



Isotopic composition of water-soluble nitrate in bulk atmospheric deposition at Dongsha Island: sources and implications of external N supply to the northern South China Sea

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Abstract. Increased reactive nitrogen (N_r , $NO_3^- + NH_4^+$ + dissolved organic nitrogen) emission from the Asian continent poses profound threats to ecosystem safety from terrestrial throughout the ocean proper. To quantify atmospheric N_r input, diagnose its sources, and evaluate influence on marine nitrogen cycle of the South China Sea (SCS), an oligotrophic marginal sea adjacent to the emission hot spot China, we conducted measurements of concentrations of nitrate and ammonium as well as other major ions and dual isotopes of nitrate ($\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$) in atmospheric deposition collected from Dongsha Island off southern China. The $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ for dry deposition averaged at -2.8‰ and $+58.8\text{‰}$, ranging from -7.5 to $+3.7\text{‰}$ and from $\sim +17$ to $+88\text{‰}$, respectively. Wet deposition, although with limited samples, showed a similar flux-weighted mean in $\delta^{15}N_{NO_3}$ (-2.6‰) yet a significantly higher mean in $\delta^{18}O_{NO_3}$ ($+78.8\text{‰}$). The dual isotope ratios showed an anti-correlation and an inverse seasonality; the $\delta^{15}N_{NO_3}$ values were higher in summer compared to those in winter, while the $\delta^{18}O_{NO_3}$ values were higher in winter than those in summer. In winter, not only dual isotopic compositions of nitrate but also the ammonium and nitrate dry deposition fluxes were relatively uniform, demonstrating a persistent influence of fossil fuel combustion sourced from Asian continental outflows via the northeasterly monsoon winds. More variable isotopic values in summer likely suggest varying sources and dynamical formation processes of dry deposition nitrate. Biomass burning and lightning are suggested to be responsible for the observed higher $\delta^{15}N_{NO_3}$ values in summer. Atmospheric nitrate and ammonium

deposition together was estimated to be $\sim 50\text{ mmol N m}^{-2}\text{ year}^{-1}$, with the dominance of nitrate in dry deposition but ammonium slightly higher in wet deposition. If not including this additional fertilization of atmospheric inorganic nitrogen deposition to enhance the carbon sequestration, CO_2 release out of the SCS would be double than that of the present amount, $460 \pm 430\text{ mmol C m}^{-2}\text{ year}^{-1}$. Our study demonstrates that atmospheric deposition may serve as an important external N_r supplier to the SCS; however it is difficult to separate the isotopic signal from N_2 fixation (-2 – 0‰) due to their similarity in $\delta^{15}N_{NO_3}$. More studies related to isotopic composition of nitrogen speciation in atmospheric N_r deposition, their relative contributions and source identification, and the role of typhoons in the SCS are required.

1 Introduction

The input of newly bioavailable nitrogen to the ocean is thought to largely control the efficiency of the biological pump, and thus export, of carbon from the surface ocean, and subsequently to modulate the levels of atmospheric CO_2 (Falkowski et al., 1998). For decades, human activities have significantly contributed to the emission of reactive nitrogen (N_r) to the atmosphere, a considerable proportion of which is transported and deposited onto the coastal regions and even the remote ocean proper (Dentener et al., 2006; Gruber and Galloway, 2008; Reay et al., 2008). The global simulated flux of atmospheric N_r deposition to the ocean has rapidly

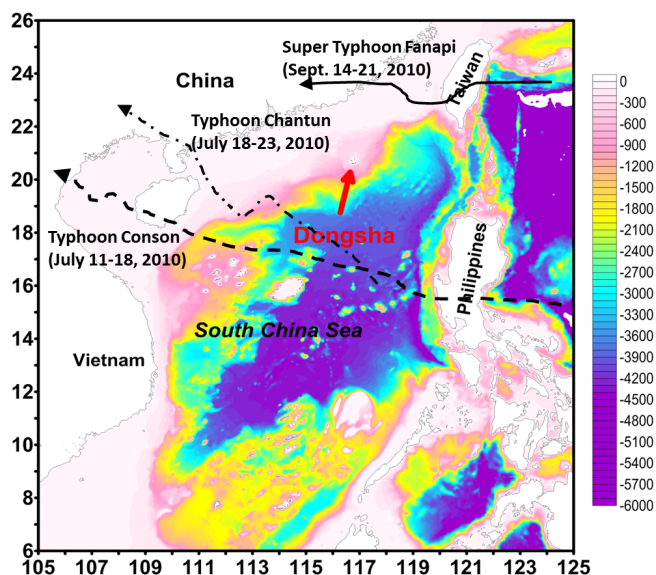


Fig. 1. Map of the South China Sea and sampling location of Dongsha Island. The arrow curves denote the pathways of three typhoons that passed over the northern or southern regions of Dongsha during the sampling periods.

increased to $\sim 67 \text{ Tg N year}^{-1}$ since the mid-1800s, and this value is comparable with the estimates of present oceanic N_2 fixation and would account for $\sim 40\%$ of external N supply to the surface ocean, mostly due to anthropogenic emissions (Galloway et al., 2004, 2008; Duce et al., 2008, and references therein). Such external anthropogenic input from the atmosphere apparently has a prominent impact on marine nitrogen cycle and associated biogeochemistry, as well as the community structure of ecosystem, particularly in oligotrophic marginal seas sensitive to N_r availability (Zhang et al., 2004; Bonnet et al., 2005; Duarte et al., 2006; Galloway et al., 2008; Kim et al., 2011). However, direct observations on the magnitude of atmospheric N_r deposition to the ocean are limited. In order to better constrain the influence of atmospheric N_r 's inputs and evaluate its role in marine nitrogen cycling, field measurements for the quantification of atmospheric N_r deposition and its main sources are urgently required.

Nitrate, the most stable compound of atmospheric N_r (Galloway et al., 2008), is formed from homogeneous and heterogeneous oxidation of NO_x , which could be derived from both natural (e.g., lightning, soil emissions, wildfires) and anthropogenic (e.g., combustion of fossil fuels, vehicle exhausts) origins. Specifically, atmospheric nitrate (atmNO_3^-) is generally formed by NO_x oxidation via several complex chemical pathways, mainly including the following: (1) NO is quickly oxidized by ozone (O_3) to NO_2 and followed by hydroxyl radical (OH) oxidation during daytime. These processes are more prevalent in summer, when photochemically produced OH concentrations are generally highest. (2) Hy-

drolisis of N_2O_5 formed via combination NO_3 radical (NO_2 oxidation by O_3) with NO_2 at nighttime and this pathway is predominant during wintertime (Calvert et al., 1985). Although isotopic fractionation may occur during these processes of nitrate formation and subsequent transport of NO_3^- in the atmosphere (e.g., Freyer, 1991; Morin et al., 2009), previous studies have suggested that N isotopic composition of nitrate in atmospheric deposition could be used as fingerprints to identify NO_x sources (Heaton, 1987; Freyer, 1991; Russell et al., 1998; Yeatman et al., 2001; Hastings et al., 2003; Knapp et al., 2010). On the other hand, O isotopes in nitrate are mostly controlled by the oxidation pathways during atmospheric transport (Hastings et al., 2003; Savarino et al., 2007; Elliott et al., 2009; Wankel et al., 2010; Fang et al., 2011). However, to our best knowledge, no isotope study was conducted so far to trace the sources of atmNO_3^- deposition to China marginal seas, which has been thought to receive significant amounts of N_r emitted from China (Duce et al., 2008), the hot spot of ammonia and NO_x emissions in a global perspective (Bouwman et al., 2002; Richer et al., 2005).

The South China Sea (SCS) is one of the largest marginal seas in the world with widely oligotrophic deep basin, located in the tropical–subtropical western North Pacific. It is largely surrounded by landmasses with the densest population and vibrant economics (Fig. 1). The SCS is under the influence of East Asian monsoon system, showing that stronger northeasterly winds prevail in winter and relatively weak southwesterly winds in summer. Many studies have suggested that Asian outflow dusts and air pollutants from northern China could be detected in the SCS and its coastal regions during the winter monsoon (Wang et al., 2005; Lin et al., 2007; Hsu et al., 2007, 2013, 2014), while during the summer monsoon, biomass burning in southeastern Asia could act as another contributor (e.g., Ma et al., 2003; Lin et al., 2009). Several model results reported that N_r deposition to the SCS was higher than $500 \text{ mg N m}^{-2} \text{ year}^{-1}$ in the last decade, and it is highly likely that this amount will continue to increase in the future (An et al., 2002; Dentener et al., 2006; Duce et al., 2008). It is clear the SCS is a receptacle that accepts anthropogenic N_r deposition, which in turn alters its oligotrophic ecosystem. In addition to monsoons, the episodic tropical cyclone (typhoon) may also bring significant nitrogen of natural and/or anthropogenic origins to the ocean (Kodama et al., 2011; Kim et al., 2014). On average, 14 typhoons traverse the SCS each year (Lin et al., 2003). However, the seasonal variations of N_r deposition to the SCS basin and its relative contributions from aforementioned sources remain unclear.

Furthermore, the SCS, as well as its adjacent areas, is thought to be preferable for N_2 fixation (Capone et al., 1997; Wong et al., 2002) with relatively higher N_2 fixation rates (Chen et al., 2008a; Shiozaki et al., 2010). Based on the $\delta^{15}\text{N}$ values of suspended and sinking particulate nitrogen observation in the northern SCS, Kao et al. (2012) estimated the

Table 1. Statistical summary of average fluxes of atmospheric nitrate and ammonium depositions and flux-weighted isotopic compositions of nitrate during the sampling periods.

Sampling period (no. of samples)	NO ₃ ⁻ fluxes (±SD) (μmol N m ⁻² day ⁻¹)	NH ₄ ⁺ fluxes (±SD) (μmol N m ⁻² day ⁻¹)	δ ¹⁵ N _{NO₃} (‰ vs. air N ₂)	δ ¹⁸ O _{NO₃} (‰ vs. VSMOW)
9–19 Jul 2010 (<i>n</i> = 10 or 5*)	27 ± 19	21 ± 15	+1.6	+31.9
15–23 Sep 2010 (<i>n</i> = 13)	63 ± 59	36 ± 19	-0.5	+21.4
27 Nov–13 Dec 2010 (<i>n</i> = 27)	46 ± 39	15 ± 10	-3.7	+77.3
18 Feb 2010–2 Mar 2011 (<i>n</i> = 24 or 18*)	40 ± 21	14 ± 13	-5.3	+78.8
Overall dry deposition	43 ± 38	19 ± 15	-2.8	+58.8
Overall wet deposition (<i>n</i> = 11 or 9*)	140 ± 188	156 ± 185	-2.6	+78.8

* The dry and wet deposition sample numbers were used for isotope measurement, which are different from the respective total dry and wet deposition samples collected.

annual N-fixation flux to be $\sim 20 \pm 26$ mmol N m⁻² year⁻¹, which was similar to that reported at the BATS station (e.g., Orcutt et al., 2001) and ALOHA station (e.g., Karl et al., 1997). However, the isotope-derived estimation of N₂ fixation could be biased by N supply from atmospheric dry and wet deposition (Knapp et al., 2010; Wankel et al., 2010; Kao et al., 2012). To clarify the relative contribution of the two external inputs from the atmosphere, atmospheric N_r, and N₂ fixation, it is also necessary to quantify the magnitude of nitrate and characterize its isotopic imprints from various atmospheric inputs to the SCS.

Here we report first-hand data on the fluxes of nitrate and ammonium and the dual isotopic compositions of nitrate (δ¹⁵N_{NO₃} and δ¹⁸O_{NO₃}) in atmospheric deposition at a remote island (Dongsha) in the northern SCS. We estimate the fluxes, examine the potential sources of deposited nitrate in varying seasons, and discuss possible impacts of atmospheric nitrogen deposition on nitrogen cycling in the SCS.

2 Methods

2.1 Sample collection

Dongsha Island (atoll, Fig. 1) is located 340 km southeast of Hong Kong in the northern basin of SCS, with an area of ~ 2.8 km \times ~ 0.9 km. The water depth around this island is ~ 1000 m, and the biogeochemical characteristics (e.g., nutrients and chlorophyll *a*) in the vicinity of Dongsha are generally similar to those in the northern SCS (Liu et al., 2007, and unpublished data from M. H. Dai).

Four field experimental campaigns were conducted on Dongsha Island – July, September, November–December in 2010, as well as February–March in 2011. Table 1 provides the exact sampling periods. The wet season is generally from late May to late October, while the dry season covers November to April. We deployed a surrogate surface water glass dish (19 cm diameter and 8.5 cm depth, SCHOTT DURAN) for collecting dry deposition following the method employed by Hsu et al. (2013), which, in principle, was similar to those methods used previously (Azimi et al., 2003; Inomata et al.,

2009). The pre-cleaned container was infused with 100 mL of Milli-Q water prior to deployment; once approximately half (~ 50 mL) of the originally infused water was evaporated during deployment, the dish was replenished with additional 50 mL of Milli-Q water. The sampling duration of each sample was 12 h for the latter three sampling campaigns, but 24 h for the first campaign (July 2010). The recovered water was filtrated through polycarbonate membrane (0.45 μm pore in size and 47 mm in diameter, Nuclepore) by using pre-cleaned plastic filtration units (Nalgene Filterware 300–4100) and stored in the pre-weighed wide-mouth polypropylene (PP) bottles. The deposition samples were then subjected to in situ storage in refrigerator and to post-weighing when returning back in land-based lab in order to gravimetrically determine the recovered water volume. All samples (*n*=85) were stored at -20 °C before chemical and isotopic analysis. During the four field campaigns, 11 of 85 deposition samples were mixed with rainfall; these were therefore excluded from the dry deposition samples and treated as bulk deposition (i.e., wet plus dry deposition) samples in the present study. Note that these rain events collected in July and September were mostly caused by outer precipitating circulations of typhoons when they passed over to the north or south of Dongsha, making landfall at Taiwan towards eastern China or Hainan Island towards Vietnam, respectively (Fig. 1 and Supplement Fig. S1). The influence of tropical cyclones on deposition chemistry and isotopic signatures could be addressed to a greater or lesser extent. However the two rain-mixing deposition samples collected in December seem to be due to wintertime raining frontal systems from the north, as demonstrated by the backward trajectories (Supplement Fig. S2).

2.2 Chemical and isotopic analysis

Major ionic species (Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, Mg²⁺, K⁺, Ca²⁺, and NH₄⁺) in the deposition samples were analyzed by means of ion chromatography using ion chromatographs (model ICS-1100 for anions and model ICS-900 for cations) equipped with a conductivity detector (ASRS-ULTRA) and suppressor (ASRS-300 for ICS-1100 and CSRS-300 for

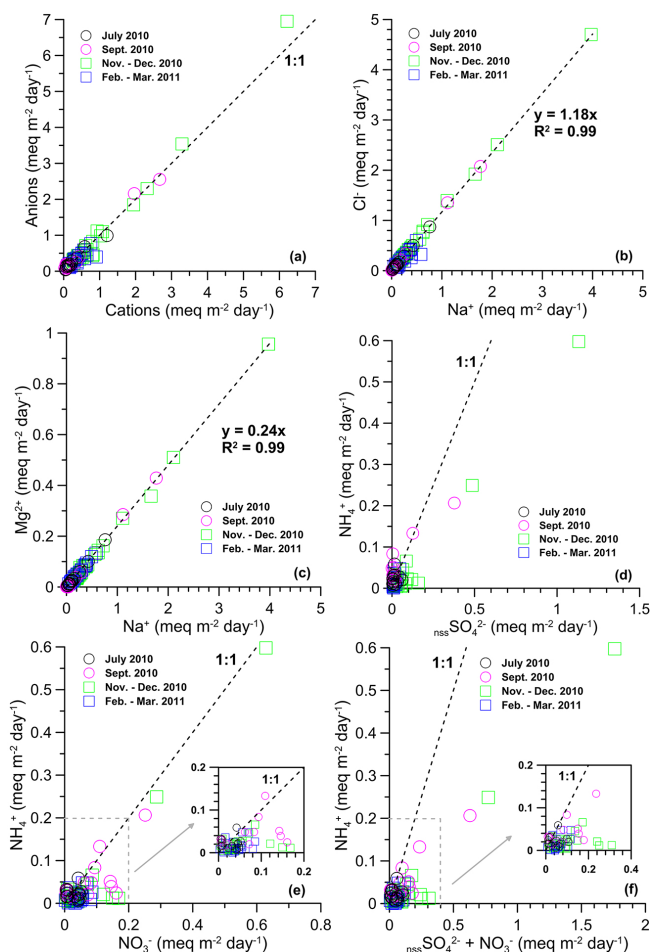


Fig. 2. Relationships for equivalent fluxes of (a) the total cations versus total anions, (b) Cl^- versus Na^+ , (c) Mg^{2+} versus Na^+ , (d) NH_4^+ versus non-sea-salt SO_4^{2-} ($_{\text{nss}}\text{SO}_4^{2-}$), (e) NH_4^+ versus NO_3^- , and (f) NH_4^+ vs. NO_3^- plus $_{\text{nss}}\text{SO}_4^{2-}$ in bulk atmospheric deposition during collection periods.

ICS-900). Separator columns (AS11-HC for anions, and CS12A for cations) and guard columns (AG11-HC for anions and CG12A for cations) were also used in the analysis. The eluents used were 22–25 mM KOH *Potassium hydroxide* for anions and 20 mM methansulfonic acid (MSA) for cations. In general, detection limits were below 0.01 mg L^{-1} for all ions except Cl^- and NH_4^+ ($\sim 0.015 \text{ mg L}^{-1}$). The concentration of non-sea-salt SO_4^{2-} ($_{\text{nss}}\text{SO}_4^{2-}$) was calculated by subtracting sea salt SO_4^{2-} ($_{\text{ss}}\text{SO}_4^{2-}$) from total SO_4^{2-} , and $_{\text{ss}}\text{SO}_4^{2-}$ was estimated by multiplying Na^+ by a factor of 0.252, where the coefficient of 0.252 is a typical sulfate-to-sodium mass ratio in seawater. Similar method was used to calculate non-sea-salt Ca^{2+} ($_{\text{nss}}\text{Ca}^{2+}$) with the coefficient of 0.0382, which is a typical calcium-to-sodium mass ratio in seawater.

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate plus nitrite (since nitrite concentration is mostly below the detection limit, hereafter referred to as nitrate) was measured by means of the “deni-

trifier method” (Sigman et al., 2001; Casciotti et al., 2002), which has been widely used to analyze nitrate dual isotopes in both seawater and freshwater, as well as in aerosol and rain (Hastings et al., 2003; Wankel et al., 2010; Fang et al., 2011). In brief, cultured denitrifying bacteria that lack N_2O reductase enzyme were used to quantitatively convert sample nitrate into N_2O ($\sim 10 \text{ nmol}$). Subsequently, the dual isotopes of N_2O gas were determined online using GasBench II coupled to a continuous flow isotope ratio mass spectrometer (IRMS, Thermo Finnigan DELTA^{plus}). Although oxygen isotopic fractionation between sample nitrate and the product N_2O during denitrification might take place, it is considerably constant in a given culture batch of denitrifier strain *Pseudomonas aureofaciens* (ATCC 13985) used (Casciotti et al., 2002). Thus, the N and O isotope ratios were corrected for drift, O isotopic exchange and blank by international nitrate isotope standards USGS 34, USGS 35, USGS32, and IAEA-N3 (Böhlke et al., 2003), as well as a laboratory working nitrate standard. Values are reported as the δ notation ($\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, where R denotes the ratios of heavy isotope to light isotope for N and O, in units of per mil, ‰). The standard deviations of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ measurements based on duplicate (for the samples with nitrate fluxes above $10 \mu\text{mol m}^{-2} \text{ day}^{-1}$) or triplicate (for the samples with nitrate fluxes below $10 \mu\text{mol m}^{-2} \text{ day}^{-1}$) analysis were generally better than ± 0.2 and $\pm 0.4 \text{ ‰}$ (1 SD), respectively. The reproducibility for a laboratory working standard is better than $\pm 0.2 \text{ ‰}$ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ over 2 years.

Previous studies showed a large mass-independent contribution of ^{17}O to the m/z 45 signal of N_2O ($^{14}\text{N}-^{14}\text{N}-^{17}\text{O}$) for $_{\text{atm}}\text{NO}_3^-$ samples could bias the results of $\delta^{15}\text{N}$ measurements from the “denitrified method” (e.g., Hastings et al., 2003; Wankel et al., 2010). Due to the limited sample for quantifying the effects of ^{17}O , we use a similar method (Wankel et al., 2010) based on the observed $\delta^{18}\text{O}$ values and the reported relationship between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Michalski et al., 2004) to correct $\delta^{15}\text{N}$ values in this study. The average corrected $\delta^{15}\text{N}$ value was decreased by $\sim 0.9 \text{ ‰}$.

3 Results

3.1 Chemistry of bulk deposition

First of all, we examined the equivalent ratios between the selected cations and anions by looking at their deposition flux correlations to evaluate the charge balance and, moreover, to identify the likely chemical forms of nitrate and ammonium that might be presented in deposited particles, as illustrated in Fig. 2. Obviously, total anions and total cations follow a nearly 1 : 1 good correlation (Fig. 2a), revealing a good charge balance in deposition samples. Furthermore, both Cl^- and Na^+ equivalent fluxes are well correlated ($R^2 = 0.99$), showing a linear regression line with a slope of 1.18 (Fig. 2b), which is close to that of average seawater

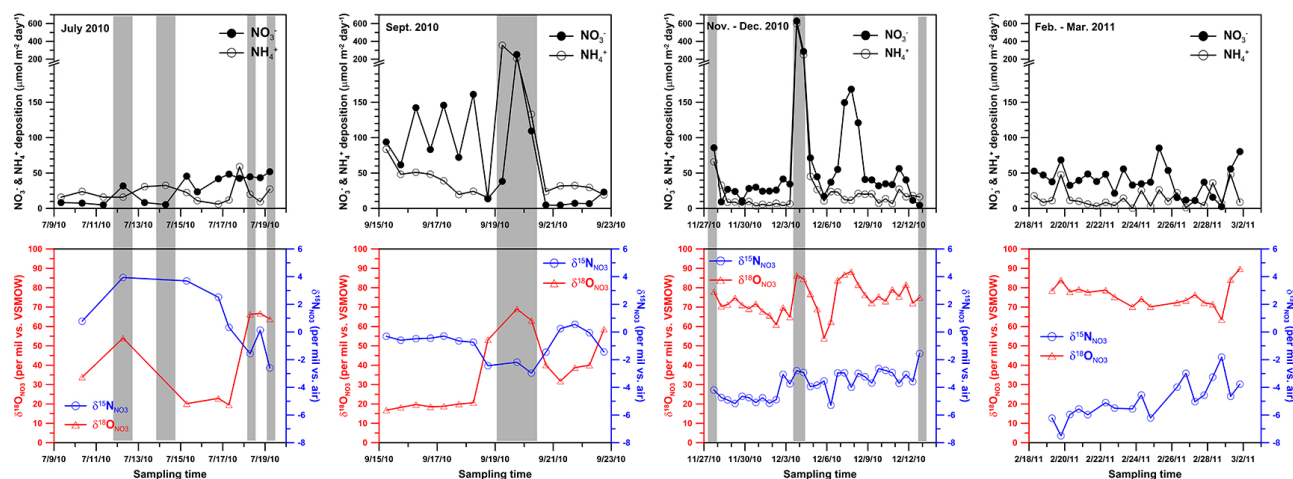


Fig. 3. Time series of fluxes of atmospheric nitrate and ammonium deposition and dual isotopic compositions of nitrate during four collection periods. The shaded areas indicate rainy events.

composition (1.17). In addition, both Na^+ and Mg^{2+} are well correlated ($R^2 = 0.99$), with a slope of 0.24 for the linear regression line (Fig. 2c), which is again consistent with that of average seawater composition (0.23). This clearly demonstrates that the origin of Cl^- , Na^+ , and Mg^{2+} is predominantly sea salt aerosols, which would thus serve as a vital component of deposition samples collected on Dongsha Island. On average, both sea-salt-derived Cl^- and the sum of Na^+ and Mg^{2+} accounted for 80 % or higher of each of the total anions and cations on the basis of equivalent amounts. Accordingly, when further looking at the correlation between ammonium and sulfate, instead of the total SO_4^{2-} , we only considered nssSO_4^{2-} (Fig. 2d). According to the correlations of NH_4^+ versus nssSO_4^{2-} (Fig. 2d), NH_4^+ versus NO_3^- (Fig. 2e), and NH_4^+ versus $(\text{nssSO}_4^{2-} + \text{NO}_3^-)$ (Fig. 2f), NH_4^+ appeared to be relatively insufficient to neutralize acid species such as anthropogenic sulfate and nitrate as most of the samples have much lower $\text{NH}_4^+/\text{nssSO}_4^{2-}$ and $\text{NH}_4^+/\text{NO}_3^-$ equivalent ratios than unity. Hsu et al. (2007) observed that marine aerosols collected over the study ocean were considerably depleted in ammonium relative to acidic components, leading to enhancing the acidity of marine aerosols (Keene and Savoie, 1998; Pathak et al., 2009). Moreover, this is in concert with the spatial distribution of ammonia emission over China, revealing that its hot spot is localized in the northern mainland (Huang et al., 2012). Also, this is consistent with the results of precipitation in the Pearl River delta, showing that the mean $\text{NH}_4^+ / (\text{nssSO}_4^{2-} + \text{NO}_3^-)$ equivalent ratio was only around 0.3–0.5 (Zheng et al., 2012), although no literature data on dry deposition composition from adjacent areas is available for comparison.

3.2 Atmospheric depositional fluxes of nitrate and ammonium

The time series of atmospheric nitrate and ammonium depositions for four collection periods are shown in Fig. 3, where rain-mixing samples in particular are indicated. Data on flux and isotope composition for dry and bulk deposition are statistically summarized in Table 1 though rain-mixing deposition samples were limited in numbers.

Nitrate and ammonium dry deposition varies largely, from 2.6 to $168 \mu\text{mol N m}^{-2} \text{ day}^{-1}$, and from 0.4 to $83.5 \mu\text{mol N m}^{-2} \text{ day}^{-1}$, respectively. Average dry deposition fluxes of nitrate and ammonium in each period have relatively smaller variability as compared to daily/diel values. The overall dry deposition averages of nitrate and ammonium throughout the sampling periods are 43 ± 38 and $19 \pm 15 \mu\text{mol N m}^{-2} \text{ day}^{-1}$, respectively. Both components show higher fluxes in the September campaign, while nitrate appears to be higher than ammonium.

Similar to dry deposition, wet deposition of nitrate and ammonium could vary largely with individual rain events. Such rain-event dependence is consistent with other studies performed around the world (Strayer et al., 2007; Zhang et al., 2011). The average rain-mixing bulk deposition ($140 \pm 188 \mu\text{mol N m}^{-2} \text{ day}^{-1}$ for nitrate and $156 \pm 185 \mu\text{mol N m}^{-2} \text{ day}^{-1}$ for ammonium, Table 1) exceeds the dry deposition by 3 to 7 times, implying that wet deposition cannot be neglected in quantification of atmospheric nitrogen deposition to the SCS though with much less frequency. Unlike in dry deposition, both nitrogen species are similarly important in contributing to nitrogen wet deposition. Moreover, it is noted that there was no concurrent variation of ammonium and nitrate in dry deposition. However, both ammonium and nitrate depositions in rainy days increased concomitantly and ammonium may even reach the same level of nitrate (Fig. 3 and Table 1).

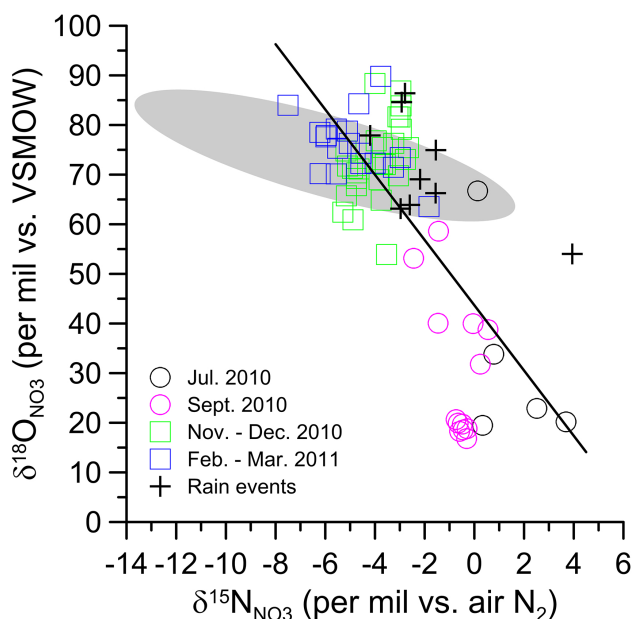


Fig. 4. Correlation between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values in dry deposition as well as rain-mixing bulk deposition. The solid line indicates the regression line for the entire data set. The shaded area covers the distribution of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of precipitation nitrate observed at Bermuda (32.27° N, 64.87° W; Hastings et al., 2003).

The $\text{NO}_3^-/\text{NH}_4^+$ ratios in dry deposition over the entire period vary widely, from 0.2 to 94, with lower ratios (range 0.2–6.9, average 2.0) in the warm periods (July and September) and higher ratios (range 0.3–94; average 6.2) in the cold period (November to March). A similar seasonal pattern was observed by Jia and Chen (2010) in a coastal city of southern China. Therefore, the overall mean $\text{NO}_3^-/\text{NH}_4^+$ ratio (2.3) higher than unity in dry deposition indicates the dominance of nitrate in atmospheric inorganic nitrogen deposition year round.

However, the $\text{NO}_3^-/\text{NH}_4^+$ ratio in wet deposition averages at ~ 0.9 revealing an opposite pattern with the dominance of NH_4^+ . Though we know atmospheric NH_4^+ is important and mainly derived from volatilized NH_3 (from waste, fertilizer, and soil), and thermogenic NH_3 (from biomass burning and fossil combustion) (Dentener and Crutzen, 1994; Jia and Chen, 2010), its isotope measurement is not yet available in our laboratory. Below, we will focus on nitrate isotopes to identify the potential sources of atmospheric nitrate.

3.3 Dual isotopic compositions of atmospheric nitrate

Nitrate $\delta^{15}\text{N}$ values in dry deposition have a wide span, varying between -7.5 and $+3.7$ ‰ with a flux-weighted average value of -2.8 ‰ (Fig. 3 and Table 1). All data fall within the wide range of previously reported $\delta^{15}\text{N}$ values for atmNO_3^- in coastal and oceanic regions (Russell et al., 1998;

Yeatman et al., 2001; Carrillo et al., 2002; Hastings et al., 2003; Baker et al., 2007; Savarino et al., 2007; Wankel et al., 2010). It seems that the $\delta^{15}\text{N}$ values exhibit a seasonality with lower values (< -3 ‰) in the northeasterly monsoon, higher values ($+1.6$ ‰) in the summer monsoon, and intermediate (-0.5 ‰) in the transitional time (autumn) (Table 1). Similar seasonal trend in $\delta^{15}\text{N}$ values of atmNO_3^- was observed previously (e.g., Hastings et al., 2003; Morin et al., 2008; Wankel et al., 2010), whereas inverse pattern was also reported in some other studies (Yeatman et al., 2001; Elliott et al., 2009). Different trends are likely attributed to the sources of atmNO_3^- and their respective nitrogen imprints varying temporally from site to site, as will be discussed later in conjunction with the $\delta^{18}\text{O}$ results.

Nitrate $\delta^{18}\text{O}$ values in dry deposition range from $+16.8$ to $+88.3$ ‰ with a flux-weighted average value of $+58.8$ ‰. The general seasonality of $\delta^{18}\text{O}_{\text{NO}_3}$ in dry deposition is different from that of $\delta^{15}\text{N}_{\text{NO}_3}$, showing higher values during the cold period and lower values in the warm season (Fig. 3 and Table 1). The overall seasonal pattern with higher $\delta^{18}\text{O}_{\text{NO}_3}$ values in winter is consistent with previous studies (Hastings et al., 2003; Wankel et al., 2010; Fang et al., 2011). However, the lower bound generally observed in the summer is far lower than the typical range reported (e.g., Böhlke et al., 2003; Hastings et al., 2003; Savarino et al., 2007), deserving further discussion (see Sect. 4.1).

Regarding wet deposition, its flux-weighted mean $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values are -2.6 and $+78.8$ ‰, falling into the range of those in dry deposition. Because of the similarity and limitation of available sample numbers, the following discussion on the dual isotopic compositions is focused on dry deposition; for discussion, sometimes wet deposition is combined with dry deposition.

4 Discussion

4.1 Interpretation for unusually low $\delta^{18}\text{O}$ values of atmospheric nitrate

A negative correlation ($R^2 = 0.52$, $n = 72$) is observed between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ in all deposition samples (Fig. 4), which is consistent with that reported for precipitation nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ at Bermuda (Hastings et al., 2003). The authors suggested that the changing sources of nitrate because of varying air masses might be responsible for the seasonal variations in $\delta^{15}\text{N}_{\text{NO}_3}$ (source-driven signals) and $\delta^{18}\text{O}_{\text{NO}_3}$ (chemistry-driven signals) values. However, the slope of the regression line in our study is much steeper, mainly due to relatively lower $\delta^{18}\text{O}_{\text{NO}_3}$ values observed.

As low as $\sim +17$ ‰ is unusual for $\delta^{18}\text{O}$ value of atmNO_3^- . The $\delta^{18}\text{O}_{\text{NO}_3}$ values are thought to be mainly controlled by relative significance between ozone ($+90$ to $+122$ ‰; Johnson and Thiemens, 1997) and OH radical (typically from

–10 to –6‰ around the SCS from the Global Network of Isotopes in Precipitation (GNIP; International Atomic Energy Agency, available from <http://isohis.iaea.org>) to nitrate formation. Higher $\delta^{18}\text{O}$ values in nitrate observed in winter are mainly due to greater contribution by O_3 to NO_x oxidation, while the lower $\delta^{18}\text{O}$ values in summer could be attributed to favorable reaction of NO_2 with OH (Hastings et al., 2003; Michalski et al., 2003; Wankel et al., 2010). Using the minimum and maximum $\delta^{18}\text{O}$ values of O_3 and OH, one might predict that $\delta^{18}\text{O}$ values of nitrate would fall within a range from $\sim +56\%$ (assuming two oxygen molecules from O_3 and one from OH) to $\sim +100\%$ (assuming 5/6 oxygen atoms from O_3 and 1/6 from OH) based on chemical reactions (see Hastings et al., 2003; Fang et al., 2011).

However, some of our summertime $\delta^{18}\text{O}_{\text{NO}_3}$ data are much lower than expected range above. A likelihood is that NO is oxidized to NO_2 by peroxy radicals that could compete with O_3 in certain environments. The oxygen molecule of peroxy radicals is suggested to derive from atmospheric O_2 (Salisbury et al., 2001, and references therein), which typically occupies lower $\delta^{18}\text{O}$ values ($\sim +23\%$), perhaps resulting in low $\delta^{18}\text{O}$ values in atmNO_3^- . The expected $\delta^{18}\text{O}$ values could be down to $+11\%$ if the reaction is taking place with peroxy radicals (Fang et al., 2011). The formation of peroxy radicals, the intermediates between OH radicals and O_3 formation or destruction, is more prevalent in polluted cities (Salisbury et al., 2001). The marine boundary layer of the study region under the influence of Asian continental outflows is known to be relatively polluted (Hsu et al., 2013).

4.2 Potential sources of atmospheric nitrate

In our study area, seasonal variation in $\text{atmNO}_3^- \delta^{15}\text{N}$ might reflect the changes in potential sources, which are driven primarily by distinct monsoon systems and episodically by tropical cyclones. During winter when the northeasterly wind is prevailing, atmNO_3^- deposition collected in the northern SCS, with $\delta^{15}\text{N}$ ranging from -7.5 to -1.8% , could be presumably predominantly derived from anthropogenic emissions originated from northern China. Recent studies showed that aside from natural sources such as soil emission, lightning, and biomass burning, all the main sources of anthropogenic NO_x emissions including industry, power plants, residential, and transportation in China are relevant to fossil fuel combustion (Lin et al., 2010; Liu et al., 2013, and references therein). Among these fossil fuels, coal is one of the primary (more than 70%; Tian et al., 2001); different types of Chinese coals exhibit the $\delta^{15}\text{N}$ values ranging from -6 to $+4\%$ with an average of $\sim -1.5\%$ (Xiao and Liu, 2011). Widory (2007) reported a particularly low $\delta^{15}\text{N}$ value, -5.3% , for coal combustion, as compared to larger values reported by Fang et al. (2011) and Felix et al. (2012). Heaton (1990) reported a range from -13 to -2% for $\delta^{15}\text{N}$ values of NO_x from vehicle exhausts. Chen et al. (2011) found that rain nitrate had low $\delta^{15}\text{N}$ values (-7.5 to -3.1%)

in the coastal area of southeastern China, which was ascribed mostly to vehicle exhausts. An intimate correlation has been found between NO_3^- and nssSO_4^{2-} in our deposition samples ($R^2 = 0.82$, $P < 0.0001$; Supplement Fig. S3), suggesting that the transport and/or sources of atmNO_3^- might be associated with SO_4^{2-} dominated by coal combustion in China. Such positive correlation has also been observed in precipitation collected from southern China, suggesting concurrent emissions from coal burning (Fang et al., 2011). Accordingly, our data might indicate the dominance of anthropogenic sources for atmNO_3^- deposited in the northern SCS, of which coal combustion is of particular importance. The back-trajectory analysis in Supplement Fig. S2, which shows that the wintertime air mass was mainly sourced from the very north of China at an altitude of ~ 1500 – 3000 m, is supportive to our conjecture.

In order to further identify the likely sources of atmNO_3^- , we examine the correlations of NO_3^- , nssSO_4^{2-} , and nssCa^{2+} deposition fluxes compared to dual isotopic compositions of atmNO_3^- (Fig. 5). Higher fluxes were almost associated with intermediate $\delta^{15}\text{N}_{\text{NO}_3}$ (-4 to 0%) but with higher $\delta^{18}\text{O}_{\text{NO}_3}$ ($+60$ to $+90\%$). Accordingly, this perhaps indicates that these larger deposition might be contributed by the deposition of $\text{Ca}(\text{NO}_3)_2$ and CaSO_4 particles that are formed through heterogeneous reactions between CaCO_3 dust and acid gases, including H_2SO_4 (SO_2) and HNO_3 (NO_x and N_2O_5) (Sullivan et al., 2007). This phenomenon of heterogeneous reaction between Asian dust bearing carbonate and anthropogenic acid gases has often been observed over the study ocean (Hsu et al., 2013). These deliquescent $\text{Ca}(\text{NO}_3)_2$ and CaSO_4 particles were readily dissolved in the solution (Milli-Q water) used in collection once they were deposited.

In contrast to the northeasterly monsoon, the summer monsoon blows relatively cleaner maritime air towards Dongsha. However, the summer monsoon winds may often pass over southeastern Asia, which is well known to be the major hot spot of biomass burning in the world (Ott et al., 2010). The occurrence of biomass burning is concentrated in the period of summer to autumn, particularly in Indonesia (Tosca et al., 2011). Low levels of atmNO_3^- in July could be carried by relatively weak southwesterly winds mainly from southern/southeastern Asia and pelagic regions, as depicted by the typical trajectories in Supplement Fig. S4. The maritime air is usually associated with considerably low levels of continentally derived air pollutants and dust (nssSO_4^{2-} and nssCa^{2+} ; see Fig. 5b–c), possibly suggesting the dominance of natural sources. To our best understanding, no $\delta^{15}\text{N}$ data are currently available for nitrate in southeastern Asian biomass-burning-dominated aerosols or precipitation. In fact, biomass burning data are also very scarce on the global scale; Kundu et al. (2010) reported the $\delta^{15}\text{N}$ ratios ranging from $+23.5$ to $+25.7\%$ for total nitrogen (but not nitrate) in $\text{PM}_{2.5}$ sourced from Brazilian biomass burning plumes, as compared to a revised $\delta^{15}\text{N}_{\text{NO}_3}$ value of

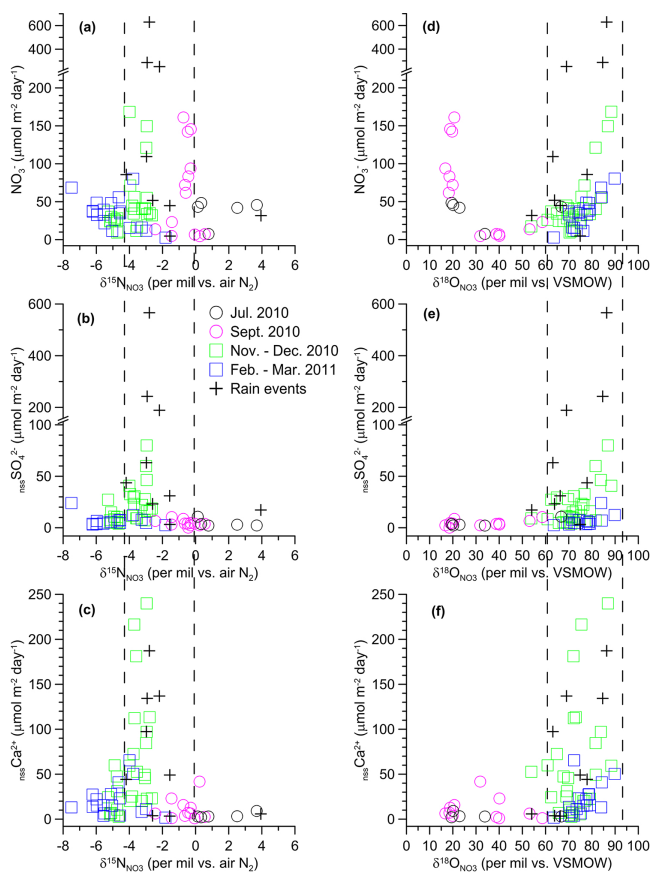


Fig. 5. Scatter plots of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values compared to atmospheric deposition fluxes of NO_3^- (a, d), nssSO_4^{2-} (b, e), and nssCa^{2+} (c, f). The dashed lines cover the $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ ranges corresponding to higher deposition fluxes of NO_3^- , nssSO_4^{2-} , and nssCa^{2+} .

$\sim +11.5\%$ recently reported by Felix and Elliott (2013). Accordingly, the involvement of relatively more biomass burning substances in summertime deposition perhaps in part accounted for the observed increase in $\delta^{15}\text{N}_{\text{NO}_3}$ values.

In addition to biomass burning, it is well known that lightning and soil emission are two vital natural sources of tropospheric NO_x in the globe (Holland et al., 1999; Schumann and Huntrieser, 2007). The $\delta^{15}\text{N}\text{-NO}_x$ produced from lightning is characterized by near-zero values (-0.5% to $+1.4\%$) (Hoering, 1957), but a much lower value (-15%) has been reported by Moore (1977). Based on a comprehensive review by Schumann and Huntrieser (2007), it has been shown that the tropical regions have higher lightning-generated NO_x emissions in summer. Lin (2012) specifically suggested that in summer contributions from natural sources combining soil emanation and lightning represent up to 30% of the NO_x in the atmosphere in eastern China, which demonstrates the significance of lightning, particularly during the episodic raining events. Although raining

events induced by tropical cyclones in July and September passing over around Dongsha (Fig. 1 and Supplement Fig. S1) would supply nitrogen deposition, rain composition could vary with distinct pathways of typhoon passage (Wai et al., 2007; Buda and DeWalle, 2009; Tsai et al., 2011). Specifically, isotopic signals along with rain chemistry have also been found to have large inter- and intra-rain-event variability during the typhoon/hurricane periods, corresponding to the changing sources of air pollutants (Liotta et al., 2008; Mullaugh et al., 2013). Therefore, the contribution of lightning-generated NO_x and its oxidation products, including $\text{HNO}_{3(g)}$ and aerosol nitrate, could be partly responsible for the observed relatively large ratios in summer. A few studies have also found similar N isotope signals (near 0‰) of atmNO_3^- in warm season (Hastings et al., 2003; Elliott et al., 2009; Morin et al., 2009). However, it is noticed that the $\delta^{15}\text{N}_{\text{NO}_3}$ values decreased from 0 to -1% before September 18 to $\sim -3\%$ after 19 September and returned back to positive ratios on 21 September. It is likely that when Typhoon Fanapi made landfall on Taiwan and Fujian on 19–20 September, its counterclockwise circulation might have swept the continental nitrate pollutants characterized by lower $\delta^{15}\text{N}_{\text{NO}_3}$, such as fossil fuel combustion and traffic exhaust, out of these areas and carried them southward to Dongsha.

The higher level of nitrate deposition and lightning-derived isotopic feature suggested that nitrate supply induced by tropical cyclone is potentially an important nitrogen source to the SCS. Indeed, previous studies suggested that lightning-derived NO_x could account for a significant amount of nitrate supply to the ocean. Hastings et al. (2003) calculated a $\sim 70\%$ contribution derived from lightning to total nitrate deposition at Bermuda. Given an average of 14 typhoons passing over the SCS annually (Lin et al., 2003) with a similar period of influence and magnitude of nitrate flux, we suggest that typhoon-induced contribution could be of considerable significance, warranting further studies to quantify its relative importance and explore such nitrate generation processes in future work.

4.3 Implications of atmospheric N_r deposition to the South China Sea

Hsu et al. (2007) recently reported an average aerosol nitrate concentration of $1.1 \pm 0.6 \mu\text{g m}^{-3}$ over the northern SCS during wintertime of 2004. If we adopted a dry deposition velocity of 1.15 cm s^{-1} for aerosol NO_3^- similar to that used in the Yellow Sea and East China Sea (Zhang et al., 2011, and references therein), dry deposition contributed by aerosol nitrate was calculated to be $18 \pm 10 \mu\text{mol N m}^{-2} \text{ day}^{-1}$, which is less than half of the mean measured nitrate dry deposition ($43 \pm 38 \mu\text{mol N m}^{-2} \text{ day}^{-1}$). This might imply that dry deposition of oxidized nitrogen gaseous species, particularly nitric acid, could be a vital contributor, though we acknowledge that those aerosol data were observed during

two short wintertime periods. On the other hand, average wet deposition of nitrate over collection periods was up to $140 \pm 188 \mu\text{mol N m}^{-2} \text{ day}^{-1}$ (Table 1). Higher inorganic nitrogen fluxes via wet deposition were also observed in the East China Sea and Yellow Sea (Zhang et al., 2011). This may suggest that wet deposition is more significant in terms of N supply to the ocean in our study area. By considering the climatology of annual non-raining and raining days at Dongsha to be 256 and 109 days, respectively, the resulting annual nitrate deposition is $26 \pm 23 \text{ mmol N m}^{-2} \text{ year}^{-1}$.

Similar to nitrate, ammonium dry deposition was also higher in September, and wet deposition was higher than dry deposition. Based on the overall dry and wet deposition of ammonium listed in Table 1, annual ammonium deposition was calculated to be $22 \pm 21 \text{ mmol N m}^{-2} \text{ year}^{-1}$ by considering the annual non-raining and raining days.

When compared to the observed results from adjacent oceanic regions (Nakamura et al., 2005; Chen et al., 2011; Zhang et al., 2011, and references therein), we found atmospheric nitrate deposition fluxes into the northern SCS were generally comparable to those reported in the Yellow Sea (YS) and open areas of the East China Sea (ECS), as well as the western North Pacific (WNP), yet considerably lower than coasts of the YS and ECS ($80\text{--}90 \text{ mmol N m}^{-2} \text{ year}^{-1}$). Ammonium depositions to the northern SCS were slightly lower than those measured over the YS, ECS, and WNP ($15\text{--}30 \text{ mmol N m}^{-2} \text{ year}^{-1}$), but considerably lower than those in coastal areas of China (up to $100 \text{ mmol N m}^{-2} \text{ year}^{-1}$). Similarly, the observed NO_3^- and NH_4^+ deposition fluxes in the northern SCS were relatively lower than those ($35\text{--}212 \text{ mmol N m}^{-2} \text{ year}^{-1}$ for nitrate and $36\text{--}163 \text{ mmol N m}^{-2} \text{ year}^{-1}$ for ammonium) in coastal urban stations in southern China (Jia and Chen, 2010; Wai et al., 2010). Such a spatial pattern with an offshore decreasing tendency implies that N_r (including nitrate and ammonium) was essentially transported from the continent via the northeasterly winds during the winter monsoon.

As compared to previously simulated results for the northern SCS ($500\text{--}1000 \text{ mg N m}^{-2} \text{ year}^{-1}$; Dentener et al., 2006; Duce et al., 2008), our N_r deposition data ($\sim 48 \text{ mmol N m}^{-2} \text{ year}^{-1}$ or $672 \text{ mg N m}^{-2} \text{ year}^{-1}$) are rather comparable. It is worth noting that dissolved organic nitrogen (DON) was not taken into account in our estimate. Recent studies suggested that organic N_r could account for $10\text{--}40\%$ of total N_r deposition to the adjacent marginal seas (Zhang et al., 2011) and open ocean (e.g., Cornell et al., 2001), therefore reminding us that our observation might be an underestimation. Also noted is that we missed sampling in spring, which is the prevailing time of Asian dust outflows, which often bring more pollutants for long-range transport (Hsu et al., 2010, 2014; Zhang et al., 2011). By taking no account of DON, our observation of $50 \text{ mmol N m}^{-2} \text{ year}^{-1}$ as total N_r deposition may stimulate a new production of $\sim 330 \text{ mmol C m}^{-2} \text{ year}^{-1}$ when the Redfield ratio is applied. This amount is comparable to the annual CO_2 emission in the outer shelf and slope of the north-

ern SCS on an areal basis ($\sim 460 \pm 430 \text{ mmol C m}^{-2} \text{ year}^{-1}$; Zhai et al., 2005, 2013). Due to its unique feature of thermocline circulation, the SCS has been taken as an upwelling basin and thus a source of CO_2 (Dai et al., 2013). Since we know that, due to significant anthropogenic alteration, there has been no pristine marine environment since the Industrial Revolution, accordingly, the primitive northern SCS might release 2 times higher CO_2 than present day if not including this fertilization from atmospheric N_r input.

From the literature data that have been obtained through various methods (Cai et al., 2002; Chen, 2005; Chen et al., 2008b; Kao et al., 2012), the reasonable value for new production in the northern SCS is $\sim 2000 \text{ mmol C m}^{-2} \text{ year}^{-1}$, though it is largely variable and uncertain among those data. Thus, atmospheric N_r would contribute $\sim 15\%$, which is obviously a significant portion for such an upwelling basin.

Meanwhile, nitrogen fixation is also considered as one of the main external nutrient sources for new production, which could contribute to the POC export flux in N-limiting systems such as the western Pacific (e.g., Liu et al., 1996; Shiozaki et al., 2010). At present, data on N-fixation rates for the oligotrophic SCS are considerably scarce (Wong et al., 2007; Chen et al., 2008a; Kao et al., 2012), widely ranging from 2.4 ± 1.7 to $240 \text{ mmol N m}^{-2} \text{ year}^{-1}$. Each of those studies inherited weakness. The upper end of the aforementioned range was derived from the nitrate anomaly method (Wong et al., 2007), which could be overestimated. One of the possible reasons is that they have assumed N supply was only derived from N_2 fixation, and neglected the effects of atmospheric deposition having substantial amounts of N and high N:P ratios (e.g., Baker et al., 2003). It is well known that the N:P ratios in atmospheric deposition are generally much higher than the Redfield N:P ratio of 16:1 (e.g., Baker et al., 2003); thus enhanced atmospheric N_r input may relax N limitation in order to suppress N_2 fixation. Inevitably, the relative importance of N_r deposition and N_2 fixation will change over time with the continuous increase in atmospheric N_r inputs in the future. Briefly, our estimate implies the significance of atmospheric deposition in supplying bioavailable nitrogen to the SCS and potentially influencing its biogeochemistry.

4.4 Isotope constraints on new nitrogen inputs to thermocline

Based on our direct observation on Dongsha, the flux-weighted average $\delta^{15}\text{N}$ of nitrate was -2.7% , which is very similar to that by N_2 fixation (-2% to 0%). Even lower averages were observed for N isotopic compositions of NH_4^+ (-12.4% to -0.6% with an annual volume-weighted mean of -7.3%) near cities on the coast of China (Jia and Chen, 2010). All these low N isotopic compositions of atmospheric N_r may lead to a similar syndrome of nitrogen fixation after mixing with nitrate from deeper water. To discern the relative contribution from atmospheric N_r and N_2 fixation to the surface ocean, we follow a similar approach adopted in

Bermuda (Knapp et al., 2010) to estimate the fraction of lowering nitrate $\delta^{15}\text{N}$ of the SCS thermocline due to atmospheric N_r deposition (f_{AND}), which is formulated as

$$f_{\text{AND}} = \left(\Delta\delta^{15}\text{N}_{\text{bt-a}} \times F_a \right) / \left(\Delta\delta^{15}\text{N}_{\text{bt-f}} \times F_f + \Delta\delta^{15}\text{N}_{\text{bt-a}} \times F_a \right) \quad (1)$$

where F_a and F_f represent the fluxes of atmospheric N_r deposition ($\sim 50 \text{ mmol N m}^{-2} \text{ year}^{-1}$) and nitrogen fixation (here we use $40 \text{ mmol N m}^{-2} \text{ year}^{-1}$), respectively; subscripts bt, a, and f stand for nitrate below thermocline, atmospheric total N_r , and N_2 fixation.

$\Delta\delta^{15}\text{N}_{\text{bt-a}}$ is the offset between $\delta^{15}\text{N}_{\text{bt}}$ ($\delta^{15}\text{N}_{\text{bt}} = \sim +6.2\text{‰}$; Liu et al., 1996; Wong et al., 2002) and $\delta^{15}\text{N}_a$ (here we used -2.7‰ , the same as that of atmNO_3^-), $\Delta\delta^{15}\text{N}_{\text{bt-f}}$ stands for the discrepancy between $\delta^{15}\text{N}_{\text{bt}}$ and $\delta^{15}\text{N}_f$, and here we take -1‰ for $\delta^{15}\text{N}_f$ (Karl et al., 1997). Accordingly, f_{AND} is estimated to be ~ 0.6 , indicating that atmospheric N_r deposition could account for $\sim 60\%$ of depression in nitrate $\delta^{15}\text{N}$ of the SCS thermocline.

Three factors may result in uncertainty of this estimate, the N-fixation rate and atmospheric DON flux and its isotopic composition, of which more efforts should be paid for atmospheric DON as little data were documented for its concentration and isotopic composition. The few reports gave a range of relatively wide $\delta^{15}\text{N}$ for atmospheric DON from -7 to $+10\text{‰}$ and it seems to be site-dependent (Cornell et al., 1995; Russell et al., 1998). From our result, we knew the observed nitrate $\delta^{15}\text{N}$ values resemble that derived from N_2 fixation. To better constrain the atmospheric impact on the nitrogen cycle in the SCS, more spatiotemporal data about N_r speciation (e.g., ammonium and DON) and their relative contributions are required in isotopic balance model.

5 Conclusions

In light of the depositional flux of N_r , dual isotopes of nitrate and ion chemistry measurements on the Dongsha Island, we suggest that the majority of atmospheric N_r deposition was sourced from mainland China driven by the prevailing winter monsoon winds, whereas contributions from tropical cyclones and southeastern Asian biomass burning could be significant in summer. Dual isotopic composition, $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$, exhibited an anti-correlation, and showed an evident seasonality in which $\delta^{15}\text{N}_{\text{NO}_3}$ was higher in summer and lower in winter. Such a $\delta^{15}\text{N}_{\text{NO}_3}$ pattern could be attributed to the change in source provenances with monsoons – that is, the predominance of coal combustion from eastern and northern China during the northeasterly monsoon compared to that of biomass burning from southeastern Asia and lightning in the summer monsoon. This study highlights the urgent need to establish the specific nitrogen isotopic composition of various potentially significant end members (emission sources) such as coal and oil combustion, vehicle exhaust, and biomass burning, particularly around eastern Asia.

Annual total atmospheric inorganic nitrogen deposition was estimated to be $\sim 50 \text{ mmol N m}^{-2} \text{ year}^{-1}$ but would increase by 10–40% if considering DON. This quantity could stimulate a new production of $\sim 330 \text{ mmol C m}^{-2} \text{ year}^{-1}$, which would mitigate $\sim 50\%$ of the CO_2 release from the northern SCS. If the atmospheric N_r emission from China continuously increases as predicted by the model, the SCS might turn from a source to a sink in terms of CO_2 sequestration. In our monitoring, the overall mean nitrate/ammonium ratio in dry deposition was ~ 2.3 , whereas the ratio can reduce to around unity for wet deposition, suggesting that ammonium plays an important role in contributing to the N cycling of oligotrophic SCS. Unfortunately, the documented N-fixation rates by different methods varied over ~ 2 orders of magnitude, revealing that researchers' appreciation of N_2 fixation is still insufficient to precisely construct a budget of N_r in the study ocean. Additionally, the similarity in $\delta^{15}\text{N}$ produced by depositional nitrate and diazotrophs further complicated the application of the isotope model to the euphotic zone. More comprehensive studies are urgently needed on isotopic compositions of nitrogen speciation in deposition on varying spatiotemporal scales as well as their relative importance versus potential impacts on N cycling in the SCS.

Supplementary material related to this article is available online at <http://www.biogeosciences.net/11/1833/2014/bg-11-1833-2014-supplement.pdf>.

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