



Characterization of aerosol acidity at a high mountain site in central eastern China

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ABSTRACT

Aerosol acidity plays an important role in the formation of secondary organic aerosols. In the present study, strong and aerosol acidity properties of PM_{2.5} were evaluated based on the highly time-resolved measurements of PM_{2.5} ionic compositions obtained at the highest mountain site in central eastern China in spring and summer of 2007. Overall, PM_{2.5} was weakly acidic at Mt. Tai with 57.2% and 81.3% of the observations being acidic aerosols in spring and summer, respectively. Strong and aerosol acidities showed higher levels in summer (mean ± stand deviation: 142.65 ± 115.23 and 35.27 ± 30.88 nmol m⁻³) and lower concentrations in spring (64.82 ± 75.07 and 25.25 ± 32.23 nmol m⁻³). Aerosol pH exhibited an opposite seasonal trend with less acidic aerosols in summer compared to the aerosols in spring due to high water content in the particles in summer. Strong acidity showed a well-defined diurnal profile with a broad peak during the daytime, while aerosol acidity was at relatively low level in the daytime. The effects of ambient RH and atmospheric aging on the acidities of PM_{2.5} were examined. Aerosol water content facilitated the release of free H⁺ in the aerosol droplet via hydrolysis processes of bisulphate and acidic aerosols were often associated with more processed air masses. Several cases with formation and accumulation of secondary organic aerosols occurring were investigated. The results indicated that the increase of secondary organic aerosols was probably due to effects of acidity promotion and aqueous phase formation. This is the first attempt to investigate aerosol acidity based on high resolution measurements of aerosol ions in central eastern China.

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1. Introduction

Fine particles (i.e., PM_{2.5}) are well known to be associated with human health, air quality deterioration, and even global climate change (Charlson et al., 1992; Nel, 2005). Aerosol acidity is an important property of particles. It can influence aerosol phase reactions by altering the uptake of precursors and the partitioning of volatile and semi-volatile compounds between the gas phase and particle surfaces (Grassian, 2001; Usher et al., 2002; Hatch and Grassian, 2008). It can also catalyze heterogeneous reactions to enhance the formation of secondary inorganic aerosols (Underwood et al., 2001; Ullerstam et al., 2002; Manktelow et al., 2010) and secondary organic aerosols (SOA) (Jang et al., 2002; Gao et al., 2004; Cao and Jang, 2010). Therefore, understanding of aerosol acidity and its impact is a fundamental issue in aerosol sciences.

Acidity of fine aerosols is mainly determined by the balance of acidic ionic components with basic ones, namely, sulfate (SO₄²⁻), nitrate (NO₃⁻) and ammonium (NH₄⁺). There are two indicators of particle acidity: strong acidity (H⁺_{strong}) and actual free acidity of aerosol (H⁺_{air}). H⁺_{strong} is the total amount of acid contributed by the strong acids, such as sulfuric and/or nitric acid, in the aqueous extract of the aerosols collected on the filter or from semi-continuous sampler. H⁺_{air}, defined as the moles of free hydrogen ions in the aqueous phase of aerosols per unit of air (nmol m⁻³), is the actual acidity in the droplets of the aerosol. However direct measurement of H⁺_{air} is not possible since the aqueous water of the aerosol is very small. Indirect methods, such as thermodynamic models, including Aerosol Inorganic Model (AIM-II) (Clegg et al., 1998), ISORROPIA (Nenes et al., 1998), SCAPE2 (Meng et al., 1995) and GFEMN (Ansari and Pandis, 1999), can supply suitable approaches for predicting H⁺_{air} and pH can also be calculated based on the output H⁺_{air} and liquid volume of the particles. H⁺_{strong} not only contains the actual free hydrogen ion in the aqueous phase of aerosols (H⁺_{air}), also includes other hydrogen ion released from either undissociated sulfuric acid or bisulfate in the presence of

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large excesses of water. Thus in amount $[H^+]_{\text{strong}}$ is the sum of $[H^+]_{\text{air}}$, $[HSO_4^-]$ and any other $[H^+]$ in the solid phase with sulfate and/or nitrate at equilibrium (Pathak et al., 2009; Yao et al., 2006). Thus H^+_{air} is a more accurate indicator of aerosol acidic nature (Pathak et al., 2009) and more relevant than strong acidity in understanding the chemical behavior and subsequent environmental impacts of atmospheric aerosols.

Several applications have been reported the performance of AIM-II (<http://www.aim.env.uea.ac.uk/aim.htm>) is the most accurate in evaluating the acidity nature of particles (Ansari and Pandis, 1999; Pathak et al., 2003; Yao et al., 2006). So AIM-II was selected to calculate H^+_{air} in this study. On the other hand, most of previous studies were based on integrated measurements (i.e., 24-h filter measurements) of ion concentrations, which cannot provide useful information on the time evolution of aerosol acidity and its impacts on aerosol phase reaction processes. Furthermore, long-time integrated sampling of particulate matter also leads to many artifacts (Nie et al., 2010), which in turn interfere with AIM-II's calculation of aerosol acidity. Highly time-resolved data of ion concentrations are valuable for investigating temporal variation of aerosol properties and for detailed process analysis of aerosol pollution; however only a few studies are based on the real time measurement (Zhang et al., 2007; Takahama et al., 2006; Tanner et al., 2009).

Central eastern China is home to three megacities, i.e., Beijing, Tianjin, and Shanghai, and parts or the entirety of Hebei, Shandong, Henan, Hubei, and Jiangsu provinces. It is the largest emitter in China for many chemically and radioactively important pollutants such as SO_2 and particles (Zhang et al., 2009), and thus is of particular interest with regard to air quality studies. High concentrations of carbonaceous aerosols have also been reported at Mt. Tai (the highest mountain in this area), and it was also reported that substantial SOA was formed through both photochemical process and cloud processing (Wang et al., 2011, 2012). This abundant SOA may be attributed to the high concentration of precursors (e.g., VOC) and atmospheric oxidants (e.g., O_3) (Gao et al., 2004; Suthawaree et al., 2010). Intensive field observations were conducted at Mt. Tai in spring and summer of 2007. In this study hourly measurements of SO_4^{2-} , NO_3^- and NH_4^+ were used to investigate the acidity of $PM_{2.5}$ including strong acidity, aerosol acidity and pH. This is the first attempt to investigate aerosol acidity based on such high resolution measurements of aerosol ions at a mountain site in China. Several factors that influence the acidity were discussed. To date conflicting conclusions have been obtained by different measurements about the influence of acidity on the SOA formation (Takahama et al., 2006; Zhang et al., 2007; Tanner et al., 2009; Rengarajan et al., 2011). It is thus worthwhile to investigate the relationship between acidity and SOA formation in this mountain site.

2. Experiment and methods

2.1. Experiment

Two phases of field experiments were conducted at the peak of Mount Tai ($36^\circ 16' N$, $117^\circ 6' E$, 1534 m a.s.l.) from March 21 to April 23 (spring campaign) and from June 15 to July 15 (summer campaign) in 2007. Mount Tai is the highest mountain on the central eastern plain of China. It is located 15 km north of Tai'an city (population: $\sim 500,000$) and about 230 km from the Bohai and Yellow Seas. Previous study indicated that Mount Tai is relatively isolated from local emissions and most air masses arriving at Mount Tai have undergone long-range transport (Zhou et al., 2010), thus it is an ideal location to study the regional-scale air pollution and atmospheric processes in central eastern China.

The details of the measurement station had been described (Zhou et al., 2010).

A large suite of air pollutants including trace gases and aerosol parameters were measured during the campaigns (Zhou et al., 2010). In this paper, only a brief description is presented. Ionic compositions in $PM_{2.5}$ were measured on an hourly basis by using a semi-continuous ambient ion monitor (Model URG 9000B), which had been described in Zhou et al. (2010). Ten inorganic ions, i.e., F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} were determined by two ion chromatographs. The detection limits (at the 99% confidence level) are 0.054, 0.010, and $0.045 \mu g m^{-3}$ for SO_4^{2-} , NO_3^- , and NH_4^+ which were used in this study, with measurement uncertainties of approximate $\pm 10\%$ (Zhou et al., 2010). On other species relevant to this study (e.g., OC, EC, NO_x , O_3 , NH_3 and CO), detailed descriptions of measurement techniques, accuracy and precision, and quality assurance/quality control methods were described elsewhere (Wang et al., 2003, 2011).

2.2. Calculation of aerosol acidities

2.2.1. Strong acidity

In the present work, hourly concentrations of SO_4^{2-} , NO_3^- and NH_4^+ were used to evaluate the acidic characteristics of $PM_{2.5}$. These three ions were selected due to the fact that they contributed more than 90% of the total ionic compounds in $PM_{2.5}$ and thus controlled aerosol acidity (Zhou et al., 2010). And water soluble organic ions only contributed less than 1% to the total ions. This method is not adapted for the area with large fraction of coarse or organic aerosol. Neutralization degree (denoted by F in this paper), defined as the extent to which acidic aerosol is neutralized, was derived from the mole concentration ratio of NH_4^+ to $(2 \times SO_4^{2-} + NO_3^-)$.

$$F = [NH_4^+] / (2 \times [SO_4^{2-}] + [NO_3^-]) \quad (1)$$

where $[NH_4^+]$, $[SO_4^{2-}]$ and $[NO_3^-]$ denote the mole concentrations ($nmol m^{-3}$) of each species in air. F ranges from 0 (no neutralization has occurred) to $1 \pm \sigma$ (anions have been neutralized fully by NH_4^+), in which σ stands for the analytical error based on error propagation of corresponding ion's measurement uncertainty. On average, $\sigma = 10\%$ was estimated for the present method.

For acidic aerosols with $F < 1$, strong acidity was estimated from the difference between mole concentrations of $(2 \times SO_4^{2-} + NO_3^-)$ and NH_4^+ .

$$[H^+]_{\text{strong}} = [H^+] + [HSO_4^-] \approx (2 \times [SO_4^{2-}] + [NO_3^-] - [NH_4^+]) \quad (2)$$

It is worth noting that a small portion of data was excluded from the acidity analysis in this study. These data were mainly obtained from several dust storm cases in spring when mineral ions and carbonic acid accounted for a larger fraction of the aerosol mass, and from cloud/fog events in summer when the concentrations of ions were very low. Finally, a total of 430 and 443 sets of hourly data were available for the calculation of strong acidity, accounting for $\sim 71\%$ and $\sim 63\%$ of the total measurements in spring and summer, respectively.

2.2.2. Aerosol acidity and pH

Aerosol acidity was calculated by the online version of Aerosol Inorganic Model II (AIM-II) with gas-aerosol interaction disabled (Clegg et al., 1998). Hourly measurements of SO_4^{2-} , NO_3^- , NH_4^+ , ambient temperature (T), relative humidity (RH), and the calculated H^+_{strong} were entered into the model as inputs. After calculation, the model outputted the aqueous phase concentrations of free ions

including H^+ , SO_4^{2-} , NO_3^- , NH_4^+ and HSO_4^- , and water content in the aerosol droplets per m^3 air. The pH was predicted by the mole concentrations of free H^+ in the aqueous phase of particle droplets,

$$\text{pH} = -\log \left[\gamma \times \left[\text{H}^+ \right]_{\text{air}} / (V_{\text{aq}}/1000) \right] \quad (3)$$

where γ and V_{aq} denote the activity coefficient of H^+ (mol m^{-3}) and the volume of particle aqueous phase in air ($\text{cm}^3 \text{m}^{-3}$).

The H^+ predicted by AIM-II highly depends on the presence of an aqueous phase in the thermodynamic equilibrium. When ambient RH is lower than the deliquescence point (DRH), the particle is considered by AIM-II to exist as a pure solid phase and thus there was no output for the H^+ . In addition, the model cannot predict the H^+ for fully neutralized aerosols (i.e., $F \geq 1$). That means only the aerosol acidity of acidic ones were considered. In the present study, a total of 214 and 339 sets of hourly data had valid output to evaluate the aerosol acidity of $\text{PM}_{2.5}$ in spring and summer, respectively.

3. Results and discussion

3.1. General results

3.1.1. Overview of aerosol acidity

Fig. 1 shows the frequency distributions of neutralization degrees of $\text{PM}_{2.5}$ obtained in the spring and summer phases at Mt. Tai. In the present study, acidic aerosol is defined as the sample with a neutralization degree lower than 0.9. $\text{PM}_{2.5}$ samples collected at Mt. Tai showed a general weakly acidic nature. In spring, 57.2% of the valid samples were acidic aerosols with an average F (\pm standard deviation) of 0.88 (± 0.23), while 81.3% of the valid observations were acidic with a mean F of 0.78 (± 0.17) in summer. Furthermore, about 28.1% of the observations in spring were more acidic with F smaller than 0.75, compared to an approximate fraction of 48.5% in summer. These results indicate higher acidities of particles in summer than those in spring.

Strong acidity, aerosol acidity, and pH of $\text{PM}_{2.5}$ at Mt. Tai and other compositions modeled by AIM-II are summarized in Table 1. Fig. 2 shows the time series of $[\text{H}^+]_{\text{air}}$ and pH together with other acidity indicators ($[\text{H}^+]_{\text{strong}}$ and F) for the study periods. The average concentration of H^+ (\pm standard deviation) was 64.82 (± 75.07) nmol m^{-3} in spring, which was much lower than that of 142.65 (± 115.23) nmol m^{-3} in summer. This is in line with the higher frequency of acidic particles in summer. The mean concentration of total water-soluble ions in spring was about 25% lower

than that in summer (Zhou et al., 2010) with most accounted for sulfate. Thus higher acidities were observed in summer.

Similar to strong acidity, aerosol acidities of $\text{PM}_{2.5}$ in summer (mean = 35.27 nmol m^{-3}) were also higher than those in spring (mean = 25.25 nmol m^{-3}). The amount of H^+ accounted for about 20% of the strong acidity in summer, which was slightly lower than that of 24% in spring. In contrast, aerosol pH was much higher with a mean value of $-0.04 (\pm 1.01)$ in summer than that in spring ($\text{pH} = -0.32 \pm 1.38$), indicating lower acidity in summer than that in spring. This is because the aerosol water content was almost two times higher in summer (mean = 78.57 $\mu\text{g m}^{-3}$) than in spring (mean = 47.89 $\mu\text{g m}^{-3}$), which led to less ionic strength ($19.39 \pm 11.09 \text{ mol kg}^{-1}$ water in summer compare to $21.48 \pm 12.86 \text{ mol kg}^{-1}$ water in spring) and less H^+ in the aqueous phase. The impact of aerosol water content on the aerosol acidity of $\text{PM}_{2.5}$ will be discussed in section 3.3.1.

3.1.2. Comparison with other studies

We compared the acidities of $\text{PM}_{2.5}$ at Mt. Tai with the data obtained from other areas in the world (Table 2). The strong acidity of $\text{PM}_{2.5}$ at Mt. Tai was much higher than those reported in US, Korea, Japan, India, Hong Kong Guangzhou and Lanzhou, but lower than those in Beijing and Shanghai (Table 2). The seasonal variation at Mt. Tai was opposite to that in Durham in New England (Ziemba et al., 2007) and Hong Kong (Pathak et al., 2003), which may be caused by different air mass transportation. According to the limited reports, we can find the aerosol acidity of aerosol in Mt. Tai was higher than those from Indian, Pittsburgh, Guangzhou and Lanzhou, but lower than Beijing and Shanghai, which was similar to the case of strong acidity.

The overall acidity of aerosols is balanced by both acidic and basic components. NH_3 plays an important role in neutralizing the acidic components in the atmosphere. Atmospheric NH_3 emission is often positively associated with human activities (Galloway et al., 2004). Thus more acidic aerosols are often observed in rural areas than in urban areas (Table 2), due to lower NH_3 emissions caused by less human activities in rural areas (Liu et al., 1996). However Mt. Tai, a place far from human activities, had lower aerosol acidity than a rural site in Beijing, indicating that relatively abundant NH_3 may exist in this area. This is evidenced by our measurement that the average NH_3 concentration at this mountain site was 10.06 and 13.75 ppb in spring and summer respectively, higher than the concentration reported in the rural site in Beijing in 2007 (annual average: 4.5 ± 4.6 ppb) (Meng et al., 2011). In this study the fractions of acidic sulfate and nitrate ($[\text{H}^+]_{\text{strong}}/[2 \times \text{SO}_4^{2-} + \text{NO}_3^-]$) with

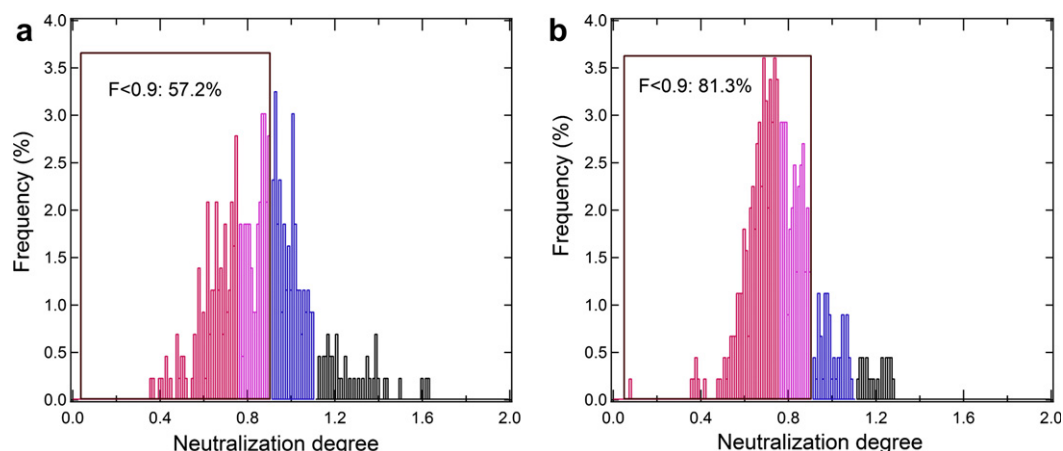


Fig. 1. Frequency distributions of neutralization degrees of $\text{PM}_{2.5}$ in (a) spring and (b) summer campaigns at Mt. Tai with acidic frequency in the box.

Table 1
Statistics of strong acidity ($[H^+]_{\text{strong}}$), neutralization degree (F) and aerosol acidity ($[H^+]_{\text{air}}$) modeled by AIM-II in $PM_{2.5}$ in spring and summer campaigns at Mt. Tai.

	Spring			Summer		
Strong acidity	All valid data	$F < 0.75$	$0.75 < F < 0.9$	All valid data	$F < 0.75$	$0.75 < F < 0.9$
Number	430	121 (28.1%)	125 (29.1%)	443	215 (48.5%)	145 (32.7%)
F	0.88 ± 0.23	0.64 ± 0.09	0.83 ± 0.05	0.78 ± 0.17	0.65 ± 0.08	0.82 ± 0.04
H^+_{strong} (nmol m^{-3})	64.82 ± 75.07	134.38 ± 76.01	72.82 ± 53.44	142.65 ± 115.23	209.42 ± 110.29	118.42 ± 72.54
Aerosol acidity	All valid data			All valid data		
Number	214			339		
H^+_{air} (nmol m^{-3})	25.25 ± 32.23			35.27 ± 30.88		
pH	-0.32 ± 1.38			-0.04 ± 1.01		
HSO_4^- (nmol m^{-3})	67.66 ± 57.65			121.34 ± 79.05		
$H^+_{\text{strong}}^a$ (nmol m^{-3})	111.52 ± 82.64			180.02 ± 104.4		
$\text{HSO}_4^-/H^+_{\text{air}}$	3.8 ± 2.51			4.74 ± 2.99		
$H^+_{\text{air}}/H^+_{\text{strong}}^a$	0.24 ± 0.14			0.2 ± 0.11		
Water content ($\mu\text{g m}^{-3}$)	47.89 ± 77.14			78.57 ± 136.99		
RH (%)	65 ± 22			70 ± 16		
T (K)	277.98 ± 4.32			291.35 ± 2.24		

^a Stands for the strong acidity for the aerosol with valid H^+_{air} .

these two anions concentrations were also compared (Fig. 3). The results showed that high $[H^+]_{\text{strong}}/[2 \times \text{SO}_4^{2-} + \text{NO}_3^-]$ ratios were accompanied with low to moderate anion concentrations in both spring and summer. This trend was opposite to that in many other locations where a limited amount of ammonia was available (Liu et al., 1996). It was reported that short or long range transport of air mass from other areas dominated the source of the aerosol at Mt. Tai during the study (Zhou et al., 2010). Thus the NH_3 concentration in this mountain site was probably affected by upslope transport of low-land emissions or by transport from areas with high NH_3 emissions.

The observations at Mt. Tai showed the existence of high ammonia emission which to a large extent neutralized the aerosol acidity. However the aerosol acidity at Mt. Tai was still at a high level compared with that in many other sites in the world, which suggests extremely serious acidity pollution in this area.

3.2. Diurnal variations

Fig. 4 shows the diurnal profiles of H^+_{strong} , H^+_{air} and pH, together with RH and water content in aerosols obtained at Mt. Tai. Overall, H^+_{strong} exhibited a well-defined diurnal pattern in both

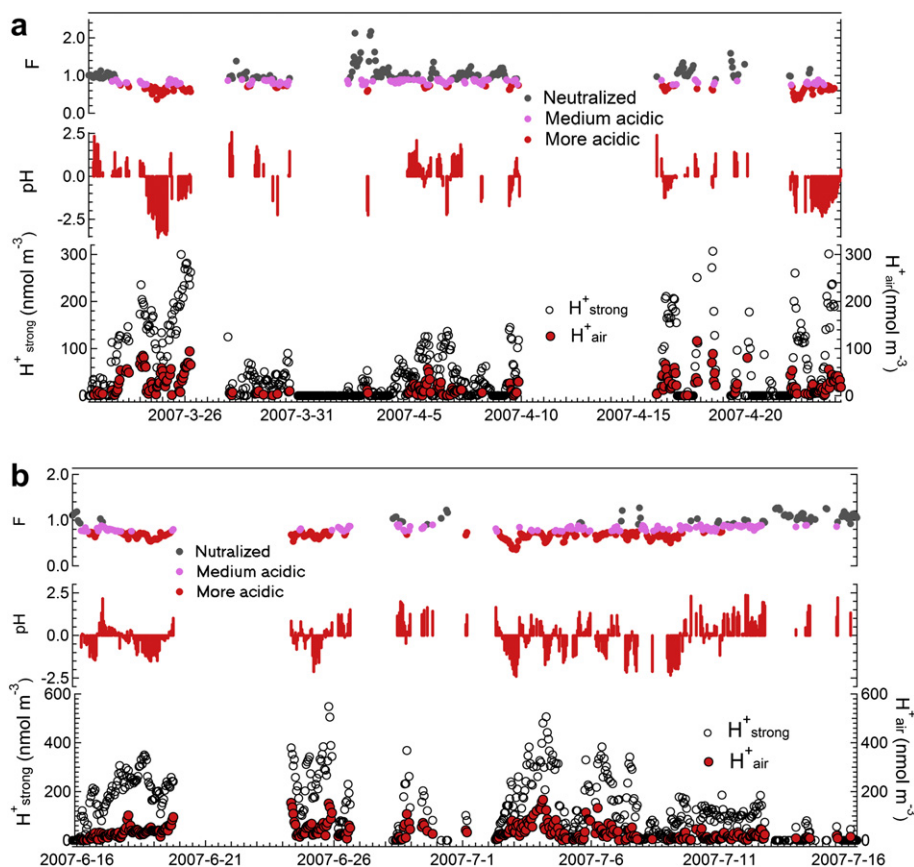


Fig. 2. Temporal variations of H^+_{strong} , H^+_{air} , pH and F of $PM_{2.5}$ in (a) spring and (b) summer campaigns at Mt. Tai.

Table 2
Comparison of aerosol acidity of PM_{2.5} at Mt. Tai and other sites in the world.

	Location	Study periods	H ⁺ _{strong}	H ⁺ _{air}	Reference ^a
Mt. Tai, China (1532 m)	36°16' N, 117°6' E	2007 Mar.–Apr. 2007 Jun.–Jul.	64.82 ± 75.07 142.65 ± 115.23	25.25 ± 32.23 35.27 ± 30.88	This study
Camp Dodge, US (452 m)	41° 42' N, 93° 42' W	1991–1997 1998–2007	25.9 ± 44.4 24.0 ± 27.9		Murray et al., 2009
Lakes of the Clouds, US (1540 m)	46°48' N, 89°45' W	1991–1997 1998–2007	18.2 ± 31.8 25.4 ± 34.0		
Pittsburgh, US (urban site)	40°26' N, 80°0' W	2002 Sep. 1990 summer	28 38.2 ± 5.1		Zhang et al., 2007 Liu et al., 1996
Uniontown, US (semi-rural site)	39°54' N 79°43' W	1990 summer	128.0 ± 2.6		
State College, US (semi-rural site)	40°47' N, 77°51' W	1990 summer	68.6 ± 3.6		
New England, ^b US (rural site)	43°6' N, 70°56' W	2000–2004 spring 2000–2004 summer	7.46 6.58		Ziemba et al., 2007
Seoul, Korea (urban site)	37°34' N, 126°58' E	1996 fall	5.9		Lee et al., 1999
Goto, Japan (urban site)	32°50' N, 129°0' E	1997 Jan. and Dec.	24.2		Shimohara et al., 2001
Dazaifu, Japan (urban site)	33°31' N, 130°31' E	1997 Jan. and Dec.	11.4		
Ahmedabad, India (semi-arid region)	23°02' N, 72°32' E	2006 Dec. ~ 2007 Jan.	11–250		Rengarajan et al., 2011
Beijing, China (280 m rural site)	40°21' N, 116°18' E	2005 Jun.–Aug.	390 ± 545	228 ± 344	Pathak et al., 2009
Shanghai, China (urban site)	31°27' N, 121°06' E	2005 May–Jun.	220 ± 225	96 ± 136	
Lanzhou, China (suburban site)	36° N, 104° E	2006 Jun.–Jul.	65 ± 44	7 ± 6	
Guangzhou, China (suburban site)	22°42' N, 113°30' E	2004 May	70 ± 58	25 ± 29	
Hong Kong, China (rural and urban sites)	22° N, 114° E	2000 spring 2000 summer	49 27		Pathak et al., 2003

^a This study used the online ion determination method, Zhang et al. (2007) used the aerosol mass spectrometer method and other studies used the filter-based method.

^b Medium data.

seasons. In spring, H⁺_{strong} had high concentrations ([H⁺]_{strong}: 55.45~81.67 nmol m⁻³) in the afternoon and evening, and low levels ([H⁺]_{strong}: 37.36~54.06 nmol m⁻³) at night and in the early morning. While in summer, it showed a broader daytime peak with a maximum value of 173.5 nmol m⁻³ compared to the nighttime with a minimum value of 78.99 nmol m⁻³. These patterns were consistent with those of major secondary inorganic ions, namely, SO₄²⁻, NO₃⁻ and NH₄⁺ (Zhou et al., 2010), and to some extent coincided with those of Semi-volatile organic carbon (SVOC) and Non-volatile organic carbon (NVOC) (Wang et al., 2011). Such diurnal variations were a result of the upslope transport of polluted air from the lowland areas due to the mountain-valley breeze and enhanced convective mixing during the daytime (Ren et al., 2009; Zhou et al., 2010). Much newly-formed sulfate may lead to enhanced acidity in the aerosol in the summer campaign.

Compared to H⁺_{strong}, diurnal profiles of H⁺_{air} and pH were less various. This is in large part due to the fact that the level of H⁺_{air} is a complex function of not only the concentrations of SO₄²⁻, NO₃⁻ and NH₄⁺, also a function of water content. In spring, H⁺_{air} generally showed low concentrations (~8.25 nmol m⁻³) in the afternoon.

Low RH and less particle water (H₂O_p) in the afternoon in spring may lead to more solid-phase transitions in aerosols, resulting in low concentrations of free H⁺ in the aqueous phase of aerosol. Aerosol pH showed the highest acidity concentration in the aqueous phase in the afternoon, which may be attributed to the low aerosol water content in the afternoon. In summer, H⁺_{air} generally showed low concentrations during the daytime, consistent with the broad peak of pH. An interesting phenomenon is that pH showed similar diurnal trends with RH. The correlation of pH and RH for all the hourly measurements was examined, and excellent correlations in both seasons ($R=0.96$ in spring and $R=0.91$ in summer) were derived, suggesting RH plays a significant role in the acidity characteristics of aerosols. The specific impact of ambient RH on aerosol acidity will be discussed in detail in the following section.

3.3. Factors affecting acidity

3.3.1. Aerosol water content

As stated above, water content in aerosol droplets plays a key role in the acidity of PM_{2.5}. One of the effects is the release of free

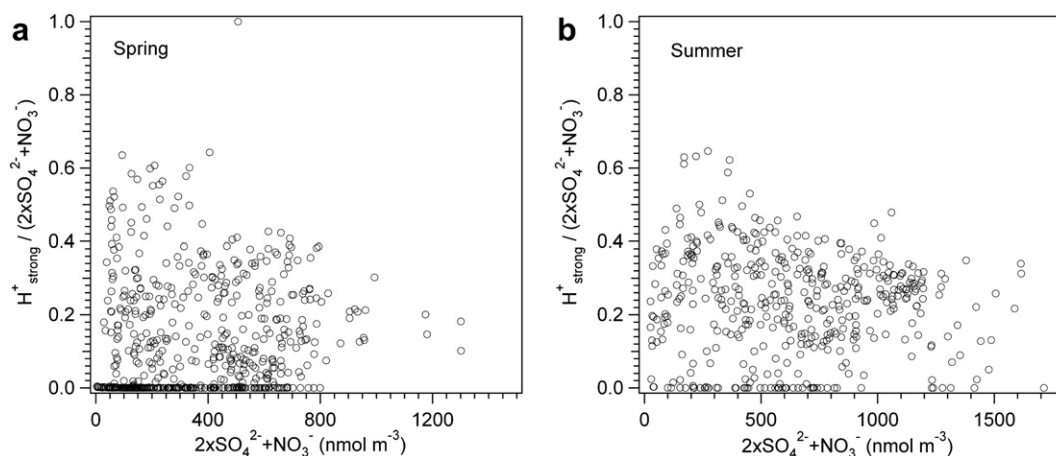


Fig. 3. Mole ratios of acid to sulfate and nitrate vs. sulfate and nitrate concentrations in PM_{2.5} at Mt. Tai for (a) spring and (b) summer campaigns.

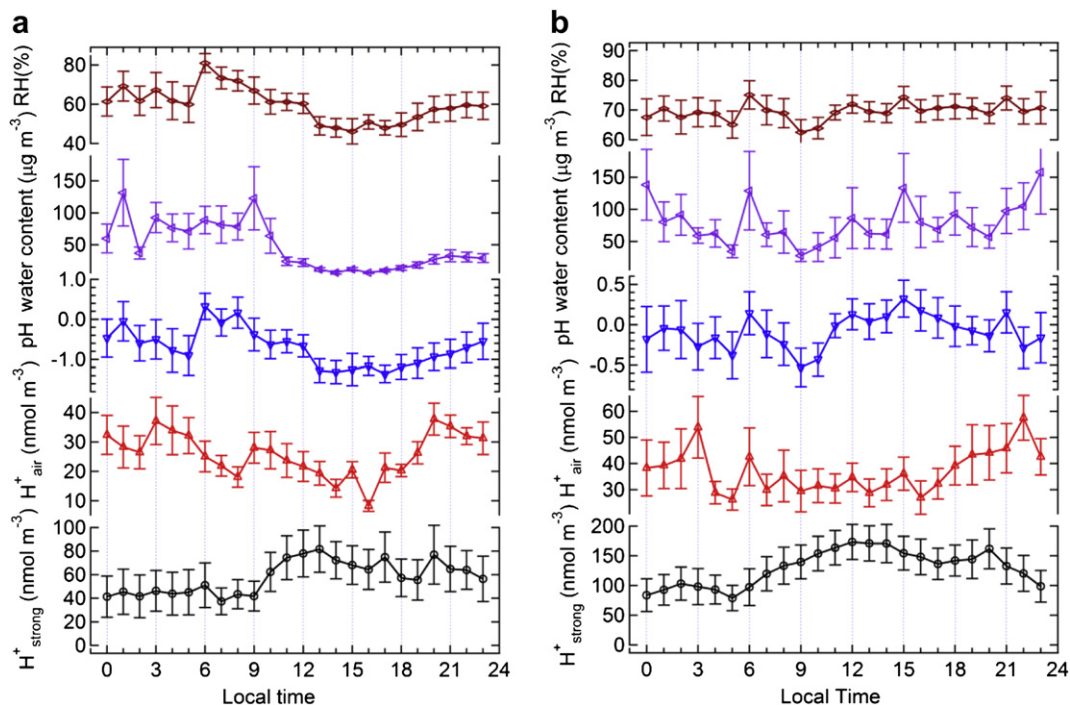


Fig. 4. Average diurnal variations of H^{+}_{strong} , H^{+}_{air} , pH, RH and water content in $PM_{2.5}$ at Mt. Tai during (a) spring and (b) summer campaigns. Note that the diurnal variations of H^{+}_{air} , pH, RH and water content are only for periods when AIM-II gave valid outputs as shown in Fig. 2, and whisker stands for 1/4 standard deviation.

H^{+} from HSO_4^{-} in the liquid phase of the aerosol (Yao et al., 2007). To evaluate the impact of the HSO_4^{-} hydrolysis process on the aerosol acidity, the relationship of $[HSO_4^{-}]/[H^{+}_{\text{air}}]$ against RH was examined (Fig. 5). Under conditions with $RH > 65\%$, the mole ratio of $[HSO_4^{-}]/[H^{+}_{\text{air}}]$ decreased with increasing RH, indicating that increasing aerosol water led to the dissociation of HSO_4^{-} to form free H^{+} . According to the outputs of AIM-II, the DRH for the aerosols in the present study were estimated at a range of 60%~65%, which further evidences that dissociation of HSO_4^{-} in aerosols is dependent on the difference between ambient RH and DRH (Pathak et al., 2003).

The interaction between water content and aerosol acidity is complicated. Some water content measurements found that when the aerosol was acidic, it could retain water at low RH, preventing the aerosol from drying in summer (Khlystov et al., 2005). On the other hand, elevated water content can supply a larger water surface to uptake more SO_2 , H_2SO_4 and HNO_3 , and accelerate the oxidation of SO_2 in the aqueous phase to increase aerosol acidity, especially when H_2O_2 or metal oxidants exist in the particles (Seinfeld and Pandis, 2006). And these new formed sulfate and nitrate will again uptake more water due to their hygroscopic characteristics. Also, particle water can also facilitate the release of free H^{+} from HSO_4^{-} in the liquid phase of the aerosol (Yao et al., 2007). These are the reasons why low values of H^{+}_{air} ($nmol\ m^{-3}$) were observed when H_2Op were low in the afternoon in spring, and in summer, H^{+}_{air} showed similar trend with H_2Op during the daytime (Fig. 4). However high water content can also dilute proton concentrations in acidic aerosols, leading to the decrease of acidity in the aqueous phase ($nmol\ L^{-1}$). This is evidenced by a similar pH trend with H_2Op (Fig. 4). This is also consistent with the results that higher average H_2Op (mean = $78.57\ \mu g\ m^{-3}$) with higher pH value (mean = -0.04) in summer than that in spring ($H_2Op = 47.89\ \mu g\ m^{-3}$; pH = -0.32), indicating the final result is dilution over the H^{+} formation in the aqueous phase.

3.3.2. Atmospheric processing

In this section, the relationship between aerosol acidities and atmospheric processing of air masses is explored. The ratio of NO_x to NO_y is usually used to evaluate the extent of atmospheric processing of air masses (Mao and Talbot, 2004). In the present study, $-\log(NO_x/NO_y)$ was used as a proxy of photochemical age of air masses arriving at Mt. Tai, with larger values indicating higher degree of atmospheric aging (Kleinman et al., 2008). Fig. 6 shows the correlation between H^{+}_{strong} and air mass age for both seasons. From the figure, H^{+}_{strong} correlated very well with the air mass age with R of 0.94 and 0.88 in spring and summer, respectively; indicating aerosols were more acidic in more processed air masses. The RMA slopes in Fig. 6 indicated increases of ~ 9.20 and $\sim 18.25\ nmol\ m^{-3}$ in H^{+}_{strong} for each increment of 0.01 in photochemical age in spring and summer respectively. This positive correlation was similar to the result observed by Quinn et al. (2006) in a cruise measurement during second New England Air Quality Study (NEAQS, 2004) which reported that more acidic aerosol was measured as the distance from the source region increased. To understand the positive correlation between H^{+}_{strong} and air mass age, we examined the relationship among air mass age with main acidity-affecting aerosol species, namely SO_4^{2-} , NO_3^{-} and NH_4^{+} (see Fig. 7). All these species showed good positive correlation with the air mass age, indicating they were produced during the aerosol processing. However, more SO_4^{2-} and NO_3^{-} were formed during the processing without an equivalent increase in NH_4^{+} , leading to an accumulation of H^{+} .

3.4. Relationships between aerosol acidity and secondary organic aerosol formation

A prominent advantage of high time-resolved measurements is that they provide an opportunity to investigate aerosol chemical processes in more detail. In this section, the relationship between acidity and secondary organic aerosol for summer campaign were

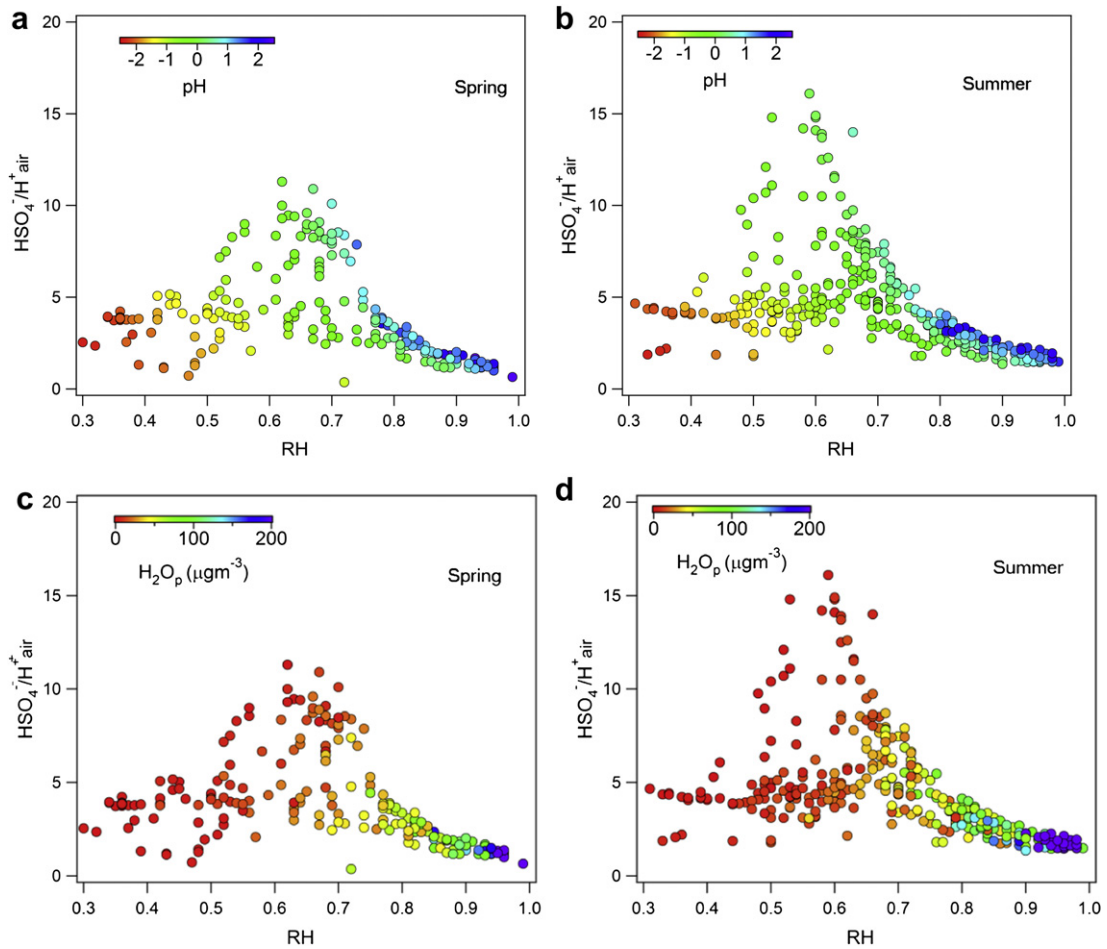


Fig. 5. Variations of $[\text{HSO}_4^-]/[\text{H}^+]_{\text{air}}$ ratios with RH for spring and summer campaigns (a and b colored by pH, c and d by aerosol water content). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

investigated. 18 out of 29 days of validate data were examined (11 days influenced by fog and rain were excluded). Because changes of wind direction were often observed in the morning and evening due to the influence of valley wind at this mountain site, the time series between 8:00 to 18:00 were investigated. Air parcel with similar wind direction are assumed underwent similar aerosol formation processes. The concentration of secondary organic

carbon (SOC) was estimated by EC-tracer method which had been already described (Wang et al., 2012).

3.4.1. Case of SOC increase with high acidity

If acidity enhanced SOA formation exists, possible evidence would be illustrated by an increase of the SOC concentration accompanying or following a period of high H^+ concentrations

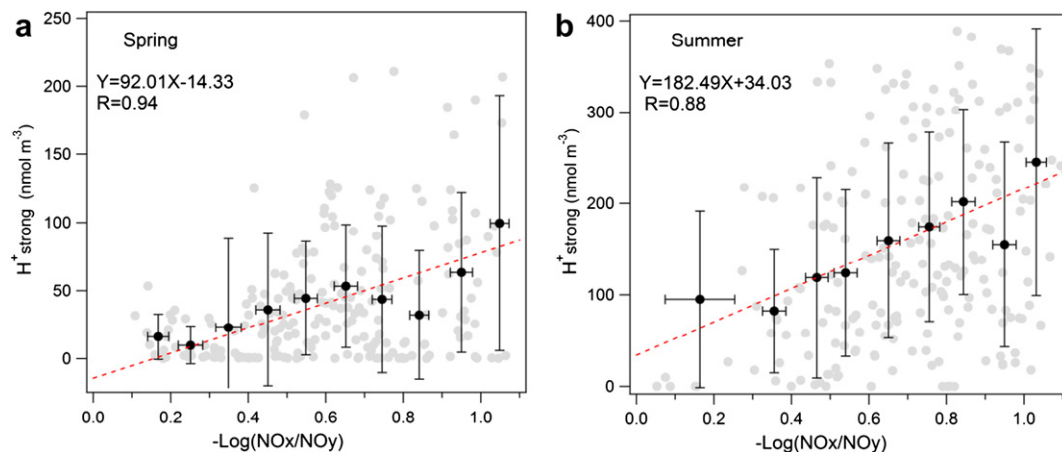


Fig. 6. Correlation between H^+ strong and air mass age in (a) spring and (b) summer campaigns (Grey data points are the H^+ strong during the campaigns, dark data points are the average values of H^+ strong in each specific age bin, and whisker stands for standard deviation).

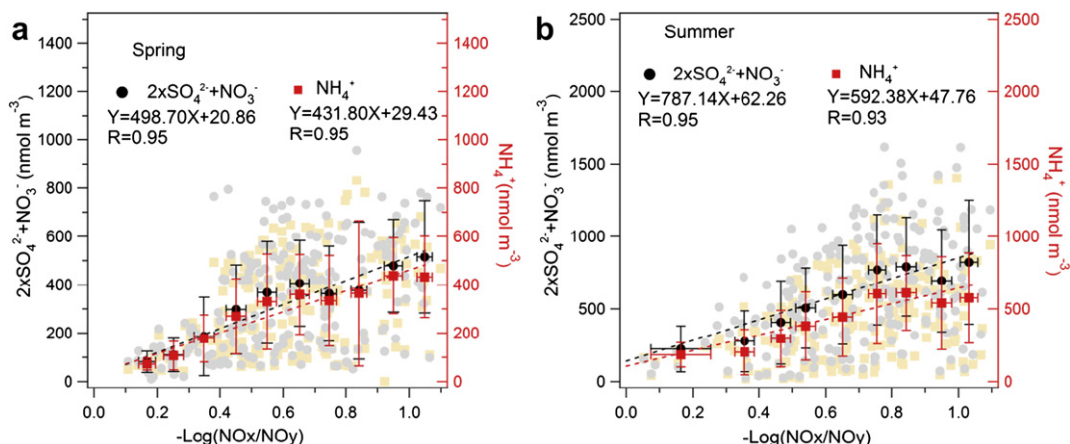


Fig. 7. Correlation between ions and air mass age in (a) spring and (b) summer campaigns (Light data points are the ions concentrations during the campaigns, solid clear data points are the average values of ions concentrations in each specific age bin, circle stands for anion, square stands for cation, and whisker stands for standard deviation).

with similar wind direction (Takahama et al., 2006). Fig. 8 illustrates an event of SOC formation accompanied with high $[H^+]_{\text{air}}$ on July 3rd. Time series of H^+_{air} , SOC, SO_4^{2-} , O_3 and CO, H_2O_p together with surface wind were plotted. During this event, SOC and SO_4^{2-} were quickly formed and accumulated in the morning with SOC and sulfate concentrations increasing from 2.82 and $24.25 \mu\text{g m}^{-3}$ at 8:00 to 5.63 and $47.53 \mu\text{g m}^{-3}$ at 14:00. The SOC concentrations were continued to stay high compared with other data in summer. The aerosol water was at a high level (H_2O_p : $57 \sim 136 \mu\text{g m}^{-3}$) during this increase. Thus the increase of sulfate may relate to both gas and aqueous phase oxidation and both high water content and sulfate concentration lead to a high concentration of H^+_{air} (nmol m^{-3}). SOA could be formed by gas-particle partitioning of photochemical oxidation products (Seinfeld and Pandis, 2006) and aqueous phase reactions (Blando and Turpin, 2000; Wang et al.,

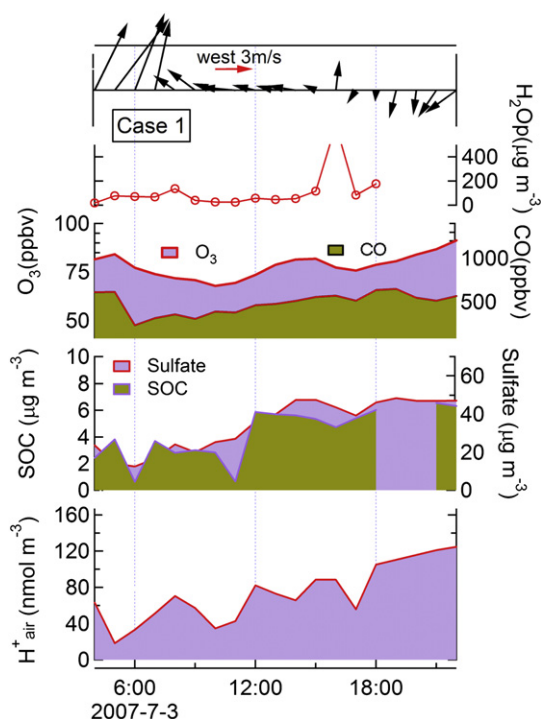


Fig. 8. Time series for the concentrations of H^+_{air} , SOC, O_3 , CO, water content and related surface wind direction on July 3rd.

2012). The correlation relationship between O_3 and CO can be used as an indicator of photochemical activity (Cooper et al., 2002). In this case, the RMA slope of O_3/CO was relatively low (slope: 0.05) compared with the whole summer condition (slope: 0.09), whereas the $[H^+]_{\text{air}}$ was high and continued to increase during the event. Thus such high levels of H^+_{air} coupled with a large amount of water content in the particle droplet possibly suggested that the high acidity of aerosols could promote the production of SOA through heterogeneous reactions (Jang et al., 2002; Gao et al., 2004). Another possibility is enhanced H_2O_p or cloud processing increased the SOA formation from aqueous phase reactions (Kamens et al., 2011; Zhou et al., 2011; Wang et al., 2012). At Mt. Tai, more than half of the investigated days (10 out of 18 days) were of this type, where inorganic acidity and SOC increased together under conditions of constant wind direction. This phenomenon at Mt. Tai was probably due to the effects of acidity promotion and aqueous phase formation. To be noted, the SOC may sometimes lag off the increase of H^+_{air} .

3.4.2. Case in no clear relationship was observed

In some cases no obvious relationship was observed between SOC concentration and acidity (8 cases), suggesting possibilities of other processes dominating the change in organic aerosol. Fig. 9 shows an example on July 10th. SO_4^{2-} was quickly formed and accumulated during the daytime with its concentrations increased from $17.67 \mu\text{g m}^{-3}$ at 8:00 to $33.29 \mu\text{g m}^{-3}$ at 12:00. But it began to decrease after 12:00 and stayed at a medium concentration. SOC showed a general increasing trend from $1.17 \mu\text{g m}^{-3}$ at 8:00 to $3.43 \mu\text{g m}^{-3}$ at 15:00. However, $[H^+]_{\text{air}}$ was relatively low (range: $1.36 \sim 11.5 \text{ nmol m}^{-3}$) and exhibited a decreasing trend due to low water content ($H_2O_p < 20 \mu\text{g m}^{-3}$). This implied no direct relationship between acidity in the aqueous phase and the formation of secondary aerosols in this air mass. Given the relatively high slope of O_3/CO (slope: 0.10), gas phase oxidation was believed important to contribute to the production of secondary aerosol in this event. And we found the cases that SOC increased with low acidity normally had high O_3/CO slopes (range: 0.10–0.16).

The SOC concentration did not necessarily follow the variation of the acidity. In fact, the variation of SOC concentration was often observed to lag off that of the acidity. This phenomenon may result from the requirement of time for the accumulation of the SOC when the acidity goes up, or from the continued formation of the SOC after the acidity goes down. Another possibility is that the acidity is under the threshold of affecting SOC formation. The wind direction of these two cases is very different, which may suggest different air

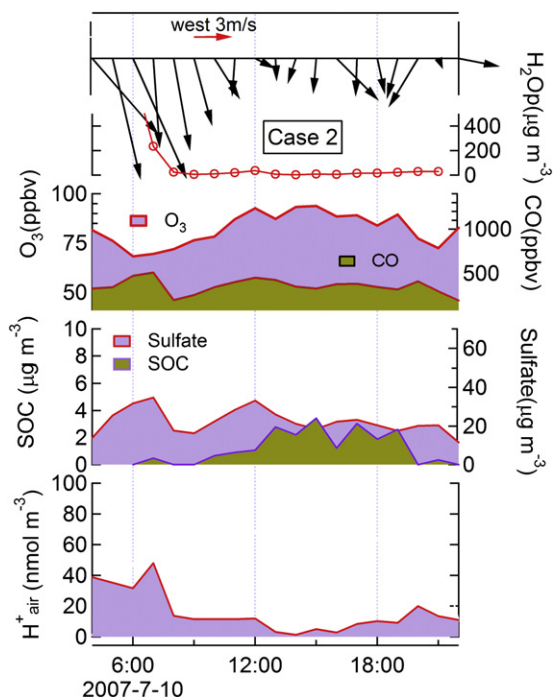


Fig. 9. Time series for the concentrations of H^+_{air} , SOC, O_3 , CO, water content and related surface wind direction on July 10th.

mass sources. All the air sources were checked each hour during the summer campaign and generally two categories were found. The acidities of aerosols from east (51.3% of the campaign) and south (7.0% of the campaign) were high with $[H^+]_{strong}$ at $161.32 \pm 116.12 \text{ nmol m}^{-3}$ and $[H^+]_{air}$ at $41.13 \pm 32.43 \text{ nmol m}^{-3}$ respectively. While when the air blew from the north direction (8.1% of the campaign), and west or northwest direction (33.62% of the campaign), the acidities were relatively low ($[H^+]_{strong}$: $115.87 \pm 108.77 \text{ nmol m}^{-3}$; $[H^+]_{air}$: $27.40 \pm 27.16 \text{ nmol m}^{-3}$). This indicated the air mass from east and south brought highly polluted aerosol in the summer campaign at Mt. Tai. This is consistent with the results that low pH of wet deposition was observed at Mt. Tai when the air mass came from the south and east in previous study (Wang et al., 2008).

4. Summary

Near continuous measurements of water-soluble ions in $PM_{2.5}$ were made in the spring and summer of 2007 at Mt. Tai, the highest mountain in central eastern China. The hourly data were used to estimate the strong and aerosol acidities of $PM_{2.5}$. Aerosol acidities characteristics and their relationship with SOC formation were investigated.

$PM_{2.5}$ was on average weakly acidic with approximate 57.2% and 81.3% of the samples being acidic particles in spring and summer, respectively. Strong acidity had higher concentrations in summer with an average of $142.65 \text{ nmol m}^{-3}$ and lower levels in spring with a mean value of $64.82 \text{ nmol m}^{-3}$. Similarly, aerosol acidity also showed elevated concentrations in summer (mean = $35.27 \text{ nmol m}^{-3}$) compared to lower levels in spring (mean = $25.25 \text{ nmol m}^{-3}$). In contrast, aerosol pH exhibited an opposite seasonal trend with less acidic aerosol in summer (mean = -0.04) and more acidic ones in spring (mean = -0.32). Aerosol acidities of $PM_{2.5}$ at Mt. Tai were much higher than those reported for other locations in US, Korea, and Japan, but

reasonably lower than those obtained from Beijing and Shanghai, in central eastern China. Strong acidity showed broad maximum levels during the daytime in both seasons. Aerosol acidity generally showed relatively low concentrations during the day. Several factors influencing aerosol acidities, such as ambient RH, existing state of sulfate, and atmospheric aging of air masses were investigated. Water content in aerosol droplets can enhance the release of free H^+ through the hydrolysis process of HSO_4^- , but also dilute the proton concentrations in the liquid phase. Acidic aerosols were often associated with more processed air masses. Time evolution of sulfate, SOC and aerosol acidity in several events of secondary organic aerosols production was examined. SOC formation with high acidities and high water content possibly suggested that aerosol acidity and aqueous phase reaction may play significant parts in the secondary organic aerosol formation in central eastern China.

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