Aerosol Elemental and Molecular Mixing State Measurements via Multimodal X-Ray and Electron Microscopy

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Abstract

Climate relevant aerosol properties depend on how different chemical species are distributed among individual particles (mixing state). Scanning Transmission X-ray Microscopy and SEM have been applied to several ARM field campaigns: GoAmazon2014/15, HI-SCALE, and ACE-ENA.

In the GoAmazon2014/15 campaign, three sampling sites were setup around the industrial city of Manaus. Two sampling sites (ZF2 and ATTO) served as less polluted background for the site downwind of Manaus (T3). Here Scanning Transmission X-ray Microscopy coupled with Near Edge X-ray Absorption Fine Structure spectroscopy (STXM-NEXAFS) has been combined with Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX) on individual particles[1,2] to calculate diversity parameters (D_i) and mixing state index (χ)[3]. This highlighted the difference in diversity between the biogenic background and the anthropogenic emissions from Manus.

During the Holistic Interactions of Shallow Clouds, Aerosols, and Land-Ecosystems (HI-SCALE) campaign in the Southern Great Plains of Oklahoma, aerosols were collected during dry periods and immediately after rain events. Here a unique type of particle, the Airborne Solid Organic Particle (ASOP) was investigated. This particle class (thought to be brown carbon) was observed to cause an increase in angstrom exponent.

Inorganic dominant particles, composed mostly of sulfates and organics, have been sampled from the ACE-ENA campaign. STXM was used to determine the distribution of carbonaceous components (soot, inorganics, and organics) and total Organic Volume Fraction (OVF) of these particles. The particle average OVF is low and the is comparable with fresh sea spray aerosols.

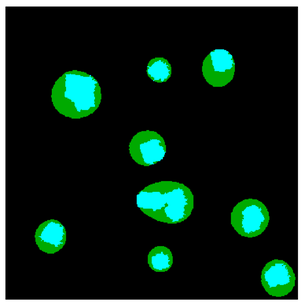
Methods

Quantitative Elemental Mass Fraction Determination

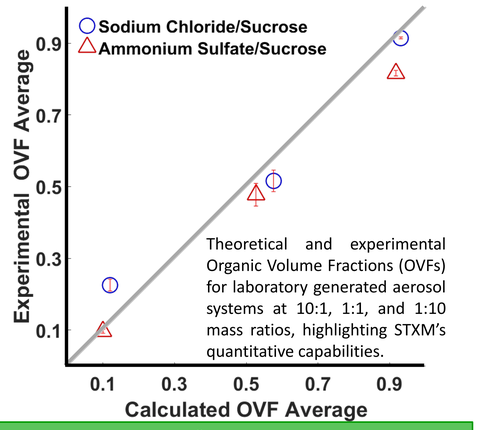
$$1)\ OD_i = \rho t \sum_{a=1}^{n} f_a \mu_{a,i} \quad 2)\ \frac{f_1}{f_2} = \frac{rel.\%_1}{rel.\%_2} \quad 3)\ \sum_{a=1}^{n} f_a = 1$$

SEM/EDX data is converted to absolute masses by solving a system of ~14 equations. 1) Beer-Lambert law, 2) multiple relationships between absolute and relative mass fractions, 3) approximation that all elements analyzed account for 100% of the sample mass. Here OD_i is optical density at energy "i", ρ is density, t is thickness, μ is the mass absorption coefficient for element "a" at energy "i", f_a is the mass fraction of element "a".

Validation with Standard Aerosols



Organic dominant (green) an inorganic dominant (blue) phases of laboratory generated aerosols from a 1:1 mass ratio NaCl/Sucrose solution.



Theoretical and experimental Organic Volume Fractions (OVFs) for laboratory generated aerosol systems at 10:1, 1:1, and 1:10 mass ratios, highlighting STXM's quantitative capabilities.

Future Work

- Expanding the calculated mixing state parameter χ to include nitrates and sulfates
- Determining the sub-particle spatial distribution of nitrates, sulfates
- Calculating the mixing state and particle diversity (D_i) from the matched HI-SCALE data
- Identifying elemental or spectral characteristics of ASOPs and relating them to brown carbon
- ACE-ENA samples previously imaged with STXM to be analyzed with SEM/EDX.
- Continued data collection to characterize clean marine and polluted air masses during ACE ENA IOP 1 and IOP 2

References

1. Piens, Dominique S., et al. "Measuring mass-based hygroscopicity of atmospheric particles through in situ imaging." *ES&T* (2016).
2. O'Brien, Rachel E., et al. "Chem. imaging of ambient aerosol particles: Observational constraints on mixing state..." *J. of Geophys: Atmos.* (2015)
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5. Kilcoyne, A. L. D., et al. "Interferometer-controlled scanning transmission X-ray microscopes at the Advanced Light Source" J. of Sync. Rad. (2003)
6. Fraund, M., et al. "Elemental Mixing State of Aerosol Particles Collected in Central Amazonia during GoAmazon2014/15", Atmosphere (2017)
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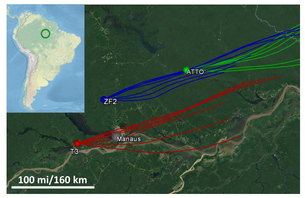
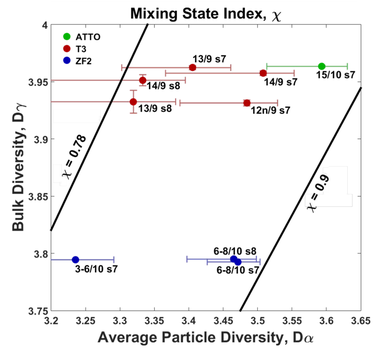
GoAmazon2014/15



Representative HYSPLIT trajectories

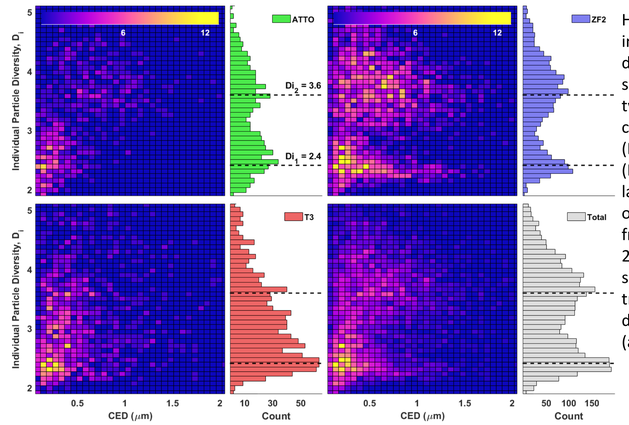
Trade winds show north eastern wind direction. Above is a National Oceanic and Atmospheric Administration (NOAA) HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model showing representative trajectories over our sampling periods[4].

Elemental Mixing State



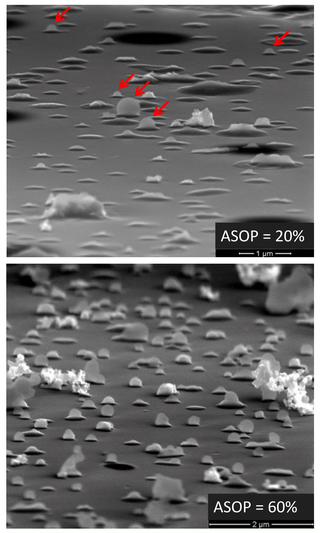
Mixing state[3] of samples taken at ATTO (green), ZF2 (blue), and T3 (red). Error bars shown are reduced by a factor of one-tenth. Differences in χ were not statistically significant, owing to the large elemental mass variation found in aerosol particles.

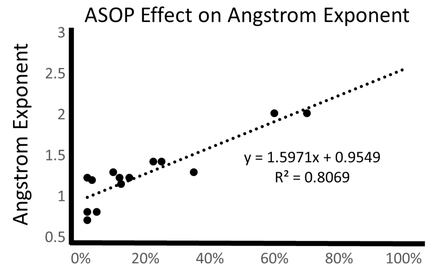
Aged and Fresh Diversity Modes



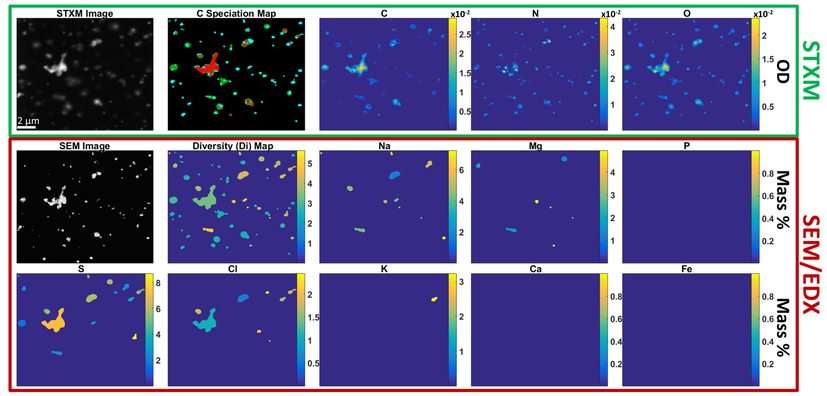
Histograms of individual particle diversity separated by sampling site show two diversity modes corresponding to fresh (D_i=2.4) and aged (D_i=3.6) emissions. T3 lacks the aged mode, owing to many more fresh emissions. 2D histograms showing the slight trend of higher diversity particles (aged) being larger.

HI-SCALE SGP



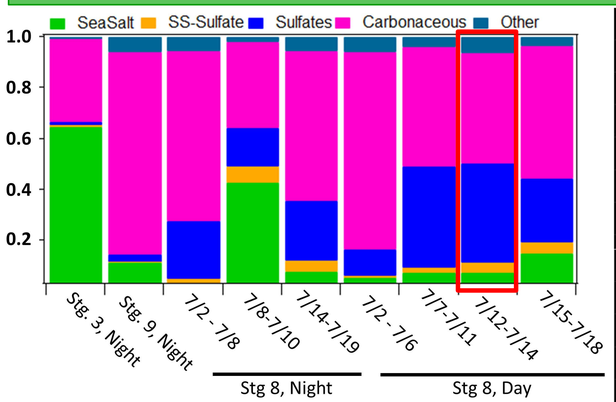


(left) Tilted SEM images showing spherical glassy particles (labeled), thought to be Airborne Solid Organic Particles (ASOP). The % of ASOP present varies between samples and is hypothesized to increase after rain events.
(above) Correlation between red/blue angstrom exponent and ASOP% (as visually identified with high aspect ratios from tilted SEM images). When the correlation line is extended to 100% ASOP an angstrom exponent value of ~2.5 is observed, which is consistent with brown carbon.

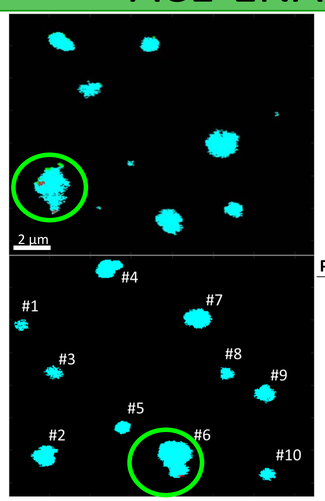


Elemental maps of a HI-SCALE sample. The green rectangle contains STXM images with optical density maps for C, N, and O along with a carbon speciation map (red for soot, blue for inorganics, green for organics). The red rectangle contains SEM/EDX images with elemental mass percent maps for selected elements as well as an individual particle diversity (D_i) map.

ACE-ENA

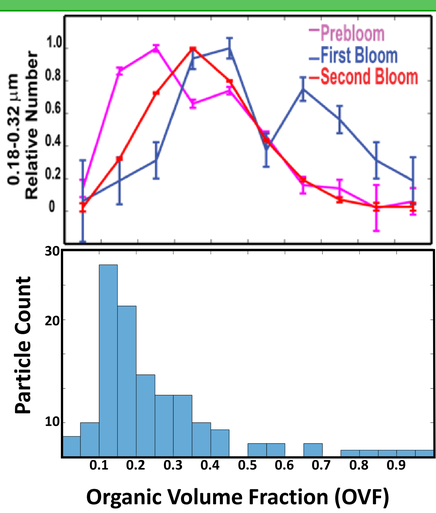


Particle classification from SEM/EDX data. The sample boxed in red was analyzed with STXM where mostly carbonaceous and sulfate aerosols were seen.



(left) Carbon speciation maps show mainly inorganic dominant particles. A few particles (green circles) have small soot inclusions.

Particle	OVF
1	0.225
2	0.215
3	0.237
4	0.0798
5	0.126
6	0.227
7	0.119
8	0.149
9	0.181
10	0.148



(top left) OVF histograms from laboratory generated sea spray aerosols[7]. Bloom conditions listed refer to the two phytoplankton blooms that occurred in the filtered seawater. (bottom left) OVF histogram for ACE-ENA samples (stage 7 and 8, 0.56 – 0.32 and 0.32 – 0.18 μm size ranges respectively).

The ACE-ENA samples compare most closely with prebloom conditions where less biological activity was observed.