Supplemental Information

Side-by-Side Comparison of Four Techniques Explains the Apparent Differences in the Organic Composition of Generated and Ambient Marine Aerosol Particles

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Marine OM Measurement Techniques

The composition of the organic component of both ambient and generated marine aerosol particles differ substantially in recently reported results (Rinaldi et al. 2010; Bates et al. 2012). The cause of the difference, attributed to either different OM measurement approaches or differences in seawater properties that produce the marine particles, is still unresolved (Rinaldi et al. 2010). The purpose of this study is to resolve the discrepancy in OM composition of generated marine aerosol as observed by Fourier transform infrared (FTIR) spectroscopy and high resolution time of flight aerosol mass spectrometry (HR-ToF-AMS) measurements through the use of multiple measurement techniques including FTIR spectroscopy, HR-ToF-AMS, evolved gas analysis (EGA), scanning transmission X-ray microscopy near edge absorption fine structure (STXM-NEXAFS), and a light scattering module of the HR-ToF-AMS (LS-ToF-AMS).

Given the complexity of the organic composition of marine aerosol particles, characteristics can be determined through the combination of techniques that provide complementary information. The measurement techniques vary in the fraction of OM they can quantify and in the degree to which the organics can be speciated. Spectroscopy techniques (FTIR, Raman, and nuclear magnetic resonance) can be used to determine the functional group composition, while mass spectrometry techniques (gas chromatography mass spectrometry and aerosol mass spectrometry) can be used to determine mass fragments. These techniques and others have been utilized to measure the organic composition of ambient and generated marine aerosol particles. The multiple techniques used and the general organic compositions of marine aerosol determined by each are shown in Table S1.

Table S1: Organic composition of generated and ambient marine aerosol particles measured using different techniques.

Technique Used^a	OM Composition	Reference
Ambient		
FT-ICR MS; H-NMR	Biomolecules with high aliphaticity	(Schmitt-Kopplin et al. 2012)
FTIR spectroscopy and STXM-NEXAFS	Polysaccharides	(Russell et al. 2010)
GC-MS	Oxo-, mono-, and di-carboxylic acids	(Kawamura and Gagosian 1987)
GC-MS	Low molecular weight saturated fatty acids	(Mochida et al. 2002)
GC-MS	Low molecular weight fatty acids, fatty alcohols, and sterols	(Fu et al. 2011)
GC-MS; EGA	Saccharides; isoprene products	(Fu et al. 2013)
H-NMR	WIOM; WSOM	(Facchini et al. 2008)
H-NMR	Diethyl and dimethyl amine salts	(Facchini et al. 2010)
H-NMR; LC-MS	Lipids, fatty acids, short chain aliphatics; WSOC	(Decesari et al. 2011)
HPLC	Proteins, amino acids, and polysaccharides in gels	(Kuznetsova et al. 2005)
HPLC	Free amino acids in WSOC	(Matsumoto and Uematsu 2005)
HR-ToF-AMS	Hydrocarbons; oxygenated hydrocarbons	(Ovadnevaite et al. 2011)
HR-ToF-AMS	N/A	(Shank et al. 2012)
IC; EGA	WSOC and TOC	(Yoon et al. 2007)
IC; IC-EIT-MS; EGA	WIOM; levoglucosan, glucose	(Kaku et al. 2006)
IC; solid/liquid phase elemental analysis	WSOC: methanesulfonic acid, alkylammonium salts, dicarboxylic acids	(Rinaldi et al. 2010)
IC; TOC liquid analysis; EGA	WIOC; WSOC aliphatic and partially oxidized humic-like substances	(Cavalli et al. 2004)
IC; TOC liquid analysis; EGA	Enriched in WIOC with high molecular weight; Enriched in WSOC (partly oxidized species with extended aliphatic moieties)	(O'Dowd et al. 2004)

IC; TOC liquid analysis; EGA; Eddy covariance	WIOC; WSOC	(Ceburnis et al. 2008)
IC-EIT-MS	Dicarboxylic acids, carbohydrates	(Crahan et al. 2004)
STXM-NEXAFS	Polysaccharides, proteins, and phytoplankton fragments	(Hawkins and Russell 2010)
TEM	Marine microorganisms; microcolloidal aggregates	(Leck and Bigg 2005)
TEM	WIOC aggregates; exopolymeric gels	(Bigg 2007)
TEM	Exopolymers	(Bigg and Leck 2008)
TOC Analyzer	WSOC, WIOC, TOC	(Sciare et al. 2009)
Generated		
FTIR spectroscopy and HR-ToF-AMS	Polysaccharide-like, alkyl-like, pattern of CH-fragments	(Bates et al. 2012)
H-NMR	WIOM: colloids	(Facchini et al. 2008)
H-NMR	WIOM: lipo-polysaccharides	(Facchini et al. 2010)
Raman microspectroscopy	Aliphatic hydrocarbons	(Ault et al. 2013)
TOC Analyzer	WSOC	(Keene et al. 2007)

^aRelevant acronyms: Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS); Fourier transform infrared (FTIR); gas chromatography mass spectrometry (GC-MS); proton nuclear magnetic resonance (H-NMR); liquid chromatography mass spectrometry (LC-MS); high performance liquid chromatography (HPLC); high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS); ion chromatography (IC); evolved gas analysis (EGA); ion chromatography electrospray ion trap mass spectroscopy (IC-EIT-MS); scanning transmission X-ray microscopy with near-edge X-ray absorption fine structure (STXM-NEXAFS); transmission electron microscopy (TEM); total organic carbon (TOC); water insoluble organic mass/carbon (WIOM/C); water soluble organic mass/carbon (WSOM/C).

Marine Aerosol Measurements during WACS

During the WACS cruise, the R/V *Ronald H. Brown* traveled from Boston, MA, to Bermuda, stopping in the colder, eutrophic seawater of George's Bank and the warmer, oligotrophic seawater of the Sargasso Sea. The nascent (or newly generated) SSA particles, referred to as generated marine aerosol particles, were generated with the Sea Sweep. These particles were free of influence from ambient air and were transported from the sea surface to the research vessel for sampling through a humidity and temperature-controlled inlet.

FTIR spectroscopy

Ambient and generated marine particles were collected on pre-scanned 37 mm Teflon filters (Pall Inc., 1 μ m pore size) for 1 to 8 hours, after passing through a diffusion drier filled

with silica gel and a 1 μm cut cyclone. The cyclone has a 100% particle transmission efficiency for particles with aerodynamic diameters (d_a) less than 750 nm (Gussman et al. 2002), shown in Figure S1. Five ambient and sixteen generated samples were collected. The filters were analyzed aboard the R/V *Ronald H. Brown* using Fourier transform infrared (FTIR) spectroscopy (Tensor 27 spectrometer, Bruker, Billerica, MA). The filters were then frozen and transported back to San Diego, CA, for further analysis. The generated marine samples were dehydrated using the method outlined by Frossard and Russell (2012) to remove interference of sea salt hydrate bound water with the organic signal in the FTIR spectra.

The FTIR spectrum from each filter was baselined and integrated at specific peak locations to determine the peak areas of the organic functional groups using an automated algorithm outlined by Maria et al. (2002) and revised by Russell et al. (2009) and Takahama et al. (2012). The absorptivity and molar masses were used to convert peak area to mass for each functional group including: organic hydroxyl (C-O-H), alkane (C-C-H), amine (C-N-H), carboxylic acid (COOH), and non-acid carbonyl (C=O). Alkene (C=C-H) and aromatic functional groups were below the detection limit in all of the samples. The total OM for each sample was calculated as the sum of the organic functional groups. 20% uncertainty is shown in Figure 2, based on Maria et al. (2002).

HR-ToF-AMS

A high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) (Aerodyne, Billerica, MA) was used to measure the non-refractory submicron particle composition of the ambient and generated marine particles including ammonium, sulfate, nitrate, sea salt, and OM concentrations (Canagaratna et al. 2007; DeCarlo et al. 2006). Ambient and generated particles passed through a diffusion drier filled with silica gel and a 1 μm cut cyclone before sampling. The AMS lens has 100% particle transmission efficiency for particles with d_a from 90 to 700 nm (Figure S1) and 30% transmission efficiency for 1 μm particles (d_a) (Williams et al. 2013). The HR-ToF-AMS alternated between sampling in V-mode (both pToF and mass spectrum modes), W-mode, and LS-mode, which is discussed in the next section, on a 2-minute cycle for each mode. The V and W-mode data was analyzed using the ToF-AMS HR Analysis 1.10H program (Pika, D. Sueper, available at <http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html>). However, only V-mode data were used in this study. pCO₂ concentrations were measured during the cruise (Wanninkhof et al. 2013) and used in the ToF-AMS HR analysis program to correct for CO₂ gas phase influence. The ionization efficiency (IE) was obtained using the method described by Jimenez et al. (2003). 20% uncertainty in the HR-ToF-AMS measurements are shown in Figure 2 (Drewnick et al. 2005).

LS-ToF-AMS

A light scattering (LS) module on the HR-ToF-AMS (LS-ToF-AMS) was used to optically detect single particles before characterizing with the mass spectrometer, as described by Liu et al. (2013). The LS-ToF-AMS has the lens efficiency of the HR-ToF-AMS, but the smallest particles with significant optical signal are $d_a = 180$ nm (Figure S1). Using the LS data processing software Sparrow 1.04D (available at <http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html#Sparrow>), single particles were observed and classified based on their vaporization behavior. Briefly, in order to determine a sufficient chemical signal, ten high intensity ion fragments (m/z 36, 41, 43, 44, 48, 55, 57, 58, 64, 81) were

selected to make up the mass intensity profile for each particle (Liu et al. 2013). Based on the intensity profiles, particles were separated by those that had light scattering and mass spectral signals (LS+MS) and those that only had light scattering signals (LS-only). The LS-only particles were optically detected but not sufficiently vaporized with total mass spectral signal to noise less than 3.

In addition to the optically detected particles, more triggers were saved but did not have detectable optical signals, as described by Liu et al. (2013) as an additional duty cycle due to an unusual noise spike in the LS channel. During sampling, the coincident particles (e.g., more than one particle is optically detected in one cycle) were less than 0.5% of the total particles and are not included in this analysis, consistent with Liu et al. (2013).

STXM-NEXAFS

Ambient and generated particles were collected on silicon nitride windows (Si_3N_4 , Silson Ltd, Northampton, England) using a Streaker (PIXE International Corp., Tallahassee, FL) for impaction. The windows were frozen after collection to prevent evaporation. Generated particles were collected from 22:00 to 01:00 UTC starting on 21 August 2012. Ambient particles were collected from 19:00 to 00:00 UTC starting on 23 August 2012. The windows were analyzed at the Advanced Light Source at Lawrence Berkeley National Laboratory using scanning transmission X-ray microscopy with near-edge X-ray absorption fine structure (STXM-NEXAFS) at atmospheric temperature and under dry He at 1 atm (Hawkins and Russell 2010; Takahama et al. 2007; Kilcoyne et al. 2003; Takahama et al. 2010). Scans of selected single particles were done from 278 to 320 eV to determine the X-ray absorption spectra of the carbon K-edge, and functional groups were identified by their absorption (Hawkins and Russell 2010). Image scans of the particles were used to determine the diameter, morphology, and organic composition of the single particles. Due to instrument and analysis constraints, the number of single particles analyzed by STXM-NEXAFS is limited (Bahadur et al. 2010). From the particles impacted on the silicon nitride windows, 26 generated and 18 ambient particles were analyzed.

The generated particle diameters (d_p) ranged from 0.65 to 3.1 μm , and the ambient particle diameters (d_p) ranged from 0.39 to 2.59 μm . Using a density of 1.1 g cm^{-3} for the low O/C particles and 2.05 g cm^{-3} for the high O/C particles (based on a sea salt density of 2.165 g cm^{-3} and an average sea salt fraction of 89%), the aerodynamic particle diameters ranged from 0.72 to 6.4 μm and 0.47 to 5.3 μm for generated and ambient marine particles, respectively (Figure S1).

OC and IC measurements

Ambient and generated particles ($<1.1 \mu\text{m}$ at 60% relative humidity) were collected on pre-combusted quartz fiber filters using a two stage impactor downstream of a charcoal denuder (Bates et al. 2004). They were analyzed with a Sunset Laboratory thermal/optical analyzer to determine the concentrations of organic carbon (OC) with evolved gas analysis, hereafter referred to as EGA OC. Particles ($<1.1 \mu\text{m}$) were also collected on Millipore Fluoropore filters with a Berner-type multijet cascade impactor. The substrates were extracted and analyzed using ion chromatography (IC) to quantify inorganic ions including Na^+ , Cl^- , sulfate, nitrate, and ammonium (Quinn et al. 1998).

Sea salt concentrations for the generated marine particles were calculated as $3.26 \cdot \text{Na}^+$ concentrations measured by IC, based on the calculation by Quinn et al. (submitted) and the ratio of ions in seawater (Holland 1978). Ambient sea salt concentrations were calculated using measured Cl^- plus $1.47 \cdot \text{Na}^+$ concentrations to account for the depletion of Cl^- in the atmosphere (Holland 1978). As described by Quinn et al. (in review) using these measurements, the generated marine particle mass was 89% sea salt and 11% OM. The ambient particle mass was 3% sea salt, 59% OM, and 38% other mass (Table S2).

Table S2: Mass fractions of OM, non-sea salt sulfate, ammonium, methanesulfonic acid (MSA), and sea salt in ambient and generated marine particles (based on Quinn et al., (in review)).

	Ambient	Generated
OM (FTIR)	0.59	0.11
Non-sea salt sulfate	0.25	
Ammonium	0.11	
MSA	0.02	
Sea salt	0.03	0.89

Aerosol physical measurements

Ambient and generated marine aerosol size distributions were measured using differential mobility particle sizers (DMPS, Aitken and Accumulation) and an aerodynamic particle sizer (APS, TSI model 3321) as described by Bates et al. (2012). The number and mass size distributions for the generated and ambient marine particles are shown in Figure S1.

The 100% transmission efficiency aerodynamic diameter (d_a) ranges for FTIR spectroscopy, HR-ToF-AMS, and LS-ToF-AMS, in addition to the range of particles analyzed by STXM-NEXAFS, are included in Figure S1 and listed in Table 1. Figure S1 shows the overlap of the d_a ranges with the maximum concentration ranges for the LS-ToF-AMS, HR-ToF-AMS, and FTIR measurements. The STXM-NEXAFS technique measured particles with larger d_a but overlaps with the other techniques at their largest d_a values.

Figure S1: Normalized (bottom) number and (middle) mass size distributions of generated and ambient marine aerosol particles. (top) Ranges of aerodynamic diameters of particles measured with the different techniques, based on Table 1. The solid lines represent 100% particle transmission efficiency for HR-ToF-AMS and FTIR, the lowest detectable diameters to diameters with 100% transmission efficiency for LS-ToF-AMS, and the diameters of particles measured for STXM-NEXAFS. Dashed lines show the reduced collection on filters and reduced sensitivity for FTIR and 50% transmission efficiency for HR-ToF-AMS and LS-ToF-AMS. At 1 μm , the HR-ToF-AMS and LS-ToF-AMS have particle transmission efficiencies of 30%.”

Comparison of HR-ToF-AMS and FTIR OC with EGA OC

The OC mass measured by FTIR spectroscopy was calculated from the total moles of carbon in each sample. On average, the total OC mass measured by FTIR spectroscopy was a factor of 1.06 greater than that measured with the Sunset EGA ($r = 0.61$) with an average overall percent difference of 3% (Figure S2a). HR-ToF-AMS OC was calculated using the ratio of OM/OC and OM. Overall, comparison with EGA OC gave a slope of 0.31 and a correlation of $r = 0.67$ (Figure S2b). The HR-ToF-AMS and FTIR OM have similar masses after the CE_{IC} is applied (Figure S2c), and the ambient samples correlate well ($r = 0.88$).

Figure S2: Correlations of (a) FTIR OC with EGA OC; (b) HR-ToF-AMS OC with EGA OC; and (c) HR-ToF-AMS OM (using CE_{IC}) with FTIR OM. Markers are colored as generated (dark blue) and ambient (bronze). The overall (ambient and generated together) slopes and correlations are given. Two samples were not included in the correlations due to filter sampling problems and high humidity.

Table S3: Ambient and generated marine particle OM, OC, and O/C values measured with FTIR spectroscopy, HR-ToF-AMS, and EGA (OC only). HR-ToF-AMS OC was calculated with HR-ToF-AMS OM/OC elemental ratios. HR-ToF-AMS values do not have a CE applied.

	Ambient	Generated
OM ($\mu\text{g m}^{-3}$)		
FTIR	2.09 ± 1.74	3.23 ± 1.52
HR-ToF-AMS	0.58 ± 0.32	0.65 ± 0.36
OC ($\mu\text{g m}^{-3}$)		
EGA	1.16 ± 0.63	1.68 ± 0.75
FTIR	1.04 ± 0.79	1.67 ± 1.01
HR-ToF-AMS	0.33 ± 0.12	0.49 ± 0.30
O/C		
FTIR	0.55 ± 0.17	0.51 ± 0.22
HR-ToF-AMS	0.63 ± 0.11	0.20 ± 0.08

Figure S3: Time series of (top) IC sea salt concentration, (middle) FTIR spectroscopy and HR-ToF-AMS (no CE applied) OM concentrations, and (bottom) FTIR and HR-ToF-AMS O/C ratios. The bars at the top represent the type of sample: ambient (bronze) and generated (dark blue) marine aerosol.

HR-ToF-AMS Sea Salt

The heater temperature of the HR-ToF-AMS was set to 650°C to vaporize more of the sea salt components (Ovadnevaite et al. 2012). The HR-ToF-AMS measurements were used to calculate the mass of sea salt by identifying and scaling specific sea salt ions based on the method outlined by Ovadnevaite et al. (2012). The concentrations of four different combinations of the sea salt ions, outlined in Table S4, were averaged over the impactor sampling times. A least squares fit was used to fit the concentrations from the ion groups in Table S4 to the IC measured sea salt to determine a HR-ToF-AMS sea salt scaling factor, which is the inverse of the sea salt collection efficiency (CE_{SS}). The combination of sea salt ions Cl^+ , HCl^+ , $NaCl^+$, Na_2Cl^+ , KCl^+ , $MgCl^+$ and their isotopes were used to calculate the final scaling factor based on the correlation to IC sea salt and the combined ion signal. The ambient scaling factor is 12, and the generated marine particle scaling factor is 79, which are similar to those used by Ovadnevaite et al. (2012) of 2.5 and 51, respectively, calculated for laboratory generated sea salt. The larger sea salt scaling factors measured here may be due to a decreased lens transmission efficiency of larger sea salt particles, compared to the monodisperse 300 nm particles used by Ovadnevaite et al. (2012). Increasing the number of HR-ToF-AMS sea salt ions in the comparison to IC sea salt decreases the resulting scaling factor. While $NaCl^+$ compared well to the IC sea salt ($r > 0.70$), the scaling factor was very high for both ambient (1302) and generated (1729) marine particles making the corresponding CE_{SS} values very low and indicating that additional ions are needed for the scaling. The concentration of Na^+ is unreliable as a sea salt ion due to its persistence in

the HR-ToF-AMS system and was therefore not used to calculate the scaling factor (Ovadnevaite et al. 2012). The moderate correlations of the HR-ToF-AMS ions and the IC sea salt suggest that the sea salt collection efficiency may also have a size dependence. A more accurate CE could be determined using variations in size and lens transmission efficiency.

Table S4: Comparison of sea salt scaling factors ($1/CE_{SS}$) used to scale HR-ToF-AMS sea salt to IC measured sea salt. The correlation coefficient is shown in parentheses for each case. The average of un-scaled and scaled sea salt is shown for each set of ions.

		Scaling factor (correlation coefficient, r)		Average of HR-ToF-AMS sea salt ($\mu\text{g m}^{-3}$)			
				Un-scaled		Scaled ^b	
HR-ToF-AMS ions used to calculate sea salt	Reference Values	Ambient	Generated	Ambient	Generated	Ambient	Generated
NaCl^+	51 ^a	1302 (0.98)	1729 (0.71)	9.5e-5	0.015	0.12	25.2
Na^+ , Cl^+ , HCl^+ , NaCl^+ , $^{37}\text{Cl}^+$, H^{37}Cl^+ , $\text{Na}^{37}\text{Cl}^+$	2.5 ^a	0.216 (0.65)	27 (0.55)	0.43	1.0	0.09	28.2
NaCl^+ , Na_2Cl^+ , KCl^+ , MgCl^+ , $\text{Na}^{37}\text{Cl}^+$, $\text{Na}_2^{37}\text{Cl}^+$, K^{37}Cl^+ , $^{41}\text{KCl}^+$, $^{41}\text{K}^{37}\text{Cl}^+$, $\text{Mg}^{37}\text{Cl}^+$	N/A	126 (0.20)	707 (0.67)	9.1e-4	0.037	0.12	25.8
Cl^+ , HCl^+ , NaCl^+ , Na_2Cl^+ , KCl^+ , MgCl^+ , $^{37}\text{Cl}^+$, H^{37}Cl^+ , $\text{Na}^{37}\text{Cl}^+$, $\text{Na}_2^{37}\text{Cl}^+$, K^{37}Cl^+ , $^{41}\text{KCl}^+$, $^{41}\text{K}^{37}\text{Cl}^+$, $\text{Mg}^{37}\text{Cl}^+$	N/A	12 (0.52)	79 (0.59)	9.9e-3	0.35	0.12	27.6

^a(Ovadnevaite et al. 2012); laboratory generated sea salt (300 nm, relative humidity = 65%) and vaporizer temperature of 650°C

^bAverage IC sea salt values: ambient = $0.10 \mu\text{g m}^{-3}$ and generated = $26.7 \mu\text{g m}^{-3}$

HR-ToF-AMS CE Calculations

The HR-ToF-AMS collection efficiency (CE) was calculated by comparing the concentration of HR-ToF-AMS sulfate and the concentration of sulfate from filters measured with IC, as discussed by Canagaratna et al. (2007) and calculated by Bates et al. (2012) for similar measurements. The sulfate based CE (CE_{IC}) was calculated separately for the ambient and generated marine particles to allow for the differences in CE values based on particle type. With the direct comparison to independently measured sulfate, other factors contributing to the CE, such as particle shape, phase, and acidity are taken in to account but not directly calculated (Matthew et al. 2008; Huffman et al. 2005; Middlebrook et al. 2012). This method also includes lens transmission efficiency, which affects the larger particles, such as the OM associated with sea salt. When comparing the HR-ToF-AMS sulfate loadings to IC sulfate only, we obtained a CE_{IC} of 0.35 for ambient, and a CE_{IC} of 0.17 for the generated particles. The different CE_{IC}

values for ambient and generated marine particles indicate that the CE_{IC} incorporates variations in detection efficiency as a function of particle size. The CE_{IC} values were used to scale the OM for comparison with FTIR measured OM.

The CE_{IC} values for generated particles are less than typical AMS CE values of 0.5 (Canagaratna et al. 2007) because a large fraction of the generated particle mass (89%) is sea salt, which does not vaporize efficiently at 650°C (due to its refractory nature and tendency to bounce off the vaporizer) and therefore has a much lower CE (CE_{SS}). For this reason, and to compare directly to LS-ToF-AMS that produces a total CE for all particles through optical detection, a total CE (CE_{total}) for the HR-ToF-AMS was calculated separately for the ambient (CE_{totalA}) and generated (CE_{totalG}) particles using: $CE_{total} = CE_{SS} * X_{SS} + CE_{other} * X_{other}$. The value of CE_{other} is assumed to be 0.5 (Canagaratna et al. 2007), and X is the fraction of the respective mass measured by IC and/or EGA. The calculated CE_{totalG} (0.07) is less than CE_{totalA} (0.49), indicating that only a small fraction of the total mass is vaporized by the HR-ToF-AMS under the standard operational conditions due to the presence of sea salt. The standard comparison of total particle mass to integrated particle mass size distributions was not included due to differences in sampling conditions between the HR-ToF-AMS and the particle sizing instruments.

STXM-NEXAFS Particle Morphologies

The particle morphologies associated with these spectral types were unique to the OM types. The low O/C particle type mainly had round or irregular shaped particles with uniformly distributed carbon absorbance. A large fraction of the high O/C particles have the shapes characteristic of polysaccharides on sea salt, with a cuboidal inner-structure surrounded by a high O/C organic (Hawkins and Russell 2010; Russell et al. 2010). Four of the 17 ambient high O/C particles were round and did not have characteristics of organics on sea salt. These particles may be from oxidization of alkyl-like particles or secondary formation in the atmosphere. Their spectra are similar to secondary organic aerosol particles identified by Takahama et al. (2007). STXM-NEXAFS measurements are too limited (in size range and sample number) to be quantitatively representative of the OM particle.

LS-ToF-AMS and HR-ToF-AMS

The composition of the LS-ToF-AMS particles has a much larger fraction of low O/C OM than the HR-ToF-AMS for both the generated and ambient marine particles. This difference may be attributed to a number of factors. (i) The high and low O/C separation for the LS-ToF-AMS was based on a single particle clustering, where the HR-ToF-AMS OM separation was based on the mass fragment groups of the overall average mass spectra. (ii) Additionally, spectra with less than 6 organic ions were not used in the LS-ToF-AMS clustering as their composition was not representative of the particle. However, those spectra are included in the overall HR-ToF-AMS OM due to the overall mass averaging during sampling. The same idea applies to the spectra that were saved by the light scattering mode. If a significant mass spectrum was not observed, then that spectrum was not used. For the HR-ToF-AMS, all of the mass spectra are averaged, so the lack of ions in an individual spectrum does not affect the total. The low OM signal from the generated particles is better included in the bulk averaged HR-ToF-AMS than in the individual particles detected by LS-ToF-AMS. (iii) The LS-ToF-AMS has a smaller range of

measured particles than the HR-ToF-AMS. The smallest particle with significant optically detected signal is 180 nm (d_a). This is a higher cutoff than the HR-ToF-AMS, which has a particle transmission efficiency of 100% at 90 nm (d_a). The LS-ToF-AMS particle size detection range falls within the size range of the maximum in particle mass concentration but does not have much overlap with the maximum in number concentration for the generated marine particles. (iv) Particles that contain less volatile species, such as sea salt, can bounce off of the vaporizer (Huffman et al. 2005).

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