Atmospheric ammonia and particulate ammonium from agricultural sources in the North China Plain

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ABSTRACT

Atmospheric ammonia (NH_3) and particulate ammonium (NH_4^+) were measured using passive samplers and particulate samplers at four rural and two suburban sites in the North China Plain (NCP) from August 2006 to September 2009. The annual mean concentrations of NH_3 and NH_4^+ in PM_{10} across the sites were 15.6 and 12.4 $\mu g\ m^{-3}$, respectively. Higher concentrations of NH_3 and NH_4^+ were found at the rural sites compared with the suburban sites. NH_3 concentrations were highest in summer and lowest in winter, showing positive correlations with N fertilizer application rates and temperature in each season. Particulate NH_4^+ showed significant positive correlations with particulate SO_4^{2-} and NO_3^- at the six sites. The annual mean concentrations of secondary inorganic particles (sum of NH_4^+, SO_4^{2-} and NO_3^-) accounted for 26.1–41.3% of the PM_{10} concentration across all sites. The formation of inorganic NH_4^+ particles was limited mainly by the availability of H_2SO_4 and HNO_3 and partly by NH_3. The total NH_x deposition in the NCP averaged 43.5 kg N $ha^{-1}\ yr^{-1}$, accounting for 84.1% of the mean NH_3 emission intensity. The serious particulate NH_4^+ pollution and high NH_x deposition suggest the urgency of reducing NH_3 emission from agricultural sources in the NCP.

1. Introduction

Ammonia (NH_3) is the most abundant basic gas in the atmosphere. The primary sources for atmospheric NH_3 are agricultural emissions such as domestic animals, nitrogen (N) fertilizer application and biomass burning (Bouwman et al., 1997; Galloway et al., 2004). Once emitted to the atmosphere, NH_3 will deposit onto the earth's surface near sources in large quantities as dry deposition. Ammonia can also react with acidic species (e.g., H_2SO_4, HNO_3, HCl) to form secondary inorganic particles (e.g., $(NH_4)_2SO_4$, NH_4NO_3, and NH_4Cl) (Asman et al., 1998). These secondary particles have been regarded as the main contributor to fine particulate matter (PM), which is harmful to human health and reduces visibility (Erisman and Schaap, 2004; Pinder and Adams, 2007) and is also implicated in climate change due to its effects on direct and indirect radiative forcing (Adams and Seinfeld, 2001; Haywood and Boucher, 2000). The deposition of NH_3 and particulate ammonium (NH_4^+) in natural or semi-natural ecosystems may cause eutrophication, soil acidification and loss of biodiversity (Bergström and Jansson, 2006; Bouwman et al., 2002; Stevens et al., 2004).

Due to the negative effects on the environment, environmental scientists have concentrated on atmospheric ammonia and particulate ammonium since the 1990s (Sutton et al., 2008). Concentrations of atmospheric NH_3 and pNH_4^+ have been measured at many sites worldwide to check pollution levels and estimate dry deposition fluxes as well as for calibrating deposition models (e.g., Erisman and Schaap, 2004). For example, the mean concentration of NH_3 was as high as 10.48 $\mu g\ m^{-3}$ at a commercial hog farm in eastern North Carolina, USA (McCulloch et al., 1998). In comparison, mean NH_x ($NH_3 + NH_4^+$) concentration was only 2.21 $\mu g\ m^{-3}$ at Mt. Mitchell, NC, USA (Aneja et al., 1998). Walker et al. (2004) reported NH_x 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 $ha^{-1}\ yr^{-1}$, respectively. Measuring NH_3 and pNH_4^+ is time consuming, complicated and costly, but recently, Clarisse et al. (2009) found that infrared spectra, obtained by the IASI/MetOp satellite can be used to map global NH_3 concentrations from space. Though this method needs much improvement, it offers a new and easier way to check NH_3 pollution levels over large regions.

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In previous studies, we found very high NH_3 emission intensities (from 40 to 120 kg N ha^{-1} yr^{-1}) in the North China Plain (NCP), which were mainly caused by high NH_4-based fertilizer application rates and large numbers of intensive livestock farms (Cai et al., 2004; Yan et al., 2003; Zhang et al., 2010). Such high emission intensities may consequently cause high NH_3 concentrations and pollution. Considering the concomitant large emission intensities of both SO_2 and NO_x in this region (Lu et al., 2010; Richter et al., 2005; Streets and Waldhoff, 2000), we suspect that secondary inorganic particle pollution due to the reaction between NH_3 and acids from SO_2 and NO_x could be a major problem. High bulk deposition of reduced N has partly proved this (e.g., Liu et al., 2006; Zhang et al., 2008).

Croplands account for about 60% of the NCP. Therefore, NH_3 emission from N fertilized croplands will have a very important influence on local air quality and pollution. However, direct measurements of atmospheric NH_3 and NH_4^+ concentrations are scarce. In this paper, we present measurements of atmospheric NH_3 and particulate NH_4^+ as well as particulate NO_3^-, SO_4^{2-} and Cl^- concentrations at six typical sites in the NCP. The spatio-temporal characteristics of the measured compounds, correlations between particulate NH_4^+ and particulate NO_3^-, SO_4^{2-} and Cl^- as well as the NH_3/NH_x ratios were analyzed. The emission, transport, transformation and deposition of NH_x and the benefits from agricultural NH_3 emission controls in reducing the PM pollution in this intensively managed agricultural region are discussed.

2. Materials and methods

2.1. Sampling sites

Six monitoring sites were selected based on land use categories, distance from the city, and NH_3 emission intensity. The six sites were Dongbeiwang (DBW), Shangzhuang (SZ), Quzhou (QZ), Huimin (HM), Wuqiao (WQ) and Shouguang (SG), and their locations are shown in Fig. 1. The NH_3 emission intensities in the year 2008 in a 5 km × 5 km resolution for each site, calculated with the census database from China's statistic datasets and emission factors recalculated by the RAINS model (Zhang et al., 2010), are shown in Table 1.

Both DBW and SZ are suburban sites in the northwest suburb of Beijing. They are 20 and 33 km away from the city center of Beijing, respectively. Croplands account for about 40% of the total land area; other main land uses are residential, commercial houses, small scale livestock farms and roads. The DBW and SZ sites were surrounded by agricultural fields growing mainly winter wheat and summer maize in rotation. The unique difference between the two locations is that SZ is far from a main road (c 2 km) while DBW is much closer to a main road (c 0.2 km).

The four rural sites were located in QZ, WQ, HM and SG counties. These are 51, 39, 51 and 25 km away from their nearest cities (Xingtai, Dezhou, Binzhou and Weifang, respectively) and have arable land coverages of about 75%. Winter wheat, summer maize, cotton and greenhouse vegetables are the main crops in QZ, WQ and HM, while greenhouse vegetables are the main crops in SG. Ammonia emission intensities at the four rural sites can be ranked as high due to the large area of arable land and high N fertilizer application rates. The sites QZ, SG and SZ were about 2 km away from the main roads, while the distance of WQ and HM to the nearest main roads was more than 10 km.

In the winter wheat/summer maize rotations, N fertilizer application rates are usually as high as 500–600 kg N ha^{-1} yr^{-1} (Ju et al., 2009). Nitrogen fertilizers are used as basal fertilizers at the beginning of October (for winter wheat) and in late June or at the beginning of July (for summer maize), and used as a top-dressing in March or/and April (for winter wheat) and July and
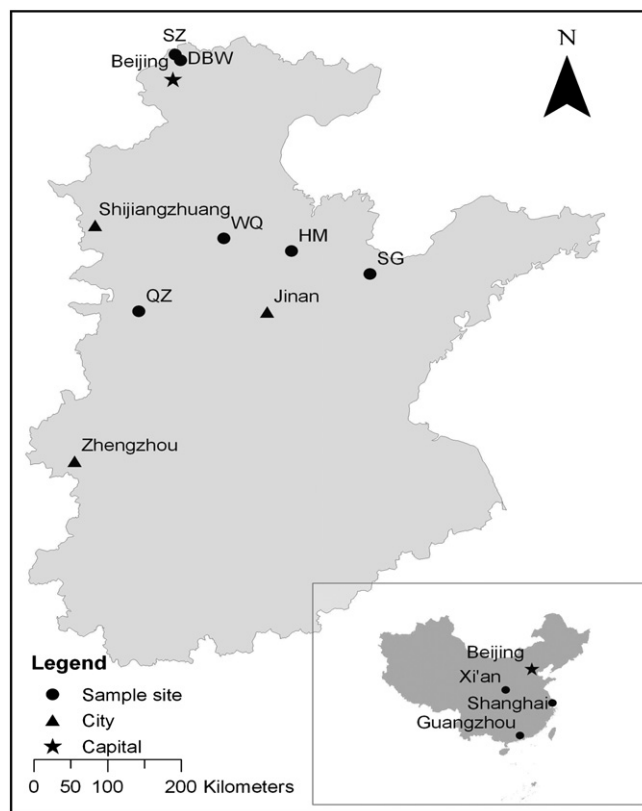

Fig. 1. Map of sampling sites in the North China Plain.

August (for Summer maize). For greenhouse vegetable production, double-cropping is typical without supplementary heating or illumination and total N fertilizer application rates are extremely high at 1000–2000 kg N ha^{-1} yr^{-1}. Basal fertilizers are used in summer, while top-dressing fertilizers are applied in the other three seasons.

2.2. Meteorological factors

The climate of the North China Plain is sub-humid temperate. Annual average precipitation ranges from 400 to 700 mm with approximately 70% of the precipitation occurring in the summer (June to August). Highest relative humidity and lowest wind speed are often found in the summer, while lowest relative humidity and highest wind speed usually occur in spring and part of the winter. The meteorological data (air temperature, wind speed, wind direction, precipitation, and relative humidity) at SZ, WQ, HM and SG were obtained from local meteorological bureaus, while those at DBW and QZ sites were recorded at weather stations in the fields not far from the sampling sites.

2.3. Sampling methods and chemical analysis

Sampling was conducted during August 2006 to September 2009. Two sampling strategies were used for different sampling sites. Ammonia and particulate matter concentrations were measured monthly at DBW, QZ and SZ (sampling strategy 1) and seasonally at WQ, HM and SG. (sampling strategy 2). Detailed sampling and analytical methods are as follows.

2.3.1. NH_3

NH_3 concentrations were measured with Radiello® passive samplers (Aquaria, Italia). Three NH_3 samplers per site for each

Table 1
Mean NH_3, NO_2, HNO_3 and SO_2 concentrations at six sites in the NCP.

Site	Sampling frequency	NH_3 emission intensity kg N ha^{-1} yr^{-1}	NH_3 µg m^{-3}	NO_2 µg m^{-3}	HNO_3 µg m^{-3}	SO_2 µg m^{-3}
DBW	Monthly	55.4	14.0 ± 7.3	71.2 ± 21.8	1.9[a]	39.0[c]
QZ	Monthly	85.8	16.2 ± 10.3	39.6 ± 27.8	2.3 ± 1.9	22.3 ± 8.9
SZ	Monthly	46.2	9.4 ± 6.3	37.6 ± 15.1	1.9[a]	39.0[c]
HM	Seasonally	83.7	8.9 ± 3.3	17.7 ± 11.8	n.d.[b]	57.3[d]
SG	Seasonally	79.9	24.2 ± 20.9	31.1 ± 15.1	n.d.	101.6[d]
WQ	Seasonally	76.0	21.0 ± 22.2	16.9 ± 11.8	n.d.	52.5[d]

[a] Cited from Wu et al. (2009).
[b] Not determined.
[c] Mean SO_2 concentration in Beijing during 2007–2009 reported by BEPB (2010).
[d] SO_2 concentrations at HM, SG and WQ were taken from the first half-year mean values for 2010 in nearby cities Jinan, Weifang and Shijiazhuang, respectively, which were reported by the Ministry of Environmental Protection of China (MEPC, 2010).

sampling period were exposed in a PVC shelter (2 m above the ground), which protected the samplers from precipitation and direct sunlight. The NH_3 concentrations were measured for a month by exposing the samplers for two weeks in the middle of each month during August 2006 to July 2007 at DBW and QZ, and

from October 2007 to September 2009 by exposing the samplers for half a month at QZ and SZ. For the seasonal NH_3 concentration measurements at WQ, HM and SG, ammonia concentrations were measured once in each season (autumn, winter, spring and summer) by exposing the passive samplers for six days. After
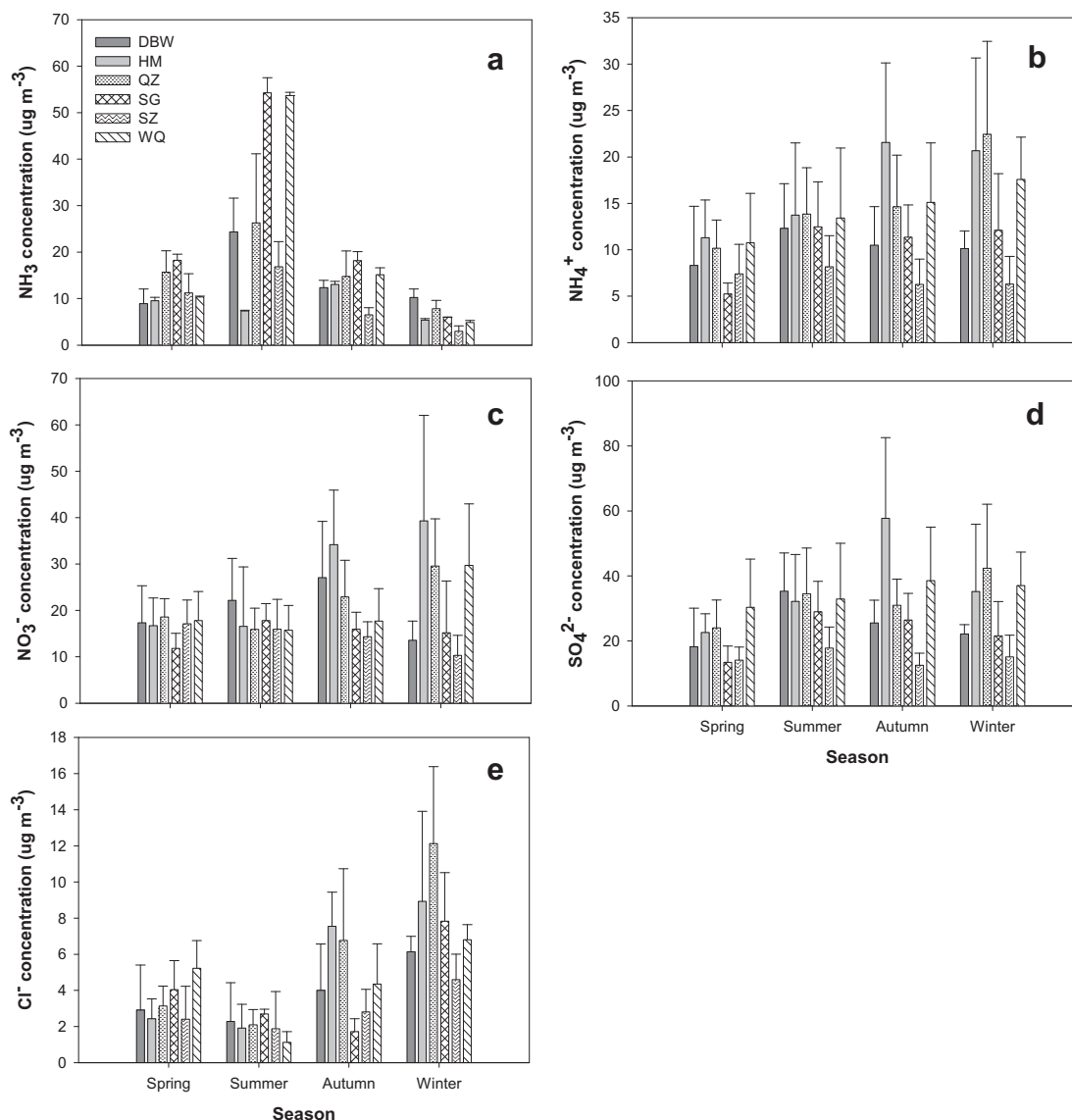

Fig. 2. Seasonal mean concentrations of NH_3 (a), particulate NH_4^+ (b), NO_3^- (c), SO_4^{2-} (d) and Cl^- (e) in PM_{10} across sites. Error bars mean the standard deviations.

exposure, absorption cartridges of the passive samplers were put into airtight plastic tubes and kept in a refrigerator at 4 °C until chemical analysis, which was made within two months. The cartridges were extracted with 10 ml high-purity water (18.2 MΩ) for 2 min using a VORTEX type stirrer, and the NH_4^+-N in the extractant measured by a continuous flow analyzer (TRAACS 2000, Germany). Field blank measurements were made each month or each season at every site.

2.3.2. Particulate matter

A portable particulate sampler (frmOMNI, BGI Inc., USA) was used to sample PM_{10} and $PM_{2.5}$ during August 2006 and August 2007. During this sampling period, five daily PM_{10} and five daily $PM_{2.5}$ (three in first half of a month and two in the second half of a month) samples were collected at DBW and QZ in each month, while three daily PM_{10} and three daily $PM_{2.5}$ samples were obtained at WQ, HM and SG in each season (autumn, winter, spring and summer). High volume samplers (TH1000C, Tianhong Co., China) were used to sample PM_{10} during October 2007 to September 2009 at SZ and QZ. A 24-h PM_{10} sample was obtained every other day except the days without electricity or when mechanical problems occurred. Detailed measurement and analysis methods for particulate matter and particulate dissolvable inorganic ions (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, K^+, Ca^{2+}, Mg^{2+} and Na^+) were described by Shen et al. (2009). Briefly, concentrations of PM_{10} or $PM_{2.5}$ were calculated according to weight differences between filters before and after sampling; while concentrations of particulate inorganic anions and cations were measured by ion chromatography (DX-120, Dionex, USA) and ICP-AES (Optima 3300DV, USA), respectively.

3. Results and discussion

3.1. NH₃ concentrations

Mean NH_3 concentrations across sampling sites are shown in Table 1. The mean NH_3 concentrations were in the range 8.9–24.2 μg m^{-3}, showing a positive correlation with NH_3 emission intensity (46.2–85.8 kg N ha^{-1} yr^{-1}). The mean NH_3 concentration was highest at SG, which could be due to the large quantities of NH_3 emission from greenhouse vegetable production in Shouguang County, where farmers use extremely high rates of N fertilizers (e.g., 1900 kg N ha^{-1} as chemical N fertilizer and an additional 1000 kg N ha^{-1} as organic manure) in the field every year to obtain high yields. In comparison, the mean NH_3 concentrations were 11–23 μg m^{-3} at sites with emission intensities in the range of 50–200 kg NH_3–N ha^{-1} yr^{-1} in the Netherlands (Buijsman et al., 1998). Unexpectedly, the mean NH_3 concentration was lowest at HM (7.3 μg m^{-3}), a site with moderate NH_3 emission intensity. As there were several heavy rainfall events at HM during the summer sampling, rainfall scavenging may have caused this. Lower NH_3 concentration was also observed at SZ, which also had the lowest emission intensity among the six sampling sites. Though DBW has similar NH_3 emissions to SZ, the small distance (200 m) to the main road means that DBW was easily affected by NH_3 emissions from cars and other vehicles with catalytic converters (Cape et al., 2004).

Owing to the high NH_3 emission intensities, the NH_3 concentrations at the sampling sites were higher than those measured at many agricultural sites in American, Asian, and European countries (e.g., Burkhardt et al., 1998; Edgerton et al., 2007; Hong et al., 2002; Horváth and Sutton, 1998; Walker et al., 2004 and references therein). Similar high NH_3 concentration (14.1 μg m^{-3}) to those measured in this study was reported at an agricultural site with fruit production in the Guanzhong Plain in Northwest China (Cao et al., 2009).
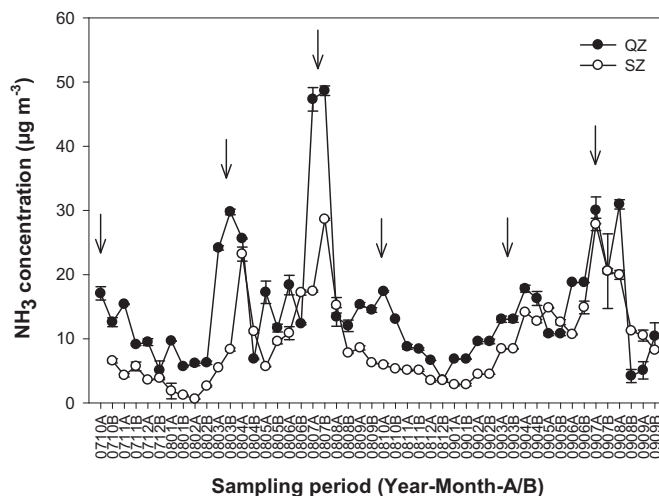

Fig. 3. Half-monthly mean NH_3 concentrations measured at Quzhou (QZ) and Shangzhuang (SZ) during October 2007 and September 2009 (A—the first half of a month, B—the second half of a month). Downward arrows represent N fertilizer applications during the sampling periods.

The ammonia concentrations at the six sampling sites showed distinct seasonal variations (Fig. 2). Averaged NH_3 concentrations across the sites were 12.3 ± 3.8, 30.5 ± 19.4, 13.3 ± 3.9 and 6.2 ± 2.5 μg m^{-3} in spring, summer, autumn and winter, respectively. Ammonia concentrations in summer were 3.9, 1.5 and 1.3 times higher than those in winter, spring and autumn, respectively. Nitrogen fertilizer applications have a major impact on atmospheric NH_3 concentrations. As shown in Fig. 3, NH_3 concentrations increased sharply after N fertilizer application in October and March or April for winter wheat, and in July or August for summer maize at QZ and SZ. This is most probably due to NH_3 volatilization from urea, the most common N fertilizer in China. As reported by Ju et al. (2009), due to the very large amounts of N fertilizer applied, N loss from NH_3 volatilization in the NCP accounted for 19 and 25% of the applied N fertilizer for winter wheat and summer maize, respectively. As NH_3 volatilization is promoted by higher temperatures, atmospheric NH_3 concentration may be indirectly affected by air temperature. As shown in Fig. 4, NH_3 concentrations increased exponentially with the increase in air temperature at the sampling sites, which was consistent with the findings of Yamamoto et al. (1995) and Robarge et al. (2002).
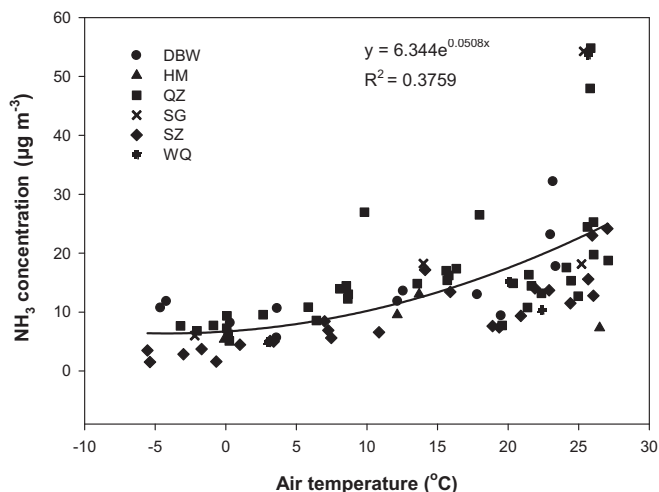

Fig. 4. Correlation between air temperature and NH_3 concentration across the sites.

Table 2
Mean mass concentrations of PM_{10}, $PM_{2.5}$, and ions (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-) in PM_{10} and $PM_{2.5}$. Data in the parenthesis are standard deviations.

Site	No.	PM			NH_4^+			NO_3^-			SO_4^{2-}			Cl^-		
		PM_{10}	$PM_{2.5}$	Ratio	PM_{10}	$PM_{2.5}$	Ratio	PM_{10}	$PM_{2.5}$	Ratio	PM_{10}	$PM_{2.5}$	Ratio	PM_{10}	$PM_{2.5}$	Ratio
DBW	54	204.8 (102.0)	136.2 (67.3)	0.66	10.0 (7.9)	8.8 (6.7)	0.88	19.9 (16.3)	15.1 (11.4)	0.76	25.5 (20.1)	22.4 (16.2)	0.88	3.7 (3.3)	2.8 (2.5)	0.75
QZ1[a]	54	223.9 (156.1)	159.6 (93.8)	0.71	16.1 (13.6)	15.5 (12.4)	0.96	22.3 (18.2)	19.1 (13.2)	0.86	36.1 (24.3)	31.2 (21.6)	0.87	7.0 (7.5)	6.0 (7.4)	0.86
HM	12	195.4 (97.4)	148.6 (88.2)	0.76	16.8 (8.8)	13.0 (8.9)	0.77	26.7 (17.3)	18.1 (17.0)	0.68	36.9 (20.7)	30.4 (19.6)	0.82	5.2 (4.1)	3.7 (4.2)	0.71
SG	11	153.9 (66.3)	111.2 (37.2)	0.72	9.9 (4.7)	9.7 (4.2)	0.98	12.8 (5.8)	11.2 (4.6)	0.88	21.5 (10.3)	21.7 (10.3)	1.00	4.6 (2.9)	4.3 (2.9)	0.94
WQ	12	171.7 (84.2)	125.3 (61.8)	0.73	14.5 (6.8)	13.1 (5.4)	0.90	21.7 (11.1)	18.0 (9.3)	0.83	34.7 (14.9)	29.0 (14.8)	0.83	4.4 (2.6)	3.1 (2.3)	0.70
QZ2[a]	288	171.1 (111.7)	n.d.	n.d.[b]	12.9 (12.2)	n.d.	n.d.	19.9 (14.6)	n.d.	n.d.	29.1 (23.1)	n.d.	n.d.	5.5 (5.4)	n.d.	n.d.
SZ	298	138.7 (111.6)	n.d.	n.d.	6.6 (7.7)	n.d.	n.d.	13.7 (13.7)	n.d.	n.d.	15.9 (23.7)	n.d.	n.d.	2.0 (3.3)	n.d.	n.d.

[a] QZ1 and QZ2 mean concentrations of PM_{10}, $PM_{2.5}$ and ions at Quzhou were measured during period 1 (from August 2006 to July 2007) and period 2 (from October 2007 to September 2009), respectively.
[b] Not determined.

3.2. Particulate NH_4^+, NO_3^-, SO_4^{2-} and Cl^- concentrations

Table 2 shows mass concentrations of PM_{10}, $PM_{2.5}$, and inorganic ions (particulate NH_4^+, NO_3^-, SO_4^{2-} and Cl^-) in PM_{10} and $PM_{2.5}$ at the six sites. The mean concentrations of particulate NH_4^+ in PM_{10} ranged from 6.6 to 16.8 µg m^{-3}, while those of $PM_{2.5}$ ranged from 8.8 to 15.5 µg m^{-3} (no data for $PM_{2.5}$ at SZ). The concentrations of particulate NH_4^+ in $PM_{2.5}$ accounted for 77–98% of PM_{10} across the sampling sites (Table 2), indicating that most of the NH_4^+ particles were in the fine fraction. In general, NH_4^+ concentrations increased with the increase of NH_3 emission intensities, with higher concentrations at rural sites than at suburban sites. The seasonal trends in NH_4^+ concentrations were different from those of NH_3. As shown in Fig. 2, NH_4^+ concentrations were higher in summer at suburban sites, but higher in autumn and winter at rural sites. This difference may reflect the influences of primary air pollutants (here taken to be NH_3, NO_x and SO_2) on the formation of secondary ammonium particles (e.g., $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3). In other words, the high NO_x and SO_2 concentrations and relative low NH_3 concentrations at the suburban sites may make the NH_3 concentration a restricting factor in secondary ammonium particle formation, while the high NH_3 concentrations and relatively low NO_x and SO_2 concentrations at the rural sites may make the NO_x and SO_2 concentrations the restricting factors there. Therefore, because NH_3 concentrations were highest in summer at the suburban sites (Fig. 2), and NO_x and SO_2 concentrations highest in winter at the rural sites (Meng et al., 2008; Shen et al., 2009), particulate NH_4^+ concentrations were also highest in summer and winter at the suburban and rural sites, respectively. Similar to NH_3 concentrations, particulate NH_4^+ concentrations in this study were much higher than those measured at agricultural sites worldwide (Hong et al., 2002; Horváth and Sutton, 1998; Walker et al., 2004),

while particulate NH_4^+ concentrations at the suburban sites in Beijing were comparable with those reported at other urban sites in Beijing (He et al., 2001; Wang et al., 2005).

Similar to particulate NH_4^+, concentrations of particulate NO_3^-, SO_4^{2-} and Cl^- were also very high at the sites (Table 2 and Fig. 2). For example, mean concentrations of particulate NO_3^- and SO_4^{2-} in PM_{10} were as high as 12.8–26.7 µg m^{-3} and 15.9–36.9 µg m^{-3}, respectively. The concentrations of these three ions were also much higher than those measured in other regions (Gietl et al., 2008; Hong et al., 2002; Walker et al., 2004), but were comparable with those measured in urban sites with serious pollution problems in China (He et al., 2001; Wang et al., 2005). The masses of particulate NO_3^-, SO_4^{2-} and Cl^- in $PM_{2.5}$ accounted for 68 to almost 100% of those in PM_{10}, indicating that these ions were also comprised of mostly fine particles. The concentrations of particulate NO_3^-, SO_4^{2-} and Cl^- showed different seasonal variations at the sites (Fig. 2). The seasonal variation of particulate NO_3^- was similar to that of particulate NH_4^+, with higher concentrations in summer at suburban sites and in winter at rural sites. Concentrations of particulate SO_4^{2-} were highest in summer and lowest in spring, indicating that SO_2 emission intensity and temperature have important influences on the formation of sulphate (Khoder, 2002). Particulate Cl^- concentrations across the sites were highest in winter and lowest in summer, which corresponds to coal consumption patterns.

3.3. Correlations between particulate NH_4^+ and SO_4^{2-}, NO_3^- and Cl^-

Pearson correlation coefficients between molar concentrations of particulate NH_4^+ and NO_3^-, SO_4^{2-} and Cl^- in PM_{10} and $PM_{2.5}$ are shown in Table 3. There were significant positive correlations between NH_4^+ and NO_3^- as well as NH_4^+ and SO_4^{2-} at the six

Table 3
Correlation coefficients (R^2) between molar concentrations of NH_4^+ and NO_3^-, SO_4^{2-} and Cl^- in PM_{10} and $PM_{2.5}$.

Site	No.	NO_3^- vs NH_4^+		SO_4^{2-} vs NH_4^+		Cl^- vs NH_4^+		($NO_3^- + SO_4^{2-}$) vs NH_4^+		($NO_3^- + SO_4^{2-} + Cl^-$) vs NH_4^+	
		PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
DBW	54	0.768**	0.718**	0.777**	0.796**	0.279**	0.128*	0.903**	0.893**	0.897**	0.874**
QZ1[a]	54	0.884**	0.850**	0.796**	0.776**	0.376**	0.509**	0.954**	0.921**	0.919**	0.928**
HM	12	0.845**	0.801**	0.806**	0.765**	0.414*	0.681**	0.946**	0.942**	0.895**	0.935**
SG	11	0.731*	0.706*	0.758*	0.893**	0.064	0.046	0.814*	0.848*	0.840*	0.841*
WQ	12	0.441*	0.396*	0.799**	0.874**	0.096	0.200	0.825**	0.848**	0.749**	0.773**
QZ2[a]	288	0.783**	n.d.[b]	0.746**	n.d.	0.355**	n.d.	0.860**	n.d.	0.843**	n.d.
SZ	298	0.823**	n.d.	0.788**	n.d.	0.228**	n.d.	0.890**	n.d.	0.866**	n.d.

** significant at 0.01 level, *significant at 0.05 level.
[a] QZ1 and QZ2 mean concentrations of NH_4^+, NO_3^-, SO_4^{2-} and Cl^- at Quzhou were measured during period 1 (from August 2006 to July 2007) and period 2 (from October 2007 to September 2009), respectively.
[b] Not determined.

Table 4
Mean (±standard deviation) molar ratios of aerosol components (NH_4^+, NO_3^-, Cl^- and SO_4^{2-}), with standard deviations in parenthesis, calculated from daily average concentrations in $PM_{2.5}$ and PM_{10} at the sampling sites.

Site	$PM_{2.5}$			PM_{10}		
	NO_3^-/NH_4^+	Cl^-/NH_4^+	NH_4^+/SO_4^{2-}[b]	NO_3^-/NH_4^+	Cl^-/NH_4^+	NH_4^+/SO_4^{2-}
DBW	0.49 ± 0.17	0.16 ± 0.15	1.13 ± 0.66	0.58 ± 0.21	0.19 ± 0.19	0.92 ± 0.66
QZ1[a]	0.39 ± 0.15	0.17 ± 0.11	1.58 ± 0.60	0.41 ± 0.15	0.20 ± 0.15	1.36 ± 0.49
HM	0.38 ± 0.18	0.14 ± 0.12	1.52 ± 0.88	0.44 ± 0.13	0.16 ± 0.10	1.34 ± 0.29
SG	0.35 ± 0.10	0.28 ± 0.21	1.61 ± 0.52	0.43 ± 0.14	0.24 ± 0.17	1.46 ± 0.62
WQ	0.40 ± 0.11	0.14 ± 0.12	1.65 ± 0.84	0.47 ± 0.16	0.17 ± 0.13	1.16 ± 0.37
QZ2[a]	n.d.[c]	n.d.	n.d.	0.47 ± 0.15	0.20 ± 0.15	1.35 ± 0.82
SZ	n.d.	n.d.	n.d.	0.55 ± 0.23	0.19 ± 0.16	1.18 ± 0.84

[a] QZ1 and QZ2 mean concentrations of NH_4^+, NO_3^-, SO_4^{2-} and Cl^- at Quzhou were measured during period 1 (from August 2006 to July 2007) and period 2 (from October 2007 to September 2009), respectively.
[b] NH_4^+ represents the molar concentration of NH_4^+ that is not associated with NO_3^- ($NH_4^+ - NO_3^-$).
[c] Not determined.

sampling sites, and the positive correlations between NH_4^+ and Cl^- were also significant at four sites (DBW, HM, QZ and SZ). However, the correlation coefficients between NH_4^+ and the sum of NO_3^- and SO_4^{2-} at most of the sampling sites were higher than those between NH_4^+ and the sum of NO_3^-, SO_4^{2-} and Cl^-. This indicates that particulate NH_4^+ was probably mainly associated with particulate NO_3^- and SO_4^{2-}, and so particulates are likely to be NH_4NO_3, $(NH_4)_2SO_4$ and/or NH_4HSO_4, which are the secondary products of high concentrations of NH_3, SO_2 and NO_x measured (Table 1).

Further analysis showed that molar ratios of NO_3^-/NH_4^+ and $(NH_4^+ - NO_3^-)/SO_4^{2-}$ were from 0.41 to 0.59 and from 0.95 to 1.43 respectively, across the sites (Table 4). Molar ratios of NO_3^-/NH_4^+ were higher at the suburban sites (DBW and SZ) than at the rural sites (QZ, WQ, HM and SG), corresponding to relatively higher NO_2 concentrations and lower NH_3 concentrations in the suburban sites compared with the rural sites (Table 1). Molar ratios of $(NH_4^+ - NO_3^-)/SO_4^{2-}$ were close to 1.0 at the suburban sites, while they were larger than 1.0 at the rural sites. This indicates that ammonium particles mainly existed as NH_4NO_3 and NH_4HSO_4 at the suburban sites and NH_4NO_3, NH_4HSO_4 and $(NH_4)_2SO_4$ at the rural sites (Walker et al., 2004).

The mean concentrations of secondary inorganic particles (here referring to the sum of NH_4^+, SO_4^{2-} and NO_3^-) across the sites were as high as 36.1–80.4 $\mu g\ m^{-3}$ (with an average of 59.6 $\mu g\ m^{-3}$), which accounted for 24.2–41.2% (with an average of 33.5%) of the PM_{10} concentrations (Table 1). The Chinese Ministry of Environmental Protection had established an ambient standard for PM_{10} of 100 $\mu g\ m^{-3}$ on an annual average basis. The concentration of secondary inorganic particles at our sampling sites sometimes reached 60% of this standard. Furthermore, the concentration of secondary particles exceeded the standard set by the US Environmental Protection Agency for PM_{10} (50 $\mu g\ m^{-3}$ on an annual average basis) at most of the sampling sites. Therefore, a reduction of the concentration of secondary inorganic particles should be a target for the NCP to improve air quality.

3.4. Ratios of NH_3 to NH_x

The ratio of NH_3 to NH_x had 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 dry deposition of NH_3 contributes most to NH_x deposition. NH_4^+ in this system derives from long-range transport and local formation. In contrast, when the ratio of NH_3 to NH_x is less than 0.5, it indicates that atmospheric NH_x is strongly affected by long-range transport of pNH_4^+ and NH_x deposition is dominated by dry and wet

depositions of NH_4^+. Fig. 5 shows the seasonal ratios of NH_3 to NH_x across the sites. The ratios for most of the sites were higher than 0.5 in spring, summer and autumn, while lower than 0.5 in winter with only a few exceptions at HM and DBW (Fig. 5). This suggests that NH_x was strongly influenced by local sources in spring, summer and autumn, while it was mainly affected by long-range transport in winter. It also can be inferred that NH_3 dry deposition could contribute a large part of the NH_x deposition in spring, summer and autumn, but a small part in winter across all the sites. Higher values for the ratio of NH_3 to NH_x at DBW in winter may be caused by NH_3 emitted from vehicles near the sampling sites as NH_3 emission from soils and plants was suppressed due to very cold weather. Lower values at HM in summer were likely caused by the under-estimation of NH_3 concentrations because of the heavy rainfall, as discussed earlier.

3.5. Emission, transport, transformation and deposition of NH_3 in the NCP

Using the monitored and published data, we initially estimated the emission, transport, transformation and deposition of NH_3 in the NCP (Fig. 6). We assumed that the main source of NH_3 emission in the cropland region is NH_3 volatilization from N fertilizer, which was 1.62 Mt NH_3–N yr^{-1} in 2004 as reported by Zhang et al. (2010). When dividing the emission amount by the area of the NCP (about 320,000 km^2), we obtained the averaged NH_3 emission intensity from N fertilizer in the NCP of 51.7 kg NH_3–N yr^{-1}. As it is hard to
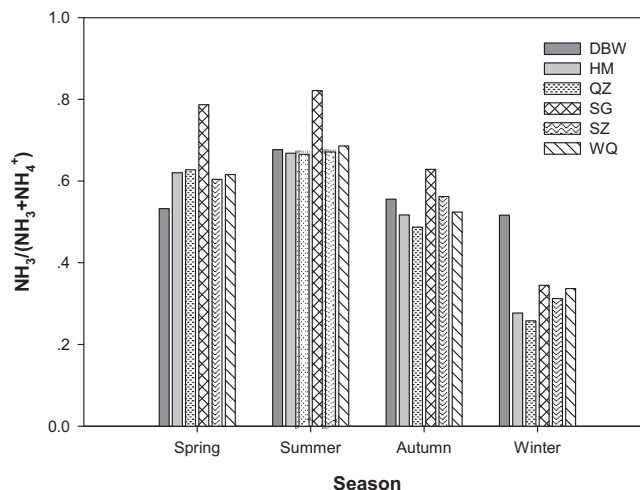

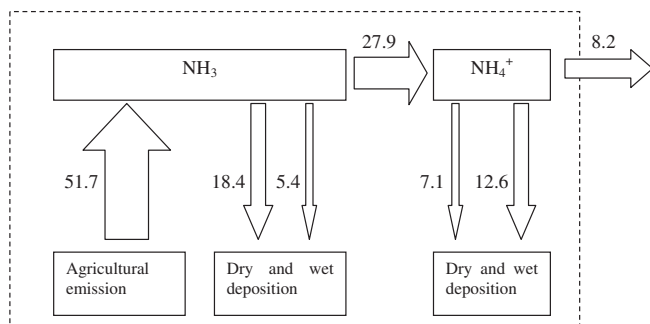**Fig. 5.** Seasonal molar ratios of NH_3 to $NH_3 + NH_4^+$ at the sites.

Fig. 6. An approximation of NH_x emission, transport, transformation and deposition in the cropland regions of the NCP (unit: kg N ha^{-1} yr^{-1}). NH_3 emission intensity was obtained from Zhang et al. (2010). NH_x wet deposition was obtained from Zhang et al. (2008), and the ratio of wet deposition of NH_3 to NH_x was taken to be 0.3, as suggested by Asman (2001). The dry depositions of NH_3 and NH_4 were estimated using the simplified inferential method (Shen et al., 2009).

measure dry deposition of NH_3 and particulate NH_4^+ directly using the micrometeorological methods, the dry deposition rates in this study were calculated from the products of measured NH_3 and NH_4^+ concentrations and literature-based mean dry deposition velocities of NH_3 (0.74 cm s^{-1}) and NH_4^+ (0.24 cm s^{-1}) in agricultural regions (Hanson and Lindberg, 1991). For NH_3, the compensation point (5 µg N m^{-3} as an empirical value in croplands (Denmead et al., 2008)) was subtracted from the mean NH_3 concentration when calculating dry deposition. The calculated mean NH_3 and NH_4^+ dry depositions (18.4 and 7.1 kg N ha^{-1} yr^{-1}, respectively) at the sites in this study were used to represent the approximate mean values in the NCP. For wet deposition, the mean value of NH_x wet deposition during 2004–2005 in the NCP (18.0 kg N ha^{-1} yr^{-1}) as given by Zhang et al. (2008) was used. As there was no discrimination between wet deposition of NH_3 and NH_4^+ by Zhang et al. (2008), here we assumed NH_3 wet deposition accounts for 30% of NH_x deposition as suggested by Asman (2001). As NH_3 has a low residential time (several hours to 5 days) in the atmosphere, we assumed the emitted NH_3 will be completely transformed to NH_4^+ except for that deposited as dry and wet deposition. The calculated amount of NH_3 transformed was 27.9 kg N ha^{-1} yr^{-1}, accounting for 54.0% of the emitted NH_3. As particulate NH_4^+ has a longer residential time, after any dry and wet deposition it can be transported long-distances. Here we estimated that about 8.2 kg NH_4^+–N ha^{-1} yr^{-1} or 0.26 Mt yr^{-1} in total would be transported from the NCP to surrounding terrestrial and marine ecosystems. This may cause secondary aerosol pollution in other regions and negative ecological impacts on natural and semi-natural ecosystems, for example the forests located in the east and west, grasslands to the north, and the Bohai and Yellow Seas in the northeast and east of the NCP. The total NH_x deposition is 43.5 kg N ha^{-1} yr^{-1} with NH_3 and NH_4^+ deposition contributing to 54.7% and 45.3%, respectively. This high NH_x deposition together with moderate NO_x deposition (Zhang et al., 2008; Shen et al., 2009) is another reason for reducing excess N fertilizer application in the

NCP: the overuse of N fertilizer in China (including the NCP) has caused significant acidification of croplands (Guo et al., 2010), large NH_3 volatilization loss and substantial N_2O emission (Ju et al., 2009; Zhu and Chen, 2002) and groundwater nitrate pollution (Zhang et al., 1996).

It should be stressed that all of the data in the Fig. 6 were calculated by simple estimation or were approximate values from the literature. For example, the dry deposition values were not obtained from *in situ* measurement, but from a simple inferential method. The ratio of wet deposition of NH_3 to NH_x was also an empirical value. Besides, the dry and wet deposited NH_4^+ may include that from sources other than N fertilizer, e.g., livestock manure, plants and soils. Thus, the dry and wet deposited NH_4^+ from N fertilizer in the NCP may be overestimated, while the transported NH_4^+ may be underestimated. To obtain a more precise value for NH_3 emission, transport, transformation and deposition in the NCP, we strongly recommend *in situ* measurements of atmospheric concentrations, emissions, and wet and dry deposition of NH_x. Moreover, deposition models such as FRAME (Singers et al., 1998; Kryza et al., 2009), MM5/CMAQ (Wu et al., 2008a, b) should be used to give more detailed data on NH_x net fluxes and transportation between the NCP and surrounding regions.

3.6. The benefits of agricultural NH_3 emission control to atmospheric PM reduction

Using an inorganic aerosol equilibrium model proposed by Ansari and Pandis (1998), we estimated the response of secondary inorganic PM (sum of particulate NH_4^+, NO_3^- and SO_4^{2-}) to NH_3 concentrations at our sites. Data of seasonal concentrations of NH_3, HNO_3, particulate NH_4^+, NO_3^- and SO_4^{2-} as well as air temperature and relative humidity at QZ and SZ were used to calculate the input parameters for the model (Table 5). According to the model, although PM was sensitive to both H_2SO_4 and HNO_3 (d(PM)/d(SO_4^{2-}) = 1–1.34 and d(PM)/d(NO_3^-) = 0.9–1.3) there was a nonlinear response to NH_3 (d(PM)/d(NH_3) = 0.2–3.5) in all four seasons at SZ and in spring and summer at QZ. As shown in Table 5, the free NH_3 ([NH_3(g)] + [NH_4^+(a)] − 2[SO_4^{2-}(a)]) concentrations were very high in most seasons at both sites. Therefore, it can be inferred that inorganic PM would be sensitive to H_2SO_4 or HNO_3. As the total nitrate concentrations ([HNO_3(g)] + [NO_3^-(a)]) were also high at the sites, which suggests that further formation of NH_4NO_3 is possible, there would be a nonlinear response of PM to NH_3. This indicates that reducing NH_3 concentrations could be an effective method for alleviating secondary inorganic PM pollution in the NCP, especially in suburban or urban areas. Using the CMAQ model, Liu et al. (2005) argued that control NH_3 emission was one of the most efficient ways of reducing PM pollution in north China, besides the reduction of primary SO_2, NO_x and aerosol emissions. This is also the case for SO_2 and NO_x as precursors of secondary particles. However, although PM_{10} is routinely measured in large Chinese cities, NH_3, an important precursor of secondary particles, is not (Chan and Yao, 2008). Considering the high PM_{10} and secondary inorganic particle concentrations at both rural and

Table 5
Temperature and relative humidity, averaged concentrations (ppb) of free ammonia (NH_3^F) and total nitrate (HNO_3^T) and gas ratio (GR) in four seasons at QZ and SZ.

Season	QZ					SZ				
	T	RH	NH_3^F	HNO_3^T	GR	T	RH	NH_3^F	HNO_3^T	GR
Spring	Medium	Low	24.1	8.9	2.7	Medium	Low	19.1	8.4	2.3
Summer	High	High	38.7	8.0	4.8	High	High	26.3	8.0	3.3
Autumn	Medium	High	25.3	10.1	2.5	Medium	High	11.8	6.7	1.7
Winter	Low	Low	19.1	12.4	1.5	Low	Low	5.7	5.0	1.1

Note: T: air temperature, RH: relative humidity, NH_3^F = [NH_3(g)] + [NH_4^+(a)] − 2[SO_4^{2-}(a)], HNO_3^T = [HNO_3(g)] + [NO_3^-(a)], GR = NH_3^F/HNO_3^T.

suburban sites in the NCP (Table 2) and the dependence of secondary inorganic particles on local NH_3 emissions, we suggest that NH_3 emissions from agricultural sources should be measured and controlled to improve air quality in the NCP.

4. Conclusions and summary

(1) Atmospheric NH_3 and particulate NH_4^+ concentrations were very high at six agricultural sites in the North China Plain, with annual mean concentrations of NH_3 and NH_4^+ of 15.6 and 12.4 $\mu g\ m^{-3}$, respectively, reflecting high NH_3 emission intensities from agriculture.

(2) Both NH_3 and particulate NH_4^+ concentrations showed distinct spatio-temporal variations. Compared with suburban sites, higher NH_3 and NH_4^+ concentrations were found at rural sites due to large NH_3 emissions from fertilizer N. NH_3 concentrations were highest in summer and lowest in winter at both rural and suburban sites, while highest NH_4^+ concentrations occurred in winter and summer at all six sites. Nitrogen fertilizer application, air temperature and gas-to-particle conversion reactions have important influences on this seasonality.

(3) Annual mean concentrations of secondary NH_4^+ related particles (sum of NH_4^+, SO_4^{2-} and NO_3^-) in PM_{10} were 36.2–80.4 $\mu g\ m^{-3}$ and accounted for 26.1–41.3% of the PM_{10} concentration at the sites. Serious secondary inorganic particle pollution in the NCP 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 concentrations on NH_3 concentrations suggests that controlling NH_3 emission from agricultural sources could be an efficient way to reduce secondary inorganic particle pollution in the NCP, besides the reduction of SO_2 and NO_x emissions from industry, power plants and transport.

(4) NH_x dry and wet deposition averaged 43.5 kg N $ha^{-1}\ yr^{-1}$ at the sites. The heavy NH_x pollution and deposition should be considered in non-point source pollution (e.g., eutrophication) control and integrated cropland N management.

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