Global-scale multi-season observations of the organic mass fraction of sea salt particles

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Sea spray organics: import and questions

The amount of organic material in sea spray is potentially relevant for a few reasons:

1. Higher organic mass fractions reduce sea salt particles' hygroscopicity and therefore their ambient size and light scattering.
2. Higher organic mass fractions reduce hygroscopity and potentially CCN activity.
3. Higher sea salt organic mass fractions can be associated with higher sea spray number fluxes.

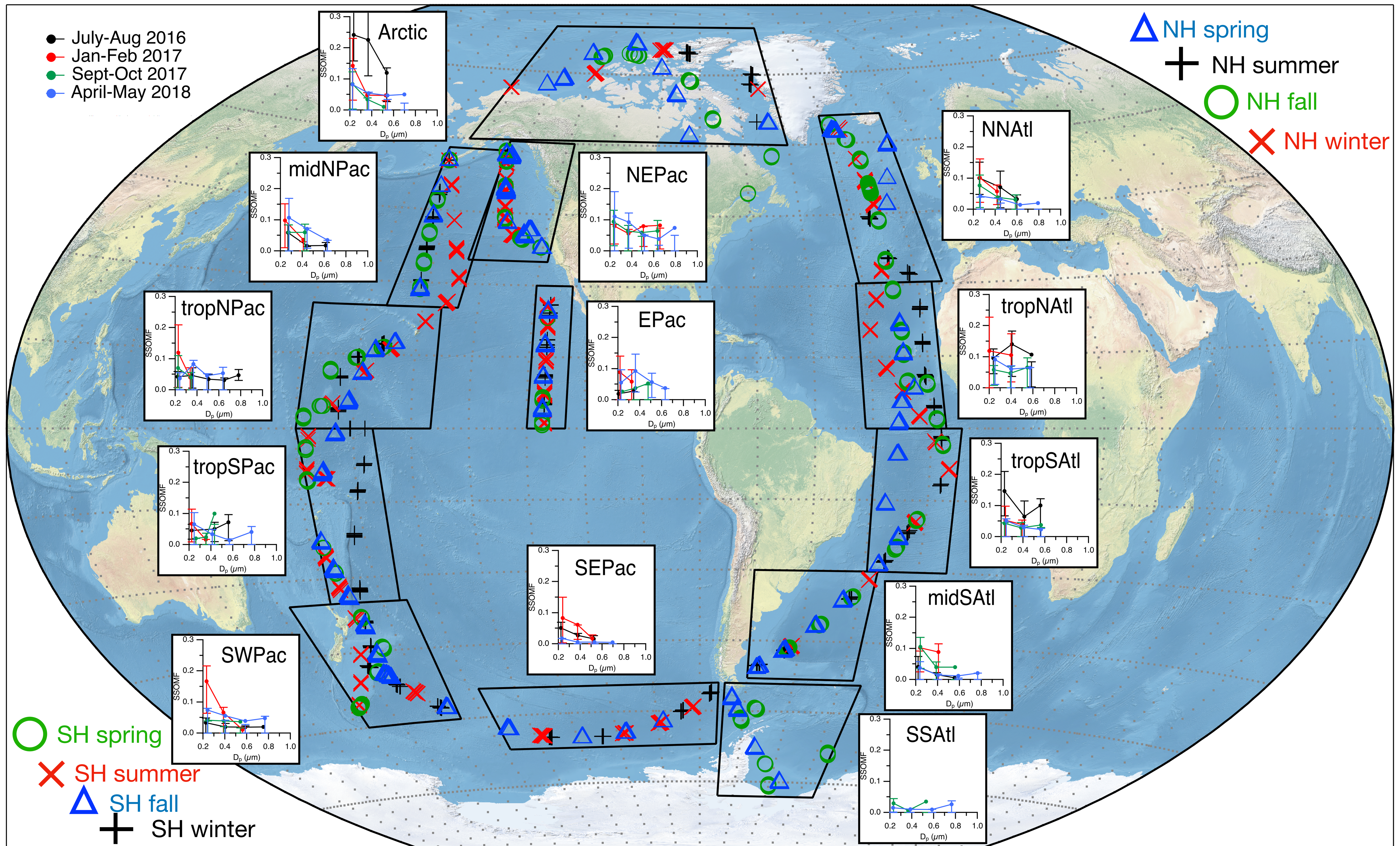
There is considerable uncertainty in how much organic matter is in sea spray, and what controls this. We think we know a few things:

1. The smaller the sea spray particle, the higher the organic content.
2. Most of the organics present in submicron sea spray are probably from broadly distributed dissolved seawater organic carbon[1,2,3].
3. However, under some conditions, there can be substantial increases to sea spray organics as a result of more recent surface ocean biological production[4,5].
4. Perhaps the most puzzling result of recent years is that the enormous North Atlantic seasonal phytoplankton bloom appears to show no substantial seasonal cycle in primary sea spray aerosol composition and properties[6].

A new global-scale dataset of organic content of sea salt (or sea spray) aerosol

The ATom series of missions provided an unprecedented in situ snapshot of the remote atmosphere in four seasons, over a wide range of altitudes (marine boundary layer to 10 km) and latitudes.

We quantified the size-resolved organic mass fraction of thousands of individual sea salt particles detected over this mission, from particles of about 0.13 to 0.8 μm dry diameter. The lower limit is set by optical particle detection and the upper limit by a change in ionization regime. We describe the particles as "sea salt" because we require the salt cations to identify them, but our ability to detect sea spray particles with as little as 1% sea salt content by mass means that these results probably represent "sea spray" more broadly, i.e. including the majority of highly organic-enriched sea spray particles.

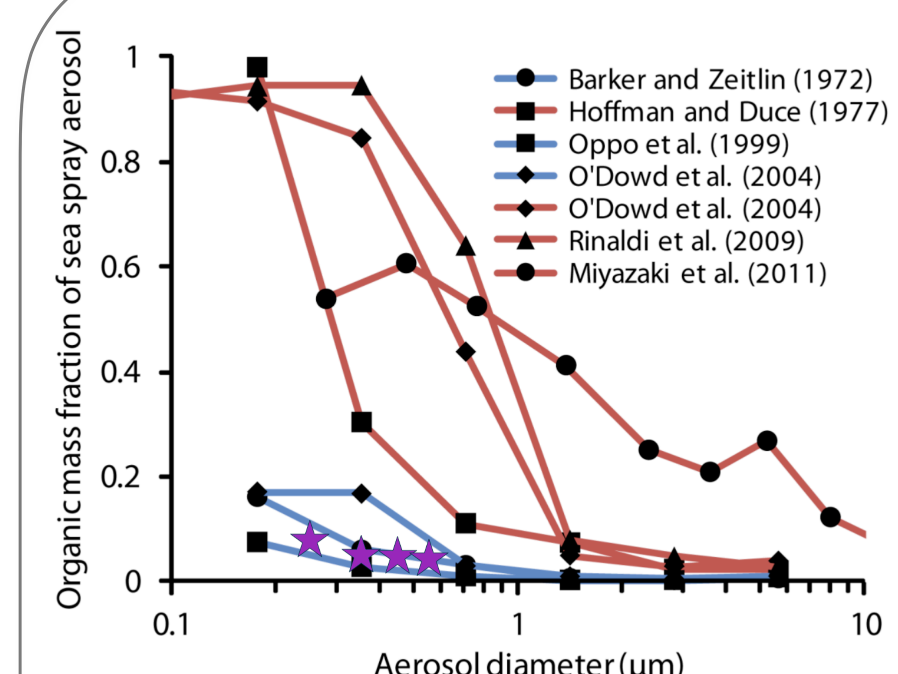


Regional MBL Fresh Sea Salt Organic Mass Fraction (SSOMF) vs Diameter

Measurements of the organic mass fraction of sea salt particles (SSOMF) in the marine boundary layer (MBL), grouped by region and season. Only particles with no measurable non-sea-salt sulfate are included to get the best estimate of only primary organics. The colors correspond to the different seasons of the four Atom missions, with locations of MBL sampling indicated on the map. Means are plotted as solid circles, and the 25%-75% interquartile range is shown as error bars.

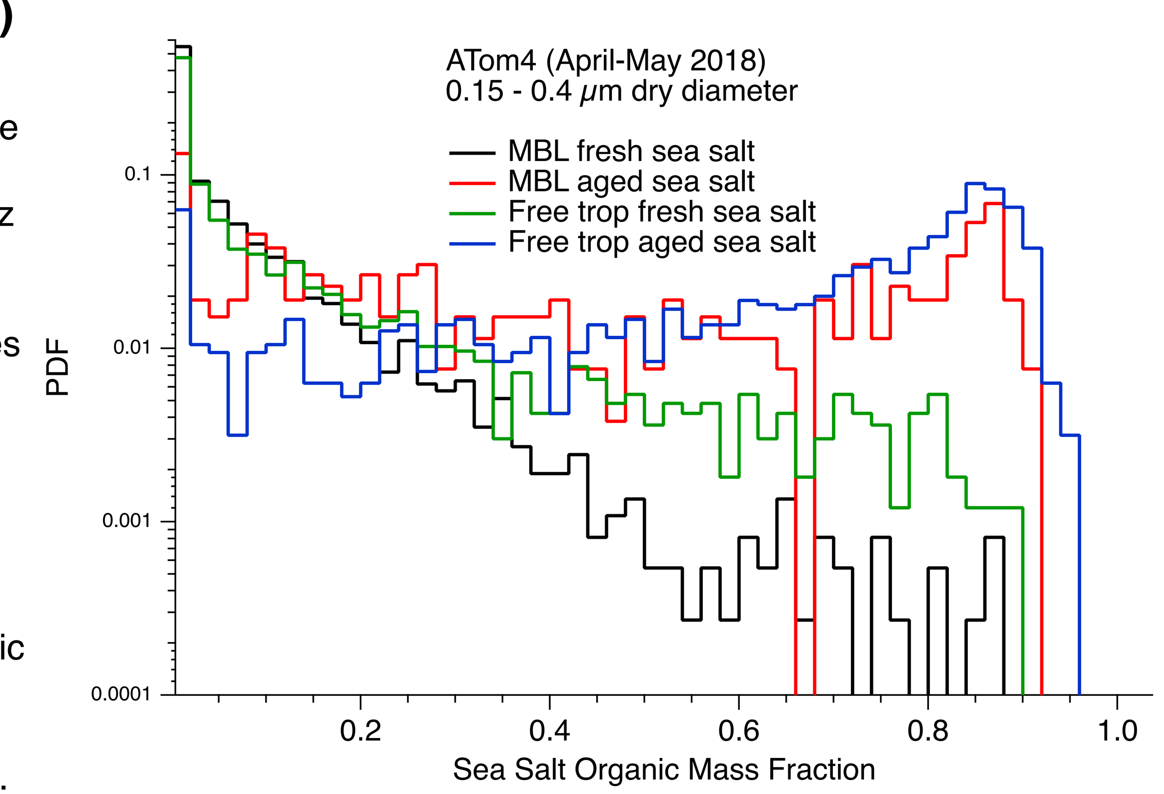
Conclusions:

1. **Mean sea spray organic mass fractions are low** (< 20% even at 200 nm), but the range is quite large.
2. **Seasonal cycles appear weak** but may exist in some regions.
3. **Atmospheric aging can cause large increases in sea salt organics**, especially for small particles.
4. **High organic mass fraction regions must be highly heterogeneous**, localized in space and time presumably to biologically active regions.



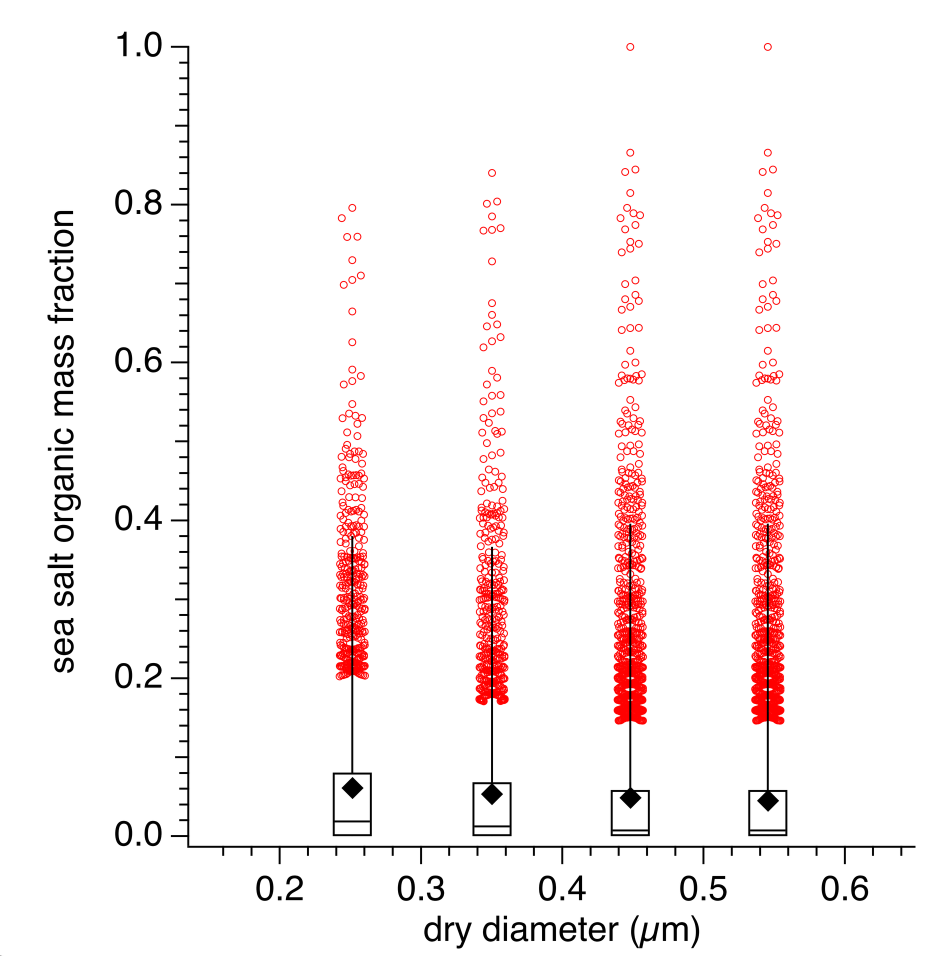
Present study global mean MBL fresh sea salt values (purple stars) compared with literature review studies (CITE Gantt). Red lines were considered biologically active regions and blue were not.

Distribution of organic mass fraction in small sea salt particles (0.15- 0.4 *µm* dry diameter)



Aged sea salt is identified by detectable non-sea-salt sulfate, measured as SO^+ (m/z 48) above the fresh sea salt ion fraction. Fresh sea salt particles in both the marine boundary layer (MBL) and free troposphere are very likely to have < 2% organic mass fraction. They can reach very high organic mass fractions (> 80%), but such particles are very rare. Fresh sea salt in the free troposphere is slightly more likely to have a higher organic mass fraction, perhaps due to more efficient scavenging of saltier particles. The fraction of aged particles in the troposphere is higher (close to 50%) in the free troposphere compared to the MBL (< ~ 20%).

Aging of small sea salt particles is accompanied by an increase in their organic mass fractions. Aged sea salt has a similar distribution in the MBL and the free troposphere, though they are on average saltier in the MBL, presumably due to less aging overall.



Global MBL fresh sea salt organic mass fraction vs diameter

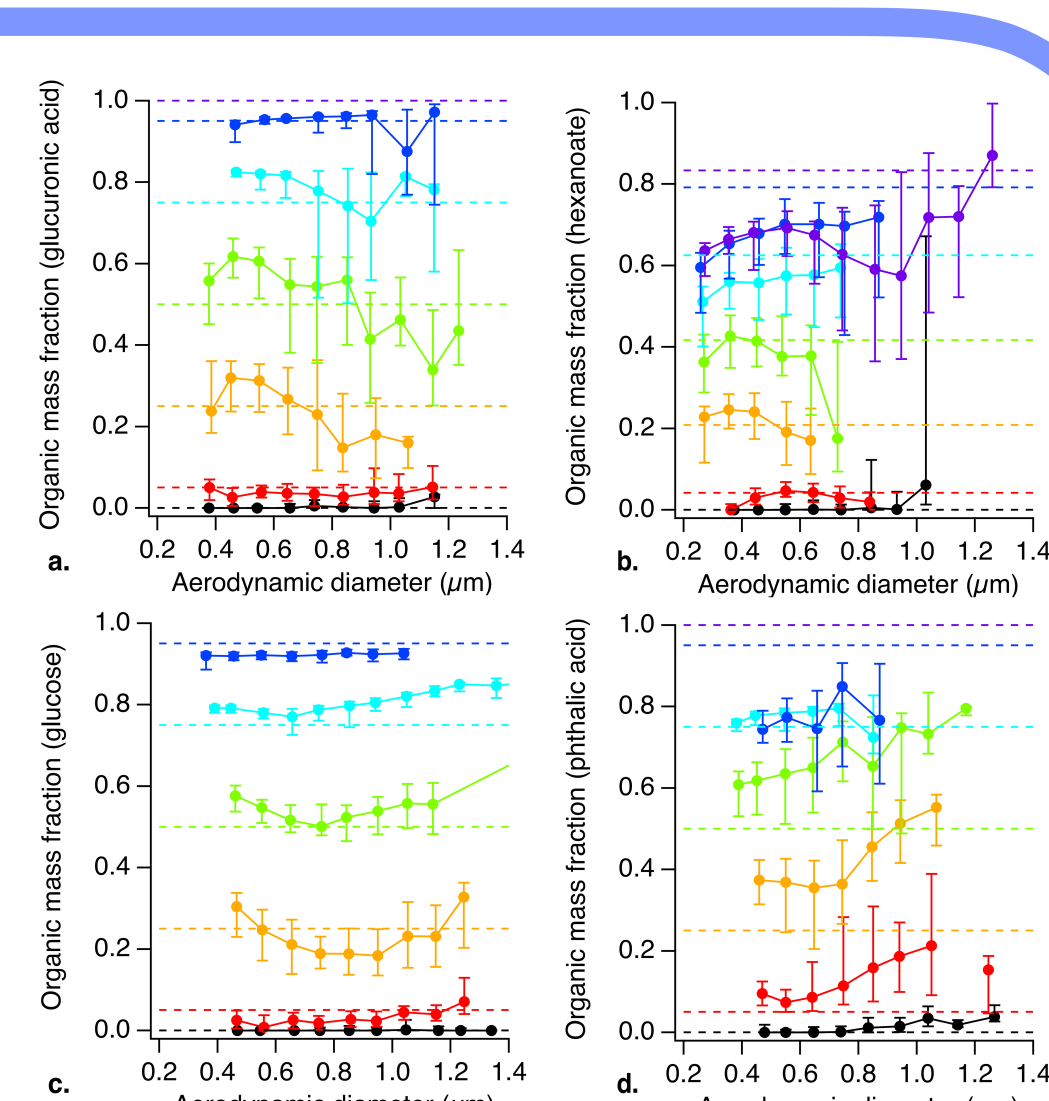
This plot includes almost all the fresh sea salt organic mass fraction data from the marine boundary layer. Slightly smaller and larger diameter data exist but are excluded because they may be biased due to sampling limitations. Diamonds are mean values. Boxes are 0.1 μm wide from 0.2 to 0.6 μm. Boxes are 25th-75th quantiles with median as line in middle. Whiskers are 2nd and 98th percentiles. Outliers (Tukey method) are plotted as red circles. Sea salt organic mass fractions span a very wide range but are very low in the median or mean.

Quantifying sea salt organic mass fraction (SSOMF) using Particle Analysis by Laser Mass Spectrometry (PALMS)

The NOAA PALMS single particle mass spectrometer can identify sea salt with high accuracy using relationships among key detected ions in individual particle spectra. Organic ions are sometimes present in the spectra, and the main two (C^+ at m/z 12 and CO^+ at m/z 28) were used to develop a calibration for SSOMF of individual sea salt particles.

Lacking a truly representative marine organic standard, we tried to cast as wide a chemical net as possible while only choosing compounds which had good solubility and low vapor pressure so that nebulized calibration aerosol would be of well-known composition. We included sodium hexanoate as an aliphatic and phthalic acid as an aromatic, alongside glucose and glucuronic acid (an analog for marine polysaccharide gel monomers).

The plot at right shows calibration signals (solid circles) with the calibration curve applied, including modifications for size-dependent effects. The dashed lines show the actual SSOMF of the calibration aerosol. The results show fairly good agreement across a wide size range for the diverse compounds.



References:

1. P. K. Quinn et al., Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol. Nat. Geosci. 7, 228–232 (2014).
2. Lawler, M. J., et al.: North Atlantic marine organic aerosol characterized by novel offline thermal desorption mass spectrometry: Polysaccharides, recalcitrant material, and secondary organics, Atmos. Chem. Phys., 20(24), 16007–16022, doi:10.5194/acp-2020-562, 2020.
3. Beaupré, S. R., et al.: Oceanic efflux of ancient marine dissolved organic carbon in primary marine aerosol, Sci. Adv., 5(10), 1–10, doi:10.1126/sciadv.aax6535, 2019.
4. O'Dowd, C., Facchini, M. and Cavalli, F.: Biogenically driven organic contribution to marine aerosol, Nature, 431(October), doi:10.1038/nature02970.1., 2004.
5. Prather, K. A. , et al. : Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol., Proc. Natl. Acad. Sci. U. S. A., 110(19), 7550–5, doi:10.1073/pnas.1300262110, 2013.
6. Bates, T. S., et al. Variability in Marine Plankton Ecosystems Are Not Observed in Freshly Emitted Sea Spray Aerosol Over the North Atlantic Ocean, Geophys. Res. Lett., 47(1), doi:10.1029/2019GL085938, 2020.
7. Gantt, B. and Meskhidze, N.: The physical and chemical characteristics of marine primary organic aerosol: A review, Atmos. Chem. Phys., 13(8), 3979–3996, doi:10.5194/acp-13-3979-2013, 2013.

Acknowledgements:

Ken Aiken (NOAA ESRL) provided Igor Pro-based software for projecting and transforming the map.