Chinese coastal seas are facing heavy atmospheric nitrogen deposition

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Received 29 May 2014, revised 7 July 2014
Accepted for publication 18 August 2014
Published 24 September 2014

Abstract
As the amount of reactive nitrogen (N) generated and emitted increases the amount of N deposition and its contribution to eutrophication or harmful algal blooms in the coastal zones are becoming issues of environmental concern. To quantify N deposition in coastal seas of China we selected six typical coastal sites from North to South in 2011. Concentrations of NH3, HNO3, NO2, particulate NH4+ (pNH4+) and pNO3− ranged from 1.97–4.88, 0.46–1.22, 3.03–7.09, 2.24–4.90 and 1.13–2.63 μg N m−3 at Dalian (DL), Changdao (CD), Linshandao (LS), Fenghua (FH), Fuzhou (FZ), and Zhanjiang (ZJ) sites, respectively. Volume-weighted NO3−–N and NH4+–N concentrations in precipitation varied from 0.46 to 1.67 and 0.47 to 1.31 mg N L−1 at the six sites. Dry, wet and total deposition rates of N were 7.8–23.1, 14.2–25.2 and 22.0–44.6 kg N ha−1 yr−1 across the six coastal sites. Average N dry deposition accounted for 45.4% of the total deposition and NH3 and pNH4+ contributed to 76.6% of the dry deposition. If we extrapolate our total N deposition of 33.9 kg N ha−1 yr−1 to the whole Chinese coastal sea area (0.40 million km2), total N deposition amounts to 1.36 Tg N yr−1, a large external N input to surrounding marine ecosystems.

Keywords: reactive N, atmospheric deposition, coastal sea, eutrophication, China

1. Introduction

Human activities have generated increasingly more reactive nitrogen (N) since 1860, the symbolic year of the industrial revolution, because of increased food production and energy consumption worldwide (Galloway et al 2008). China is the world’s largest consumer of fertilizer N, with annual fertilizer N consumption of about 32 Tg N (Guo et al 2010). Power plants and transportation are the important sectors for NOx emissions in China. During 2000–2010 the installed capacity of thermal power plants and the vehicle population increased by 195% and 300%, respectively (Wang and Hao 2012). All of these human activities have led to large NH3 and NOx...
emissions and have resulted in elevated N deposition especially over the last three decades (Liu et al. 2013, Cui et al. 2013). Negative impacts of N deposition include reduction of species diversity and altered biological productivity and soil acidification and eutrophication (Allen et al. 2011, Erisman et al. 2013), and have affected the Earth’s climate system via direct and indirect pathways (Erisman et al. 2011). It is therefore important to determine the magnitude of N deposition and predict its impact on the health of different sensitive ecosystems (Rattray and Sievering 2001).

The oceans comprise the largest and most important ecosystems on Earth. The oceans are reactive N emission sources controlled mainly by natural processes and are also important sinks for N deposition (Duce et al. 2008). Reactive N enters the oceans via rivers, biological N2 fixation, and atmospheric deposition. As the generation and emission of reactive N have increased, total N deposition to the oceans has more than tripled to ∼67 Tg N yr$^{-1}$ in 2000 compared with the value (∼20 Tg N yr$^{-1}$) in 1860 (Duce et al. 2008). As a consequence, N deposition plays an increasingly important role in the oceans, especially in coastal zones where the N inputs are largest (Seitzinger et al. 2010). Atmospheric N deposition was found to increase the N abundance of the North Western Pacific Ocean, and the excess N inputs and other elements such as phosphorus (P) have led to eutrophication of the coastal marine ecosystems (Conley et al. 2009, Kim et al. 2011). Coastal eutrophication will lead to widespread hypoxia and anoxia, habitat degradation, alteration of food-web structure, loss of biodiversity, and increased frequency, spatial extent and duration of harmful algal blooms (Howarth 2008).

China has long coastlines (total length about 18 000 km). The provinces located in the coastal areas have benefitted enormously from the new economic policies and have made great progress. For example, the GDP of the coastal provinces Guangdong, Shandong, Jiangsu, and Zhejiang are among the top four economically significant regions in China. Economic development also increases activities that release reactive N to the environment. However, studies on the influence of these reactive N emissions on the coastal areas are relatively limited at present. The coasts of China, connecting the mainland of China with the Pacific Ocean and the sources from the mainland are contributing to coastal eutrophication through atmospheric and riverine transport of nutrients (including N). As a result, harmful algal blooms have been observed in the coastal seas (Conley et al. 2009, Chen et al. 2011, Liu et al. 2011). In this study, six coastal sampling sites were set up in China, located at the Bohai Sea, Yellow Sea, East China Sea, and South China Sea. The gaseous and particulate N concentrations and inorganic N concentrations in rain samples were measured and N dry and wet deposition rates to coastal seas were estimated. The objectives of this study were to evaluate the current situation regarding reactive N concentrations and pollution in the air and precipitation of coastal areas and to estimate N dry and wet deposition values and their potential impacts on Chinese marine ecosystems.

2. Materials and methods

2.1. Sampling sites

The study included six sampling sites and all the sampling sites were located in the coastal region (near the sea) or on islands. The sampling sites were set up in Liaoning, Shandong, Zhejiang, Fujian, and Guangdong provinces, respectively (figure 1). The specific sites are Dalian (DL, 38°44′N, 120°31′E), Changdao island (CD, 37°55′N, 124°44′E), Linshan island (LS, 35°45′N, 120°08′E), Fenghua (FH, 29°36′N, 121°31′E), Fuzhou (FZ, 26°10′N, 119°21′E), and Zhanjiang (ZJ, 21°12′N, 110°17′E), respectively. Dalian is a coastal city and is famous for business development. DL is an urban site...
where the mean annual temperature is 8–11 °C and the annual rainfall varies between 550 and 1000 mm. DL belongs to the warm temperate and semi-humid monsoon and marine climatic zone. CD is largest island in Shandong province, located in the joint of the Bohai Sea and the Yellow Sea with about 40 000 inhabitants. CD island is remote and does not have industry or agricultural activities near the sampling site. LS is located in the Yellow Sea belonging to Jiaonan city (region), Shandong province. There are about 2700 inhabitants on the island. FH is located in Chunhu town, Fenghua city, Zhejiang province. It is a typical coastal area of the East China Sea and has an advanced fishery. FZ is surrounded by hills and has low population density. The FZ site is surrounded by some agricultural land growing tobacco and paddy rice without large livestock farms or industry. ZJ is located in Leizhou Peninsula, Zhanjiang city, Guangdong province, close to the South China Sea. The climate is tropical with relatively high temperatures, high rainfall, and high plant cover. This area is rich in tropical fruits and farmers use large quantities of fertilizers for fruit production. Although only the DL is located at real urban site, all sampling sites (except FZ) are affected by rapid urbanization (e.g., increased traffic vehicles and population intensities) in coastal area of China. Besides the local N sources, all coastal sites receive atmospheric N transport from both inland (mainly agricultural sources) and marine (including international ship emissions) ecosystems.

2.2. Equipment for collecting reactive N components and sampling period

Reactive N components were collected by the DELTA (DEnuder for Long-Term Atmospheric Sampling) system which is an active sampling equipment, fulfilling long-time sampling and thus cost saving and it is widely used in the European N deposition monitoring network (Flechard et al. 2011). Atmospheric HNO₃, NH₃, particulate NO₃ and NH₄ can be captured by the coated wall of the denuders and the subsequent filters. The sampling time is one month. The coating solution is 5% m/v citric acid in methanol for absorbing NH₃, and 1%(m/v) K₂CO₃+1%(m/v) glycerol in methanol for collection of HNO₃. The coating solution was 13%(m/v) citric acid in methanol added to the filters absorbing pNH₄, and the coating solution which absorbs pNO₃ is 5%(m/v) K₂CO₃+10%(m/v) glycerol in methanol. The extraction solution is 0.05% H₂O₂ for the denuders and filters absorbing NO₃ (10 ml) and the extraction solution for NH₃ and pNH₄ is high purity water (denuders 6 ml and filters 10 ml). The NH₄—N and NO₃—N concentrations in the samples were analyzed by an AA3 continuous-flow analyzer (Bran + Luebbe GmbH, Norderstedt, Germany). The DELTA system also absorbs SO₄ by the denuders and filters. SO₄— concentration was measured by ion chromatography (761 Compact, Switzerland). Atmospheric concentrations of NO₂ were sampled by passive samplers (UK Environmental Change Network Diffusion tubes) extensively described in Luo et al. (2013). Monthly reactive N concentrations were collected mostly starting from August or September 2010 and ending in May or June 2012. The detailed sampling periods and the numbers of reactive N and SO₄— samples at the six sites are listed in table 1.

Table 1. The start and end sampling periods and total monthly sampling numbers of reactive N and pSO₄²⁻ during the entire sampling period at the six coastal sites.

| Site | Sampling period | No. of NH₃ | No. of HNO₃ | No. of NO₂ | No. of pNO₃ | No. of pNH₄ | No. of pSO₄²⁻ |
|------|----------------|------------|------------|-----------|------------|------------|-------------|
| DL   | September 2010–April 2012 | 20         | 20         | 15        | 20         | 20         | 12          |
| CD   | September 2010–June 2012   | 22         | 22         | 19        | 22         | 22         | 17          |
| LS   | February 2011–May 2012     | 15         | 15         | 15        | 15         | 15         | 11          |
| FH   | August 2010–May 2012       | 22         | 22         | 21        | 22         | 22         | 20          |
| FZ   | April 2010–July 2012       | 28         | 28         | 21        | 28         | 28         | 16          |
| ZJ   | August 2010–May 2012       | 22         | 22         | 12        | 22         | 22         | 16          |

2.3. Rain water collection and N wet deposition calculation

Rain water samples were collected by precipitation collectors directly after every rainfall event. Wet deposition of N was collected in situ by precipitation collectors (SDM6, Tianjin Weather Equipment, China). The sampling period was one complete year (2011). The samples were analyzed for concentration of NH₄—N and NO₃—N using the AA3 continuous-flow analyzer mentioned above. Wet deposition of NH₄—N and NO₃—N was then calculated by the following two equations:

\[ N \text{ deposition per event (kg N ha}^{-1}\) = precipitation (mm) × \text{NH}_4^-\text{N or NO}_3^-\text{N concentration in rainwater (mg N L}^{-1}\) × 0.01. \]

\[ N \text{ deposition per month or year (kg N ha}^{-1}\) = 0.001 × \sum N \text{ deposition per event in a month or year.} \]

2.4. N dry deposition estimation

Compared with wet deposition N dry deposition is relatively complicated because it changes with the meteorological conditions and the surface characteristics. In the inferential model the dry deposition flux can be expressed by

\[ F = C × V_a \]  (1)

and \( V_a \) can be expressed by

\[ V_a = (R_a + R_b + R_c)^{-1}. \]  (2)

Here, \( R_a \) is the aerodynamic resistance, \( R_b \) is the quasi-laminar boundary layer resistance, and \( R_c \) is the surface or canopy
resistance. In the three resistances, $R_a$ is dependent on the meteorological conditions and it should be calculated for a range of atmospheric stabilities, and $R_b$ is mainly about the gas own characteristic. $R_c$ is quite complicated in inferential model and difficult for dry deposition calculation due to the different surface features and gas or particles species (Erisman and Pul Van 1994).

In this study we did not have enough equipment or suitable methods to calculate the dry deposition velocities at the ocean surface. In addition, studies on N dry deposition velocities above the ocean surface are very limited, so we decided to use the deposition velocities from the Chinese literature on the ocean. We therefore cited deposition velocities of the gases $\text{NH}_3$, $\text{HNO}_3$, and $\text{NO}_2$ from Zhang et al (2010) and those of particulate $\text{pNH}_4^+$ and $\text{pNO}_3^-$ from Zhang et al (2004).

3. Results

3.1. Atmospheric concentrations of reactive N components

Atmospheric concentrations of reactive N components are shown in figure 2. Annual average $\text{NH}_3$ concentrations were 2.73, 3.50, 3.97, 7.34, 2.13, and 5.62 $\mu$g N $\text{m}^{-3}$ at sites DL, CD, LS, FH, FZ, and ZJ, respectively. The concentrations of $\text{NH}_3$ were higher at FH and ZJ than at the other sites because of the high level of agricultural activity. $\text{HNO}_3$ and $\text{NO}_2$ concentrations ranged from 0.46 to 1.22 $\mu$g N $\text{m}^{-3}$ and 3.10 to 7.19 $\mu$g N $\text{m}^{-3}$ across all six sites. The lowest concentrations of $\text{HNO}_3$ and $\text{NO}_2$ were observed at FZ and the highest were found at FH and CD, reflecting the weak effects of power plants, industry and transportation on the concentrations measured at FZ but strong effects on FH and CD because of the large population densities and advanced economic activities. Average $\text{pNO}_3^-$ concentrations were 1.14–2.68 $\mu$g N $\text{m}^{-3}$ at the six sampling sites. The highest value was measured at CD and the lowest at FZ. Average concentrations of $\text{pNH}_4^+$ were 4.16, 4.45, 4.78, 4.07, 2.29, and 3.30 $\mu$g N $\text{m}^{-3}$ at sites DL, CD, LS, FH, FZ, and ZJ, respectively. Air concentrations of $\text{pNH}_4^+$ at the North coastal sites (DL, CD and LS) were almost twice of those at the Southern FZ site, whereas the concentrations of $\text{pNH}_4^+$ at FH and ZJ were close to the North coastal sites. Three North sampling sites located close to the North China Plain, an intensively managed agricultural region, and the higher $\text{pNH}_4^+$ concentrations in this area showed agricultural source impacts on secondary aerosols (e.g., NH$_2$-based PM$_{2.5}$).

3.2. Seasonal variation in reactive N concentrations

Table 2 shows the seasonal variation in reactive N concentrations at the six sampling sites. A peak $\text{NH}_3$ concentration was found in summer at all sites (except DL) because high temperatures together with N fertilization in summer induce high $\text{NH}_3$ emissions from various sources. The lowest concentration of $\text{NH}_3$ was observed in winter at all sampling sites. The air concentration of $\text{pNH}_4^+$ was highest in spring or winter. The results may be explained by low rainfall in the spring and winter, and in addition, coal consumption for heating in the winter and spring can also stimulate the formation of particulate NH$_4^+$. HNO$_3$ concentrations did not show notable seasonal variation across the six sampling sites. Peak concentrations of $\text{pNO}_3^-$ were observed in winter or spring and lowest in the summer. Seasonal variation in $\text{pNO}_3^-$ is similar to that of $\text{pNH}_4^+$ in air as mentioned above. The meteorology and heating stimulate higher $\text{pNO}_3^-$ pollution especially in North China in winter. The $\text{pNO}_3^-$ concentrations were 24.2% higher at coastal sites of North China (DL, CD and LS) than at sites of South China (FH, FZ and ZJ) in winter. Concentrations of $\text{NO}_2$ mainly peaked in winter or spring and had a close relationship with heating, especially in North China.

3.3. N wet deposition

Rainfall distribution showed seasonal and regional variations. South China sampling sites had more rainfall than the Northern sites. The latter had lesser or even no rain in winter and spring but the Southern sites experienced more rain in these two seasons. The inorganic N concentrations in rainwater were 0.46–1.67 mg N L$^{-1}$ for NO$_3^-$ and 0.47–1.31 mg N L$^{-1}$ for NH$_3$–N (table 3). Nitrogen concentrations in rainwater followed the pattern in atmospheric reactive N concentrations. For example, CD and FZ had the highest and lowest inorganic N concentrations in rainwater in relation to the highest and lowest concentrations of atmospheric reactive N at the two sites, respectively. N wet deposition ranged from 14.2 to 25.2 kg N ha$^{-1}$ yr$^{-1}$. N wet deposition rate was controlled by the N concentration in rainwater and the amount of annual rainfall. The NH$_3$/NO$_3^-$ ratio was lower than 1.0 except at ZJ, so wet deposition of NO$_3^-$ was slightly higher than that of NH$_3$–N in our study.

3.4. N dry deposition

Annual N dry deposition was 12.9, 16.9, 15.2, 23.1, 7.8 and 18.0 kg N ha$^{-1}$ at DL, CD, LS, FH, FZ, and ZJ sampling sites, respectively (figure 3(a)). The estimated dry deposition velocities of NH$_3$, HNO$_3$, NO$_2$, $\text{pNH}_4^+$ and $\text{pNO}_3^-$ averaged 0.626, 0.63, 0.005 34, 0.27 and 0.27 cm s$^{-1}$, respectively, which were taken directly from (Zhang et al 2004, 2010). NH$_3$ and $\text{pNH}_4^+$ were the major parts in the N dry deposition because they have both higher concentrations and higher deposition velocities, and the total NH$_3$ and $\text{pNH}_4^+$ contribution to the dry deposition was 72.1–81.7%. FH had the highest N dry deposition rate because of the highest reactive N concentrations (especially NH$_3$ and NO$_2$). FZ had the lowest dry deposition rate because all reactive N components were very low at this site. In general, the N dry deposition rate is comparable to the N wet deposition in our study (except FZ). Given the wet N deposition, the annual total N deposition rates were 29.9, 32.8, 31.1, 44.6, 22.0, 43.2 kg ha$^{-1}$ yr$^{-1}$ at DL, CD, LS, FH, FZ, and ZJ (figure 3(b)), respectively.
4. Discussion

4.1. The atmospheric reactive N conditions in coastal areas of China

NH₃ and NOₓ are two primary reactive N species in air which are emitted mainly from human activity. Rapid economic development in China has led to continuing increases in NH₃ and NOₓ emissions since the 1980s (Liu et al. 2013). However, the N emissions varied from region to region and also from season to season due to the large differences in population density, economic function, land use types and weather conditions. The NH₃ emission ‘hot-spots’ were in Hebei, Henan, Shandong and Jiangsu provinces (Clarisse et al. 2009, Zhang et al. 2010), while the NOₓ emission ‘hotspots’ were in some well developed regions such as Jing-Jin-Ji (Beijing-Tianjin-Hebei) Region, the Yangtze River Delta and the Pearl River Delta (Richter et al. 2005, Gu et al. 2012). In this study the NH₃, HNO₃ and NO₂ concentrations were much lower than our previous results on the North China Plain (Shen et al. 2009, Luo et al. 2013), but are comparable to the results from three South China sampling sites in Hunan province (Shen et al. 2013).

Atmospheric pNH₄⁺, pNO₃⁻ and pSO₄²⁻ are important components of secondary aerosols. Particulate pollution is a major public concern and there are many studies focusing on urban regions (Chan and Yao 2008). Our data show that atmospheric concentrations of pNH₄⁺ and pNO₃⁻ or pSO₄²⁻ made an important contribution to the formation of secondary particulates (e.g., NH₄NO₃ and (NH₄)₂SO₄) and their transportation to the coastal sea. China

Figure 2. Atmospheric concentrations of reactive N ((a) NH₃, (b) HNO₃, (c) NO₂, (d) pNO₃⁻, (e) pNH₄⁺) at six sites during sampling periods. Solid line represents median values and dotted line represents average values.
has made great progress in controlling particulate matter but concentrations remain high because industrial development has offset the PM control technology and the conditions of particulate pollution are even more problematic in the cities of North China (Wang and Hao 2012). Compared with particulate NH$_4^+$ and NO$_3^-$ concentrations on the North China Plain (Luo et al. 2013), the concentrations of pNH$_4^+$ and pNO$_3^-$ at the six coastal sites were lower especially at one Southeast sampling site (FZ). China uses large amounts of coal which accounts for about 70% of its energy consumption. SO$_4^{2-}$ is therefore one of the most important components in particulate matter (Chan and Yao 2008). The SO$_4^{2-}$/NO$_3^-$ ratio is very low in this study (SO$_4^{2-}$/NO$_3^-$ ratios were 0.48, 0.49, 0.69, 0.49, 0.87, 0.50 at DL, CD, LS, FH, FZ, and ZJ, respectively), reflecting the possibly higher contribution of the transportation sector and rapid urbanization to the present-day air pollution. Our results are consistent with recent reports of decreasing SO$_4^{2-}$/NO$_3^-$ trends in Beijing and Shanghai (Shen et al. 2011b, Huang et al. 2012). Natural processes can also produce aerosols. Cusack et al. (2012) found crustal material and marine aerosol comprising 9% and 2% respectively of the total sum of the chemical components at a sampling site in Spain. In addition, forest fires and volcanic eruption form large amounts of natural-source aerosols.

Regarding seasonal variation and taking NH$_3$ as an example, we know that fertilized soils, animal/human

| Table 2. Seasonal variation in atmospheric reactive N components across the six coastal sampling sites (mean ± SD, μg N m$^{-3}$). |
|---|---|---|---|---|
| Site | Spring | Summer | Autumn | Winter |
| NH$_3$ | DL 2.47 ± 2.46 | 3.80 ± 0.95 | 3.89 ± 2.91 | 1.12 ± 0.78 |
|     | CD 5.52 ± 3.28 | 6.65 ± 2.13 | 3.50 ± 1.31 | 0.77 ± 0.67 |
|     | LS 4.65 ± 0.94 | 6.86 ± 4.37 | 1.84 ± 1.52 | 1.82 ± 0.77 |
|     | FH 8.22 ± 4.01 | 11.88 ± 4.28 | 7.44 ± 4.75 | 2.84 ± 1.63 |
|     | FZ 1.78 ± 0.90 | 3.98 ± 1.94 | 1.39 ± 0.42 | 0.73 ± 0.38 |
|     | ZJ 6.81 ± 3.02 | 9.23 ± 3.11 | 5.59 ± 2.07 | 1.94 ± 0.97 |
| pNH$_4^+$ | DL 3.68 ± 1.71 | 3.55 ± 0.99 | 3.72 ± 1.33 | 5.47 ± 2.53 |
|      | CD 5.53 ± 4.50 | 5.07 ± 1.47 | 4.21 ± 2.02 | 3.30 ± 1.29 |
|      | LS 5.02 ± 1.40 | 3.28 ± 2.43 | 4.10 ± 1.09 | 7.18 ± 2.30 |
|      | FH 3.12 ± 1.69 | 3.48 ± 1.68 | 3.57 ± 1.94 | 5.69 ± 1.21 |
|      | FZ 2.74 ± 1.25 | 1.89 ± 1.78 | 2.23 ± 0.45 | 2.09 ± 1.17 |
|      | ZJ 2.56 ± 1.50 | 1.96 ± 1.98 | 4.29 ± 0.88 | 3.61 ± 2.12 |
| HNO$_3$ | DL 0.71 ± 0.49 | 0.72 ± 0.21 | 1.11 ± 0.31 | 1.03 ± 0.43 |
|     | CD 1.05 ± 0.47 | 1.05 ± 0.20 | 1.40 ± 0.32 | 1.27 ± 0.89 |
|     | LS 0.99 ± 0.16 | 0.78 ± 0.22 | 0.82 ± 0.55 | 0.78 ± 0.67 |
|     | FH 1.37 ± 0.26 | 1.09 ± 0.27 | 0.87 ± 0.52 | 1.56 ± 0.32 |
|     | FZ 0.50 ± 0.14 | 0.61 ± 0.13 | 0.36 ± 0.21 | 0.37 ± 0.18 |
|     | ZJ 0.93 ± 0.48 | 0.36 ± 0.21 | 0.97 ± 0.32 | 1.05 ± 0.29 |
| pNO$_3^-$ | DL 1.55 ± 1.14 | 1.44 ± 0.24 | 1.78 ± 0.78 | 3.12 ± 2.23 |
|       | CD 3.38 ± 1.75 | 2.17 ± 0.43 | 2.63 ± 0.91 | 2.33 ± 0.69 |
|       | LS 1.88 ± 0.41 | 1.49 ± 0.24 | 1.32 ± 1.05 | 3.89 ± 2.15 |
|       | FH 2.17 ± 0.67 | 1.55 ± 0.87 | 1.78 ± 0.70 | 2.76 ± 0.35 |
|       | FZ 1.30 ± 0.36 | 1.08 ± 0.30 | 1.06 ± 0.31 | 1.05 ± 0.19 |
|       | ZJ 1.63 ± 0.57 | 0.75 ± 0.51 | 1.95 ± 0.70 | 3.27 ± 0.89 |
| NO$_2$ | DL 5.45 ± 1.10 | 3.82 ± 0.78 | 4.20 ± 1.66 | 5.07 ± 1.25 |
|      | CD 6.21 ± 0.89 | 4.87 ± 0.43 | 5.51 ± 1.04 | 6.53 ± 0.87 |
|      | LS 5.74 ± 1.80 | 3.72 ± 0.74 | 4.12 ± 0.88 | 5.94 ± 0.50 |
|      | FH 7.11 ± 2.08 | 5.24 ± 0.74 | 6.75 ± 1.14 | 8.52 ± 2.07 |
|      | FZ 3.76 ± 0.60 | 3.40 ± 1.01 | 2.04 ± 0.52 | 2.93 ± 0.69 |
|      | ZJ 4.05 ± 0.94 | 4.36 ± 0.39 | 3.96 ± 0.53 | 4.49 ± 0.25 |

| Table 3. Inorganic N concentrations in precipitation and wet deposition at the six coastal sampling sites. |
|---|---|---|---|---|---|---|---|
| Site | Rainfall N concentration (mg N L$^{-1}$) | N wet deposition (kg N ha$^{-1}$ yr$^{-1}$) |
|     | NO$_3^-$–N | NH$_4^+$–N | Total | NO$_3^-$–N | NH$_4^+$–N | Total |
| DL | 660.8 | 1.36 | 1.21 | 2.57 | 9.01 | 7.98 | 16.99 |
| CD | 531.8 | 1.67 | 1.31 | 2.98 | 8.86 | 6.97 | 15.83 |
| LS | 731.4 | 1.15 | 1.02 | 2.17 | 8.45 | 7.44 | 15.89 |
| FH | 1120.6 | 1.04 | 0.88 | 1.92 | 11.7 | 9.86 | 21.56 |
| FZ | 1528.4 | 0.46 | 0.47 | 0.93 | 7.00 | 7.23 | 14.23 |
| ZJ | 1952.0 | 0.87 | 1.11 | 1.98 | 12.0 | 13.2 | 25.20 |
manures and biomass burning are major NH$_3$ emission sources worldwide. These emission sources have a close relationship with temperature and high temperatures stimulate NH$_3$ emission in summer (Shen et al. 2011a). The oceans are important natural sources of NH$_3$ emissions (Olivier et al. 1998) and high temperatures also stimulate NH$_3$ emissions from the oceans in summer. Meteorological conditions may affect the air quality in the coastal sea in different seasons. The wind comes mainly from the sea in the summer and brings relatively clear air from the ocean which is also an explanation for the lower pNH$_4^+$ and pNO$_3^-$ concentrations in summer. Wind comes mainly from the West or North in winter and the sampling sites were affected by the land sources. As a result, particulate pollution is usually higher in winter and spring. There are always sand storms from Inner Mongolia in spring and there can be long-range transport to the China seas affecting the air quality in this region and to a lesser extent the Yellow Sea followed by the Bohai Sea, the East China Sea, and the Northern South China Sea (Tan et al. 2012).

Precipitation can remove various components from the atmosphere, so the precipitation N concentrations have a close relationship with the atmospheric concentrations of NH$_3$ and NH$_4^+$ (Xiao et al. 2012). As reported by Liu et al. (2013), inorganic N concentrations in precipitation show remarkable differences in different regions of China. The average concentration was 1.20 mg N L$^{-1}$ for NH$_4^+$–N, and 0.97 mg N L$^{-1}$ for NO$_3^-$–N at a South China site in Guangzhou city (Jia and Chen 2010). Chen and Mulder (2007) reported lower inorganic N concentrations in precipitation (NH$_4^+$–N 0.29–2.33 mg N L$^{-1}$ and NO$_3^-$–N 0.20–1.11 mg N L$^{-1}$) at four South China sites in Hunan, Chongqing and Guizhou. Our study reflects the consistency of rainwater N concentrations with rainfall distribution in different regions. The North China sites had higher N concentrations in precipitation than the South China sites due to the lower rainfall and higher atmospheric reactive N concentrations (Zhang et al. 2008). This study confirms the higher inorganic N concentrations in rainwater at coastal sites of North China than South China. The lower inorganic N concentration in rainwater at FZ in our study compares well with the inorganic N concentration in rainwater (1.74 mg N L$^{-1}$) in Xiamen (Chen et al. 2011).

4.2. Impact of N deposition on the coastal ocean ecosystems

Nitrogen wet and dry deposition in coastal areas in our study was overall lower than that in intensive agricultural areas of China. For example, on the North China Plain, N wet and dry
deposition ranged from 60–102 kg N ha$^{-1}$ yr$^{-1}$ due to high air pollution and the inter-annual variability of rainfall (Pan et al. 2012, Luo et al. 2013). Nitrogen wet deposition in the Taihu Lake region and Shanghai area in East China was estimated to be about 30 kg N ha$^{-1}$ yr$^{-1}$ (Xie et al. 2008) and 58 kg N ha$^{-1}$ yr$^{-1}$ (Mei and Zhang 2007), respectively. Jia and Chen (2010) reported an N wet deposition of 52.8 kg N ha$^{-1}$ yr$^{-1}$ at a South urban sampling site of Guangzhou. However, N wet deposition on the lower Liaohe River Plain in Northeast China was only 14.5 kg N ha$^{-1}$ yr$^{-1}$ (Yu et al. 2011) and close to our results.

For the coastal sea area, streams and rivers are additional nutrient sources to estuarine and coastal marine environments. The inputs of N and P increased rapidly by erosion from arable lands or carrying human wastewater, so the coastal sea is more affected by human activity than only by air pollution (Smith et al. 1999). Atmospheric N deposition represents a long-term low level fertilization effect for the ocean and has consequences for the natural biogeochemical cycles of N and increases the productivity of the oceans (Duce et al. 2008). Compared with the riverine N input into the coastal ocean, N deposition may have long range impacts on the open ocean downwind of the primary source regions, especially in Eastern North America, Europe, and South and East Asia (Doney et al. 2007). China is one of the hotspots of global reactive N emissions and deposition (Galloway et al. 2008, Liu et al. 2013). Several studies have quantified potential reactive N long range transport. For example, a modeling study showed that the high emissions of reactive N in China made a significant contribution to Japan’s HNO$_3$ deposition through long-range transport (Holloway et al. 2002). The Yellow Sea regions showed high N deposition through long-range transport from East Asia (Kim et al. 2010). Total N deposition averaged 33.9 kg N ha$^{-1}$ yr$^{-1}$ for all the sampling sites in this study. If we consider this to be representative of N deposition for the sea area, it makes a significant contribution in addition to the river or the groundwater N entering the oceans. Assuming an annual mean N deposition of 33.9 kg N ha$^{-1}$, the total N deposition into the whole Chinese coastal seas (total area approx. 0.4 million km$^2$, calculating from 18,000 km length of boundary line of territorial waters with 22 km width of territorial waters) can amount to 1.36 Tg N yr$^{-1}$. It is a large N nutrient input from atmospheric deposition, which is comparable to inorganic N output of 1.61 Tg N yr$^{-1}$ from the Yangtze River to the East China Sea (Yan et al. 2010) and estimated feed N input (~1.5 Tg N yr$^{-1}$) from coastal aquaculture (www.zg3n.com.cn/2012/0904/15059.html).

Although no systematic studies show the total N input from riverine source, aquaculture and deposition (three major N sources in coastal zones), the contribution of N deposition to Chinese coastal N input (accounting to about 30% of total N input) should not be neglected. Such high levels of N deposition in particular NH$_3$/NH$_4^+$ deposition may lead to secondary N$_2$O emissions either from soils or marine ecosystems (Matson et al. 2002, Duce et al. 2008), due to nitrification and denitrification. Our monitoring results are 3–8 times higher than the modeled N deposition rates (2.5–11 kg N ha$^{-1}$ yr$^{-1}$) in the East China Sea (Zhang et al. 2010). One possible explanation may be that we focus on the coastal sea and atmospheric reactive N concentrations and deposition show a decreasing gradient downward from the shore and are therefore significantly lower for the whole sea area. Another possibility is that the modeling results underestimate N wet and dry deposition in the coastal areas.

In addition, the coastal ocean environment is also affected by P and iron inputs and other complex chemical process (Deutsch et al. 2007), so it is quite complicated to quantify the environmental impact of N deposition to the coastal ocean and further research is also needed to quantify all the nutrient fluxes from mainland China to the ocean. Nitrogen dry deposition velocities were taken directly from the literature (e.g., Zhang et al. 2004, 2010) and are therefore highly uncertain, leading to uncertainties for the dry deposition rates in this study, and this needs more accurate estimation in future studies.

5. Conclusion

This study provides an updated evaluation of present-day atmospheric reactive N conditions in Chinese coastal regions. Our data show lower atmospheric reactive N concentrations in the coastal area than previous results in North China but large rates of N dry and wet deposition. The annual total N deposition ranged from 22.0 to 44.6 kg N ha$^{-1}$ and averaged 33.9 kg N ha$^{-1}$ at the six sampling sites along the coastal zones. Average N dry deposition account for 45.4% of the total deposition demonstrating that it is important part of the total deposition. The significant relationships between pNH$_4^+$ and pNO$_3^-$ and/or pSO$_4^{2-}$ concentrations suggest that pollution transportation may make an important contribution to the formation of secondary aerosols (including PM$_{2.5}$) in Chinese coastal regions. Ratios of pSO$_4^{2-}$/pNO$_3^-$ were very low in this study reflecting a large contribution of the transportation sector to current air pollution in China. High levels of N deposition in the coastal seas remind us to pay more attention to the impacts of atmospheric reactive N pollution and deposition on the sensitive coastal zones and surrounding marine ecosystems.

Acknowledgements

We thank Dr Peter Christie for correcting the English of the manuscript, Ms Zong Xiaoyan for analyzing N wet deposition and Mr Chang Yunhua for helping us to draw the monitoring site distribution figure. This work was supported by the Chinese National Basic Research Program (2014CB954202), the Chinese National Fund for Distinguished Scholars and the Innovative Group Grant from the NSFC (31121062).
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