Supplementary Information for

Formation mechanisms of atmospheric nitrate and sulfate during the winter haze pollution periods in Beijing: gas-phase, heterogeneous and aqueous-phase chemistry

Pengfei Liu, Can Ye, Chaoyang Xue, Chenglong Zhang, Yujing Mu*, Xu Sun

This PDF file includes:

- M1. Sample analysis for WSIs, OC and EC.
- M2. Measurements for atmospheric H_2O_2 and HONO.
- M3. The Mass transport for multiphase reactions.
- Figure S1. The location of the sampling site.
- Figure S2. Time series of meteorological parameters (wind speed, wind direction, ambient temperature and RH), O_3 and $PM_{2.5}$ during the sampling period.
- Figure S3. The correlations between the concentrations of $PM_{2.5}$ and CO in the three cases during the sampling period.
- Figure S4. The average mass proportions of the species in $PM_{2.5}$ in the three cases during the sampling period.

Supplementary Information:

M1. Sample analysis for WSIs, OC and EC

As for the filter samples, half of each filter was extracted ultrasonically with 10 mL ultrapure water for 30 minutes. The supernatants were filtered by a type of microporous membrane (diameter, 13mm; pore size, 0.45 μm) and the WSIs in the filtrates were analyzed by an ion chromatography (Wayeal IC6200, China). Five cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) were separated through a cation column (TSKgelSuperIC-CR, 4.6 mm ID × 15 cm) with the solvent (2.2 mmol L^{-1} methane sulfonic acid and 1 mmol L^{-1} 18-crown-6) flow rate of 0.7 mL min^{-1} and column temperature of 40 °C. Four anions (Cl^-, NO_3^-, SO_4^{2-} and NO_2^-) were separated via an anion column (IC SI-52 4E, 4.0 mm ID × 25 cm) with the solvent (3.6 mmol L^{-1} sodium carbonate) flow rate of 0.8 mL min^{-1} and column temperature of 45 °C. The relative standard deviation (RSD) of each ion was not more than 0.5 % for the reproducibility test. The detection limits (S/N=3) were less than 1 μg L^{-1} for the cations and anions. At least three filter blanks were simultaneously analyzed for every 60 filter samples, and the mean blank values were about 30 μg L^{-1} for Na^+, Ca^{2+}, NO_2^-, NO_3^- and SO_4^{2-}, 20 μg L^{-1} for NH_4^+ and Cl^-, 10 μg L^{-1} for Mg^{2+} and K^+. All ion concentrations were corrected for the blanks.

A quarter of each filter was heated with temperature programming to 140 °C, 280 °C, 480 °C and 580 °C in the helium atmosphere for analyzing OC1, OC2, OC3 and OC4, respectively, and then to 580 °C, 780 °C and 840 °C in the atmosphere of 98 % helium and 2 % oxygen for analyzing EC1, EC2 and EC3, respectively, by using a thermal optical carbon analyzer (DRI-2001A). The pyrolyzed OC (POC) is defined as the carbon fraction that has combusted after the initial introduction of oxygen and before the laser reflectance signal returns its original value, and it is assigned to the OC fraction (Ma et al., 2016;Zhang et al., 2013). Then, OC = OC1 + OC2 + OC3 + OC4 + POC and EC

= EC1 + EC2 + EC3 – POC. The method calibration was performed with a concentration gradient of KHP standards (R^2 = 0.9997, N=5). A replicate sample was detected for every 10 filter samples, and the RSD of OC and EC was less than 5 %. The detection limits were 0.82 μgC cm^{-2} and 0.20 μgC cm^{-2} for OC and EC, respectively.

M2. Measurements for atmospheric H_2O_2 and HONO

Atmospheric H_2O_2 was measured by a wet liquid chemistry fluorescence detector (AL 2021; AERO laser, Germany). When atmospheric H_2O_2 is stripped by a faintly acid solution (pH = 5.8-6.0), organic peroxides are simultaneously detected by the catalysis of the horseradish peroxidase and then the reaction with *p*-hydroxyphenyl-acetic acid. In order to divide between H_2O_2 and organic peroxides, two channels are designed and H_2O_2 is selectively destroyed by catalase prior to the detection of fluorescence in one channel. Thus, the difference of the signal between the two channels can represent the H_2O_2 concentration. The calibrations were performed with liquid H_2O_2 standards (33.3 μg L^{-1}) for both channels in every 1-3 days. There is an uncertainty of 10 %, a calibration RSD of 0.25 %, a detection limit of less than 50 ppt and a noise of less than 2 % at full scale for the H_2O_2 monitor. Although some organic peroxides such as $HOCH_2OOH$ and $CH_3C(O)OOH$ have been found to decompose into H_2O_2 in the collection solution at pH > 5 (O'Sullivan, 1996), their decomposition to H_2O_2 during the short period of the sampling progress could be neglected due to their relatively slow hydrolysis rate (1−2 days) (O'Sullivan, 1996) and extremely low atmospheric concentrations (He et al., 2010).

Atmospheric HONO was measured by a wet chemical method that is named after stripping coil (SC) equipped with ion chromatograph (IC) and was described in detail by our previous studies (Xue et al., 2019a;Xue et al., 2019b). Briefly, hourly HONO samples were absorbed by ultrapure

water in the SC with the gas flow rate of 2 L min^{-1} and the absorption solution flow rate of 0.2 mL min^{-1}. After sampling, the liquid samples were stored in a refrigerator around 4 °C and then analyzed by IC in three or four days. The flow calibrations including the gas and liquid were performed once a day, and the collection efficiency was more than 90 % and the correlations between the SC-IC and other techniques were close to 0.9 (slope = 0.94~1.06) (Xue et al., 2019a).

M3. The Mass transport for multiphase reactions

The formula of a standard resistance model was adopted for evaluating the effects of mass transport (Seinfeld and Pandis, 2006):

$$\frac{1}{R_{S,aq}} = \frac{1}{R_{aq}} + \frac{1}{L_{aq,lim}} \quad \text{(S-R1)}$$

where $R_{S,\,aq}$ is the sulfate production rate, R_{aq} is the aqueous-phase reaction rate of oxidants which could be calculated by the equations of R1-R4, and $L_{aq,\,lim}$ is the limiting mass transfer rate (M s^{-1}) which could be calculated by the formulas as follows (Seinfeld and Pandis, 2006):

$$L_{aq,lim} = min\{L_{aq}(SO_2), L_{aq}(O_{xi})\} \quad \text{(S-R2)}$$

$$L_{aq}(X) = k_{MT}(X) \cdot [X] \quad \text{(S-R3)}$$

where [X] represents the aqueous-phase concentrations of SO_2 or the oxidants O_{xi} such as O_3, H_2O_2 and NO_2, which could be calculated based on Henry's law (R5-R7). The mass transfer rate coefficient $k_{MT}(X)$ (s^{-1}) is expressed by the equations as follows (Seinfeld and Pandis, 2006):

$$k_{MT}(X) = [\frac{R^2}{3D} + \frac{4R}{3\alpha v}]^{-1} \quad \text{(S-R4)}$$

where R is the aerosol radius (0.15 μm), D is the gas-phase molecular diffusion coefficient (0.2 $cm^2\ s^{-1}$ at 293 K), v is the average molecular speed (3×10^4 cm s^{-1}), and α is the mass accommodation coefficient (0.11, 0.23, 2×10^{-3} and 2×10^{-4} for SO_2, H_2O_2, O_3 and NO_2, respectively) on the droplet surface (Jacob, 2000;Seinfeld and Pandis, 2006).

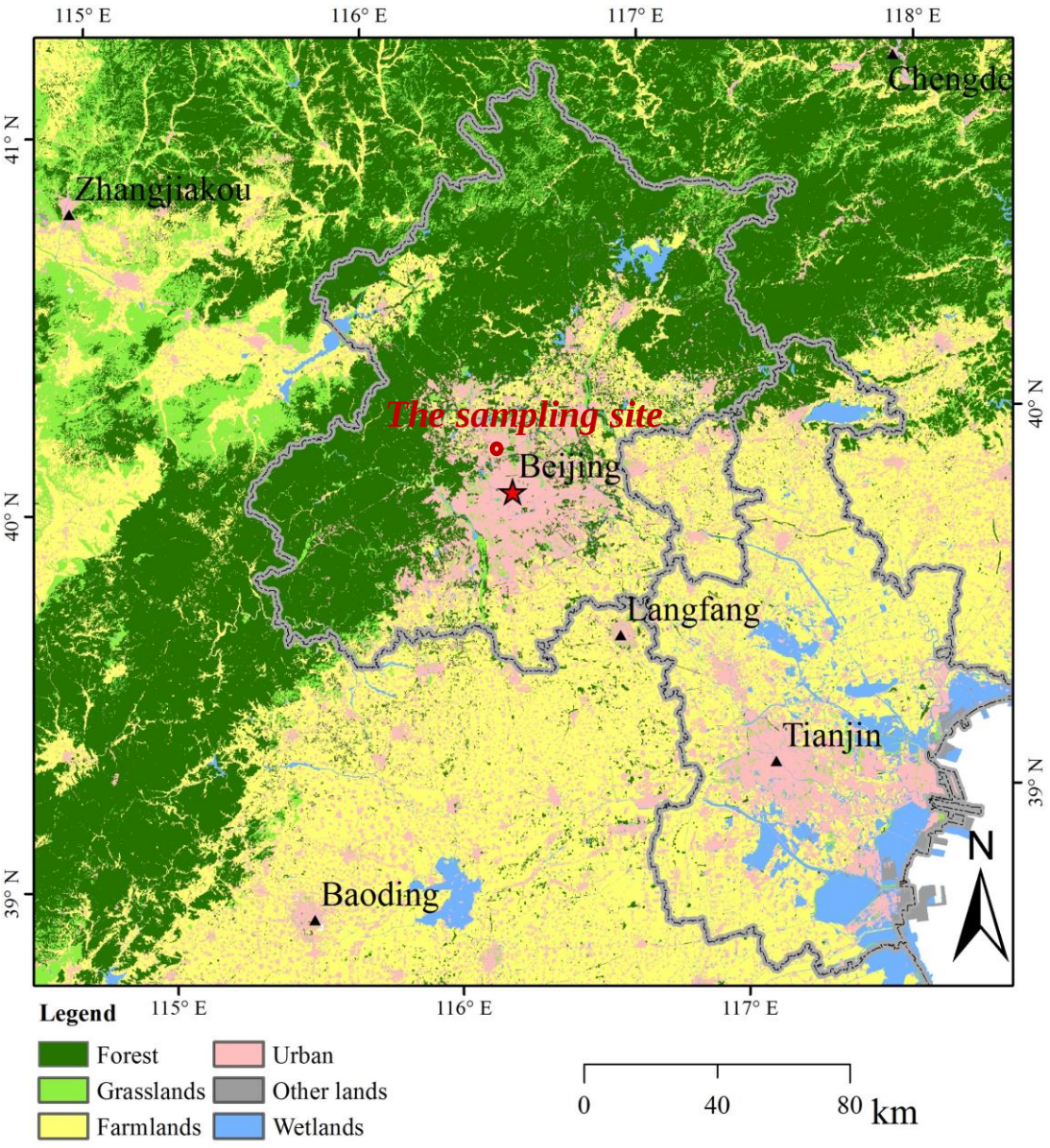

Figure S1. The location of the sampling site.

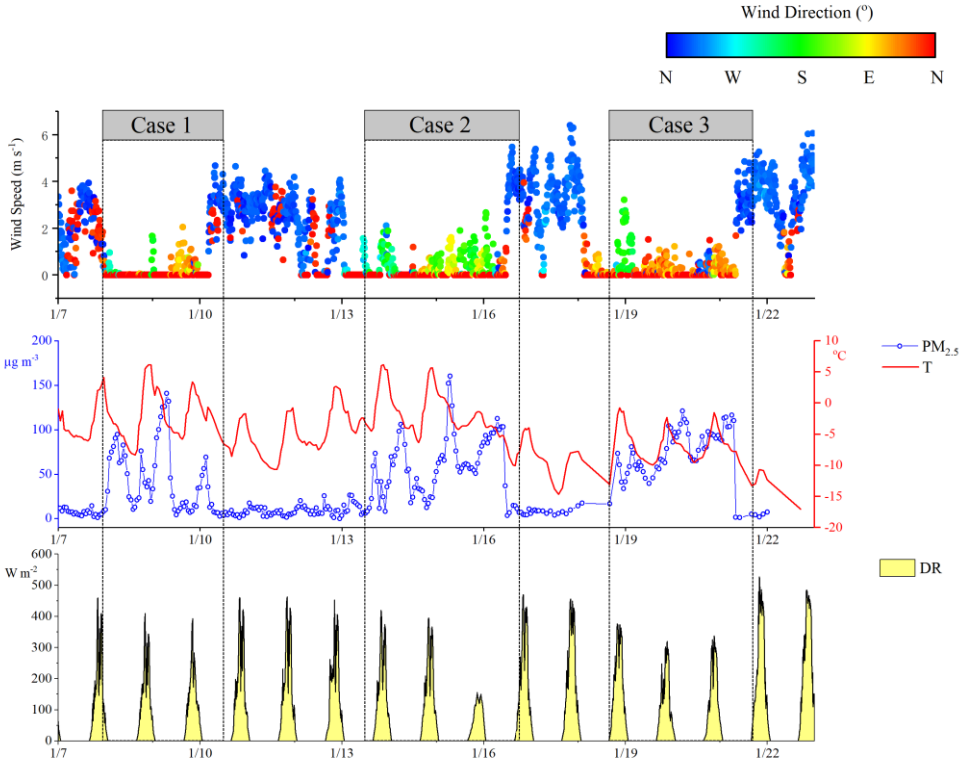

Figure S2. Time series of meteorological parameters (wind speed, wind direction, ambient temperature and DR) and $PM_{2.5}$ during the sampling period.

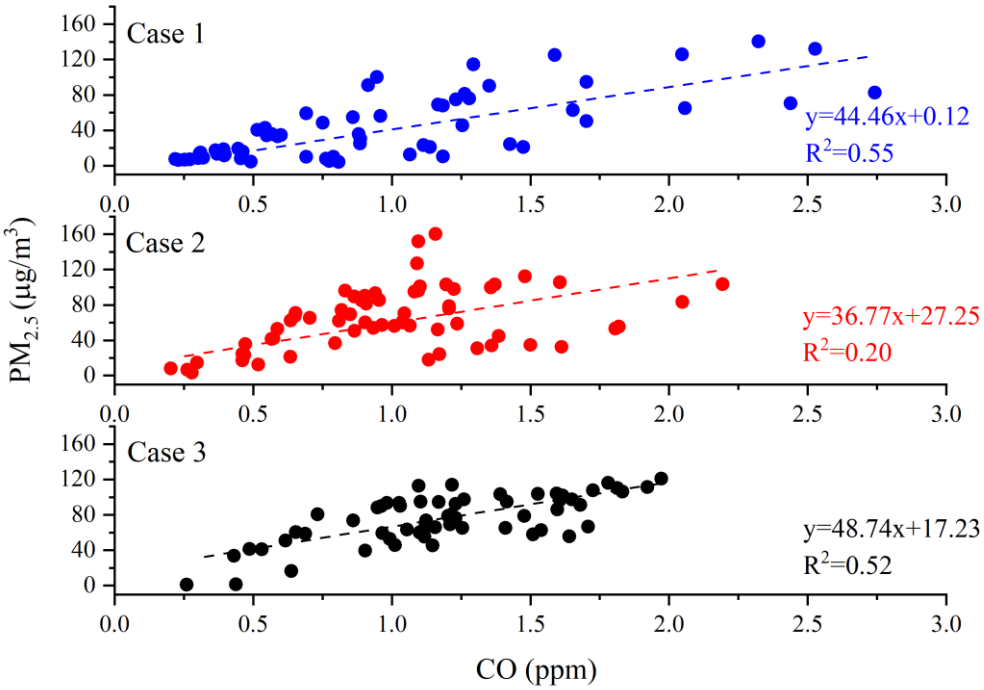

Figure S3. The correlations between the concentrations of $PM_{2.5}$ and CO in the three cases during the sampling period.

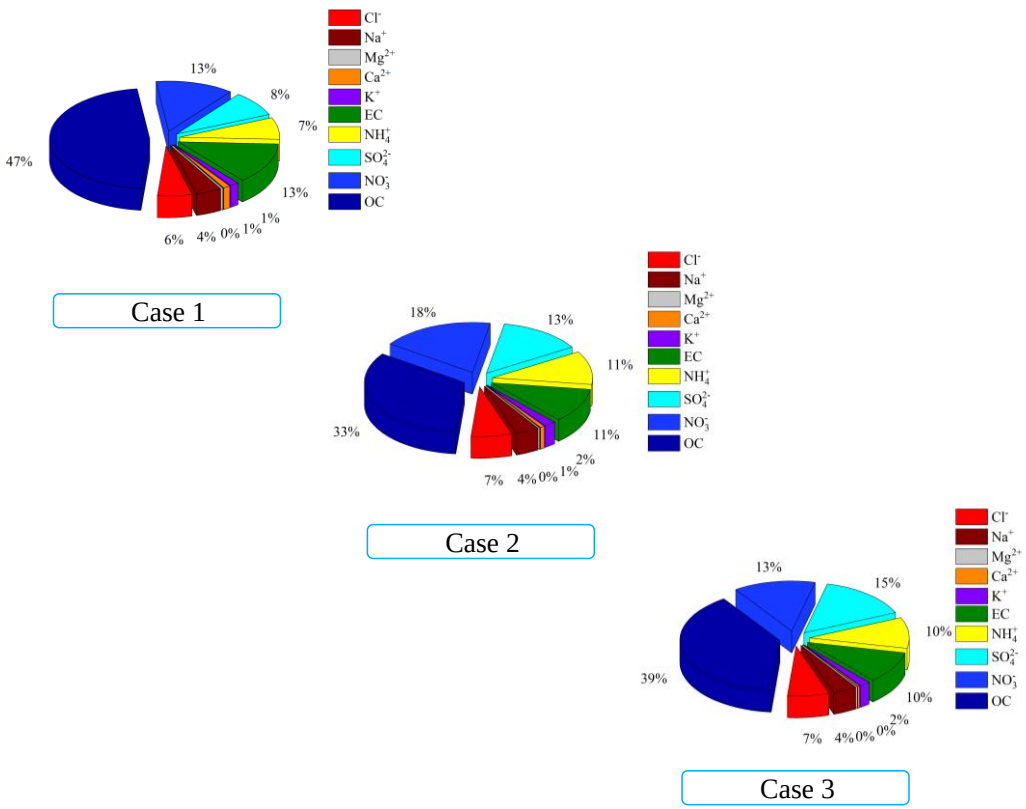

Figure S4. The average mass proportions of the species in $PM_{2.5}$ in the three cases during the sampling period.

References

He, S. Z., Chen, Z. M., Zhang, X., Zhao, Y., Huang, D. M., Zhao, J. N., Zhu, T., Hu, M., and Zeng, L. M.: Measurement of atmospheric hydrogen peroxide and organic peroxides in Beijing before and during the 2008 Olympic Games: Chemical and physical factors influencing their concentrations, Journal of Geophysical Research, 115, 10.1029/2009jd013544, 2010.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmospheric Environment, 34, 2131-2159, 2000.

Ma, X., Wu, J., Zhang, Y., Bi, X., Sun, Y., and Feng, Y.: Size-Classified Variations in Carbonaceous Aerosols from Real Coal-Fired Boilers, Energy & Fuels, 30, 39-46, 10.1021/acs.energyfuels.5b01770, 2016.

O'Sullivan, D. W. J. J. o. P. C.: Henry's Law Constant Determinations for Hydrogen Peroxide, Methyl Hydroperoxide, Hydroxymethyl Hydroperoxide, Ethyl Hydroperoxide, and Peroxyacetic Acid, 100, 3241-3247, 1996.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics, from Air Pollution to Climate Change, Wiley, 429-443 pp., 2006.

Xue, C., Ye, C., Ma, Z., Liu, P., Zhang, Y., Zhang, C., Tang, K., Zhang, W., Zhao, X., Wang, Y., Song, M., Liu, J., Duan, J., Qin, M., Tong, S., Ge, M., and Mu, Y.: Development of stripping coil-ion chromatograph method and intercomparison with CEAS and LOPAP to measure atmospheric HONO, The Science of the total environment, 646, 187-195, 10.1016/j.scitotenv.2018.07.244, 2019a.

Xue, C., Ye, C., Zhang, Y., Ma, Z., Liu, P., Zhang, C., Zhao, X., Liu, J., and Mu, Y.: Development and application of a twin open-top chambers method to measure soil HONO emission in the North China Plain, Sci. Total Environ., 659, 621-631, 10.1016/j.scitotenv.2018.12.245, 2019b.

Zhang, R., Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of $PM_{2.5}$ in Beijing: seasonal perspective, Atmospheric Chemistry and Physics, 13, 7053-7074, 10.5194/acp-13-7053-2013, 2013.