Point-by-Point Response to Reviewers' Comments

Manuscript Ref: amt-2020-156

Title: An inter-laboratory comparison of aerosol in organic ion measurements by Ion Chromatography: implications for aerosol pH estimate

Journal: Atmospheric Measurement Techniques

Comments from Reviewer #3

General Comments:

General Response: Thanks for the reviewer's suggestions. Modifications have been done according to reviewer's comments. Please see our point-to-point response of reviewer's comments below.

Specific comments:

1. In Section 2, more experimental details should be given so that the possible reasons for the data difference between different labs can be evaluated. For example, how the purity of the ultrapure water in each lab was assured? What type of syringe filter (Teflon, Nylon or others?) is employed to filtrate the extract prior to analysis? What types of vial (e.g., glass or PTFE vial?) was used for analysis (glass vial may bring Na+ contamination)? What model/what power of ultrasonicator is used during the extraction? Are they consistent in all labs? These experimental procedures may be important for the data accuracy and resulting in the data difference. Those details would be helpful for the discussion of the potential reasons for the inconsistency; it is also useful for those who are setting up the protocol to conduct proper analysis of ionic species in aerosol. So, I suggest the authors try to include those details if available.

Response: Thanks for the reviewer's very constructive suggestion. All experimental details mentioned by the reviewer has been provided in Table S1, including the type of extraction vials, model and purity of the ultrapure water, type and power of ultrasonicator, type of the syringe and syringe filters, type of the vials that used in ion analysis. In addition, the calibration and QA/QC details are also provided in Table S2. However, this is no clear relationship between the differences of these information with the differences of WSIIs measured by each lab. One thing that worth noting is the need of using certified reference materials for quality control, which we have mentioned in our revised manuscript **line 278-285** and copied below:

"As shown in Table 2, the DA of most ions measured by Lab-4 were < 100%, while those of Lab-1 were much higher, especially for major ions (>100%). Corresponding to this, the ion concentrations in Lab-4 were mostly lower than other labs, while those of Lab-1 were mostly higher than other labs. For Lab-6 which was also observed to

have lower DA of ions such as SO_4^{2-} (89.2%) and NH_4^+ (88.4%) in 10 labs; its SNA concentrations and total ions accounted for 24.5±5.6 % and 28.7±6.0% of $PM_{2.5}$, respectively, the second lowest among all labs. Hence, it is very important to run certified reference materials before any sample analysis to ensure accuracy and good quality of data."

2. This study showed a similar trend of aerosol pH among the 10 labs and concluded that although there is large variation in aerosol ion concentration measurements, the estimated aerosol pH from the ISORROPIA-II model is more consistent. However, the 10 labs actually shared the same set of gaseous NH3 concentration, and it has been known that the concentration of gaseous NH3 may be one of the most important components during the estimation of acidity. Therefore, the consistent aerosol pH may not reflect the uncertainty of measurement of other ionic species. I suggest the authors should also consider the measurement uncertainty of gaseous NH3 concentration when comparing aerosol pH in different labs.

Response: Thanks for the reviewer's suggestion. Reviewer #2 has a similar comment (#4). Please see our response below:

Because the ammonia analyzer applied in this study has a precision of 0.2 ppb and maximum drift of 0.2 ppb over 24h. We have investigated the pH of the original NH_3 ± 0.2 ppb, the results showed the pH difference is smaller than 0.01 in each sample of 10 labs, which is neglectable. However, as the uncertainty of NH_3 measured by different instruments was not known, we also investigated the difference of pH at (original NH_3) ± 1 ppb, ± 5 ppb, ± 10 ppb, with other parameters like ions, temperature and RH remained the same. ISORROPIA II model was also run in forward mode and metastable state. The largest difference was found at ± 10 ppb, the difference of pH with the original ones ranged between 0.001-0.417 with average of 0.117. Hence, the effect of measurement uncertainty of NH_3 on pH calculation is considered small and neglectable.

3. The authors may also consider showing the predicted gas-aerosol partitioning of NH3 and comparing the results with the measurements in different labs. Compared to aerosol pH, the gas-aerosol partitioning may be a more sensitive parameter.

Response: Thanks for the reviewer's advice. We have added the comparison of predicted NH_3 by the ISORROPIA-II model and the measured NH_3, please see added sentence below (**line 522-525** in the revised manuscript):

"The predicted gas-phase NH_3 by ISORROPIA-II was well correlated with the measured NH_3 with slope of 1.02 and R^2 of 0.95 (Fig. S6), which demonstrated the accuracy of thermodynamic calculations by the model (Song et al., 2018)."

We agree with the reviewer that aerosol pH could also be estimated from the gas-particle phase partitioning of NH_3 (Hennigan et al., 2015):

$$\{H^+\} = \frac{K_W\{NH_4{}^+\}}{K_H K_b p_{NH_3}}$$

where $\{H^+\}$ is the activity of H^+ in atmospheric particles, K_H, K_b and K_W are temperature-dependent constant, p_{NH3} is the gas-phase partial pressure of ammonia, and $\{NH_4^+\}$ is the activity of aqueous aerosol ammonium in mol/L. However, this method is not completely independent as the calculation of $\{NH_4^+\}$ requires the use of aerosol water content obtained from ISORROPIA-II model. Besides, because of the extremely low RH of the samples (around 20%), the existence forms of most ions are in solid salts, and the estimated water content by ISORROPIA-II in reverse mode at stable state was 0 in all samples. Therefore, pH in this study was calculated by ISSOROPIA-II in forward at metastable state, assuming the salts do not precipitate under supersaturated conditions. If using the gas-particle partitioning equation above to estimate H^+, the results will be heavily overestimated as most NH_4^+ are not in aqueous phase under extremely low RH. This is also in agreement with previous studies that low RH (<20%) was not be considered for pH calculation as the aerosol water content is close to 0 (Song et al., 2018; Jia et al., 2020). We have also addressed the uncertainties of pH estimation in our study. Please see **line 558-564** in the revised manuscript.

"ISORROPIA-II gives more consistent aerosol pH values among different laboratories. But there are uncertainties within this calculation: 1) RH during some periods in this study was relatively low (around 20%), and as a result, aerosol water content is very low. Under such conditions, ions are mostly existed in solid phase. Hence, pH of aerosols with very low RH may not be reliable; 2) the calculation of AWC only considered for inorganics in this study. Water associated with organics also contribute to AWC. For example, Guo et al. (2015) indicated that it accounts for 29-39% of total $PM_{2.5}$ water in southeastern United States."

References:

Guo, H., Xu, L., Bougiatioti, A., Cerully, K., Capps, S., Hite, J., Carlton, A. M., Lee, S.-H., Bergin, M., Ng, N., Nenes, A., and Weber, R.: Fine-particle water and pH in the southeastern United States, ATMOSPHERIC CHEMISTRY AND PHYSICS, 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15, 2775-2790, 10.5194/acp-15-2775-2015, 2015.

Jia, S., Chen, W., Zhang, Q., Krishnan, P., Mao, J., Zhong, B., Huang, M., Fan, Q., Zhang, J., Chang, M., Yang, L., and Wang, X.: A quantitative analysis of the driving factors affecting seasonal variation of aerosol pH in Guangzhou, China, Science of The Total Environment, 725, 138228, https://doi.org/10.1016/j.scitotenv.2020.138228, 2020.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

4. There are 5 days with pH > 7. Since the ISSORPIA-II is running in forward mode, pH>7 would require extremely high concentration of NH3 in gaseous phase which is almost impossible for ambient air environment. Dr. Song Shaojie, one of the co-authors of this manuscript, has conducted a comprehensive analysis on the issue of pH in 2018 (Song et al., 2018). I would suggest the authors should double check their input parameters in ISORROPIA-II.

Response: Thanks for the reviewer's advice. This suggestion is similar to the comment #3 from the reviewer #2. The model was run by Dr Shaojie Song in this study. We have carefully checked the inputs and provided the daily averaged concentrations of NH_3 in Table S3. The NH_3 concentration level in this study (17.2±2.2 ppb) is in consistent with previous study in Beijing during winter (18±9 ppb) (Song et al., 2018). In our study, RH was only around 20% for most samples. NH_3 concentrations on the first three days were around 19-20 ppb, while on the pH<7 days were around 16-17 ppb. At very low RH, particles can only absorb a small amount of water at metastable state (Song et al., 2018). A relatively higher NH_3 concentration may have caused increase of pH at low RH. Our sensitivity test of NH_3 showed when other inputs remained the same, the change of NH_3 on the final pH results was small. Hence, the difference of pH between samples was mainly affected by the equilibrium of ions.

In addition, the equilibrium of water (H_2O) with OH^-(aq) + H^+(aq) is temperature-dependent. For highly dilute aqueous systems, the values of pK_w (= $-\log_{10}[K_w]$; K_w is the temperature-dependent equilibrium constant on molality basis) at 25 °C (13.99) and 0 °C (14.95) can result in corresponding pH values of 6.995 and 7.475, respectively, both of which are considered neutral (Bandura and Lvova, 2006; Pye et al., 2020). In our study, the temperature of 8 samples ranged between -4.4~4.3 °C (Table S3). Hence, except relatively alkalic nature of the 5 aerosol samples, another possible reason of the higher pH values in these samples could be the lower temperature. In addition, we also tested the aerosol pH of samples at different RH. The results showed that the aerosol pH significantly decreased with the pH of all samples < 6.5. Hence, the low RH for the samples may have led to the abnormally high pH values in samples.

Please see **<u>line 536-548</u>** in the revised manuscript for added discussion:

"It should be noted that higher pH (>7) of those samples could be due to the lower temperature (-4.4~4.3 °C) during the sampling period (Table S3), in addition to their relatively alkalic nature. The equilibrium of water (H_2O) with OH^-(aq) + H^+(aq) is temperature-dependent. For highly dilute aqueous systems, the values of pK_w (= $-\log_{10}[K_w]$; K_w is the temperature-dependent equilibrium constant on molality basis) at 25 °C (13.99) and 0 °C (14.95) can result in corresponding pH values of 6.995 and 7.475, respectively, both of which are considered neutral (Bandura and Lvova, 2006; Pye et al., 2020). In addition, the low RH in these samples (Table S3) may have also contributed to the high pH values we calculated. Different RH values were tested for aerosol pH among 10 labs. The results (Fig. S7) showed that at different RH (40%, 50%, 60%, 70%, 80%), the pH values in 10 labs were consistent; and the pH values were mostly lower than 6 in all samples. Hence, higher pH (>7) of some samples could be resulted from the combination of lower temperature, RH, and the nature of the aerosols."

Added references:

Bandura, A., and Lvova, S.: The Ionization Constant of Water over Wide Ranges of Temperature and Density, Journal of Physical and Chemical Reference Data - J PHYS CHEM REF DATA, 35, 10.1063/1.1928231, 2006.

Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr, J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I. T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, Atmos. Chem. Phys., 20, 4809-4888, 10.5194/acp-20-4809-2020, 2020.

5. In lines 582-585, the authors attributed the large variation of ammonium measurement to the volatility of NH3 and suggested to use fresh prepared standard solution. I agree with the suggestion to use fresh prepared standard solution. However, I doubt the reason given by the authors. NH3 (as molecular) are indeed volatile. However, in acid or neutral solution, NH3 is mainly in the form of NH4+ which is not volatile. The authors may check the pH of the standard solution. I also suggest the authors to check the calibration curve of NH4+. Depending on the instrument, the calibration curve of NH4+ can be either linear or non-linear, which should be treated carefully and often causes large uncertainty.

Response: Thanks for the reviewer's suggestions. As the reviewer mentioned, we have carefully checked the calibration results provided by all labs. The results provided by different labs were calculated based on the curves they obtained, which showed the calibration curves of NH_4^+ in different labs could be linear or non-linear. The calibration details are summarized in Table S1. From our routine IC analysis, we discovered the NH_4^+ concentration in stock solutions could decline over time. Hence, we think ammonium is unstable. As suggested by the reviewer, "volatile" may be less appropriate. Hence, we changed the original description to " Stock $NH4^+$ solutions that are used for the preparation of calibration standards should be freshly prepared to ensure a high detection accuracy.". Please see **line 617-618** in the revised manuscript.

6. Other minor issue: a) Line 206: The description may be misleading. In the forward mode of ISORROPIA-II, the total concentrations of gas + aerosol is fixed.

b) Lines 229-230: I suggest the authors to show the result of water blanks to support their interpretation.

c) Line 435: [F-/19] should be [F-/9]?

Response: Thanks for the reviewer's suggestions. Please see our responses below:

a) To avoid misleading of the description, the original sentence "In this study, the model was run only in forward mode (gas and aerosol concentrations of species are fixed) in the thermodynamically metastable phase state" has been modified as " In this study, the model was run only in forward mode (with gas + aerosol inputs) in

the thermodynamically metastable phase state". Please see **line 212-213** in the revised manuscript.

b) The result of water blanks has been added in the context. The original sentence "This may be due to contamination in the water blanks or the IC system." has been revised as " This may be due to contamination in the water blanks or the IC system, as the average concentration of K^+ in 3 water blanks of Lab-7 was 8.0 ng/L, much higher than the median value of 10 labs (3.4 ng/L).". Please see **line 236-238** in the revised manuscript.

c) The molar mass of F^- is 18.998 g/mol, hence, [F^-/19] in the original equation is correct.