A13F-2514: Characteristics of In Situ Fine Fraction Aerosol Spectra from 300-700 nm Observed Around the Korean Peninsula During KORUS-OC

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In situ aerosol extinction and absorption spectra covering the 300-700 nm range at ≤ 1 nm spectral resolution were measured aboard the R/V Onnuri during the Korea U.S. – Ocean Color (KORUS-OC) cruise around the Korean Peninsula from May 21 through June 3, 2016. Total absorption spectra were obtained from aerosols collected on glass fiber filters and subsequently placed in the center of an integrating sphere (Labsphere DRA-CA-30) attached to a dual beam spectrophotometer (Cary 100 Bio UV-Visible Spectrophotometer, 0.2 nm spectral resolution). Absorption spectra from methanol and deionized water extracts of aerosols collected on Teflon filters were measured in a liquid waveguide capillary cell (World Precision Instruments LWCC-3100, ~0.4 nm spectral resolution). Extinction spectra were measured with a custom built instrument (SpEx, ~0.8 nm spectral resolution). The measurements were obtained at a height of ~10 m above the sea surface with an inlet that limited the measured aerosols to diameters ≤ 1.3 µm. All four sets of spectra exhibit curvature in log-log space with 2nd order polynomials providing a better fit to the measured spectra than power law fits. The deionized water extracts were also analyzed with an ion chromatograph (Dionex ICS-3000 Ion Chromatography System) and with an aerosol mass spectrometer (Aerodyne Research, Inc. HR-ToF High Resolution Aerosol Mass Spectrometer) to examine chemical composition. These data indicate the optical spectra are sensitive to differing chemical properties of the measured ambient aerosols and suggest differing sources and/or atmospheric processes influence the observed optical signatures. The measured suite of spectra are combined to examine the spectral characteristics of single scattering albedo, as well as to examine the contribution of soluble absorbing chromophores to the total absorption spectra. Additional measurements made during the affiliated Korea U.S. - Air Quality (KORUS-AQ) campaign will be used to provide further insight on the observed spectral characteristics.

Characteristics of *in situ* fine fraction aerosol spectra from 300-700 nm observed around the Korean Peninsula during KORUS-OC

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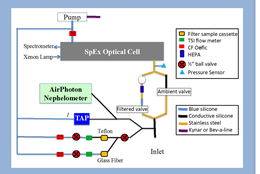
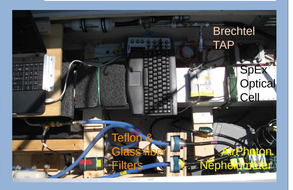
Abstract

In situ aerosol extinction and absorption spectra covering the 300-700 nm range at ≤ 1 nm spectral resolution were measured aboard the R/V Onnuri during the Korea U.S. – Ocean Color (KORUS-OC) cruise around the Korean Peninsula from May 21 through June 3, 2016. Total absorption spectra were obtained from aerosols collected on glass fiber filters and subsequently placed in the center of an integrating sphere (Labsphere DRA-CA-30) attached to a dual beam spectrophotometer (Cary 100 Bio UV-Visible Spectrophotometer, 0.2 nm spectral resolution). Absorption spectra from methanol (MeOH) and deionized water (DIW) extracts of aerosols collected on Teflon filters were measured in a liquid waveguide capillary cell (World Precision Instruments LWCC-3100, ~0.4 nm spectral resolution). Extinction spectra were measured with a custom built instrument (SpEx, ~0.8 nm spectral resolution). The measurements were obtained at a height of ~10 m above the sea surface with an inlet that limited the measured aerosols to diameters ≤ 1.3 µm. All four sets of spectra exhibit curvature in log-log space with 2nd order polynomials providing a better fit to the measured spectra than power law fits. The DIW extracts were also analyzed with an ion chromatograph (Dionex ICS-3000 Ion Chromatography System) and with an aerosol mass spectrometer (Aerodyne Research, Inc. HR-ToF High Resolution Aerosol Mass Spectrometer) to examine chemical composition. These data indicate the optical spectra are sensitive to differing chemical properties of the measured ambient aerosols and suggest differing sources and/or atmospheric processes influence the observed optical signatures. The measured suite of spectra are combined to examine the spectral characteristics of single scattering albedo, as well as to examine the contribution of soluble absorbing chromophores to the total absorption spectra. Additional measurements made during the affiliated Korea U.S. - Air Quality (KORUS-AQ) campaign will be used to provide further insight on the observed spectral characteristics.

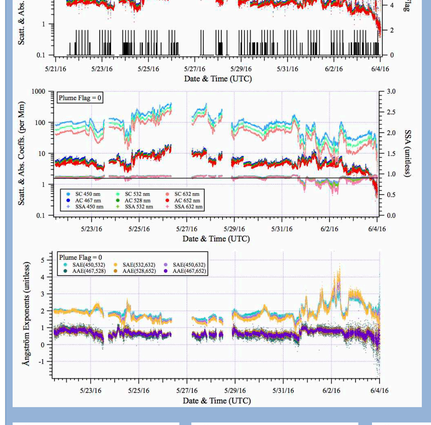
Introduction: KORUS-OC & *In Situ* Aerosol Measurements

- Affiliated with airborne KORUS-AQ & KOCOA cruise
  - joint missions to study S. Korean air quality (AQ) & OC
- Under view of S. Korean Geostationary Ocean Color Imager (GOCI)
  - providing hourly OC & aerosol optical depth (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)



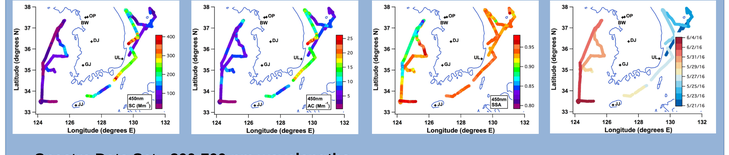


- **1 minute Data Set: 3 visible wavelengths**
  - Scattering (AirPhoton Nephelometer model IN101: 450, 532, and 632 nm)
  - Absorption (Brechtel Tricolor Absorption Photometer, TAP, model 2901: 467, 528, and 652 nm)

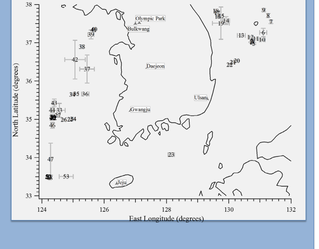


Key Points

- 1 min scattering and absorption coefficients (SC and AC, respectively) used to flag ship plume interceptions (Left: compare top 2 panels)
- Single scattering albedo (SSA) decreases occur when scattering decreases (middle panel at left)
- Absorption Ångström Exponents show little variability with time or wavelength pair used in calculation (Left: bottom panel)
- Scattering Ångström Exponents show some variability with wavelength pair, along with an increase in values late in cruise (Left: bottom panel)
- The cruise track (Below: right panel, excluding periods within the S. Korean Territorial Seas) was to the east of the peninsula for the 1st half of the cruise, then crossed to the west for the 2nd half of the cruise.
- 450 nm SC, AC, and SSA mapped to show peak values observed to the east, lowest values to the west (Below: left 3 panels)



- **Spectra Data Set: 300-700 nm wavelengths**
  - Extinction (Spectral Aerosol Extinction (SpEx) instrument, 4 min resolution)
  - Total Absorption (Glass fiber filter measured in center of integrating sphere (Labsphere DRA-CA-30) attached to dual beam spectrometer (Cary 100 Bio UV-Visible Spectrophotometer)
  - DIW- and MeOH-soluble Absorption (extracts from Teflon filters measured in liquid waveguide capillary cell (World Precision Instruments LWCC-3100)
  - Filters sampled ~ 3 hr daytime, 12 hr nighttime (Right: mean sampling locations)



- **Chemical Analyses of DIW Extracts**
  - Dionex ICS-3000 Ion Chromatography System
  - Aerodyne High Resolution – Time Of Flight Aerosol Mass Spectrometer (HR-TOF AMS)

Relationship of 365 nm Optical Properties to Water-soluble Chemical Composition

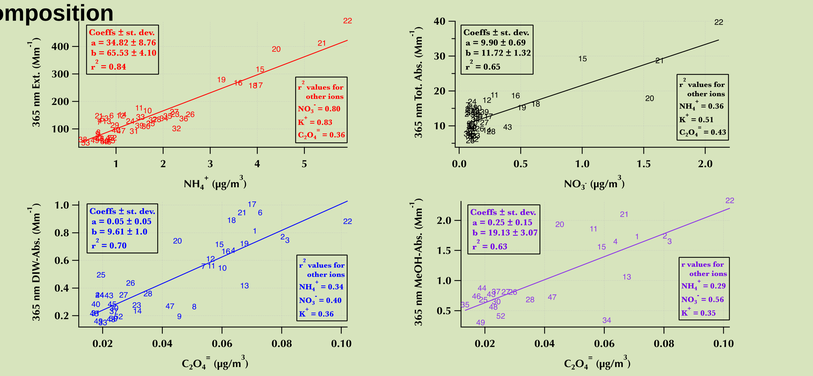


Figure 1. Relationships between 365 nm optical properties and water-soluble ions differ with extinction (upper left) best correlated with NH_4^+, total absorption with NO_3^- and K^+, and soluble absorption to $C_2O_4^=$. Filter numbers used as markers.

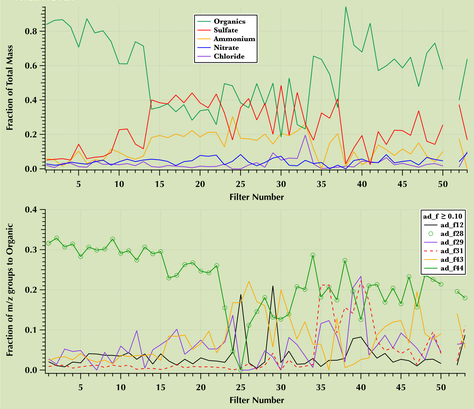


Figure 2. Time series of AMS major contributions to total aerosol mass (top) and major m/z group contributions to organic mass (bottom).

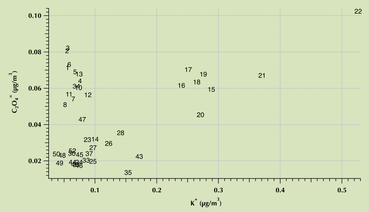


Figure 3. Enhanced soluble absorption related to $C_2O_4^=$ splits into two groups: with and without enhanced K^+.

Key Points

- Filters 1-22 collected in East Sea
- 365 nm Extinction and Total Absorption enhanced with increased pollution sources (filters #15-22)
- $C_2O_4^=$ has known combustion and cloud-processing sources suggesting that…
- Enhanced 365 nm soluble Absorption related to combustion (with enhanced K^+, #15-22) and to cloud processing (#1-12)

Characterizing Spectral Shapes

•Aerosol interaction with light is wavelength dependent often characterized by a power law: $\mathbf{p(\lambda) = \lambda^{-\alpha}}$
where, α is known as the Ångström exponent and p may be scattering, absorption, extinction, etc.
[e.g. Ångström , 1929; Moosmüller, & Chakrabarty, 2011]
-taking the derivative, the Ångström exponent describes a wavelength-independent line in log space:
$\alpha = -\,d \ln p(\lambda) / d \ln \lambda$, or for 2 wavelengths, $= -\ln (p(\lambda_2)/p(\lambda_1)) / \ln (\lambda_2/\lambda_1)$

•Ambient observations of total atmospheric column aerosol extinction have shown that spectra exhibit curvature in log space
and this curvature can be represented with a 2nd order polynomial: $\mathbf{\ln p(\lambda) = a_0 + a_1 \ln \lambda + a_2 (\ln \lambda)^2}$
[e.g., Eck et al., 1999 and 2001; Schuster et al., 2006]
- Fine aerosols exhibit negative curvature; the presence of sufficient coarse aerosols results in positive curvature

•The sampling inlet for our system had a 50% size cut of 1.3 µm diameter particles, hence all of our measurements were of the fine fraction. ***In all cases the measured spectra sets were better fit with a 2nd order polynomial than a line*** (e.g., Fig. 4).

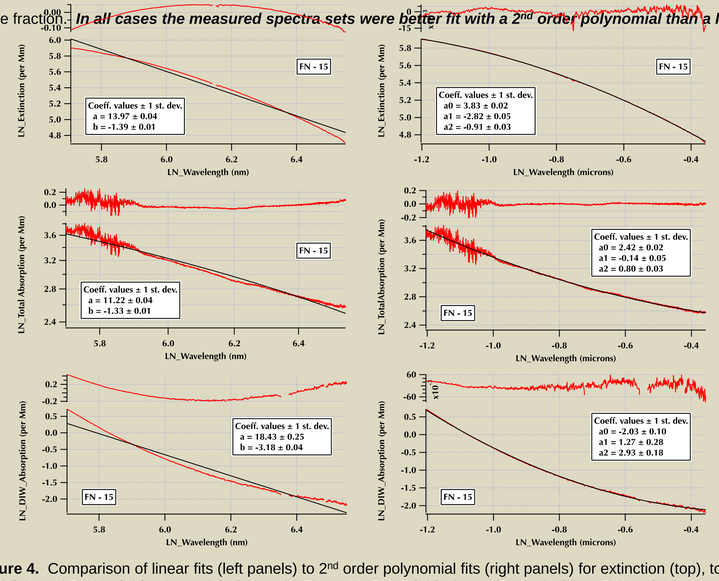


Figure 4. Comparison of linear fits (left panels) to 2nd order polynomial fits (right panels) for extinction (top), total absorption (middle), and DIW-soluble absorption (bottom). Fits to MeOH-soluble (not shown) similar to DIW-soluble absorption.

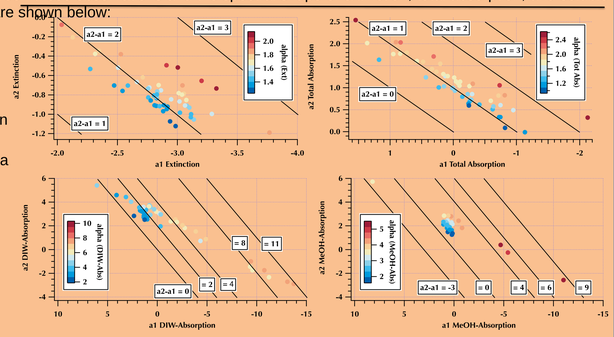
Exploring Information Content of 2nd order Spectral Fit Parameters: a_2 and a_1

•Extinction (or AOD) Ångström exponents are typically used to distinguish particle sizes, i.e., $\alpha < 1$ indicates coarse dust or sea salt aerosols with diameters > 1 µm, while > 2 indicates small combustion aerosols with diameters < 1 µm

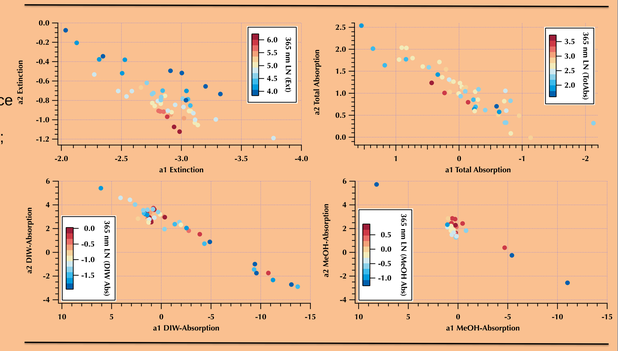
•Previous studies using ambient total column measurements and/or models have investigated sensitivities of the 2nd order polynomial coefficients and considered additional information content they may offer [e.g., Eck et al., 2001; Schuster et al., 2006]

•Here, we can map various *in situ* observations into a_2 vs. a_1 coefficient space following Schuster et al. [2006] to examine the relationship between these observations and the spectral shape of extinction, total absorption, and soluble absorption; a few examples are shown below:

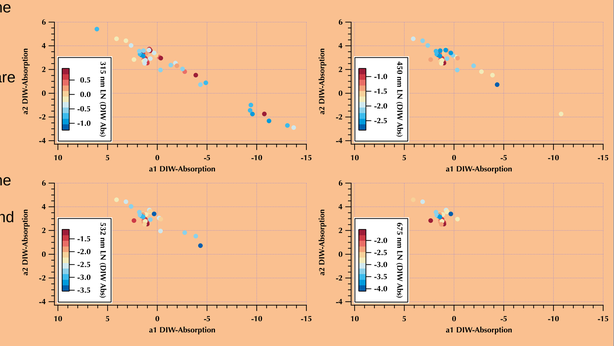
- **$\alpha \sim a_2 - a_1$**
  - Schuster et al. [2006] identified this empirical relationship for extinction coefficients
  - Similarly, separation as a function of α is found across all spectra sets, although the above empirical relationship does not strictly hold



- **Magnitudes**
  - Extinction shows clear separation in a_2-a_1 space as a function of the magnitude of extinction; This holds for all wavelengths (365 nm shown)
  - This is not the case for any of the absorption spectra

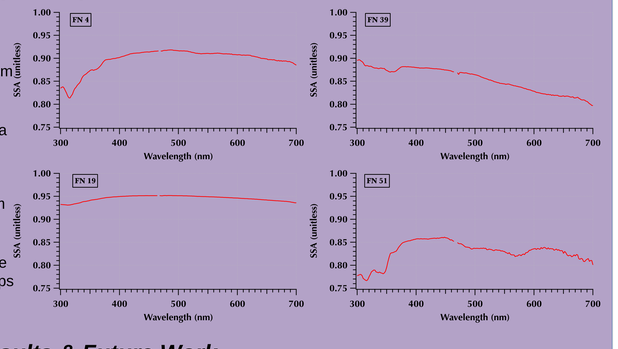


- **DIW-soluble Absorption Wavelength-Dependence**
  - Blanks used to determine limits of detection for all spectra
  - Only values 3 sigma above the mean blank are retained
  - The strong wavelength-dependence of brown carbon results in many partial spectra over the 300-700 nm range for the soluble absorbers
  - Extreme values for a_2 and a_1 for both DIW- and MeOH-Abs arise from partial spectra
  - All Ext and Total Abs spectra were complete spectra resulting in a more limited range of values for a_2 and a_1



SSA & Total Absorption Spectra

- SSA spectra exhibit diverse features throughout the cruise
- These features arise from the Total Abs spectra
- Unlike Ext and soluble-Abs spectra, there was a lot of structure in Total Abs spectra (here, smoothed over 10 nm using a boxcar algorithm prior to 2 nm averaging for SSA calculations)
- That structure limited the utility of the a_2 vs a_1 maps for either Total Abs or SSA



Implications of Results & Future Work

•*In situ* aerosol spectral measurements have been combined with other *in situ* aerosol measurements showing that both targeting specific wavelengths, as well as evaluating the spectral shape, can provide insight into the linkages between chemical and optical aerosol properties

•Work is ongoing to fully assess these data and investigate the results obtained within the broader KORUS-AQ data set; Efforts are also underway to refine and expand the spectral measurement capabilities as deployed during KORUS-OC

•Future studies combining these spectral measurement techniques with more extensive microphysical and chemical information will likely provide a wealth of new information regarding key aerosol characteristics responsible for particular optical signatures

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Acknowledgments. *The authors gratefully acknowledge the support of the KORUS-OC,* KOCOA, *and KORUS-AQ science teams, the outstanding support provided by our hosts, and financial support from the NASA/NIA cooperative agreement NNL09AA00A*