

# Supplementary Materials: Detailed Source-Specific Molecular Composition of Ambient Aerosol Organic Matter Using Ultrahigh Resolution Mass Spectrometry and $^1\text{H}$ NMR. *Atmosphere* 2016, 7, 79, doi:10.3390/atmos7060079

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## Supplementary Methods

### *Aerosol Sample Collection*

Marine TSP samples ( $n = 4$ ) were collected aboard the R/V Knorr (Woods Hole, Massachusetts, USA) 14 m above sea level in the north Atlantic Ocean. Three of the samples were collected as part of the 2011 US GEOTRACES program cruise [1] (during the fall (27.5830°N, 49.6328°W, 24–26 November 2011; 27.5543°N, 49.5538°W, 26–27 November 2011; and 26.3083°N, 45.3897°W, 27–28 November 2011). The fourth sample was collected as part of the 2014 second Western Atlantic Climate Study [2] during the summer (33.3466°N, 63.3168°W, 2 June 2014). Backward air mass trajectories were used to identify the samples as marine-influenced, (*i.e.*, having minimal influence from 5 day back trajectories that reach continental areas).

Mixed source TSP samples ( $n = 3$ ) were collected at sea level during the summer (16–17 August 2011, 24–25 June 2013, and 25–26 June 2013) at the Virginia Institute of Marine Science in Gloucester Point, Virginia, USA (37.2482°N, 76.5005°W). The area is typical of a rural environment on the East Coast of the United States and is expected to have contributions from several natural (*i.e.*, biogenic SOAs) and anthropogenic sources (e.g., fossil fuel combustion, industrial emissions).

Biomass burning TSP samples ( $n = 2$ ) were collected at sea level during the summer (21 August 2011, 24–25 August 2011) in Suffolk, Virginia, USA (36.8934°N, 76.5020°W) <30 km downwind of heavy smoke pollution from a fire burning at the Great Dismal Swamp (Suffolk, Virginia, USA; 36.6100°N, 76.4662°W). The smoldering-peat fire was caused by a lightning strike where peat, brush, and downed trees fueled the fire.

Urban TSP samples ( $n = 5$ ) were collected ~60 m above sea level on the roof of an academic building during the summer (4–5 August 2014, 5 August 2014, 5–6 August 2014, 6 August 2014, and 6–7 August 2014) at Drexel University in downtown Philadelphia, Pennsylvania, USA (39.9545°N, 75.1858°W). The area is urban, and the collected TSP are expected to have strong anthropogenic contributions from fossil fuel, vehicle, industrial, and cooking emissions as each was clearly visible from the sampling site.

A new and pre-combusted QM/A filter was stored alongside the 2011 mixed source and biomass burning aerosols, and these filters were analyzed as storage filter blanks. At the beginning of the sampling period for the urban (4 August 2014), marine (7 November 2011 and 1 June 2014), and 2013 mixed source (24 June 2013) aerosols, a new and pre-combusted QM/A filter was attached to the air sampler for 5 min without drawing any air, and was stored under identical conditions. These filters were analyzed as field filter blanks for their respective aerosol samples.

### *Aerosol Mass and Carbon Measurements*

The QM/A filters were weighed before and after sampling to determine the TSP mass loadings (Table 1), and the fraction of non-carbonate carbon on each filter was determined using a FlashEA 1112 elemental analyzer (Thermo Scientific, Waltham, Massachusetts, USA) according to methods previously described [3]. Black carbon (BC) amounts were determined using chemothermal oxidation (CTO-375) [4]. Triplicate filter plugs were exposed to HCl vapor for 24 h to remove inorganic

carbonates. The filters were heated using a controlled temperature program where the temperature was held at 375 °C for 4 h. The material remaining (*i.e.*, BC) was analyzed for total carbon using the same method described above for TC analysis, and percentages are expressed relative to the TC values. TSP, BC, and TC values were not determined for the marine aerosols due to limited sample availability.

### Solvent Extractions

Solvent extracts of the aerosols and respective filter blanks were obtained by combining aerosol filter plugs of known OC masses with ultrapure water (Millipore Synergy Ultrapure Water System, Darmstadt, Germany) or pyridine (Sigma-Aldrich, St. Louis, Missouri, USA, ≥99.9%) and thoroughly mixed on an orbital shaker (150 RPM, 4 h, 21 °C). Insoluble particles were removed using a syringe with a 0.45 μm PTFE filter cartridge. The percent of water soluble organic carbon (WSOC) in each filtrate was determined by evaluating the non-purgeable organic carbon using a Shimadzu (Kyoto, Japan) TOC-VCPH analyzer. The measured WSOC was compared with the TC content to determine the %WSOC. The %PSOC was determined by dissolving each of the aerosol samples into pyridine- $D_5$  and comparing spectral signals determined by  $^1H$  NMR to that of a glucose standard. The methods and calculations for this pyridine extraction efficiency determination are described in detail elsewhere [3]. The calculation for PSOC percentage by the  $^1H$  NMR technique omits aromatic peaks due to interference by the exchanged pyridine protons. Because the biomass burning samples are expected to have high aromatic contributions, as indicated by the high %BC and increased signal in aromatic region of the  $^1H$  NMR spectrum for the WSOM (discussed in Section 3.4), the H/C values are expected to be high, and the %PSOC value may be considered a low estimation (Table S1).

For FTICR-MS analyses, the water extracts were desalted using an established procedure for Agilent PPL solid-phase extraction cartridges [5]. The desalted sample was eluted in methanol (Acros Organics, Geel, Belgium, 99.9%), and will be referred to as WSOM<sub>PPL</sub> to differentiate it from WSOM. The solvent extracts were stored at -8 °C until FTICR-MS analysis, typically within 24 h of preparation.

### Supplementary Tables and Figures

**Table S1.** Percent area contributions from the major proton regions and calculated H/C ratios in  $^1H$  NMR spectra for aerosol PSOM.

Aerosol source (Collection date)	Functional Group Region (Chemical Shift)			Calculated H/C	%PSOC
	H-C-O (3.2–4.4 ppm)	H-C-C= (1.95–3.2 ppm)	H-C (0.7–1.95 ppm)		
Mixed source (24–25 June 2013)	2.5	21.0	76.0	1.98	54.1
Mixed source (25–26 June 2013)	6.4	25.5	67.0	1.94	35.7
Biomass burning (21 August 2011)	1.5	15.8	82.7	1.99	51.4
Biomass burning (24–25 August 2011)	2.6	17.3	80.2	1.98	80.0
Urban (4–5 August 2014)	5.4	19.5	75.1	1.95	41.5
Urban (5 August 2014)	4.7	22.7	72.5	1.96	44.2
Urban (5–6 August 2014)	5.5	22.2	72.2	1.95	52.0
* Urban (6 August 2014)	-	-	-	-	-
Urban (6–7 August 2014)	5.0	22.5	72.6	1.96	38.0

\* Not determined.

**Table S2.** Total formulas and average elemental properties for aerosol WSOM<sub>PPL</sub> and PSOM from each emission source determined using FTICR mass spectra. The distribution of molecular formulas based on atomic content and  $AI_{mod}$  structure type are listed as number of formulas with the percentage of total formulas in parentheses directly below.

	<b>Marine Aerosols <i>n</i> = 4</b>	<b>Biomass Burning Aerosols <i>n</i> = 2</b>	<b>Urban Aerosols <i>n</i> = 5</b>	<b>Mixed Source Aerosols <i>n</i> = 3</b>
Total formulas	4570	7891	10,701	6134
<b>Atomic Content</b>				
CHO	1880 (41.1%)	2617 (33.2%)	3318 (31.0%)	2182 (35.6%)
CHON	741 (16.2%)	2699 (34.2%)	3472 (32.4%)	1574 (25.7%)
CHOS	953 (20.9%)	1560 (19.8%)	1910 (17.8%)	1333 (21.7%)
CHONS	614 (13.4%)	961 (12.2%)	1560 (14.6%)	944 (15.4%)
CHOP(N,S)	382 (8.4%)	54 (0.7%)	441 (4.1%)	101 (1.6%)
<b>Structure Type</b>				
Aliphatic	1718 (37.6%)	1864 (23.6%)	4024 (37.6%)	2442 (39.8%)
Olefinic/alicyclic	2371 (51.9%)	4186 (53.0%)	5621 (52.5%)	3086 (50.3%)
Aromatic	247 (5.4%)	1318 (16.7%)	583 (5.4%)	353 (5.8%)
Condensed aromatic	234 (5.1%)	523 (6.6%)	473 (4.4%)	253 (4.1%)

**Table S3.** Total formulas and average elemental properties for aerosol WSOM<sup>-</sup>, WSOM<sup>+</sup>, and PSOM<sup>-</sup> from each emission source determined using FTICR-MS. Atomic content and structure type values are expressed as the number of formulas. The values in parentheses are the percentage of total molecular formulas in each sample, an average for each source.

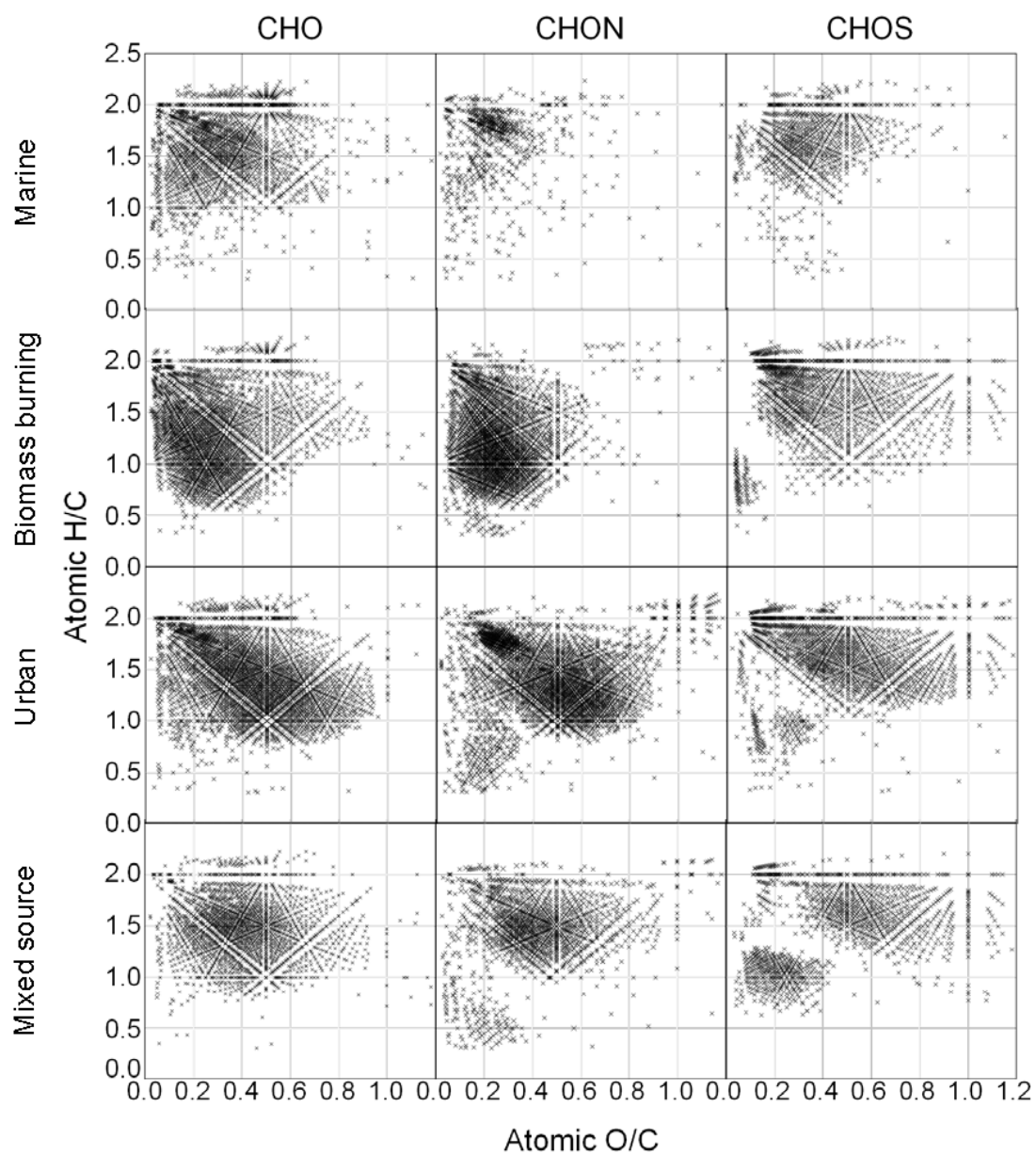
	Marine Aerosols <i>n</i> = 4			Biomass Burning Aerosols <i>n</i> = 2			Urban Aerosols <i>n</i> = 5			Mixed Source Aerosols <i>n</i> = 3		
	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>
<b>Total Formulas</b>	<b>1267 ± 551</b>	<b>1257 ± 238</b>	<b>547 ± 297</b>	<b>3526 ± 49</b>	<b>3259 ± 545</b>	<b>2654 ± 62</b>	<b>4527 ± 557</b>	<b>2061 ± 148</b>	<b>2295 ± 528</b>	<b>2143 ± 552</b>	<b>2065 ± 471</b>	<b>1347 ± 340</b>
Average O/C	0.35	0.27	0.32	0.33	0.28	0.35	0.53	0.38	0.54	0.45	0.39	0.55
Average H/C	1.59	1.56	1.60	1.24	1.29	1.49	1.41	1.46	1.53	1.46	1.44	1.56
Average Al <sub>mod</sub>	0.13	0.21	0.15	0.33	0.35	0.17	0.14	0.21	0.10	0.14	0.22	0.07
Atomic Content												
CHO	591 (48%)	818 (65%)	76 (15%)	1401 (40%)	1271 (37%)	806 (30%)	1848 (41%)	1154 (56%)	592 (26%)	1059 (51%)	1024 (50%)	355 (27%)
CHON	113 (11%)	174 (14%)	63 (11%)	1182 (34%)	1596 (48%)	440 (17%)	1329 (29%)	626 (30%)	492 (21%)	379 (17%)	736 (34%)	109 (7%)
CHOS	422 (30%)	22 (2%)	226 (38%)	795 (23%)	62 (2%)	991 (37%)	927 (21%)	10 (<1%)	721 (31%)	567 (26%)	12 (<1%)	621 (47%)
CHONS	47 (4%)	195 (15%)	74 (15%)	131 (4%)	314 (10%)	402 (15%)	325 (7%)	236 (11%)	428 (19%)	97 (4%)	239 (12%)	253 (18%)
* CHOP(N,S)	94 (7%)	-	108 (21%)	18 (<1%)	-	16 (1%)	97 (2%)	-	61 (3%)	42 (2%)	-	9 (<1%)
Structure Type												
Aliphatic	460 (36%)	393 (32%)	240 (44%)	641 (18%)	386 (12%)	939 (35%)	1645 (36%)	603 (29%)	1251 (55%)	757 (34%)	647 (31%)	836 (63%)
Olefinic/alicyclic	757 (60%)	714 (56%)	259 (47%)	1922 (55%)	1970 (60%)	1503 (57%)	2797 (62%)	1231 (60%)	947 (41%)	1330 (63%)	1144 (55%)	480 (35%)
Aromatic	20 (2%)	80 (6%)	20 (4%)	811 (23%)	646 (20%)	199 (7%)	69 (1%)	121 (6%)	47 (2%)	49 (2%)	140 (7%)	26 (2%)
Condensed Aromatic	29 (2%)	71 (6%)	28 (5%)	153 (4%)	257 (8%)	13 (<1%)	16 (<1%)	107 (5%)	49 (2%)	8 (<1%)	134 (7%)	5 (<1%)

\* Phosphorous was not included in atomic allowances for positive ESI.

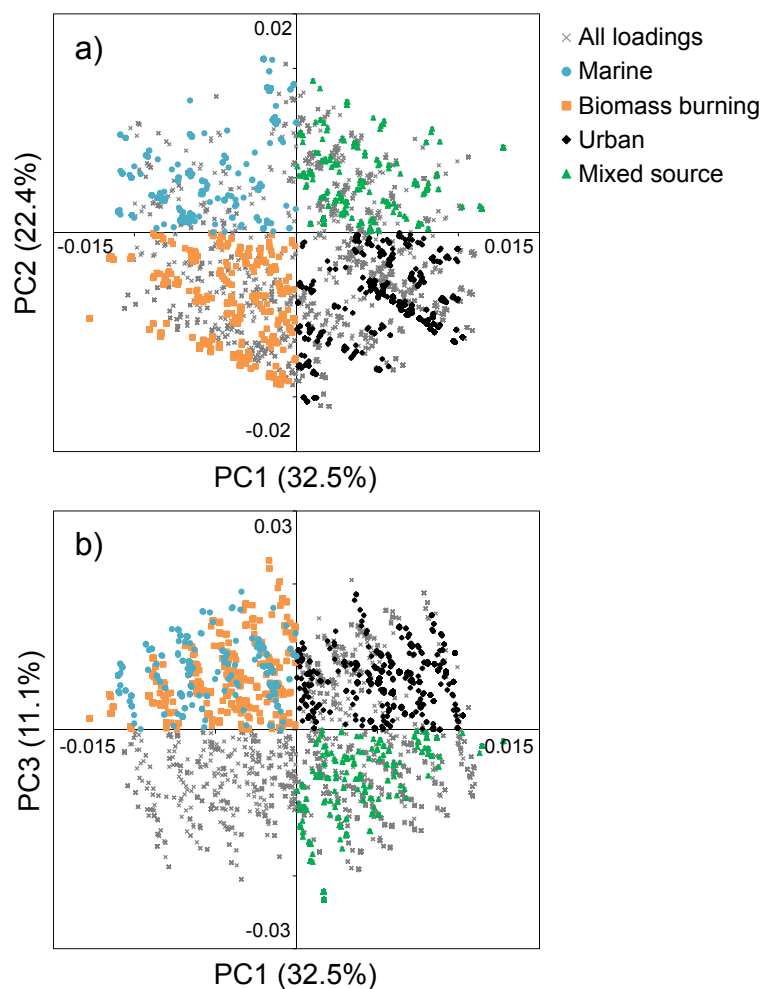
**Table S4.** Total formulas and average elemental properties for aerosol WSOM<sup>-</sup>, WSOM<sup>+</sup>, and PSOM from each emission source identified by PCA. Distributions of formulas based on atomic content and Al<sub>mod</sub> structure type are listed as percentage of total formulas.

	Marine Aerosols			Biomass Burning Aerosols			Urban Aerosols			Mixed Source Aerosols		
	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>	WSOM <sup>-</sup>	WSOM <sup>+</sup>	PSOM <sup>-</sup>
Average O/C	0.29	0.23	0.28	0.27	0.24	0.27	0.58	0.47	0.57	0.33	0.36	0.36
Average H/C	1.56	1.56	1.58	1.14	1.18	1.36	1.33	1.43	1.44	1.41	1.55	1.47
Average Al <sub>mod</sub>	0.16	0.21	0.16	0.41	0.42	0.28	0.16	0.18	0.14	0.20	0.17	0.16
Atomic Content												
CHO	29%	61%	14%	38%	33%	36%	35%	54%	23%	55%	56%	75%
CHON	9%	15%	12%	47%	62%	32%	40%	36%	36%	12%	34%	5%
CHOS	47%	1%	39%	11%	<1%	21%	14%	<1%	17%	23%	2%	17%
CHONS	6%	23%	16%	4%	4%	10%	9%	10%	20%	<1%	8%	4%
* CHOP(N,S)	6%	-	19%	<1%	-	<1%	2%	-	4%	9%	-	0%
Structure Type												
Aliphatic	27%	28%	34%	7%	3%	18%	33%	32%	47%	9%	29%	16%
Olefinic/alicyclic	67%	59%	57%	56%	61%	62%	65%	61%	48%	79%	64%	80%
Aromatic	2%	6%	5%	32%	31%	19%	2%	3%	3%	3%	4%	5%
Condensed Aromatic	4%	6%	4%	5%	5%	<1%	<1%	4%	3%	2%	3%	0%

\* Phosphorous was not included in atomic allowances for positive ESI.

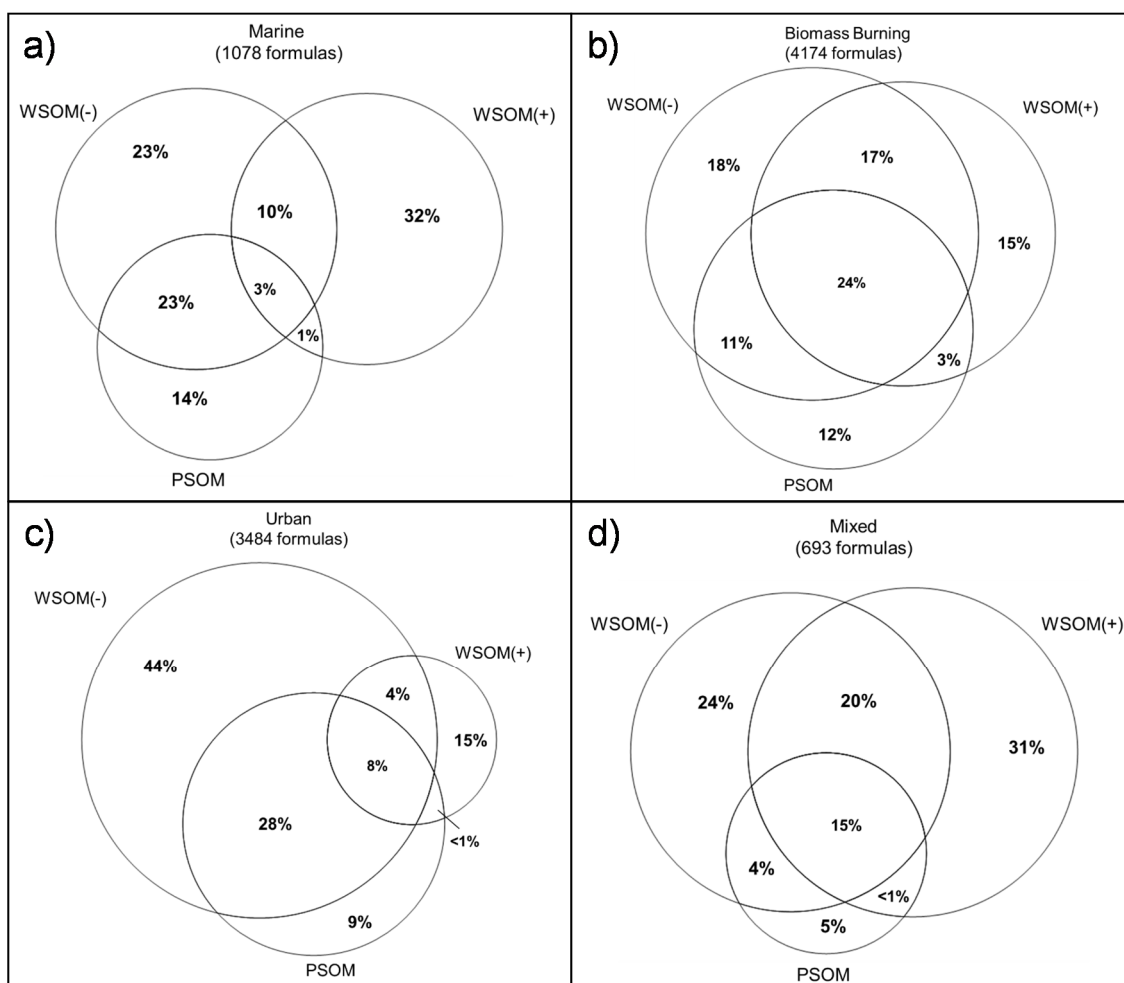


**Figure S1.** Van Krevelen diagrams for molecular formulas identified in the FTICR mass spectra for the marine, biomass burning, urban, and mixed source aerosols. Each row represents a different source, and each column represents only those formulas with a specific elemental makeup (CHO, CHON, or CHOS). Each “x” represents one or more molecular formulas.



**Figure S2.** The loadings for (a) PC1 and PC2 and (b) PC1 and PC3 from the PCA analysis of the FTICR-MS molecular formulas.

The PC loadings are shown in Figure S2. Each formula was assigned as an important loading to the Marine (blue), Biomass Burning (orange), Urban (black), or Mixed Source (green) samples or as not being an important loading to any of the sources (grey) based on the similarity of the PC loading to the PC scores for the samples. Each of the marine samples have a negative PC1 score, a positive PC2 score, and a positive PC3 score. PC variables (molecular formulas) that had loadings that were negative for PC1, positive for PC2, and positive for PC3 were assigned as important to the Marine samples. The mixed source samples have a positive PC1, a positive PC2, and a negative PC3 score, the biomass burning samples have a negative PC1, a negative PC2, and a positive PC3, and the urban samples have a positive PC1, a negative PC2, and a positive PC3. The PC variables with the corresponding loadings were assigned to each of those sources. This resulted in the identification of 1078 formulas characteristic for marine aerosols, 693 formulas for mixed source aerosols, 4174 formulas for biomass burning aerosols, and 3484 formulas for urban aerosols. The remaining PC variables (5379 formulas) were determined to contain characteristics that are represented by multiple sources indicating that they are not diagnostic of a particular source and may be ubiquitous in aerosol OM or inconsistently present in a given source.



**Figure S3.** Venn diagrams showing the relative distribution of PCA molecular formulas present in any of the three solvent/ionization methods (WSOM<sup>-</sup>, WSOM<sup>+</sup>, and PSOM) for each aerosol source. Areas of overlap represent percentages of molecular formulas that appear in two or more of those samples. Areas with no overlap represent the percentage of molecular formulas unique to that individual solvent/ionization method.

## References

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