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Photochemical aging of aerosol particles in different air masses arriving at Baengnyeong Island, Korea

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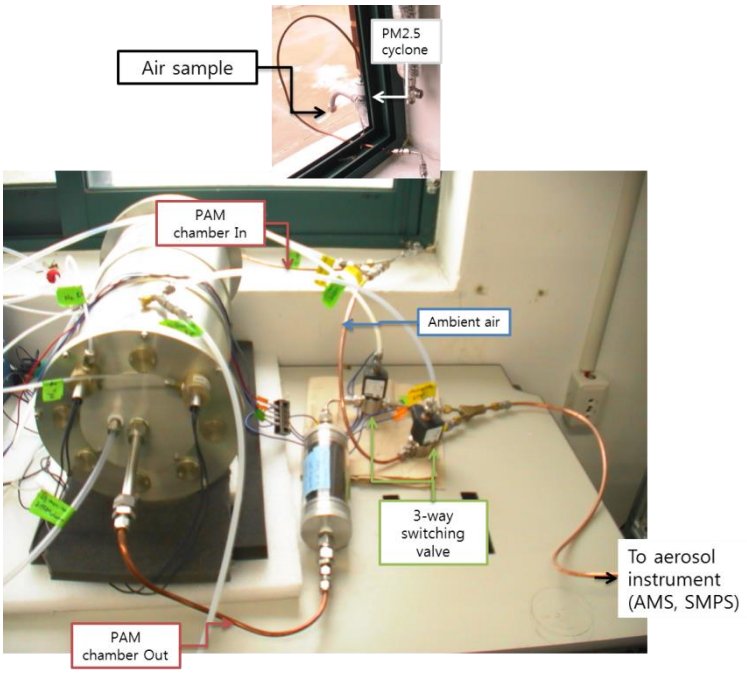
S1. The sampling setup of the PAM reactor



[Figure S1. The PAM reactor sampling setup]

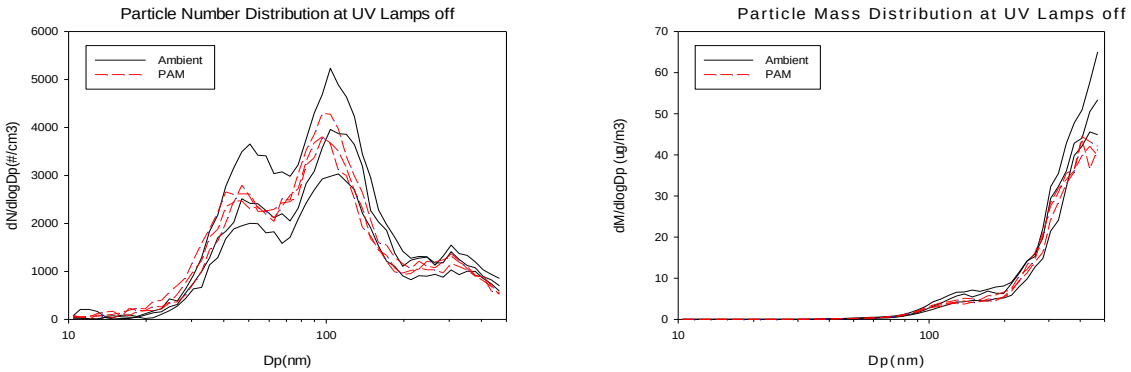
In our experimental setup, the PAM reactor was installed beside the window in the laboratory and ambient air was pulled through a copper tubing (~ 30 cm) from PM2.5 cyclone outside the laboratory. The ambient air from the PM2.5 cyclone was introduced into the PAM reactor through an inlet plate and endcap and then rapidly dispersed before entering the reactor through a Silconert-coated (Silcotech, Inc.) stainless steel screen. Aerosol sampling tubes were 1/4 inch OD copper and stainless steel tubes and gas sampling tubes were 1/4 inch OD PFTE Teflon tubes. The ambient and PAM reactor through air samples were alternately switched to the aerosol measurement instruments by using a 3-way switching valve every 6 minute. The 3-way switching valve might cause the evaporation of ambient and PAM aerosols when it was getting hot during operation. When PAM aerosol was introduced in the measurement instruments, ambient aerosol was bypassed to outside and vice versa. The total flow rate to the PAM reactor and ambient

sampling was set to 5 liters per minute. We tried to set up the PAM reactor as close as possible to the PM2.5 cyclone and the AMS/SMPS instruments as shown in the figure above. The aerosol particles and gases loss due to the PAM reactor and through the tube surfaces contributes to the mass concentration measurement uncertainty.

S2. The wall loss test

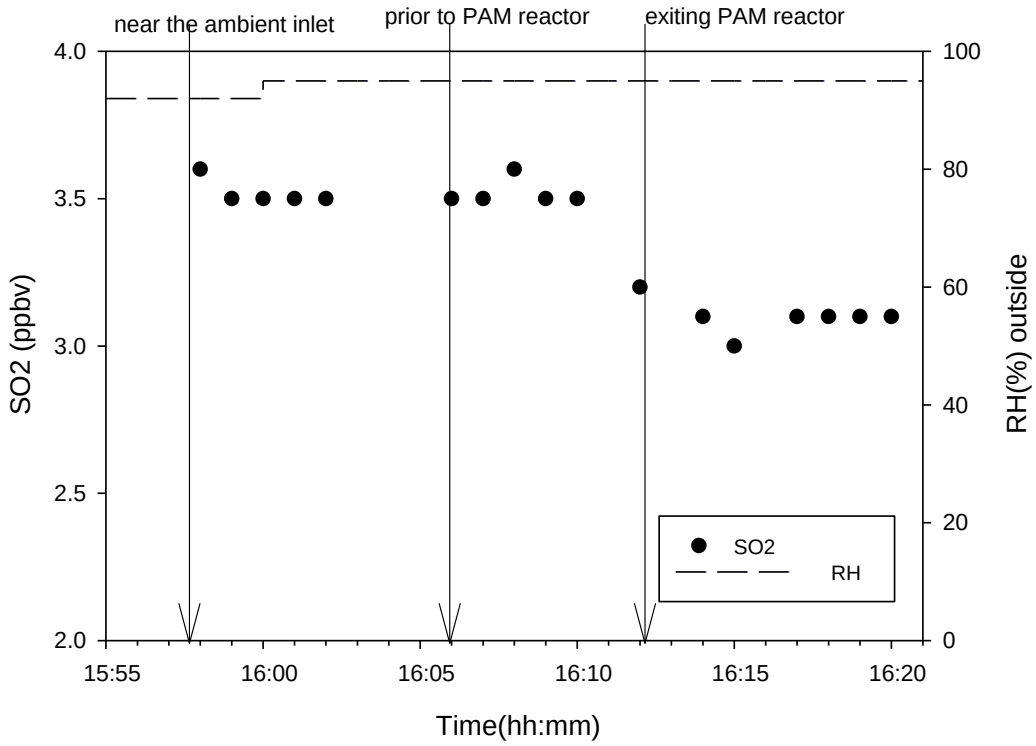
We conducted the loss test for 1) ambient aerosol and 2) SO_2 during the experiment in 2011. Its results are discussed below and the LVOCs fate is calculated using the method in Palm et al. (2016).

First, PAM reactor was run for ambient air without lamp-on and the SMPS signals of air entering and exiting the PAM reactor were compared to estimate the physical loss of aerosol to the wall. In experimental setup, ambient air entering the PAM reactor was introduced into SMPS alternately with air exiting the PAM reactor. For the test, this cycle was repeated three times. Because entering and exiting air was not simultaneously measured, there could be some error caused by the variation of ambient air. However, there was no detectable variation in ambient air, judged from gaseous concentrations for less than an hour of test period. The mass of ambient aerosol and aerosol exiting the PAM reactor (without lamps on) was 13.1 ± 2.06 μg m^{-3} and 11.6 ± 0.46 μg m^{-3}, respectively, resulting in about 12 % of aerosol mass in the PAM reactor (Figure below). However, the decrease in mass was due to the loss of pre-existing aerosols but not newly formed secondary aerosols from condensable gases.



[Figure S2-1. SMPS particle number distribution (left) and mass distribution (right) for wall loss test. Red and black color indicate air exiting and entering the PAM reactor.]

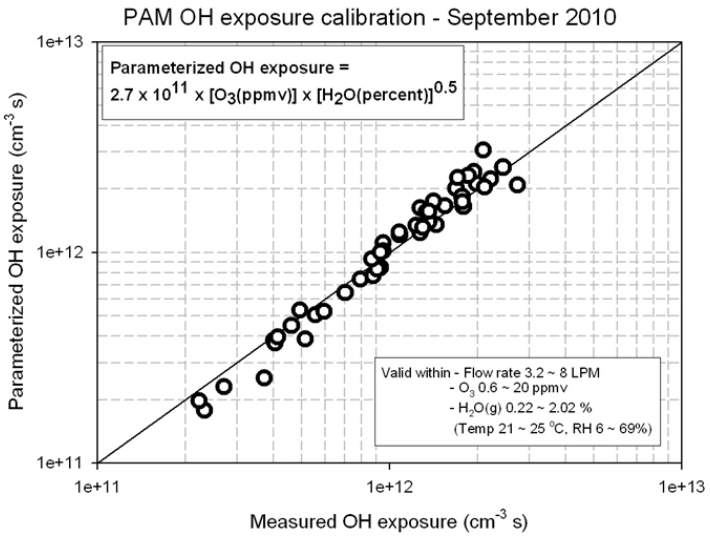
Second, we have tested SO_2 loss by the wall during the experiment. For this test, we used ambient air instead of standard SO_2 mixtures in a wide range of concentrations. When air was pulled through the PAM reactor inlet plate, SO_2 was measured first for ambient air in front of the inlet, and then before it entered and after it exited the PAM reactor (Figure below). SO_2 concentrations prior to and after the PAM reactor were 3.5 ppbv and 3.1 ppbv, respectively, leading to SO_2 loss of 11 ± 7 %. There was loss in the sampling inlet line. The detailed information on SO_2 measurement is given below.



[Figure S2-2. SO_2 loss test results in PAM reactor]

S3. Calibration of OH exposure in the PAM reactor

We used the OH exposure calibration which was done with a mixture of pure air and SO_2(g) in the laboratory by Kang et al. (2011a). The full manuscript can be found in J. KOSAE Vol. 27, No. 5 (2011) pp. 534~544, Journal of Korean Society for Atmospheric Environment, DOI: http://dx.doi.org/10.5572/KOSAE.2011.27.5.534.

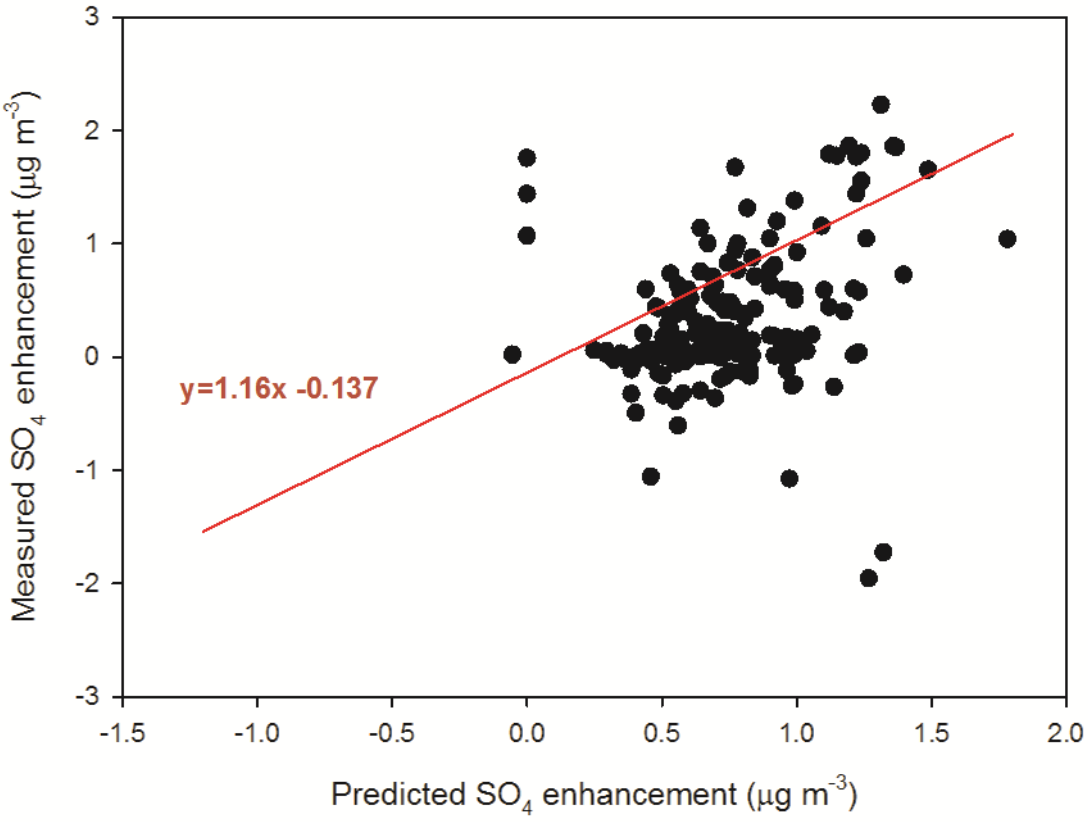


[Figure S3. OH exposure calibration curve for this PAM reactor. (cited from Kang et al., (2011a)]

S4. Comparison between calculated and measured sulfate formation in PAM reactor

We calculated the sulfate formation using SO_2 measurements from sampling through and bypassing the PAM chamber, assuming that SO_2(g) was converted to sulfate(p) by reaction with OH inside the PAM reactor. For this estimation, we adopted 2 ppbv offset for ambient SO_2 measurement, SO_2 gas loss of 11 % in the PAM reactor, and condensable sulfate loss by wall and exiting the reactor of about 38%. At 4.6 days of OH exposure, 43% of SO_2 will be consumed in the PAM reactor based on $k_{SO2+OH} = 1x10^{-12}$ cm^3 $molec^{-1}$ s^{-1}. The measured SO_4 enhancement was obtained by subtracting the ambient SO_4 concentration from the SO_4 concentration measured in PAM chamber. For this comparison, AMS measurements were averaged hourly to be consistent with the SO_2 measurement. The figure below compares the measured and predicted SO_4 enhancement, showing that the measured explained well the expected (slope = 1.16 and an intercept = -0.137. We used the total least squares regressions (http://www.real-statistics.com/regression/total-least-squares/), which is minimizing the sum of the squared Euclidean distances from the points to the regression line similar to orthogonal distance regression. The correlation between the measured and predicted was deteriorated by the very low measured SO_4 enhancement against a wide range of sulfate expected to be enhanced. Not to mention, uncertainty was involved in the measurement of SO_2

concentration, loss assessment of SO_2 and condensable sulfate, and the AMS measurement of particles smaller than 50 nm.



[Figure S4. Measured SO_4 enhancement vs. calculated SO_4 enhancement.]

S5. Estimating the condensation sink

In addition, we estimated the loss of condensable gases by wall deposition, exiting the reactor, and further OH reaction competing with condensation on existing particles, based on Palm et al. (2016) and model posted in https://sites.google.com/site/pamwiki/hardware/estimation-equations. Although the model calculating the possible loss of condensable gases was developed a couple of years after this experiment was performed, the physical setup of our PAM reactor was very similar to the ones used in Palm et al. (2016), Ortega et al. (2013), and (2016).

We used the same constants as those in Palm et al. (2016), but for wall loss in our experiment, we used a measured loss percentage of SO_2 of 11%. A proportion to condensing on the existing particles (Faerosol denoted in Figure S5) associates to the condensation sink (CS). The details of aerosol CS calculation were available in a previous paper (Salimi et al., 2015). Faerosol variation with respect to time was due to the existing particles concentration variation. About 20~70% of condensable organic gases were estimated to be condensed on existing particles, contributing to mass increase in PAM reactor. It is similar to the case of high condensation sink (CS) shown in figure 5 of Palm et al. (2016). In our study the fraction of low-volatility gases that were not condensed in the PAM reactor was higher for organic-dominated case (~40%) than sulfate-dominated case (~30%) because of greater CS in latter than former.

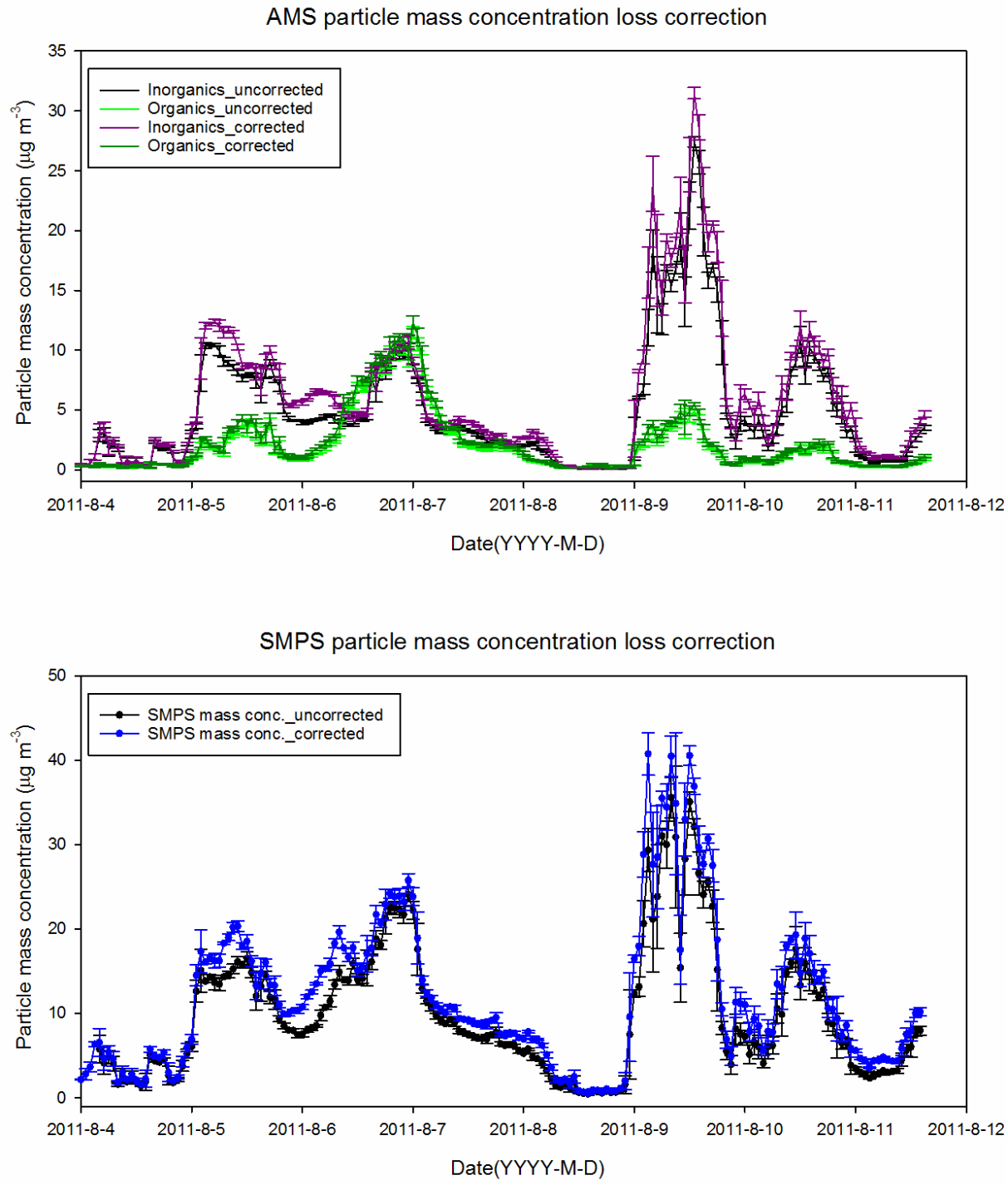
For conversion of SO_2 to sulfate, the fraction of additional OH reaction-induced loss was set to 0 because of no more reactions between SO_2 and OH as described in Palm et al. (2016). The estimated fraction of sulfate condensation on existing particles was in the range of 40~90% and the rest were expected to be lost by walls and exit the reactor without being condensed.

[Figure S5. Fractional loss of SO_2 (upper) and condensable organics (down) in PAM reactor]

S6. Correction of the particle mass concentration in PAM reactor with condensation loss

We corrected the particle mass concentration measured in PAM reactor with condensation loss by the exiting the reactor and the wall. For AMS measurement, we used a loss of sulfate for sulfate, nitrate, ammonium, and chloride concentration and used

a loss of organics for organics concentration. For SMPS measurement, we used a composition dependent loss (organics/(organics+inorganics)*organics loss+inorganics/(organics+inorganics)*sulfate loss) for the total particle mass concentration. The figure S6 shows the uncorrected and corrected particle mass concentration in PAM reactor. The errors are 2σ confidence. Note that the correction range of the particle mass concentrations were mostly overlapped with the error range.

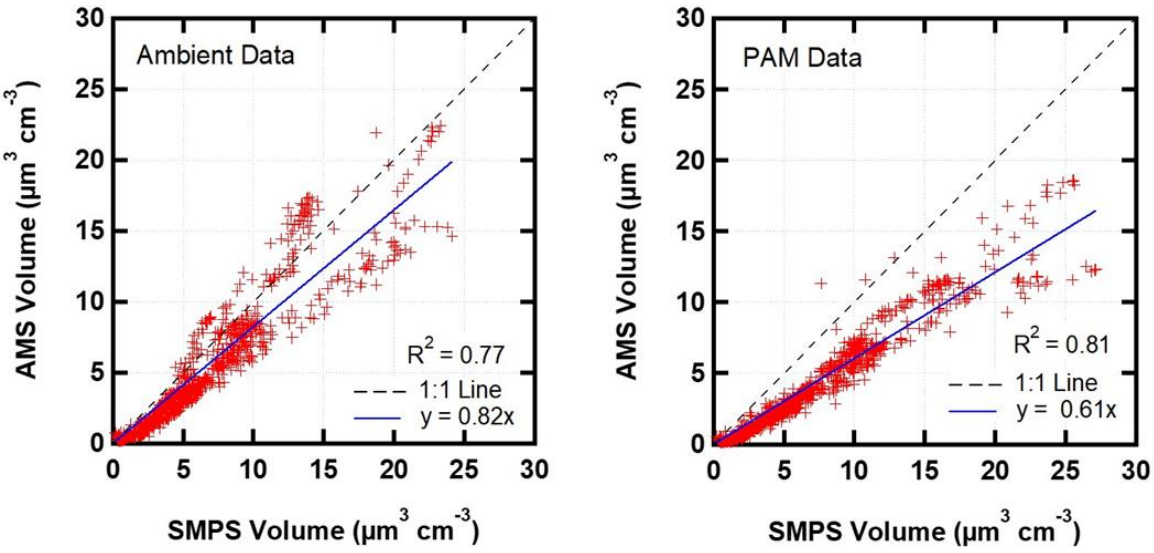


[Figure S6. Time series of uncorrected AMS and SMPS particle mass concentration and corrected particle mass concentration with condensable gases loss. The errors are 2σ confidence.]

S7. A comparison of AMS vs SMPS

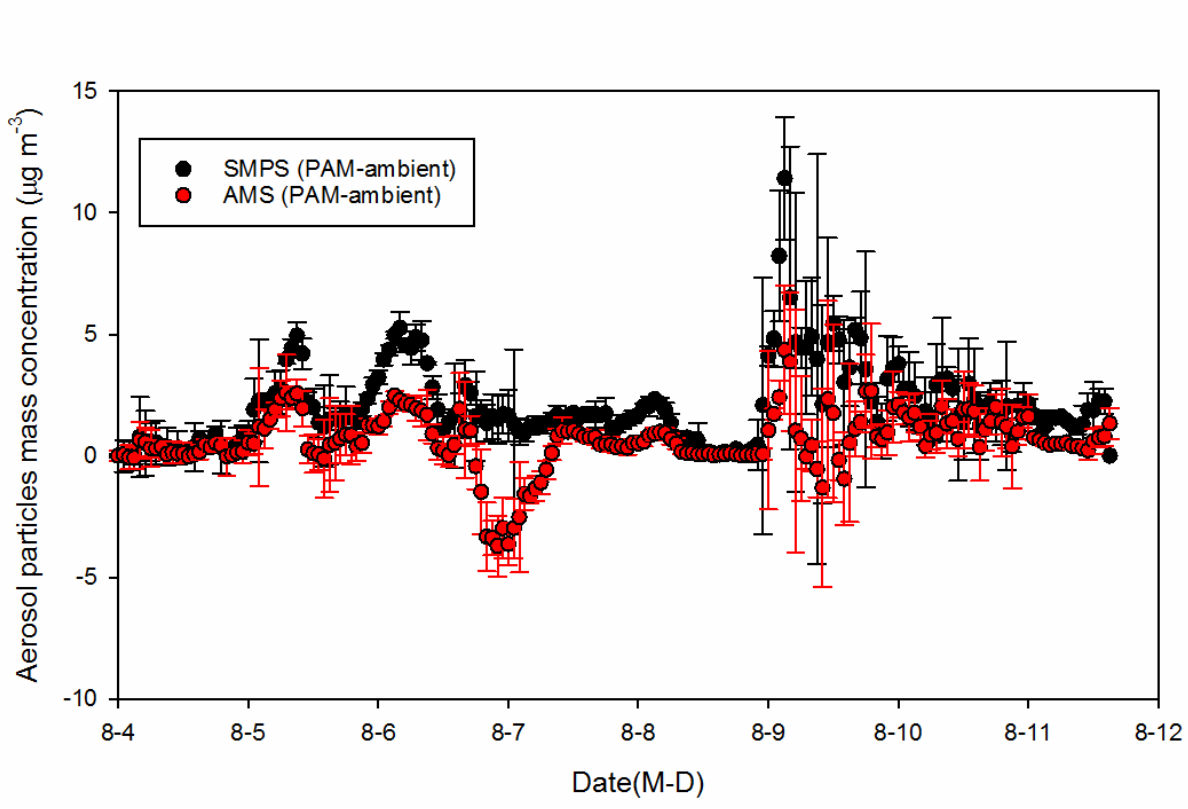
Aerosol particles volume concentration obtained from AMS and SMPS was compared each other for ambient and PAM aerosol particles. Particle volume concentration from SMPS was directly obtained by the SMPS measurement, and particle volume concentration from AMS was extracted by the measured particle mass concentration divide by composition dependent density.

Figure 2(c) in the manuscript is a time series of AMS and SMPS particle volume concentration and Figure S7-1 is a scatter plot of AMS and SMPS particle volume concentration. For ambient aerosol particles, the AMS and SMPS particle volume concentrations agree to within measurement uncertainties, but for the PAM aerosol particles, the SMPS volume concentration was greater than AMS volume concentration by a factor of 1.6. While this difference can be explained by the measurement uncertainties of the two instruments, it is also possible that elemental carbon and soil particles are being detected by the SMPS but not by the AMS. In ambient aerosol particles data for the organics-dominated episode, the AMS volume concentration was slightly greater than or similar to that of the SMPS, but in sulfate dominated episode, AMS volume concentration was smaller than that of the SMPS.



[Figure S7-1. Scatter plots of SMPS aerosol volume concentration and AMS aerosol volume concentration.]

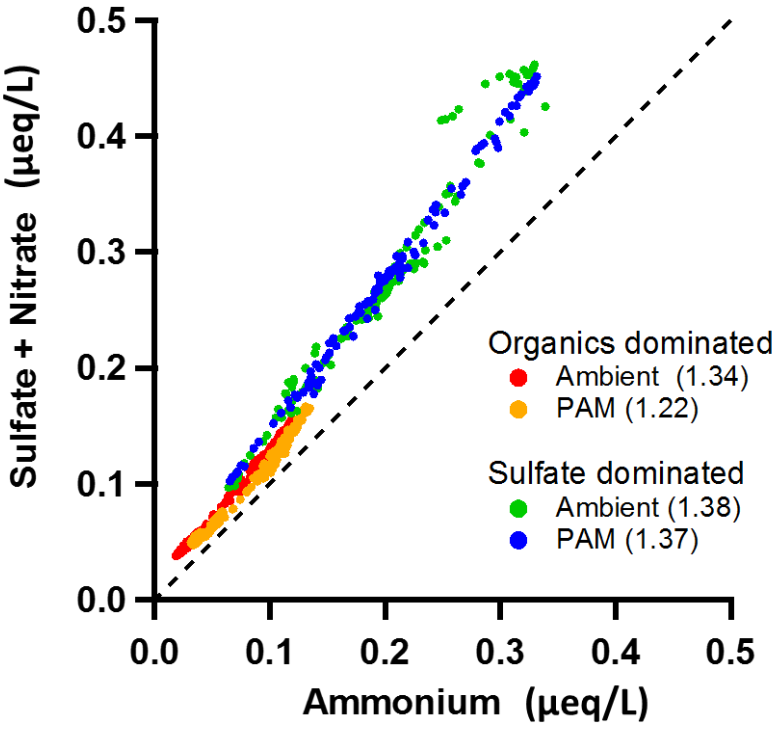
The mass concentration changes between the PAM aerosol particles and the ambient aerosol particles were determined for both the AMS and the SMPS (Figure S7-2). For most of the data, the SMPS mass concentration difference is equal to or slightly greater than the AMS mass concentration difference. However, there are also periods during which the AMS mass concentration difference is much less than the SMPS mass concentration difference. These discrepancies occur for days when the mass concentrations are greatest in the organic-dominated period and the sulfate-dominated period and thus do not depend on the origin of the aerosol particles. The reasons for these discrepancies are under investigation, but they do not affect our conclusions.



[Figure S7-2. The difference in mass concentrations between the PAM aerosol and ambient aerosol measured by SMPS and AMS. Data are averages for 6 minutes with 2σ confidence intervals.]

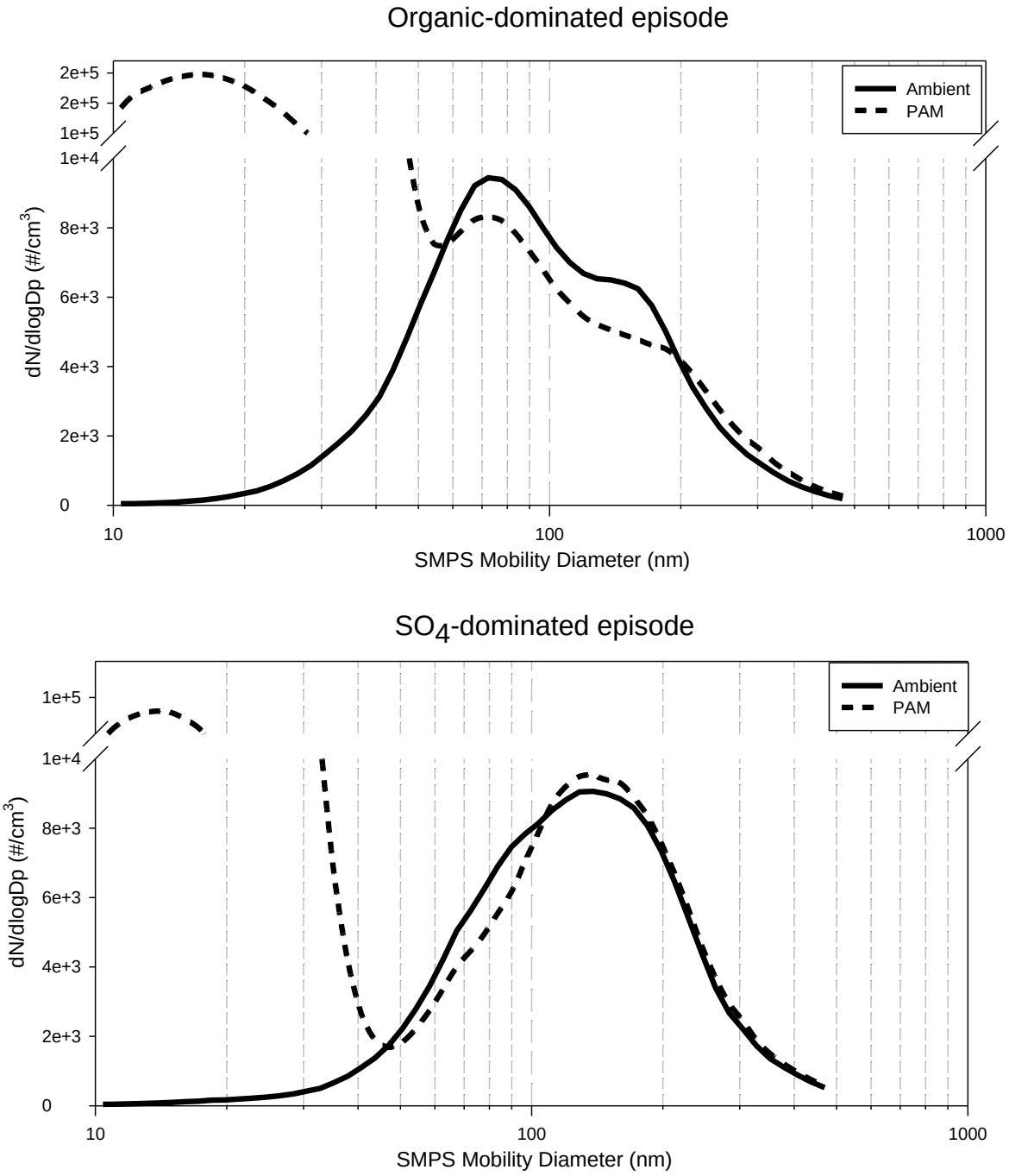
S8. Ammonium balance with sulfate and nitrate

We plotted the ammonium balance with sulfate and nitrate for ambient and PAM observation for each episode. The chloride concentration was under 0.4 μg m^{-3} which was less than 1/10 of nitrate concentration, thus we only used sulfate and nitrate. The inorganic aerosols were overall acidic, and the acidity in PAM aerosol was similar to ambient aerosol in sulfate dominated episode. It is because of the sulfate enhancement in sulfate dominated episode while nitrate in PAM reactor was depleted a lot than ambient nitrate. In organics dominated episode, both of sulfate and ammonium was enhanced in PAM reactor while nitrate was depleted. Thus, the acidity was rather decreased in PAM reactor.



[Figure S8. The normality balance of ammonium with sulfate and nitrate in ambient and PAM aerosol for organics dominated and sulfate dominated episodes. The numbers on the figure legend were the acidity of aerosols obtained from [sulfate+nitrate](µeq/L)/ammonium(µeq/L).]

Figure S9. Ambient and PAM particle size distribution for organic-dominated and sulfate-dominated episode. The dN/dlogDp (# cm^{-3}) of particles smaller than 50 nm in diameter for organic-dominated episode was about an order of magnitude greater than that for sulfate-dominated episode.



Salimi, F., Crilley, L. R., Stevanovic, S., Ristovski, Z., Mazaheri, M., He, C., Johnson, G., Ayoko, G., and Morawska, L.: Insights into the growth of newly formed particles in a subtropical urban environment, Atmos. Chem. Phys., 15, 13475-13485, https://doi.org/10.5194/acp-15-13475-2015, 2015.