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 #2

General response: Thanks for the reviewer's comments. More details have been provided and discussed. Please see our point-to-point response of reviewer's comments below.

1. My 1st concern is that the authors used large space to show the differences in the WSIs measurement, but did not discuss on the possible reasons.

Response: To address this concern, we have added more experimental details to the manuscript: (1) calibration and QA/QC details are provided in Table S1; (2) extraction details such as the model and power of ultrasonicator used for extraction, syringe filter, vials used for detection are provided in Table S2; (3) instrument and analytical method details are provided in Table 1. All of these could have led to the differences in WSIIs measurements. However we are not able to pinpoint what factor(s) caused the differences except for some of the potential reasons discussed below (**line 278-285** in the revised manuscript):

"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."

Our data highlighted the potential uncertainties in the IC analysis, which has been usually considered the standard / easy measurement. Based this intercomparison and the data analyses, we have proposed ways to improve the accuracy of the ionic composition analyses, please see below (**line 605-628** in the revised manuscript):

"

1. Literature aerosol ion data based on online and offline methods should be treated with a degree of uncertainty in mind. The uncertainties are particularly large for minor ions like Ca^{2+} from the aerosol filters-based ion chromatography analysis.
2. The ion-balance approach is not recommended for estimating aerosol acidity due to its large uncertainty. Instead, in situ aerosol pH may be used to represent acidity, and can be calculated from thermodynamic model considering gas-aerosol equilibrium (e.g., NH_4^+ and NH_3). This requires the measurements of aerosol composition as well as NH_3.
3. Certified reference materials should be used on a regular basis to assess the accuracy and reliability of the measurement method. Calibration standards should be re-prepared and the IC performance should be checked when the detection accuracy is largely deviated from 100% (e.g., > 110% or < 90%).
4. The detection accuracy of ammonium varied significantly among 10 labs (88.4-135.0%) with median value close to 100%. Stock NH_4^+ solutions that are used for the preparation of calibration standards should be freshly prepared to ensure good detection accuracy.
5. Robust quality control processes should be put in place to avoid contamination, particularly for those ions with low concentrations, such as K^+ and Na^+. For example, water blanks should be run before any standard or sample analyses to ensure no contamination from water blanks or the IC system.
6. Some batches of commercial quartz filters may be contaminated with Na^+ and PO_4^{3-}, and thus testing each batch of blank filters is necessary before any field sampling (data not shown here). Filter washing may be needed in some cases.
7. Ionic concentration from ACSM observations should be calibrated although the observed trend is robust. Future research should be carried out to compare the offline ASCM and IC using the same filters to clearly identify the discrepancies between the two methods."

2. The calculation of aerosol pH using ISORROPIA-II is dependent on gas-phase NH3 too much, which is not an easy species to measure. For most cases, especially measurement based on filter sampling, NH3 would not be measured simultaneously.

Response:

NH_3 is an important factor in affecting aerosol acidity. pH calculated in reverse mode (aerosol phase as input) is sensitive to measurement errors, while calculations in forward mode (gas plus aerosol phase as inputs) are affected much less by measurement errors (Song et al., 2018). It is true that NH3 is not measured in many filter-based observations but it is important to include NH_3 in ISORRPIA II for pH calculation.

3. Fig. 6: There were 5 of the 8 samples showed a pH higher than 7. It is, to me, a bit too high. According to my best knowledge, except for dust samples, the pH of most aerosols should be lower than 7. Did the authors measure the pH of sample solutions before IC measurement? Were the 5 samples alkaline?

Response: Thanks for the reviewer's question. We didn't measure the pH of the sample solutions before IC measurement. It is difficult to collect sufficient sample material to measure aerosol pH without perturbing its acidity and is not a standard method (Pye et al., 2020). Regarding the high pH (>7) of 5 samples, please see our explanation below:

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 these 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 aerosol."

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.

4. Since the same concentration of NH3 was used in ISORROPIA-II to estimate the pH of aerosol, I somehow doubt the similarity of estimated pH among different labs were due to the same input of gas-phase NH3 (As mentioned in comment 2).

Response: To address this comment, we have investigated the influence of NH_3 concentration on the pH calculation. In addition, we have also considered the measurement uncertainty of NH_3 on pH estimation. Please see our explanation 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 (Ge et al., 2019). We has 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. We also investigated the difference of pH at (original NH_3, Table S3) ± 1 ppb, ± 5 ppb, ± 10 ppb, with other parameters like ions, temperature and RH remained the same. 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 similarity of the pH in different labs was not due to the use of same set of NH_3.

5. Section 3.2.3: I don't think this part is relevant to the topic of this work. Suggest to omit it.

Response: Thanks for the reviewer's suggestion.

Because NO_3^- and SO_4^{2-} are individually different among 10 labs (Fig. 1). The trend of NO_3^-/SO_4^{2-} could be different from either NO_3^- or SO_4^{2-}. However, as this section is too short, it has been incorporated into section 3.2.1. The original Fig. 3 has also been moved to supplemental information (Fig. S1). Please see **line 266-270** in the revised manuscript.

6. Similar to the last comment, I don't understand why the authors make a comparison with ACSM. It is a bit out of the scope of this work.

Response: Because IC and ACSM are two important techniques to investigate inorganic ions, with one carried out online and one offline. One of the original reasons to carry out the intercomparison for ioninc aerosol species is that we have found large difference in the AMS / ACSM and offline filter analyses during the APHH-China field campaigns. We think the intercomparison between ACSM and IC results provides useful insights about the potential uncertainties in the analytical methods for ionic aerosol species. Considering this, we also added a recommendation for future research to compare the offline ASCM and IC using the same filters to clearly identify the discrepancies between the two methods. Please see **line 627-628** in the revised manuscript: "Future research should be carried out to compare the offline ASCM and IC using the same filters to clearly identify the discrepancies between the two methods.".

7. The figure quality needs to be improved.

Response: Thanks for the reviewer's suggestion. The quality of all figures has been improved. Please see updated figures in the revised manuscript and supplemental information.