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Aerosol pH and its influencing factors in Beijing

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Abstract

Acidity (pH) plays a key role in the physical and chemical behavior of aerosol and cannot be measured directly. In this work, aerosol liquid water content (ALWC) and size-resolved pH are predicted by thermodynamic model (ISORROPIA-II) in 2017 of Beijing. The mean aerosol pH over four seasons is 4.3±1.6 (spring), 4.5±1.1 (winter), 3.9±1.3 (summer), 4.1±1.0 (autumn), respectively, showing the moderate aerosol acidity. The aerosol pH in fine mode is in the range of 1.8 ~ 3.9, 2.4 ~ 6.3 and 3.5 ~ 6.5 for summer, autumn and winter, respectively. And coarse particles are generally neutral or alkaline. Diurnal variation of aerosol pH follows both aerosol components (especially the sulfate) and ALWC. For spring, summer and autumn, the averaged nighttime pH is 0.3~0.4 unit higher than that on daytime. Whereas in winter, the aerosol pH is relatively low at night and higher at sunset. SO_4^{2-} and RH are two crucial factors affecting aerosol pH. For spring, winter and autumn, the effect of SO_4^{2-} on aerosol pH is greater than RH, and it is comparable with RH in summer. The aerosol pH decreases with elevated SO_4^{2-} concentration. As the NO_3^- concentration increases, the aerosol pH firstly increases and then decreases. Sulfate-dominant aerosols are more acidic with pH lower than 4, whereas nitrate-dominated aerosols are weak in acidity with pH ranges 3~5. In recent years, the dominance of NO_3^- in inorganic ions may be another reason responsible for the moderately acidic aerosol. ALWC has a different effect on aerosol pH in different seasons. In winter, the increasing RH could reduce the aerosol pH whereas it shows a totally reverse tendency in summer, and the elevated RH has little effect on aerosol pH in spring and autumn when the RH is between 30% and 80%. The dilution effect of ALWC on H_{air}^+ is only obvious in summer. The elevated NH_3 and NH_4^+ could reduce aerosol acidity by decreasing H_{air}^+ concentration exponentially.

Key words: Aerosol pH, Size distribution, Influening factors, Beijing

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1. Introduction

Acidity or pH, which drives many processes related to particle composition, gas-aerosol partitioning and aerosol secondary formation, is an important aerosol property (Jang et al., 2002; Eddingsaas et al., 2010; Surratt et al., 2010). The aerosol acidity has a significant effect on the aerosol secondary formation through the gas-aerosol partitioning of semi-volatile and volatile specials (Pathak et al., 2011a; Guo et al., 2016). Recent studies have shown that aerosol acidity could promote the generation of secondary organic aerosol by affecting the aerosol acid-catalyzed reactions (Rengarajan et al., 2011;). Moreover, metals can become soluble by acid dissociation under lower pH conditions (Shi et al., 2011; Meskhidze et al., 2003) or by forming a ligand with organic species, such as oxalate at higher pH (Schwertmann et al., 1991). In addition, higher aerosol acidity could lower the acidification buffer capacity and affect the formation of acid rain. The investigation in aerosol acidity is conducive to better understand the important role of aerosols in acid deposition and atmospheric chemical reactions.

The hygroscopic components in the aerosols include water-soluble inorganic ions and part of organic acid (Peng, 2001; Wang et al., 2017). The deliquescence relative humidity for the mixed-salt is lower than that of any one component (Seinfeld and Pandis, 2016), hence the ambient aerosols are generally droplets containing liquid water. The aerosol pH actually is the pH of the aerosol liquid water. The aerosol acidity is usually estimated by the charge balance of measurable cations and anions. A net negative balance correlated with an acidic aerosol and vice versa (Zhang et al., 2007; Pathak et al., 2011b; Zhao et al., 2017). Generally, a larger value of the ion balance implies a stronger acidity or stronger alkaline. Nevertheless, an ion balance or other similar proxies fail to represent the true aerosol pH because the aerosol acidity estimated by this way is measured through the aerosol water extract, which poorly predicts the concentration of hydronium ion in the aerosol liquid water (Guo et al., 2015; Hennigan et al., 2015). Moreover, due to the large amounts of water is used for extraction, the results cannot reflect the characteristics of the in-situ aerosol acidity, and it cannot be applied to study the influence of aerosol acidity on gas-particle conversion. In-situ aerosol acidity, defined as the free H^+ concentration in the liquid phase of a particle, is an important parameter that actually affects the chemical behavior of the particle, which could be calculated by hydrogen ion concentration and the aerosol liquid water content (ALWC).

It is critical to obtain the ALWC in calculating aerosol acidity. One way to calculate the ALWC is based upon the assumption that the volume of ALWC is equal to subtracting the volume of dry aerosol particles from that of wet particles (Guo et al., 2015; Bian et al. 2014; Engelhart et al. 2011). Under this assumption, ALWC could be calculated by the size-resolved hygroscopic growth factors (g(D, RH)) combining particle size distribution (PNSDs) or by the hygroscopic growth factor of aerosol scattering coefficient (f(RH)) (Bian et al. 2014; Guo et al., 2015; Kuang et al., 2017a). The g(D, RH), defined as the ratio of the diameter of the wet particle at a certain relative humidity to the corresponding diameter at dry conditions, could be measured by H-TDMA (Hygroscopic Tandem Differential Mobility Analyzer) (Liu et al., 1978; Swietlicki et al., 2008; Liu et al., 2011). And the f(RH) could be observed by the wet & dry nephelometer system (Covert et al., 1972; Rood et al. 1985; Yan et al., 2009; Kuang et al., 2016, 2017b).

Another way to calculate the ALWC is based on the aerosol chemical components with thermodynamic models, such as ISORROPIA-II, AIM, ADDEM etc. (Nenes et al., 1998; Fountoukis and Nenes, 2007, Clegg et al., 1998, Topping et al., 2005a, b). Based on the aerosol chemical components as well as temperature and relative humidity, the aerosol thermodynamic models could output both ALWC and concentration of the hydronium ion in air (moles H^+ per volume of air, denoted hereafter as H_{air}^+), which offers a more precise approach to acquire aerosol pH (Pye et al., 2013). Among these thermodynamic models, ISORROPIA and ISORROPIA-II are most widely used owing to its rigorous calculation and performance on computational speed. ISORROPIA simulates the gas-particle partitioning in the H_2SO_4, NH_3, HNO_3, HCl, Na^+, H_2O system, while its second version, ISORROPIA-II, adds Ca^{2+}, K^+, Mg^{2+} and the corresponding salts to the simulated particle components in thermodynamic equilibrium with water vapor and gas-phase precursors.

Comparisons were made in some studies to investigate the consistency of calculated ALWC derived from the above methods. In the North China Plain, Bian et al. (2014) found that the ALWC calculated using size-resolved hygroscopic growth factors and the PNSD agreed well with that calculated using ISORROPIA II at higher relative humidity (>60%). Relatively good consistency was also found in the study of Engelhart et al. (2011) in USA based on the similar method. Guo et al. (2015) compared the ALWC calculated by f (RH) with the total predicted water by organics and

inorganics. The total predicted water was highly correlated and on average within 10 % of the *f*(RH) measured water. Though good consistencies in ALWC were found among these methods, the H_{air}^{+} could only be obtained by thermodynamic models, which have been applied to predict aerosol acidity in many studies (Nowak et al., 2006; Fountoukis et al., 2009; Weber et al., 2016; Fang et al., 2017).

When calculating aerosol acidity with thermodynamic models, the aerosol is assumed internally mixed and the bulk properties of aerosol are used, without considering variability of chemical compositions with particle size. However, the size-resolved characteristics of aerosol chemical components are obviously different. Among inorganic ions, SO_4^{2-}, NO_3^-, Cl^-, K^+, NH_4^+ are mainly concentrated in fine mode, whereas Mg^{2+}, Ca^{2+} are abundant in coarse mode (Zhao et al., 2017). The aerosol acidity is the result of the balance between the soluble acidic (SO_4^{2-}, NO_3^-, Cl^- and some soluble organic acids) and alkaline (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) component in the aerosol. The gas precursor NH_3, HNO_3, and HCl for main water-soluble ions as well as ambient temperature and relative humidity are also important factors affecting the aerosol acidity. In some countries where PM concentration is very low, the pH diurnal variation was mainly driven by meteorological conditions (Guo et al., 2015, 2016; Bougiatioti et al., 2016). In China, however, the annual average $PM_{2.5}$ concentration in some mega cities was ~2 times higher than the national standard value (35 μg m^{-3}) and the inorganic ions account for 40%~50% to $PM_{2.5}$, especially in the North China Plain (Zou et al., 2018; Huang et al., 2017; Gao et al., 2018). Hence it can be expected that the aerosol composition is also a crucial factor on pH, which cannot be ignored.

The North China Plain is the region with the most severe aerosol pollution in China. Nevertheless, few studies have focused on aerosol pH at this region. Cheng et al. (2016) estimated the averaged pH by ISORROPIA-II, and Wang et al. (2016) derived the particle pH by using a molar ratio approach in Beijing, their results show that the aerosol acidity was close to neutral. However, Liu et al. (2017) and Shi et al. (2017) found that fine particles in the North China Plain were moderately acidic based on the hourly measured particulate water-soluble ions and precursor gases along with ISORROPIA-II, with an average pH of 4.2 in winter of Beijing and 4.9 in Tianjin. These results are all significantly higher than that in the United States or Europe, where aerosols are often highly acidic with a pH lower than 3.0 (Guo et al., 2015, 2016; Bougiatioti et al., 2016; Weber et al., 2016;

Young et al., 2013). The differences in aerosol pH in the North China Plain mainly result from the different calculated methods (ion balance & thermodynamic equilibrium models). Several studies have shown that the ion balance and reverse-mode calculations of thermodynamic equilibrium models are not applicable to interpret the aerosol acidity (Hennigan et al., 2015; Liu et al. 2017; Song et al., 2018). Moreover, the change of the chemical composition of $PM_{2.5}$ in the North China Plain in recent years also contributed to the differences in aerosol pH. The observations in previous studies exploring aerosol acidity in the North China Plain were almost conducted before 2015. In the recent three years, the chemical composition of $PM_{2.5}$ in Beijing has undergone tremendous changes. Nitrate has replaced sulfate and is dominant in inorganic ions in most cases (Zhao et al., 2017; Huang et al., 2017; Ma et al., 2017). Moreover, studies about seasonal variation of aerosol pH and size-resolved aerosol pH are rare in the North China Plain, and the key factors affecting aerosol acidity are still not well understood.

In this work, thermodynamic model ISORROPIA-II with forward mode is utilized to predict ALWC and aerosol pH in Beijing. The hourly measured $PM_{2.5}$ inorganic ions and precursor gases in four seasons during 2016 to 2017 are used to analyze the seasonal and diurnal variation of aerosol acidity, and the sensitivity analysis is conducted to identify the key factors that affecting the aerosol pH. In our previous studies, the multi-stage cascade impactors (MOUDI-122) were used for size-resolved aerosol sampling during 2013 to 2015. The actual relative humidity inside the impactors was calculated, and the size distribution of water-soluble ions, organic carbon, and elemental carbon in three seasons were discussed (Zhao et al., 2017; Su et al., 2018). Based on these size-resolved results, the pH for aerosol in different size ranges could also be modeled, which can help to evaluate whether it is appropriate to calculate the overall pH of $PM_{2.5}$ ignoring the differences in particle size.

2. Data Collection and Methods

2.1 Site

The measurements were performed at the Institute of Urban Meteorology in Haidian district of Beijing (39°56’N, 116°17’E). The sampling site was located next to a high-density residential area, without significant air pollution emissions around the site. Therefore, the observation data could represent the air quality levels of the urban area of Beijing.

2.2 Online data collection

Water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) of $PM_{2.5}$ and trace gases (HCl, HNO_3, HNO_2, SO_2, NH_3) in the ambient air were measured by an online analyzer (MARGA) at hourly temporal resolution during the spring (April and May in 2016), winter (February in 2017), summer (July and August in 2017) and autumn (September and October in 2017). The more details about MARGA can be found at ten Brink et al. (2007). The $PM_{2.5}$ and PM_{10} mass concentrations (TEOM 1405DF), the hourly ambient temperature and relative humidity were also synchronously attained.

Hourly concentrations of $PM_{2.5}$, PM_{10}, and water-soluble ions in $PM_{2.5}$, as well as meteorological parameters during the observation, are shown in Figure 1. In spring, two dust events occurred (21-22, April and 5-6, May). During the first dust event, the wind came predominantly from the north with mean wind speed 3.5 m s^{-1}. And the PM_{10} concentration reached 425 μg m^{-3} while the $PM_{2.5}$ concentration was only 46 μg m^{-3} on the peak hour. Similarly, the second dust event was resulted from the strong wind come from the northwest direction. In the following pH analysis based on MARGA data, it is assumed that the particles were internally mixed, and the chemical compositions were the same for particles of different sizes in $PM_{2.5}$. Hence, these two dust events were excluded from this analysis.

2.3 size-resolved chemical compositions

A Micro-Orifice Uniform Deposit Impactor (MOUDI-120) was used to collect size-resolved aerosol samples with the calibrated 50% cut sizes of 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.1, 6.2, 9.9 and 18 μm. Size-resolved sampling was conducted during July 12-18, 2013; January 13-19, 2014; July 3-5, 2014; October 9-20, 2014; and January 26-28, 2015. Fifteen, fourteen, and eighteen sets of samples were obtained for the summer, autumn and winter, respectively. Except for two sets of samples, all the samples were collected in daytime (from 08:00 to 19:00) and nighttime (from 20:00 to 7:00 the next day), respectively. One hour of preparation time was set for filter changing and nozzle plate washing with ethanol. The water-soluble ions were analyzed from the samples by using an ion chromatography (DIONEX ICS-1000). The detailed information about the features of MOUDI-120, the procedures of sampling, pre-treatment, and laboratory chemical analysis (including the quality assurance & quality control) were described in our previous papers (Zhao et al., 2017; Su et al., 2018).

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2.4 Aerosol pH prediction

As mentioned in the Introduction, pH of ambient aerosols could be predicted by the thermodynamic model such as AIM and ISORROPIA, AIM is considered an accurate benchmark model while ISORROPIA has been optimized for use in chemical transport models. Currently, ISORROPIA-II, adds K^+, Mg^{2+}, Ca^{2+} (Fountoukis and Nenes, 2007), could calculate the equilibrium H_{air}^+ (particle hydronium ion concentration per volume air) and ALWC with reasonable accuracy by taking water-soluble ions mass concentration, temperature and relative humidity as input. The H_{air}^+ and ALWC were then used to predict aerosol pH by the Eq. (1).

$$\mathrm{pH} = -\log_{10} \mathrm{H}_{aq}^{+} \cong -\log_{10} \frac{1000\mathrm{H}_{air}^{+}}{ALWC_{i}} \tag{1}$$

Where H_{aq}^+ (mole L^{-1}) is the hydronium ion concentration in the ambient particle liquid water. H_{aq}^+ can also be deemed to be the H_{air}^+ (μg m^{-3}) divided by the concentration of ALWC associated with inorganic species, $ALWC_i$ (μg m^{-3}). Both inorganic and part of organic species in particles are hygroscopic. However, the pH prediction is not highly sensitive to the water uptake by organic species ($ALWC_o$), unless the $ALWC_o$ mass fraction to the total particle water is close to 1 (Guo et al., 2015, 2016). And similar result was also found in Beijing in Liu et al. (2017). Hence the aerosol pH could be fairly predicted by ISORROPIA-II with just measurements of inorganic species in most cases.

In ISORROPIA-II, forward and reverse mode are provided to predict ALWC and H_{air}^+. In forward mode, known quantities are T, RH and the total (i.e. gas+aerosol) concentrations of NH_3, H_2SO_4, HCl and HNO_3. Reverse mode calculates the equilibrium partitioning given the concentration of only aerosol composition together with RH and T as input. In this work, the online ion chromatography MARGA was used to measure both inorganic ions of $PM_{2.5}$ and precursor gases, hence ISORROPIA-II was run in the "forward mode" for aerosols in metastable condition. Moreover, the forward mode was reported less sensitive to measurement error than the reverse mode (Hennigan et al., 2015; Song et al., 2018).

Running ISORROPIA-II in the forward mode with only aerosol concentrations as input may result in a bias in predicted pH due to repartitioning of ammonia in the model, leading to a lower predicted pH when gas-phase data are not available (Hennigan et al., 2015). In this work, no $NH_{3(g)}$

was available for the size-resolved pH prediction. We determined aerosol pH in the fine mode through an iteration procedure that used the measured particulate species and ISORROPIA-II to predict gas species, detailed information could be found in Fang et al. (2017) and Guo et al. (2017). As for coarse mode particles, equilibrium is not considered between the gas and particles due to kinetic limitations (Dassios et al., 1999; Cruz et al., 2000), the pH was determined by ignoring the gas phase and ISORROPIA-II was run in forward mode with zero gas concentrations.

The accuracy of the aerosol pH prediction is primarily assessed by the reproduction of semivolatile components partitioning between gas and particle phases. A comparison between predicted NO_3^-, NH_4^+ and measured values colored by RH is shown in Figure 2. Overall, the model captures the measured NO_3^-, NH_4^+, and the predicted NO_3^-, NH_4^+ are on average within ±20% of the measurements, with R^2>0.9, and best agreement is observed at RH above 60%.

Figure 1

3. Results and Discussion

3.1 Overall summary of aerosol pH over four seasons

The averaged $PM_{2.5}$ concentration is 62±36, 60±69, 39±24, 59±48 μg m^{-3} in spring, winter, summer and autumn observation, respectively. Among all ions measured, NO_3^-, SO_4^{2-}, NH_4^+ are three dominant species, accounting for 83% ~ 87%. Compared with other seasons, the averaged concentration of primary inorganic ions (Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}) was higher in spring. The aerosol in Beijing showed the moderate acidity with aerosol pH was 4.3±1.6, 4.5±1.1, 3.9±1.3 and 4.1±1.0 in spring, winter, summer and autumn observation, respectively. The overall winter aerosol pH is comparable to the result found in Beijing (4.2, winter) from Liu et al. (2017) and lower than that (4.9, winter and spring) in Tianjin (Shi et al., 2017), another mega city about 120 km away from Beijing. The summer aerosol pH was lowest among all four seasons, implying the higher aerosol acidity. The seasonal variation of aerosol pH in this work was similar to the result from Tan et al. (2018) except for spring, which was winter (4.11 ± 1.37) > autumn (3.13 ± 1.20) > spring (2.12 ± 0.72) > summer (1.82 ± 0.53). Noted that the observation in Tan et al. (2018) was conducted in 2014 of Beijing, the distinction in aerosol composition may be responsible for the lower aerosol pH in

their work.

The acid liquid surface has a catalytic effect on the gas-liquid reaction process, and the presence of the oxidant can significantly increase the reaction rate and promote the formation of secondary aerosols (Liu et al., 2012). How the moderate acidity of aerosol in the North China Plain affect the formation of secondary aerosols needs to be further investigated.

Figure 2

Wind dependence of $PM_{2.5}$, NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+} concentration and the averaged pH are shown in Figure 3 and Fig. S1. In spring and summer, the high aerosol pH occurs with both NW and SW strong winds (wind speed >3 m s^{-1}) while the low aerosol pH occurs with calm winds (wind speed <2 m $s^{-1)}$ and SW winds with wind speed lower than 3 m s^{-1}. For winter, we surprisingly found that the high aerosol pH is mainly concentrated in the SSW direction, while the aerosol pH in northerly winds is as low as 3~4. In autumn, the aerosol pH accompanied by NW winds is much higher than that accompanied by souther winds. Generally, the northerly winds usually occur with cold front systems and high wind speeds, which could sweep away air pollutants but raise dust in which the crustal species (Ca^{2+}, Mg^{2+}) content are higher.

Haze episodes usually occur with SW and SE winds and calm winds in Beijing, the air pollutants are transported to Beijing from other cities located in SW and SE directions, leading to the accumulation of pollutants. Beijing is surrounded by mountains on three sides, and south Beijing is plain. The industry is mainly concentrated in the south of Beijing, and there are plenty of emission sources in these two major transport pathways from southwest and southeast directions, leading to the higher $PM_{2.5}$ concentration. We find that the aerosol pH is negatively correlated with $PM_{2.5}$ concentration in spring, summer, and autumn whereas it shows the positive relationship in winter.

To further investigate the aerosol pH performance under different pollution level over four seasons, the $PM_{2.5}$ concentration is classified into three groups with 0~75 μg m^{-3}, 75~150 μg m^{-3} and >150 μg m^{-3}, representing clean, polluted and heavily polluted days, respectively. Overall, as the air quality deteriorates, ALWC and H_{air}^+ all increased, but the aerosol acidity performs differently. In spring, summer, and autumn, the pH on clean days is the highest (Table 1), then followed by polluted days and heavily polluted days. In winter, however, the averaged pH on polluted days (5.4±1.0) is the highest, then followed by heavily polluted days (4.4±0.9) and clean days (4.3±1.1).

Figure 3

Table 1

3.2 Diurnal variation of aerosol pH, ALWC, and H_{air}^+

The diurnal variation for ALWC is similar over four seasons, but distinctions are found in H_{air}^+ and pH diurnal variations (Figure 4). Generally, nighttime mean ALWC is higher than daytime and reached a peak at near 04:00 ~ 06:00 (local time). After sunrise, the increasing temperatures resulted in a rapid drop in RH, leading to the obvious loss of particle water, ALWC reached the lowest level in the afternoon. For spring, summer, and autumn, the significant H_{air}^+ peak starting at roughly 12:00 and reaching a maximum between 16:00 and 18:00, the low ALWC and high H_{air}^+ resulted in the minimum pH in the afternoon. The averaged nighttime pH is 0.3~0.4 unit higher than that on daytime for spring, summer, and autumn, respectively. However, for winter, H_{air}^+ in the nighttime is slightly higher than that in the daytime, and the aerosol pH is relatively low at night and higher at sunset. Noted that the diurnal variation of aerosol pH is all consistent with the diurnal variation of SO_4^{2-} over four seasons, it seems that the SO_4^{2-} is a key factor affecting aerosol pH.

Figure 4

The distinguishing diurnal patterns of aerosol pH over four seasons indicate that aerosol composition is a key factor for the diurnal variation of aerosol pH, which is very different from what Guo et al. (2015) found in the southeastern United States: the pH diurnal variation is largely driven by meteorological conditions due to the dilution of ALWC to H_{air}^+, not aerosol composition. The biggest reason for the discrepancy is that the hygroscopic components in particles such as $(NH_4)_2SO_4$ and NH_4NO_3 in Beijing are much higher than that in the southeastern United States (lower than 5 μg m^{-3}) while the mean RH is lower. Thus the influence of aerosol composition on pH cannot be ignored in Beijing.

3.3 Factors affecting ALWC, H_{air}^+ and aerosol pH

As mentioned above, the aerosol chemical composition has a non-negligible effect on aerosol pH. In this work, the effects of aerosol chemical components (NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}) and precursor gases (NH_3, HNO_3), as well as meteorological parameters (RH, T) on aerosol pH are performed

through a sensitivity analysis over four seasons. When assessing how a factor affects aerosol acidity, ALWC, or H_{air}^+, the real-time measured values of an evaluated factor and the averaged values for other factors in each season are input in ISORROPIA-II. For example, the magnitude of the deviation for calculated aerosol pH can reflect the effect of an evaluated factor on the aerosol acidity. The higher the deviation, the greater the effect, vice versa. Noted that the sensitivity analysis in this work only reflects the characteristics during the observation period, further work is needed to determine whether the sensitivity analysis is valid in other environments. And the sensitivity analysis in this paper only focused on single factor variations, however, in reality, changes in one factor could alter other factors and made it more complicated.

As show in Table 2, for ALWC, the largest deviation is observed when RH is taken as the evaluated factor, then followed by SO_4^{2-} and NO_3^- (NO_3^- and SO_4^{2-} in autumn), which means that the RH affect ALWC most and SO_4^{2-} and NO_3^- are major hygroscopic components in the aerosol. SO_4^{2-} is the most influential factor for H_{air}^+, and RH, NO_3^-, and NH_3 are also important factors affecting H_{air}^+. Synthetically, SO_4^{2-} and RH are two crucial factors affecting aerosol pH. For spring, winter and autumn, the effect of SO_4^{2-} on aerosol pH is greater than the RH, and it is comparable with RH in summer. Figure 4-6 and S2-S7 show how these factors affecting the aerosol acidity, ALWC and H_{air}^+ in detail over four seasons. The sensitivity analysis for ALWC and H_{air}^+ are similar over four seasons, while the sensitivity analysis of RH on aerosol pH in summer is different from the other three seasons. In this study, the sensitivity analysis in winter and summer are chosen for detailed description since winter is of a lot of concern due to the poor air quality while the photochemical reactions are strongest in summer.

Table 2

The positive linear relationships between SO_4^{2-}, NO_3^-, HNO_3 concentration and ALWC as well as negative linear relationship between Ca^{2+} concentration and ALWC are observed in the sensitive analysis. Exponential relationships between RH and ALWC are observed, and the ALWC increased rapidly with increasing RH, especially when the RH higher than 80%. Elevated NH_4^+ and NH_3 concentration could increase ALWC slightly. As for temperature, ALWC decreased with the increasing temperature nonlinearly. High temperature could affect gas-aerosol portioning, shifts the equilibrium from NO_3^- to HNO_3, underpredicted the NO_3^- and NH_4^+ concentration, thus decreasing

the ALWC. In addition, the higher temperature could also decrease RH and results in low ALWC in the real atmosphere.

Figure 5

As mentioned above, SO_4^{2-} and RH are the most important factors on H_{air}^+. An exponential growth of H_{air}^+ with elevated SO_4^{2-}, RH, NO_3^-, and T are found, whereas an exponential decrease of H_{air}^+ with elevated NH_3 and NH_4^+ are found. Though H_{air}^+ concentration decreased linearly with the augment of Ca^{2+} concentration, Ca^{2+} concentration is generally lower than 3 μg m^{-3} and generates a little variation in H_{air}^+ compared to other factors. It should be noted that a "U" shape between NO_3^- and H_{air}^+ are found in spring (Fig.S2), H_{air}^+ drops with the increasing NO_3^- concentration within ~20 μg m^{-3} and then starts to grow with the increasing NO_3^- concentration. The addition of NH_3 or NH_4^+ has a much more obvious effect on H_{air}^+ than ALWC. The higher the NH_3 concentration in the atmosphere, the more NH_3 will dissolve in the aerosol liquid water and balance the H_{air}^+ partially. Increasing temperature or RH alone will increase H_{air}^+ when other influencing factors were fixed, which is consistent over four seasons.

Figure 6

The effects of all these factors on aerosol pH is actually a superposition of the effects on ALWC and H_{air}^+. Synthetically, the effect of chemical components (NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}) and precursor gases (NH_3, HNO_3), as well as meteorological parameters (RH, T) on aerosol pH is shown in Figure 7. The most important influencing factor on aerosol acidity is SO_4^{2-}. The aerosol pH decreases about 2.8 (5 to 2.2), 6.0 (6 to 0), 1.0 (3.8 to 2.8), and 1.1 (4 to 2.9) unit with SO_4^{2-} concentration goes up from 0 to 40 μg m^{-3} in spring, winter, summer, and autumn, respectively. In spring and winter, the ALWC is low, the variation of SO_4^{2-} concentration could generate dramatic changes in aerosol pH. In section 3.1, the aerosol pH shows an obvious seasonal variation, the aerosol pH is generally low in summer whereas highest in winter, which is consistent with the SO_4^{2-} mass faction in total ions. The SO_4^{2-} mass faction in total ions in summer is highest among four seasons with 32.4%±11.1%, whereas it is lowest in winter with 20.9%±4.4%. Similarly, the low aerosol pH on clean days in winter also relates to the leading position of SO_4^{2-} (Table 1).

The second important factor on aerosol acidity is RH. In the North China Plain, the severe haze episodes usually occur with very high RH at a stable whether condition, resulting in the considerable ALWC. In this work, except for summer, the increasing RH could reduce the aerosol pH significantly when RH lower than ~30%, and then the aerosol pH decreases slowly or keeps almost a constant at ~4 when the RH is between 30~80%, and the aerosol pH starts to increase with the further increasing RH. However, the aerosol pH increases continuously ~1.5 unit (2.5 to 4) when RH goes up from 20% to 96% in summer. The $PM_{2.5}$ concentration is lowest in summer, while the RH is relatively high, the high ALWC tends to dilute H_{air}^+ and increase aerosol pH. The sensitivity analysis suggests that ALWC has a different effect on aerosol pH in different seasons, the dilution effect of ALWC on H_{air}^+ is obvious only in summer.

Figure 7

Different from SO_4^{2-}, the effect of NO_3^- on aerosol pH is not always same. In winter, summer and autumn, the aerosol pH increases first and then starts to decrease when NO_3^- concentration is larger than ~30 μg m^{-3}. There seems to be a threshold for the effect of NO_3^- on aerosol acidity. From a mathematical point of view, the H_{air}^+ concentration increased exponentially with elevated NO_3^- concentration, especially at higher NO_3^- concentrations, whereas the ALWC increase linearly with elevated NO_3^- concentration. When NO_3^- concentration is less than the threshold, ALWC plays a dominant role, while when the NO_3^- concentration is greater than the threshold, the H_{air}^+ has a greater effect and the aerosol acidity begins to increase.

Moreover, in spring, the aerosol pH increases continuously with the addition of NO_3^-, which is not consistent with the previous thought that addition of anion could reduce the aerosol pH. Same results are found in Guo et al. (2017): at a constant ALWC, more NO_3^- is measured at higher pH. Based on the measured $NO_3^-/2SO_4^{2-}$ ratio (mole $mole^{-1}$) of this work, we find that aerosol pH is generally between 3~5 when the aerosol anionic composition is dominated by nitrate ($NO_3^-/2SO_4^{2-}>1$), whereas when $NO_3^-/2SO_4^{2-}<1$, about 86% of aerosol pH is lower than 4 (Figure 8). In recent years, the average annual concentration of SO_4^{2-} in Beijing decreased significantly due to the strict emission control measures for industries and power plants, in most cases NO_3^- dominates inorganic ions (Zhao et al., 2017; Huang et al., 2017; Ma et al., 2017), which may be

another reason responsible for the moderately acidic aerosol.

Elevated NH_3 and NH_4^+ could reduce aerosol acidity by decreasing H_{air}^+ concentration exponentially. In this work, NH_3 is rich in spring (21.5±8.7 μg m^{-3}), summer (19.6±6.4 μg m^{-3}) and autumn (16.8±8.0 μg m^{-3}), and poor in winter (4.9±2.8 μg m^{-3}). The ratio of [TA]/2[TS] provides qualitative description for the ammonia abundance, where [TA] and [TS] are the total (gas + aqueous + solid) molar concentrations of ammonia and sulfate. The rich-ammonia is defined as [TA] > 2[TS], while if the [TA] < 2[TS], then it is defined as poor-ammonia (Seinfeld and Pandis, 2016). In this work, the ratio of [TA]/2[TS] is much higher than 1 and belongs to rich-ammonia (Fig. S8). In the poor-ammonia case, there is insufficient NH_3 to neutralize the available sulfate, hence the aerosol will be acidic. Whereas in the rich-ammonia case there is excess ammonia, the remaining ammonia after reaction with sulfuric acid will be available to react with nitric acid to produce NH_4NO_3, so that the aerosol phase will be neutralized to a large extent. However, the moderate aerosol acidity suggests that though there is excess ammonia in the atmosphere, due to the limited ALWC compared with the cloud liquid water content and precipitation, in most cases the aerosol will not be alkaline.

Furthermore, elevated Ca^{2+} concentration could increase the aerosol pH and the change of HNO_3 concentration has little effect on pH. Elevated temperature in favor of enhancement the aerosol acidity by reducing ALWC and increasing H_{air}^+.

Figure 8

3.4 Size distribution of aerosol components and pH

According to the average $PM_{2.5}$ concentration during every sampling period, all the samples are also classified into three groups (clean, polluted, heavily polluted) with the same rule described in Section 3.2. A severe haze episode occurred during the autumn sampling, hence there were more heavily polluted samples for autumn than that in other seasons. Figure 9 shows the averaged size distributions of PM components and pH on clean, polluted and heavily polluted days in summer, autumn and winter, respectively. The NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, K^+, OC, and EC were mainly concentrated in the size range with aerodynamic diameters between 0.32~3.1μm, while Mg^{2+} and Ca^{2+} were predominantly distributed in the coarse mode. As shown in Figure 9, the concentration levels for all chemical components increased with the increasing pollution. During the haze episodes,

the sulfate and nitrate in the accumulated mode increased significantly. However, the increase of Mg^{2+} and Ca^{2+} in the coarse mode were not as obvious as secondary ions, mainly due to the low wind speed and calm atmosphere which make it more difficult to raise dust during the heavy pollution. More detailed information about size distributions of mass concentration for all analyzed species during three seasons is shown in Zhao et al. (2017) and Su et al. (2018).

Figure 9

The aerosol pH for both accumulation mode and coarse mode in summer were lowest among three seasons, then followed by autumn and winter. In summer, the predominance of sulfate in the fine mode resulted in a low pH, ranging between 1.8 and 3.9. The sensitivity analysis of this work shows sulfate plays a key role in predicting pH, its high hygroscopicity leads to the formation of the aqueous drops and provides H_{air}^{+} (Fang et al., 2017). Aerosol pH for fine particles in autumn and winter are in the range of 2.4 ~ 6.3 and 3.5 ~ 6.5, respectively. As for coarse particles, the predicted pH is approximately near or even higher than 7 for all of the three seasons in this work. It should be noted that assuming coarse mode particles in equilibrium with the gas phase generally overestimates acidity (pH<4) (Fang et al., 2017).

On heavily polluted days, the aerosol pH in coarse mode showed a marked fall in autumn and winter. For example, the pH in stage 3 (3.1-6.2 μm) declined from 7.8 on clean days to 4.5 on heavily polluted days in winter, implying that the aerosols in coarse mode during severe hazy days would become weak acid from neutral. The obvious increase of nitrate in coarse mode may responsible for this. Moreover, the significant decrease of mass ratios of Ca^{2+} and Mg^{2+} also weakened the alkaline.

The size distribution of aerosol pH and all analyzed chemical components in the daytime and nighttime are illustrated in Figure 10. For summer and autumn, the pH in the nighttime is higher than that in the daytime. Whereas, in winter, the pH is higher in the daytime. The diurnal variation for aerosol pH based on MOUDI data is consistent with the online data. In the daytime of summer and autumn, the solar radiation is strong and photochemical reaction is active as well as the RH is lower, leading to a lower aerosol pH than nighttime. In winter, the averaged RH during the sampling period is 43%, leading to a low ALWC, but the SO_4^{2-} and NO_3^{-} in the nighttime are obviously higher due to the lower boundary layer. Therefore, H_{air}^{+} is more abundant in nighttime while the low ALWC

had little effect on pH.

Figure 10

5. Summary and conclusions

Aerosol acidity is important for the formation of secondary aerosol and is of many challenges to be measured directly. In this work, ISORROPIA-II with forward mode is applied to calculate the H_{air}^+ and ALWC based on the 1-h $PM_{2.5}$ inorganic ions, precursor gases (HCl, HNO_3, NH_3) and RH, T. Moreover, the size distribution of pH is predicted based on the MOUDI samples with the same way, the gas-phase NH_3, HNO_3 and HCl are determined through an iteration procedure. In Beijing, the mean aerosol pH over four seasons is 4.3±1.6 (spring), 4.5±1.1(winter), 3.9±1.3(summer), 4.1±1.0 (autumn), respectively, showing the moderate aerosol acidity. The seasonal variation of aerosol pH is closely related to the SO_4^{2-}. Overall, the aerosol is more acidic on hazy days than clean days. The aerosol pH in fine mode is in the range of 1.8 ~ 3.9, 2.4 ~ 6.3 and 3.5 ~ 6.5 for summer, autumn and winter, respectively. As for coarse particles, the predicted pH is approximately near or even higher than 7.

Due to the significantly high level of hygroscopic components in particulate matter in Beijing, pH has a diurnal trend that follows both aerosol components (especially the sulfate) and ALWC. For spring, summer and autumn, the averaged nighttime pH is 0.3~0.4 unit higher than that on daytime. However, in winter, H_{air}^+ in nighttime is slightly higher than that in daytime and the aerosol pH is relatively low at night and higher at sunset. This result is very different from that found in southeastern United States: the pH diurnal variation is largely driven by meteorological conditions.

A sensitivity analysis is performed in this work to investigate how aerosol components, precursor gases and meteorological conditions affect aerosol acidity. The RH affects ALWC most, then followed by SO_4^{2-} and NO_3^-. For H_{air}^+, SO_4^{2-} is the most influential factor, and RH, NO_3^-, NH_3 are also important factors affecting H_{air}^+. Synthetically, SO_4^{2-} and RH are two crucial factors affecting aerosol pH. For spring, winter and autumn, the effect of SO_4^{2-} on aerosol pH is greater than RH, and it is comparable with RH in summer. The aerosol pH decreases with elevated SO_4^{2-} concentration, the variation of SO_4^{2-} concentration could generate dramatic changes in aerosol pH in spring and winter. As the NO_3^- concentration increases, the aerosol pH firstly increases and then decrease at a

inflection point with 30 μg m^{-3}. In this work, sulfate-dominant aerosols are more acidic with pH lower than 4, whereas nitrate-dominated aerosols are weak in acidity with pH ranges 3~5. In recent years, the SO_4^{2-} concentration of $PM_{2.5}$ in Beijing decreased significantly due to the strict emission control measures, in most cases NO_3^- dominates inorganic ions, which may be another reason responsible for the moderately acidic aerosol.

ALWC has a different effect on aerosol pH in different seasons. In winter, the increasing RH could reduce the aerosol pH whereas it shows a totally reverse tendency in summer, and the elevated RH has little effect on aerosol pH in spring and autumn when the RH is between 30% and 80%. The sensitivity analysis of this work highlights the diverse influence of ALWC on aerosol pH, the dilution effect of ALWC on H_{air}^+ is only obvious in summer. The elevated NH_3 and NH_4^+ could reduce aerosol acidity by decreasing H_{air}^+ concentration exponentially. In the North China Plain, the ammonia is rich, the remaining ammonia after reaction with sulfuric acid will be available to react with nitric acid to produce NH_4NO_3, so that the aerosol phase will be neutralized to a large extent. However, the moderate aerosol acidity suggests that though there are excess ammonia in the atmosphere, in most cases the aerosol will not be alkaline due to the limited ALWC.

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Table captions

Table 1. The averaged $PM_{2.5}$ and NO_3^-, SO_4^{2-}, NH_4^+ mass concentration as well as RH, ALWC, H_{air}^+, pH on clean, polluted and heavily polluted days over four seasons.

Table 2. Sensitivity of aerosol chemical components (NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3) and meteorological parameters (RH, T) to aerosol acidity, ALWC and H_{air}^+. The larger magnitude of the deviation represents the larger impact.

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Table 1

Spring	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC	H_{air}^+	pH
	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	
Averaged	62±36	14.9±14.6	9.7±7.9	7.9±7.3	17±30	4.7E-06±9.5E-06	4.3±1.6
Clean	44±17	7.9±6.6	6.2±3.7	4.8±3.2	10±21	3.5E-06±8.4E-06	4.5±1.9
Polluted	100±21	30.8±14.3	16.4±5.9	15.4±5.8	28±34	5.6E-06±7.4E-06	3.9±0.7
Heavily polluted	169±12	45.3±8.5	36.3±4.9	29.4±2.3	77±60	1.9E-05±6.1E-06	3.6±0.3
winter	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC	H_{air}^+	pH
Averaged	60±69	13.7±21.0	7.3±8.7	7.3±10.0	17±37	9.0E-06±1.3E-04	4.5±1.1
Clean	22±20	3.6±3.9	2.8±1.8	2.2±2.0	4±11	2.6E-07±4.2E-07	4.3±1.1
Polluted	107±21	18.9±8.6	11.0±5.7	11.0±4.7	31±42	1.2E-05±6.9E-05	5.3±1.2
Heavily polluted	209±39	59.7±21.8	26.2±6.3	29.1±8.7	77±51	5.2E-05±3.4E-04	4.5±0.7
Summer	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC	H_{air}^+	pH
Averaged	39±24	9.5±9.5	8.6±7.5	7.2±5.6	51±68	1.6E-05±1.6E-05	3.9±1.3
Clean	33±18	7.3±6.8	7.0±6.0	5.9±4.0	41±61	1.3E-05±1.6E-05	3.9±1.3
Polluted	87±13	26.5±10.5	20.7±7.0	17.6±4.8	102±85	3.1E-05±1.7E-06	3.5±0.4
Autumn	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC	H_{air}^+	pH
Averaged	59±48	18.5±19.5	6.5±5.9	8.2±8.2	91±145	1.1E-05±1.5E-05	4.1±1.0
Clean	33±21	7.6±7.4	4.4±4.1	3.8±3.5	37±72	5.1E-06±9.4E-06	4.2±1.2
Polluted	105±21	33.8±11.6	14.3±6.3	16.0±4.6	182±172	1.8E-05±1.3E-05	3.9±0.4
Heavily polluted	174±18	63.4±15.4	25.0±15.9	29.0±5.1	315±212	3.6E-05±2.6E-05	3.9±0.3

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Table 2

Impact Factor		SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	RH	T	NH_3	HNO_3
Spring	D-ALWC	**3.8**	**2.0**	0.2	0.9	**14.2**	0.7	0.3	0.1
	D-H_{air}^+	**1.4E-05**	6.9E-07	2.9E-07	7.0E-07	**2.1E-06**	9.1E-07	**1.2E-06**	2.4E-08
	D-pH	**0.7**	0.4	0.2	0.3	**0.5**	0.4	0.3	0.0
Winter	D-ALWC	**3.2**	1.5	0.6	0.2	**16.6**	0.4	0.1	0.1
	D-H_{air}^+	**2.6E-04**	5.8E-07	2.5E-06	1.9E-07	5.9E-07	2.8E-07	2.5E-07	1.9E-07
	D-pH	**1.4**	0.4	0.9	0.1	**1.3**	0.4	0.2	0.0
Summer	D-ALWC	**10.0**	**9.1**	0.5	1.8	**43.9**	2.1	0.8	0.3
	D-H_{air}^+	**1.7E-05**	2.5E-06	2.0E-06	1.6E-06	5.0E-06	3.0E-06	**4.1E-06**	5.8E-08
	D-pH	**0.3**	0.1	0.1	0.1	**0.3**	0.2	**0.2**	0.0
Autumn	D-ALWC	**10.3**	**16.7**	0.2	1.1	**83.5**	2.0	0.3	0.4
	D-H_{air}^+	**1.6E-05**	**1.5E-05**	1.9E-06	4.8E-07	6.7E-06	3.0E-06	2.5E-06	4.6E-08
	D-pH	**0.3**	0.2	0.2	0.0	**0.2**	**0.3**	0.2	0.0

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Figure captions

Figure 1. Time series of relative humidity (RH), temperature (T) (a, e, i, m); $PM_{2.5}$, PM_{10}, and NH_3 (b, f, g, n); dominant water-soluble ion species: NO_3^-, SO_4^{2-}, NH_4^+ (c, g, k, o); aerosol pH colored by $PM_{2.5}$ concentration (d, h, l, p) over four seasons.

Figure 2. Comparisons of predicted NO_3^-, NH_4^+ to measured values based on (a, b) online ion chromatography data and (c, d) MOUDI data.

Figure 3. Wind dependence map of aerosol pH over four seasons. In each picture, the shaded contour indicates the average of variables for varying wind speeds (radial direction) and wind directions (transverse direction).

Figure 4. Diurnal patterns of predicted aerosol liquid water content (ALWC) (a-d); H_{air}^+ predicted by ISORROPIAII (i-l); predicted aerosol pH (m-p) over four seasons. Mean and median values are shown, together with 25% and 75 % quantiles.

Figure 5. Sensitivities of chemical components (NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3) as well as meteorological parameters (RH, T) to ALWC in summer and winter.

Figure 6. Sensitivities of chemical components (NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3) as well as meteorological parameters (RH, T) to H_{air}^+ in summer and winter.

Figure 7. Sensitivities of chemical components (NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3) as well as meteorological parameters (RH, T) to pH in summer and winter.

Figure 8. Measured $NO_3^-/2SO_4^{2-}$ ratio (mole $mole^{-1}$) versus predicted pH colored by ambient RH. NO_3^-, SO_4^{2-} dominant zone denotes $NO_3^-/2SO_4^{2-} > 1$ or < 1.

Figure 9. The size distribution of aerosol pH and all analyzed chemical components on clean (a, d, g), polluted (b, e, h) and heavily polluted days (c, f, i) in summer, autumn and winter.

Figure 10. The size distribution of pH and all analyzed chemical components in the daytime (a, c, e) and (b, d, f) nighttime in summer, autumn and winter.

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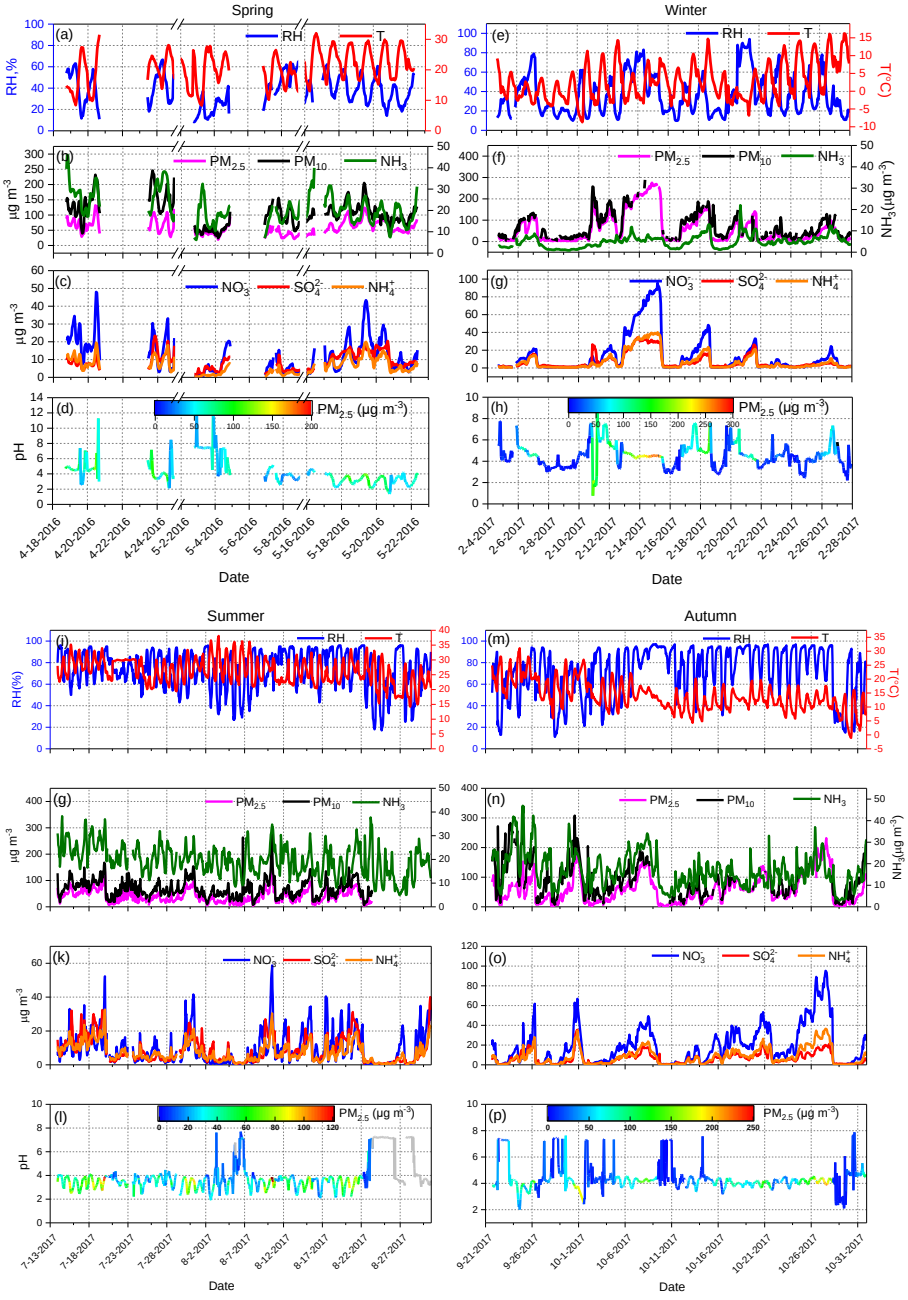

Figure 1.

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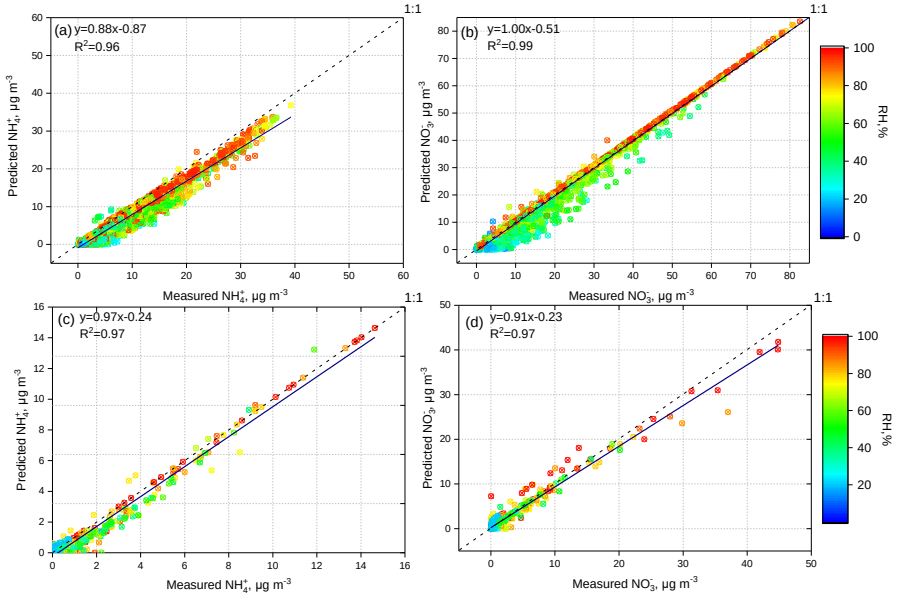

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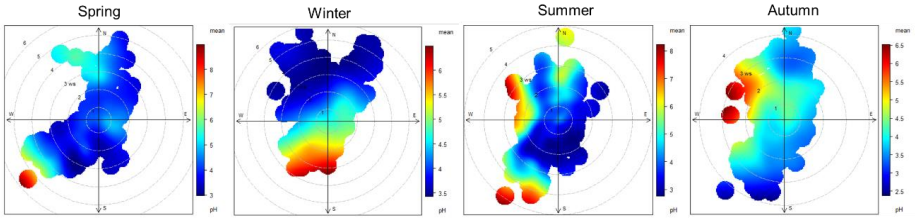

Figure 3.

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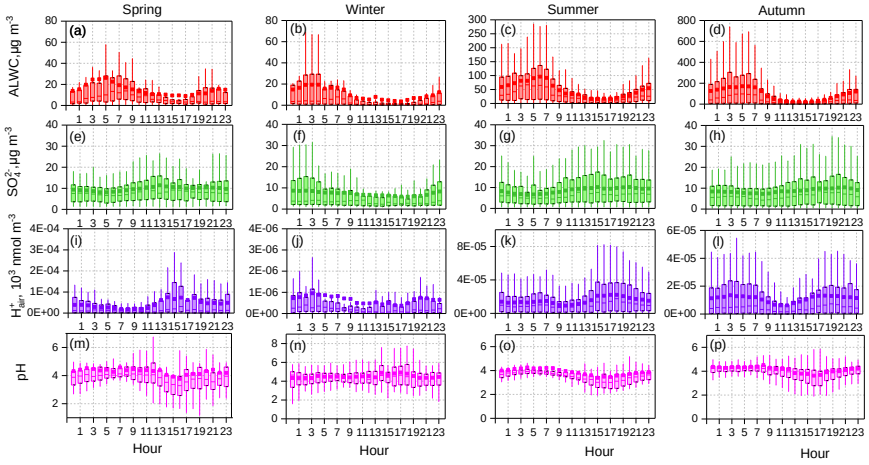

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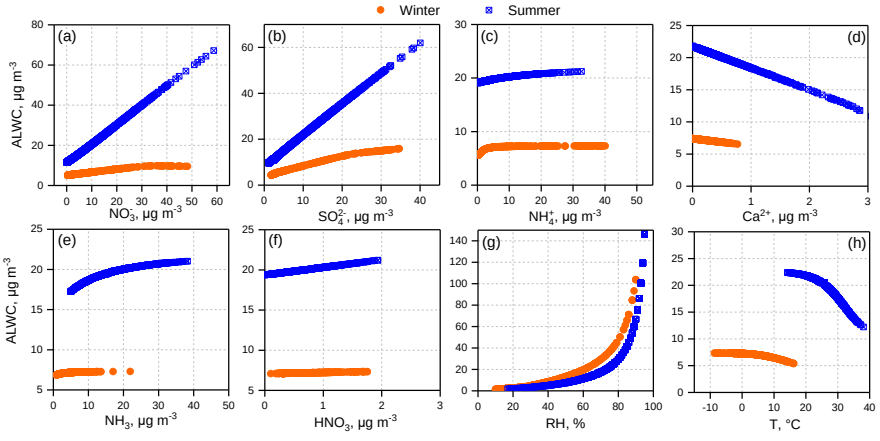

Figure 5.

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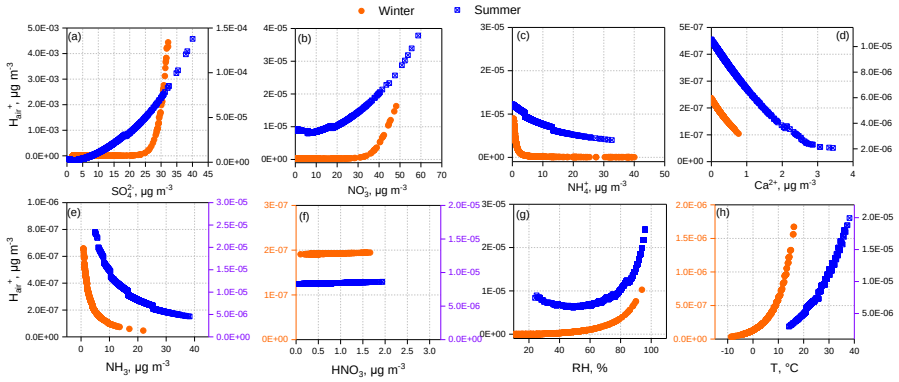

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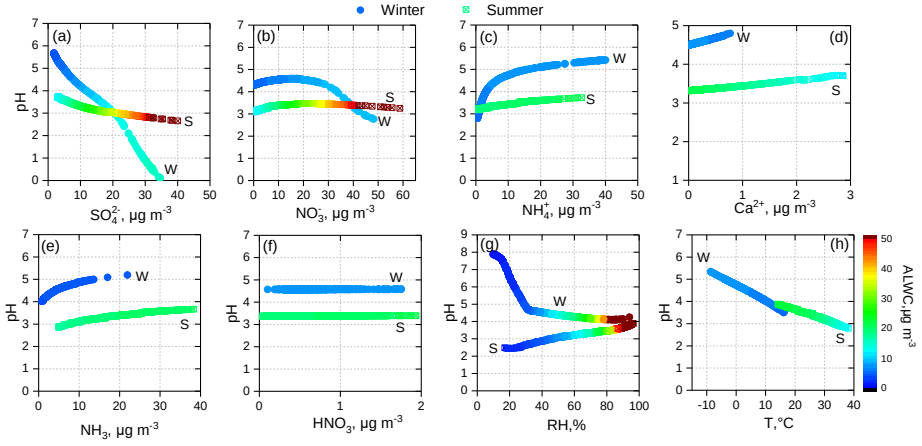

Figure 7.

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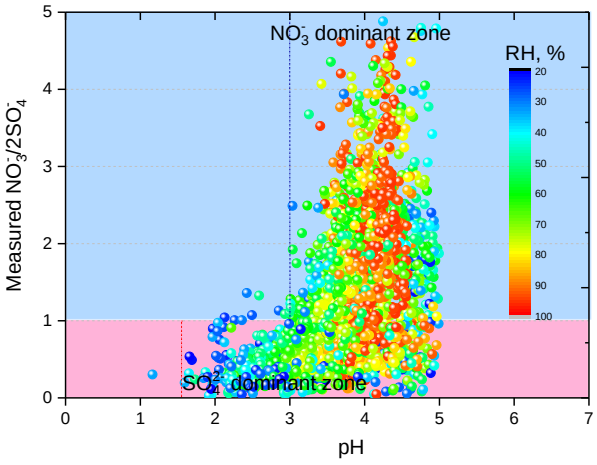

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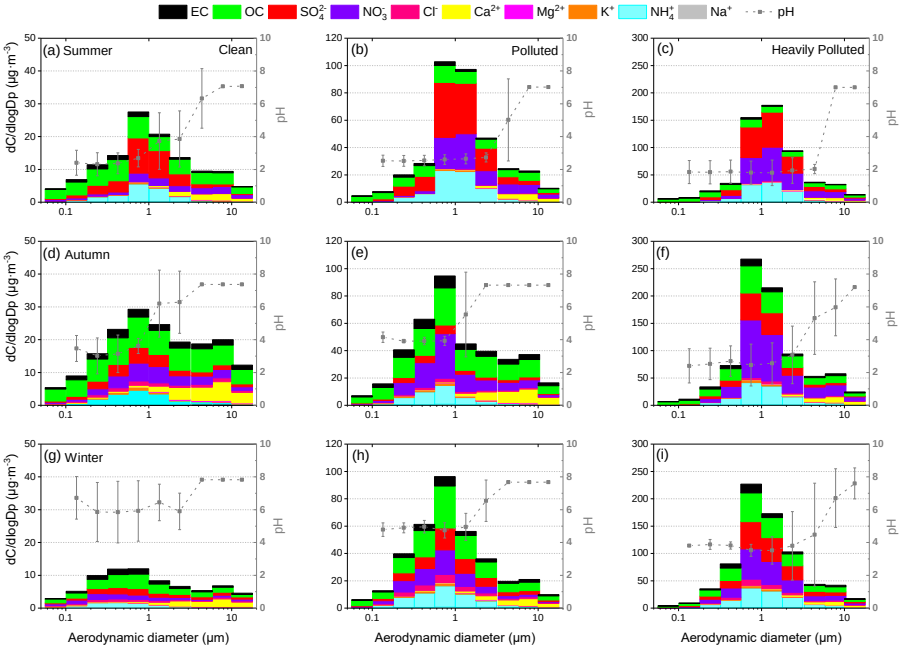

Figure 9.

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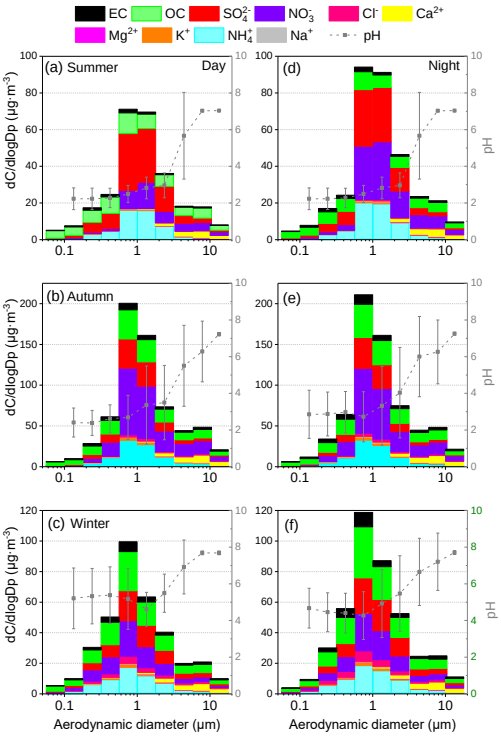

Figure 10.