Seasonal Variation of Ammonia and Ammonium Aerosol at a Background Station in the Yangtze River Delta Region, China

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ABSTRACT

The measurement of atmospheric NH_3 was conducted by mean of passive samplers from September 2009 to December 2010 at Lin'an regional background station located in the economically blooming Yangtze River Delta (YRD) region in eastern China. NH_4^+ in fine particles was also measured in 2010 at this site. The NH_3 concentration ranged from 0.1 to 41.8 ppb, with the annual average of 16.5 ± 11.2 ppb in 2010. The daily NH_4^+ concentrations ranged from 0.02 to 19.2 $\mu g/m^3$, with an annual average of 4.3 ± 3.5 $\mu g/m^3$. NH_3 concentrations were highest in summer and lowest in winter, showing positive correlations with agricultural activities and temperature. The highest concentrations of NH_4^+ were in autumn coinciding with the period of active open burning of agricultural residues. The mean mass ratio of NH_3/NH_x is estimated to be 0.8 ± 0.1 during 2010, indicating that NH_x was mainly influenced by local sources around Lin'an. The air mass back trajectory analysis suggests that both local sources and long-distance transport played important roles in the observed ammonium aerosol at Lin'an. High NH_x deposition in this regional background station suggests the urgency of reducing NH_3 emission in the YRD region.

Keywords: Passive sampling; Atmospheric nitrogen; $PM_{2.5}$; Air mass back trajectory.

INTRODUCTION

Gaseous ammonia (NH_3) is the third most abundant nitrogen containing compounds and is the primary alkaline trace gas in the atmosphere. Ammonia is a very reactive gas and plays a major role in the neutralization of atmospheric sulfuric and nitric acid to form ammonium salts, thereby affecting the acidity of cloud water and aerosols (Asman *et al.*, 1998; Roelle and Aneja, 2002; Krupa, 2003; Heeb *et al.*, 2006; Zhang *et al.*, 2010). The most recent consideration for NH_3 emissions on the global scale is linked to climate change based on its ability to form $PM_{2.5}$, specifically ammonium sulphate and ammonium nitrate. These aerosols can possibly increase the earth's albedo. Particulate ammonium (NH_4^+) has a longer atmospheric lifetime than NH_3, therefore, it can be transported over relatively long distances. Deposition of

NH_3 and NH_4^+ to the Earth's surface can fertilize nitrogen-limited ecosystems, and have detrimental effects such as eutrophication, soil acidification, and biodiversity loss in sensitive ecosystems (Galloway *et al.*, 2003; Ellis *et al.*, 2011). It is necessary to characterize the magnitude and spatiotemporal variability of atmospheric NH_3 and associated ammonium aerosols.

Due to the negative effects on the environment, atmospheric NH_3 and NH_4^+ have been measured at some sites worldwide to check pollution levels and estimate dry deposition fluxes as well as for calibrating deposition models. For example, Walker *et al.* (2004) reported NH_x ($NH_3 + NH_4^+$) concentrations being 7.16, 3.71 and 1.49 $\mu g/m^3$ at sites located in counties with total NH_3 emission densities of 48.0, 22.8 and 3.20 kg NH_3-N/ha/yr, respectively.

With the accelerated process of urbanization in many regions of China, anthropogenic emissions produced by human activities have increased rapidly and are expected to have significant impacts on the environment and regional climate. In previous study, we found that the spatial variability of the NH_3 concentration was large in China, with higher levels in North China, Southwest China and East China

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(Meng *et al.*, 2010). Some studies showed that agricultural sources determined the temporal and spatial NH_3 concentration distribution in some locations (Cao *et al.*, 2009; Ianniello *et al.*, 2010; Shen *et al.*, 2011).

The concentrations of ammonia and ammonium aerosol at atmospheric background sites can better reflect the impacts of human activities and natural processes on the compositions of the atmosphere because such observation results can better represent a "well mixing" status of the air. The Yangtze River Delta (YRD) is located in the eastern part of China, is one of China's most developed and heavy-polluted regions. Most previous studies in YRD focused on the conventional pollutants, such as SO_2, NO_x and PM_{10}, while the knowledge on reduced nitrogen is still limited. In the current study, we present for the first time NH_3 continuous measurement from September 2009 to December 2010 at Lin'an regional background station in YRD, characterizing the seasonal variation of ammonia and ammonium. In addition, we investigate the relative contributions of NH_3 to NH_x deposition and long-range transport on the ammonium aerosol in YRD. We expect the results presented here to provide useful information of the spatial variation of background ammonia and ammonium aerosol in eastern China. These findings illustrate the potential importance of NH_3 emissions to particulate formation in YRD. This will improve our understanding beyond the present limited information and our future acid deposition, air-quality and climate modeling, and health studies.

EXPERIMENT

Measurement Site

Lin'an regional atmospheric background station (30°18'N, 119°04'E, altitude 138.6 m) is located in the southern edge of the Yangtze Delta region in China. The site is one of the World Meteorological Organization Global Atmosphere Watch (WMO/GAW) network stations. It is 11 km north of the Lin'an Township, 53 km west of Hangzhou, and 210 km southwest Shanghai, the latter two are major population centers. The site is surrounded by hills well covered by vegetation and there is no big village within 3 km surrounding area. The site represents the background atmosphere of the economically developed Yangtze River Delta in China. The detail information about the site can be seen in our previous paper (Meng *et al.*, 2010; Qi *et al.*, 2012).

Sampling, Analysis and QA/QC Procedures

Ogawa passive samplers (Ogawa USA, Inc., Pompano Beach, Florida) were used to determine the time-averaged concentrations of NH_3 at Lin'an. The efficacy of passive samplers in measuring atmospheric NH_3 shown in previous studies (Roadman *et al.*, 2003; Cao *et al.*, 2009; Meng *et al.*, 2010) helped in the selection of passive sampling use in this study. The prepared samplers were sealed in individual airtight storage vials in the laboratory and shipped in a cooling box to Lin'an site. The samplers were deployed in the thermometer screen (1.5 m above the ground), which protects the samplers from rain and direct sunshine. To prevent the collection filters from deterioration, measures

were taken to reduce the time in which the collection filters or the loaded samplers were exposed to warmer conditions. All collection filters were sealed and stored in the refrigerator before being loaded into the samplers. Samplers were transported to and from the field in an ice box. Upon retrieval, the exposed samplers were frozen until analysis. At Lin'an, each sampler was exposed about 10 days and a total of 116 samples were collected from September 2009 to December 2010. The field blank was a loaded sampler taken to and from the field with the other samplers but never removed from its air-tight vial. Field blank measurements were made each month at the site. Both the laboratory and field blanks were prepared and processed at the same time and in the same way as the deployed samplers to determine if contamination occurred during the sampler loading, transport, or analysis.

Trace gases were simultaneously determined by a pulsed UV fluorescence analyzer (TEI, model 43TCL) for SO_2 and a chemiluminescence analyzer (TEI, model 42CTL) for NO_2. All instruments were housed in an air-conditioned room. Zero and span checks were done every week to identify for possible analyzer malfunction and zero drifts. The multi-point calibrations were performed at approximately 1-month interval. More details for instrumentation and data process may be found in the papers by Lin *et al.* (2011). The average SO_2 and NO_2 concentrations measured by continuous analyzers were calculated by hourly averaged values during the sampling period.

Daily aerosol $PM_{2.5}$ samples were collected using the MiniVol portable sampler (Airmetrics, Oregon, USA) operating at a flow rate of 5 L/min from January to December 2010 at Lin'an. $PM_{2.5}$ samples were collected on 47 mm Whatman quartz microfiber filters (QM/A), which were pre-combusted at 850°C for 3-h before sampling to remove contaminants. After collection, the loaded filters were placed in clean polystyrene petri dishes and stored in a refrigerator at about 4°C to prevent the evaporation of volatile components. All those filters were weighed with an analytical balance (Sartorius $1/10^5$) after stabilizing under constant temperature $(20 \pm 5°C)$ and humidity $(40 \pm 2\%)$ before and after sampling. The precisions (based on replicate weighing) were less than 5 µg per filter before and after sampling. The filters were reweighed whenever the difference between replicate weighing was out of that range. A total of 223 valid $PM_{2.5}$ samples were collected during 2010 at Lin'an.

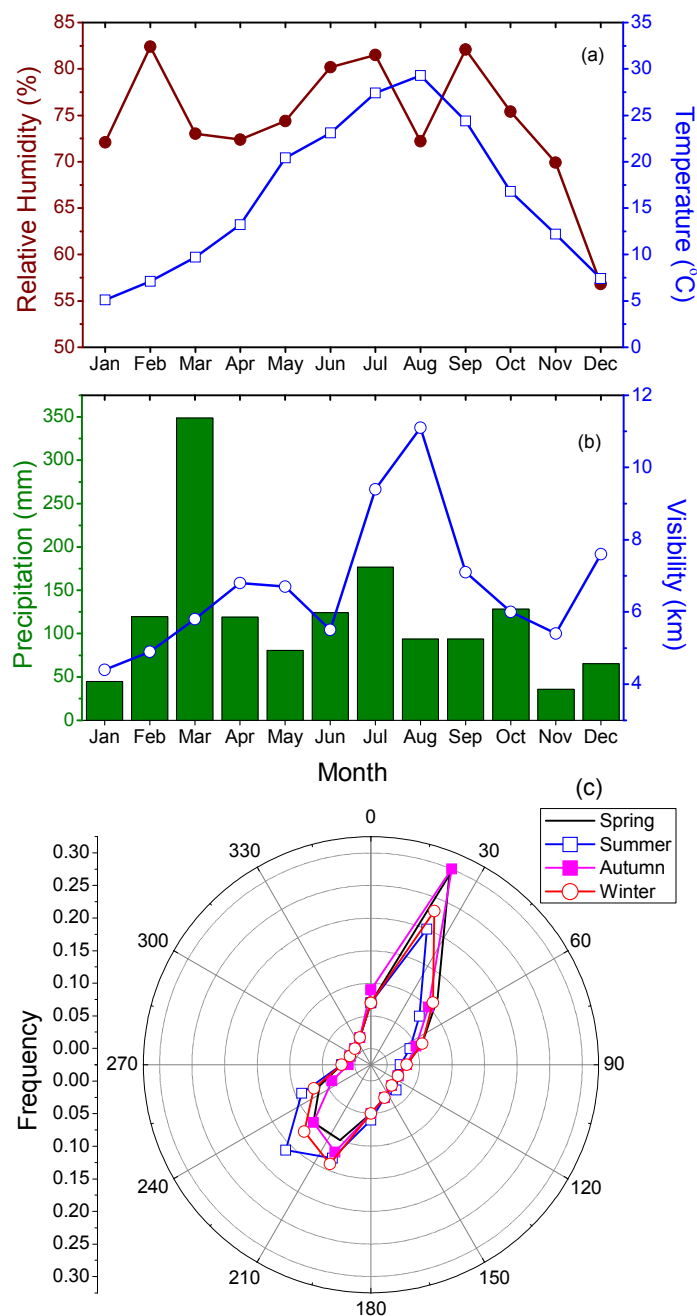In the laboratory, NH_3 samples were analyzed following the manufacturer's protocols (Ogawa, http://www.ogawausa. com). The two filters of sample were analyzed, and the mass transfer coefficient at 25°C is 31.1 cm^3/min. The NH_3 collection filters were put into 25-mL glass vials containing 8 mL ultrapure water for 30 min with occasional shaking. The ammonium extract was analyzed using Dionex ICS-3000 Ion Chromatography (Dionex, USA) with a CG12A 4 mm guard column and a CS12A 4 mm analytical column. The CSRS (cation self-regenerating suppressor) was set at 50 mV. The detector used was a CD conductivity detector. The eluent was methanesulfonic acid (MSA). The concentrations of NH_4^+, NO_3^-, SO_4^{2-} and Cl^- in $PM_{2.5}$ samples (N = 122) were also determined by using Dionex ICS-3000. Standard reference materials produced by the National Research

Center for Certified Reference Materials were analyzed for quality control and assurance purposes. The concentrations of NH_3 and $PM_{2.5}$ were corrected using field blanks.

Meteorology at Lin'an

Meteorological parameters were recorded at Lin'an regional atmospheric background station during the sampling period. Fig. 1 presents the variations of temperature, relative humidity, visibility, precipitation and wind direction rose at Lin'an in 2010. The monthly average highest temperature was recorded as 29.3°C in August and the lowest was 5.1°C in January 2010 (Fig. 1(a)). The annual precipitation was 1413.8 mm in 2010. The rainfall mainly concentrated

in spring (419 mm) and summer (230 mm). Visibility was relatively low during the winter and relatively high in the summer, with a mean value of 5.2 km and 9.1 km, respectively (Fig. 1(b)). The prevailing wind directions were from the northeast and southwest sectors (Fig. 1(c)). The monthly average wind speed was higher in spring (1.9 m/s) and winter (1.8 m/s) and lower in summer and autumn (1.6 and 1.5 m/s), indicating that the long-range transport of aerosols from outside Lin'an is more efficient in spring and winter. This was especially the case during spring dust periods when daily average wind speed reached 4.7 m/s. It has a typical subtropical monsoon climate with distinct four seasons.

Fig. 1. Monthly average relative humidity and temperature (a), precipitation and visibility (b) and wind frequency (c) during measurement period at Lin'an station in 2010.

RESULTS AND DISCUSSION

Concentration Level and Comparison with Other Areas

The statistics of the mean concentrations for the measured species and meteorological parameters from September 2009 to December 2010 are listed in Table 1. The 10-day mean concentration of NH_3 at Lin'an ranged from 0.1 to 41.8 ppb during the sampling period. The average concentration of NH_3 with one standard deviation (SD) was 16.5 ± 11.2 ppb, which was higher than that (10.2 ppb) observed from June 2008 to December 2009 at Shangdianzi (40°39′N, 117°07′E, 293.3 m a.s.l.) regional background station in Northern China reported by Meng *et al.* (2011) (Table 2). The NH_3 level at Lin'an in this study was higher than that (8.2 ppb) in 2007–2008 at Waliguan (36°17′N,100°55′E, 3816.0 m) in Qinghai (Meng *et al.* 2010) and that (14.1 ppb) at Xi'an suburban site (Cao *et al.*, 2009). The NH_3 level at Lin'an was lower than that (20.1 ppb) observed at Dongbeiwang site in Northern China. It is noted that Dongbeiwang is a suburban site in the northwest suburb of Beijing, which had higher NH_3 emission intensity of 55.4 kg N/ha/yr in 2008 (Shen *et al.*, 2011).

The values at Lin'an during 2009–2010 were much higher than that (4 ppb) during 1999–2000 reported by Carmichael *et al.* (2003) (Table 2). Such differences may indicate an increase of NH_3 levels in YRD. According to the inventory study by Dong *et al.* (2010), the national total atmospheric ammonia emissions were estimated to be 11.06 million tons (Mt) in 1994 and quickly increased to 16.07 Mt in 2006. This increase should have enhanced the NH_3 levels in many regions of China. In this study, the NH_3 levels at Lin'an were higher than those observed in 2007–

2008 (Meng *et al.*, 2010). The possible reasons for the difference in NH_3 levels between the two studies are both changes in emissions and sampling frequency. As one of the fastest developing regions in China, the emission of air pollutants has changes significantly in the past decade. For the YRD region in 2010, the emission of NH_3 was estimated as 1439 kt (Fu *et al.*, 2013). Zhejiang province had also undergone rapid economic development, with energy consumption increasing by 34% during the period 2008 to 2010 (Zhejiang Statistical Yearbook, 2011). It can thus be expected that anthropogenic emissions should have increased between the study periods. Another possibility is that the sampler was exposed about 10 days and three times per month at Lin'an during 2009–2010. However, the samples were collected about 10 days and once a month in previous study. In addition, the more strict QA/QC procedures were adopted in this study.

The relatively high concentrations of NH_3 observed at Lin'an in this study resulted from ongoing agricultural activity, including fertilizer use, vegetation and livestock as well as industrial processes in the region surrounding this site. Fu *et al.* (2013) reported that the fertilizer application and livestock are the largest emission sources for NH_3 in YRD. The NH_3 emission factors for fertilizer application were estimated based on fertilizer types and their application rate, while NH_3 emissions of livestock included cattle, pigs, horses, and chickens. Livestock and fertilizer application were estimated to contribute over 90% of NH_3 emissions in the YRD region in 2010.

Dong *et al.* (2010) used emission factor to estimate the atmospheric ammonia emissions, and analyzed its geographical distributions in China. They found that emissions

Table 1. Summary statistics of average concentration of measured species and meteorological parameters during measurement period at Lin'an station.

Species	Mean	Standard Deviation	Minimum	Maximum
NH_3 (ppb)	16.5	11.2	0.1	41.8
SO_2 (ppb)	6.4	4.2	0.9	16.8
NO_2 (ppb)	10.8	5.2	3.6	20.5
$PM_{2.5}$ ($\mu g/m^3$)	58.2	50.8	1.4	442
NH_4^+ ($\mu g/m^3$)	4.3	3.5	0.02	19.2
SO_4^{2-} ($\mu g/m^3$)	9.6	6.1	0.5	31.7
NO_3^- ($\mu g/m^3$)	7.6	7.5	0.3	50.1
Cl^- ($\mu g/m^3$)	2.1	2.2	0.04	12.7
T (°C)	18.1	8.3	–1.4	33.6
RH (%)	75	16	4	99
WS (m/s)	2.0	1.2	0.0	12.9

Table 2. Comparison of NH_3 concentrations in Lin'an with previous measurements.

Location	Type	Period	Concentration (ppb)	Reference
Lin'an, China	Regional background	2009.09–2010.12	18.2 ± 14.2	This study
Lin'an, China	Regional background	2007.01–2008.12	8.5 ± 8.3	Meng *et al.* (2010)
Shangdianzi, China	Regional background	2009.09–2010.07	10.2 ± 10.8	Meng *et al.* (2011)
Dongbeiwang, China	Rural	2006.08–2009.09	20.1 ± 10.5	Shen *et al.* (2011)
Waliguan, China	Regional background	2007.01–2008.12	8.2 ± 5.8	Meng *et al.* (2010)
Xi'an, China	Suburban	2006.04–2007.04	14.1 ± 11.1	Cao *et al.* (2009)
Lin'an, China	Regional background	1999.09–2000.05	4	Carmical *et al.* (2003)

from provinces including Henan, Shandong, Hebei, Sichuan and Jiangsu accounted for 40.8 percent of national emissions. The monitoring results showed that NH_3 concentrations were higher in agricultural and urban regions with large population density. For example, the annual mean concentrations of NH_3 and NH_4^+ in PM_{10} at four agricultural sites in the North China Plain were 15.6 and 12.4 $\mu g/m^3$ (Shen *et al.*, 2011). Cao *et al.* (2009) and Meng *et al.* (2011) reported the higher NH_3 concentrations (18.6 and 22.8 ppb) at urban sites in Xi'an and Beijing, respectively. The regional background NH_3 concentration in Yangtze River Delta in eastern China was higher than that observed at Shangdianzi regional background station in northern China, but was lower than that observed at Longfengshan regional background station in northeast China (Meng *et al.*, 2010).

The mean concentrations of SO_2 and NO_2 were 6.4 ± 4.2 and 10.8 ± 5.2 ppb, respectively, during the sampling period (Table 1). It is not surprising to see that the observed concentrations of SO_2 and NO_2, especially SO_2 at Lin'an during 2009-2010 were lower than those in 2007-2008 (Meng *et al.*, 2010). The significantly lower concentrations of SO_2 may be attributable to the implementation of stricter emission control measures by the government. The daily concentrations of $PM_{2.5}$ at Lin'an were in the range of 1.4–442 $\mu g/m^3$, with a mean and SD of $58.2 \pm 50.8 \mu g/m^3$. For the YRD region in 2010, the total emissions of SO_2, NO_x and $PM_{2.5}$ were estimated as 2147 kt, 2776 kt, and 643 kt, respectively, while emissions of SO_2 have declined 49% from 2005 to 2010 (Fu *et al.*, 2013).

The daily NH_4^+ concentrations ranged from 0.02 to 19.2 $\mu g/m^3$, and the average concentration within one standard deviation was $4.3 \pm 3.5 \mu g/m^3$ during 2010 (Table 1). This result was lower than that of 6.4 $\mu g/m^3$ obtained at Shangdianzi station from June 2008 to December 2009 (Table 3). The average concentrations of SO_4^{2-}, NO_3^- and Cl^- in $PM_{2.5}$ at the Lin'an site during 2010 were 9.6 ± 6.1, 7.6 ± 7.5 and $2.1 \pm 2.2 \mu g/m^3$, respectively. SO_4^{2-} and NO_3^- concentrations were lower than those in Shangdianzi (12.3 and 11.6 $\mu g/m^3$ for SO_4^{2-} and NO_3^-, respectively); meanwhile the concentrations of Cl^- was higher than that in Shangdianzi (1.3 $\mu g/m^3$ for Cl^-) during the period from June 2008 to December 2009 (Meng *et al.*, 2011). Air masses with maritime origin were primarily responsible for the rise of Cl^- in $PM_{2.5}$.
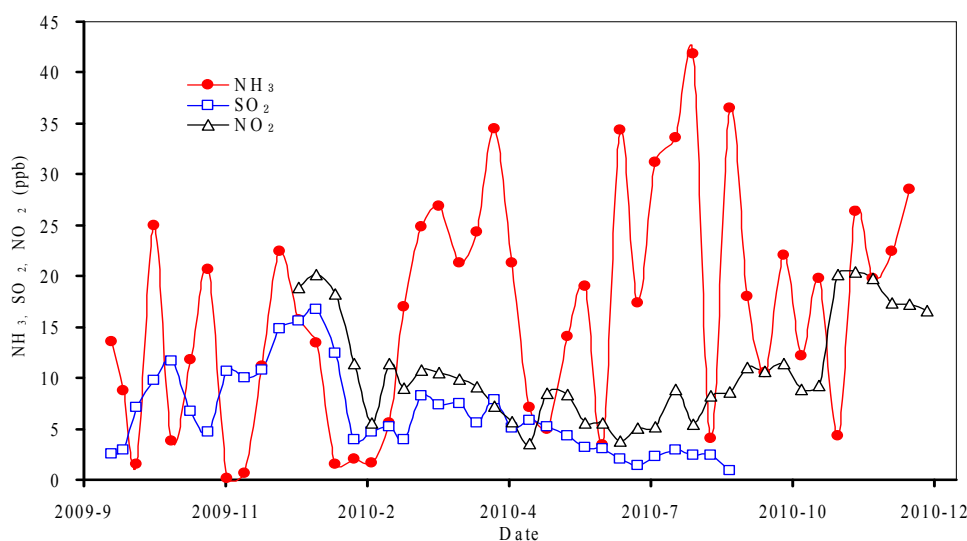
Ambient Ammonia

Fig. 2 shows the temporal variation of NH_3 at Lin'an from September 2009 to December 2010. NH_3 increased gradually from March and reached the highest values in July, and then decreased. The peak NH_3 value was 41.8 ppb on 11–21 August 2010 and the lowest concentrations of NH_3 (0.1 ppb) appeared during 21 November to 1 December 2009. NH_3 levels were higher in spring as the temperature increased suddenly causing the release of NH_3 from natural and fertilized soils and vegetation, most of which was accumulated in winter from human sources produced NH_3. The monthly temperatures were 23.5°C, 27.5°C and 29.3°C in June, July and August, respectively, with the low temperatures in January and February 2010 at Lin'an (Fig. 1(a)). The maximum value of NH_3 was consistent with the highest ambient temperature in August. As there were several heavy rainfall events during the summer, rainfall scavenging may have caused lower NH_3 values (3.4 and 4.0 ppb) during 21 June–1 July and 21–31 August 2010. The minimum monthly value appeared in February 2010. Nitrogen fertilizer applications had a major impact on atmospheric NH_3 concentrations. NH_3 concentrations increased sharply after N fertilizer application for a rice field in June at Lin'an. This is most probably due to NH_3 volatilization from urea, the most common N fertilizer in China.
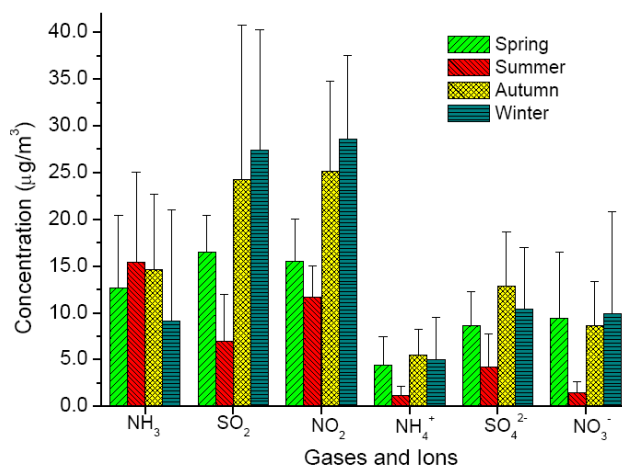
The seasonal variations of ammonia concentrations depended on its source and meteorological conditions. Fig. 3 shows the seasonal mean concentrations of NH_3, other trace gases and ionic species in $PM_{2.5}$ at the site during the measurement period. Error bars mean the standard deviations. NH_3 exhibited a distinct and significant seasonal variation with highest concentrations in summer and lowest in winter. Seasonal average concentrations of NH_3 at Lin'an were 12.7 ± 7.7, 15.4 ± 9.6, 14.6 ± 8.1 and $9.1 \pm 11.9 \mu g/m^3$ in spring, summer, autumn and winter, respectively. Higher concentrations in summer may reflect both the influence of fertilizer application to surrounding farmland and higher volatility of NH_3 during warm season. This seasonal cycle in ambient concentrations is in agreement with the temperature dependence of aqueous-phase partitioning between NH_3 and NH_4^+, as well as the equilibrium between aqueous- and gas-phase NH_3 as predicted by Henry's law, which results in increased ammonia emissions from fertilizers, animal manure, soils, and vegetation with increasing temperature

Table 3. Concentrations of NH_4^+, SO_4^{2-} and NO_3^- in $PM_{2.5}$ at Lin'an station and a city site in same region and a background station in Northern China.

Location	Period	Ion	Concentration ($\mu g/m^3$)				Reference
			Spring	Summer	Autumn	Winter	
Lin'an	2010	NH_4^+	4.4	1.2	5.5	5.0	This Study
		SO_4^{2-}	8.6	4.2	12.9	10.4	
		NO_3^-	9.4	1.5	8.6	9.9	
Shangdianzi	2008.06–2009.12	NH_4^+	7.4	9.0	5.8	4.7	Meng *et al.* (2011)
		SO_4^{2-}	15.8	22.7	10.2	8.9	
		NO_3^-	13.2	11.2	10.3	9.6	
Shanghai	2003.09–2005.01	NH_4^+	4.1	2.4	3.6	4.4	Wang *et al.* (2006)
		SO_4^{2-}	11.7	5.4	8.7	12.8	
		NO_3^-	9.1	2.6	3.7	8.5	

Fig. 2. Temporal variations of the 10-day average NH_3, SO_2 and NO_2 concentration at Lin'an from September 2009 to December 2010.

Fig. 3. Seasonal variations of NH_3, other trace gases and ionic species in $PM_{2.5}$ at Lin'an station during the measurement period. Error bars mean the standard deviations.

(Asman *et al.*, 1998).

The season cycles of SO_2 and NO_2 were different from those of NH_3. At Lin'an site, the concentration of SO_2 in winter (10.5 ppb) was 4 times higher than that in summer (2.7 ppb). The lowest concentrations of NO_2 appeared in summer and the highest levels of NO_2 were observed in winter. This indicates a different source of NH_3 from those of SO_2 and NO_2. In cold season, SO_2 and NO_2 accumulated due to high emissions from heating, weak photochemical conversion and atmospheric mixing; and in warm and rainy seasons, SO_2 and NO_2 were easily removed by rapid photochemical conversion, precipitation scavenging, and fast atmospheric diffusion.

Ambient Ammonium Aerosol

As shown in Fig. 4, strong temporal variations in $PM_{2.5}$ mass concentrations were observed at Lin'an. The several severe high $PM_{2.5}$ episodes occurred in spring due to the intrusion of dust from the northwest of China. For example,

the highest value of daily average $PM_{2.5}$ mass (442 μg/m³) occurred when a super dust storm attacked Lin'an on 20 March 2010. This was verified by the backward trajectory (see last section), in which the air mass came from the northwest of China. The dust events also caused the high mass concentrations (319 μg/m³) of $PM_{2.5}$ coupled with the high Ca^{2+} ions (9.5 μg/m³), an indicator of soil/dust on 21 March 2010. Therefore, it must be noted that the air pollution in Lin'an might be under the influence of local emissions as well as long range transport from outside areas. It is evident from Fig. 4 that the negative correlation existed between $PM_{2.5}$ and visibility. The minimum daily value of $PM_{2.5}$ (1.4 μg/m³) occurred on 9 July, while the highest daily visibility (17.2 km) observed on this day. A fog episode was monitored on 21 May 2010, when the daily $PM_{2.5}$ concentration was 313 μg/m³ and the daily visibility was 1.9 km. A discussion of the impacts of $PM_{2.5}$ and water-soluble ions on visibility is given in next section.

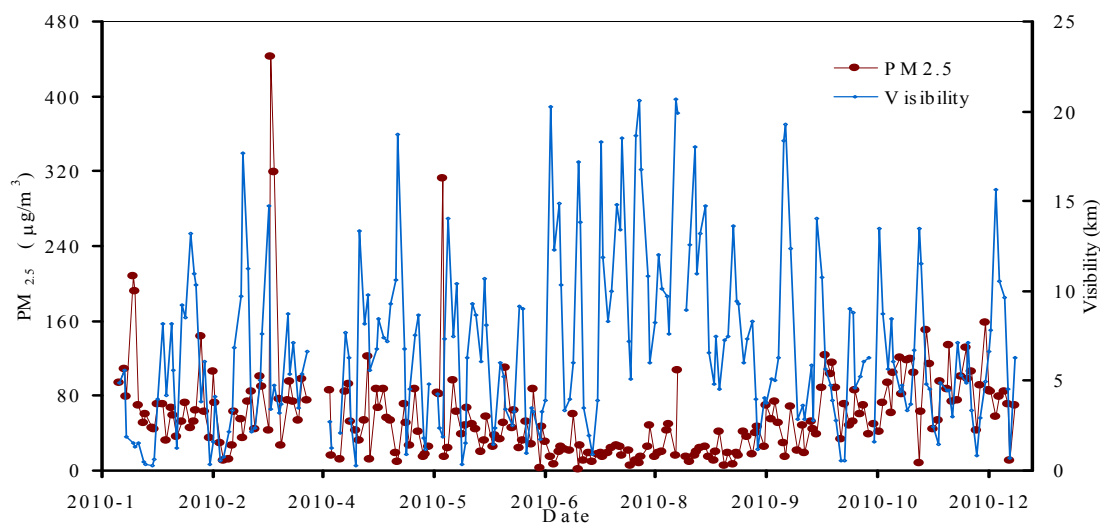The concentrations of $PM_{2.5}$ appeared good correlated with

Fig. 4. Temporal variations of the daily $PM_{2.5}$ concentration and visibility at Lin'an in 2010.

SO_2 and NO_2 (R = 0.96 for SO_2 and 0.74 for NO_2), which might be due to the fact that SO_2 and NO_2 contributed to the formation of $PM_{2.5}$.

The annual average concentration of total water-soluble ion in $PM_{2.5}$ was 28.5 ± 17.7 μg/m³, accounting for 47% of $PM_{2.5}$ mass concentration. Especially, the secondary aerosol components SO_4^{2-}, NO_3^- and NH_4^+ shared the largest part of the total water-soluble ions (69%). During sampling period in 2010, the highest daily concentration of NH_4^+ (19.2 μg/m³) occurred on 29 January and the lowest value (0.02 μg/m³) on 5 March at Lin'an.

NH_4^+ is formed from its gaseous precursor NH_3 through gas phase and aqueous-phase reactions with acidic species. Among the reaction products, $(NH_4)_2SO_4$ is preferentially formed and the least volatile; NH_4NO_3 is relatively volatile and NH_4Cl is the most volatile. Volatility increases with increasing air temperature and decreasing humidity (Zhang *et al.*, 2008). As shown in Fig. 3, the average concentrations of NH_4^+ were 4.4, 1.2, 5.5 and 5.0 μg/m³ in spring, summer, autumn and winter, respectively. It was noted above NH_4^+ concentration was highest in autumn. SO_4^{2-} emission comes mainly from industrial combustion and industrial process, and SO_4^{2-} concentration was also expected to be higher in autumn due to the preference of the formation of $(NH_4)_2SO_4$. Thus, the seasonal cycles of SO_4^{2-} concentrations should be similar to NH_4^+ at Lin'an. This can be seen from Fig. 3, the average concentrations of SO_4^{2-} in spring, summer, autumn and winter were 8.6, 4.2, 12.9 and 10.4 μg/m³, respectively. The results showed clearly that the concentrations of the secondary ions such as NH_4^+ and SO_4^{2-} were higher in autumn and winter and lower in summer. The highest concentrations of NH_4^+ and SO_4^{2-} in autumn were coincided with the period of the active open burning of agricultural residues after the harvest of summer rice. This result also differs from that at Shangdianzi (Table 3), which indicated that the NH_4^+ and SO_4^{2-} concentrations in $PM_{2.5}$ were relatively low in autumn and winter and were relatively high in summer and spring during the measurement period from June 2008 to December 2009. As the tracer of biomass burning, the highest concentration (1.6 ± 0.7 μg/m³) of K^+ was found in autumn, which could be due to the biomass burning activities in autumn around Lin'an. Previous measurement at Lin'an has shown impacts from biomass burning in autumn (Wang *et al.*, 2002). Our observation suggested that biomass/biofuel burning could be a major source of the observed NH_4^+ and possibly of other trace gases and water-soluble inorganic ions as well in autumn.

The average concentrations of NO_2 were 28.6 and 11.7 ppb in winter and summer, respectively. NO_3^- is largely formed from the oxidation of NO_x and NH_4NO_3 is the main form of the fine fraction of NO_3^- in $PM_{2.5}$. The average concentrations of NO_3^- in spring, summer, autumn and winter were 9.4, 1.5, 8.6 and 9.9 μg/m³, respectively. The lower temperature in winter favors the existence of NH_4NO_3 while the higher temperature in summer favors the evaporation of NH_4NO_3 into nitric acid gas. This theory partially explains the high concentration of NO_3^- in winter. The NO_3^- concentrations at Lin'an were significantly lower in summer than in other seasons. This was different from that observed in Shangdianzi where the concentrations of NO_3^- were higher in spring and summer. The concentrations of the secondary aerosol had a good agreement with Shanghai located in Yangtze River Delta (Table 3). At Lin'an, the concentrations of these secondary ions were lowest in summer might attribute to the relatively clean marine air mass from southeast or southwest.

Relationship between Ammonia and Ammonium Aerosol

In the present study, the ratios of gaseous NH_3 to particulate NH_4^+ (NH_3/NH_4^+) were more than 1, with the highest NH_3/NH_4^+ ratio in summer, implying that abundant NH_3 gas existed in the atmosphere in summer. The lowest NH_3/NH_4^+ ratio appeared in winter 2010.

The ratio of NH_3 to NH_x (NH_3+ NH_4^+) have been used to identify the source of NH_x and the relative contribution of NH_3 and NH_4^+ to NH_x deposition (Walker *et al.*, 2004). When the value is higher than 0.5, it signifies that NH_x is mainly from local NH_3 sources and the dry deposition of

NH_3 dominate the NH_x deposition. The mean ratio of NH_3/NH_x was 0.8 ± 0.1 in 2010, suggesting that NH_x was mainly influenced by local sources around Lin'an. It can also be inferred that NH_3 dry deposition would dominate NH_x deposition at this location. NH_4^+ presented in this system was contributed by long-range transport and local formation as discussed below in next section.

With respect to the percentage of the total mass, on average, SO_4^{2-} was the most important species on average in $PM_{2.5}$ at Lin'an. Nitrate contributes more significantly to the total mass during colder months when SO_2 oxidation rates were reduced in response to lower concentrations of oxidants such as OH. The average molar ratios of NH_4^+ to SO_4^{2-}, NH_4^+ to NO_3^- and NH_4^+ to Cl^- were 2.3, 2.1 and 3.8, respectively.

There were significant positive correlations between NH_4^+ and SO_4^{2-} as well as NH_4^+ and NO_3^- at Lin'an. The correlation coefficients (R) of NH_4^+ versus SO_4^{2-}, NO_3^- and Cl^- were 0.91, 0.84 and 0.33, respectively, all at a very significant level ($P < 0.001$). This indicates that particulate NH_4^+ was probably mainly associated with particulate SO_4^{2-} and NO_3^-, likely to be as $(NH_4)_2SO_4$ and/or NH_4HSO_4, NH_4NO_3 at Lin'an.

The relationships of observed NH_4^+ molar concentrations vs. the sum of $2SO_4^{2-}$ and NO_3^- concentrations in 2010 are shown in Fig. 5. In $PM_{2.5}$, a ratio of the equivalents of ammonium to the sum of sulfate plus nitrate that is more than one indicates a fully neutralization of acidic aerosols. The mean molar ratios were 0.82, 0.53, 0.78 and 0.80 in spring, summer, autumn and winter, respectively, indicating the partial neutralization of acidic aerosols at Lin'an. The result agrees with previous study at same site (Wang *et al.*, 2003), which indicates that abundant NH_3 is present to neutralize H_2SO_4 in spring at Lin'an. The excess of NH_4^+ was inferred to be associated with NO_3^- and Cl^-. The ambient levels of ammonium ions were sufficiently high to fully neutralize the sulfates and nitrates, indicating that large

amounts of ammonia were resulting from the agricultural practices of the region in spring.

Fine nitrates were strongly correlated with sulfate in spring (R = 0.82) and winter (R = 0.90), but a weak correlation in summer (R = 0.45) and autumn (R = 0.57). The large nitrate/sulfate ratios (mean mass ratio = 0.90) in spring and winter suggested that the reaction $NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s)$ or (aq) favored the presence of solid-phase ammonium nitrates.

Visibility is an important index for assessment of background environmental air quality. Fig. 6 presents the power curve fitting of visibility with $PM_{2.5}$, NH_4^+, SO_4^{2-} and NO_3^-. The correlation coefficients (R^2) between visibility and $PM_{2.5}$, NH_4^+, SO_4^{2-} and NO_3^- were 0.56, 0.85, 0.68 and 0.44, respectively. NH_4^+ and visibility were found to be inversely correlated at a very significant level ($P < 0.0001$). The relationships between visibility and $PM_{2.5}$, SO_4^{2-} and NO_3^- could be best fit using a power curve function, suggesting that the impacts of $PM_{2.5}$, NH_4^+, SO_4^{2-} and NO_3^- in $PM_{2.5}$ on visibility were relatively large.

Influence of Air Mass on the Levels of Ammonium Aerosol

The different air mass origins could influence the levels of the fine particles because the different air masses traveling through the different regions may bring aerosols with different chemical components (Wang *et al.*, 2005). To gain an insight into the impact of transport on ammonium aerosol at Lin'an, air mass backward trajectories were calculated and analyzed in combination with corresponding pollutants concentrations using the HYSPLIT4 model (Meng *et al.*, 2012). As can be seen in Fig. 7, the trajectories in Clusters 2 come from the local areas over Lin'an, and it was the most important cluster to the Lin'an site, contributing 34% of air masses. Based on the statistics, the number of trajectories in Cluster 1, 2, 3 and 5 accounts to 74% of the all trajectories. As more than 74% air masses originated
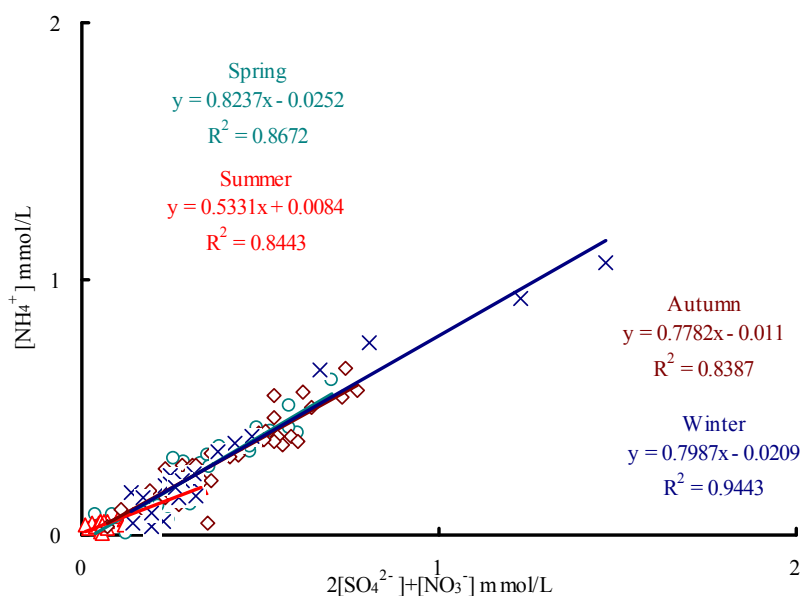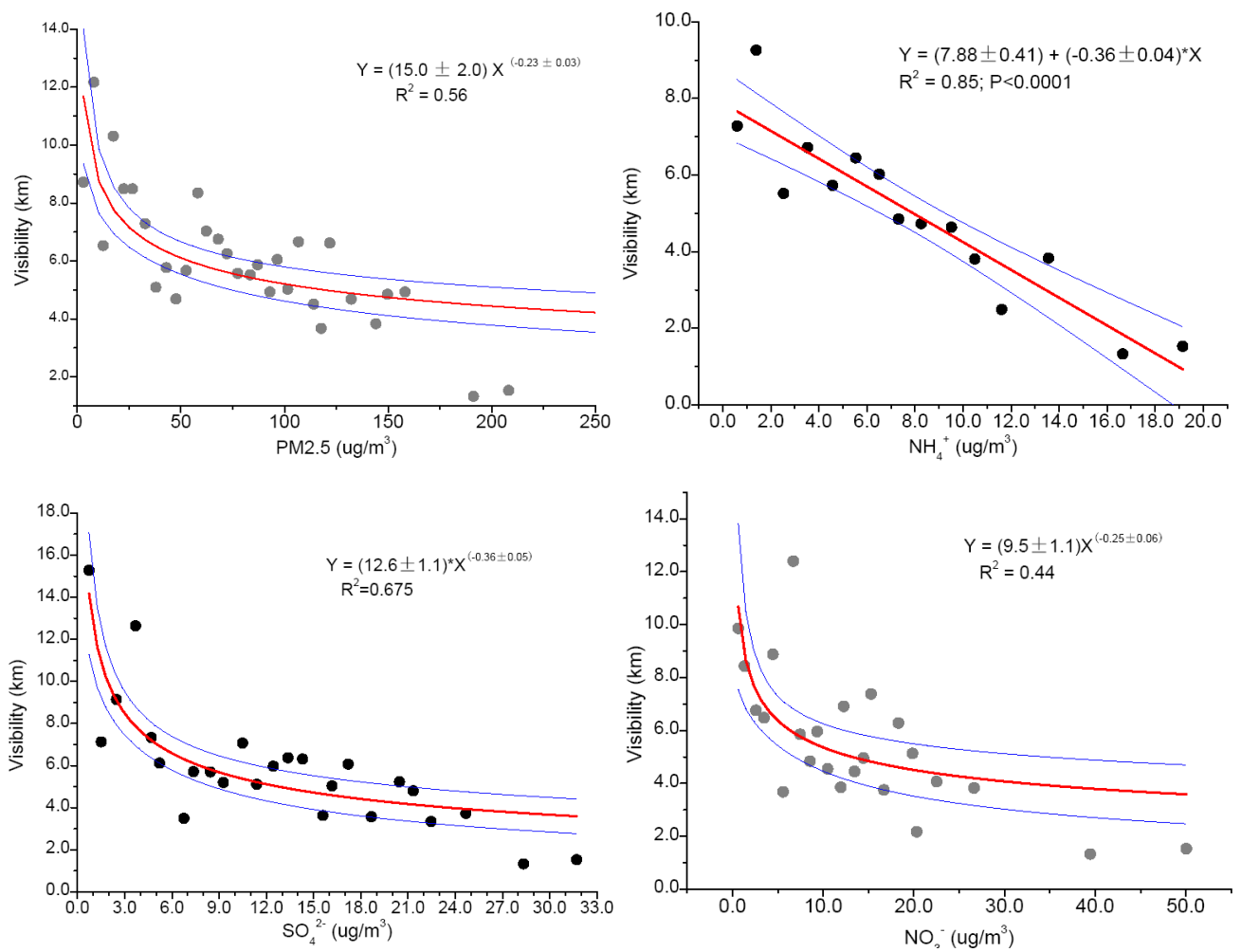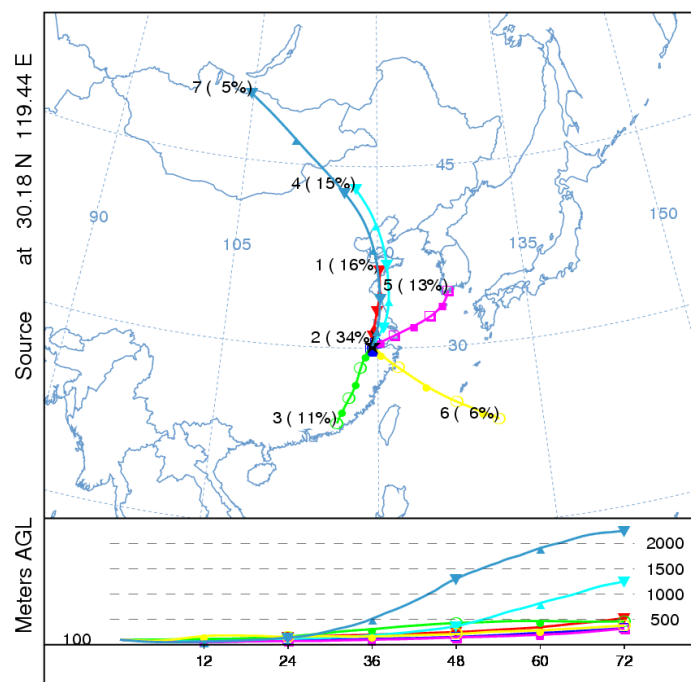

Fig. 5. Relationship of observed NH_4^+ molar concentrations vs. sum of $2SO_4^{2-}$ and NO_3^- concentrations in 2010.

Fig. 6. The curve fitting of visibility with $PM_{2.5}$, NH_4^+, SO_4^{2-} and NO_3^- at Lin'an in 2010.

Fig. 7. 72-h backward trajectories for 100 m above ground level at Lin'an in 2010.

Table 4. Occurrence frequency and mean values of NH_4^+, SO_4^{2-} and NO_3^- in $PM_{2.5}$ for each type of air masses arriving at Lin'an during sampling period in 2010.

Air mass	Spring	Summer	Autumn	Winter	Ratio (%)	NH_4^+	SO_4^{2-}	NO_3^-
Cluster 1	70	31	75	57	16	5.5	11.9	9.9
Cluster 2	131	114	107	134	34	5.9	12.6	10.0
Cluster 3	17	113	4	22	11	2.8	5.5	4.9
Cluster 4	70		60	85	15	4.1	8.6	7.0
Cluster 5	59	56	59	18	13	3.1	10.0	5.6
Cluster 6	15	50	26	1	6	0.9	2.5	2.0
Cluster 7	2		29	39	5	3.0	7.9	6.6

from or passing over the Yangtze River Delta region can influence the surface measurements at Lin'an station, the observation results at Linan station can well represent the background changes of atmospheric components in the Yangtze River Delta region. The Cluster 4 and 7 represent air parcels mainly from the northwest, while Cluster 6 represents air mass originating from the sea.

In order to know the seasonal variations of air trajectories, the occurrence frequencies of each type of air masses arriving at Lin'an in different seasons were calculated and shown in Table 4. Based on this table, trajectories in cluster 1, 2 and 5 can occur in any season, trajectories in clusters 3 and 6 occur mainly in warmer season, and trajectories in cluster 4 and 7 occur mainly in colder season.

Since the emission sources of pollutants are unevenly distributed in the areas surrounding the Lin'an site, air masses from different directions containing different levels of pollutants. The corresponding mean concentrations of NH_4^+, SO_4^{2-} and NO_3^- in $PM_{2.5}$ in different clusters of backward trajectories are also included in Table 4 in order to characterize the dependences of the pollutants concentrations on air masses.

Large differences in the concentrations of NH_4^+, SO_4^{2-} and NO_3^- existed among the different clusters, with cluster 2 corresponding to the highest NH_4^+, SO_4^{2-} and NO_3^- levels (5.9, 12.6 and 10.0 μg/m³, respectively), and cluster 1 corresponding to the second highest NH_4^+, SO_4^{2-} and NO_3^- levels (5.5, 11.9 and 9.9 μg/m³, respectively). The cluster 4 had the third highest concentration of ammonium and nitrate levels and higher sulfate levels, with cluster 7 corresponding to the higher concentrations of nitrate, ammonium and sulfate. Local and regional sources as well as long-distance transport played important roles in the observed ammonium aerosol in Lin'an station. The SO_4^{2-} concentration was greatly impacted by SO_2 produced by industrial emissions and fossil fuels burning. With the northern air southward, long-distance transport of high concentrations sulfate led to increase the SO_4^{2-} concentration in Lin'an area in cold season. NO_3^- in the atmosphere was mainly from the chemical conversion process and NO_x emissions were primarily from motor vehicle exhausting and coal burning. In recent years, with the rapid growth of the motor vehicles in Yangtze River Delta region, there was an increasing trend in the emissions of NO_x year by year. Air mass from Shanghai, Hangzhou and surrounding cities were primarily responsible for the rise of nitrates and other water-soluble ions in $PM_{2.5}$.

Based on Table 4, more samples prevailed in the SW and SE sectors in the summer, which was expected to bring cleaner air masses into surface. This explains the lowest NH_4^+, SO_4^{2-} and NO_3^- levels corresponding to clusters 3 and 6.

CONCLUSIONS

Continuous measurements of atmospheric ammonia and ammonium aerosol were conducted from September 2009 to December 2010 at Lin'an regional station in the Yangtze Delta region in China. The average concentrations of NH_3 and NH_4^+ were 16.5 ± 11.2 ppb and 4.3 ± 3.5 μg/m³, respectively. NH_3 concentrations were the highest in summer and the lowest in winter at Lin'an, while the highest NH_4^+ concentrations occurred in autumn. Agricultural activities, biomass burning, air temperature and gas-to-particle conversion reactions have important influences on this seasonality. At Lin'an site, NH_x is strongly influenced by local NH_3 sources and dry deposition of NH_3. The secondary inorganic particle pollution at Lin'an is a reflection of the high emission intensities of NH_3, NO_x and SO_2 in this region. High NH_3/NH_x ratios and the dependence of secondary inorganic $PM_{2.5}$ concentrations on NH_3 concentrations suggest that controlling NH_3 emission from agricultural, biomass burning and livestock sources could be an efficient way to reduce secondary inorganic particle pollution in the Yangtze Delta region in China, besides the reduction of SO_2 and NO_x emissions from industry, power plants and transport. The high NH_3/NH_x ratio and air mass back trajectory analysis suggest that the higher ammonia and ammonium aerosol levels observed at Lin'an were due to a combination of regional-scale primary emissions in the Yangtze River Delta region and long-range transport of NH_x from northeastern of China.

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