Response to Anonymous Referee #1

Song et al.

Comments are in black and responses are in blue.

This manuscript needs minor reversion before acceptance for publication.

Our responses to specific comments are provided below.

(1) As the authors stated, some papers reported the aerosol pH in Beijing, I suggest it should be declared clearly what are the correct results in the abstract and conclusion, also to let the readers know, which method is correct to estimate a reasonable aerosol pH.

The abstract and conclusion have been revised to highlight the appropriate applications of thermodynamic modeling and the reasonable range of aerosol water pH inferred from such method.

Revisions made in the manuscript:

> *"**Abstract.** pH is an important property of aerosol particles but is difficult to measure directly. Several studies have estimated the pH values for fine particles in North China winter haze using thermodynamic models (i.e., E-AIM and ISORROPIA) and ambient measurements. The reported pH values differ widely, ranging from close to 0 (highly acidic) to as high as 7 (neutral). In order to understand the reason for this discrepancy, we calculated pH values using these models with different assumptions with regard to model inputs and particle phase states. We find that the large discrepancy is due primarily to differences in the model assumptions adopted in previous studies. Calculations using only aerosol phase composition as inputs (i.e., reverse mode) are sensitive to the measurement errors of ionic species and inferred pH values exhibit a bimodal distribution with peaks between −2 and 2 and between 7 and 10, depending on whether anions or cations are in excess. Calculations using total (gas plus aerosol phase) measurements as inputs (i.e., forward mode) are affected much less by these measurement errors. In future studies, the reverse mode should be avoided whereas the forward mode should be used. Forward mode calculations in this and previous studies collectively indicate a moderately acidic condition (pH from about 4 to about 5) for fine particles in North China winter haze, indicating further that ammonia plays an important role in determining this property. The particle phase state assumed, either stable (solid plus liquid) or metastable (only liquid), does not significantly impact pH predictions. The unrealistic pH values of about 7 in a few previous studies (using the standard ISORROPIA model and stable state assumption) resulted from coding errors in the model, which have been identified and fixed in this study."*

> *"**Conclusions.** This study suggests that the significant discrepancy of fine particle pH, ranging from about 0 (highly acidic) to about 7 (neutral), calculated in previous studies of North China winter haze is due primarily to differences in the ways in which the E-AIM and ISORROPIA thermodynamic equilibrium models have been applied. The reverse mode calculations (only using aerosol phase composition as inputs) lead to erroneous results of pH since they are strongly affected by ionic measurement errors (especially under ammonia-rich conditions), and therefore should be avoided in future winter haze studies. The forward mode calculations (using the total (gas plus aerosol phase) compositions as inputs) account for additional constraints imposed by the partitioning of semi-volatile species and are affected much less by the measurement errors, and therefore, should be used in future studies. The forward mode calculations in this and previous studies collectively indicate, during North China winter haze events, that aerosol particles are moderately acidic with pH values ranging from about 4 to about 5. The assumed particle phase state (stable or metastable) does not significantly affect the pH calculations of ISORROPIA after coding errors in its standard model being fixed. A few previous studies, in which the standard ISORROPIA model was used and the stable state was assumed, predicted unrealistic pH values of around 7, and should be re-evaluated. In agreement with previous studies, we confirm that ammonia plays an important role in determining particle pH under winter haze conditions in northern China."*

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(2) The "forward stable" module was modified by the authors, although I did not read it in detail, the results seem more reasonable than previous runs. If possible, please contact GIT group to confirm it.

Our modification of the ISORROPIA source code for the "forward stable" mode has been confirmed by its developers.

(3) Some recent studies declared the aerosol pH could be close to 7 due to the high ammonia level, please use the sensitivity test to show if it is possible. The implications of aerosol pH should be very important for atmospheric reactions.

The sensitivity of pH to ammonia concentration levels has been examined in a few previous winter haze studies (e.g., Liu et al., 2017 and Guo et al., 2017). Thus, in this study we cited their results in Sect. 3.2.3 in the revised manuscript and also provided a similar sensitivity test. Our conclusions are the same as those from these previous studies.

Revisions made in the manuscript:

> *"By analyzing the sensitivity of pH to ammonia concentrations, recent studies have emphasized the important role of ammonia in determining winter haze particle pH (Guo et al., 2017b; Liu et al., 2017a). It was suggested, under ammonia-rich conditions, that a 10-fold increase in gas phase NH_3 concentrations roughly corresponds to one unit increase in pH (i.e., a 10-fold decrease in H^+ activity) (Guo et al., 2017b). This is obvious, since the equilibrium of dissolution and dissociation of ammonia in water can be expressed as: $NH_{3(g)} + H^+_{(aq)} \leftrightarrow NH^+_{4(aq)}$. These sensitivity tests have also indicated that atmospheric relevant ammonia concentrations are not high enough to achieve a fully neutralized condition (pH of around 7) for aerosol particles (Guo et al., 2017b; Liu et al., 2017a). The sensitivity tests conducted in this study are consistent with these previous studies (Fig. S9 in the Supplement)."*

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophys. Res. Lett., 44, 5213-5221, doi:10.1002/2017GL073210, 2017a.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Sci. Rep., 7, 12109, doi:10.1038/s41598-017-11704-0, 2017b.

(4) Please have some discussion on the aerosol water content effects on pH values especially when RH was high.

In the revised manuscript, we have added more discussion in Sect. 3.2.3 on the effects of ammonia concentrations and RH on the pH values predicted by ISORROPIA and E-AIM. We think it does not make much sense to directly compare aerosol water content and pH values, because the aerosol water content predicted by the thermodynamic equilibrium models depends on the amount of chemical species and RH values in the input. If the input RH and excess ammonia remain constant, increasing the amount of chemical species would increase aerosol water content but would not change predicted pH values significantly. On the other hand, if the excess ammonia and the amount of chemical species in the input remain constant, increasing RH values would affect predicted pH values, but this effect is different for E-AIM and ISORROPIA. Thus we choose to evaluate the effect of changing RH on the predicted pH values.

Below is a new figure in the supplement of the revised manuscript. It shows the sensitivity of pH to NH_x concentrations and RH. The model inputs include total H_2SO_4 = 30 µg m^{-3}, total HNO_3 = 51 µg m^{-3}, temperature = 278 K, and varying RH (from 30% to 90%) and total NH_x concentrations (from 25 to 100 µg m^{-3}). The inputs are calculated from our field measurements during haze episodes (RH > 60%) as the average temperature and average concentrations of total H_2SO_4, and HNO_3. Na^+ and K^+ are accounted for as equivalent NH_4^+, and Cl^- as equivalent NO_3^-. The required NH_x concentrations calculated for the input total H_2SO_4 and HNO_3 concentrations are about 24 µg m^{-3}. The curves in panels (c and d) show the average pH in each bin for NH_x concentrations or RH.

Panel (d) of this figure shows the relationship of RH and pH. We find that the pH from ISORROPIA is insensitive to RH and the variability of pH is less than 0.3 unit. On the other hand, pH from E-AIM increases by 0.8 unit with increasing RH from 30% to 90%. The reason for this difference in pH between ISORROPIA and E-AIM remains unclear, and is discussed briefly in Sect. 3.2.1.

(a) ISORROPIA pH

(b) E-AIM pH

(c) Excess NH$_x$ vs. pH

(d) RH vs. pH