

## **Point-by-Point Response to Reviewer #2's further Comments**

Manuscript Ref: amt-2020-156

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

Journal: Atmospheric Measurement Techniques

### **Further comments from Reviewer #2**

#### **General Comments:**

I still have one concern about the influence of NH<sub>3</sub> on the estimation of aerosol pH, as follows:

1. The NH<sub>3</sub> concentration in this study was so high that always enough to neutralize the acidic components. Even assuming the uncertainty of  $\pm 10$  ppb, the low limit of NH<sub>3</sub> concentration would be larger than 5 ppb, which was still high enough to “constrain” the aerosol pH and result in similar pH obtained among different labs. But it is not necessarily to mean the measurement bias of water-soluble ions is not important.

**Response:** Thanks for the reviewer's valuable comment. To address the concern mentioned by the reviewer, we conducted a sensitivity test for NH<sub>3</sub>. Please see added discussions below:

“To investigate the effect of NH<sub>3</sub> concentration on aerosol pH, we conducted a sensitivity test which showed the aerosol pH of samples measured by 10 labs at NH<sub>3</sub> levels of 0.5, 1, 2, 5 and 10 ppb (Fig. S8). When the concentration of NH<sub>3</sub>  $\geq 2$  ppb, the aerosol pH estimates of the 10 labs were generally consistent and less affected by the variation of ion concentrations. But there is more variation of aerosol pH in the 10 labs when NH<sub>3</sub> concentration was under 2 ppb. This suggests when NH<sub>3</sub> concentration  $< 2$  ppb, the aerosol pH could be more affected by the variation of ion concentrations.”

Please see **line 568-574** in the revised manuscript.

2. The NH<sub>3</sub> measurement in this study was a daily averaged value. BUT NH<sub>3</sub> would have strong diurnal variation. Although the average concentration was very high, it was still possible that NH<sub>3</sub> concentration was low enough to induce a large change of aerosol pH.

**Response:** Thanks for the reviewer's comment. We recognize that there is a diurnal variation in aerosol composition and NH<sub>3</sub> concentrations. However, as mentioned in the manuscript, the daily ammonia concentrations during the study period ranged from  $13.9 \pm 0.6$  to  $20.1 \pm 0.7$  ppb. The small standard deviation ( $< 1$  ppb) of the daily average (derived from the original 5-minute data during each sampling day) suggest the diurnal variation of NH<sub>3</sub> concentration was not significant and would not cause a large change

of aerosol pH, especially when the NH<sub>3</sub> concentrations were relatively high. In addition, the lowest 5-minute average NH<sub>3</sub> concentration during the whole sampling period was 12.4 ppb, higher than 10ppb. Fig. S8 shows that the results of aerosol pH in 10 labs at 10ppb were consistent. Hence, we believe the diurnal variation of NH<sub>3</sub> in this study would not induce a large change of aerosol pH. However, future studies should consider the impact of the diurnal variation of NH<sub>3</sub> on aerosol pH if the NH<sub>3</sub> concentration was lower than 2 ppb, as mentioned in point 1 above.

The sentence “ The daily ammonia concentrations during the study period ranged from 13.9±0.6 to 20.1±0.7 ppb with an average of 17.2±2.2 ppb.” has been changed as

“The daily ammonia concentrations during the study period derived from 5-minute data ranged from 13.9±0.6 to 20.1±0.7 ppb (average: 17.2±2.2 ppb). The small standard deviations of the daily average (< 1 ppb) suggest that the diurnal variation of NH<sub>3</sub> was not significant. Hence, aerosol pH was only investigated using daily mean NH<sub>3</sub> concentrations.” Please see **line 515-518** in the revised manuscript.

A recommendation is added based on the above discussions.

“The variation of ion concentrations is expected to strongly affect aerosol acidity estimated by ISORROPIA II when the NH<sub>3</sub> concentration is low (e.g., < 2 ppb in this case). Additionally, the impact of the diurnal variation of NH<sub>3</sub> on aerosol acidity is worthy of investigation, particularly when the NH<sub>3</sub> concentration is low.” Please see **line 620-623** in the revised manuscript.