Chapter 7
Enrichment of Atmospheric Ammonia and Ammonium in the North China Plain

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Abstract Atmospheric ammonia and ammonium in PM_{10} were measured at six sites (two suburban sites and four rural sites) in the North China Plain (NCP) between August 2006 and September 2009, i.e. for 3 years. The annual mean concentrations of ammonia and ammonium were 7.3–19.9 μg N m^{-3} with an average of 12.8 μg N m^{-3} and 5.6–13.1 μg N m^{-3} with an average of 9.6 μg N m^{-3} respectively, at the sampling sites. Both ammonia and ammonium concentrations were higher at the rural sites than at the suburban sites, highlighting the importance of agricultural sources for atmospheric ammonia and ammonium. Higher ammonia concentrations were observed in the nitrogen (N) fertilization seasons, indicating that ammonia emission from N fertilizer application was an important source of atmospheric ammonia in the NCP. Based on the measured ammonia and ammonium concentrations and their deposition velocities taken from literatures, the annual mean NH_x (NH_3 plus NH_4^+) dry deposition rate was 25.6 kg N ha^{-1} $year^{-1}$ among the six sampling sites. The high NH_x concentrations and dry deposition rates in the NCP indicated agricultural sources were a large contributor to air pollution, and should be taken into account in the control of regional air pollution.

Keywords Ammonia • Dry deposition • Nitrogen deposition • Particulate ammonium

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7.1 Introduction

Ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. Once it has entered the atmosphere, it can deposit to land surface directly in gas form or react with acidic gases (e.g., H_2SO_4, HNO_3 and HCl) to form secondary ammonium particles, aerosols which can then be removed by dry and wet deposition, or be transported long distances (Sutton et al. 1993; Asman et al. 1998). The formation of ammonium particles can affect air quality, human health and solar radiation (Erisman and Schaap 2004; Pinder and Adams 2007; Adams and Seinfeld 2001), while the deposition of ammonia and particulate ammonium can cause eutrophication, acidification and loss of biodiversity in natural and semi-natural ecosystems (Bergström and Jansson 2006; Bouwman et al. 2002; Stevens et al. 2004).

The North China Plain (NCP) is a region with intensive crop and animal production. The overuse of nitrogen (N) fertilizer and inappropriate treatment of animal faeces have led to large NH_3 emissions in recent years. For example, Zhang et al. (2010) estimated NH_3 emissions from dense areas of agricultural sources exceeded 100 kg N ha^{-1} in 2004 in the NCP. High NH_3 emission density in this region suggests a very high NH_x (NH_3 + wet NH_4^+) deposition. Wet deposition monitoring in this region partly supports this trend (Zhang et al. 2008). Dry NH_x deposition monitoring in this region has been hindered by a shortage of monitoring instruments. The objectives of this study were to: (1) monitor concentration dynamics of ammonia and particulate ammonium and reveal the transformation from ammonia to particulate ammonium in the NCP; and (2) infer the dry deposition of NH_x, which mainly originates from agricultural sources, in the NCP.

7.2 Materials and Methods

7.2.1 Sampling Sites

Sampling was conducted at six agricultural sites in the North China Plain. The six sites include Dongbeiwang (DBW), Shangzhuang (SZ), Quzhou (QZ), Huimin (HM), Wuqiao (WQ) and Shouguang (SG). Their locations are shown in Fig. 7.1. DBW and SZ are suburban sites surrounded by small-scale cultivated lands mainly growing winter wheat and summer maize in rotation. QZ, WQ and HM are rural sites surrounded by large-scale cultivated lands for winter wheat, summer maize and cotton production, while SG is the rural site surrounded by large-scale greenhouse vegetable fields.

7.2.2 Sampling Methods and Chemical Analysis

Both passive and particle samplers were used to collect atmospheric NH_3 and particulate NH_4^+ respectively at all the sampling sites. Monthly NH_3 and particulate

Fig. 7.1 Locations of sampling sites in the North China Plain

NH_4^+ concentrations were monitored at DBW (from August 2006 to July 2007), SZ (October 2007 to September 2009) and QZ (from August 2006 to September 2009), while typically seasonal NH_3 and particulate NH_4^+ concentrations were monitored at WQ, HM (from August 2006 to July 2007) and SG (from September 2008 to August 2009). Detailed information about the sampling methods and chemical analysis are reported in Shen et al. (2009).

7.2.3 Estimation of Dry Deposition

Dry deposition (DD) of NH_3 and particulate NH_4^+ were inferred from the measured concentrations (C) and cited deposition velocities (V_d) based on the following function:

$$DD = (C - C_0) \times V_d \quad \text{(Eq. 7.1)}$$

where C_0 is the compensation point. A compensation point of 5 μg N m^{-3}, which is a common value for a variety of crops (Denmead et al. 2008) was used for estimating the dry deposition of NH_3. The compensation point of NH_4^+ was considered to be 0 μg N m^{-3}.

7.3 Results and Discussion

7.3.1 NH_3 Concentrations

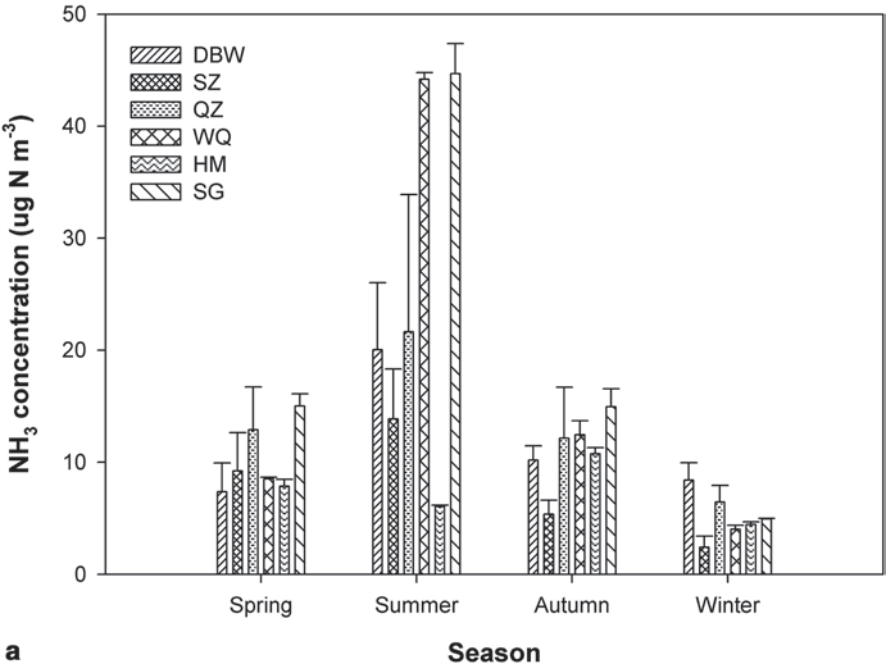
Annual mean NH_3 concentrations ranged between 7.3 and19.9 μg N m^{-3} with an average of 12.8 μg N m^{-3} at the sampling sites (Tab. 7.1). NH_3 concentrations at the rural sites (QZ, WQ, HM and SG) exceeded those at the suburban sites (DBW and SZ), with the exception of much lower NH_3 concentration at HM caused by rainfall scavenging during the summer sampling. As the area of cultivated land in rural areas is much larger than that in suburban sites in the NCP (ca.75% *vs* ca.30%), NH_3 emission intensities from N fertilizer application for crop production are also higher in those rural areas than in suburban areas. Thus greater NH_3 emission rates led to high NH_3 concentrations at rural sites. The NH_3 concentration was highest at SG (Tab. 7.1), where extremely large amounts of N fertilizers (e.g. >2,000 kg N ha^{-1} $year^{-1}$) were used to attain high yields of greenhouse vegetables (Guo et al. 2010).

Ammonia concentrations showed distinct seasonal variation at the six sampling sites (Fig. 7.2). The seasonally averaged NH_3 concentrations across the six sampling sites were 10.1, 25.1, 11.0 and 5.1 μg N m^{-3} respectively, in spring, summer, autumn and winter. Summer NH_3 concentrations were 3.9, 2.5 and 1.3 times higher than NH_3 concentrations in winter, spring and autumn, respectively. Nitrogen fertilizer application and high temperature most likely caused the highest NH_3 emission rates and subsequently higher NH_3 concentrations in the summer. In contrast, the winter temperatures were very low and almost no fertilizers were used, conditions that are not conducive to NH_3 formation. Consequently NH_3 emissions were low at all the sampling sites.

Table 7.1 Estimates of NH_3 and particulate NH_4^+ dry depositions at sampling sites

Site	NH_3 μg N m^{-3}	NH_4^+ μg N m^{-3}	DD_{NH3} kg N ha^{-1} $year^{-1}$	DD_{NH4+} kg N ha^{-1} $year^{-1}$	DD_{NHx} kg N ha^{-1} $year^{-1}$
DBW	11.5	8.0	15.2	6.1	21.3
SZ	7.7	5.6	6.3	4.2	10.5
QZ	13.3	11.7	19.4	8.9	28.3
WQ	17.3	13.1	28.7	9.9	38.6
HM	7.3	11.3	5.4	8.6	14.0
SG	19.9	8.0	34.8	6.1	40.9
Average	12.8	9.6	18.3	7.3	25.6

Dry deposition velocities are 0.74 and 0.24 cm s^{-1} for NH_3 and NH_4^+ respectively according to Hanson and Lindberg 1991
Compensation point for NH_3 is 5 μg N m^{-3} based on Denmead et al. 2008, while that for NH_4^+ is zero



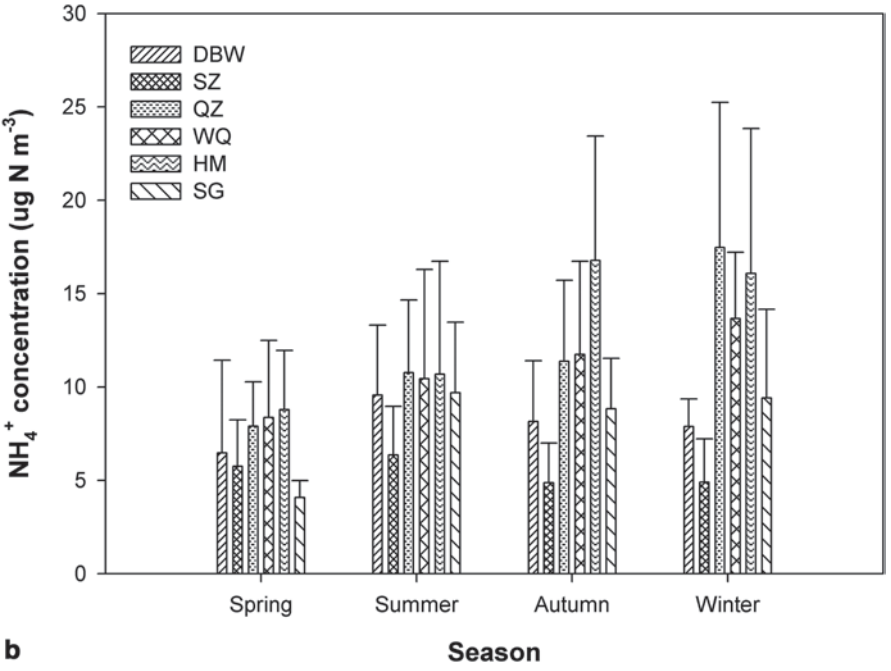


Fig. 7.2 Average concentrations and the standard deviations (mean square errors) of NH_3 (**a**) and particulate NH_4^+ (**b**) in the four seasons at the sampling sites

7.3.2 Particulate NH_4^+ Concentrations

Mean particulate NH_4^+ concentrations ranged from 5.6 to 13.1 μg N m^{-3} with an average of 9.6 μg N m^{-3} at the six sampling sites. NH_4^+ concentrations were also higher at rural sites than at suburban sites. This is likely to be caused by higher NH_3 concentrations at rural sites. The seasonal trends for NH_4^+ concentrations at the sampling sites were different from those for NH_3. As shown in Fig. 7.2, higher NH_4^+ concentration occurred in the summer at the rural sites, compared with autumn and winter at the suburban sites. Different seasonal variation patterns of particulate NH_4^+ at the sampling sites can be ascribed to a number of factors i.e. factors affecting gas to particle conversion, meteorological conditions and rainfall washout, which can influence particulate NH_4^+ concentrations.

A previous study showed that particulate NH_4^+ occurred mainly in the form of fine secondary particles, e.g. $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3, at two sites in the NCP (Shen et al. 2009). In this study, we found higher particulate NH_4^+ concentrations at six sampling sites in the NCP, indicating that particulate SO_4^{2-} and NO_3^- concentrations would also be higher at these sampling sites. The occurrence of high concentrations of secondary particles in the NCP has implications for human health, air quality and solar radiation in this region. For example, heavy PM_{10} pollution has caused high rates of mortality and morbidity in Beijing in recent years (Zhang et al. 2007). In order to reduce the damage caused by these ammonium related particles, it is very important to control NH_3 emissions from agricultural sources (e.g., N fertilization and animal husbandry) in the NCP.

7.3.3 Dry Deposition of NH_3 and NH_4^+.

At the sampling sites, dry deposition rates were inferred based on the measured concentrations and deposition velocities taken from the literature. This enabled estimation of the atmospheric deposition of reduced nitrogen (NH_x) to croplands and its potential impacts on natural and semi-natural ecosystems. As shown in Tab. 7.1, the average NH_x dry deposition was 25.6 kg N ha^{-1} $year^{-1}$. Considering high NH_x wet deposition in the NCP (18 kg N ha^{-1} $year^{-1}$, according to Zhang et al. 2008), the total mean deposition (wet plus dry) of NH_x can be as high as 44 kg N ha^{-1} $year^{-1}$ at the sampling sites. Such levels of NH_x deposition should be considered in N fertilizer management for crop production to improve N fertilizer use efficiency as well as reducing N loss to environment (e.g. atmosphere, groundwater and rivers) in the NCP. The high NH_x deposition may have contributed to eutrophication of lakes (Song et al. 2005) and cropland acidification (Guo et al. 2010) in China. Such negative effects have been documented by many monitoring and modelling experiments worldwide (Bergström and Jansson 2006; Bouwman et al. 2002; Stevens et al. 2004).

7.4 Conclusions

Atmospheric NH_3 and NH_4^+ concentrations (7.3–19.9 μg N m^{-3}) and their dry and wet deposition (average 43.6 kg N ha^{-1} $year^{-1}$) were very high across six monitoring sites in the NCP, reflecting large NH_3 emission from N fertilizer application and intensive domestic livestock production in the region. There were significant spatio-temporal variations of atmospheric NH_3 and NH_4^+ concentrations due to different NH_3 emission intensities and meteorological conditions at different seasons and locations. A number of negative effects originating from high atmospheric ammonium particles and NH_x deposition indicate NH_3 emissions, induced mainly from agricultural sources, should be reduced substantially in the NCP. Further study will be focused on developing more precise NH_x flux measurement techniques as well as reliable measures for controlling NH_3 emission from agricultural production in the NCP.

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References

Adams, P. J., & Seinfeld, J. H. (2001). General circulation model assessment of direct radiative forcing by the sulfate-nitrate-ammonium-water inorganic aerosol system. *Journal of Geophysical Research (Atmospheres)*, *106*(D1), 1097–1111.

Asman, W. A. H., Sutton, M. A., & Schjorring, J. K. (1998). Ammonia: Emission, atmospheric transport and deposition. *New Phytologist, 139,* 27–48.

Bergström, A.-K., & Jansson, M. (2006). Atmospheric nitrogen deposition has caused nitrogen enrichment and eutrophication of lakes in the northern hemisphere. *Global Change Biology, 12,* 635–643.

Bouwman, A. F., Van Vuuren, D. P., Derwent, R. G., & Posch, M. (2002). A global analysis of acidification and eutrophication of terrestrial ecosystems. *Water, Air & Soil Pollution, 141,* 349–382.

Denmead, O. T., Freney, J. R., & Dunin, F. X. (2008). Gas exchange between plant canopies and the atmosphere: Case-studies for ammonia. *Atmospheric Environment, 42,* 3394–3406.

Erisman, J. W., & Schaap, M. (2004). The need for ammonia abatement with respect to secondary PM reductions in Europe. *Environmental Pollution, 129,* 159–163.

Guo, J. H., Liu, X. J., Zhang, Y., Shen, J. L., Han, W. X., Zhang, W. F., Christie, P., Goulding, K., Vitousek, P., & Zhang, F. S. (2010). Significant soil acidification in major Chinese croplands. *Science, 327,* 1008–1010.

Hanson, P. J., & Lindberg, S. E. (1991). Dry deposition of reactive nitrogen compounds: A review of leaf, canopy and non-foliar measurements. *Atmospheric Environment, 25A*, 1615–1634.

Pinder, R. W., & Adams, P. J. (2007). Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the eastern United States. *Environmental Science & Technology, 41,* 380–386.

Shen, J. L., Tang, A. H., Liu, X. J., Fangmeier, A., Goulding, K. T. W., & Zhang, F. S. (2009). High concentrations and dry deposition of reactive nitrogen species at two sites in the North China Plain. *Environmental Pollution, 157,* 3106–3113.

Song, Y. Z., Qin, B. Q., Yang, L. Y., Hu, W. P., & Luo, L. C. (2005). Primary estimation of atmospheric wet deposition of Nitrogen to aquatic ecosystem of lake Taihu. *Journal of Lake Sciences*, *17*(3), 226–230 (in Chinese).

Stevens, C. J., Dise, N. B., Mountford, J. O., & Gowing, D. J. (2004). Impact of nitrogen deposition on the species richness of grasslands. *Science, 303,* 1876–1879.

Sutton, M. A., Pitcairn, C. E. R., & Fowler, D. (1993). The exchange of ammonia between the atmosphere and plant communities. *Advances in Ecological Research, 24,* 301–393.

Zhang, M. S., Song, Y., & Cai, X. H. (2007). A health-based assessment of particulate air pollution in urban areas of Beijing in 2000–2004. *Science of the Total Environment, 376,* 100–108.

Zhang, Y., Liu, X. J., Fangemeier, A., Goulding, K. T. W., & Zhang, F. S. (2008). Nitrogen inputs and isotopes in precipitation in the North China Plain. *Atmospheric Environment, 42,* 1436–1448.

Zhang, Y., Dore, A. J., Ma, L., Liu, X. J., Ma, W. Q., Cape, J. N., & Zhang, F. S. (2010). Agricultural ammonia emissions inventory and spatial distribution in the North China Plain. *Environmental Pollution, 158,* 490–501.