

Supporting Information for

Secondary Marine Aerosol Plays a Dominant Role over Primary Sea Spray

Aerosol in Cloud Formation

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Supporting Information

Control Experiment for MART-OFR Study

A control experiment was conducted to determine whether the majority of the AMS signal originated from seawater emissions, rather than background contamination. A brief description follows: the MART tank was filled with ultrapure water (18 M Ω), instead of seawater. Other experiment conditions, OFR settings and aerosol sampling instruments were kept the same with all other SMA experiments. The AMS was used to monitor the background aerosol chemical compositions from the OFR for this control experiment. The concentration of background concentrations of sulfate, nitrate, ammonium and organic aerosol concentrations were 0.015 ± 0.003 , 0.004 ± 0.003 , -0.002 ± 0.015 and 0.121 ± 0.041 $\mu\text{g}/\text{m}^3$, respectively, which corresponds to 1%, 4%, 0.5%, and 14% of the minimum concentration of each analyte measured during the bloom. The low background concentration of the inorganic ions indicate that background aerosols were not a significant source of the AMS signals during the SMA experiments. However, the background comprises a larger fraction of the organic aerosol, which could have affected our experimental results.

Gas-Phase Measurements

Ammonia can partition to the particle phase and form a major component of SMA particles. The following analysis was done to make sure that our experiment system was not contaminated with ammonia. The input air source is a zero-air generator (ZAG, Model 1001, Sabio) which was used to scrub contaminants from the air before it was introduced to the MART tank; however, it does not completely remove all trace gases, including ammonia. To ensure trace amounts of ammonia transmitted by the ZAG were not skewing the experimental results, we compared the ammonia signal measured by chemical ionization time-of-flight mass

spectrometry (CI-TOFMS) during the bloom to the ZAG baseline. The operating principles of the instrument are described elsewhere.¹ The CI-TOFMS was operated with a high pressure inlet at 12 mTorr using $\text{H}_3\text{O}(\text{H}_2\text{O})_n^+$ ions generated by passing humidified N_2 through a Po-210 source (20mCi, NRD). The normalized counts per second (ncps) were calculated using the intensity of the reagent water cluster at m/z 37. The signal at $m/z = 18$, corresponding to NH_4 , was used as a proxy for NH_3 concentration. To establish a baseline for the ZAG, zero air was pushed through the headspace of a clean MART tank filled with milliQ H_2O and sampled by the CI-TOFMS. During the bloom, the instrument sampled the gases from the MART headspace after they had passed through OFR. The ammonia signal (Fig. S8) from the bloom was significantly higher than the baseline throughout the experiment, with the normalized counts ranging from 20-40 times higher. This result indicates that the most of ammonia in the MART headspace gases, and thus the ammonium in the OFR-generated SMA, were derived from the seawater itself and that the contribution from the ZAG were minimal.

CCN Measurements of SSA and SMA

The DMA sample-to-sheath flow ratio used during the experiments was 1:5 for nascent sea spray aerosol and 1:10 for SMA produced in the OFR. A smaller sheath flow ratio was used for the nascent sea spray due to its low particle concentration. Decreasing the sheath flow ratio affects activation behavior by broadening the DMA transfer function, and thus allowing a wider range of particle diameters to pass through the DMA. Assuming an ideal, triangular-shaped transfer function, decreasing the sheath flow ratio from 1:10 to 1:5 has the effect of broadening the width of the transfer function for 50nm particles at half height from $\Delta Z_p = 5$ nm to $\Delta Z_p = 10$ nm.² This difference is not expected to significantly affect the SR-CCN measurement.

Figure S1. Schematic drawing of experimental setup. The phytoplankton bloom was grown in a 2,400 L outdoor tank. Each day, 120 L of seawater were transferred to the MART for aerosol generation, and then returned to the outdoor tank after sampling. Primary sea spray aerosol was generated using a plunging waterfall, while secondary marine aerosols were generated using a PAM-OFR to oxidize the headspace gases.

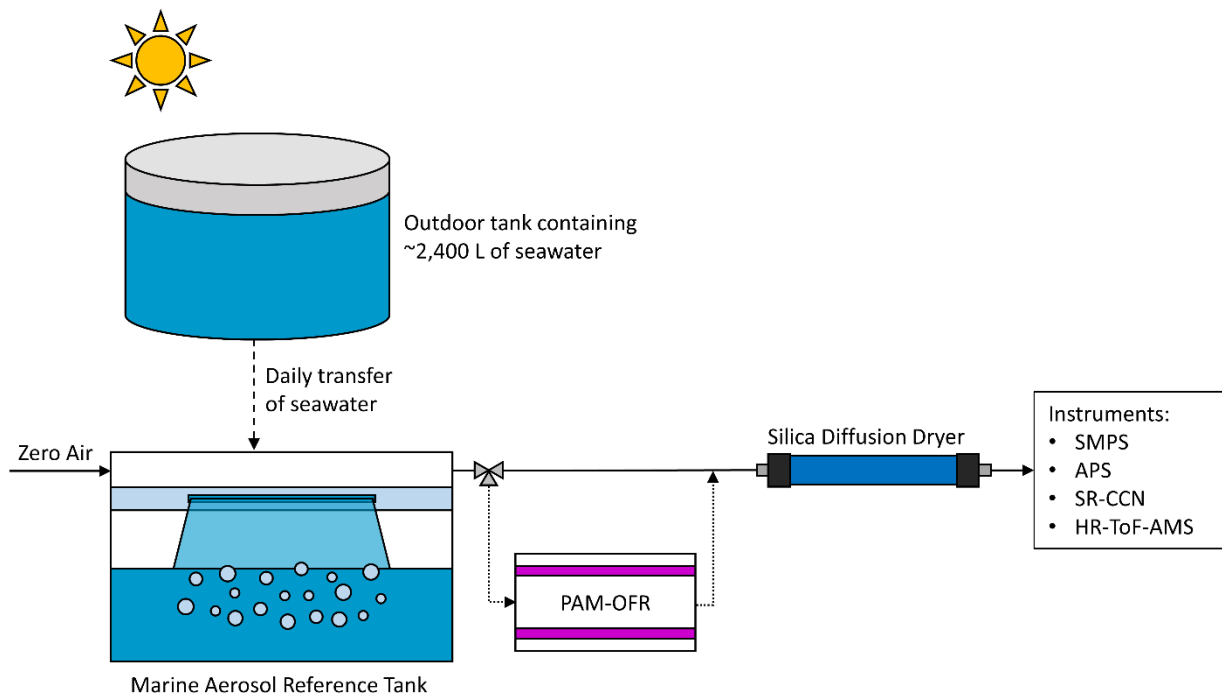


Figure S2. Time series of the average number concentrations and CCN (0.2%) concentrations for primary SSA during a mesocosm experiment. The CCN (0.2%) concentration was calculated from the aerosol size distributions and the measured hygroscopicity parameters, which were used to calculate the activation diameter of SSA at a supersaturation of $SS = 0.2\%$. The seawater chlorophyll-a concentration is shown for reference. Error bars represent $\pm 1\sigma$.

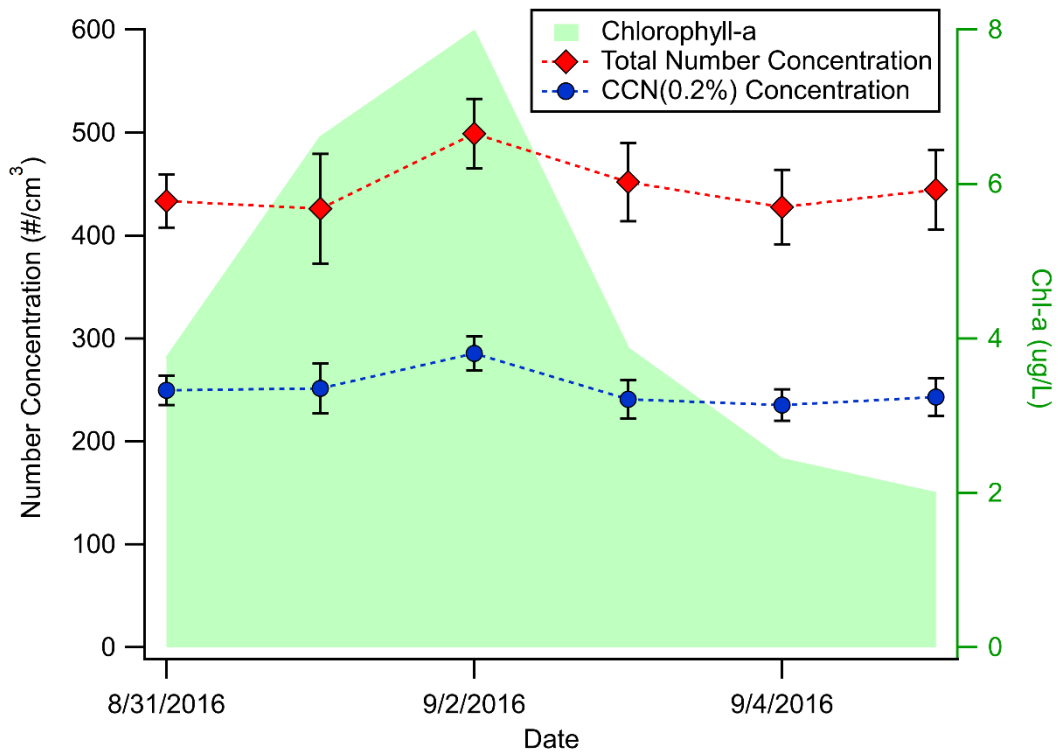


Figure S3. SMPS number size distributions of SMA generated in the PAM-OFR.

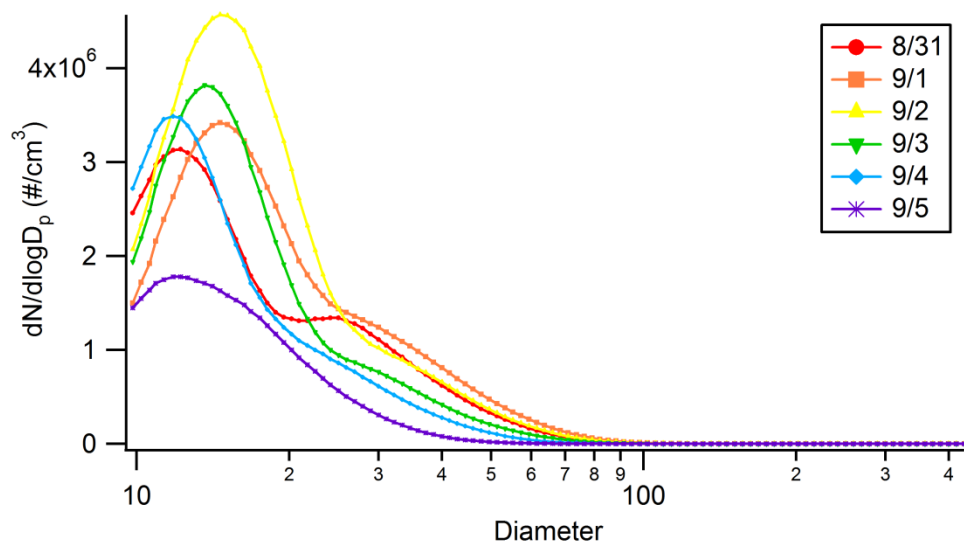


Figure S4. a) SR-CCN activation curve for 50 nm nascent SSA particles. b) SR-CCN activation curves for 50 nm OFR-generated SMA particles.

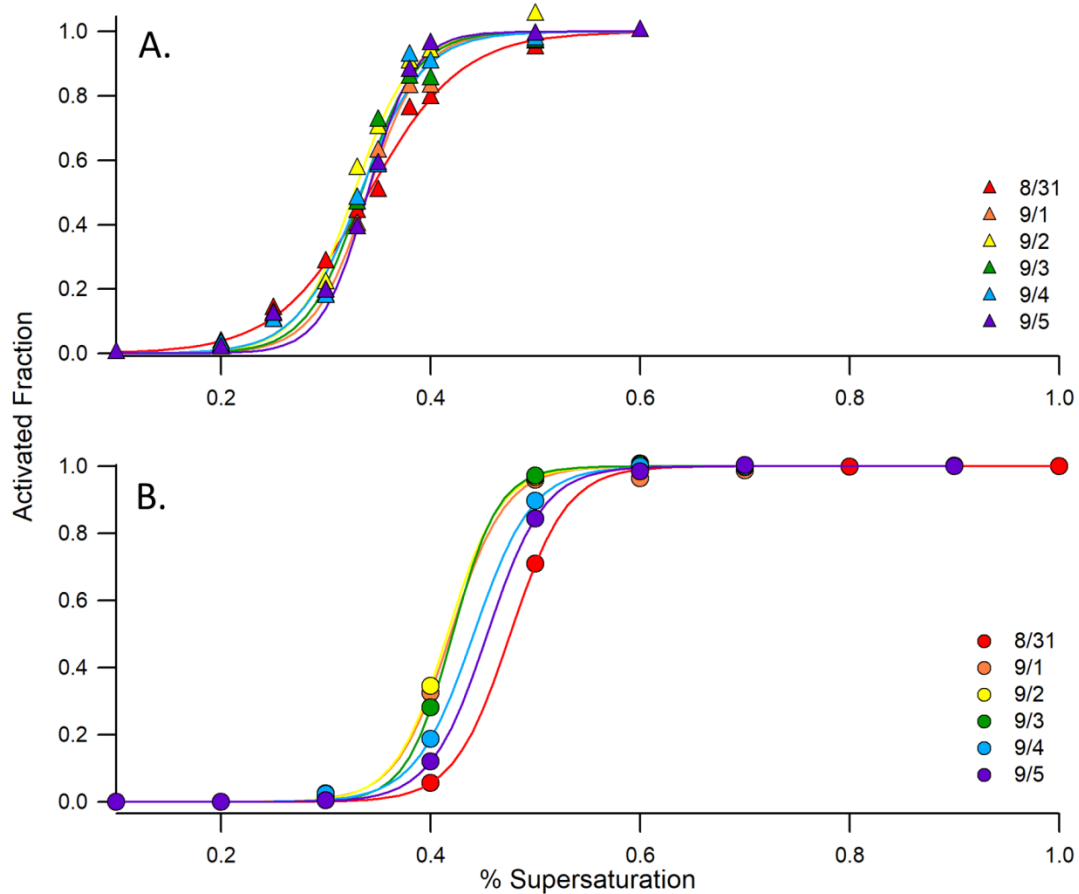
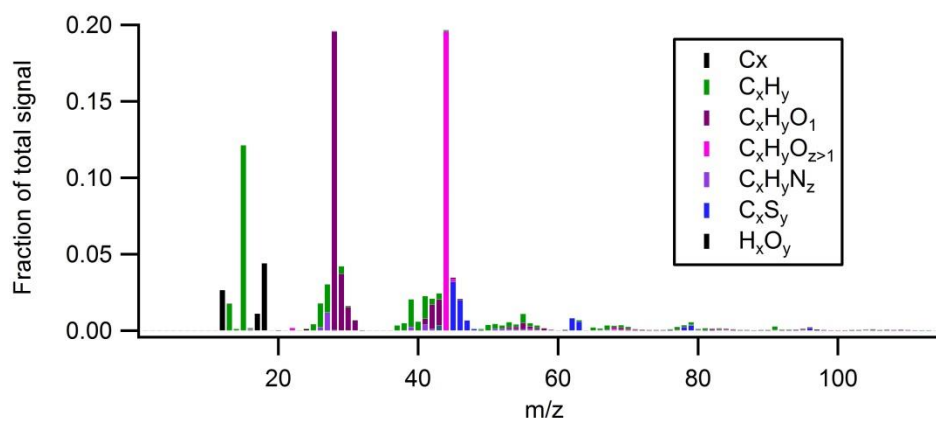


Figure S5. Average AMS spectra for organic species in (a) SMA and (b) SSA during bloom.

A. SMA



B. SSA

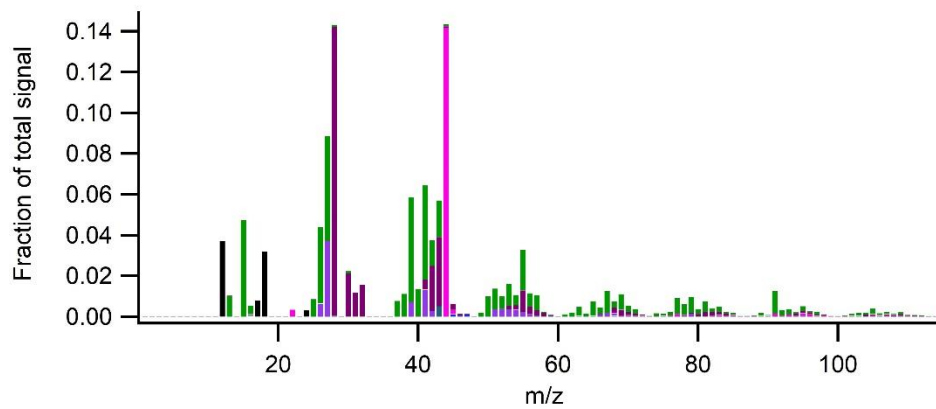
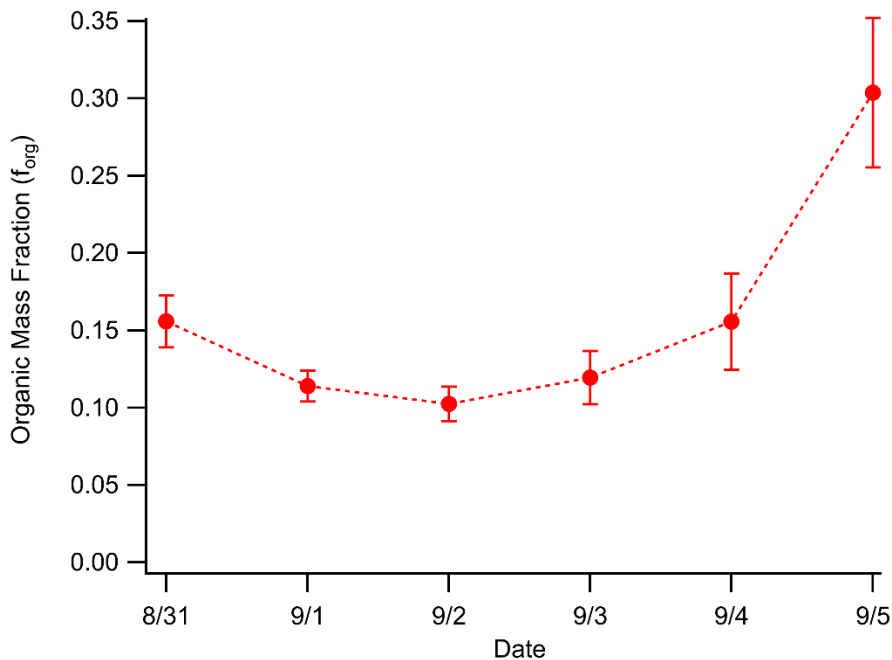


Figure S6. a) Organic mass fraction (f_{org}) of SMA over the course of the phytoplankton bloom, measured by the HR-TOF-AMS. The mass fraction of organics decreases during the peak of the bloom and then increases during the death phase. b) The molar ratio of ammonium to sulfate in SMA during the bloom. Error bars represent $\pm 1\sigma$.

A. Organic mass fraction



B. Molar ratio of ammonium to sulfate ($[\text{NH}_4]/[\text{SO}_4]$)

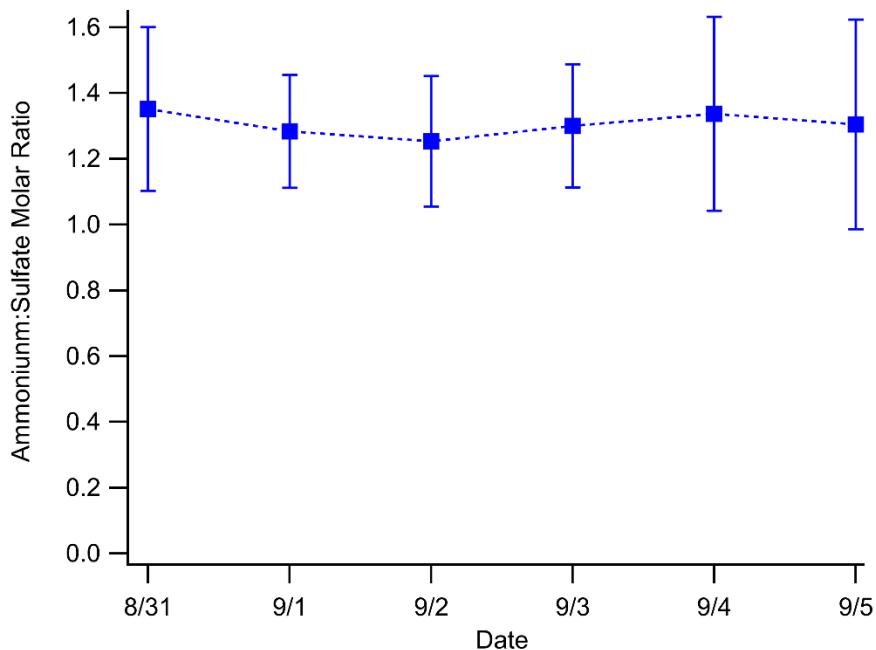


Figure S7: Elemental ratios (H/C and O/C) of the organic species in secondary marine aerosol, as measured by HR-TOF-AMS.

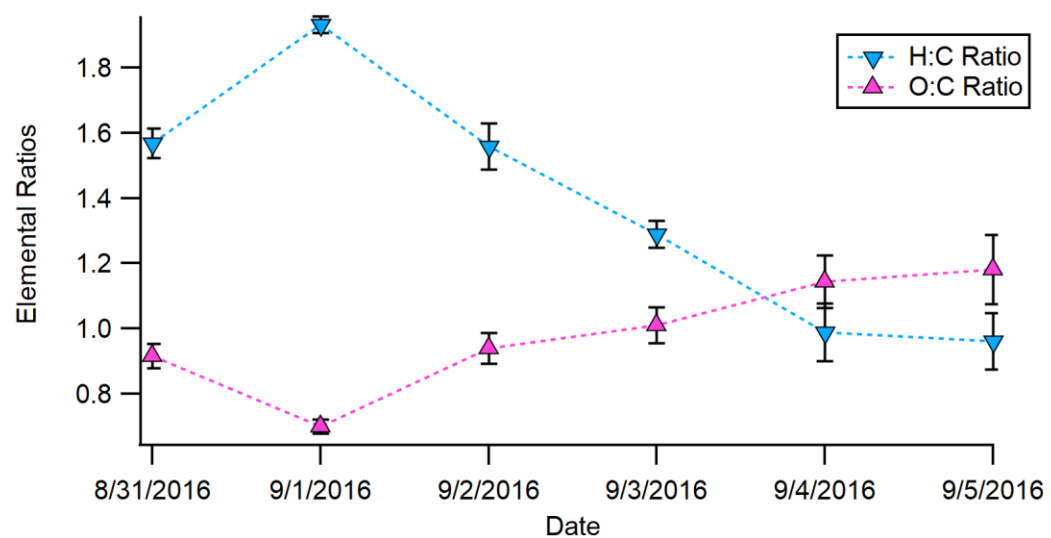
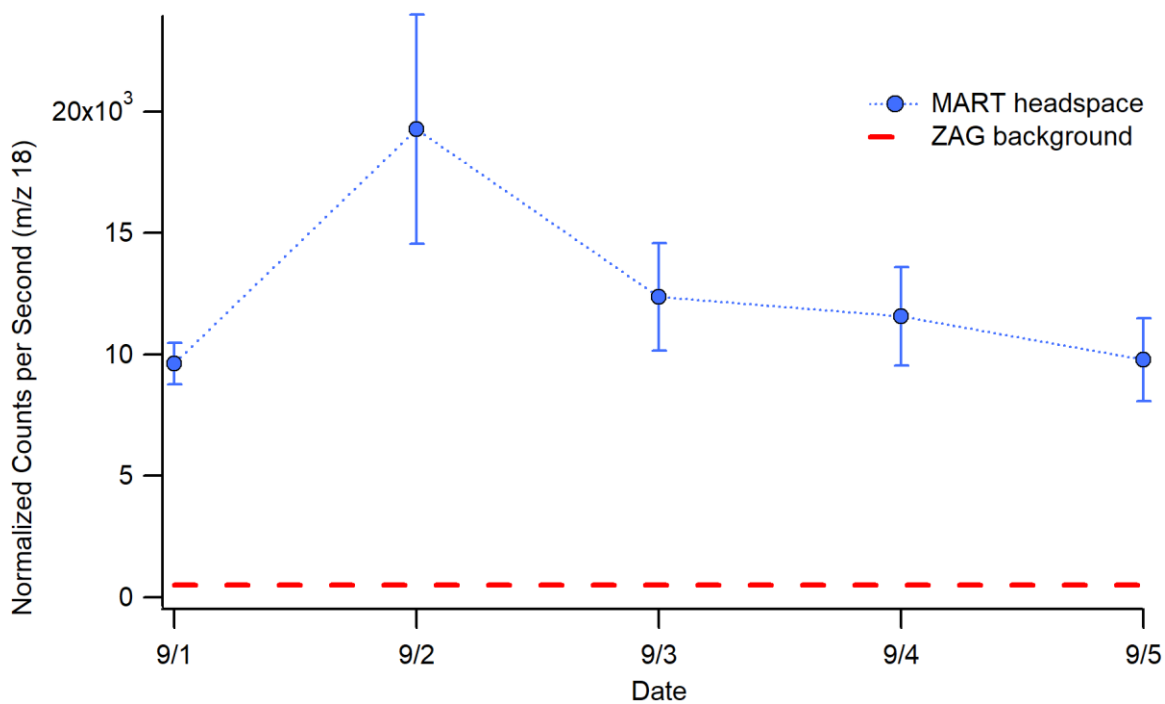


Figure S8. Ammonia measurement by CI-TOFMS from the headspace of the MART. The background was measured once prior to the start of the experiment and is shown here as the dashed line.



References

1. Bertram, T. H.; Kimmel, J. R.; Crisp, T. A.; Ryder, O. S.; Yatavelli, R. L. N.; Thornton, J. A.; Cubison, M. J.; Gonin, M.; Worsnop, D. R., A field-deployable, chemical ionization time-of-flight mass spectrometer. *Atmospheric Measurement Techniques* **2011**, 4 (7), 1471-1479.
2. Knutson, E. O.; Whitby, K. T., Aerosol classification by electric mobility: apparatus, theory, and applications. *Journal of Aerosol Science* **1975**, 6 (6), 443-451.