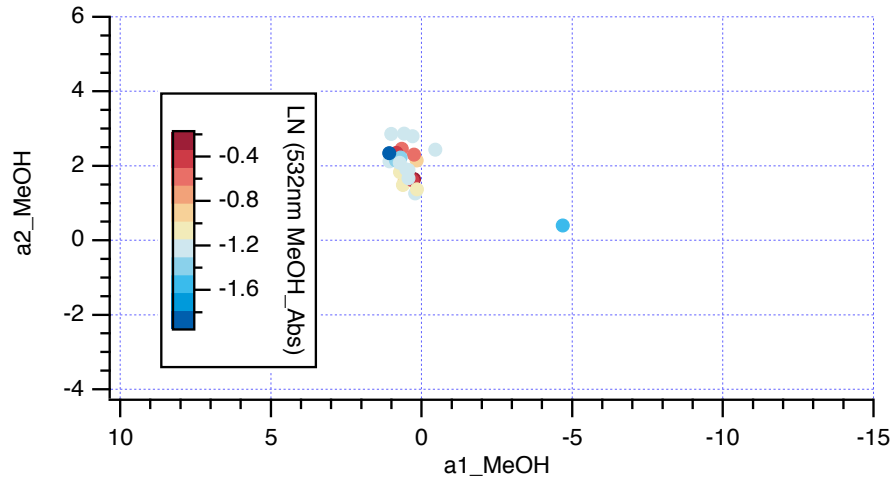
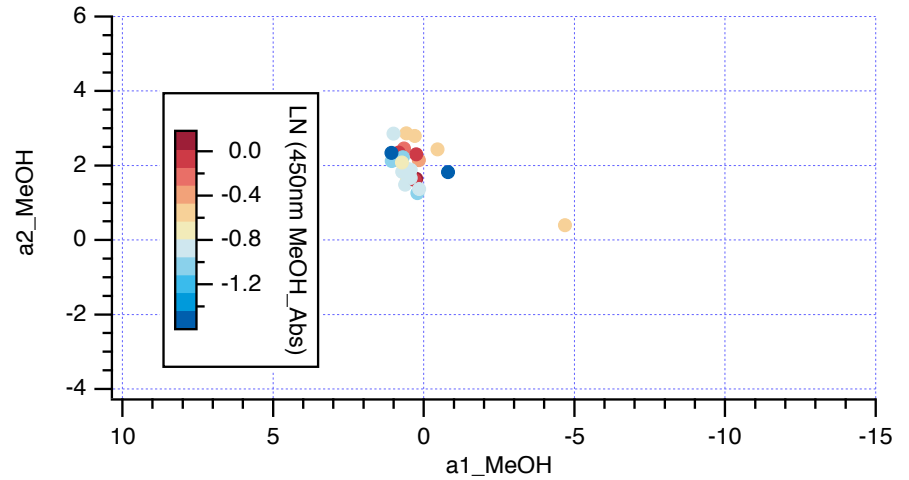
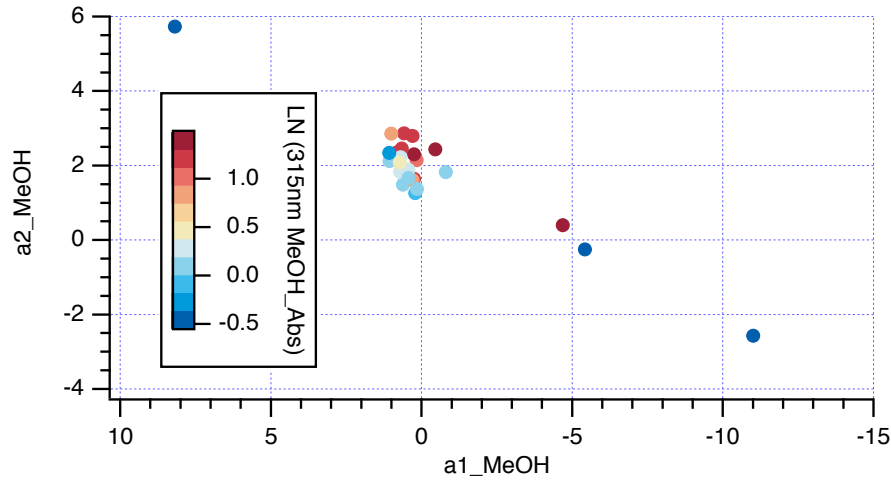




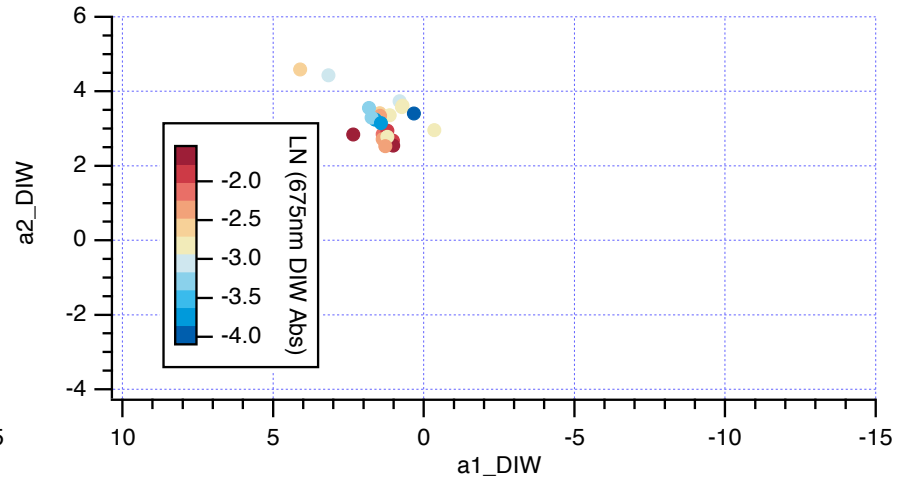
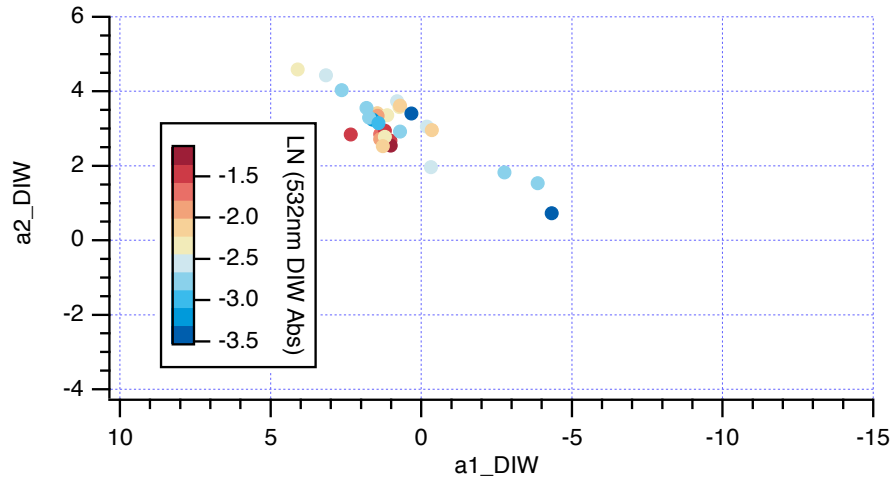
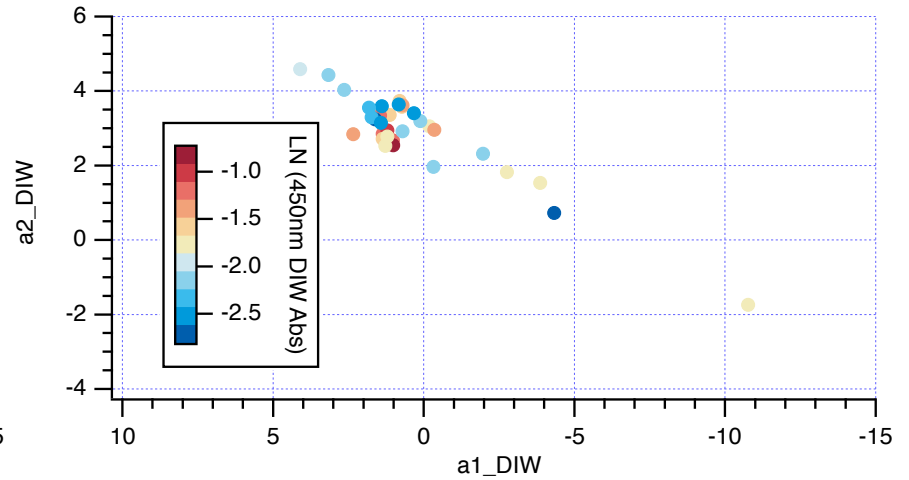
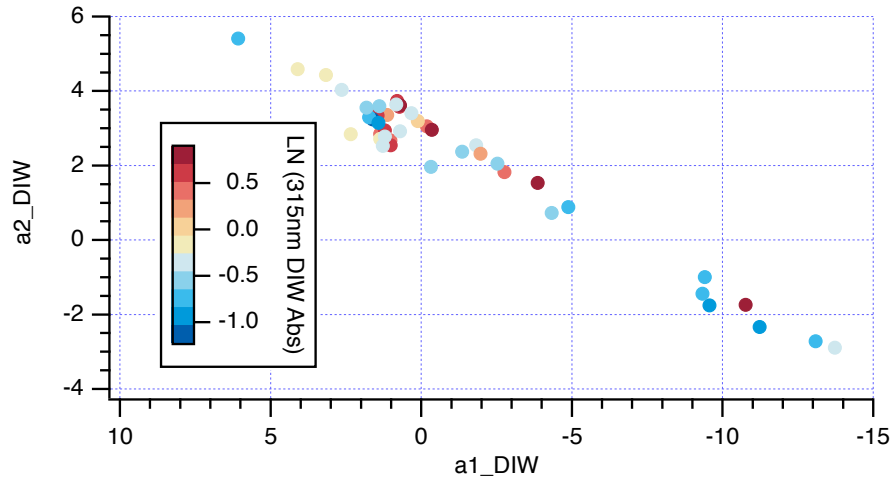




Methanol-Absorption @ 4 wavelengths

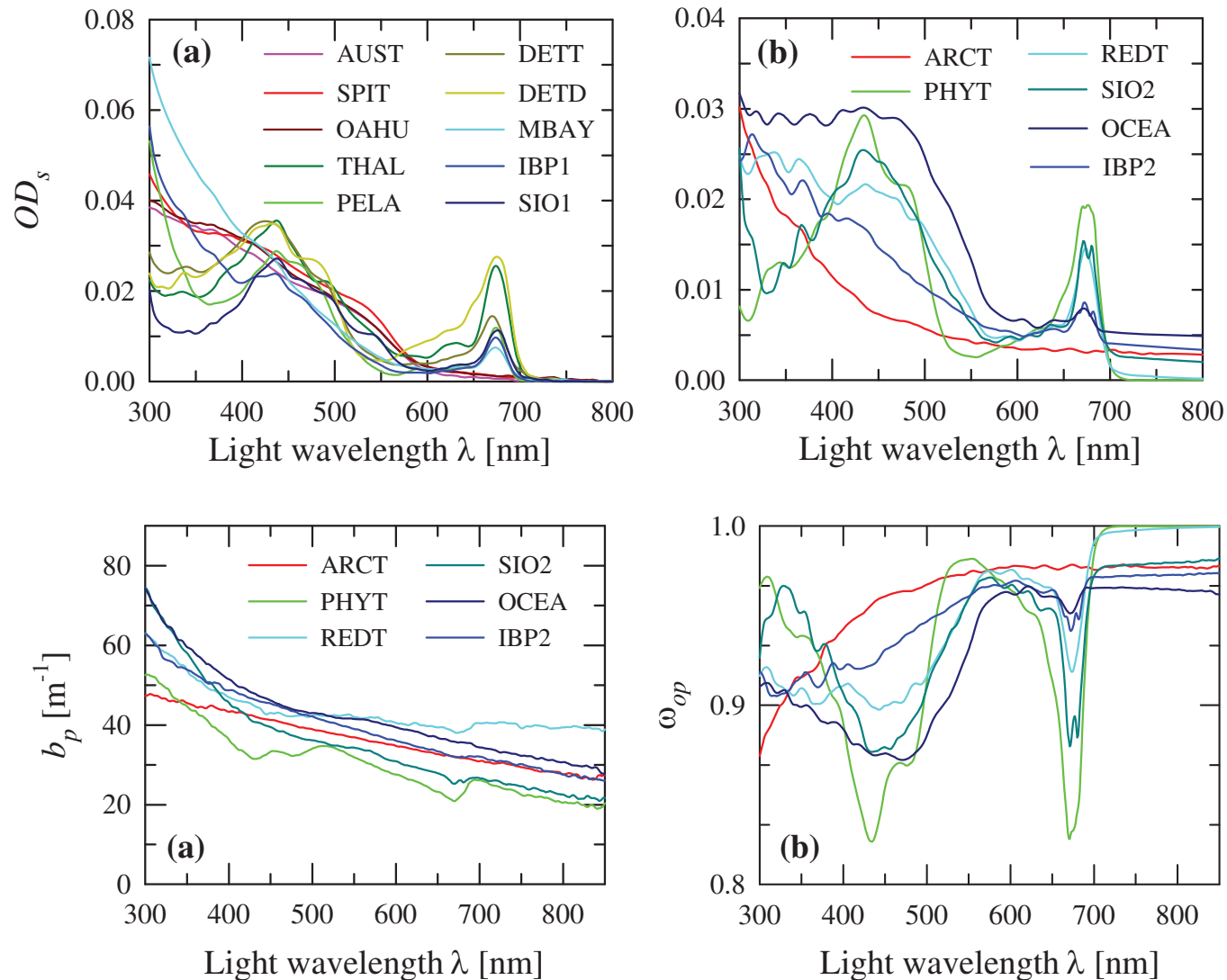


DIW-Absorption @ 4 wavelengths



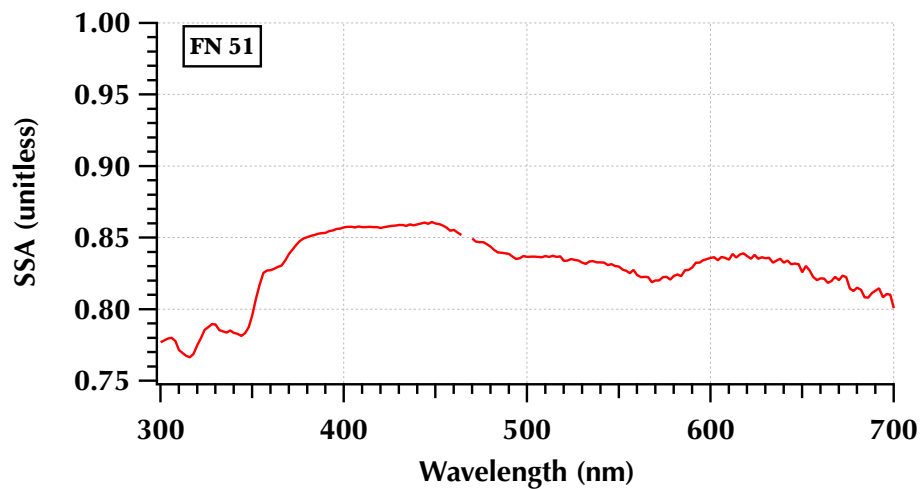
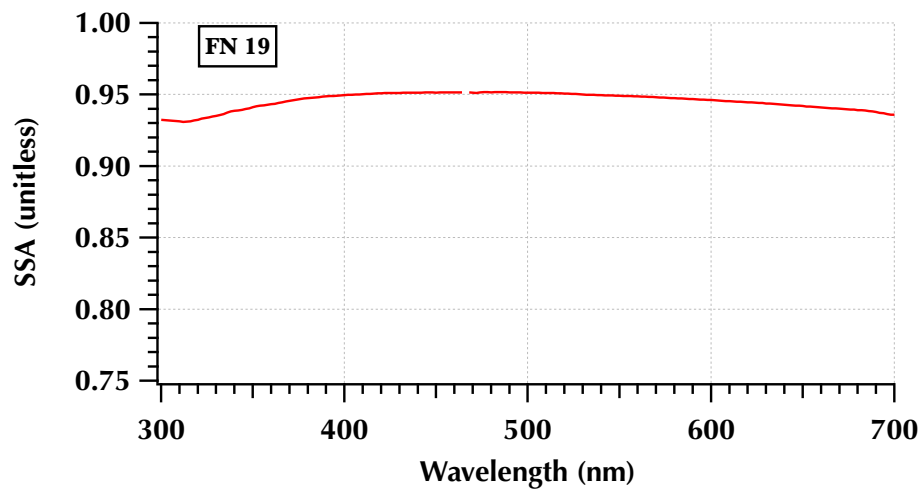
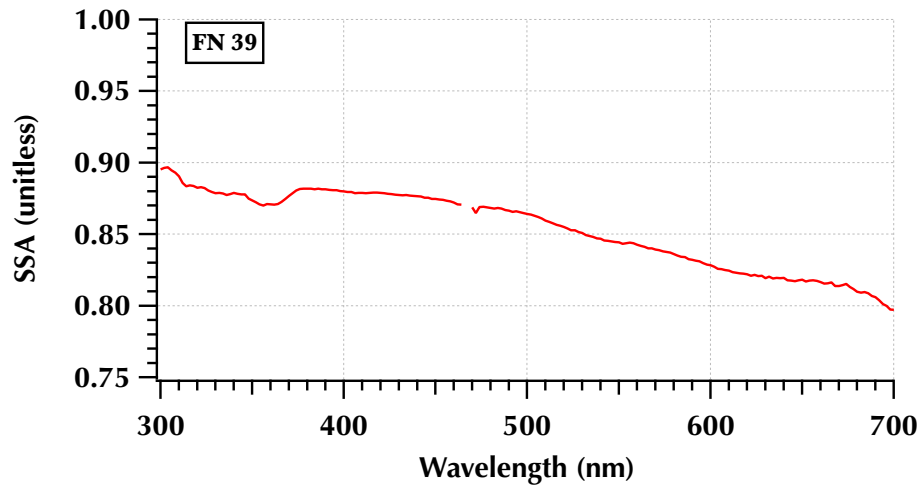
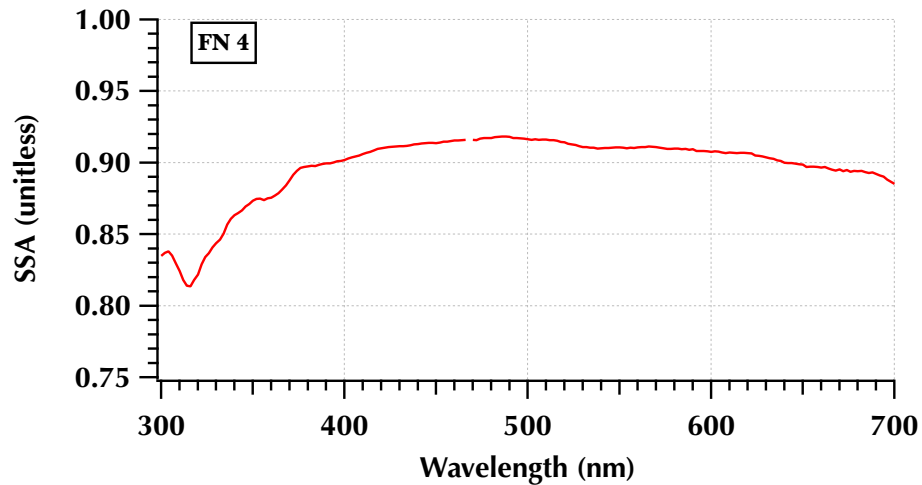
Additional Spectral Analyses...

Seawater Particle Spectra



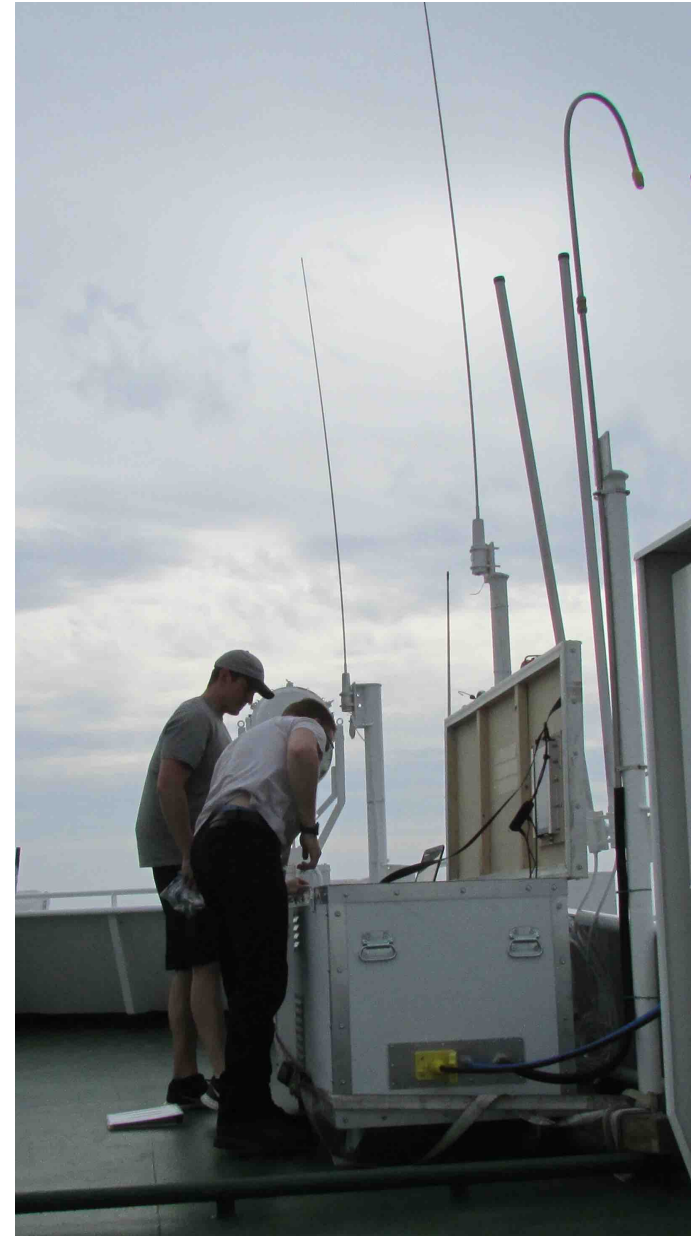
[Stramski et al., Applied Optics, 54(22), 6763-6782, 2015]

SSA Examples

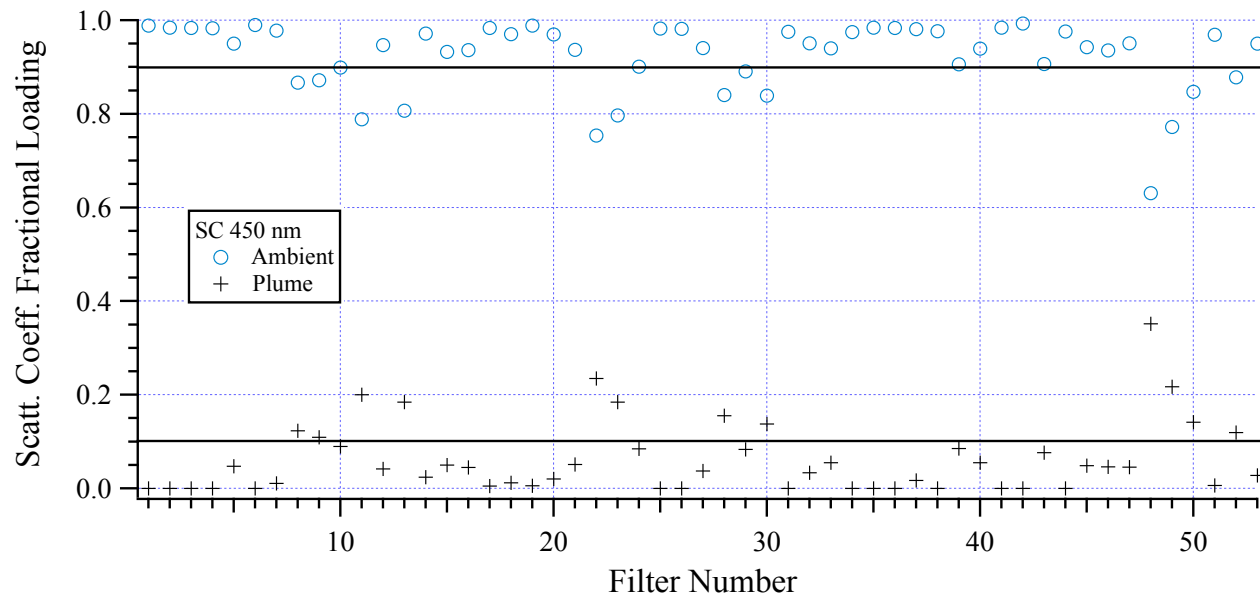
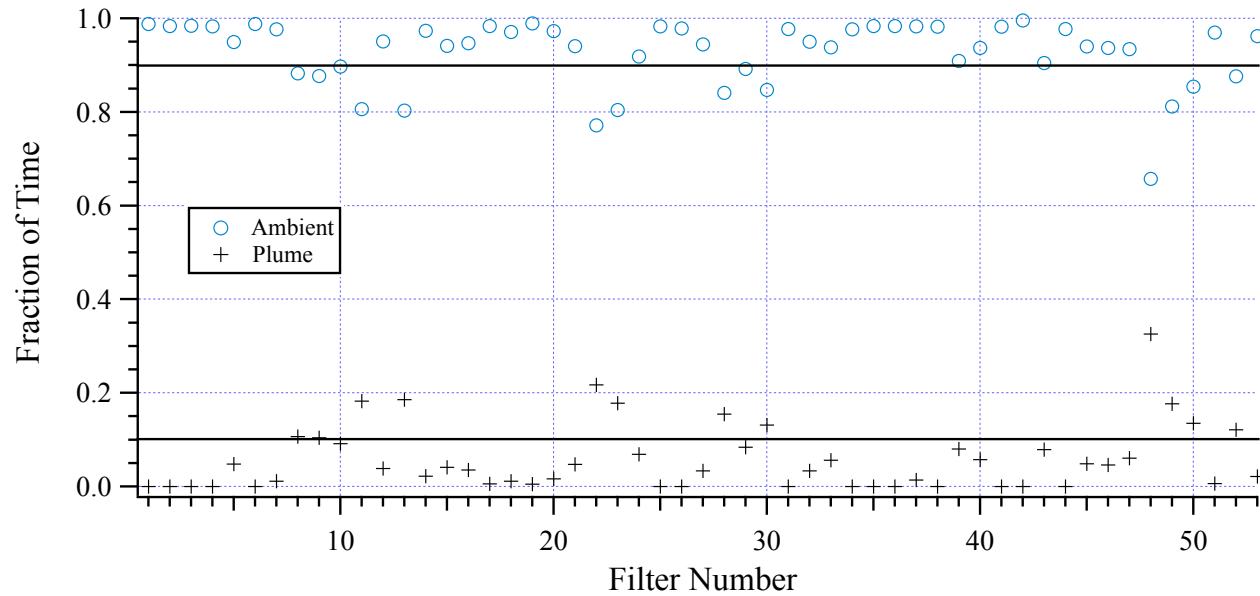


Acknowledgments

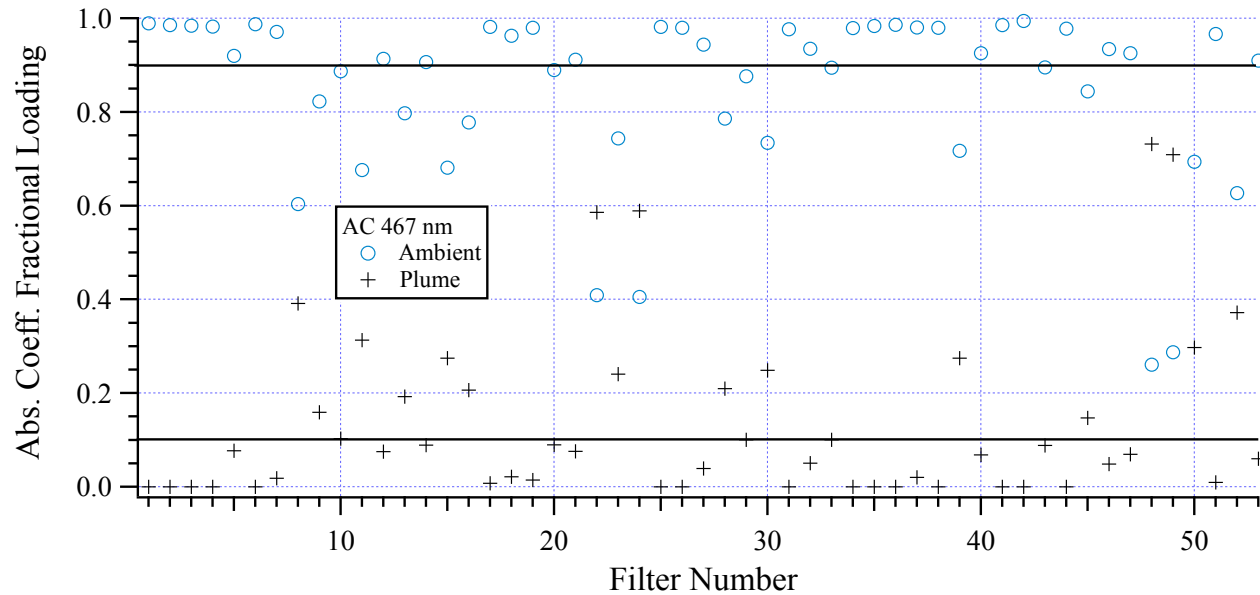
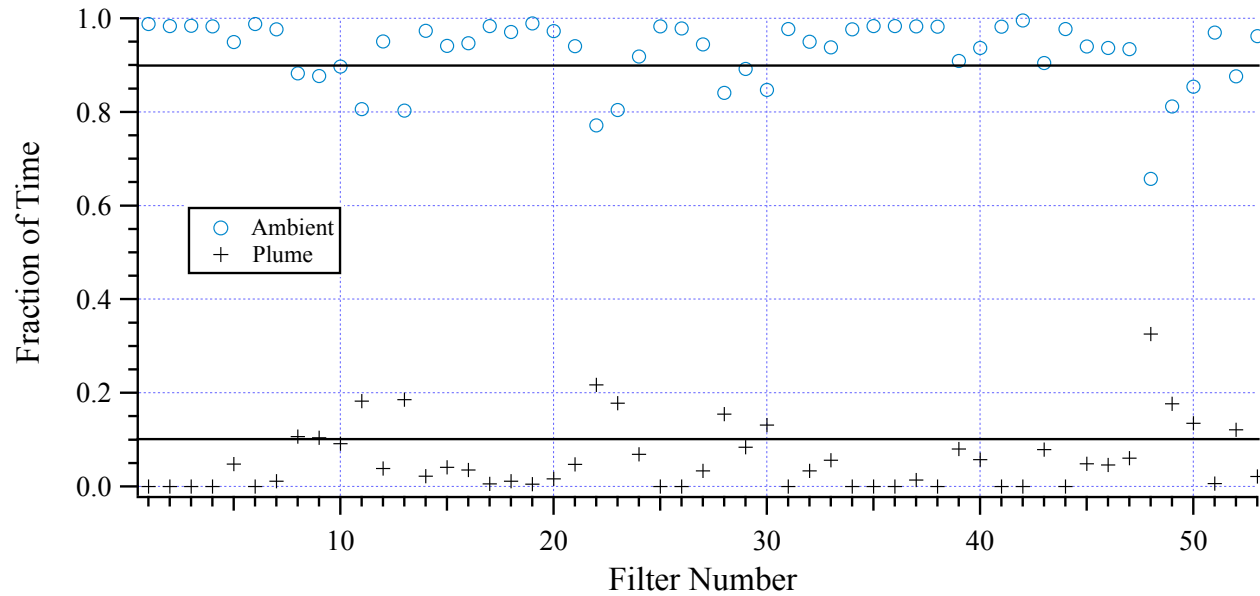
- *The authors gratefully acknowledge the support of the KORUS-OC, KOCOAA, and KORUS-AQ science teams, the outstanding support provided by our hosts, and financial support from the NASA/NIA cooperative agreement NNL09AA00A*
- *Particular thanks are due to Ryan Stauffer & Brian Lamb for making these measurements at sea*
- *Thanks also to Amin Nehrir, Fred Brechtel, Vanderlei Martins, & Claire Robinson for helpful discussions*



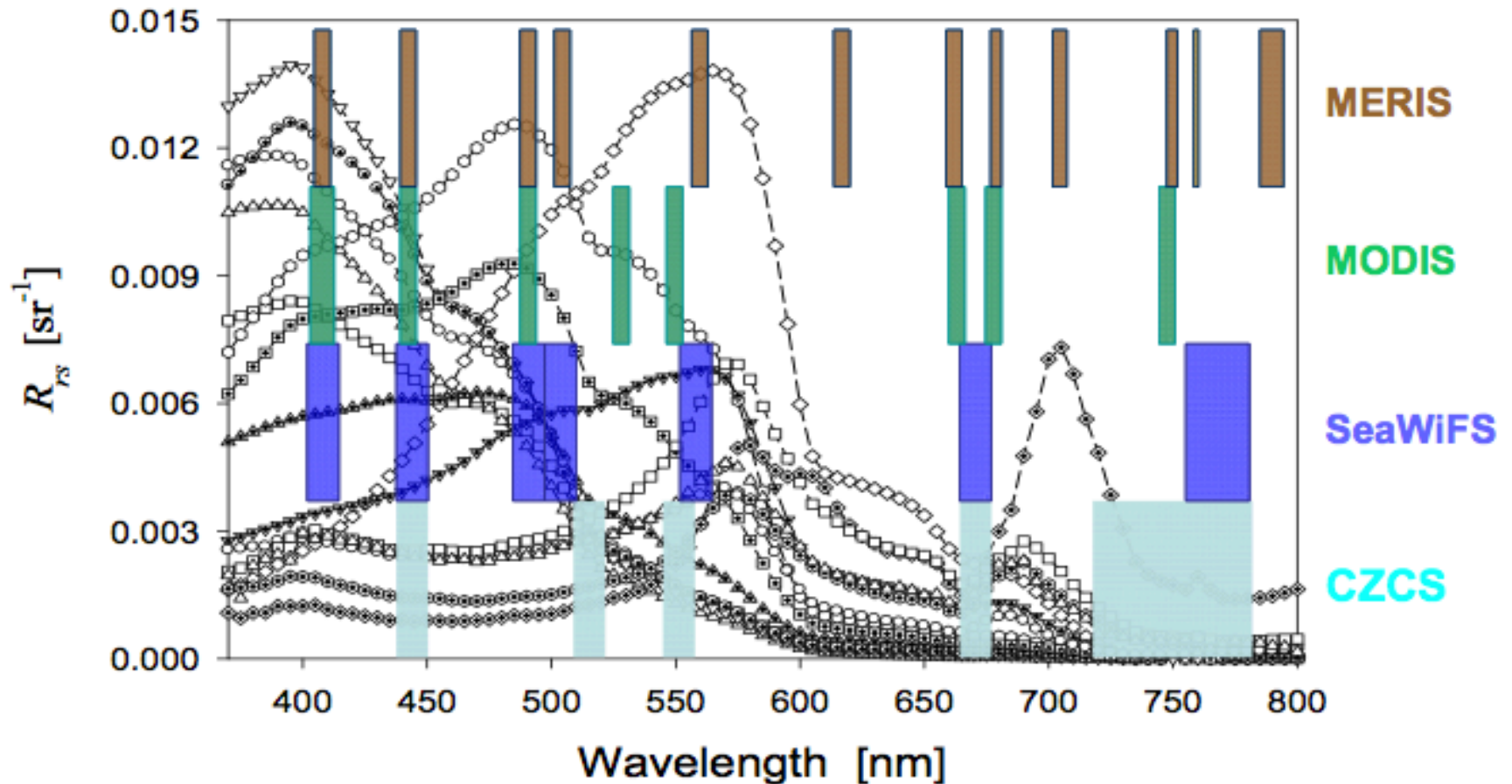
Filter Data Set: Evaluating Ship Stack Emissions



Filter Data Set: Evaluating Ship Stack Emissions



Coastal Ocean Color



Remote-sensing reflectance R_{RS} (sr^{-1}) from 384 spectra (~ 350 - 800 nm, ~ 3 nm resolution)
12-year cruise data set ranging from open ocean to coastal environments overlaid with
satellite spectral bands.

[Lee et al., 2007]