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Evidence for organic N deposition and its anthropogenic sources in China

Ying Zhang[1], Lixia Zheng[1], Xuejun Liu[1,*], Tim Jickells[2], John Neil Cape[3], Keith Goulding[4], Andreas Fangmeier[5], and Fusuo Zhang[1, *]

[1] College of Resource and Environmental Sciences, China Agricultural University, Beijing 100094, China; [2] School of Environment Sciences, University of East Anglia, Norwich, NR4 7TJ, UK; [3] Centre for Ecology and Hydrology, Bush Estate, Penicuik, EH26 0QB, UK; [4] Rothamsted Research, Harpenden, Herts, AL5 2JQ, UK; [5] Institute for Landscape and Plant Ecology, University of Hohenheim, Stuttgart 70593, Germany.

* To whom correspondence should be addressed, E-mail: xuejun.13500@gmail.com, zhangfs@cau.edu.cn.

Abstract

Organic nitrogen (N) is an important component of the atmospheric deposition of reactive N, but its sources are essentially unknown. Assessing whether this dissolved organic N (DON) is of natural, anthropogenic or mixed origin is critically important in attempting to determine the scale of human perturbation of the global N cycle. Here we report evidence for atmospheric organic N deposition and its anthropogenic sources in China. Precipitation samples were collected and analyzed from fifteen rural, suburban and urban sites during 2005 and 2006. The average deposition of DON was 8.6 kg ha^{-1} yr^{-1} with a volume-weighted concentration of 111 μmol L^{-1}, which was much higher than in other regions of the world. The contribution of DON to total dissolved N (TDN) was approximately 30% on average, agreeing well with other reported data in the literature. Parallel collections of wet-only and bulk deposition showed wet deposition to be 68% on average, indicating a significant dry deposition component. Combining data from the Chinese sites with those from elsewhere in the world, significant ($p<0.0001$) correlations between DON and NH_4-N, NO_3-N and TDN suggest that atmospheric organic N originates from similar sources to dissolved inorganic N (DIN) (NH_4-N and NO_3-N), which are largely attributed to anthropogenic emissions from both agricultural and industrial sources.

Keywords: Atmospheric deposition, organic N, inorganic N, anthropogenic sources

1. Introduction

The global N cycle is being greatly perturbed by human activity and, in turn, impacts on ecosystems causing further global change. A very significant component of the perturbed global N cycle is the atmospheric

transport of fixed N (Holland et al., 1999; Paerl and Whitall, 1999; Matson et al., 2002; Galloway et al., 2004). Organic N represents an important component of atmospheric N (Cornell et al., 1995; Keene et al., 2002; Cape et al, 2004), but its sources are essentially unknown (Cornell et al., 2003). Assessing whether this material is of natural, anthropogenic or mixed origin is critically important in attempting to determine the scale of human perturbation of the atmospheric N cycle.

Atmospheric organic N probably comprises a wide range of compounds from volatile gases through to aerosols, with both primary (e.g. soil re-suspension, soot particles) and secondary production processes, e.g. the reaction of atmospheric oxidised (e.g. nitric acid) and reduced (e.g. ammonia) N gas phase species with gas or aerosol organic matter. Investigation of individual compounds (Cornell et al., 2003) or the isotopic composition of atmospheric organic N (Kelly et al., 2005) has failed to provide clear evidence of whether anthropogenic or natural sources dominate, although it appears that most of the carbon is of natural origin (Kelly et al., 2005). An alternative approach to identifying the source is to investigate relationships between organic N and ammonium and nitrate in the atmosphere, which are known to be predominantly of anthropogenic origin except in the most remote regions of the world. This approach has been tried before on data from particular regions with results that suggest a relationship, but it is only a weak one (Cape et al., 2004; Neff et al., 2002). Here we have re-evaluated the relationship between atmospheric organic N and inorganic N deposition from a number of sites around the world, incorporating new data from China. Since the Chinese data are new we present the methods by which it was measured and its interpretation before combining it with other published data to consider the global pattern. The objective of this study is to gauge the magnitude of organic N deposition in China, where N deposition is known to be high (Liu et al., 2006; Zhang et al., 2006; He et al., 2007; Zhang et al., in press), and the origins of atmospheric organic N in China and worldwide.

2. Material and Methods

2.1. Monitoring sites

Rain samples were collected at fifteen monitoring sites (Fig.1; Table 1) in China, mainly from the North China Plain (NCP) (sites 1-9). Other sites were from the Northeast China (site 10), the Changjiang River Delta (site 11), an Inner Mongolian pasture area (site 12), Northwest China (site 13) and the Tibetan

Altiplano (sites 14 and 15). The monitoring sites were located in different ecosystems such as farmland, coast, pasture and forest. The location and monitoring period for each site are shown in Fig.1 and Table 1.

2.2. Collection, storage and measurement of rainwater

Precipitation samples (bulk deposition) were collected daily using a stainless steel bucket (SDM6, Tianjin Weather Equipment Inc., China). The buckets were cleaned with deionized water before rain collection to avoid contamination (e.g. from bird faeces). Chloroform (1 ml L^{-1}) was added to inhibit the growth of micro-organisms and subsequent N transformation. Rainwater samples were filtered (0.45 μm pore size) and stored at -20 ^{o}C until analysis to avoid transformation of organic N (Cornell et al., 2003; Cape et al., 2001).

DIN (NH_4-N and NO_3-N) in rainwater was analyzed with a Continuous Flow Analyzer (TRAACS 2000, Bran-Luebbe Inc., Germany). TDN in rainwater was analyzed using the alkaline persulfate-oxidation (to nitrate) method (Bronk et al., 2000) followed by ultraviolet spectrophotometry (Shimadzu UV-2201, Shimadzu Inc., Japan). Organic N was then calculated by difference (TDN minus DIN).

Three Automatic Wet-only Samplers (APS series, Wuhan Tianhong Inc., China), which collected rainwater samples only while the rainfall was occurring based on detection by rain sensors were separately installed at DBW, QZ and WQ (for the site key see Fig 1). The collection and analysis of wet deposition were the same as for bulk deposition.

2.3. Statistical analysis

We used linear regression to analyze the relationship between DON and NH_4-N, NO_3-N and TDN in precipitation and report significant correlations (if $p<0.05$, 0.001 or 0.0001).

3. Results and discussion

3.1. Spatial variation of DON deposition

Volume-weighted concentrations, deposition and the proportion in the total deposition of NH_4-N, NO_3-N and DON at the 15 sites are summarized in Fig.2. DON concentration ranged from 14-176 μmol L^{-1} (Fig. 2a), averaged 111 μmol L^{-1}, and varied greatly between sites. In NCP (Fig 1b), the intensive agricultural area where DIN deposition was very high (Zhang et al., in press), the concentration of DON ranged from 43 to

151 μmol L^{-1}. Both higher concentrations and deposition were found at CEF, DBW and HM (Fig 2a, 2b). Sites CEF and DBW are located in sub-urban areas, exposed to multi-pollutant emissions, while HM is located in a typical intensive agricultural region with large N fertilizer applications. At a national scale, the DON concentration at UR, also located in farmland, was comparable with other areas, but the deposition was very low because of the lower rainfall (<200mm) in this arid region. The lowest deposition was found at DL in Inner Mongolia, a semi-arid temperate pasture region with little agricultural activity. At DA, QD and FH sites in the coastal area, both the concentration and deposition of DON are relatively high, accounting for its greater contribution to TDN compared with inorganic N. The N deposition at these three sites is probably influenced by both agricultural and coastal sources. Considerably higher proportions of DON to TDN (79% and 72%) compared to other sites were found at GGS and LZ (Fig. 2c) in the remote Tibetan area (almost) without anthropogenic influence, suggesting a significant natural background of DON deposition. The lower DIN concentrations and depositions here agreed with other data in the same Tibetan area (Ren et al., 1999; Kang et al., 2000), but this is the first time that a major contribution of DON to atmospheric N deposition, probably from natural sources, has been reported.

The contribution of DON to TDN deposition was very variable across the fifteen monitoring sites and ranged from 4% to 79%, being about 30% on average (Fig. 2c). This is consistent with results observed at other sites around the world (Peierls et al., 1997; Russell et al., 1998; Scudlark et al., 1998; Morales et al., 2001; Keene et al., 2002; Cape et al., 2004; Möller et al., 2005; Ham and Tamiya, 2006; Ham et al., 2006; Calderón et al., in press). However, the DON concentrations at most sites in China were substantially higher (with a median value of 117 μmol L^{-1}) compared to other sites around the world (with a median value of 13 μmol L^{-1}) (Fig.3). The maximum TDN concentration was up to 412 μmol L^{-1}. Taking the rainfall into account, the annual TDN deposition ranged from 6 to 54 kg ha^{-1} yr^{-1}, being 29 kg ha^{-1} yr^{-1} on average. The 30% contribution of DON to TDN shows that DON must be measured when estimating TDN and its potential ecological significance (Näsholm et al., 1998; Breemen, 2002; Weigelt et al., 2003).

3.2. Difference of DON from bulk and wet deposition

DON in both bulk and wet-only deposition was measured at three sites: DBW, QZ and WQ (Table 2). Volume-weighted DON concentrations in bulk deposition (145-161 μmol L^{-1}) were consistently higher than those in wet-only deposition (62-150 μmol L^{-1}). The proportion of wet/bulk deposition for DON was

68% on average, and 80% and 77% respectively for inorganic N and total N deposition, with small variations across the three sites. The lower contribution of DON to TDN in wet deposition implied that a larger proportion of DON occurred as dry deposition - particulates, aerosols and reactive gases. Considering that all three sites are located in agricultural areas and the difference between bulk and wet deposition arises mainly from coarse size particulates, we suggest that atmospheric dust, bacteria, organic debris, pollen and spores were the main sources.

3.3. Relationship between organic N and ammonium, nitrate and total N in precipitation

No significant correlation was found between volume-weighted DON and NH_4-N, NO_3-N and TDN concentrations in precipitation at the 15 sites in China. However, robust positive correlations (Fig. 4) were found between volume-weighted DON and NH_4-N, NO_3-N and TDN concentrations in precipitation after data from another 37 sites around the world are included (Scudlark et al., 1998; Russell et al., 1998; Campbell et al., 2000; Cornell et al., 2001; Neff et al., 2002; Mace et al., 2003a, b; Cape et al., 2004; Ham and Tamiya, 2006; Ham et al., 2006). The slope of the relationship between DON and TDN implies that organic N represents approximately 22% (R^2=0.68, $p<0.0001$) of TDN deposition (Fig. 4c), consistent with other estimates (e.g. Cornell et al., 2003; Keene et al., 2002; Nakamura et al., 2007).

The positive correlations between DON and NH_4-N (R^2=0.38, $p<0.0001$) and NO_3-N (R^2=0.46, $p<0.0001$) suggest the same (or at least similar) origins for a substantial component of the organic, ammonium and nitrate N. We therefore interpret the relationships in Fig. 4 to mean that organic N deposition on a global scale has a significant anthropogenic component and should be treated as an enhancement of the global N cycle rather than as only a component of the natural background, although there were two sites in our study and other sites from remote locations that show a natural DON source as well. Our results do not identify the specific sources of organic N deposition, but if the carbon component is of natural origin (Kelly et al., 2005) and the nitrogen of anthropogenic origin, this implies an important role for its formation by gas to particle reactions, consistent with the limited aerosol size distribution data available for aerosol organic N, although an important dust related DON component has been identified as well in the work of Mace et al. (2003b).

4. Conclustion

We found clear evidence of atmospheric organic N deposition in China for the first time. The flux of DON deposition ranged from 1 to 27 kg ha^{-1} a^{-1}. The volume-weighted concentration of DON in rain in China was 111 μmol L^{-1}, much higher than the average reported values for the rest of the world. DON deposition comprised approximately 30% of TDN deposition, agreeing well with other data from around the world, although as in other studies this proportion is very variable. This relatively constant proportion of DON and the strong correlation between DON and DIN deposition suggest similar origins, which are largely attributed to anthropogenic emissions from both agricultural and industrial sources.

Acknowledgements

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References

Breemen, N., 2002. Natural organic tendency. Nature **415**, 381-382.

Bronk, D.A., Lomas, M.W., Glibert, P.M., Schukert, K.J., Sanderson, M.P., 2000. Total dissolved nitrogen analysis: comparisons between the persulfate, UV and high temperature oxidation methods. Marine Chemistry **69**, 163-178.

Calderón, S. M., Poor, N.D., Campbell, S.W. Estimation of the particle and gas scavenging contribution to wet deposition of organic nitrogen. Atmospheric Environment, in press.

Campbell, J.L., Hornbeck, J.W., McDowell, W.H., Buso, D.C., Shanley, J.B., Linkens, G.E., 2000. Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry **49**, 123-142.

Cape, J.N., Anderson, M., Rowland, A.P. & Wilson, D. 2004. Organic nitrogen in precipitation across the United Kingdom. Water, Air, and Soil Pollution: Focus **4**, 25-35.

Cape, J.N., Kirika, A., Rowland, A.P., Wilson, D.S., Jickells, T.D., Cornell, S., 2001. Organic nitrogen in precipitation: real problem or sampling artefact? The Scientific World **1**(S2), 230–237.

177 Cornell, S., Rendell, A., Jickells, T., 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans.
178 Nature **376**, 243-246
179 Cornell, S.E., Jickells, T.D., Cape, J.N., Rowland, A.P., Duce, R.A., 2003. Organic nitrogen deposition on
180 land and coastal environments: a review of methods and data. Atmospheric Environment **37**,
181 2173-2191.
182 Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asener, G.P.,
183 Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R.,
184 Vörösmarty, C.J., 2004. Nitrogen cycles: past, present, and future. Biogeochemistry **70**, 153-226.
185 Ham, Y., Tamiya, S., 2006. Contribution of dissolved organic nitrogen deposition to total dissolved nitrogen
186 deposition under intensive agricultural activities. Water, Air & Soil Pollution **178**, 5-13.
187 Ham, Y., Tamiya, S., Choi I., 2006. Contribution of dissolved organic nitrogen deposition to nitrogen
188 saturation in a forested mountainous watershed in Tsukui, Central Japan. Water, Air & Soil Pollution
189 **178**, 113-120.
190 Hayashi, K., Komada, M., Miyata, A., 2007. Atmospheric deposition of reactive nitrogen on turf grassland
191 in Central Japan: comparison of the contribution of wet and dry deposition. Water Air & Soil Pollution:
192 Focus **7**, 119-129.
193 He, C., Liu, X., Fangmeier, A., Zhang, F., 2007. Quantifying the total airborne nitrogen input into
194 agroecosystems in the North China Plain. Agriculture, Ecosystem & Environment **121**, 395-400.
195 Holland, E.A., Dentener, F.J., Braswell, B.H., Sulzman, J.M., 1999. Contemporary and pre-industrial global
196 reactive nitrogen budgets. Biogeochemistry **46**, 7-43.
197 Kang, S.C., Qin, D.H., Yao, T.D., Ren, J.W., 2000. A study on precipitation chemistry in the late summer in the
198 northern slope of Mt. Xixiabangma. Acta Scientiae Circumstantiae **20**, 574-578.
199 Keene, W.C., Montag, J.A., Maben, J.R., Southwell, M., Leonard, J., Church, T.M., Moody, J.L., Galloway,
200 J.N., 2002. Organic nitrogen in precipitation over Eastern North America. Atmospheric Environment
201 **36**, 4529-4540.
202 Kelly, S.D., Stein, C., Jickells T.D. 2005. Carbon and nitrogen isotopic analysis of atmospheric organic
203 matter. Atmospheric Environment **39**, 6007-6011.
204 Liu, X., Ju, X., Zhang, Y., He, C., Kopsch, J., Zhang, F., 2006. Nitrogen deposition in agroecosystems in the
205 Beijing area. Agriculture, Ecosystems & Environment **113**, 370-377.

206 Mace, K.A., Duce, R.A., Tindale, N.W. 2003a. Organic nitrogen in rain and aerosol at Cape Grim,
207 Tasmania, Australia. Journal of Geophysical Research **108**, doi:10.1029/2002JD003051.
208 Mace, K.A., Kubilay, N.; Duce, R.A., 2003b. Organic nitrogen in rain and aerosol in the eastern
209 Mediterranean atmosphere: An association with atmospheric dust. Journal of Geophysical Research **108**,
210 doi:10.1029/2002JD002997.
211 Matson, P., Lohse, D.A., Hall, S.J., 2002. The globalization of nitrogen deposition: consequences for
212 terrestrial ecosystems. Ambio **31**, 113-119.
213 Morales, J.A., Sanchez, L., Velasquez, H., Borrego, B., Nava, M., Portillo, D., Cana, Y., Morillo, A.,
214 Albornoz, A., Socorro, E., 2001. Nutrient loading by precipitation in the maracaibo lake basin,
215 Venezuela. Water, Air & Soil Pollution **130**, 511-516.
216 Möller, A., Kaiser, K., Guggenberger, G., 2005. Dissolved organic carbon and nitrogen in precipitation,
217 throughfall, soil solution, and stream water of the tropical highlands in northern Thailand. Journal of
218 Plant Nutrition and Soil Science **168**, 649-659.
219 Nakamura, T., Ogawa, H., Maripi, D. K., Uematsu, M., 2006. Contribution of water soluble organic nitrogen
220 to total nitrogen in marine aerosols over the East China Sea and western North Pacific. Atmospheric
221 Environment **40**, 7259-7264.
222 Näsholm, T., Ekblad, A., Nordin, A., Giesler, R., Högberg, M., Högberg, P., 1998. Boreal forest plants take
223 up organic nitrogen. Nature **392**, 914-916.
224 Neff, J.C., Holland, E.A., Dentener F.J., McDowell W.H., Russell K.M., 2002. The origin, composition and
225 rates of organic nitrogen deposition: A missing piece of the nitrogen cycle? Biogeochemistry **57/58**,
226 99-136.
227 Paerl, H.W., Whitall, D.R., 1999. Anthropogenically-derived atmospheric nitrogen deposition, marine
228 eutrophication and harmful algal bloom expansion: is there a link? Ambio **28**, 307-311.
229 Peierls, B.L., Paerl, H.W., 1997. Bioavailability of atmospheric organic nitrogen deposition to coastal
230 phytoplankton. Limnol Oceanogr **42**, 1819-1823.
231 Ren, J., 1999. A study of chemical characteristics of snow, precipitation and surface water in the basin of the
232 Glacier No.29 in Danghe Nanshan, Qilian Mountains. Journal of Glaciology and Geocryology **21**, 151-154.
233 Russell, K.M., Galloway, J.N., Macko, S.A., Moody, J.L., Scudlark, J.R., 1998. Sources of nitrogen in wet
234 deposition to the Chesapeake Bay region. Atmospheric Environment **32**, 2453-2465.
235 Scudlark, J.R., Russell, K.M., Galloway, J.N., Church, T.M., Keene, W.C., 1998. Organic nitrogen in

precipitation at the Mid-Atlantic U.S. coast-methods evaluation and preliminary measurements. Atmospheric Environment **32**, 1791-1728.

Weigelt, A., King, R., Bol, R., Bardgett, R.D., 2003. Inter-specific variability in organic nitrogen uptake of three temperate grassland species. Journal of Plant Nutrition and Soil Science **166**, 606-611.

Zhang, Y., Liu, X.J., Zhang, F.S., Ju X.T., Zou G. Y., Hu K. L., 2006. Spatial and teporal variation of atmospheric nitrogen deposition in North China Plain. Acta Ecological Sinica **26**, 1633-1639.

Zhang, Y., Liu, X.J., Fangmeier, A., Goulding, K.T.W., Zhang, F.S.. Nitrogen inputs and isotopes in precipitation in the North China Plain. Atmospheric Environment, in press.

245 **Table 1.** Location and monitoring periods of the 15 sites in China in this study.

Site No.	Location	Monitoring periods	Type of site
1	Changping (CP), Beijing	2005.5-2006.10	Farmland
2	Campus Experimental Farm (CEF) of China Agricultural University, Beijing	2005.5-2006.11	Farmland & sub-urban
3	Dongbeiwang (DBW), Beijing	2005.2-2006.11	Farmland & sub-urban
4	Shunyi (SY), Beijing	2005.5-2006.10	Farmland
5	Baoding (BD), Heibei	2005.10-2006.8	Farmland
6	Quzhou (QZ), Hebei	2005.5-2006.10	Farmland
7	Wuqiao (WQ), Hebei	2005.5-2006.10	Farmland
8	Huimin (HM), Shandong	2005.10-2006.12	Farmland
9	Qingdao (QD), Shandong	2006.3-2006.12	Farmland & coastal
10	Dalian (DA), Liaoning	2006.2-2006.12	Farmland & coastal
11	Fenghua (FH), Zhejiang	2004.12-2005.9	Farmland & coastal
12	Duolun (DL), Inner Mongolia	2006.5-2006.10	Pasture
13	Urumchi (UR), Xingjiang	2006.3-2006.10	Farmland
14	Gonggashan (GGS), Sichuan	2005.10-2006.7	Forest
15	Linzhi (LZ), Tibet	2005.5-2006.12	Forest

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247 **Table 2.** Comparison of bulk and wet DON deposition at DBW, QZ and WQ sites.

Site	No.*	Bulk (μmol/L)			Wet (μmol/L)			Ratio of Wet/Bulk		
		DIN	DON	TDN	DIN	DON	TDN	DIN	DON	TDN
DBW	47	433	152	586	336	62	397	0.77	0.40	0.68
QZ	27	446	145	591	339	99	438	0.76	0.68	0.74
WQ	20	292	161	454	263	150	413	0.90	0.93	0.91
Mean	31	390	153	543	313	103	416	0.80	0.68	0.77

248 * Rain events here only refer those collections including both wet and bulk deposition during the same

249 period (DBW from May 2003 to Sep 2005, QZ and WQ from May to Sep 2005).

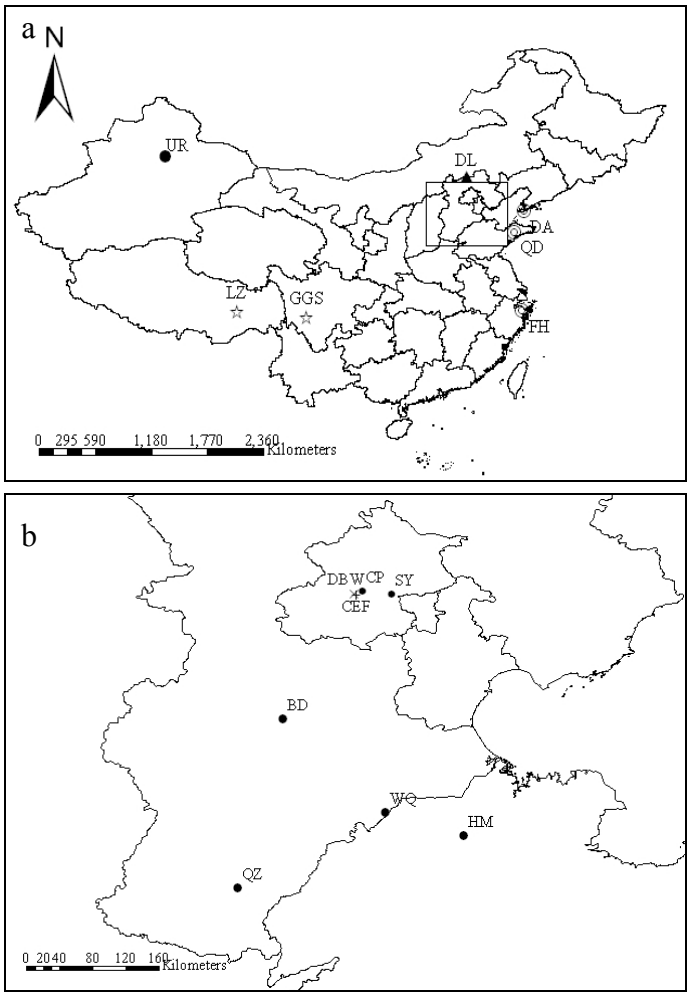


Figure 1. Distribution of the monitoring sites in China (a) and the North China Plain (b). Site symbols in the figure denote different ecosystems (● farmland; ▲ pasture; □ farmland in coastal area; □ forest; × farmland in sub-urban area; + farmland and husbandry in sub-urban area).

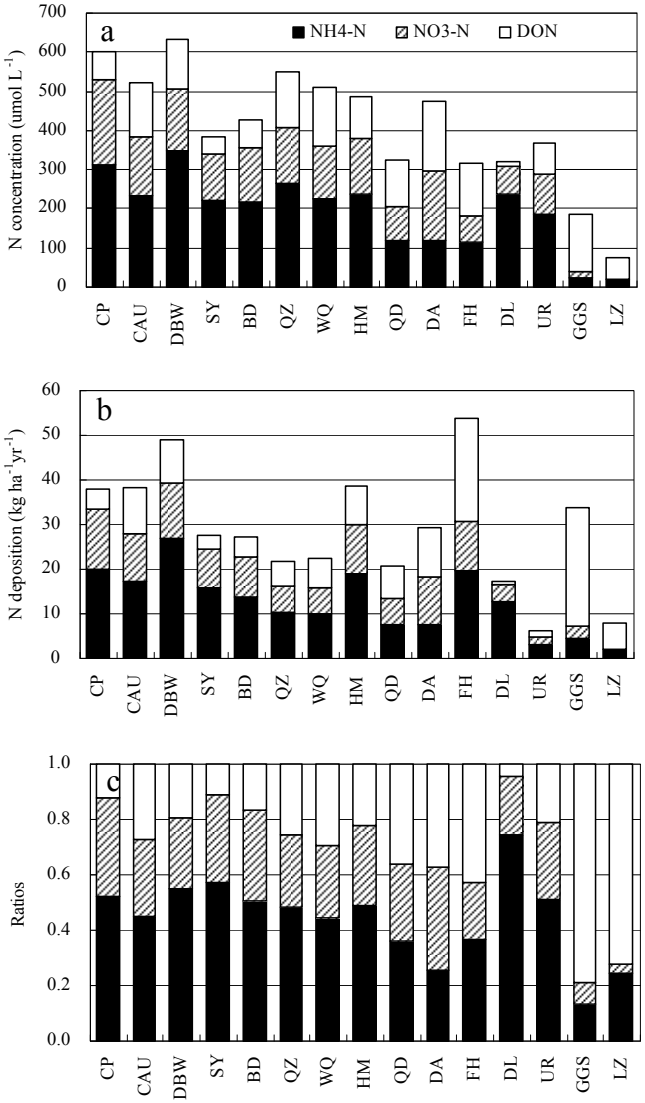


Figure 2. Atmospheric bulk N deposition at the 15 monitoring sites used in this study. (a. volume-weighted concentration of NH_4-N, NO_3-N and DON (μmol L^{-1}); b. annual deposition of NH_4-N, NO_3-N and DON (kg ha^{-1} yr^{-1}); c. ratios of NH_4-N, NO_3-N and DON to TDN).

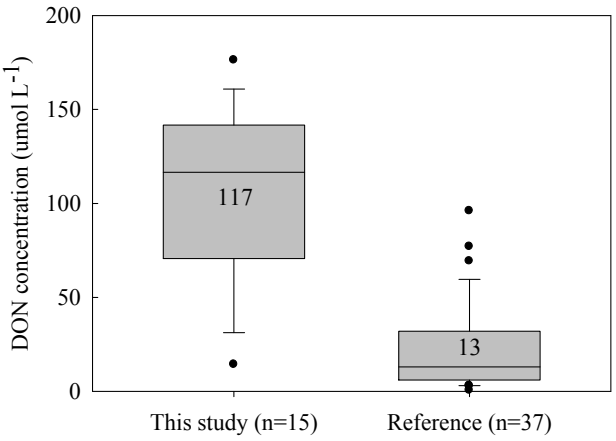
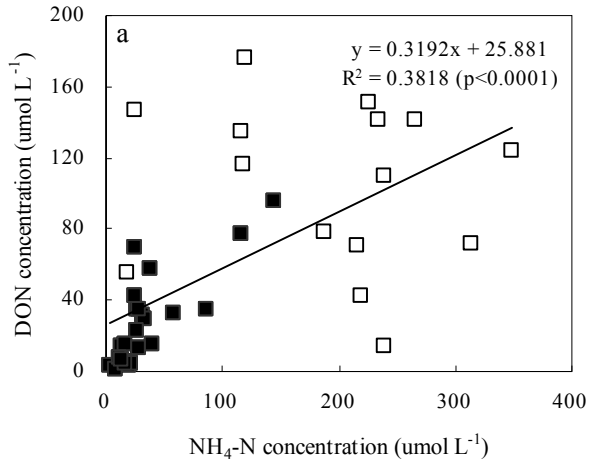


Figure 3. Distribution of the organic N concentration from precipitation in this study and other references (Cornell et al., 1995; Peierls et al., 1997; Russell et al., 1998; Scudlark et al., 1998; Campbell et al., 2000; Morales et al., 2001; Keene et al., 2002; Cape et al., 2004; Möller et al., 2005; Ham and Tamiya, 2006; Ham et al., 2006; Hayashi et al., 2007; Calderón et al., in press). The numbers in the boxes are median values.



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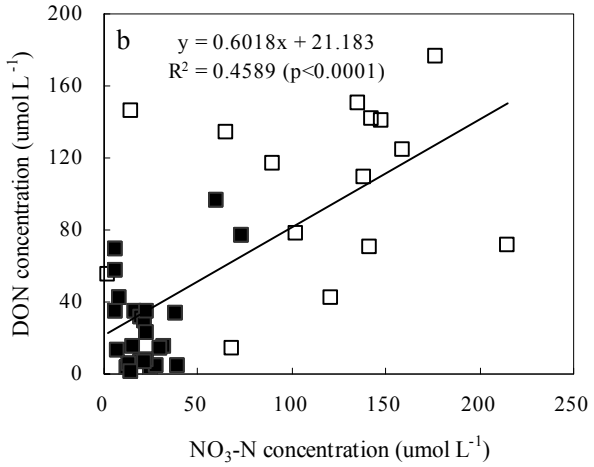

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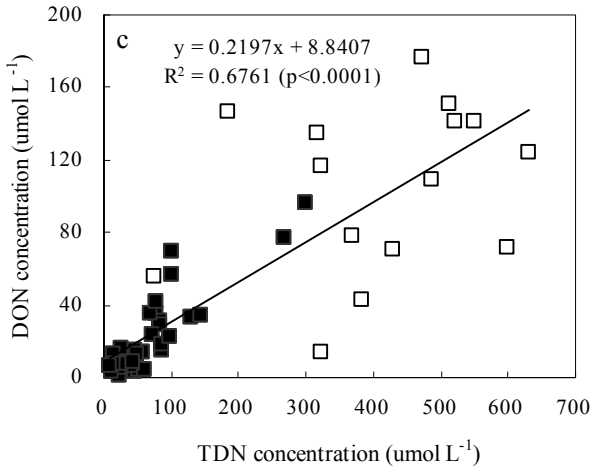

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274 **Figure 4.** Relationship between volume-weighted DON and NH_4-N (a), NO_3-N (b) and TDN (c) in
275 precipitation (bulk deposition) at the 15 sites in China (□) and 37 sites in other regions around the world (■)
276 (Cornell et al., 1995; Peierls et al., 1997; Russell et al., 1998; Scudlark et al., 1998; Campbell et al., 2000;
277 Morales et al., 2001; Keene et al., 2002; Cape et al., 2004; Möller et al., 2005; Ham and Tamiya, 2006; Ham
278 et al., 2006; Hayashi et al., 2007; Calderón et al., in press).