

## ***Interactive comment on “Observation of nitrate dominant PM<sub>2.5</sub> and particle pH elevation in urban Beijing during the winter of 2017” by Yunying Xie et al.***

**Anonymous Referee #2**

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This article evaluates the ongoing changes in the pH and nitrate content of PM2.5 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 and to make it a useful contribution to the literature.

The authors use a detailed set of pollution measurements made in Beijing from Dec 2017 – Feb 2018 and compare they typical values measured for various pollutants (e.g. NO<sub>2</sub>, SO<sub>2</sub>) 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 PM2.5 constituents by

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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 ~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?

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 CO<sub>2</sub> 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 PM2.5 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.

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 PM2.5

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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.

In particular, the statement on Lines 253-254 is very confusing: 'Less predicted H<sup>+</sup> ion in aerosol liquid water is found to be the major cause of the higher pH...' A lower concentration (or activity) of H<sup>+</sup> 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<sup>+</sup> 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 if you already know the pH, which is well above the pKa in almost all cases.

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.

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. NH<sub>3</sub> and HNO<sub>3</sub>) 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.

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Specific 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 be useful for the authors to identify which of the papers may have reported pH values that are in need of revision.

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.

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.

Page 8, Line 279 and Figure 9 - The authors use inconsistent language and definitions for the ratio of particle NH<sub>4</sub><sup>+</sup> to total ammonium (conversion ratio in Figure 9 and 'ammonia partition fraction' on Line 279).

Reference list - Wang 2016a and Wang 2016b are the same reference

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