SUPPLEMENTAL INFORMATION

for the paper

Organic particle types by single-particle measurements using a time-of-flight aerosol mass spectrometer coupled with a light scattering module

Shang Liu[1,2], Lynn M. Russell[1], Donna T. Sueper[3,4], and Timothy B. Onasch[4,5]

[1]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA

[2]Now at Earth Systems Observations, Los Alamos National Lab, Los Alamos, New Mexico, USA

[3]Cooperative Institute for Research in Environmental Studies, University of Colorado, Boulder, Colorado, USA

[4]Center for Aerosol and Cloud Chemistry, Aerodyne Research Inc., Billerica, Massachusetts, USA

[5]Chemistry Department, Boston College, Chestnut Hill, Massachusetts, USA

Comparison of number concentration measured by LS-ToF-AMS and SMPS

Average particle detection rate (particles detected per second) for each saved LSSP mode file (run number) was scaled by the overall duty cycle (for the same file) to calculate total particle number concentration. Time series of LS-ToF-AMS- and SMPS-measured number concentrations were averaged to 30-min intervals for comparison. Total number concentration for 560- to 1000-nm d_{va} (400- to 715-nm d_g) particles compared reasonably well—the linear fit has a slope of 0.89 (the SMPS-measured concentration was 11% higher) and an intercept of 6.25, and the number concentrations correlated with an R of 0.7 (Fig. S1).

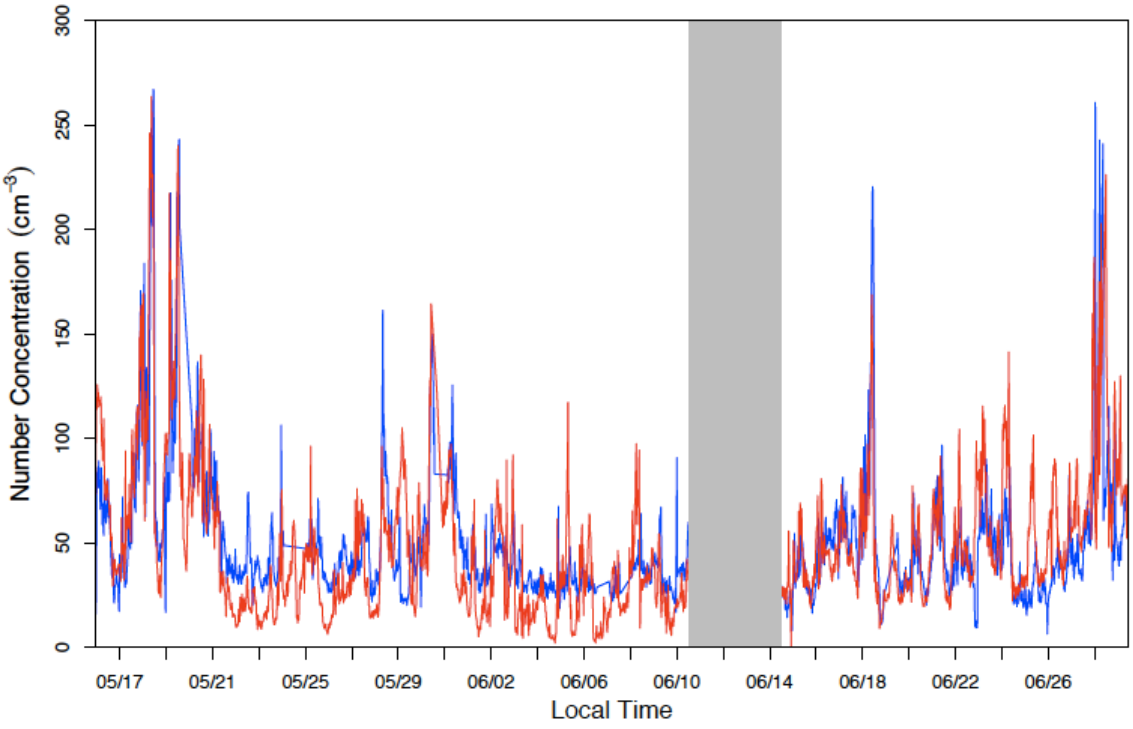


Figure S1. Time series of SMPS-measured (red) and LS-ToF-AMS-derived (blue) number concentration for particles in 560- to 1000-nm d_{va} (400- to 715-nm d_g) size range.

40

41 Comparison of ions generated by single particles of different vaporization types

42

43 The ions associated with the prompt and delayed, null, and non-particle events were

44 compared using (a) the sum of non-background ions (i.e., *m/z* 15, 27, 30, 41, 43, 44, 46,

45 48, 55, 57, and 64) and (b) all the ions in the mass spectra. The non-particle events are the

46 noise spikes in the light scattering channel that are characterized by near-zero light

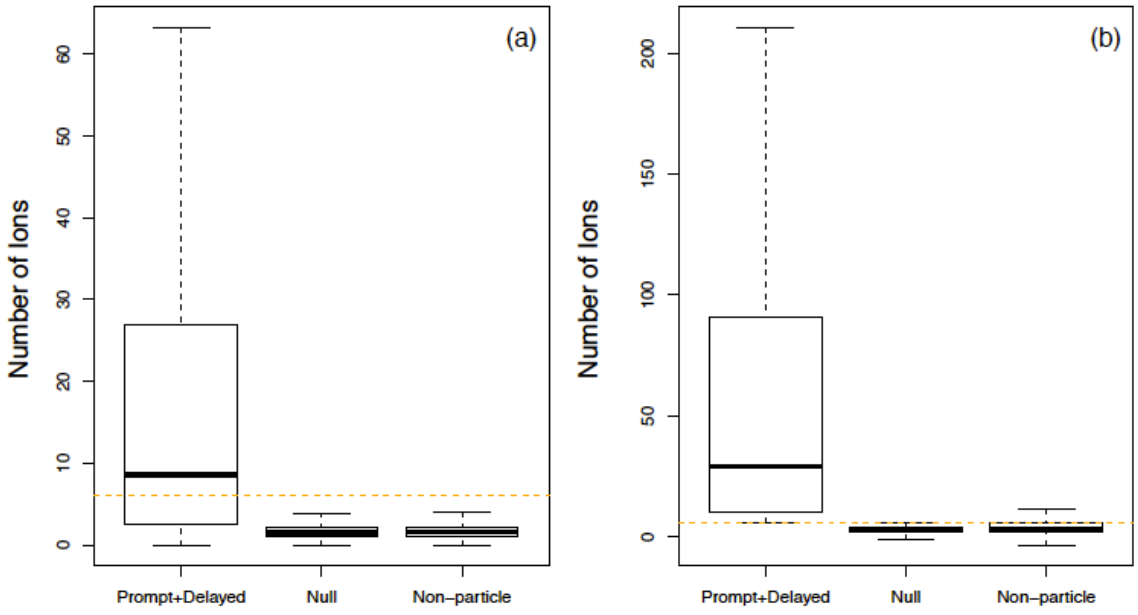
47 scattering signals. In both cases, prompt and delayed particles have significantly higher

48 number of ions than in null- and non-particle events. For the non-particle and null-

49 particle events, there are typically 2-4 ions, which are below the 6-ion detection limit

50 (Fig. S2).

51



52

53

54 Figure S2. Comparison of number of ions associated with prompt and delayed, null, and

55 non-particle events by using (a) the major ions including *m/z* 15, 27, 30, 41, 43, 44, 46,

48, 55, 57, and 64 and (b) using all ions (*m/z* 1 to *m/z* 111). Horizontal lines indicate the threshold of 6 ions.

Duty cycle versus particle number concentration

The dependence of duty cycle (data saving duty cycle calculated from the comparator circuit) on particle number concentration (from the SMPS measurement) for particles from 180–1000 nm d_{va} is shown in Fig. S3. The duty cycle is weakly or not dependent on particle number concentration.

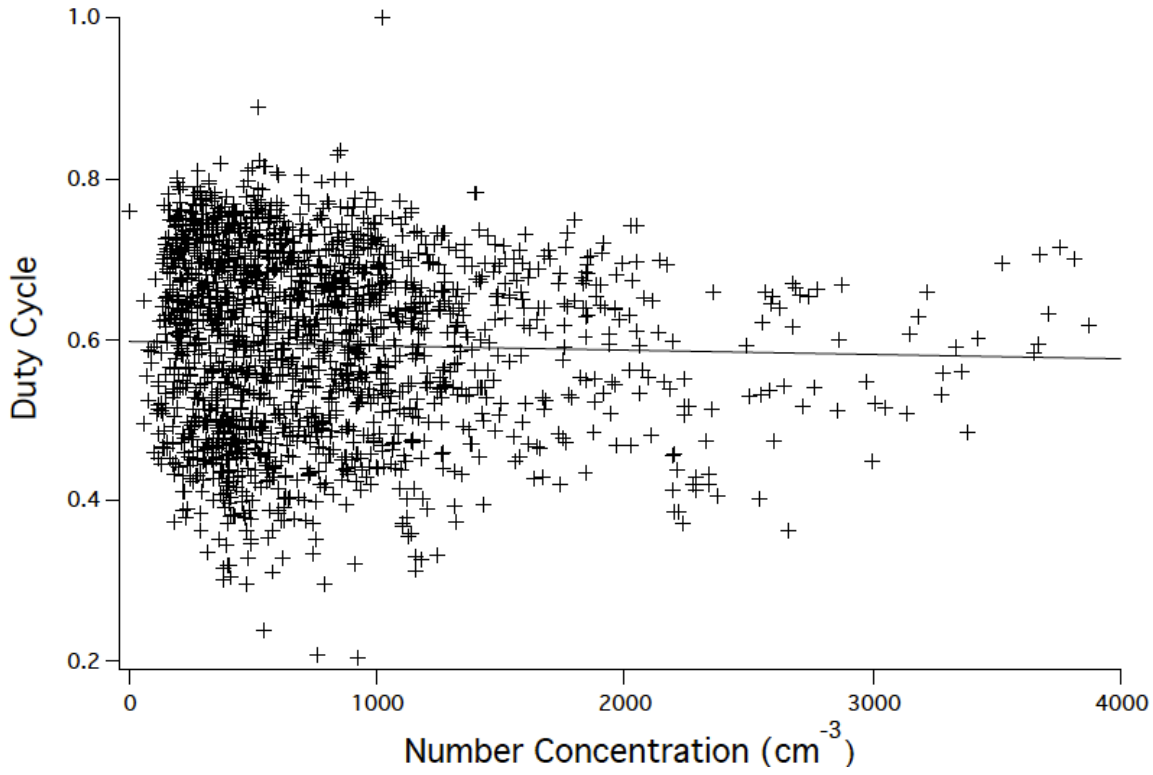


Figure S3. Data saving duty cycle (number of particles saved using LSSP over total number of LS-circuit counted particles) versus SMPS measured particle total number

concentration (130 to 715 nm d_m). The line represents the linear fit of the points with a slope of -5.6×10^{-6}.

Comparison of mass-based and number-based collection efficiency

The discrepancy of the mass-based and number-based collection efficiency (CE) may result from the differences of the operation modes. The mass-based CE was derived from the MS mode, whereas the number-based CE was determined using the LSSP mode. On average, the concentration measured by the MS mode was twice the concentration measured by the PToF mode (Liu et al., in press) and therefore the LSSP mode (the LSSP is in agreement with the PToF mode for particles larger than 600 nm d_{va}; Fig. 2c), suggesting that the null particles, which have chemical signals less than 6 ions per particle, and probably some of the prompt and delayed particles evaporated slower than the LSSP/PToF measurement window (~6 ms) but fast enough to be detected in the MS mode (10 s). The slowly vaporized particles that were not detected by the LSSP mode may result in a lower number-based CE.

Selecting particles for cluster analysis

Although the threshold of 6 ions is good for distinguishing particles from background noise, particles with low ions may not have sufficient chemical signatures to be correctly classified. In order to find at what signal level (number of ions) particles can be accurately classified on a single particle basis, we applied the K-means cluster analysis

on ten subsets of the prompt and delayed single particle spectra, with each subset containing spectra that have more ions than a threshold. The thresholds include 6, 12, 18, 30, 40, 50, 60, 80, 100, and 120 ions.

The results of the cluster analyses are shown in Fig. S4. The clusters are labeled as C1, C2, C3, C4, and C5, and similar clusters from different solutions (thresholds) are aligned in the same column for comparison. The blank panels in the results of 6-30 ions indicate that the clusters were not available in these solutions. Five major clusters were identified.

The clusters identified using different thresholds show differences and similarities. For example, the clusters identified using thresholds of 6-30 ions were not consistent, i.e., C3 only showed up in 12-ion and 30-ion solutions, and the number fractions of C2 and C5 were different among these solutions. It is likely that a fraction of the particles with low chemical ions were classified inconsistently, resulting in the cluster differences. In contrast, the clusters identified in the 40-120 ion solutions are very consistent in both cluster spectrum and number fraction, suggesting that particles with more than 40 ions likely have enough chemical signals to be accurately categorized so that the results are independent of the threshold values. Therefore, although particles with less than 40 ions and more than 40 ions have similar number size distributions (Fig. S5), including the low-ion particles in the cluster analysis decreases the robustness of the cluster analysis. Accordingly, we use 40 ions as the threshold for single-particle classification and the clusters identified from particles with more than 40 ions are used in the manuscript.

In order to identify similarities between the single-particle clusters and ensemble PMF factors, we compare their mass spectra and time series. Although the mass spectra of C1-C5 were separately identified as clusters, some of the mass spectra had similar chemical signatures. To simplify the clusters for comparison to the mass-based factors, the clusters with similar chemical signatures were combined, i.e., C1 and C4 were combined because they were both characterized by high-intensity of m/z 44 in their mass spectra, and C3 and C5 were combined because they had significant peaks at m/z 27, 29, 41, 43, and 57 that are characteristic of HOA. C14 (number-weighted combination of C1 and C4), C2, and C35 (number-weighted combination of C3 and C5) are termed as Cluster I, Cluster II, and Cluster III, respectively.

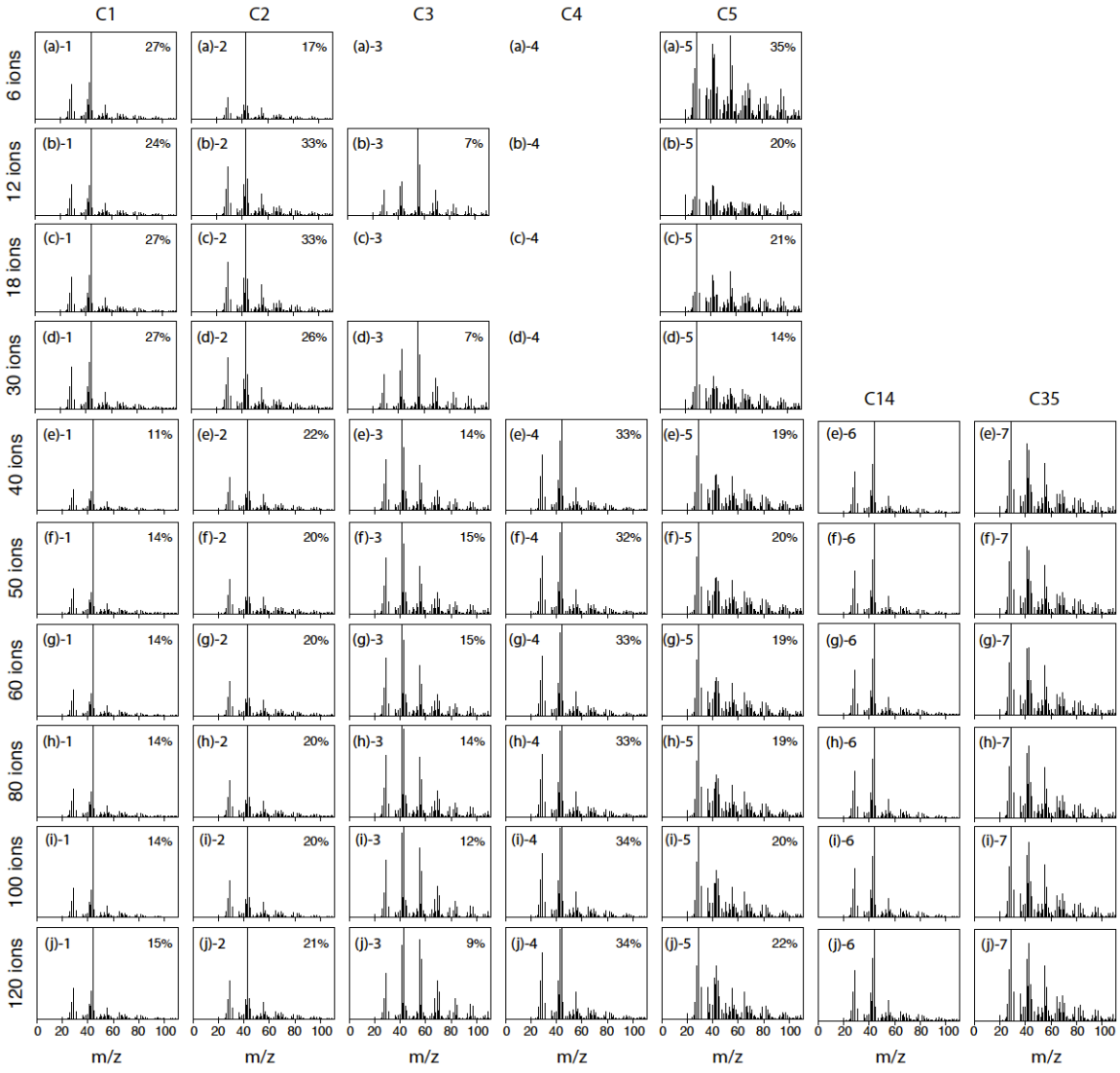
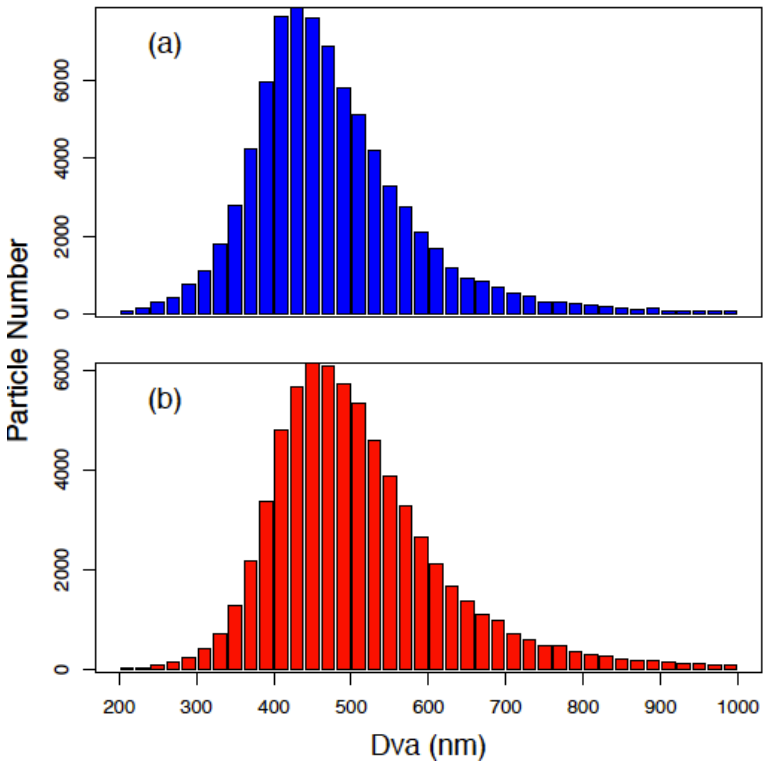


Figure S4. Columns C1-C5 represent cluster centroids for the clusters identified using thresholds of 6, 12, 18, 30, 40, 50, 60, 80, 100, and 120 ions. Column C14 represents number-weighted combination of clusters C1 and C4, and column C35 represents number-weighted combination of clusters C3 and C5. The percentage in the panel represents the number fraction of the cluster.



131

132 Figure S5. Number size distribution for (a) particles with 6-40 ions and (b) particles with

133 more than 40 ions.

134

Correlation of the single-particle clusters and the ensemble-derived PMF factors

Table S1. Cross correlation of the mass fraction time series for the three single-particle clusters (Clusters I, II, and III) and the ensemble-derived factors. Person's correlation coefficients are shown.

	High O/C alkane SOA + high O/C aromatic SOA	Low O/C alkane SOA	COA + PO SOA + Nighttime OA
Cluster I	0.69	-0.29	-0.60
Cluster II	0.00	0.23	-0.02
Cluster III	-0.65	0.19	0.60