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Characterization of Atmospheric Ammonia over Xi'an, China

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Abstract

Continuous measurements of atmospheric ammonia (NH_3) between April 2006 and April 2007 were conducted at an urban site and a suburban site in Xi'an, northwest China. NH_3 was collected using Ogawa passive samplers every sixth day. At the same time, NH_4^+ in fine particles was collected using battery-powered mini-volume samplers. The annual average concentrations of NH_3 were 12.9 μg/m^3 and 14.1 μg/m^3, at the urban and suburban sites, respectively. The NH_3 concentrations reached a maximum (~22.8-35.3 μg/m^3) in June and July and were minimum (~3.0-4.7 μg/m^3) in December, which was closely linked with NH_3 volatilization under different ambient temperatures. The seasonal variation in NH_3 was summer > spring > autumn > winter at both sites, which may be ascribed to the impact of biological emission sources such as agricultural activity. NH_3 and NH_4^+ aerosol concentrations were weakly correlated, implying that gas-particle reactions are influenced by many factors such as sources, meteorology and removal. Average NH_3/NH_4^+ ratios varied from 0.1 to 25.3, with an annual average of 4.0. High NH_3 concentrations at Xi'an had a significant influence on atmospheric acidity and the formation of secondary NH_4^+ aerosol.

Keywords: NH_3; NH_4^+; Aerosol, Agricultural activity.

INTRODUCTION

Atmospheric ammonia (NH_3) is an air pollutant of increasing interest, and along with sulfur dioxide (SO_2) and nitrogen oxides (NO_x), is one of three main primary pollutants leading to acidic deposition. In the past, much more attentions has been paid to SO_2 and NO_x, than to NH_3. However, with decreasing SO_2 emissions throughout Europe, and an increased appreciation of the role of NH_3 and NO_x in causing eutrophication of ecosystems, scientific attention on NH_3 has grown (Sutton *et al.*, 1998). As the dominant basic atmospheric species, NH_3 can react with acidic

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species to form ammonium sulfate, ammonium nitrate, or ammonium chloride, or may be deposited on the Earth's surface (Aneja *et al.*, 2000). Due to these neutralization reactions which involve rapid gas-to-particle conversion (Lemmetty *et al.*, 2007), NH_3 has recently come under scrutiny with respect to fine particulate matter ($PM_{2.5}$) regulations, impacting human health, visibility, and climate change (Barthelmie and Pryor, 1998). The high NH_3 concentration in Asia reflects increasing NH_3 emissions from agricultural activities (including fertilizer use), livestock and the use of biofuels (such as animal dung) as domestic fuel (Carmichael *et al.*, 2003). Ammonia is highly soluble in water and its major sink in the atmosphere is via wet deposition. The residence time of NH_3 in the lower level of the atmosphere is a few hours, although in a calm environment it may exist for one week (Kapoor *et al.*, 1992). In addition, due to its high reactivity, NH_3 exhibits a relatively short atmospheric lifetime, so its ambient concentration is greatly influenced by local sources.

Thus, it has become clear that NH_3 is an important gas in relation to different environmental issues. Sufficient data on NH_3 concentrations have been reported from various remote, rural, urban and suburban sites in the world (Galloway *et al.*, 1987; Khemani *et al.*, 1987; Kulshrestha *et al.*, 1996; Lenhard and Gravenhorst, 1980; Likens *et al.*, 1987; Possanzini *et al.*, 1988; Tuncel and Ungor, 1996; Chou and Wang, 2007). However, to date the concentrations and temporal variation of NH_3 in China are currently unknown. Xi'an is located on the Guanzhong Plain, one of the national food producing areas of China, at the south edge of the Loess Plateau 400 m above sea level at 33°29'-34°44' N, 107°40'-109°49' E. Xi'an is also the largest city in northwestern China with a population of about seven million, which is a typical urban environment in north China. In this work, a one-year NH_3 monitoring program between April 2006 and April 2007 was performed at two monitoring stations in order to better understand the atmospheric concentration of ammonia, its temporal variation and possible sources.

EXPERIMENT

Sampling Sites

Two sites were selected for study. The field descriptions are as follows and the location of the sites are shown in Fig. 1.

Institute of Earth Environment site: This monitoring site was located in an urban-scale zone surrounded by a residential area ~15 km south of downtown Xi'an. It was situated on the rooftop of the Institute of Earth Environment, Chinese Academy of Sciences building, 10 m above ground level, and represented the urban monitoring site.

Emperor Qin's Terra-Cotta Museum site: This monitoring site was located on the third floor roof (~10 m above ground level) of the Emperor Qin's Terra-Cotta Museum in Lintong district, which is about 40 km southeast of downtown Xi'an. It is considered a suburban microenvironment. Fields around the site are covered with a variety of fruit trees

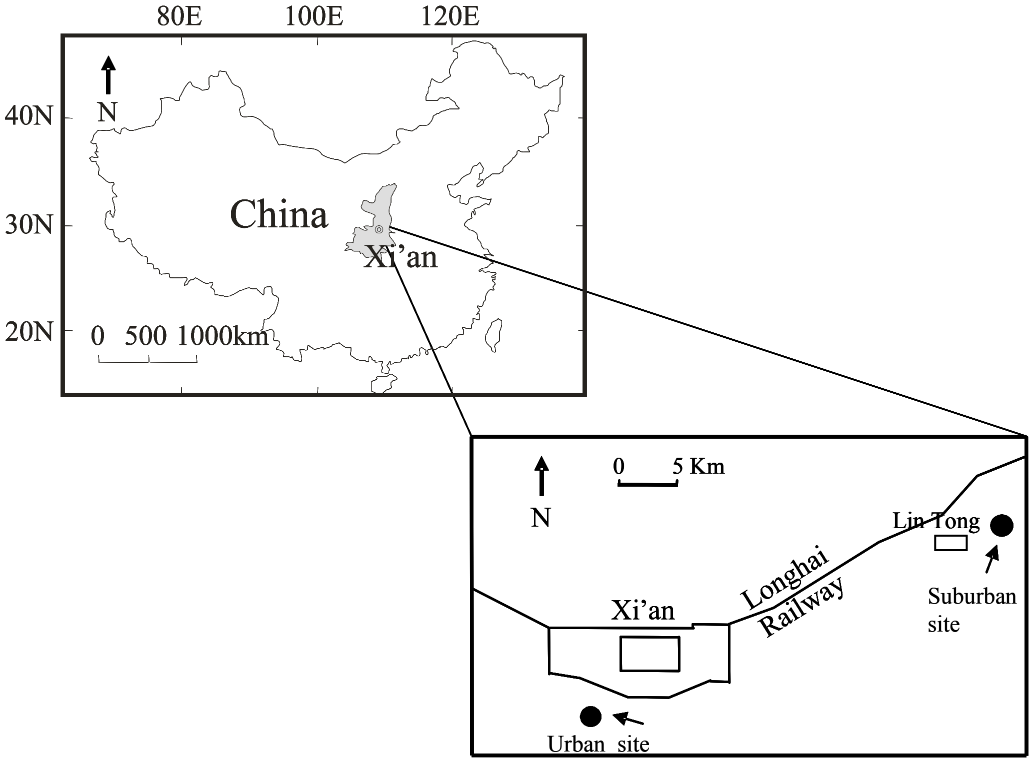

Fig. 1. The sampling locations in Xi'an, China

and agricultural activity is the major NH_3 emission.

Sample Collection

Ammonia samples were collected using Ogawa passive samplers (Ogawa USA., Inc., Pompano Beach, Florida, USA, ogawausa.com). The Ogawa passive sampler is a useful tool for monitoring atmospheric NH_3 concentrations. The advantages of passive samplers are that they are less expensive, easily deployed and do not require access to electricity (Rabaud *et al.*, 2001; Carmichael *et al.*, 2003; Roadman *et al.*, 2003). The efficacy of passive samplers in measuring atmospheric NH_3 shown in previous studies (Tate, 2002; Carmichael *et al.*, 2003; Thöni *et al.*, 2003; Wilson and Serre, 2007) helped in the selection of passive sampling use in this study. Ammonia was collected on 14.5 mm citric acid-coated cellulose filters every sixth day from 15 April 2006 to 14 April 2007 at the two sampling sites.

Daily aerosol ($PM_{2.5}$) samples were collected using the battery-powered mini-volume samplers (Airmetrics, Oregon, USA) operating at flow rates of 5 L/min (Cao *et al.*, 2006; Huang *et al.*, 2007). PM samples were collected on 47 mm Whatman quartz microfiber filters (QM/A).

NH_3 and NH_4^+ Analyses

After collection, samples were refrigerated at 4°C. The NH_3 and $PM_{2.5}$ filters were then transferred (using forceps) to acidwashed glass vials containing 3.0 and 10.0 mL of deionized water, respectively. The vials were sonicated for 60 min, and the extract was filtered through a 13-mm diameter, 0.2-mm Acrodiscs in-line filter using a 10 ml syringe. The syringe and filter were pre-rinsed with deionized water and 1-2 mL of sample solution. Filtering removes glass-fiber filter particles, which cause positive absorbance artifacts during analysis. The ammonium citrate extract was analyzed using Dionex-600 Ion Chromatography (Dionex Inc., Sunnyvale, CA, USA) with a CG12A 4 mm guard column and a CS12A 4 mm analytical column. The CSRS (cation self-regenerating suppressor) was set at 62 mV. The detector used was a CD25A conductivity detector. The eluent was methanesulfonic acid (MSA). A mass transfer coefficient of 0.249 cm^2/s was utilized to calculate the NH_3 concentrations from NH_4^+ measurements (Tate, 2002). The concentrations of NH_3 and NH_4^+ in $PM_{2.5}$ filters were corrected using field blanks.

RESULTS AND DISCUSSION

Temporal Variations of Ammonia

Fig. 2 shows the temporal variation in NH_3 at the two observation sites. The concentrations of NH_3 at the urban site ranged from 0.35 $\mu g/m^3$ to 40.0$\mu g/m^3$, with an annual average of 12.9 $\mu g/m^3$. The NH_3 concentrations at the suburban site tended to be slightly higher than those at the urban site, and varied from 0.86$\mu g/m^3$ to 54.8$\mu g/m^3$, with an annual average of 14.1$\mu g/m^3$. The NH_3 concentrations at the urban site were highly correlated with those at the suburban site (r = 0.74, significance level 99%). The high correlation of NH_3 at two typical sites may point to the regionally uniform distribution of NH_3 concentration in Xi'an and showed no evidence that local point sources of NH_3 dominated ambient measurements.

The NH_3 concentrations at the urban and suburban sites showed a similar trend, i.e., NH_3 increased gradually from April to July, and reached the highest values during June and July, and then decreased until the following March. The peak NH_3 value was 37.0 $\mu g/m^3$ at the urban site and was 54.8 $\mu g/m^3$ at the suburban site in July. NH_3 concentrations and ambient temperatures in June and July reached maximum values with minimum values in January. The annual average temperature was found to be 16.0°C, with the highest daily temperature (32°C) in July and the lowest temperature (0°C) in January at the urban site. The annual average temperature was 15.6°C at the suburban site, with the highest daily temperature (33.5°C) in June and the lowest temperature (-1.4°C) in January. NH_3 levels were found to be highly correlated (r = 0.68 for the urban site, r = 0.72 for the suburban site) with ambient temperature. As expected, ambient NH_3 concentrations showed a positive correlation with temperature because increasing temperatures: (i) increased NH_3 sources by enhancing volatilization of NH_3 and (ii) decreased the stability of NH_4NO_3 aerosols. Various studies have shown strong correlations between air temperature and ammonia concentration, suggesting that

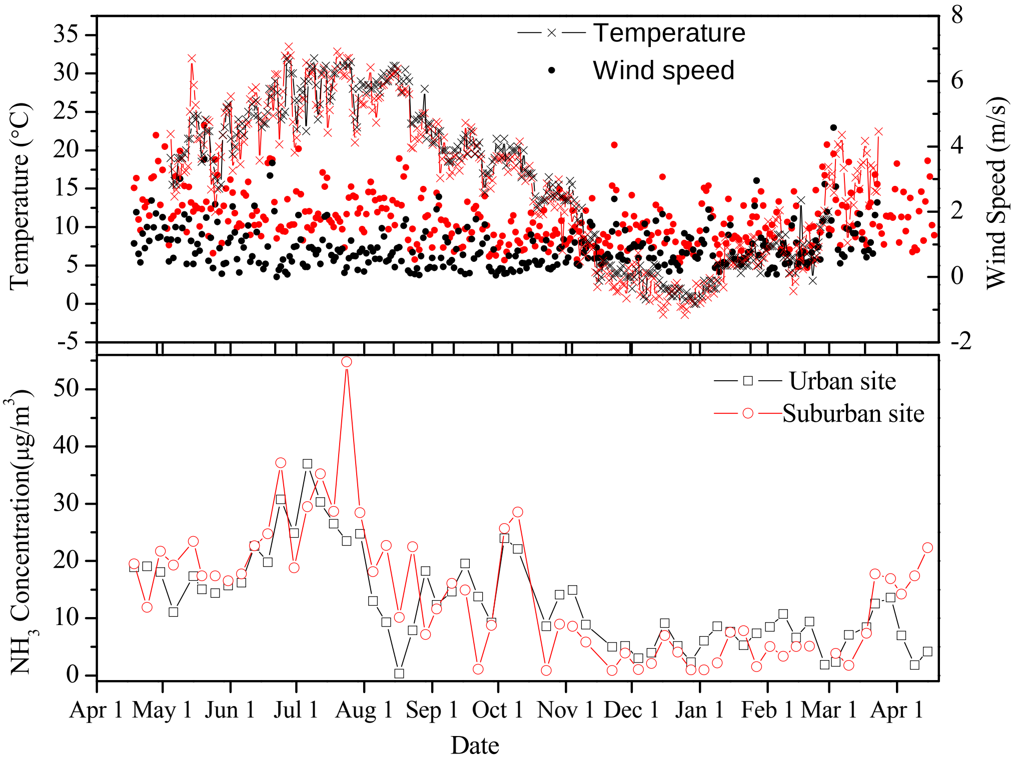

Fig. 2. Temporal variations of NH_3, temperature and wind speed. Black curves refers to these variables at urban site and red curves refers to these variables at suburban site.

temperature is an important variable in influencing NH_3 volatilization from animal waste (Aneja *et al.*, 2000). NH_3 levels were found to be poorly correlated (r = -0.19 for the urban site, r = -0.08 for the suburban site) with wind speed, which indicated that dispersion conditions were good at both sites. NH_3 concentrations decreased dramatically during August and September, reflecting the important role wet removal plays in influencing the temporal variation in ambient NH_3 levels, which is consistent with increasing relative humidity promoting the formation and stability of NH_4^+ aerosols. NH_3 values increased significantly in October at both sites, which can be ascribed to the impact of biomass burning after the harvest season on the Guangzhou plain (Cao *et al.*, 2005).

The monthly average NH_3 concentrations at the two sites are summarized in Table 1. Monthly averages were maximum in July and minimum in December. NH_3 at the urban and suburban site were 28.4 μg/m^3 and 35.3 μg/m^3, respectively, in July, which was approximately 5 and 10 times higher than those in December. At the suburban site, the monthly average NH_3 concentrations followed the order July > June > May > April > August > October > September, while NH_3 concentrations were less than 10.0 μg/m^3 in the remaining months. The variations in NH_3 concentrations at both sites were quite similar, indicating that NH_3 concentrations were primarily related to contributions from area emission sources such as agricultural activities.

Table 1. Concentrations of NH_3 at Xi'an ($\mu g/m^3$)

Month		06-Apr	06-May	06-Jun	06-Jul	06-Aug	06-Sep	06-Oct	06-Nov	06-Dec	07-Jan	07-Feb	07-Mar
Urban site	Average	18.7	14.7	22.8	28.4	9.7	13.9	17.2	8.5	4.7	7.0	7.4	6.0
	Max.	19.1	17.4	30.8	37.0	18.2	19.6	24.0	14.9	9.1	8.6	10.8	8.5
	Min.	18.1	11.1	16.2	23.5	0.4	9.2	8.6	5.0	2.3	5.3	1.9	2.4
Suburban site	Average	17.7	18.8	24.2	35.3	16.1	10.5	16.0	4.8	3.0	4.0	4.6	9.5
	Max.	21.7	23.4	37.1	54.8	22.7	16.1	28.5	8.6	7.0	7.8	5.1	17.7
	Min.	11.9	16.5	17.7	28.4	7.1	1.1	0.9	0.9	1.0	1.0	3.3	1.8

Seasonal Variations

Fig. 3 shows the distribution of NH_3 concentrations over four seasons. Seasonal average concentrations of NH_3 were 16.2 $\mu g/m^3$, 20.3 $\mu g/m^3$, 14.7 $\mu g/m^3$ and 6.1 $\mu g/m^3$ in spring, summer, autumn and winter, respectively, at the urban site. Seasonal average concentrations of NH_3 were 18.4 $\mu g/m^3$, 25.2 $\mu g/m^3$, 11.9 $\mu g/m^3$ and 3.6 $\mu g/m^3$ in spring, summer, autumn and winter, respectively, at the suburban site. The seasonal variation in NH_3 was summer > spring > autumn > winter at both sites. The seasonal changes in NH_3 levels are consistent with the view that NH_3 originates largely from natural emissions, which are at a minimum during winter. Higher concentrations during the summer season may reflect both higher volatility of NH_3 and the influence of fertilizer application to surrounding farmland during this period. Higher NH_3 volatility from city garbage and animal husbandry activities can also increase ambient NH_3 concentrations during the summer months. Low NH_3 concentrations in winter were probably due to reduced NH_3 volatilization when the air temperature was frequently below freezing and there was snow cover on the fields, as well as infrequent agricultural activities. These findings also indicated that non-biological emission sources such as industrial production and vehicle emissions did not have a significant impact on the distribution of ambient NH_3. Similar seasonal trends in NH_3 were also found in other studies (Danalatos and Glavas, 1999; Bari *et al.*, 2003). These authors suggested that high levels of NH_3 were associated with high volatility of particulate NH_4^+ under high temperatures in summer.

The scatter of NH_3 at the suburban site was larger than at the urban site in spring, summer, and autumn (Fig. 3). During winter, the scatter of NH_3 at the suburban site was smaller than that at the urban site. The large scatter of NH_3 at the suburban site may be due to NH_3 emissions originating mainly from agricultural sources and their spatial distribution was therefore closely linked to agricultural production. However, the NH_3 concentrations at the suburban site were closer during winter, which can be attributed largely to reduced NH_3 volatilization as a result of frozen surfaces in the surrounding farmland.

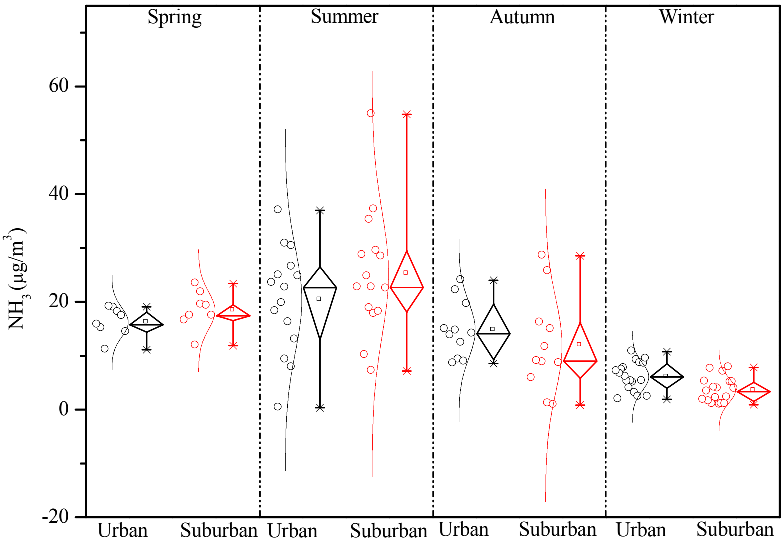

Fig. 3. Distribution of NH_3 concentrations during four seasons. The box plots indicate the mean 6-day concentration and the min, 1st, 25th, 50th, 75th, 99th and max percentiles. A normal curve is fitted to the measurements.

Relationship between NH_3 and NH_4^+ in Fine Aerosol

NH_3 is the only alkaline gas in the atmosphere, and thus plays a major role in the neutralization of atmospheric sulfuric and nitric acid. NH_3 readily reacts with these acids to form ammonium salts and thus is an important constituent of aerosols and precipitation (Erisman *et al.*, 1988). To realize the transformation of NH_3 and NH_4^+, the NH_4^+ in $PM_{2.5}$ was simultaneously observed at the urban site. Fig. 4 illustrates the time series of NH_3 and NH_4^+, where NH_4^+ concentrations ranged between 0.83 μg/m^3 and 34.0 μg/m^3, with an average of 8.3 μg/m^3. NH_4^+ concentrations increased gradually from April to December and then decreased until the following April, i.e., NH_4^+ followed a different trend to NH_3. The NH_3 concentrations were higher than NH_4^+ concentrations in $PM_{2.5}$ in spring and summer and were comparable to NH_4^+ concentrations especially in September and October. However, NH_3 concentrations were less than NH_4^+ concentrations in winter. Once emitted into the atmosphere, NH_3 may undergo conversion to NH_4^+ aerosol. The rate of this conversion, which is largely unknown, will have an important bearing on the regional impact of NH_3 distribution. The conversion of NH_3 to NH_4^+ aerosol depends on the concentration of acids in the atmosphere, temperature, and water availability (Koerkamp *et al.*, 1998; Kobara *et al.*, 2007), as will flux rates of NH_3 (Nemitz *et al.*, 2001). NH_3 concentrations were weakly correlated with NH_4^+ concentrations and the Spearman correlation was not significant ($r = 0.12$). This suggests that gas-particle reactions are influenced by many factors (such as sources, meteorology and removal).

Average NH_3/NH_4^+ ratios varied from 0.1 to

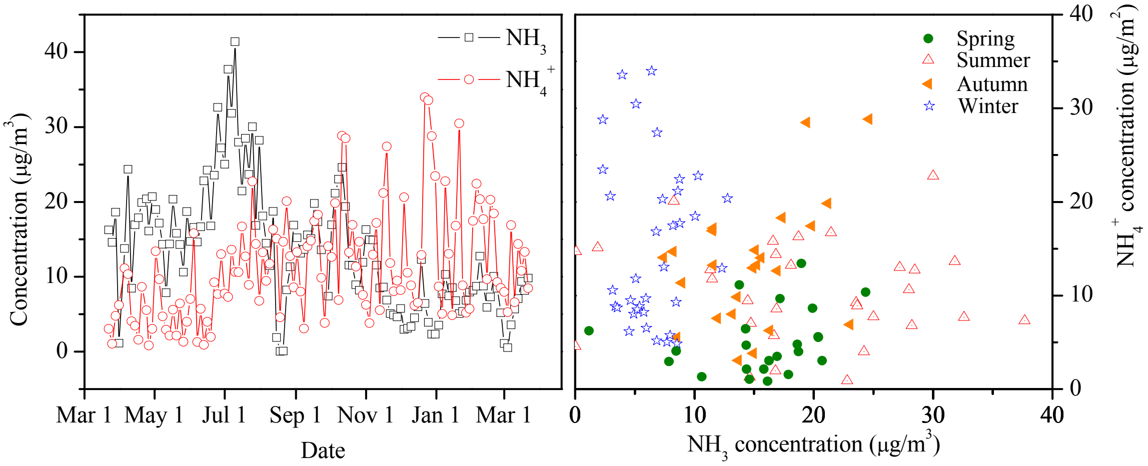

Fig. 4. Temporal variations of NH_3 and NH_4^+ in $PM_{2.5}$ at urban site (left), scatte plots between NH_3 and NH_4^+ concentrations (right).

25.3, with an annual average of 4.0. Most NH_3/NH_4^+ ratios in this study were high when compared to a "background" value of 0.1 for a U.S. site and 0.5 in Europe as reported by Lindberg *et al.* (1990). This suggests that abundant NH_3 gas existed in the atmosphere over Xi'an. The rate of ammonification is influenced by temperature, pH and water availability. Higher NH_3/NH_4^+ ratios were found in summer, implying that NH_3 gas is not neutralized completely by acidic species. However, most NH_3/NH_4^+ ratios were close to or less than 1.0, which indicated that NH_3 gas was neutralized completely by acidic species due to decreased NH_3 in ambient air and increased SO_2 concentrations from residential heating during winter.

Comparison of NH_3 Concentration with Other Area

Table 2 lists NH_3 levels at different urban and suburban sites throughout the world. The NH_3 level (12.9 μg/m^3) at the urban site in Xi'an was lower than that reported in Delhi, India (32.6 μg/m^3) (Kapoor *et al.*, 1992), Lahore, Pakistan (21.1-81.3 μg/m^3) (Biswas *et al.*, 2008) and the Northern Adriatic area, Croatia (12-20 μg/m^3) (Alebic-Juretic, 2008). NH_3 level at Xi'an was 2-5 times higher than that reported at Pune, India (2.0 μg/m^3) (Khemani *et al.*, 1987), Yokohama, Japan (5.3 μg/m^3) (Yamamoto *et al.*, 1988), Chicago, USA (1.63 μg/m^3) (Lee *et al.*, 1993), Hamilton, Canada (4.28 μg/m^3) (Brook *et al.*, 1997), Nara, Japan (2.4 μg/m^3) (Matsumoto & Okita, 1998), Seoul, South Korea (4.43 μg/m^3) (Lee *et al.*, 1999), Baltimore, USA (3.3 ± 2.1 μg/m^3) (Larsen *et al.*, 2001), Salzburg, Austria (2.7-28 μg/m^3), Munich, Germany (2.4-11 μg/m^3) (Loflund *et al.*, 2002), Zurich, Switzerland (7.5 μg/m^3) (Thoni *et al.*, 2003), Clinton, USA (5.32 μg/m^3), Kinston, USA (2.46 μg/m^3), Morehead City, USA (0.58 μg/m^3) (Walker *et al.*, 2004), Seoul, South Korea (4.81-6 μg/m^3) (Kang *et al.*, 2004) and Hong Kong (2.1 μg/m^3) (Yao *et al.*, 2006). NH_3 concentrations (14.1 μg/m^3) at the suburban site in Xi'an was close to those in

Agra, India (10.2 ± 6.4 µg/m^3) (Singh *et al.*, 2001), and the Northern Adriatic area, Croatia (6-28 µg/m^3) (Alebic-Juretic, 2008). Higher levels of NH_3 at Xi'an were probably due to emissions from farmland, animal waste, ammonia-based fertilizers and soil.

CONCLUSIONS

Measurements of atmospheric NH_3 using the Ogawa passive sampler technology were conducted between April 2006 and April 2007 at an urban and a suburban site in Xi'an. The annual average concentrations of NH_3 were 12.9 µg/m^3 and 14.1 µg/m^3 at the urban and suburban sites, respectively. NH_3 concentrations reached a maximum in June and July and were minimum in January, which was significantly associated with NH_3 volatilization under different ambient temperatures. The seasonal variation in NH_3 was summer > spring > autumn > winter at

Table 2. Comparison of NH_3 concentrations at Xi'an with other ares. (unit: µg/m^3)

Location	Period	Type	Concentration	Reference
Xi'an, China	Apr. 2006-Apr. 2007	Urban	12.88 ± 8.17	This study
		Suburban	14.08 ± 11.12	
Pune, India		Urban	2.00	Khemani *et al.* (1987)
Yokahama, Janpan		Urban	5.30	Yamamota *et al.* (1988)
Delhi, India		Urban	32.60	Kapoor *et al.* (1992)
Chicago, USA	Apr. 1990-Mar. 1991	Urban	1.63	Lee *et al.* (1993)
Hamilton, Canada	1992-1992	Urban	4.28	Brook *et al.* (1997)
Nara, Japan	June 1994-May 1995	Urban	2.40	Matsumoto and Okita (1997)
Seoul, South Korea	Oct. 1996-Sep. 1997	Urban	4.43	Lee *et al.* (1999)
Agra, India	July-Sep. 1997	Suburban	10.2 ± 6.4	Singh *et al.* (2001)
Baltimore, USA	Mar. 1997-Mar. 1999	Urban	3.3 ±2.1	Larsen *et al.* (2001)
Salzburg, Austria	Aug. 2000-Jan. 2001	Urban	2.7~28	Loflund *et al.* (2002)
Munich, Germany			2.4~11	
Rome, Italy	May 2001-Mar. 2002	Urban	3.8~45.6	Perrino *et al.* (2002)
Zurich, Switzerland	Autumn 1999-2000	Urban	7.50	Thoni *et al.* (2003)
Clinton, USA	Jan. 2000-Dec. 2000	Urban	5.32	Walker *et al.* (2004)
Kinston, USA	May 2000-Dec. 2000		2.46	
Morehead City, USA	Jan. 2000-Dec.2000		0.58	
Seoul, South Korea	Oct.-Nov. 2001	Urban	4.81~6	Kang *et al.* (2004)
Hong Kong	Autumn 2000	Urban	2.1	Yao *et al.* (2006)
Northern Adriatic area, Croatia	1998-2005	Urban	12~20	Alebic-Juretic (2008)
		Suburban	6~28	
Lahore, Pakistan	Dec. 2005-Feb. 2006	Urban	21.1~81.3	Biswas *et al.* (2008)
Munster, Germany	Jan. 2006.	Urban	<34.77	Gietl *et al.* (2008)

both sites, which was ascribed to the impact biological emission sources such as agricultural activity. NH_3 and NH_4^+ aerosol concentrations were weakly correlated, implying that gas-particle reactions are influenced by many factors such as source, meteorology and removal. High NH_3 concentrations at Xi'an had a significant influence on atmospheric acidity and the formation of secondary NH_4^+ aerosol.

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