Supplement of North Atlantic marine organic aerosol characterized by novel offline thermal desorption mass spectrometry: polysaccharides, recalcitrant material, and secondary organics

Michael J. Lawler et al.

Correspondence to: Michael J. Lawler (mlawler@uci.edu)

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Table S1: Number of samples analyzed by TDCIMS from each size class and type.

<table>
<thead>
<tr>
<th>Sea Sweep</th>
<th>Marine</th>
<th>Continental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;180 nm</td>
<td>&lt;180 nm</td>
</tr>
<tr>
<td>N1: Nov. 2015</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>N2: May 2016</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>N3: Sept. 2017</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>N4: March-April 2018</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure S1. Estimated center timing of desorption for each high resolution ion for an ambient marine PM1 filter analysis (08:00 Sept 13, 2017–07:00 Sept 14, 2017 UTC). Center of desorption was estimated by fitting a Guassian function to the desorbed ion. Warm colors show times of higher signal. Points right of the dashed line are likely to be decomposition products because they appear after the peaks typical of polysaccharides, which are detected by their thermal decomposition peaks. Points left of the dashed line are likely to include desorption peaks of intact sampled molecules. The points around 50 s are from sea salt.
Figure S2. Calibration curve for nanocellulose using the most characteristic ion for polysaccharide, C$_6$H$_5$O$_3^+$. 

Figure S3. Aldrich humic acid standard mass spectrum (black sticks) and recalcitrant factor mass spectrum (red sticks). Reported molecular formulae are positive ions, and the C$_x$H$_y$ and C$_x$H$_y$O$_z$ species should be considered H$^+$ adducts. There was not a good match between the Aldrich humics and any PMF factor identified in this study. Though the Aldrich humics are not a good match, it is worth noting that the TDCIMS sensitivity to the humics is much worse than to polysaccharide (see Figure 3). This is likely at least in part due to less structural regularity in the humics, resulting in a more diffuse spread of ion peaks.
Figure S4. TDCIMS PMF fractions for submicron NAAMES 2 (2016) ambient marine (a.) and Sea Sweep (b.) aerosol, and the same for NAAMES 3 (2017), c. and d. The fatty acid factor was excluded because of apparent gas phase-related artifacts. The Sea Sweep aerosol was dominated by the recalcitrant and polysaccharide factors, while ambient aerosol often showed higher SOA1 and SOA2 fractions. Note that these factors are not quantitative. Though we have no direct measure of the TDCIMS sensitivity to the recalcitrant material, we infer that the TDCIMS sensitivity to polysaccharides is significantly higher than the sensitivity to recalcitrant material. Polysaccharide represented a small or modest fraction of the alcohol functional group (which correlated closely with recalcitrant factor), while in these PMF fractions, the polysaccharide and recalcitrant signals are sometimes similar in magnitude for Sea Sweep aerosol. (Also see Figure S1). Similarly, we consider it more likely that the PMF fractions may provide an overestimate of the SOA:recalcitrant mass ratio rather than an underestimate.
Figure S5. Mass fractions of Mg$^{2+}$: Na$^+$ in (a) sub-180 nm and (b) submicron aerosol samples separated by season. Red circles are artificial Sea Sweep-generated sea spray. Blue circles are ambient marine aerosol. The dotted line indicates the seawater ratio of 0.12. The Mg$^{2+}$:Na$^+$ ratio was fairly consistent across seasons, aerosol types and sizes.

Figure S6. Comparison of Na$^+$ sampled on the filters as assessed by TDCIMS compared with IC. A 1:1 line is shown as a dashed line, and a quadratic fit to the data points is show in a solid line. The IC data were used for all analyses presented here.
Other cations

<table>
<thead>
<tr>
<th>Sample type</th>
<th>NH$_4^+$</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>&lt;180 nm</td>
<td>(-)0.01</td>
<td>0.54</td>
<td>0.80</td>
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<tr>
<td>marine</td>
<td></td>
<td></td>
<td>(0.03)</td>
<td></td>
</tr>
<tr>
<td>&lt;180 nm</td>
<td>(-)0.80</td>
<td>0.28</td>
<td>0.97</td>
<td>0.03</td>
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<tr>
<td>Sea Sweep</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM1 marine</td>
<td>0.03</td>
<td>0.39</td>
<td>0.96</td>
<td>0.00</td>
</tr>
<tr>
<td>PM1 Sea Sweep</td>
<td>n/a</td>
<td>0.78</td>
<td>0.97</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table S2. Coefficients of determination ($r^2$s) for linear relationships between sodium and the other 4 cations measured in sub-180 nm and submicron Sea Sweep and ambient marine samples. Bold text indicates a strong statistical relationship, with a linear slope 4 standard deviations greater than 0. Underlined text indicates a likely relationship, with a linear slope 2 standard deviations greater than 0. One case for which removing a single point changes a relationship between none and modest or none and strong are shown as “with (without)” that point and italicized. One relationship for which $r$ is negative is indicated with (-).

Figure S6. Mass fractions of Ca$^{2+}$:Na$^+$ in a. sub-180 nm and b. submicron aerosol samples organized by season. Red circles are artificial Sea Sweep-generated sea spray. Blue circles are ambient marine aerosol. The dotted line indicates the seawater ratio of 0.038. The Ca$^{2+}$:Na$^+$ ratio was highly variable and regularly showed strong enrichments with respect to seawater but no apparent seasonal cycle.