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Supplement of

Identifying precursors and aqueous organic aerosol formation pathways during the SOAS campaign

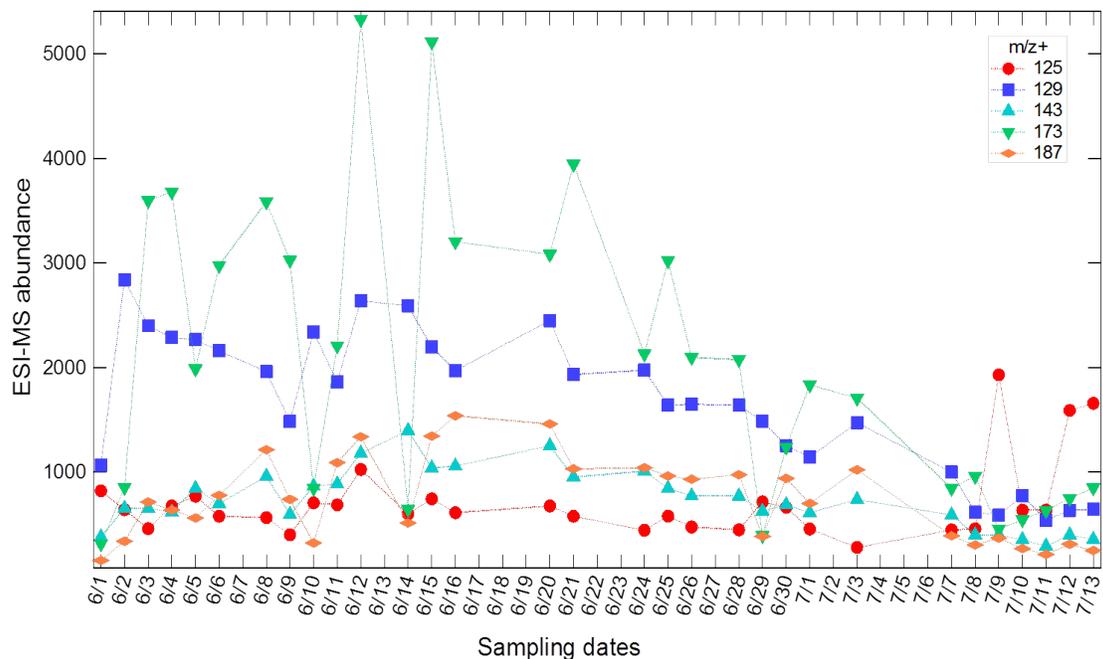
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Supplement Table S1: TOC content of sampling days

				Intensive	
Collection date	$\mu\text{M TOC}$	Collection date	$\mu\text{M TOC}$	Collection date	$\mu\text{M TOC}$
1-Jun-2013	104.9	14-Jun-2013	84.5	1-Jul-2013	82.8
2-Jun-2013	108.7	15-Jun-2013	117.0	3-Jul-2013	69.46
3-Jun-2013	127.8	16-Jun-2013	108.2	7-Jul-2013	43.33
4-Jun-2013	167.5	20-Jun-2013	131.5	8-Jul-2013	52.17
5-Jun-2013	161.4	21-Jun-2013	104.4	9-Jul-2013	56.12
6-Jun-2013	118.6	24-Jun-2013	64.3	10-Jul-2013	60.67
8-Jun-2013	120.2	25-Jun-2013	81.02	11-Jul-2013	44.49
9-Jun-2013	75.4	26-Jun-2013	86.03	12-Jul-2013	77.09
10-Jun-2013	81.5	28-Jun-2013	79.28	13-Jul-2013	63.76
11-Jun-2013	139.5	29-Jun-2013	92.0		
12-Jun-2013	179.7	30-Jun-2013	98.7		

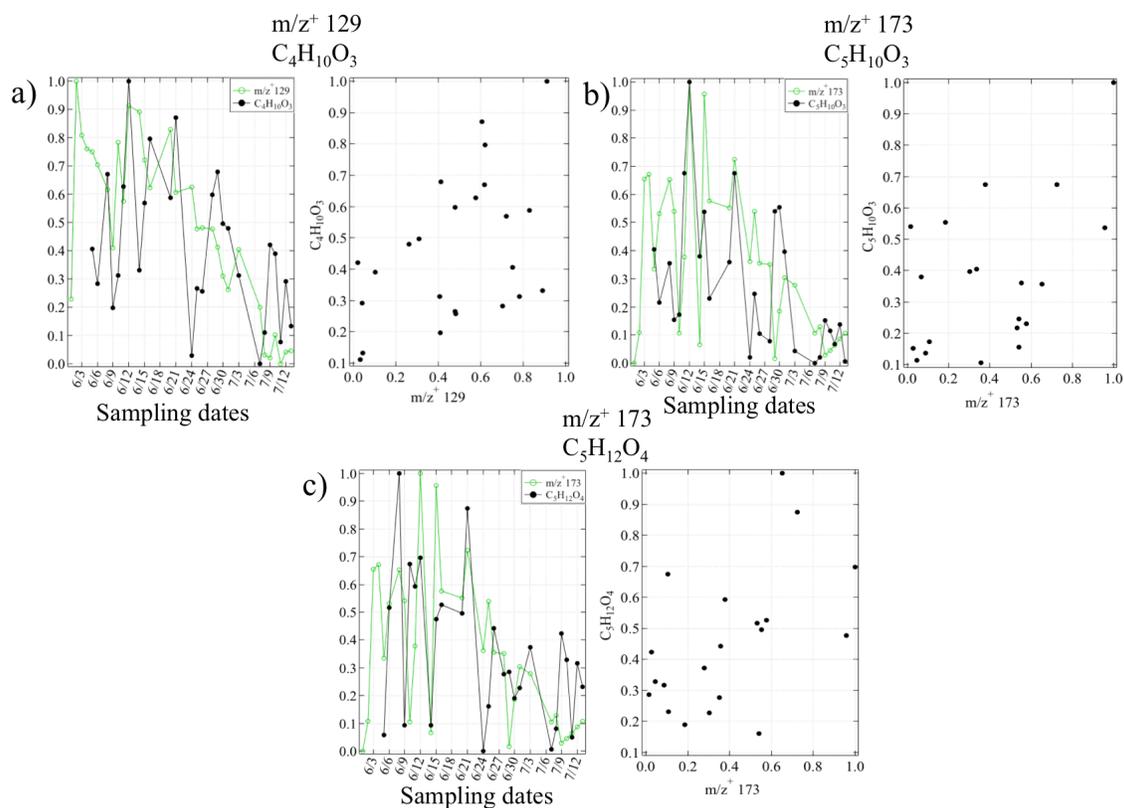


Supplement Figure S1: ESI-MS abundance of precursor masses across all sampling days.

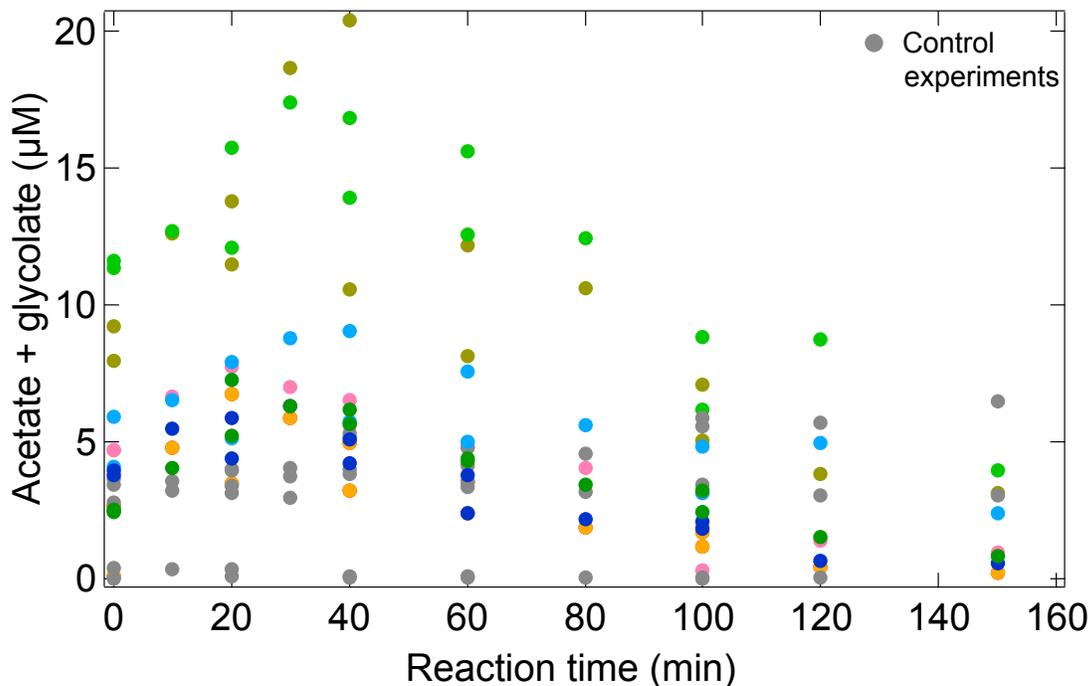
Comparison of CIMS and ESI-MS results: High-resolution time-of-flight chemical ionization mass spectrometry (HRToF-CIMS) (Lee et al., 2014), coupled to a filter inlet for gases and aerosols (FIGAERO) (Lopez-Hilfiker et al., 2014; Lopez-Hilfiker et al., 2015) was sampling ambient air in the same location (Centerville field site) as the mist chambers. Gas phase measurements from the HRToF-CIMS were made in real time through a 3/4" PTFE inlet operated at 16 standard L min⁻¹. The HRToF-CIMS employed iodide ionization, which forms organic-iodide adducts, resulting in a virtually fragmentation-free ionization. However, ions with the same mass and elemental formula cannot be distinguished. The sensitivity of the Γ CIMS depends strongly on compound structure. For example, HRToF-CIMS cannot distinguish between ISOPOOH and IEPOX but is more sensitive to ISOPOOH. The ion m/z 173 seen in the mist chamber samples

has the same mass; the sensitivity of the CIMS to this compound is unknown. The mist chamber collects a much wider variety of compounds. Thus, we expect to find compounds in the mist chamber samples that are not detected by I CIMS, and it is likely that real-time CIMS analysis facilitates measurement of some species that we will not be able to detect with the mist chambers (e.g., IEPOX).

Figure S2 shows time series of ion abundance in the aqueous mist chamber samples (8-12 hr integrated samples) and gas-phase signals of compounds with corresponding molecular formulas as measured by HRToF-CIMS (Lee et al., 2014; Lopez-Hilfiker et al., 2014). There are no strong correlations, but there are similarities in trends. Note that efficiency of ionization of compounds in the ESI-MS and CIMS varies with compound class and with the composition of the mixture (matrix); instrument sensitivity varies daily. In some cases, isobars or isomer mixtures may contribute differently to the CIMS and ESI-MS signal strength (e.g., m/z 173). Also, the ESI-MS measurements were made after collection in water, whereas CIMS measurements were made in the gas phase. Thus, there are limitations to quantitative comparisons between these measurements in the absence of authentic standards. Additionally, both techniques are highly sensitive to the structure of the compound, making comparisons challenging.



Supplement Figure S2: Normalized ion abundance from ESI-MS and HRTof-CIMS for compounds with the same elemental formula. The positive ions at (a) m/z 129 and (b, c) m/z 173 represent data from the ESI-MS (green) and the molecular formulae on the left panels of each figure are indicative of measurements from the HRTof-CIMS (black). Right panels show scatter plots.



Supplement Figure S3: Acetate + glycolate production by IC when the ambient SOAS samples are exposed to OH (colored circles). (Acetate and glycolate co-elute.) Acetate/glycolate formation is seen on some but not all days. Gray circles represent control experiments (June 11 sample + UV, June 11 sample + H₂O₂, June 30 field water blank + OH). The variability of acetic acid formation across all experiment days is 60%.

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