

Interactive comment on “Observation of nitrate dominant PM_{2.5} and particle pH elevation in urban Beijing during the winter of 2017” by Yuning Xie et al.

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We thank the referee for his/her kind and detail comments on the paper. Listed below are the point-by-point replies to the comments.

Best regards,

General comments: Comments: This article evaluates the ongoing changes in the pH and nitrate content of PM_{2.5} in Beijing as strict controls on sulfur sources are reducing particle sulfate. This is a timely and important topic and the article is within the scope of ACP, however the particle requires extensive revisions to help clarify the authors points

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and to make it a useful contribution to the literature. Response: Suggestion taken. We have extensively revised the manuscript including language modification. We will present the details in the next point-by-point replies to your comments.

Comments: The authors use a detailed set of pollution measurements made in Beijing from Dec 2017 – Feb 2018 and compare their typical values measured for various pollutants (e.g. NO₂, SO₂) to those measured in previous years in Beijing. The most important dataset for the calculation of the aerosol pH is the water-soluble gas and PM_{2.5} constituents by IGAC, however the timeseries for these measurements are not shown in the manuscript or in the SI. Given that the campaign period was ten weeks (15/12/2017 – 25/02/2018), there should be approximately 1700 hourly data points for each compound. However there only appears to be, at most, a few hundred data points in Figures 3, 6, 7, 8, 9. This implies that perhaps the data coverage of the IGAC measurements was not very extensive during the campaign period, or that the data quality were often not sufficient. It would be useful for the authors to provide more explanation about the amount of valid data used in their pH calculations and to what extent it can be viewed as representative of the entire winter season. In fact, in Figures 4 and 5, it seems that the hi-volume sampler data is used for nitrate and sulfate, rather than the hourly data – is this true and why? Response: We thank the reviewer for his/her concerning about the data points in our manuscript figures. Not all of the data points were shown in this paper. From section 3.3 it could be easily seen that the SNA composition of PM_{2.5} significantly changed during the pollution periods. Therefore, the main purpose of this article lies in the examination on the impact of nitrate fraction elevation on the pH of particles. During the winter of 2017, the pollution happened less than before and the weather was quite dry. Only data during pollutions were used to plot the referee mentioned figures. More to that, the data were chosen with a criterion of whether ALWC was sufficient. Therefore, it might seem much less data were shown in the paper but it was intended. The data measured with IGAC are hourly data. Several places in the text were modified, mainly the captions of figures. Please see page 30, line 640-642; page 31, line 645 -646; page 32, line 649-650.

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Comments: One confusing aspect of the manuscript is that the authors consistently refer to aerosol with a pH of 5.4 as 'near neutral', despite the proton activity being 40 times higher than a solution with a truly neutral pH (i.e. 7). From this, I believe they mean that a pH value of 5.4 is close to what one calculates for a solution exposed to 400 ppm of CO₂ in the ambient atmosphere. I suggest changing this language because 'neutral' has a very specific meaning, different from what is being used here. If the authors want to emphasize that the pH is close to what might be expected in the absence of high particle pollution, they could explain that a value of 5.5 is expected in 'unpolluted' conditions. However, even at very low PM_{2.5} mass loadings, the contributions of solutes other than carbonic acid/bicarbonate will dominate the ion balance and set the pH and I do not think there is anything special about a pH of 5.4. Response: Thanks for the suggestion. We revised the description to "less acidic" and "more neutralized". A pH of 5.4 is an especially important value in previous literature (Cheng et al. 2016; Wang et al.2016; Seinfeld et al.2006), which discussed the topic on whether NO₂ promotes sulfate formation in China. Please see the related discussions in the paper.

Comments: Section 3.4 addresses the main question of the publication – how changes in particle composition are linked to changes in particle pH. Because nitrate is a semi-volatile component of the particle, its gas-particle partitioning is sensitive to the particle pH (and to its LWC and temperature). Thus, it does not necessarily make sense to frame the question as 'the effect of nitrate fraction elevation on particle acidity'. I would view it from the opposite perspective – for a given amount of total ammonia, less PM_{2.5} sulfate allows the particle pH to be higher, allowing for nitrate to be present in the particle phase. In other words, the pH is not responding to the nitrate to sulfate ratio, as is suggested by the choice of axes in Figure 6. Rather, the pH is responding to the reductions in sulfate and thus leading to a change in the partitioning of nitrate. This is the converse of the explanation provided on Lines 290-291. Response: We disagree with the reviewer on the above comments. It has been found that the decrease of sulfate would not inevitably lead to an increase in particle pH and nitrate. For example,

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combing the field measurements and thermodynamic model simulations, Webber et al have investigated the variation trends of chemical composition and pH of PM_{2.5} in the southeastern US during the past 15 years (Weber et al.,2016). They found that pH of PM_{2.5} in US has kept constant in the range of 0-2 and litter change in particle ammonium nitrate, although sulfate in the fine particles has significantly decreased from about 7 $\mu\text{g}/\text{m}^3$ in 1999 to 2 $\mu\text{g}/\text{m}^3$ in 2014. However, it is not the case in China. In the past five years many studies have found that along with the sharp decreased in sulfate concentrations due to SO₂ emission controls, relative abundance of nitrate of PM_{2.5} in many cities of China has significantly increased (Ji et al., 2018; Wu et al., 2018), as those found in this study. Such a different variation trend of nitrate suggests that aerosol chemistry (e.g., acidity) in China especially in haze periods is different from that in US and other developed countries, which is the motivation of this work why we would like to investigate the impact of changes in chemical compositions of PM_{2.5} on particle acidity in Beijing. It's of our special interest to point the difference of how particle's acidity reacts to its chemical composition's change. This study highlights the difference of particle acidity calculated by the same method between China and the U.S.

Comments: In particular, the statement on Lines 253-254 is very confusing: 'Less predicted H⁺ ion in aerosol liquid water is found to be the major cause of the higher pH. . .'. A lower concentration (or activity) of H⁺ is the definition of higher pH ($\text{pH} = -\log[\text{H}^+]$), not just a major cause! Similarly, there is no reason to examine the $[\text{HSO}_4^-]/[\text{SO}_4^{2-}]$ ratio to consider the 'aerosol's ability of excess H⁺ formation' (Line 270). This ratio derived from the model output is going to be self-consistent with the pH calculated by the model given that the $[\text{HSO}_4^-]/[\text{SO}_4^{2-}]$ ratio depends on the pKa of bisulfate and the pH of the aerosol liquid water. There isn't any additional insight provided by this ratio is you already know the pH, which is well above the pKa in almost all cases. Response: We have reconsidered the comment by referee #2 and take it carefully. Our first intention is to use the ratio as a proxy of H⁺ production and to find the physiochemical nature by comparing the proxy to nitrate/sulfate ratio. However, after studying the referee#2's

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comment, we found that the ratio calculated from the result of ISORROPIA II model is almost equivalent to the pH, and thus Fig.8 is equivalent to Fig.6. Therefore, this figure and related discussion were deleted from the text. Besides this, we present more discussion on the effect of nitrate fraction elevation on NH₃ partition ratio and its potential effect in the following part. The analysis shows that the partition of NH₃ is more sensitive to nitrate content, and it is caused by the enhanced nitric acid partitioning due to higher particle pH. The deleted context were in section 3.4, before the paragraph in page 12, line 270. The added discussion were mainly in the last part of section 3.4, please refer to page12-13, line 270-288.

Comments: Generally, I found the frequent references to the mechanisms of sulfur oxidation scattered through the text to be distracting. It would be preferable to state in one section of the introduction how and why the pH might impact the sulfur oxidation mechanism and rate and then return to it in the discussion. Other mentions of it in the results section, e.g. Lines 244-247 are distracting because the observational data themselves do not evaluate this mechanism. Response: Suggestion taken. We added some introduction about SO₂ oxidation into the introduction section and shortened the NO₂ oxidation mechanism discussion in the results. See page 3, line 50-61; page 11, line 246-248;

Comments: Section 4 – The authors assess the changes in hygroscopicity in more nitrate-rich particles by comparing the ALWC when the RH is increased by 10%. The authors should clarify whether these calculations were performed using the particle components only as inputs, or the particle and gas (e.g. NH₃ and HNO₃) components as well. This is because increasing the RH would also increase the gas-to-particle partitioning of the gases, so the increase in ALWC results not just from the increased water activity in the particle, but also from dissolving more solutes into the aqueous phase for semi-volatile constituents like nitrate and ammonium. Response: Suggestion taken. In our calculation, input NH₃ was set as NH₃ plus NH₄⁺. But the input of HNO₃ was only nitrate measured, since there were no HNO₃(g) measurements. As a result,

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there will only be as much NH₄NO₃ as measured and the increase of ALWC is not from more solutes.

Specific comments: Comments: Page 3, L77 – The Song et al., 2018 reference identified a coding error in ISORROPIA that led to unreliable results for calculations done for closed, stable systems. Several of the references discussed by the authors in this section used this approach for their calculations of pH and therefore it would useful for the authors to identify which of the papers may have reported pH values that are in need of revision. Response: Right now, we couldn't get the fixed code to run the model in a more proper way. We would have further investigation on the model coding error in future work.

Comments: Page 7, Lines 215-220, Why is the ratio of ammonium/sulfate of 1.5 set as the threshold or limit for nitrate formation? It should be possible to carry out a more sophisticated analysis of the threshold for nitrate formation than what was performed in Pathak et al.2009 and 2011. Response: The RatioA-to-S is set to 1.5 by the definition of "excess ammonium", meaning that there was enough ammonia to form ammonium nitrate. Many field observations on the Chinese atmospheric aerosols including the work reported by Pathak et al., (2004) found that nitrate aerosols can be significantly detected only when molar ratio of ammonium to sulfate is larger than 1.5. Actually, there was a quite comprehensive analysis based on experiments, please refer to Pathak et al, 2004. Thus, we think it is not necessary to repeat the analysis on this threshold, which was already done by Pathak et al. We have cited this work and readers can refer to this paper for the details.

Comments: Page 7, Lines 230 -232 The Shah et al. and Weber et al. studies do not necessarily contradict each other as they each examine trends and sensitivities in pH in different seasons and regions of the U.S. Response: We found it inappropriate and rephrased the sentence. See page11, line235-237

Comments: Page 8, Line 279 and Figure 9 - The authors use inconsistent language

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and definitions for the ratio of particle NH_4^+ to total ammonium (conversion ratio in Figure 9 and 'ammonia partition fraction' on Line 279. Response: We've checked through the article and made revisions to make the language consistent on fig.9 (now as fig.8) and on page 13, line279-288.

Comments: Reference list - Wang 2016a and Wang 2016b are the same reference
Response: Thanks for the referee, we've modified this part. Other repeated reference like Cheng et al. 2016, Guo et al. 2017. See Page 19, line 417-419; Page 20, line 454 – 455; Page 25, line 560-565.

References: Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, *Sci. Adv.*, 2, e1601530, 10.1126/sciadv.1601530, 2016. Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secret, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, *P. NATL. ACAD. SCI. USA*, 113, 13630, 10.1073/pnas.1616540113, 2016. Seinfeld, J. H. and S. N. Pandis. *Atmospheric chemistry and physics: from air pollution to climate change*, John Wiley & Sons. ISBN: 978-1-118-94740-1. 2016 Ji, D., et al. Characterization and source identification of fine particulate matter in urban Beijing during the 2015 Spring Festival. *Sci. Total Environ.* 628, 430-440, 2018. Pathak, R. K., Yao, X., and Chan, C. K.: Sampling Artifacts of Acidity and Ionic Species in $\text{PM}_{2.5}$, *Environ. Sci. Technol.*, 38, 254-259, 10.1021/es0342244, 2004. Webber et al. High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years. *Nature Geoscience*, 2016, Vol.9, 282-286, DOI: 10.1038/NGEO2665 Wu, C., et al. Chemical characteristics of haze particles in Xi'an during Chinese Spring Festival: Impact of fireworks burning.

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