Supplementary Materials

Heterogeneous Formation of Particulate Nitrate under Ammonium-rich Regime during the high $PM_{2.5}$ events in Nanjing, China

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Introduction

Table S1 lists the summarized information for $PM_{2.5}$ events occurred during the experimental periods. We also presented the rates and pathways of particulate NO_3^- formation in the thigh $PM_{2.5}$ events. Figure S1 shows the equivalent concentrations of cations and anions in $PM_{2.5}$ in Nanjing during the sampling periods. Figure S2 plots average concentrations of water-soluble inorganic ions in $PM_{2.5}$ during different seasons in Nanjing City. Figure S3 shows the theoretical and observed $P_{HNO3}\cdot P_{NH3}$

values during the sampling periods. Figure S4 illustrates scatter plots of NO_3^-, SO_4^{2-} and NH_4^+ against $PM_{2.5}$ mass in Nanjing City during the sampling periods. Figure S5 shows the scatter plot of NO_3^- vs. excess-NH_4^+ molar concentrations in Nanjing during the sampling periods.

In Table S1, we defined the $PM_{2.5}$ haze days with hourly $PM_{2.5}$ concentrations of exceeding 150 μg m^{-3} and the high $PM_{2.5}$ levels should be lasted more than 3 hours. During the high $PM_{2.5}$ events, the maximum formation rate of NO_3^- (F_{NO3-}) can be calculated as:

$$F_{NO3-} = \frac{([NO_3^-]_m - [NO_3^-]_i)}{[NO_3^-]_i\ \Delta h} / ([\mathrm{CO}]_m / [\mathrm{CO}]_i)$$

where $[NO_3^-]_i$ is the nitrate concentration at the initial time during the $PM_{2.5}$ event . $[NO_3^-]_m$ is the maximum nitrate concentrations during the $PM_{2.5}$ event. Both parameters are in units of μg m^{-3}. Δh (hours) denotes the duration between the initial time and the time when NO_3^- concentration reached the maximum value during the $PM_{2.5}$ event. $[CO]_m$ is the CO concentration when the NO_3^- concentration reach the maximum value during the $PM_{2.5}$ event. $[CO]_i$ is the CO concentration at the initial time during the $PM_{2.5}$ event. Both units of $[CO]_m$ and $[CO]_i$ are in units of ppm. Here, $[CO]_m/[CO]_i$ can be considered a dilution factor of the atmosphere.

Table S1 Summarized information for occurrence of high $PM_{2.5}$ events, formation rate and potential mechanisms for particulate NO_3^-.

Events	Time of occurrence	Formation rate of NO_3^- (% h^{-1})	Behaviors of AWLC and Ox	Potential mechanisms
2016				
Case I	3/3 18:00 – 3/4 03:00	5.5	ALWC and Ox Kept constant levels	$NO_2 + OH$ / $N_2O_5 + H_2O$
Case II	3/4 08:00 – 3/4 14:00	2.4	Decreasing ALWC and increasing Ox	$NO_2 + OH$
Case III	3/4 23:00 – 3/5 03:00	26.7	Increasing ALWC and decreasing Ox	$N_2O_5 + H_2O$
Case IV	3/5 14:00 – 3/5 21:00	15.4	Increasing ALWC and decreasing Ox	$N_2O_5 + H_2O$
Case V	3/6 09:00 – 3/6 20:00	2.5	Decreasing ALWC and increasing Ox	$NO_2 + OH$
Case VI	3/14 22:00 – 3/15 04:00	6.0	Increasing ALWC and increasing Ox	$NO_2 + OH$ / $N_2O_5 + H_2O$
Case VII	3/18 09:00-3/18 18:00	13.7	Increasing ALWC and decreasing Ox	$N_2O_5 + H_2O$
Case VIII	3/19 07:00 – 3/19 16:00	11.0	Decreasing ALWC and decreasing Ox	$NO_2 + OH$ / $N_2O_5 + H_2O$
Case IX	5/7 02:00 – 5/7 08:00	4.0	Increasing ALWC and decreasing Ox	$N_2O_5 + H_2O$
2017				
Case X	1/23 17:00 -1/23 21:00	10.4	Increasing ALWC and Ox kept constant levels	$N_2O_5 + H_2O$
Case XI	2/6 00:00 – 2/6 05:00	11.4	Increasing ALWC and Ox kept constant levels	$N_2O_5 + H_2O$
Case XII	2/13 22:00 – 2/14 06:00	6.7	Increasing ALWC and Ox kept constant levels	$N_2O_5 + H_2O$

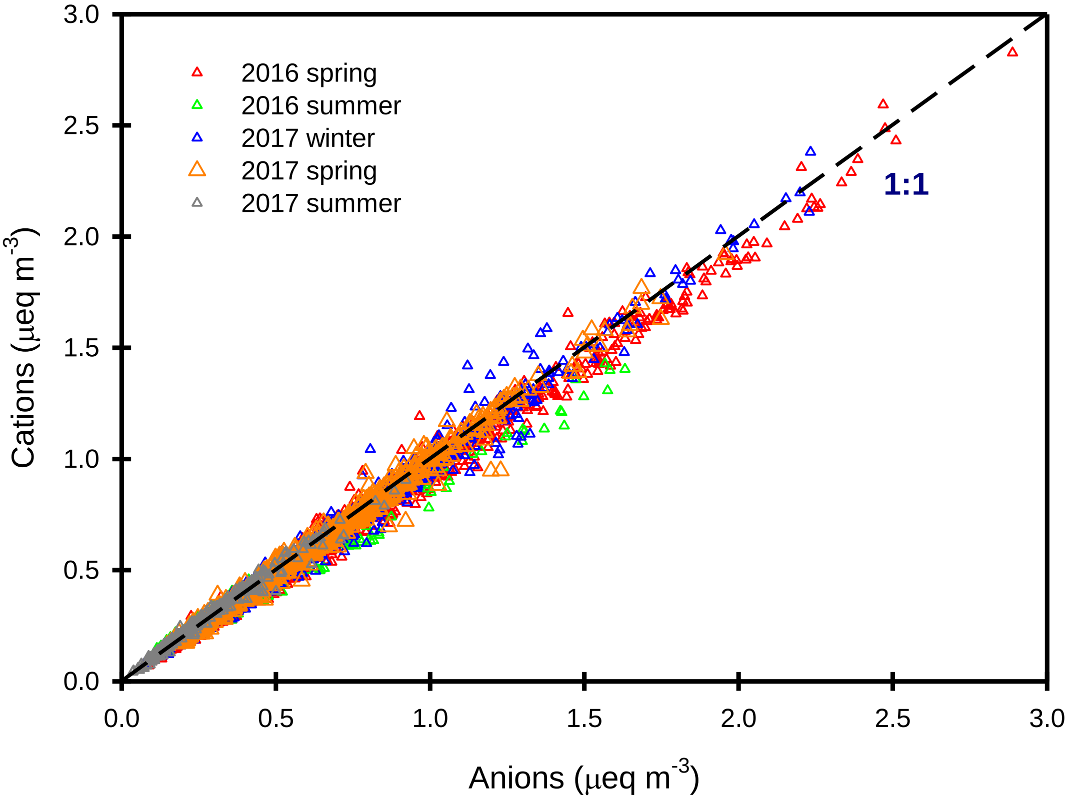

Figure S1 Equivalent concentrations of cations and anions in $PM_{2.5}$ in Nanjing during the sampling periods.

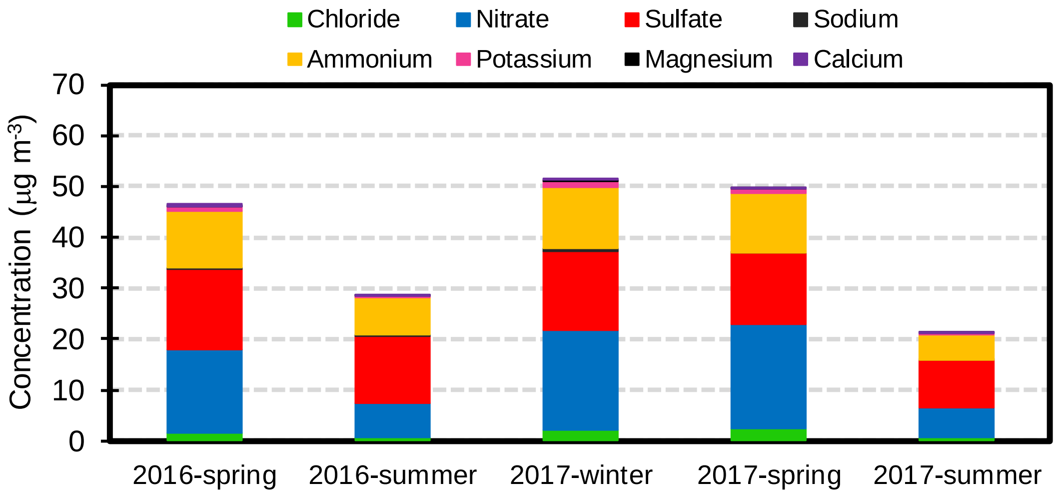

Figure S2 Average concentrations of water-soluble inorganic ions in $PM_{2.5}$ observed in Nanjing City during the different seasons.

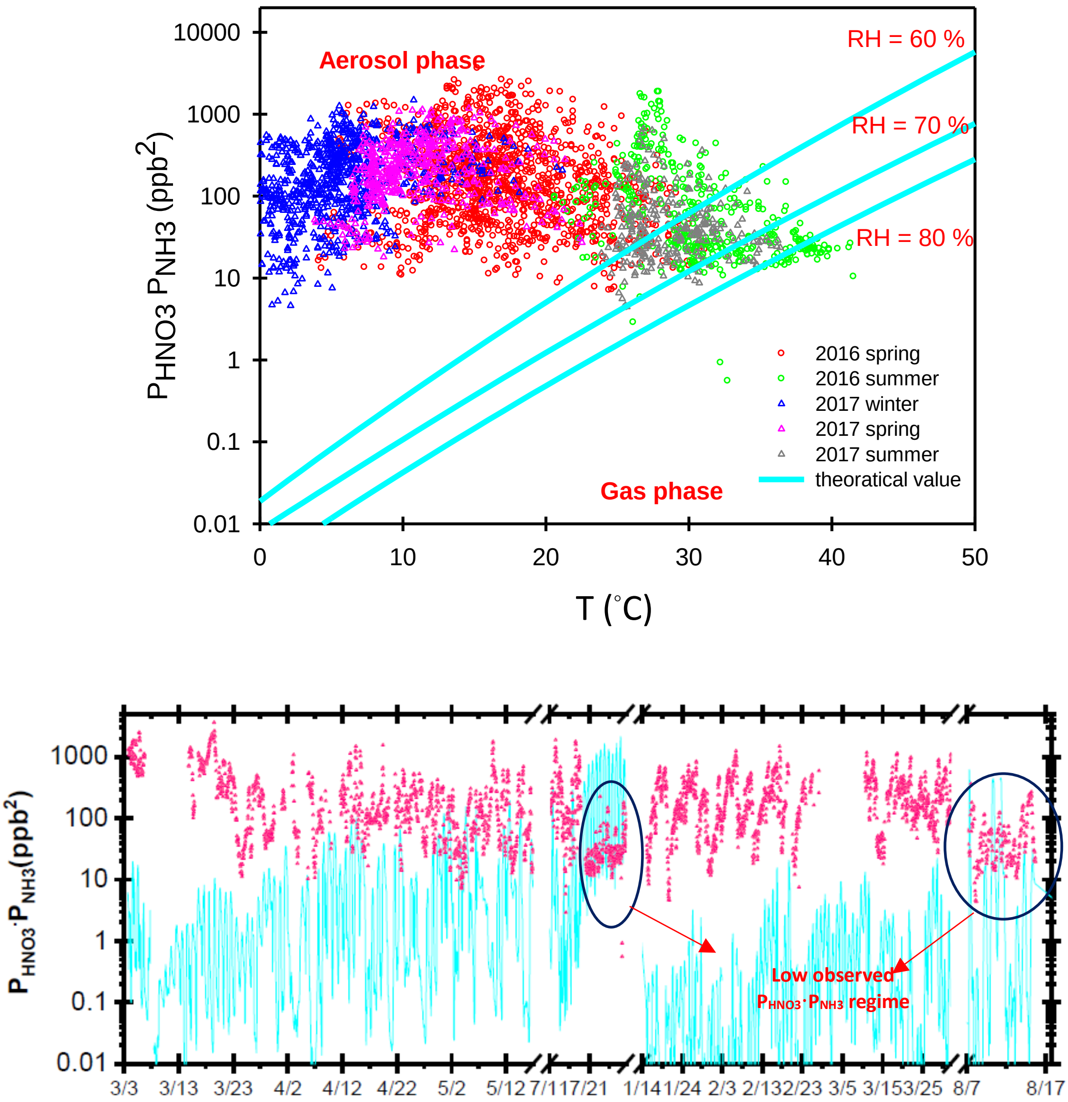

Figure S3 (a)Theoretical (solid lines) and observed (circles and triangles) equilibrium constants ($P_{HNO3}\cdot P_{NH3}$) of partitioned NO_3^- and NH_4^+ between aerosol and gas phase in different ambient temperature and relative humidity and (b) time series of theoretical (blue line) and observed $P_{HNO3}\cdot P_{NH3}$ values (pink dots) during the sampling periods.

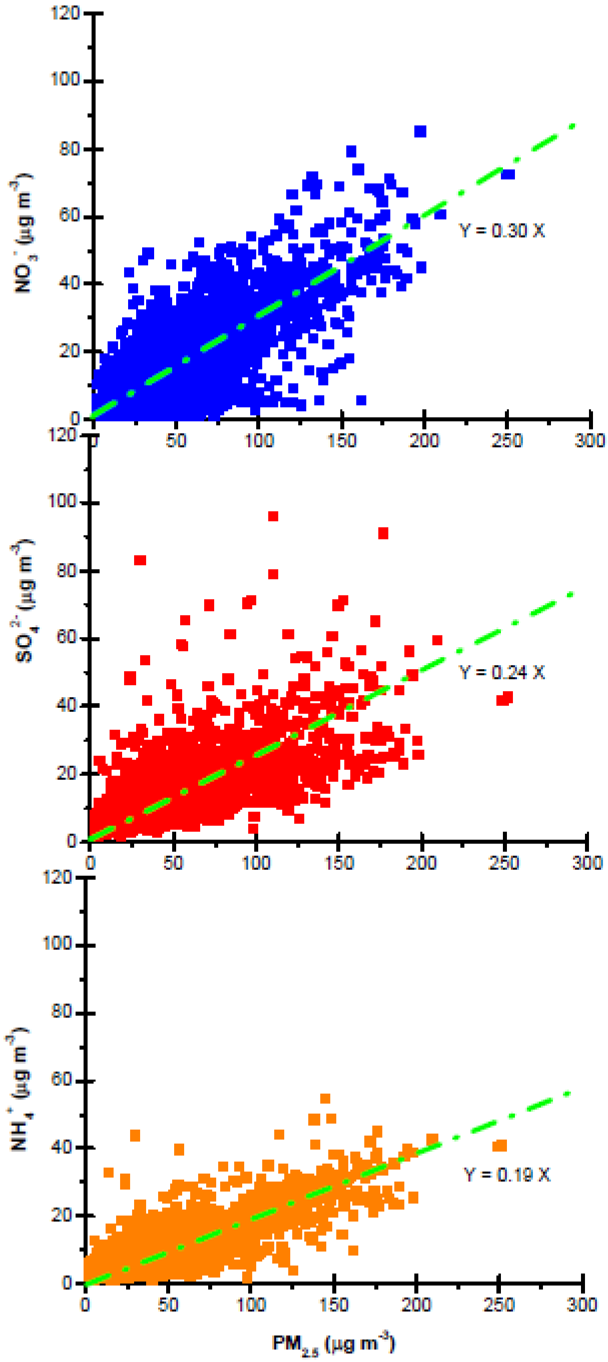

Figure S4 Scatter plots of NO_3^-, SO_4^{2-} and NH_4^+ against $PM_{2.5}$ mass in Nanjing City during the sampling periods.

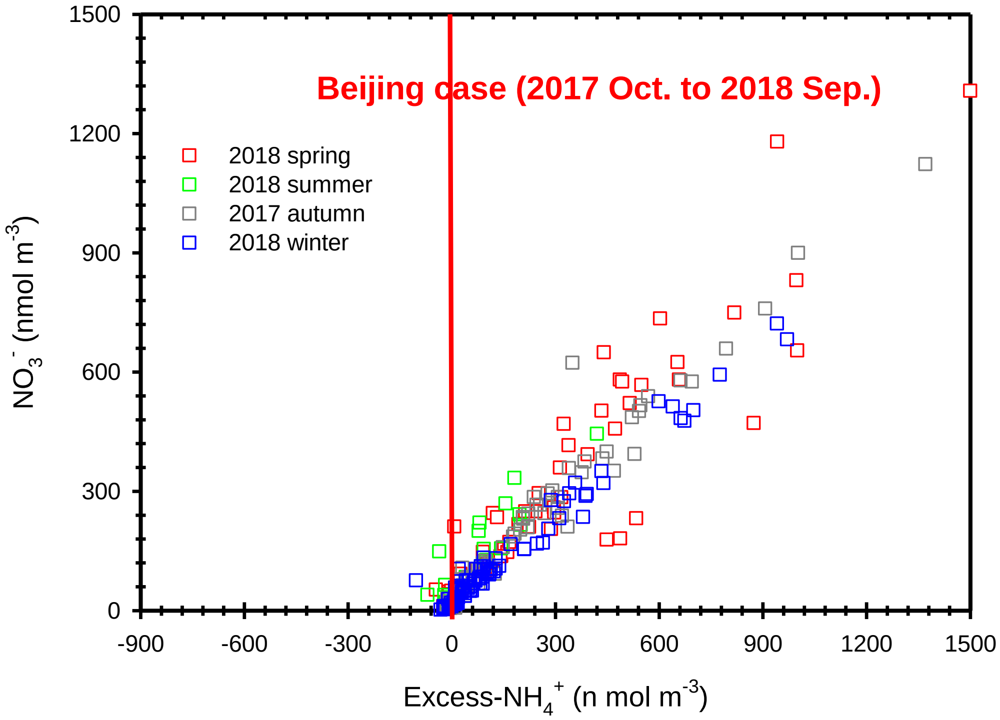

Figure S5 Scatter plot of NO_3^- vs. excess-NH_4^+ molar concentrations in Beijing from October 2017 to September 2018 (Dao et al., 2019).

References

Dao, X., Lin, Y.-C., Cao, F., Di, S.-Y., Hong, Y., Xing, G., Li, J., Fu, P., & Zhang, Y.-L. (2019). Introduction to the aerosol chemical composition monitoring network of China: objects, current status and outlook. *Bulletin of the American Meteorological Society*, accepted.