

Organic Enrichment, Physical Phase State, and Surface Tension Depression of Nascent Core-Shell Sea Spray Aerosols During Two Phytoplankton Blooms

Hansol D. Lee¹, Holly S. Morris¹, Olga Laskina¹, Camille M. Sultana², Christopher Lee³, Thilina Jayarathne¹, Joshua L. Cox², Xiaofei Wang², Elias S. Hasenecz¹, Paul J. DeMott⁴, Timothy H. Bertram⁵, Christopher D. Cappa⁶, Elizabeth A. Stone¹, Kimberly A. Prather^{2,3,7}, Vicki H. Grassian^{2,3}, and Alexei V. Tivanski^{1}*

¹Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA.

²Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093, USA.

³Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92037, USA.

⁴Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80521, USA.

⁵Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, USA.

⁶Department of Civil and Environmental Engineering, University of California, Davis, CA 95616, USA.

⁷Department of Nanoengineering, University of California, San Diego, La Jolla, CA 92093, USA.

PM_{2.5} and PM_{10-2.5} organic volume fraction measurements. The PM_{2.5} and PM_{10-2.5} organic volume fraction (OVF) results are based on daily filter samples collected for 3-6 hours and analyzed offline for organic carbon via a thermal optical analyzer and inorganic ions using ion chromatography with conductivity detection.¹⁻² Organic carbon (OC) was converted to organic matter (OM) using two OC/OM ratios: 1.8 for water soluble organic matter (WSOM) and 1.4 for water insoluble organic matter (WIOM) following Facchini et al.³ This conversion estimates the mass of O, H, N, S, P and other elements associated with organic molecules. In calculating OM mass fractions, assuming all OM is entirely water-soluble provides an upper-limit, whereas assuming all OM is water-insoluble provides a lower-limit. The OM mass estimates were converted to volume assuming a density of laminarin (1.54 g cm⁻³) and palmitic acid (0.852 g cm⁻³)

³⁾ for WSOM and WIOM, respectively, which have been previously highlighted as model SSA compounds.⁴ Inorganic mass comprised of sodium, potassium, magnesium, calcium, chloride, bromide, nitrate and sulfate was converted to volume assuming the density of sea salt (2.06 g cm⁻³). It should be noted that mass not quantified in Jayarathne et al.⁵ was ignored for these bulk OVF calculations, including water, cations (e.g. ammonium, iron, aluminum) and anions (e.g. fluoride, iodide, carbonate). An upper and lower limit for PM_{2.5} and PM_{10-2.5} OVF was calculated and plotted in Figure S1 using the estimated WSOM and WIOM volumes with inorganic volume.

Due to lack of organic-identity sensitivity from AFM OVF volume-based measurements, the data was also compared against bulk OVF values derived from PM_{2.5} and PM_{10-2.5} based on organic carbon and inorganic ion mass concentrations from Jayarathne et al.⁵ Overall, PM_{2.5} OVF results across the experiment range from 0.18 to 0.43, which is in good agreement with the AFM single particle OVF data that ranges from 0.24 to 0.44. The AFM results also agree well with previous works that quantified the OVF of SSAs collected in the same experiment and studied using scanning transmission x-ray microscopy, which reported OVF values of ~0.25 for the bloom 1 and ~0.30 for bloom 2.⁶ PM_{2.5} OVF ranges from a high of 0.39 – 0.47 on day 12 to a low of 0.16 – 0.21 on day 25. Values are higher during the beginning of the bloom 1 and reach a maximum on day 12, before the bloom 1 peak. OVF decreases after day 12 and varies less for the remainder of the experiment (0.16 – 0.21 to 0.26 – 0.34). During the bloom 1, organics, which were more surface active and aliphatic-like, were further enriched. But, there is no evident trend during the bloom 2. During the bloom 2, oxygen rich organic species were more prevalent—these species are expected to be less surface active and consequently their enrichment and the corresponding OVF would be less.⁷ PM_{10-2.5} shows significantly lower OVF compared to PM_{2.5} and exhibits even less variation across the mesocosm experiment (0.02 – 0.03 to 0.06 – 0.08), with no clear trends for either

phytoplankton bloom. This could be attributed in part to differences in the dominant organic species present, where organic enrichment increases drastically with decreasing aerosol size.⁸

The difference observed between bulk PM_{2.5} OVF and AFM OVF on day 14 can likely be attributed to OVF variation in aerosol size of larger SSA in PM_{2.5}. While PM_{2.5} contains all aerosol < 2.5 microns in size and the number fraction is dominated by sub-micron particles, aerosol mass will be dominated by the larger super-micron particles. Since the calculated OVF measurements are based on mass, PM_{2.5} OVF is likely to be less sensitive to the OVF variation found in smaller sub-micron particles that have greater organic enrichment.

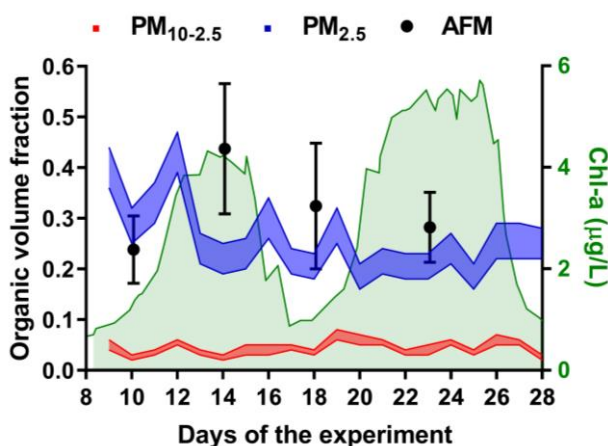


Figure S1. Temporal variation of single particle and bulk OVF results during IMPACTS 2014 study. Bulk PM_{10-2.5} and PM_{2.5} OVF values were calculated from organic carbon and inorganic ion mass concentrations taken from Jayarathne et al.⁵ The darker boundaries represent the upper and lower limits of the bulk OVF with the true value lying within the shaded region. AFM OVF averages are represented by black solid circles and error bars represent one standard deviation. Chlorophyll-a concentration is shown in green, which was taken from Wang et al.⁹

REFERENCES

1. Cavalli, F.; Facchini, M. C.; Decesari, S.; Mircea, M.; Emblico, L.; Fuzzi, S.; Ceburnis, D.; Yoon, Y. J.; O'Dowd, C. D.; Putaud, J. P.; Dell'Acqua, A., Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic. *J Geophys Res-Atmos* **2004**, *109* (D24).
2. Jayarathne, T.; Stockwell, C. E.; Yokelson, R. J.; Nakao, S.; Stone, E. A., Emissions of Fine Particle Fluoride from Biomass Burning. *Environmental Science & Technology* **2014**, *48* (21), 12636-12644.
3. Facchini, M. C.; Rinaldi, M.; Decesari, S.; Carbone, C.; Finessi, E.; Mircea, M.; Fuzzi, S.; Ceburnis, D.; Flanagan, R.; Nilsson, E. D.; de Leeuw, G.; Martino, M.; Woeltjen, J.; O'Dowd, C. D., Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. *Geophys Res Lett* **2008**, *35* (17).
4. Bertram, T. H.; Cochran, R. E.; Grassian, V. H.; Stone, E. A., Sea spray aerosol chemical composition: elemental and molecular mimics for laboratory studies of heterogeneous and multiphase reactions. *Chem Soc Rev* **2018**, *47* (7), 2374-2400.
5. Jayarathne, T.; Sultana, C. M.; Lee, C.; Malfatti, F.; Cox, J. L.; Pendergraft, M. A.; Moore, K. A.; Azam, F.; Tivanski, A. V.; Cappa, C. D.; Bertram, T. H.; Grassian, V. H.; Prather, K. A.; Stone, E. A., Enrichment of Saccharides and Divalent Cations in Sea Spray Aerosol During Two Phytoplankton Blooms. *Environmental Science & Technology* **2016**, *50* (21), 11511-11520.
6. Pham, D. Q.; O'Brien, R.; Fraund, M.; Bonanno, D.; Laskina, O.; Beall, C.; Moore, K. A.; Forestieri, S.; Wang, X. F.; Lee, C.; Sultana, C.; Grassian, V.; Cappa, C. D.; Prather, K. A.; Moffet, R. C., Biological Impacts on Carbon Speciation and Morphology of Sea Spray Aerosol. *Acs Earth Space Chem* **2017**, *1* (9), 551-561.
7. Quinn, P. K.; Collins, D. B.; Grassian, V. H.; Prather, K. A.; Bates, T. S., Chemistry and Related Properties of Freshly Emitted Sea Spray Aerosol. *Chem Rev* **2015**, *115* (10), 4383-4399.
8. Prather, K. A.; Bertram, T. H.; Grassian, V. H.; Deane, G. B.; Stokes, M. D.; DeMott, P. J.; Aluwihare, L. I.; Palenik, B. P.; Azam, F.; Seinfeld, J. H.; Moffet, R. C.; Molina, M. J.; Cappa, C. D.; Geiger, F. M.; Roberts, G. C.; Russell, L. M.; Ault, A. P.; Baltrusaitis, J.; Collins, D. B.; Corrigan, C. E.; Cuadra-Rodriguez, L. A.; Ebben, C. J.; Forestieri, S. D.; Guasco, T. L.; Hersey, S. P.; Kim, M. J.; Lambert, W. F.; Modini, R. L.; Mui, W.; Pedler, B. E.; Ruppel, M. J.; Ryder, O. S.; Schoepp, N. G.; Sullivan, R. C.; Zhao, D. F., Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol. *P Natl Acad Sci USA* **2013**, *110* (19), 7550-7555.
9. Wang, X. F.; Sultana, C. M.; Trueblood, J.; Hill, T. C. J.; Malfatti, F.; Lee, C.; Laskina, O.; Moore, K. A.; Beall, C. M.; McCluskey, C. S.; Cornwell, G. C.; Zhou, Y. Y.; Cox, J. L.; Pendergraft, M. A.; Santander, M. V.; Bertram, T. H.; Cappa, C. D.; Azam, F.; DeMott, P. J.; Grassian, V. H.; Prather, K. A., Microbial Control of Sea Spray Aerosol Composition: A Tale of Two Blooms. *Acs Central Sci* **2015**, *1* (3), 124-131.