

Response to the reviewer's comment

(Manuscript No. ACP-2019-752)

Reviewer #2

1st comment

This manuscript “Heterogeneous Formation of Particulate Nitrate under Ammonium rich Regime during the high PM_{2.5} events in Nanjing, China” by Lin et al. investigates the formation of nitrate under polluted conditions. The conclusion on the importance of the heterogeneous formation of nitrate is drawn from the good linear relationship between the nitrogen conversion ratios (Fn) and aerosol liquid water (ALW), in contrast to the poor correlation between nitrate and Ox. However, good linear relationship does not necessarily correspond to a causal relationship between the two variables. This is particularly true for the semi-volatile nitrate, the partitioning of which between gas and particle-phases is also associated with other factors such as temperature and RH. The morning peak of nitrate as reported in this manuscript (Fig. 4) could be caused by the photo-chemical production of nitrate after sun rise and the subsequent condensation on pre-existing particles before the temperature increases and RH decreases afterwards. Also, regional transport should be considered. In particular, the evaporation and re-condensation of nitrate during transport could also result in an increase of nitrate in the morning, coinciding with increase of ALW. Apart from the major issues mentioned above, there are several parts of the manuscript that need better interpretation or clarification as can be seen below.

Author's response:

Thanks for the reviewer's comment. In terms of this comment, we gave the responses as follows:

(1) Gas-phase oxidation (step1: $\text{NO}_{2(g)} + \text{OH}_{(g)} \rightarrow \text{HNO}_{3(g)}$, step2: $\text{HNO}_{3(g)} + \text{NH}_{3(g)} \rightarrow \text{NH}_4\text{NO}_{3(s,aq)}$) and heterogeneous reaction ($\text{N}_2\text{O}_{5(g)} + \text{H}_2\text{O}_{(g)} \rightarrow 2\text{HNO}_{3(aq)}$) are important

mechanisms of particulate nitrate formation. In gas-phase oxidation, the reaction rate constant of step 1 is $2.4 \times 10^{-11} (T/300)^{-1.3}$, which depends on ambient temperature (T) (Seinfeld and Pandis, 1998). Assuming the concentrations of NO_2 and OH are, respectively, 100 ppb and 10^6 molecules cm^{-3} (the typical values in the atmosphere in China), we then obtain the production rate of HNO_3 in a range of 4.5-5.2 ppb h^{-1} as the T is between 0°C (273°K) and 30°C (303°K) (see the figures in this response). However, assuming NO_2 concentration is 100 ppb and T is 25°C , we can find that the HNO_3 formation rate increased from 0.9 ppb h^{-1} ($\text{OH}=2 \times 10^5$ molecules cm^{-3}) to 23.8 ppb h^{-1} ($\text{OH}=8 \times 10^6$ molecules cm^{-3}). Obviously, OH seems to be the major factor affecting on HNO_3 production rather than T in step 1 in gas-phase oxidation reaction. In step 2, the production of nitrate particles is very sensitive to T and RH (Lin et al., 2007). For heterogeneous process, ALWC is an important factor to induce formation of liquid HNO_3 (Brown and Stutz, 2012, Chem. Soc. Rev.).

Without modeling and isotope techniques, the correlation analysis between nitrogen conversion ratio (Fn or nitrogen oxidation ratio, NOR) and other parameters (Ox, RH and ALWC) were commonly used to discuss whether gas-oxidation or heterogeneous process is a possible formation mechanism of particulate nitrate (Kohder, 2002, AE; Jansen et al., 2014, AE; Quan et al., 2015, AE). Fn is defined as the conversion ratio of NO_2 to HNO_3 (total nitrate in the text). As mentioned above, the conversion from NO_2 to HNO_3 is mainly influenced by OH, and ALWC. Therefore, we employed correlation analysis between Fn and Ox (proxy of OH) and ALWC to study the potential pathways of nitrate production; the result showed that Fn correlated well with ALWC. Apart from correlation analysis, we also selected twelve $\text{PM}_{2.5}$ episode cases to explore the variations of the concentrations of nitrate, Ox and ALWC. We found most of enhanced nitrate coincided with increasing ALWC and decreasing Ox. Thus, we concluded that heterogeneous process might be a major formation mechanism of

nitrate formation in Nanjing during the high-PM_{2.5} events ([lines 382-388 on page 15](#), [lines 389-394 on page 16](#), [lines 399-414 on page 16](#), [lines 415-440 on page 17](#) and [lines 441-448 on page 18](#)).

(2) We agreed the reviewer's comment, that is, the partition of NH₄NO₃ (semi-volatile-nitrate) between gas- and particle-phase is very sensitive to T and RH. However, F_n means the formation ratio of NO₂ to total nitrate. In other words, F_n is used to evaluate the capability of NO₂ to HNO₃ prior forming nitrate particles. As mentioned above, F_n is mainly affected by OH and ALWC through different production processes. Consequently, we used the correlation analysis between F_n vs. Ox and F_n vs. ALWC to explore the formation mechanisms of HNO₃ (also reflected the pathway of nitrate aerosol formation).

(3) As our observed data, high nitrate concentrations were found between 3 a.m. and 7 a.m.. The high nitrate concentrations in the early morning might be caused by the nitrate formation via heterogeneous reaction in the dark, and gas-phase oxidation after sunrise and the subsequent condensation on pre-existing particles before the temperature increased and RH decreased afterwards. Moreover, the lower planet boundary layer (PBL) might be another reason for enhanced nitrate in the early morning. In the revised manuscript, we have rephrase the sentences in [lines 239-244 on page 10](#).

(4) Regional transported air pollution would induce haze formation in China and is an important scientific issue. Nevertheless, it is very difficult to differentiate local and regional transported nitrate based on observations. The potential source contribution function (PSCF) is a method for identifying source region of air pollutants based on the HYSPLIT model. It is also commonly used to differentiate long-range transported air pollution from local air pollution based on observations combining with backward trajectories (Zhang et al., 2013, ACP; Hui et al., 2018, AE). The details of definition and calculation of PSCF are written in [lines 158-179](#).. To compute PSCF, the 80

percentile value of nitrate concentration was selected as the “high nitrate pollution” threshold. The results showed that the hotspots (red color) of nitrate are shown in the vicinity of Nanjing, suggesting that high nitrate pollution at the receptor site might not be contributed by long-range transported air pollution, but was likely contributed by local emissions (lines 275-284 on page 11 and lines 285-287 on page 12). In this work, the influences of ambient T, RH and long-range transported nitrate on Fn can be neglected (mentioned above). Consequently, we still used the correlation analysis between Fn and Ox (ALWC), and the variations of concentrations in NO_3^- , O_x and ALWC to investigate the formation mechanisms of particulate nitrate during the high $\text{PM}_{2.5}$ events.

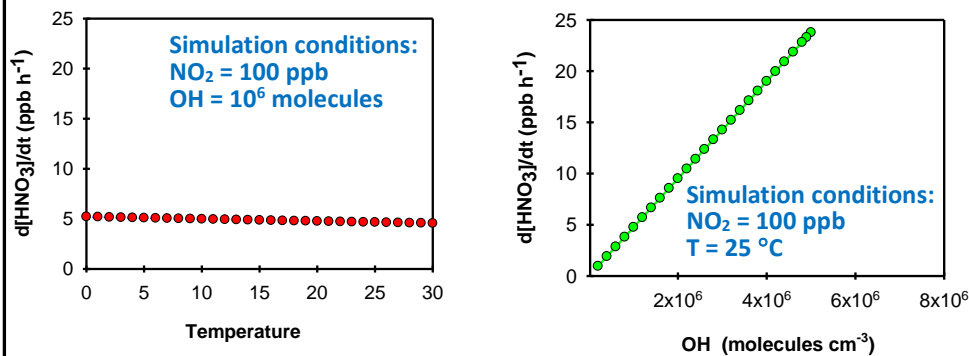


Figure The HNO_3 production rate of gas-oxidation depending on temperature and OH concentrations.

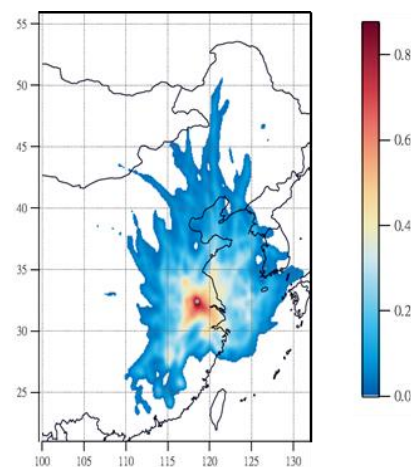


Figure 4 The PSCF maps of high nitrate pollution.

Specific comments:

2nd comment

Line 33-35. What is the absolute production rate? Please provide both $\mu\text{g m}^{-3} \text{ h}^{-1}$ and $\% \text{ h}^{-1}$.

Author's response:

As suggested, we have provided the production rate of particle nitrate in both units of $\mu\text{g m}^{-3} \text{ h}^{-1}$ and $\% \text{ h}^{-1}$ in the revised manuscript. During the sampling periods, a total of twelve high $\text{PM}_{2.5}$ events were found. Seven episodes suggested that heterogeneous processes were the major pathway of nitrate formation and two episodes indicated that gas-oxidation was the dominant formation mechanism of nitrate. On average, the production rate of nitrate aerosols via heterogeneous reaction was $12.6 \pm 7.3 \% \text{ h}^{-1}$ ($4.1 \pm 3.6 \mu\text{g m}^{-3} \text{ h}^{-1}$), which was 5 times higher than that by gas-oxidation reaction ($2.5 \pm 0.1 \% \text{ h}^{-1}$, $0.8 \pm 0.3 \mu\text{g m}^{-3} \text{ h}^{-1}$). (lines 34-36 on page 2, lines 448-450 on page 18 and Table S1)

3rd comment

Line 146-148. It is not clear what are the inputs for the ISORROPIA II model. Why use “forward” instead of “backward” mode? One should acknowledge the uncertainty of this model. Specifically, is organics causing uncertainty in the model?

Author's response:

Thanks for the reviewer's comment. ISORROPIA II is one of models to estimate aerosol liquid water content (ALWC) and has been widely used in many studies (Fountoukis and Nenes, 2007, ACP; Bian et al., 2014, ACP; Guo et al., 2015, ACP; Liu et al., 2017, GRL). The input of ISORROPIA II includes the concentrations of the observed total nitrate ($\text{HNO}_3 + \text{NO}_3^-$), total ammonium ($\text{NH}_3 + \text{NH}_4^+$), total chloride ($\text{HCl} + \text{Cl}^-$), SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+} along with measured ambient T and RH.

Two modes, such as “forward” and “reverse”, can be selected under the different input conditions. “forward” problem is always used when the quantity of ambient temperature and relative humidity along with the total concentrations (gas + aerosol) of NH_4^+ , Cl^- , NO_3^- , and aerosol concentrations of SO_4^{2-} , Na^+ , Ca^{2+} , K^+ and Mg^+ are known. On the contrary, ISORROPIA II also offers the ability to solve the “reverse problem”, in which known quantities are the concentrations of NO_3^- , SO_4^{2-} , Cl^- , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} in the aerosol phase together with ambient T and RH. In this work, we employed an online MAGAR instrument to monitored water-soluble inorganic ions in the aerosol phase and SO_2 , HNO_3 , HCl and NH_3 concentrations. We also obtained the data of ambient T and RH. Therefore, we selected the “forward” mode in ISORROPIA II model; the observed concentrations of total nitrate ($\text{HNO}_3 + \text{NO}_3^-$), total ammonium ($\text{NH}_3 + \text{NH}_4^+$), total chloride ($\text{HCl} + \text{Cl}^-$), SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+} along with measured ambient T and RH served as input of this model ([lines 143-155 on page 6 and line 156 on page 7](#)). The earlier study suggested that ISORROPIA II model can fit ALWC very well with the uncertainty of 13-20 % (Fountoukis and Nenes, 2007, ACP; Bian et al., 2014, ACP; Guo et al., 2015, ACP; Liu et al., 2017, ACP). Organic aerosols are not taken into account in ISORROPIA II model and some organic species contribute water content in aerosols. According to the results by Bougiatioti et al. (2016, ACP), ALWC would be underestimate about 28 % without considering organic aerosols. ([lines 143-148 on page 6](#))

4th comment

Line 179-180. Please provide correlation coefficient here.

Author's response:

The correlation coefficients between cation and anion were in a range of 0.98-0.99. As suggested, we have provided correlation coefficient in the revised manuscript. ([lines](#)

5th comment

Line 198-200. It is not clear how the theoretical equilibrium constants were derived? I saw large disagreement between the theoretical and observed values in every season in Fig. S3.

Author's response:

Thanks for the reviewer's comment. The reaction of $\text{HNO}_3 + \text{NH}_3$ is one of the pathway to produce particulate NH_4NO_3 . In the reaction of $\text{HNO}_{3(\text{g})} + \text{NH}_{3(\text{g})} \rightarrow \text{NH}_4\text{NO}_{3(\text{s, aq})}$, the theoretical equilibrium constant between gaseous HNO_3 and NH_3 and particle NH_4NO_3 (k_2 in the main text) can be calculated as (Mozurkewich, 1993, AE):

$$\ln(k_2) = 118.87 - \frac{24084}{T} - 6.025 \ln(T)$$

where T is ambient temperature with a unit of °K. As the relative humidity ($a_w = \text{RH}/100$) is greater than the deliquescence relative humidity of NH_4NO_3 , the influence of RH on k_2 should be considered. Thus, k_2 should be replaced by k_2' , namely:

$$k_2' = (P_1 - P_2(1 - a_w) + P_3(1 - a_w)^2) \times (1 - a_w) \times (1 - a_w)^{1.75} \times k_2$$

where

$$\ln(P_1) = -135.94 + \frac{8763}{T} + 19.12 \ln(T)$$

$$\ln(P_2) = -122.65 + \frac{9969}{T} + 16.22 \ln(T)$$

$$\ln(P_3) = -182.61 + \frac{13875}{T} + 24.46 \ln(T)$$

Using an appropriate expression for the temperature and relative humidity dependence of NH_4NO_3 thermodynamic properties, the equilibrium constant can be calculated at a specific temperature and relative humidity. Apart from theoretical equilibrium

constants, we also have observed equilibrium constants which were derived by the products of observed total nitrate ($\text{HNO}_3 + \text{NO}_3^-$) and total ammonium ($\text{NH}_3 + \text{NH}_4^+$). If the observed equilibrium constants were higher than the theoretical ones, indicating NH_4NO_3 would be produced (see in [supplementary S1](#)), otherwise the nitrate and ammonium should be partitioned into gas-phase. As shown in Figure S4b, most of the observed equilibrium constants were higher than the theoretical ones, suggesting that NH_4NO_3 was formed during the most sampling periods. However, the lower observed and higher theoretical equilibrium constants were found during the summer periods. This could partly explain the lower nitrate (or lower NH_4NO_3) concentrations during the hot seasons ([lines 229-232 on page 9 and lines 233-235 on page 10](#)).

6th comment

Line 266-268. Negative values of excess NH_4^+ means deficit instead of excess. Please reword here.

Author's response:

As suggested, we have changed the sentence of “The results revealed that and only 1 % of the excess- NH_4^+ data were lower than zero, reflecting....” to “The results revealed that and only 1 % of data showed deficit- NH_4^+ conditions, reflecting....” in [line 318 on page 13](#).

7th comment

Line 257-259. It is not clear how the criteria values were derived from the linear regression model. Is it the intercept or slope?

Author's response:

Thanks for the reviewer's comment. The criteria value can be calculated as the absolute value of intercept dividing by the slope in each linear regression model (He et al., 2012).

(lines 309-310 on page 12)

8th comment

Line 302-306. Why not correct for background values for the calculation of Fn. Background values could have a big effect on Fn, leading to large uncertainties. Also, the diffusion rate or the distribution of gas and particles are different.

Author's response:

Thanks for the reviewer's comment. Actually, Fn means nitrogen conversion ratio during each aerosol sampling duration time. Thus, we used the concentrations of NO_3^- , HNO_3 and NO_2 obtained in each sample to calculate the Fn values.

9th comment

Line 310-312. Please explain why they are comparable, and why higher than other sites rather than just comparison of values.

Author's response:

Thanks for the reviewer's comment. In this work, the conversion ratio of nitrogen (Fn) was 0.14, which was comparable to that (0.17) in Taichung city of Taiwan where both gas-oxidation and heterogeneous reaction were dominant formation mechanisms of atmospheric HNO_3 (or NO_3^-). However, our Fn value was 2.3 time higher than that (0.06) in Dokki, Egypt (Khoder, 2002, AE). The reason of significant discrepancy of Fn between this work and that in Dokki was not clearly understood, but it might be attributed to different formation processes of HNO_3 . In Dokki, gas-phase oxidation was the dominant pathway of HNO_3 production while heterogeneous process (R3) played an important role in HNO_3 formation in addition to gas-phase oxidation in Nanjing, especially during the high- $\text{PM}_{2.5}$ events. The production rate of HNO_3 by heterogeneous process was much higher than that by gas-phase oxidation. Consequently, the Fn value

was much higher in this study (lines 360-362 on page 14 and lines 363-371 on page 15).

10th comment

Line 318-319. You are saying nitrate was totally formed from gas phase reaction during the day-time. Then, where does nitrate go during the night? It disappears or is transported to downwind sites? If transported, then, the nitrate transported from your upwind site could reach your sampling site in the evening?

Author's response:

Thanks for the reviewer's comment. In this sentence, the total nitrate does not mean nitrate concentration, but means the concentrations of "total nitrate" ($\text{HNO}_3 + \text{NO}_3^-$). In the atmosphere, gas-phase oxidation ($\text{NO}_{2(\text{g})} + \text{OH}_{(\text{g})} \rightarrow \text{HNO}_{3(\text{g})}$) and heterogeneous process ($\text{N}_2\text{O}_{5(\text{g})} + \text{H}_2\text{O}_{(\text{aq})} \rightarrow 2\text{HNO}_{3(\text{aq})}$) are potential pathways of HNO_3 formation (Here, the HNO_3 means the nitric acid before forming nitrate and is also called total nitrate in this work). The product, HNO_3 , would then react with NH_3 (or would be neutralized by NH_4^+) to produce NH_4NO_3 aerosols. In this work, we used correlation analysis between F_n (nitrogen conversion ratio), Ox and ALWC together with cases studies to discuss whether gas-phase oxidation or heterogeneous process was a major formation mechanism of particulate nitrate during the high $\text{PM}_{2.5}$ levels. The equation of F_n can be expressed as:

$$F_n = \frac{G\text{NO}_3^- + P\text{NO}_3^-}{G\text{NO}_3^- + P\text{NO}_3^- + \text{NO}_2}$$

As seen, the numerator of F_n is the concentrations of total nitrate. The denominator is the total NO_2 concentrations. The results showed that there were two peaks of F_n . In the first peak, the elevated F_n coincided with increasing ALWC, suggesting heterogeneous reaction since ALWC is one of the key parameters to accelerate the

transformation of N_2O_5 to liquid HNO_3 . On the contrary, a second peak of Fn was found in the early afternoon when Ox ($\text{Ox} = \text{NO}_2 + \text{O}_3$, an index of the oxidation capacity) concentrations increased, but ALWC decreased. This suggested that the HNO_3 formation might be mainly associated with the gas-phase reaction of $\text{NO}_2 + \text{OH}$ during the daytime. To avoid misunderstanding for the reader, we have changed “total nitrate” to “ HNO_3 ” in [line 379 on page 15 in the revised manuscript](#).

11th comment

Line 329-331. You mentioned that nitrate could be formed through gas-phase processes. Here, you are saying it is not from gas-phase reactions because of poor linear correlation between Fn and Ox.

Author’s response:

Thanks for the reviewer’s comment. Both gas-phase oxidation process and heterogeneous reaction are potential formation mechanisms of particulate nitrate. In this work, the good correlation between Fn and ALWC ($R = 0.72$ and 0.76 , $p < 0.05$) in the high $\text{PM}_{2.5}$ events. On the contrary, no correlation between Fn and Ox was found under the high $\text{PM}_{2.5}$ conditions. Thus, nitrate formation during the high- $\text{PM}_{2.5}$ events in Nanjing was likely attributed to heterogeneous reactions rather than gas-phase processes. ([lines 388 on page 15 and lines 389-394 on page 16](#))

12th comment

Line 364-366. It is not clear how to get 70%. What are the absolute values of growth rate here, and in other cases?

Author’s comment

During the sampling periods, a total of twelve high $\text{PM}_{2.5}$ events were found. The significant enhancements of NO_3^- were observed during all the $\text{PM}_{2.5}$ episodes. Seven

episodes suggested that heterogeneous process ($\text{N}_2\text{O}_5 + \text{H}_2\text{O}$) might be a major pathway for nitrate formation since elevated NO_3^- levels coincided with increasing AWLC and decreasing Ox (or Ox remaining at a constant level). In the heterogeneous-process cases, five of them (Case III, Case IX, Case X, Case XI and Case XII in Table S1) were observed during the nighttime (17:00 – 6:00 on the next day), suggesting that approximately 70 % heterogeneous reaction was observed in the dark (lines 428-432 on page 17). Moreover, the growth rate of nitrate of each high $\text{PM}_{2.5}$ case is listed in Table S1. As seen, the growth rate of nitrate was from 2.4 to 26.7 % h^{-1} . On average, the production rate of NO_3^- (12.6 % h^{-1}) by heterogeneous processes was 5 times higher than that (2.5 % h^{-1}) of gas-oxidation reactions. This might explain the abrupt increase of nitrate concentrations during the high $\text{PM}_{2.5}$ events (lines 448-451 on page 18).

13th comment

Line384-385. You are assuming $\text{HNO}_3 + \text{NH}_3$ is the major pathway, but in previous part and in Table S1. Night time $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ is the major pathway.

Author's comment

Thanks for the reviewer's comment. In the revised manuscript, we have re-organized the section of "3.7 NH_3/HNO_3 limitation of nitrate aerosol formation". We used the ISORROPIA II model to evaluate whether control NH_3 or HNO_3 (NO_x) is a better way to reduce particulate NO_3^- concentrations in Nanjing since ISORROPIA II model can predict the concentrations of NO_3^- , SO_4^{2-} and NH_4^+ very well ($R^2=0.97-0.99$ with all slopes of approximately 1.0) under thermodynamic equilibrium in aerosol system (lines 462-466 on page 18, lines 467-468 on page 19 and Figure S7). In this work, we used this model to calculate concentrations of particulate nitrate depending on various total nitrate and total ammonium concentrations under high- and low-sulfate concentrations.

The results showed that nitrate aerosol formation in Nanjing during the high PM_{2.5} events was HNO₃-limited. This also reflected that control NO_x emissions can reduce particulate nitrate concentrations. (lines 481-491 on page 19 and Figure 9)

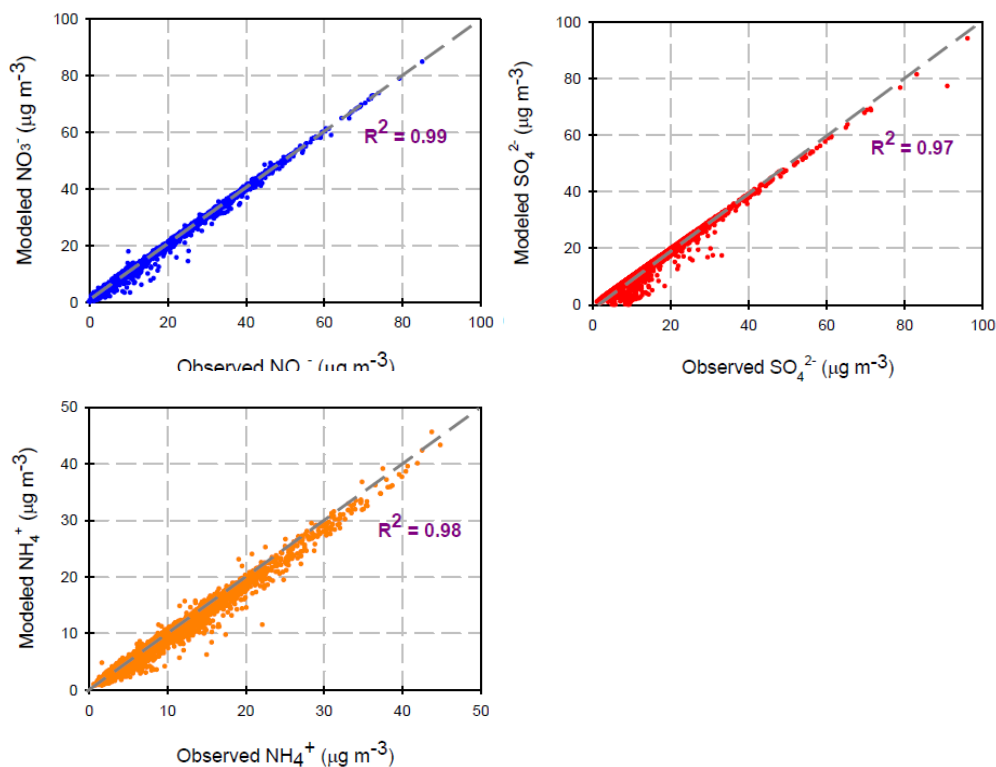


Figure S7 Scatter plots of simulated concentrations of NO₃⁻, SO₄²⁻ and NH₄⁺ against observed ones in Nanjing during the sampling periods.

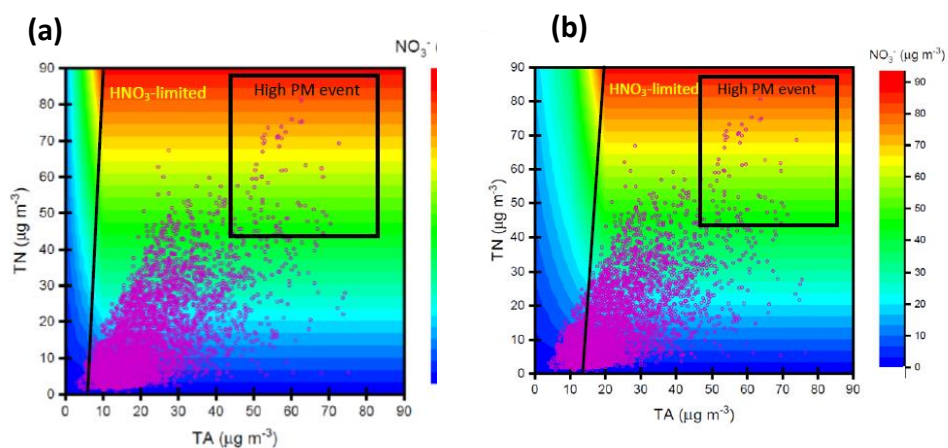


Figure 9 Nitrate concentrations simulated by ISORROPIA II model depending on TA and TN concentrations under (a) SO₄²⁻ = 10 μg m⁻³ and (b) SO₄²⁻ = 60 μg m⁻³

14th comment

Figure 1. please provide better resolution. Also, the color bar has repeated 102, and Figure 1 is not discussed in the main text. If the goal of Fig. 1 is to show the location of the sampling site, it should be in supplementary.

Author's response:

Thanks for the reviewer's comment. In the revised manuscript, we have replaced the new figure with a better resolution. However, this figure only shows the relative location of the sampling site and therefore we move this figure to the supplementary ([Figure S1](#)).

15th comment

Figure 2. Please provide year on the x-axis. Also indicate season and the cases you selected in Table S1 and Fig. 8.

Author's response:

As suggested, we have provide year on the x-axis in "new Figure 1" . Also, we have indicated the season and used shadows to pointed out the cases we selected in Table S1 and Fig. 8 in the revised manuscript.