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

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ABSTRACT

Water soluble inorganic ions such as ammonium, nitrate, and sulfate are major components of fine aerosols in the atmosphere and are widely used in the estimation of aerosol acidity. However, different experimental practices and instrumentation may lead to uncertainties in ion concentrations. Here, an inter-comparison experiment was conducted in 10 different laboratories (labs) to investigate the consistency of inorganic ion concentrations and resultant aerosol acidity estimates using the same set of aerosol filter samples. The results mostly exhibited good agreement for major ions Cl^-, SO_4^{2-}, NO_3^-, NH_4^+ and K^+. However, F^-, Mg^{2+} and Ca^{2+} were observed with more variations across the different labs. The Aerosol Chemical Speciation Monitor (ACSM) data of non-refractory SO_4^{2-}, NO_3^-, NH_4^+ generally correlated very well with the filter analysis based data in our study, but the absolute concentrations differ by up to 42%. Cl^- from the two methods are correlated but the concentration differ by more than 3 times. The analyses of certified reference materials (CRMs) generally showed good recovery of all ions in all the labs, the majority of which ranged between 90% and 110%. Better agreements were found for Cl^-, SO_4^{2-}, NO_3^-, NH_4^+ and K^+ across the labs after their concentrations were corrected with CRM recoveries; the coefficient of variation (CV) of Cl^-, SO_4^{2-}, NO_3^-, NH_4^+ and K^+ decreased 1.7%, 3.4%, 3.4%, 1.2% and 2.6%, respectively, after CRM correction. We found that the ratio of anion to cation equivalent concentrations (AE/CE) is not a good indicator for aerosol acidity estimates, as the results in different labs did not agree well with each other. Ion balance (anions − cations) calculated from SO_4^{2-}, NO_3^- and NH_4^+ gave more consistent results, because of their relatively large concentrations and good agreement among different labs. In situ aerosol pH calculated from the ISORROPIA-II thermodynamic equilibrium model with measured ion and ammonia concentrations showed a similar trend and good agreement across the 10 labs. Our results indicate that although there are important uncertainties in aerosol ion concentration measurements, the estimated aerosol pH from the ISORROPIA-II model is more consistent.

Keywords: $PM_{2.5}$, inorganic ions, aerosol acidity, ion balance, thermodynamic model

1. INTRODUCTION

Water-soluble inorganic ions (WSII), consisting of F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}, are a major component of atmospheric aerosols and can contribute up to 77% of $PM_{2.5}$ (particulate matter with aerodynamic diameter ≤ 2.5 μm) mass (Xu et al., 2019a). Secondary inorganic aerosols (SIA) including sulfate, nitrate and ammonium (SNA) often dominate water-soluble ionic species in $PM_{2.5}$, and were reported to account for more than 90% of WSII in Sichuan, China (Tian et al., 2017). In Beijing, the average SNA concentrations can range from 4.2 ± 2.9 μg/m^3 in non-haze days to 85.9 ± 22.4 μg/m^3 in heavily polluted days, and contribute to 15%-49% of $PM_{2.5}$ (Li et al., 2016). SNA can greatly influence air pollution, visibility, aerosol acidity and hygroscopicity, which are driving factors affecting aerosol-phase pH and chemistry and the uptake of gaseous species by particles (Shon et al., 2012; Xue et al., 2011; Zhang et al., 2019). Hence, the study of WSII is of great interest due to their adverse impacts.

WSII in aerosols were reported to be analyzed by multiple techniques such as Cl^- by spectrophotometry, and Ca^{2+} and Mg^{2+} by flame atomic absorption in the early 1980s (Harrison and Pio, 1983). However, this was very time-consuming as different ions required to be analyzed by different techniques. Ion chromatography (IC), which was first introduced in 1975 (Buchberger, 2001), was applied in many studies for routine measurement of atmospheric WSII due to its fast, accurate and sensitive determination in a single run (Heckenberg and Haddad, 1984; Baltensperger and Hertz, 1985). IC can be coupled with diverse detection techniques for ion analysis, such as suppressed conductivity, UV-VIS absorbance, amperometry, potentiometry, mass spectrometry, etc. (Buchberger, 2001). It has been used in various atmospheric studies for many years and is still widely applied nowadays, such as in the investigation of WSII in size-segregated aerosols (Li et al., 2013; Zhao et al., 2011; Đorđević et al., 2012), fine aerosols (Fan et al., 2017; He et al., 2017; Liu et al., 2017a) and coarse aerosols (Li et al., 2014; Guo et al., 2011; Mkoma et al., 2009). IC can also be used for the determination of both water soluble organic and inorganic ions (Yu et al., 2004; Karthikeyan and Balasubramanian, 2006).

Aerosol ion concentrations can also be measured by online methods such as the Aerosol Chemical Speciation Monitor (ACSM) or Aerosol Mass Spectrometer (AMS) (Ng et al., 2011; Sun et al., 2012). During the recent Atmospheric Pollution and Human Health in a Chinese Megacity (APHH-China) campaigns (Shi et al., 2019), we observed important discrepancies between offline aerosol IC observations from different labs and between online AMS and offline IC methods. This prompted us to carry out this intercomparison exercise.

The IC method had been validated by a common reference standard - NIST SRM 1648 (urban particulate matter) and the results for Na, K, S and NH_4^+ were compared with those from other suitable alternative analytical techniques such as AAS, UV-VIS and PIXE in previous studies (Karthikeyan and Balasubramanian, 2006). However, to the best of our knowledge, no investigation has been conducted to compare the results of different laboratories (labs) for such an important and widely used simple technique.

The aim of this work is to 1) examine the consistency of ion concentrations measured by various labs and by ACSM, 2) explore the impact of the inter-lab variability in ion concentration measurements on aerosol acidity estimates, and 3) provide recommendations for improving future WSII analysis by IC.

2. EXPERIMENTAL

2.1 Participating Laboratories

Ten laboratories from China, United Kingdom and Serbia were invited to take part in the inter-laboratory comparison of atmospheric inorganic ions, which are listed as follows: University of Birmingham; University of York; University of Belgrade; Zhejiang University; Nankai University; Ocean University of China; Beijing Normal University; Chongqing Institute of Green and Intelligent

Technology, Chinese Academy of Sciences; Institute of Chemistry, Chinese Academy of Sciences; Institute of Atmospheric Physics, Chinese Academy of Sciences. The participating laboratories were randomly coded from Lab-1 to Lab-10 and not related to the above order.

2.2 Sample and Data Collection

Eight daily $PM_{2.5}$ samples were collected on quartz filters (total area: 406.5cm^2) from 16th-23rd January 2019 by a high-volume air sampler (1.13 m^3 min^{-1}; Tisch Environmental Inc., USA) at an urban site, located at the Institute of Atmospheric Physics (IAP) of the Chinese Academy of Sciences in Beijing, China. The sampling site (116.39E, 39.98N) is located between the North Third Ring Road and North Fourth Ring Road, and approximately 200 m from the G6 Highway. It is 8 m above the ground and surrounded by high-density roads and buildings; detailed information regarding the sampling site can be found elsewhere (Shi et al., 2019). Apart from the aerosol samples, 5 field blank filters were also collected in the same manner with the pump off. All ion concentrations in this study were corrected by the values obtained from field blanks. Hourly $PM_{2.5}$ mass concentrations were obtained from a nearby Olympic Park station, the China National Environmental Monitoring Network (CNEM) website. Shi et al. (2019) showed that the $PM_{2.5}$ data at this station are close to those observed at IAP during the APHH-China campaigns. The close observed $PM_{2.5}$ concentrations at different air quality stations in Beijing provide further reassurance of the representability of the observed concentration at Olympic Park. The original hourly data was averaged to 24 h for better comparison.

An Aerodyne Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM) with a $PM_{2.5}$ aerodynamic lens was also deployed on the same roof of the building at IAP for real-time measurements of non-refractory (NR) chemical species (Organics, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) in $PM_{2.5}$ (NR-$PM_{2.5}$) with 2 min time resolution (Sun et al., 2020). Another ToF-ACSM was also used to measure the $PM_{2.5}$-associated non-refractory chemical species at the Beijing University of Chemical Technology (BUCT), which is located at the west third-Ring Road of Beijing and approximately 10 km away from the sampling location of IAP. The concentrations of non-refractory species were calculated from mass spectra using a fragmentation table (Allan et al., 2004). The ToF-ACSM data were then averaged to 24h for a comparison with those from filter analysis in our study. Note that the ToF-ACSM data at IAP on 19th and 20th and data at BUCT on 17th and 18th are excluded from the comparison due to the maintenance of the instrument. An ammonia analyzer (DLT - 100, Los Gatos Research LGR, USA) which applies a unique laser absorption technology called off-axis integrated cavity output spectroscopy was used for the ambient NH_3 measurements. It has a precision of 0.2 ppb and the original data with 5 min intervals were averaged to 24 h for the calculation of aerosol pH. More information on NH_3 measurement can be found elsewhere (Ge et al., 2019).

2.3 Sample Analysis

Filter cuts of $5cm^2$ and $6cm^2$ from the same set of samples were used for extraction in 10 labs. Filters were extracted ultrasonically for 30 minutes with 10 ml ultrapure water in all laboratories and then filtered before IC analysis. The instrument details are given in Table 1. In total, 9 ionic species were reported: F^-, Cl^-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. Other ions including Br^-, NO_2^-, PO_4^{3-} and Li^+ were not included due to their relatively low concentrations in aerosol samples.

Certified reference materials (CRM) were also determined for quality control. CRM for cations (CRM-C, Multi Cation Standard 1 for IC, Sigma-Aldrich) contains 200mg/L Na^+, 200mg/L K^+, 50mg/L Li^+, 200mg/L Mg^{2+}, 1000mg/L Ca^{2+} and 400mg/L NH_4^+. CRM for anion (CRM-A, Multi Anion Standard 1 for IC, Sigma-Aldrich) contains 3mg/L F^-, 10mg/L Cl^-, 20mg/L Br^-, 20mg/L NO_3^-, 20mg/L SO_4^{2-} and 30mg/L PO_4^{3-}. CRM-C and CRM-A were diluted 180 and 6 times, respectively.

20mL of the diluted CRM solutions were marked as unknown solutions and sent along with the aerosol samples to each lab for analysis. All CRM solutions were measured by each lab as unknown samples. All filters and solutions were kept frozen during transportation to prevent any loss due to volatilization.

Table 1. Summary of instrument and method details in 10 laboratories.

Lab No.	Instrument model (Ion Chromatograph)		Columns & suppressor		Eluent	
	Anions	Cations	Anions	Cations	Anions	Cations
1	Dionex AQUNION-1100	Dionex AQUNION-1100	IonPac^{TM} AS11-HC separation column; IonPac^{TM} AG11-HC guard column; suppressor ASRS 300	IonPac^{TM} CS12A separation column; IonPac^{TM} CG12A guard column; suppressor CSRS 300;	30 mM KOH; 1.0 ml/min.	20 mM methansulfonic acid; 1.0 ml/min.
2	Dionex ICS-1100	Dionex ICS-1100	IonPac^{TM} AS11-HC separation column; IonPac^{TM} AG11-HC guard column; suppressor ASRS 500	IonPac^{TM} CS12A separation column; IonPac^{TM} CG12A guard column; suppressor CSRS 500	KOH with gradient variation from 0 to 30 mM; 0.38 ml/min.	15 mM methansulfonic acid; 0.25 ml/min
3	Dionex ICS-600	Dionex ICS-600	IonPac^{TM} AS11-HC separation column; IonPac^{TM} AG11-HC guard column; suppressor ASRS 300	IonPac^{TM} CS12A separation column; IonPac^{TM} CG12A guard column; suppressor CSRS 300	20 mM KOH; 1.0 ml/min.	20 mM methansulfonic acid; 1.0 ml/min
4	Dionex 600	Dionex ICS 2100	IonPac^{TM} AS11 separation column; IonPac^{TM} AG11 guard column; suppressor ASRS 300	IonPac^{TM} CS12A separation column; IonPac^{TM} CG12A guard column; suppressor CSRS 300	30 mM KOH; 1.0 ml/min	20 mM methansulfonic acid; 1.0 ml/min
5	Ion Chromotragraph (ECO)	Ion Chromotragraph (ECO)	Metrosep A5-150 separation column; Metrosep A SUPP 4/5 Guard/4.0 guard column; suppressor MSM	Metrosep C4-150 separation column	3.2 mM Na_2CO_3-1.0mM $NaHCO_3$; 0.7 ml/min	1.7 mM nitric acid - 0.7mM dipicolinic acid; 0.9 ml/min
6	Metrohm (940 Professional IC Vario)	Metrohm (940 Professional IC Vario)	Metrohm A SUPP 5-250 separation column; Metrohm A SUPP 10-250 guard column; suppressor MSM-A Rotor	METROSEP C6-150 separation column; Metrohm C4 guard column	3.2 mM Na_2CO_3-1.0mM $NaHCO_3$; 0.7 ml/min	1.7 mM nitric acid - 1.7mM dipicolinic acid; 0.9 ml/min
7	Dionex ICS600	Dionex ICS600	IonPac^{TM} AS11-HC separation column; IonPac^{TM} AG11-HC guard column; suppressor ASRS	IonPac^{TM} CS12A separation column; IonPac^{TM} CG12A guard column; suppressor CSRS	30 mM KOH; 1ml/min	20 mM methansulfonic acid; 1.0 ml/min
8	Dionex ICS-900	Dionex ICS-900	IonPac^{TM} AS14 separation column; IonPac^{TM} AG14 guard column; suppressor Dionex CCRS 500	IonPac^{TM} CS12A separation column; IonPac^{TM} CG12A guard column; suppressor Dionex CCRS 500	3.5 mM Na_2CO_3-1.0mM $NaHCO_3$; 1.2 ml/min	20 mM methansulfonic acid; 1.0 ml/min
9	Dionex ICS-1100	Dionex ICS-1100	IonPac^{TM} RFICTM AS14A separation column; IonPac^{TM} RFICTM AG14A Guard column	IonPac^{TM} RFICTM CS12A separation column; IonPac^{TM} RFICTM CG12A Guard column	8.0 mM Na_2CO_3-1.0mM $NaHCO_3$; 1.0 ml/min	20 mM methansulfonic acid; 1.0 ml/min
10	Dionex ICS-2100	Dionex INTEGRION HPIC	IonPac^{TM} AS15 separation column; IonPac^{TM} AG15 guard column; suppressor ADRS 600	IonPac^{TM} CS12A separation column; IonPac^{TM} CG12A guard column; suppressor CERS 500;	38mM KOH; 0.3 ml/min.	20 mM methansulfonic acid; 1.0 ml/min.

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2.4 Coefficient of Divergence Analysis

In order to investigate the differences of ionic concentrations measured by different labs, the Pearson's correlation coefficient (R) and the coefficient of divergence (COD) were applied. COD is a parameter to evaluate the degree of uniformity or divergence of two datasets. COD and R were computed for Lab_j/Lab-Median pairs, of which Lab_j indicates the results of each lab and Lab-Median represents the median values of 10 labs. Median values are chosen here to better represent the theoretical true concentrations of the ions, as there are some outliers in some labs, and the averages may be less representative. The results of COD and R were also computed for Lab_j/Lab-Mean, Lab_j/Lab-Upper and Lab_j/Lab-Lower pairs (Supplemental Information Fig. S1-S3), where Lab-Mean, Lab-Upper and Lab-Lower represent the mean value, upper values (84% percentile) and lower values (16% percentile) of ion concentrations measured by 10 labs. COD of ionic concentrations of two datasets is determined as follows:

$$\text{COD}_{jk} = \sqrt{\frac{1}{P}\sum_{i=1}^{P}\left(\frac{X_{ij}-X_{ik}}{X_{ij}+X_{ik}}\right)^2} \qquad (1)$$

where j represents the ion concentrations measured by an individual lab-j, k stands for the median ion concentrations of 10 labs, P is the number of samples. X_{ij} and X_{ik} represent the concentration of ion i measured by lab-j and the median concentration of ion i measured by 10 labs, respectively. COD value equals to 0 implies no difference between two datasets, while a COD of 1 means absolute heterogeneity and maximum difference between two datasets (Liu et al., 2017c). A COD value of 0.2 is applied as an indicator for similarity and variability (Krudysz et al., 2008). A higher COD (>0.2) implies variability between two datasets, while lower COD (<0.2) indicates similarity between them. A COD value of 0.269 is used here as an indicator as well, as this value was also applied in other studies (Kamal et al., 2016; Wongphatarakul et al., 1998). Overall, lower COD (<0.2) and higher R (>0.8) of the lab suggest the similar variation pattern and similar ion concentrations of this lab with the median values of 10 labs.

2.5 ISORROPIA-II

ISORROPIA-II is a thermodynamic equilibrium model for predicting the composition and physical state of atmospheric inorganic aerosols (available at http://isorropia.eas.gatech.edu) (Fountoukis and Nenes, 2007). It was applied in this study to calculate the aerosol water content (AWC) and pH. Aerosol pH in this study ($\mathrm{pH_i}$) was defined as the molality-based hydrogen ion activity on a logarithmic scale, calculated applying the following equation (Jia et al., 2018; Song et al., 2019):

$$\mathrm{pH_i} = -\log_{10}\left(a_{\mathrm{H}^+_{(\mathrm{aq})}}\right) = -\log_{10}\left(m_{\mathrm{H}^+_{(\mathrm{aq})}}\gamma_{\mathrm{H}^+_{(\mathrm{aq})}}/m^{\Theta}\right) \quad (2)$$

where $a_{\mathrm{H}^+_{(\mathrm{aq})}}$ represents hydrogen ion activity in aqueous solution, $\mathrm{H}^+_{(\mathrm{aq})}$. $m_{\mathrm{H}^+_{(\mathrm{aq})}}$ and $\gamma_{\mathrm{H}^+_{(\mathrm{aq})}}$ represent the molality and the molality-based activity coefficient of $\mathrm{H}^+_{(\mathrm{aq})}$, respectively. m^{Θ} is the standard molality (1 mol kg^{-1}). Model inputs include aerosol-phase $\mathrm{Cl^-}$, $\mathrm{SO_4^{2-}}$, $\mathrm{NO_3^-}$, $\mathrm{Na^+}$, $\mathrm{NH_4^+}$, $\mathrm{K^+}$, $\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$ and gas-phase $\mathrm{NH_3}$ concentrations, along with daily averaged temperature and relative humidity (Table S2). 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, assuming salts do not precipitate under supersaturated conditions. More information regarding applications of ISORROPIA-II can be found in other studies (Guo et al., 2016; Weber et al., 2016; Song et al., 2018).

3. RESULTS AND DISCUSSION

3.1 Quality Assurance and Quality Control (QA & QC)

3.1.1 Certified reference materials (CRM) - Recovery and repeatability

Certified reference materials for both cations and anions were investigated for quality control. CRM-C and CRM-A were analyzed three consecutive times in each lab. The recovery of each ion was determined as the ratio of measured concentration divided by its certified concentration in percentage. The results of recovery of all ions are listed in Table 2.

Table 2. Recovery (%) of water-soluble inorganic ions in certified reference materials measured by 10 laboratories.

Lab NO.	F^-	Cl^-	SO_4^{2-}	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
1	111.8 ± 0.2	107.6 ± 0.1	108.5 ± 2.4	110 ± 0.5	98.2 ± 0.0	108.7 ± 0.3	99.4 ± 0.2	95.6 ± 0.3	99.6 ± 0.6
2	89.1 ± 0.4	95.1 ± 0.2	94.0 ± 1.0	94.5 ± 0.5	102.2 ± 1.0	135.0 ± 6.0	94.9 ± 4.6	95.9 ± 0.2	92.8 ± 0.5
3	101 ± 1.4	95.9 ± 0.3	132.4 ± 31.4	97.1 ± 1.0	91.4 ± 0.1	93.5 ± 0.2	92.4 ± 0.2	105.5 ± 0.3	98.7 ± 0.4
4	94.1 ± 4.0	90.4 ± 0.2	91.9 ± 1.2	91.7 ± 1.4	93.3 ± 1.7	112.2 ± 0.6	92.0 ± 2.8	98.9 ± 2.0	100.4 ± 1.1
5	94.0 ± 3.1	99.0 ± 0.0	92.4 ± 0.9	97.7 ± 0.0	85.9 ± 3.2	89.3 ± 0.5	92.1 ± 4.9	96.1 ± 0.6	101.7 ± 3.0
6	93.3 ± 0.3	110.8 ± 0.5	89.2 ± 0.1	91.4 ± 0.2	98.2 ± 1.1	88.4 ± 1.1	92.2 ± 4.9	102.0 ± 2.1	102.6 ± 1.2
7	89.4 ± 2.7	114.5 ± 21.3	100.8 ± 0.0	105.2 ± 0.2	97.0 ± 1.3	107.5 ± 0.8	72.1 ± 0.8	93.5 ± 0.4	91.9 ± 1.1
8	92.0 ± 0.0	96.6 ± 0.7	97.4 ± 1.1	96.2 ± 1.2	97.3 ± 0.0	93.8 ± 0.3	97.3 ± 0.9	94.0 ± 2.1	89.3 ± 0.6
9	102.6 ± 1.5	105.9 ± 1.0	101.9 ± 4.5	99.1 ± 3.5	101.2 ± 0.1	110.6 ± 0.2	103.0 ± 0.0	99.7 ± 0.2	102.2 ± 0.3
10	103.4 ± 1.6	103.5 ± 0.7	99.0 ± 9.3	114.2 ± 2.5	95.3 ± 4.1	91.0 ± 4.1	91.5 ± 4.7	94.8 ± 3.8	96.3 ± 2.1

As reported in Table 2, most ions were observed with a recovery in the range 90% - 110% among 10 laboratories. However, SO_4^{2-} in Lab-3 and NH_4^+ in Lab-2 were overestimated, which resulted in the recovery of 132.4%±31.4% and 135.0%±6.0%, respectively. The standard deviation of SO_4^{2-} measured by Lab-3 was the largest (31.4%), followed by Cl^- measured by Lab-7 (21.3%), which indicated their poor repeatability. Even though NH_4^+ in Lab-2 was observed with high recovery, its deviation of three repeats was relatively small, which may be attributable to the evaporation of ammonium in calibration standards in Lab-2; hence, the level it represented was higher than its real concentration. K^+ in Lab-7 was underestimated, and was observed with a recovery of only 72.1%±0.8%. This may be due to contamination in the water blanks or the IC system.

3.1.2 Detection limits

The detection limits (DLs) in this study were calculated as:

$$\mathrm{DL} = 3 \times \mathrm{SD_i} \qquad (3)$$

where $\mathrm{SD_i}$ is the standard deviation of the blank filters. The mean concentrations of the ions in blanks and DLs (3SD) of all ions are provided in Table 3.

Table 3. Mean filter blank concentrations and detection limits (3SD) (ng/m^3) of ions measured by 10 laboratories.

	F^-		Cl^-		SO_4^{2-}		NO_3^-		Na^+		NH_4^+		K^+		Mg^{2+}		Ca^{2+}	
Lab	mean	3SD	mean	3SD	mean	3SD	mean	3SD	mean	3SD	mean	3SD	mean	3SD	mean	3SD	mean	3SD
1	2.3	4.0	33.2	31.5	74.2	12.7	64.2	7.1	78.3	31.3	37.2	16.6	7.9	19.6.	3.4	3.9.	50.0	18.2.
2	0.2	0.4	10.9	11.3	15.6	2.5	35.3	14.7	11.5	8.0	20.8	5.0	3.4	1.2	3.2	6.8	38.1	54.6
3	2.8	2.0	6.3	2.7	8.7	11.7	15.3	10.5	0.5	3.4	9.6	3.9	0.0	0.0	0.0	0.0	6.8	18.8
4	59.6	195.2	103.6	229.3	85.3	25.9	50.3	159.6	22.8	29.4	59.6	123.2	19.1	26.5	10.1	1.9	376.4	90.4
5	4.2	2.7	50.9	98.6	33.4	40.8	25.7	116.5	51.6.	57.7.	46.3	54.7	22.6	9.4	45.4	9.4	268.2	49.8
6	n.a.	n.a.	251.6	7.4	55.1	53.6	24.5	0.0	56.6	35.9	35.0	46.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
7	2.1	3.9	11.4	11.8	37.9	32.7	14.5	40.3	6.1	0.0	5.8	0.0	4.9	12.4	1.4	4.5	7.6	17.3
8	n.a.	n.a.	29.0	32.8	17.4	26.1	n.a.	n.a.	8.7	22.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	20.3	27.1
9	n.a.	n.a.	n.a.	n.a.	34.8	32.8	39.5	22.7	47.4	12.1	21.2	8.3	10.1	5.4	1.6	0.2	7.1	32.4
10	29.4	1.3	19.5	21.1	59.4	21.3	78.8	102.2	24.6	53.3	33.5	34.2	31.3	82.1	4.3	0.0	10.2	14.6

Note: The detection limits were calculated based on large-volume sampling (total filter size: 406.5 cm^2; total sampling volume: 1560 m^3); n.a.: not available due to no relevant peaks being identified in the chromatography.

3.2 Mass Concentrations of $PM_{2.5}$ and Inorganic Ions

3.2.1 $PM_{2.5}$ and ion concentrations

The results for $PM_{2.5}$ and all inorganic ion concentrations measured by 10 labs are presented in Fig. 1. During January 16th – 23rd 2019, the daily mean $PM_{2.5}$ ranged from 8.4 to 53.8 $\mu g/m^3$, with an average of 31.4 $\mu g/m^3$. Among them, January 16th, 17th and 18th were deemed moderately polluted days with $PM_{2.5}$ concentration > 35 $\mu g/m^3$, while the rest were non-haze days with $PM_{2.5}$ concentrations falling in the range of 8.4-27.9 $\mu g/m^3$.

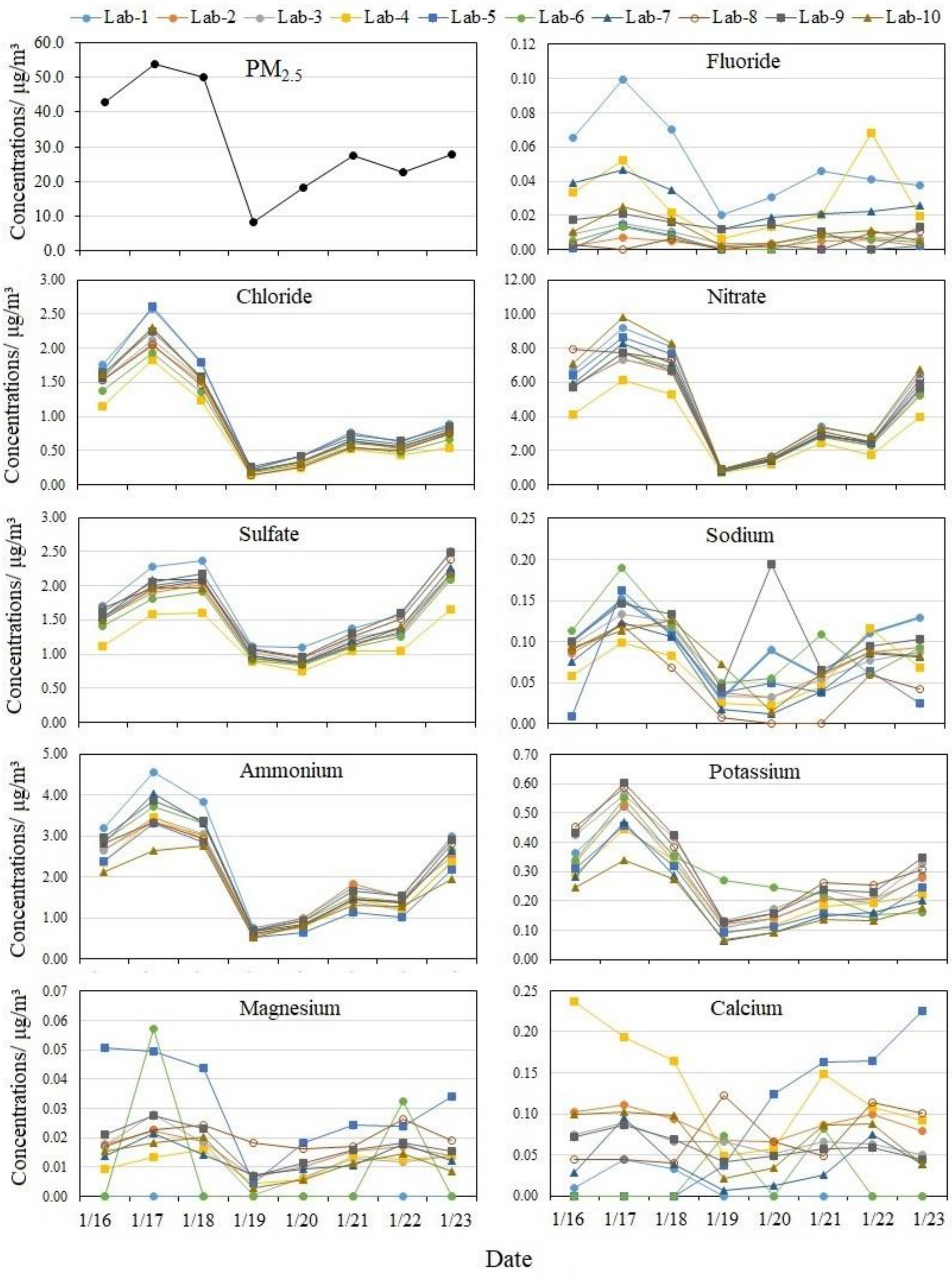

Fig. 1. The time series of mass concentrations of PM$_{2.5}$ and ions

The time series of all inorganic ions are also shown in Fig. 1 to demonstrate the consistency among different laboratories. In Fig. 1, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ showed a similar trend to $PM_{2.5}$ and good correlations among the 10 labs, suggesting the consistency and reliability of using Ion Chromatography for analysing these ions, despite various instruments and analysing methods. Larger variations of Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ concentrations between different laboratories were observed in moderately polluted days, whereas results for the non-haze days, especially for 19th and 20th, were observed with good agreement in 10 labs.

The average SNA concentrations of 8 samples varied from 6.3±3.3 (Lab-4) to 9.1±5.0 (Lab-1) $\mu g/m^3$ in 10 labs, accounting for 20.6±4.8 % to 29.0±6.7 % of the $PM_{2.5}$ mass concentrations. However, their contributions to total ions measured by each lab were not significantly different, and ranged between 83.6±2.7% and 86.3±2.3%. The total ions summed to 24.3±4.9% (Lab-4) to 33.8±7.1% (Lab-1) of $PM_{2.5}$. These results are comparable with those in another study in Beijing which found that SNA accounted for 88% of total ions and 9-70% of $PM_{2.5}$ concentrations (Xu et al., 2019b). As shown in Table 2, the recoveries of most ions measured by Lab-4 were < 100%, while those of Lab-1 were much higher, especially for major ions (>100%). For Lab-6 which was also observed to have lower recoveries of ions such as the lowest recoveries of 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.

K^+ concentrations analysed by 10 labs followed a similar trend to $PM_{2.5}$ mass, except the sample measured on a moderately polluted day (19th) by Lab-6, which is 2-3 times higher than that measured by other labs. F^- concentrations varied across 10 labs, but most of them shared a similar trend. Some labs like Lab-8 did not follow the same trend due to reporting undetectable F^- concentrations. The Na^+ concentration on the least polluted day (20th) was abnormally high in Lab-9, while its concentrations measured by other labs were generally low. This could be due to Na^+ contamination during preparation or measurement of this sample, as Na^+ concentrations in the rest of the samples measured by Lab-9 followed a similar trend as that of other labs. The alkaline ions Mg^{2+} and Ca^{2+} are mostly originated from crustal dust and mainly exist in coarse particles (Zou et al., 2018). Their mass concentrations varied considerably due to their relatively low concentrations in aerosol samples and being sometimes below the detection limits in some labs, such as Lab-6. Nevertheless, some labs like Lab-2, 3, and 10 still followed a similar trend.

3.2.2 Comparison with ToF-ACSM data

As shown in Fig. 1, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ generally exhibited similar patterns, but due to some outliers, such as NO_3^- concentration measured by Lab-8 on the 16th , the median values were selected to better represent the general levels and theoretical actual concentrations of ions measured by different labs. The scatter plots of the median mass concentrations of Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ in 10 labs (IC- Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) *versus* the non-refractory (NR) species measured by the ToF-ACSM (ACSM- Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) are shown in Fig. 2. The time series of IC and ACSM data at IAP and BUCT are plotted in Fig. S4.

Chloride is reported to arise mainly from biomass burning and coal combustion in China (Zhang et al., 2016). Its average concentration in 10 labs correlated very well with ACSM-Cl^- (R^2=0.82 for IAP). However, IC-Cl^- in IAP is 2-3 times higher than ACSM-Cl^-; this may be due to the small contribution of Cl^- to the overall mass spectrum which made it difficult to quantify by ToF-ACSM (Allan et al., 2004). Additionally, the ACSM is incapable of measuring

Cl^- in the form of KCl, as the ACSM only measures non-refractory Cl^-. Poor correlation of chloride (R^2=0.21) was also discovered between two collocated ACSMs with a much larger set of data points, while other NR species were observed with strong correlation (R^2>0.8) in another study (Budisulistiorini et al., 2014), suggesting the quantification of chloride by ACSM has large uncertainties.

Very good correlation between measured IC and ACSM data was found for NO_3^- and NH_4^+ with R^2>0.9. The lab median value of NO_3^- was very close to the ACSM-NO_3^- from the same sampling site- IAP, with a slope of 0.88 for IC-NO_3^-/ ACSM-NO_3^-, while that of BUCT was only 0.57. The slopes of IC-NH_4^+/ ACSM-NH_4^+ were 0.58 and 0.60 for IAP and BUCT, respectively. Comparing IC-NH_4^+ to ACSM-NH_4^+, the absolute concentration of IC-NH_4^+ differed the most among all ions (42%), except Cl^-. Generally, ACSM-NO_3^- and ACSM-NH_4^+ were higher than the median values of measured NO_3^- and NH_4^+ concentrations in the 10 labs. A potential reason is the high volatility of these species which leads to higher concentrations in the online ACSM observations compared to the daily filter sample measurements due to negative filter artefacts. It is also possible that the representative ions of ACSM-NO_3^- and -NH_4^+ could have significant interferences from other species in the mass spectrum, causing large uncertainties even after correction for those interferences.

Sulfate, as another important component of atmospheric secondary inorganic aerosols, plays an important role in the formation of haze (Wang et al., 2014; Yue et al., 2019). The correlation coefficient (R^2) between the measured IC-SO_4^{2-} and ACSM-SO_4^{2-} was only 0.26 for IAP with a slope of 0.54, but R^2 increased to 0.82 when excluding an outlier of the data on 23rd. The correlation of IC-SO_4^{2-} and ACSM-SO_4^{2-} from BUCT was 0.84 (R^2) with a slope of 0.56. Judging from the slopes, ACSM-SO_4^{2-} and ACSM- NH_4^+ were similarly higher than the median values of measured SO_4^{2-} and NH_4^+ concentrations in this study. The NR species followed the

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same trend as NR-$PM_{2.5}$, and chemical species measured through filter analysis also shared the same trend as $PM_{2.5}$ measured in our study.

To summarize, SO_4^{2-}, NO_3^-, NH_4^+ from lab analysis generally correlated very well with the ACSM data, but the absolute concentrations differ by up to 42%. Cl^- from the two methods is correlated but the concentration differ by more than 3 times. Crenn et al. (2015) reported the uncertainties of NO_3^-, SO_4^{2-}, and NH_4^+ in ACSM analysis were 15%, 28%, and 36%. It appears that Cl^- is less accurate in online ACSM observations. NO_3^- was comparable for the online data and filter-based data, while SO_4^{2-} and NH_4^+ in online data may be generally overestimated by a similar factor. It should be noted that higher SO_4^{2-} concentrations in online ACSM data could potentially be due to ACSM not being able to separate organosulfate from sulfate. ACSM-NO_3^-, -SO_4^{2-} and -NH_4^+ were also reported to be higher (approximately 10-20%) than filter analysis based NO_3^-, SO_4^{2-} and NH_4^+ in another study (Sun et al., 2020). Although the comparison between IC and ACSM provided important information about the data from the two methods, we recognize that we only have 8 data points here. Future studies should be carried out and include more data points in order to comprehensively study the relationship between the online ACSM data and filter-based data. We emphasize that it is essential that the filter-based observations are robustly quality controlled before any ACSM and IC intercomparison.

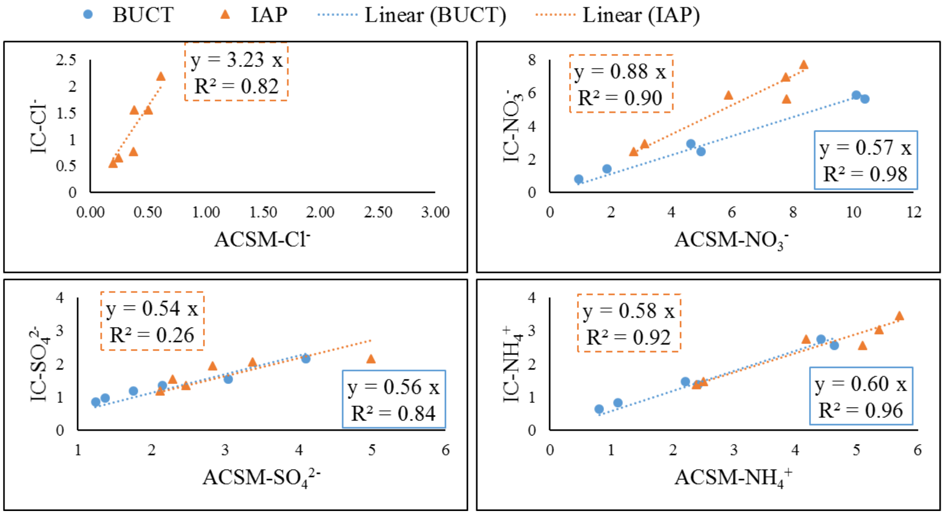

Fig. 2. Scatter plots of the median mass concentrations of Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ measured by 10 labs (IC- Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) *versus* the non-refractory (NR) chemical species from ACSM (ACSM- Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) from BUCT and IAP.

3.2.3 NO_3^-/SO_4^{2-} ratios

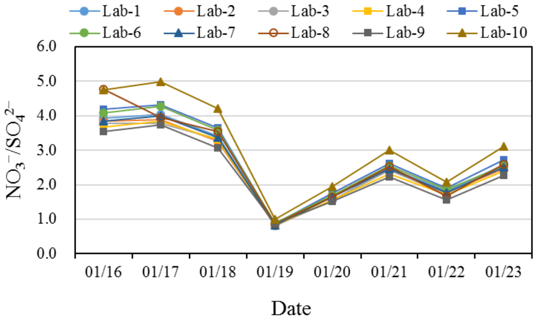

Fig. 3. Mass ratio of NO_3^-/SO_4^{2-} during the study period in 10 labs.

Good agreement was observed for the mass ratios of NO_3^-/SO_4^{2-} in most of the labs during the study period, which basically followed a similar trend as $PM_{2.5}$. On more polluted days, NO_3^-/SO_4^{2-} ratios were obviously higher than less polluted days, suggesting the dominance of mobile source contributions over stationary sources during heavily polluted days.

3.3 Divergence and Correlation Analysis

As shown above, some ions like Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ generally exhibited similar patterns, but some of the ions varied significantly in different laboratories. Therefore, the Pearson's correlation coefficient (R) and the coefficient of divergence (COD) were both calculated to identify the uniformity and divergence of ionic concentrations measured by different labs. The COD and R values of all ions for Lab_j/Lab-Median pairs are presented in Fig. 4. Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ and K^+ clearly showed high R values (>0.8) and low COD values (<0.2) in all labs, suggesting the reliability of the measurement of these ions in different labs. However, F^- and Ca^{2+} in most labs was observed with higher COD values, and Ca^{2+} was also found with lower R, suggesting heterogeneity of Ca^{2+} detection in different labs, which made this ion less reliable. Mg^{2+} was observed with good correlation (>0.7) between each lab and the Lab-Median, but a higher COD was found between Lab-3, 5, 6 with the Lab-Median. Similarly, Na^+ was also observed with good correlation (>0.7) between each lab and the Lab-Median, except Lab-9, and a higher COD was found between Lab-5, 8 with the Lab-Median.

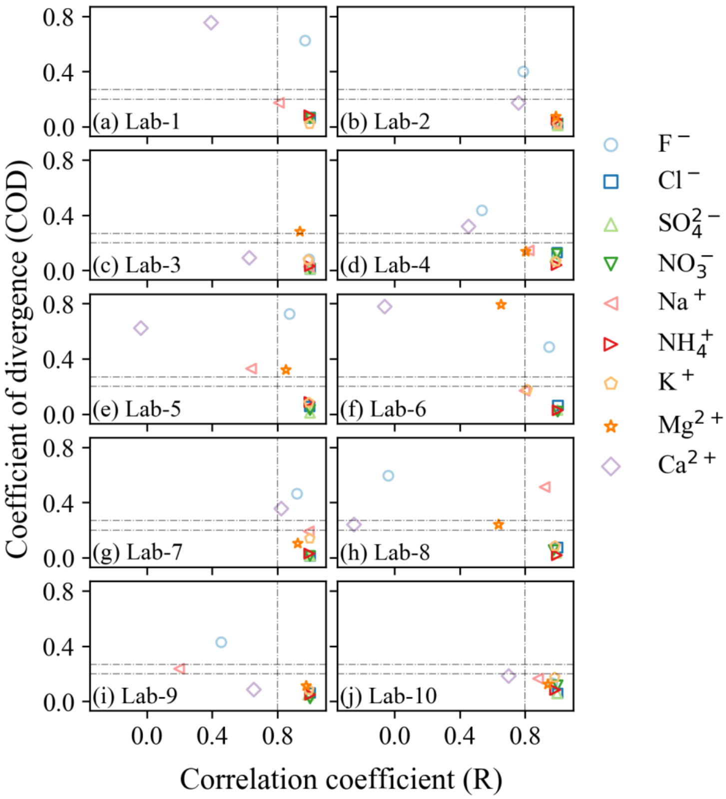

Fig. 4. Coefficient of divergence (COD) plotted against correlation coefficient (R) for all ions in each lab with the median ionic concentrations of 10 labs. (Note: vertical line indicates an R value of 0.8, and horizontal lines indicate COD values of 0.2 and 0.269, respectively).

3.4 Correction of Ion Concentrations by Recovery of CRM

The recovery of the certified reference materials was used to correct the ion concentrations in this study. The correction was conducted by dividing the measured ion concentrations by their corresponding recovery value. The coefficient of variation (CV) which can indicate the variance of data, was applied here to compare the variation of uncorrected/corrected ion concentrations among 10 labs. It was calculated as the standard deviation of ion concentrations measured by 10 labs divided by the mean and expressed in a percentage. A lower CV value indicates the closeness of data measured by 10 labs and reflects more precise results, while higher CV value reflects the opposite. As F$^-$, Na$^+$, Mg^{2+} and Ca^{2+} were undetectable in some labs, only Cl^-, SO_4^{2-}, NO_3^-, NH_4^+ and K^+ were investigated and the results are shown in Table 4.

In Table 4, Lab-7 was excluded from the calculation of CV of both uncorrected and corrected chloride, due to its poor repeatability. The CV of uncorrected chloride concentration in 8 samples varied between 11.7-19.3%, with an average of 14.3%. CV of corrected chloride concentration in 8 samples varied between 10.4-17.0%, with an average of 12.6%. The averaged CV decreased 1.7% for corrected chloride concentration. Small changes of CV were observed during moderately polluted days (16th, 17th, 18th), but more obvious changes occurred during non-haze days. These results suggested that certified reference materials can be used to correct the Cl^- concentrations for more accurate results, especially for less polluted samples.

The average CV of SO_4^{2-} surprisingly increased from 9.8% for uncorrected to 10.9% for corrected SO_4^{2-} (Supplemental Table S1). However, when excluding Lab-3 from the calculation, the averaged CV of uncorrected sulfate concentration was 10.3% and it significantly decreased to 6.9% once corrected. Therefore, it is strongly recommended that excessive recovery (>110%) with large variation should be avoided for the correction of SO_4^{2-} concentrations. Better agreements of NO_3^- and K^+ concentrations among 10 labs were also observed after correction, as indicated by lower CV values for corrected samples. Similar to other ions, the mean concentration of NH_4^+ of the 10 labs remained almost the same after correction, but the CV of corrected samples increased from 12.5% to 13.2% after correction (Supplemental Table S1). Nevertheless, it decreased 1.2% after correction when excluding Lab-2 from the calculation, the NH_4^+ recovery of which was 135.0±6.0 %. The small change of coefficient of variation here could be due to the high volatility of ammonia which leads to differing results measured by different analytical procedures in labs.

To sum up, certified reference materials should be applied for the correction of the ion concentrations. But the extreme recoveries with large inter-CRM variations should be avoided from the corrections, as this may increase the uncertainty of measurements.

Table 4. Uncorrected and CRM-corrected ion concentrations (μg/m^3) and their corresponding coefficient of variations (CV/ %).

	Uncorrected Mean (min-max)	CV/%	Corrected Mean (min-max)	CV/%	Uncorrected Mean (min-max)	CV/%	Corrected Mean (min-max)	CV/%
	Chloride				Sulfate			
2019/1/16	1.5 (1.2-1.8)	11.7	1.5 (1.2-1.7)	10.4	1.5 (1.1-1.7)	11.3	1.6 (1.2-1.7)	8.8
2019/1/17	2.2 (1.8-2.6)	12.4	2.2 (1.7-2.6)	11.3	2.0 (1.6-2.3)	9.7	2.0 (1.7-2.2)	6.0
2019/1/18	1.5 (1.2-1.8)	11.9	1.5 (1.2-1.8)	11.2	2.0 (1.6-2.4)	10.2	2.1 (1.7-2.3)	7.3
2019/1/19	0.2 (0.1-0.3)	19.3	0.2 (0.2-0.2)	16.8	1.0 (0.9-1.1)	7.9	1.0 (1.0-1.1)	4.5
2019/1/20	0.3 (0.2-0.4)	19.0	0.3 (0.3-0.4)	17.0	0.9 (0.8-1.1)	10.7	0.9 (0.8-1.0)	6.7
2019/1/21	0.6 (0.5-0.8)	12.6	0.6 (0.5-0.7)	11.0	1.2 (1.1-1.4)	8.7	1.2 (1.1-1.3)	4.7
2019/1/22	0.5 (0.4-0.7)	13.4	0.5 (0.4-0.6)	11.3	1.4 (1.0-1.6)	12.5	1.4 (1.1-1.6)	8.8
2019/1/23	0.8 (0.5-0.9)	13.9	0.8 (0.6-0.8)	12.0	2.2 (1.7-2.5)	11.6	2.3 (1.8-2.4)	8.5
Average		14.3		12.6		10.3		6.9
	Nitrate				Ammonium			
2019/1/16	6.1 (4.1-8.0)	16.5	6.1 (4.5-8.3)	15.2	2.7 (2.1-3.2)	12.7	2.7 (2.1-3.2)	12.8
2019/1/17	8.0 (6.1-9.8)	13.1	8.0 (6.7-8.9)	7.8	3.6 (2.6-4.5)	14.9	3.6 (2.9-4.2)	12.1
2019/1/18	7.1 (5.3-8.3)	12.1	7.1 (5.7-7.9)	8.4	3.1 (2.7-3.8)	10.8	3.2 (2.6-3.8)	10.2
2019/1/19	0.9 (0.7-0.9)	8.9	0.9 (0.8-1.0)	7.3	0.6 (0.5-0.8)	11.7	0.6 (0.6-0.7)	9.4
2019/1/20	1.5 (1.2-1.7)	9.8	1.5 (1.3-1.6)	7.0	0.8 (0.6-1.0)	13.1	0.8 (0.7-1.1)	13.3
2019/1/21	3.0 (2.4-3.4)	9.4	3.0 (2.7-3.3)	5.9	1.5 (1.1-1.7)	12.1	1.5 (1.3-1.7)	9.7
2019/1/22	2.4 (1.8-2.9)	12.3	2.5 (2.0-2.6)	7.9	1.3 (1.0-1.5)	12.3	1.3 (1.1-1.6)	11.8
2019/1/23	5.7 (4.0-6.8)	13.6	5.7 (4.4-6.4)	9.6	2.5 (2.0-3.0)	13.7	2.6 (2.1-3.0)	12.6
Average		12.0		8.6		12.7		11.5
	Potassium							
2019/1/16	0.3 (0.2-0.5)	19.8	0.4 (0.3-0.5)	16.2				
2019/1/17	0.5 (0.3-0.6)	15.6	0.5 (0.4-0.7)	14.9				
2019/1/18	0.3 (0.3-0.4)	14.1	0.4 (0.3-0.5)	10.8				
2019/1/19	0.1 (0.1-0.3)	48.5	0.1 (0.1-0.3)	47.7				
2019/1/20	0.1 (0.1-0.2)	31.4	0.2 (0.1-0.3)	29.7				
2019/1/21	0.2 (0.1-0.3)	20.9	0.2 (0.2-0.3)	17.0				
2019/1/22	0.2 (0.1-0.3)	20.6	0.2 (0.1-0.3)	17.8				
2019/1/23	0.3 (0.2-0.3)	25.3	0.3 (0.2-0.4)	21.3				

Average	24.5	21.9

Lab-2, 3 and 7 were excluded for calculating CV% of ammonium, sulfate and chloride, respectively.

3.5 Aerosol Acidity

In this study, aerosol acidity was evaluated applying three different parameters: Anion and Cation Equivalence Ratio, ion-balance and in situ acidity. Ion-balance was calculated by subtracting equivalent cations from anions (Zhang et al., 2007), while in-situ aerosol acidity was represented by pH or the concentration of free H^+ in the deliquesced particles under ambient conditions. In situ aerosol pH can be estimated from various thermodynamic models, for example, SCAPE, GFEMN, E-AIM and ISORROPIA (He et al., 2012; Pathak et al., 2009; Yao et al., 2006). In situ aerosol acidity is most likely to influence the chemical behavior of aerosols (He et al., 2012). Ion-balance is widely used to indicate the neutralization status of aerosols with the equivalent ratios of anions/cations in a relative way (Sun et al., 2010; Takami et al., 2007; Chou et al., 2008). It is noteworthy that ion-balance and in-situ aerosol acidity estimations are empirical approaches which are strongly dependent on the selection of ion species.

3.5.1 Anion and Cation Equivalence Ratio

The ratio of the anion molar equivalent concentrations to the cation molar equivalent concentrations (AE/CE) can be applied to reflect the potential aerosol acidity (Meng et al., 2016; Zou et al., 2018). In this study, AE and CE were calculated as:

$$\mathrm{AE} = [\mathrm{SO_4^{2-}}/96]\times 2 + [\mathrm{NO_3^-}/62] + [\mathrm{Cl^-}/35.5] + [\mathrm{F^-}/19] \qquad (4)$$

$$\mathrm{CE} = [\mathrm{NH_4^+}/18] + [\mathrm{Na^+}/23] + [\mathrm{K^+}/39] + [\mathrm{Mg^{2+}}/24]\times 2 + [\mathrm{Ca^{2+}}/40]\times 2 \qquad (5)$$

AE represents the equivalent concentrations of all anions; and CE denotes all cations equivalent concentrations.

Table 5. Anion and cation equivalent ratios (AE/CE) among 10 laboratories.

	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Lab-8	Lab-9	Lab-10
2019/1/16	1.02	1.01	1.02	0.81	1.26	0.93	1.03	1.18	0.93	1.43
2019/1/17	1.00	1.02	1.01	0.85	1.25	0.93	0.87	1.07	0.96	1.59
2019/1/18	1.03	1.03	1.04	0.84	1.26	0.96	1.03	1.14	0.95	1.28
2019/1/19	0.99	0.79	0.97	0.85	1.11	0.65	0.99	0.90	0.98	1.15
2019/1/20	1.00	0.80	0.96	0.85	1.14	0.82	1.00	0.98	0.83	1.08
2019/1/21	1.03	0.78	1.03	0.80	1.14	0.85	1.04	1.02	0.90	1.12
2019/1/22	1.04	0.79	1.04	0.80	1.16	0.90	0.97	0.91	0.93	1.09
2019/1/23	1.02	0.98	1.05	0.80	1.15	0.95	0.84	1.00	0.94	1.48

As presented in Table 5, the AE/CE ratio of all samples were compared among 10 labs. The ratios in Lab-1 and Lab-3 were close to unity. The ratios in Lab-5 and Lab-10 were above 1, indicating the deficiency of cations to neutralize all anions, while that was the contrary of Lab-4, 6 and 9. In Table 2, the recoveries of major cations (Na^+, NH_4^+, K^+) were <100% and much lower than those of the major anions (Cl^-, NO_3^-, SO_4^{2-}) in Lab-5 and 10, which may have caused lower cation concentrations than their real concentrations and a constant higher ratio of AE/CE. For Lab-9, the recoveries of all ions were very close to 100%, except NH_4^+ which was found with a recovery of >110%. Therefore, AE/CE < 1 of all samples measured by Lab-9 could be the result of overestimation of ammonium. Similarly, in addition to an ammonium recovery of >110%, generally lower anion recoveries than cations were reported by Lab-4, which may explain AE/CE < 1 in all samples measured by this lab as well. The other three labs (Lab-2, 7 and 8) were found with various AE/CE ratios with both >1 and <1 values; moderately polluted days were generally observed with a higher ratio of AE/CE. These results indicate that AE/CE ratios bear large uncertainties from different labs. Stricter quality control measures should be adopted if applying AE/CE ratios to evaluate aerosol acidity.

3.5.2 Ion Balance

The calculation of ion balance is an alternative way to evaluate the aerosol acidity (Han et al., 2016; He et al., 2012). Three methods were listed below for the calculation of ion balance in this study:

Method 1: $IB = 2[\mathrm{SO}_4^{2-}] + [\mathrm{NO}_3^-] - [\mathrm{NH}_4^+]$ (6)

Method 2: $IB = 2[\mathrm{SO}_4^{2-}] + [\mathrm{NO}_3^-] + [\mathrm{Cl}^-] - [\mathrm{NH}_4^+] - [\mathrm{Na}^+] - [\mathrm{K}^+]$ (7)

Method3:$IB = 2[\mathrm{SO}_4^{2-}] + [\mathrm{NO}_3^-] + [\mathrm{Cl}^-] - [\mathrm{NH}_4^+] - [\mathrm{Na}^+] - [\mathrm{K}^+] - 2[\mathrm{Mg}^{2+}] - 2[\mathrm{Ca}^{2+}]$ (8)

In Method 1, only SO_4^{2-}, NO_3^- and NH_4^+ were applied for the calculation (Tian et al., 2017), assuming that these three ions and H^+ alone control $PM_{2.5}$ acidity (Ziemba et al., 2007). SO_4^{2-}, NO_3^- and NH_4^+ were also used in other studies to assess aerosol acidity. For example, the mole charge ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- was applied to represent aerosol acidity (Chandra Mouli et al., 2003; Wang et al., 2019). SO_4^{2-}, NO_3^- and NH_4^+ were selected because they contributed approximately 90% of the total ionic species in fine aerosols and play predominant roles in controlling aerosol acidity (Zhou et al., 2012). Salt ions Na^+, K^+ and Cl^- were added for the calculation in Method 2. Based on this calculation, Mg^{2+} and Ca^{2+} were added in Method 3 to include the effects of crustal dust on aerosol acidity (Huang et al., 2014).

The ion balance of all labs varied applying different methods, especially for the first three heavily polluted days, as shown in Fig. 5. Positive ion balance values indicated a deficiency of cations to neutralize anions, while negative values implied an excess of cations to neutralize anions. Lab-10 showed the highest variation among all labs; when excluding Lab-10, the results of the other 9 labs agreed very well, with most of the values below 0, suggesting sufficient ammonium to neutralize sulfate and nitrate. By applying Method 1, comparable results were found. The average ion balance values in all samples were consistent in Lab-1, 2, 6, 7, 9 (0.02 μmol/m^3). When adding more ions in the calculation by adopting Methods 2 and 3, poorer agreement among all labs was exhibited. Therefore, it seems more consistent to indicate the relative ion-balanced aerosol acidity among different samples by Method 1, as SNA were the most abundant ions in atmospheric aerosols and their concentrations measured by different labs showed good agreement (Fig. 1). This method could reduce the large discrepancy of ion balance results calculated by adding other ions from the different labs, as their concentrations varied largely in different labs due to varying detection limits.

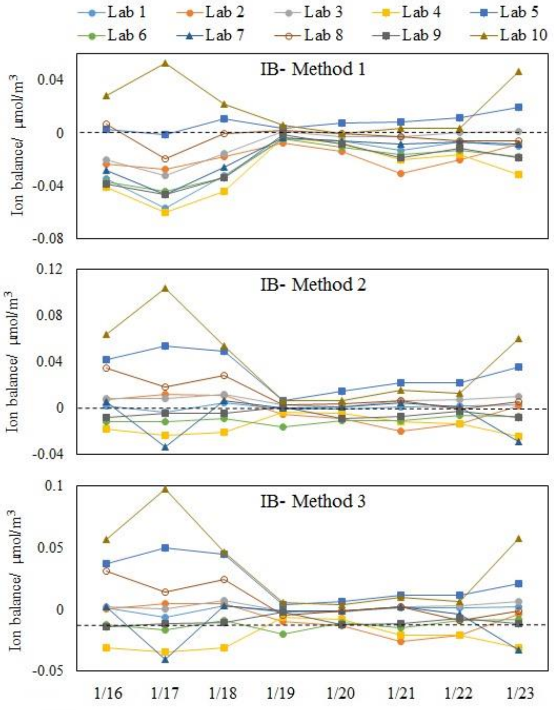

Fig. 5 Ion balance in all labs applying different methods (negative values reflect the excessive cations to neutralize anions)

3.5.3 Aerosol pH using ISORROPIA-II

A thermodynamic equilibrium model- ISORROPIA-II was applied to estimate the in-situ aerosol acidity. This was run only in forward mode, as the results from the use of reverse mode (using only particle phase composition) are reported to be unreliable (Song et al., 2018). The only gas phase data were for ammonia, but this introduces little error as concentrations of HNO_3 and HCl are likely to be very low in this high ammonia environment (Song et al., 2018).

The inputs include aerosol-phase Cl^-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} and gas-phase NH_3 concentrations. 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. Mean NH_3 concentrations during moderately polluted and non-haze days were 19.6±0.6 and 15.9±1.5 ppb, respectively. Daily temperature ranged between -4.4°C to 4.3°C with an average of 1.0°C and RH ranged from 13.8% to 40.1% with a mean value of 22.4%. The aerosol pH was calculated for all samples by the model, as well as aerosol water content (AWC. Table S3), details of the calculation of pH and AWC can be found elsewhere (Liu et al., 2017b; Masiol et al., 2020). The calculated aerosol pH results of 10 labs are presented in Fig. 6.

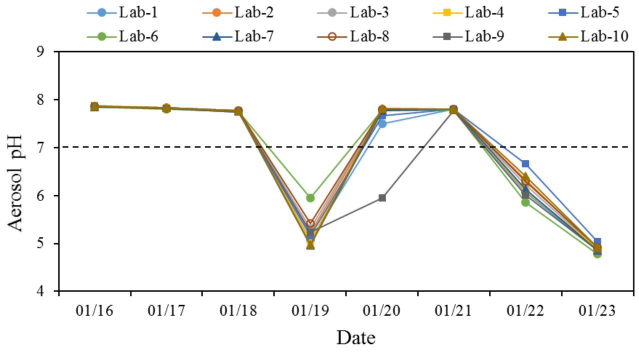

Fig. 6. Aerosol pH estimated by ISORROPIA-II using ions and ammonia in 10 labs from 16th to 23rd January 2019.

The computed aerosol pH during the study period generally exhibited good agreement among 10 labs. Lab-6 was observed with higher pH and lower ion balance than other labs on the 19th, which could be mainly due to the 2-3 times higher K^+ concentration measured by Lab-6 on that day (Fig. 1), while other ions measured by this lab were more comparable with other labs. The aerosol pH on 3 moderately polluted days was above 7, indicating an alkaline nature of aerosols during these days. This result is consistent with the discussion mentioned above that ion balance estimated by Method 1 was below 0 as more NH_4^+ neutralizes NO_3^- and SO_4^{2-}. Excellent agreement among the 10 labs for the aerosol pH during these moderately polluted days was also found. Non-haze days, especially the least polluted day on 20th, showed higher variation among the different labs. The calculated pH of 9 labs mostly fall on the same side of the neutralization line (pH=7), and only lab-9 on 20th falls onto a different side of the pH=7 line from the other labs.

NH_3 is the main driving factor affecting aerosol pH and leads to the more alkaline nature of aerosols. Wang et. al (2020) also reported that the high concentration of total ammonium (gas+aerosol) was likely an important factor causing lower aerosol acidity of fine particles during a severe haze period in Henan province, China. It is also confirmed in another study that ammonia played an important role in influencing aerosol pH during winter haze period in northern China (Song et al., 2018).

4. SUMMARY AND RECOMMENDATIONS

Despite use of variable methods and instruments for measuring ion concentrations, data from all the participating labs show a reasonably good agreement in the overall trend for major ions like chloride, sulfate, nitrate, and ammonium. The coefficients of divergence of these ions across 10 labs were lower than 0.2 and the correlation coefficients were higher than 0.8, suggesting a reasonably high reliability of measuring major ions by IC in different labs. However, the inter-lab difference can be as high as 30% if excluding the two extreme values for each day, and reached up to 100% in extreme cases if including all data. Furthermore, ions like F^-, Mg^{2+}, K^+ and Ca^{2+} were observed with large variations in different labs, which may be due to their relatively low concentrations in the atmosphere. Good correlations were found for non-refractory ion species measured by ACSM with those in our study. However, the absolute mass levels were quite different, which may be due to the interference of other ions in mass spectra and in some cases, the capture of semi-volatile species by the ACSM. Due to the limited number of datapoints in the present study, further investigations on larger datasets are necessary to confirm these findings. Certified reference materials were applied to show the detection accuracy of IC measurement in the 10 laboratories. By comparing the coefficient of variation of samples among 10 labs before and after correction by the recovery of CRM, we emphasize the importance of using certified reference materials for quality control for future ionic species analysis.

Aerosol acidity was studied through the investigation of ion-balance based acidity and in-situ acidity. Firstly, the ratios of anion equivalent concentrations to cation equivalent concentrations (AE/CE) varied significantly in different labs, which could be attributed to measurement errors, as supported by the different recoveries of ions in CRM. Secondly, by calculating the ion balance, Method 1 which only applied SNA for the calculation, was more consistent in most labs. Poor agreement of acidity estimation was observed in all labs when adding other ions like Ca^{2+} and Mg^{2+}. Finally, ISORROPIA-II was applied for estimating in-situ aerosol acidity by calculating aerosol pH in forward (gas+aerosol phases as input) mode. The results showed a similar trend between labs and exhibited a good agreement. This indicates that, if including gaseous pollutant equilibrium in the ISORPIA II model, the estimated aerosol pH is more consistent even if there are relatively large differences in the measured concentrations of ions.

Based on this analysis and our experience, we recommend that:

1. There are substantial inter-lab uncertainties in both the aerosol major and minor ions measured by ion chromatography from the filters. Literature data should be treated with this uncertainty in mind.
2. The ion-balance approach bears large uncertainty and thus should be used with caution for estimating aerosol acidity. 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)
3. Poor consistency of ion-balanced acidity in 10 labs, but good agreement of aerosol pH when applying the ISORROPIA-II model, suggests that measurement errors were not that important when including NH_3 for the determination of aerosol pH. Hence, we recommend NH_3 should be used in future aerosol pH investigations.
4. Certified reference materials should be used on a regular basis to assess the accuracy of the measurement method and ensure reliable measurements.
5. Actual aerosol observations should be corrected for CRM recoveries. But the recovery of ions with poor repeatability should be not be used for correction, as it will cause a larger discrepancy. IC performance should be checked and improved when ions exhibit poor repeatability.
6. The recovery of ammonium varied significantly among 10 labs (88.4-135.0%). As ammonium is highly volatile, it is recommended that stock solutions which are used for the preparation of calibration standards should be freshly prepared to ensure the detection accuracy.
7. As the ions like Mg^{2+} and Ca^{2+} were not detectable in some labs due to low concentrations, it is recommended that labs should consider improving their detection limits and /or correspondingly increase the size of filter cuts for future analysis.

8. Robust quality control processes should be put in place to avoid contamination, particularly for those ions with low concentrations, such as K^+ and Na^+.
9. 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).
10. Ionic concentration from ACSM observations should be calibrated although the observed trend is robust.

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Data availability. The data in this article are available from the corresponding author upon request.

Author contributions. ZS conceived the study after discovering large inter-lab variability in water-soluble inorganic ions from offline and online methods. JX prepared the paper with the help of ZS, RMH and all co-authors. JX, LW, QZ, CZ, XY, DC, WJL, MW, HT, LiL, ST, WRL, JW, GS, YH, SS, CP, YC, FY, AM, DD, SJS, IA, and JFH conducted the laboratory analysis. SS supported the aerosol pH calculation. CS supported the calculation of coefficient of divergence. YLS, LuL, FZ, KRD, CY, YL, MK provided the ACSM data and YLS supported the interpretation of the ACSM data. BG provided the NH_3 data.

Competing interests. The authors declare that they have no conflict of interest.

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