Supplement to “North Atlantic marine organic aerosol characterized by novel offline thermal desorption mass spectrometry approach: polysaccharides, recalcitrant material, secondary organics” by Lawler et al., 2020.

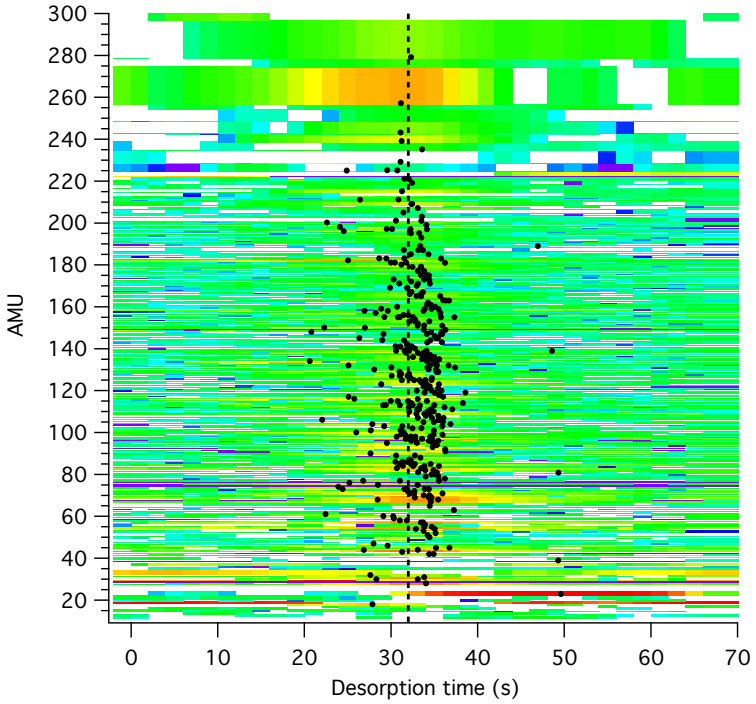

Figure S1. Estimated center timing of desorption for each high resolution ion for an ambient marine PM1 filter analysis (08:00 Sept 13, 2017– 07:00 Sept 14, 2017 UTC). Center of desorption was estimated by fitting a Guassian function to the desorbed ion. Warm colors show times of higher signal. Points 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.

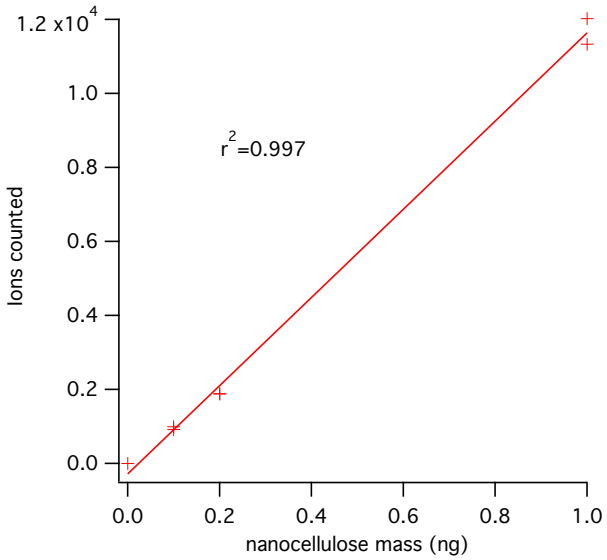

Figure S2. Calibration curve for nanocellulose using the most characteristic ion for polysaccharide, $C_6H_5O_3^+$.

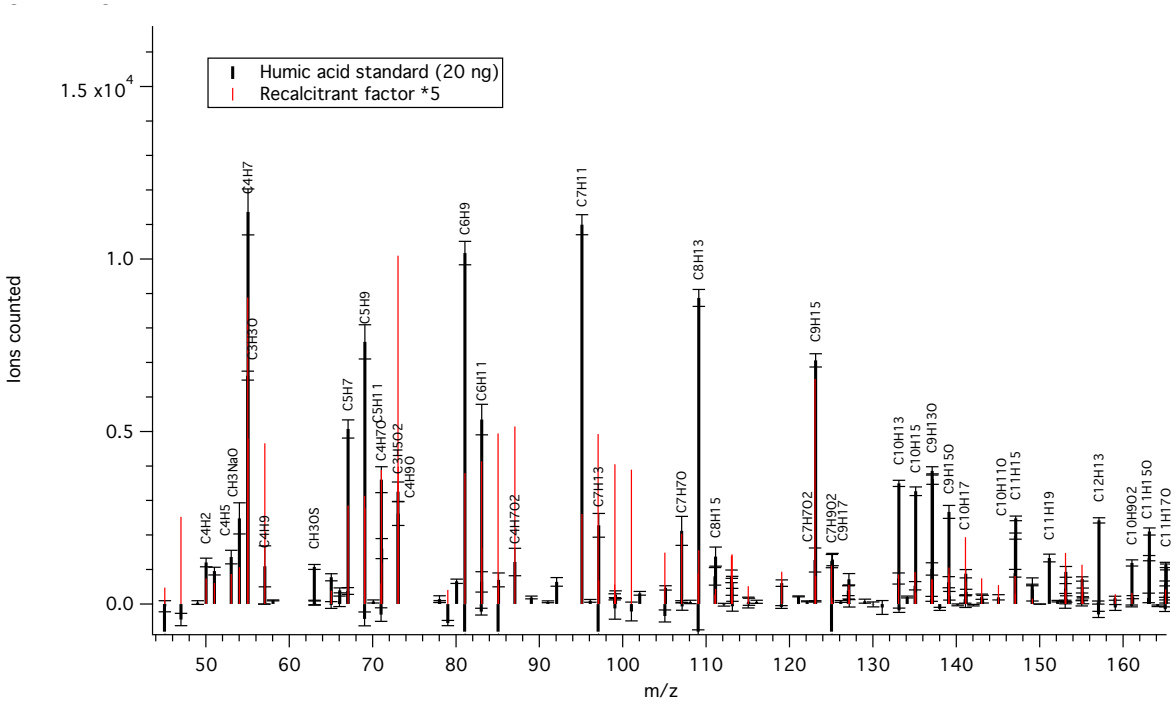

Figure S3. Aldrich humic acid standard mass spectrum (black sticks) and recalcitrant factor mass spectrum (red sticks). Reported molecular formulae are positive ions, and the C_xH_y and $C_xH_yO_z$ species should be considered H^+ adducts. There was not a good match between the Aldrich humics and any 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.

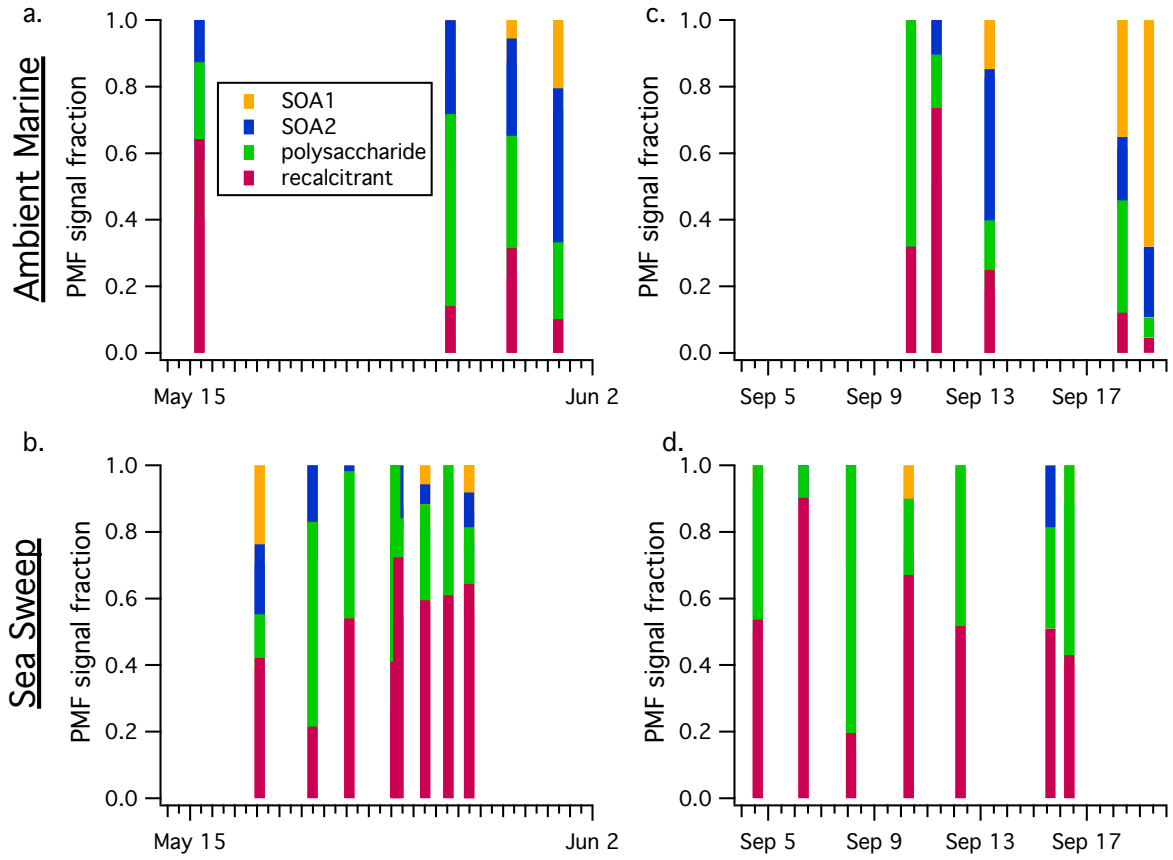

Figure S4. TDCIMS PMF fractions for NAAMES 2 (2016) ambient marine (a.) and Sea Sweep (b.) aerosol, and the same for NAAMES 3 (2017), c. and d. The fatty acid factor was excluded because of its apparent volatilization behavior. The Sea Sweep aerosol was dominated by the recalcitrant and polysaccharide 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.

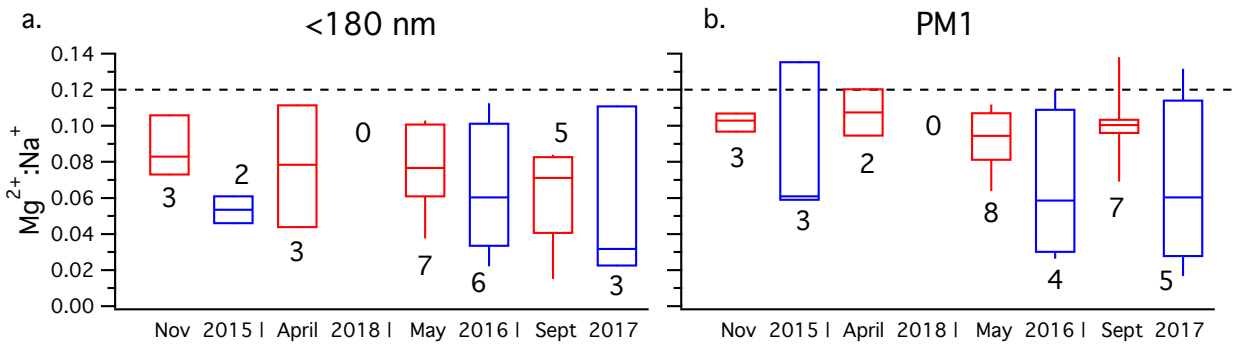

Figure S5. Mass fractions of Mg^{2+}: Na^{+} in **a.** sub-180 nm and **b.** submicron aerosol samples organized into box-and-whisker plots. Red boxes are artificial Sea Sweep-generated sea spray. Blue boxes are ambient marine aerosol. The dotted line indicates the seawater ratio of 0.12. Median, 25th and 75th percentiles are plotted as horizontal lines in boxes, and 10th and 90th percentiles are indicated by vertical lines outside boxes. The number of samples contributing to each sample type is given above the box. Any negative (below background) signals were removed from the analysis. The Mg^{2+}:Na^{+} ratio was fairly consistent across seasons, aerosol types and sizes.

		Other cations			
	Sample type	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Na^+	<180 nm marine	(-)0.01	0.54 (0.03)	0.80	0.01
	<180 nm Sea Sweep	(-)0.80	0.28	0.97	0.03
	PM1 marine	0.03	0.39	0.96	0.00
	PM1 Sea Sweep	n/a	0.78	0.97	0.38

Table S1. Coefficients of determination (r^2s) for linear relationships between sodium and the other 4 cations measured in sub-180 nm and submicron Sea Sweep and ambient marine samples.

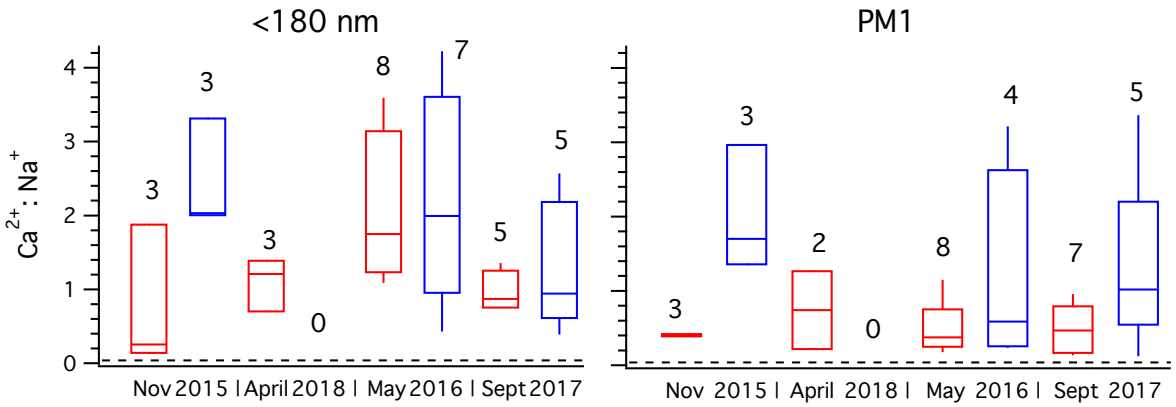

Figure S6. Mass fractions of Ca^{2+}: Na^{+} in **a.** sub-180 nm and **b.** submicron aerosol samples organized into box-and-whisker plots. Red boxes are artificial Sea Sweep-generated sea spray. Blue boxes are ambient marine aerosol. The dotted line indicates the seawater ratio of 0.038. Median, 25th and 75th percentiles are plotted as horizontal lines in boxes, and 10th and 90th percentiles are indicated by vertical lines outside boxes. The number of samples contributing to each sample type is given above the box. Any negative (below background) signals were removed from the analysis. The Ca^{2+}:Na^{+} ratio was highly variable and regularly showed strong enrichments with respect to seawater.