

Isotopic composition  
of nitrate in bulk  
atmospheric  
deposition

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# 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 Asian continent poses profound threats on ecosystem safety from terrestrial throughout the ocean proper. To diagnose the sources of atmospheric  $N_r$  input and quantify its influence on marine nitrogen cycle of the South China Sea (SCS), an oligotrophic marginal sea adjacent to the emission hotspot China, we conducted measurements of dual isotopes of water-soluble nitrate ( $\delta^{15}N_{NO_3}$  and  $\delta^{18}O_{NO_3}$ ) and concentrations of major ions for bulk atmospheric deposition collected from Dongsha Island off south China. The  $\delta^{15}N_{NO_3}$  and  $\delta^{18}O_{NO_3}$  for bulk deposition ranged from  $-7.5\%$  to  $+3.9\%$  and  $\sim +17\%$  to  $+88\%$ , respectively. A relatively uniform low  $\delta^{15}N_{NO_3}$  and high  $\delta^{18}O_{NO_3}$  endmember were observed in winter. Non-sea-salt sulfate/calcium ( ${}_{nss}SO_4^{2-}$  and  ${}_{nss}Ca^{2+}$ ) peaked as the increasing nitrate depositional flux (one exception caused by typhoon), implying a pollution source of nitrate during high deposition. Meanwhile, the flux-weighted average of  $\delta^{15}N_{NO_3}$  was  $-2.7 \pm 2.3\%$ , resembling the isotopic signature of fossil fuel combustion in inland China. More variable dual isotopic values observed in July and September suggest relatively dynamics sources and conversion chemistry. During the period affected by the peripheral circumfluence of Typhoon Fanapi, a high nitrate deposition with uniform isotopic composition ( $\delta^{15}N_{NO_3}$  of  $\sim -0.5\%$  and  $\delta^{18}O_{NO_3}$  of  $\sim +19\%$ ) was observed accompanying with low terrestrial constituents such as dust and pollutants (e.g.  ${}_{nss}SO_4^{2-}$  and  ${}_{nss}Ca^{2+}$ ). This high nitrate deposition was likely a natural endmember sourced from lightning. The summarized total atmospheric  $N_r$  deposition (AND) is  $\sim 50 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ . If without this additional AND fertilization,  $CO_2$  release (currently  $460 \pm 430 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ) from the SCS would be doubled. Our study demonstrates that AND may serve as an important external  $N_r$  supply to the SCS yet difficult to separate from N-fixation ( $-2\%$  to  $0\%$ ) due to isotopic similarity and high N:P ratio. More studies related to isotopic

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composition of nitrogen speciation and their relative contributions as well as the role of typhoon-induced input to AND are required.

## 1 Introduction

The input of newly bioavailable nitrogen to the ocean is thought to largely control the efficiency of biological pump and thus export of carbon from the surface ocean, and subsequently to modulate the levels of atmospheric CO<sub>2</sub> (Falkowski et al., 1998). For decades, human activities significantly contribute to the emission of reactive nitrogen (N<sub>r</sub>) 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<sub>r</sub> deposition to the ocean has rapidly increased to ~ 67 Tg N yr<sup>-1</sup> since the mid-1800s and the number is comparable with the estimates of oceanic N-fixation at present and would account for ~ 40 % of external N supply to the surface ocean, mostly due to anthropogenic emissions (Duce et al., 2008, and references therein; Galloway et al., 2004, 2008). Such external anthropogenic input from the atmosphere apparently results in a prominent impact on marine nitrogen cycle and associated biogeochemistry, as well as the community structure of ecosystem, particularly in oligotrophic marginal seas being sensitive to N<sub>r</sub> availability (e.g. Bonnet et al., 2005; Duarte et al., 2006; Galloway et al., 2008; Kim et al., 2011; Zhang et al., 2004). However, direct observations on the magnitude of atmospheric N<sub>r</sub> deposition to the ocean are limited. In order to better constrain the influence of atmospheric N<sub>r</sub> inputs and evaluate its role in marine nitrogen cycling, field measurements for the sources and quantification of atmospheric N<sub>r</sub> deposition are urgently required.

Nitrate, the most stable compound of atmospheric N<sub>r</sub> (Galloway et al., 2008), is formed from the homogeneous and heterogeneous oxidation of NO<sub>x</sub>, which could be derived both from natural (e.g. lightning, soil emissions, wildfires) and anthropogenic (e.g. combustion of fossil fuels, vehicle exhausts) origins. Specifically, atmospheric ni-

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trate ( ${}_{\text{atm}}\text{NO}_3^-$ ) is generally formed by  $\text{NO}_x$  oxidation by several complex chemical pathways, mainly including: (1) NO is quickly oxidized by ozone ( $\text{O}_3$ ) to  $\text{NO}_2$  and followed by hydroxyl radical (OH) oxidation during daytime. These processes are more prevalent in the summer, when photochemically produced OH concentrations are generally highest; (2) hydrolysis of  $\text{N}_2\text{O}_5$  formed via combination  $\text{NO}_3$  radical ( $\text{NO}_2$  oxidation by  $\text{O}_3$ ) with  $\text{NO}_2$  in 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  $\text{NO}_3^-$  in the atmosphere (e.g. Freyer, 1991; Morin et al., 2009), previous studies suggested that N isotopic composition of nitrate in atmospheric deposition could be used as fingerprints to identify  $\text{NO}_x$  sources (e.g. Freyer, 1991; Hastings et al., 2003; Heaton, 1987; Knapp et al., 2010; Russell et al., 1998; Yeatman et al., 2001). On the other hand, O isotopes in nitrate are mostly controlled by the oxidation pathways during atmospheric transport (Elliott et al., 2009; Fang et al., 2011; Hastings et al., 2003; Savarino et al., 2007; Wankel et al., 2010). However, to our knowledge no isotope study was conducted so far to trace the sources of  ${}_{\text{atm}}\text{NO}_3^-$  deposition onto China marginal seas, where has been thought to receive remarkable amounts of  $\text{N}_r$  supplied from the inland China (Duce et al., 2008), the hotspot of ammonia and  $\text{NO}_x$  emissions in global map (Bouwman et al., 2002; Richer et al., 2005).

The South China Sea (SCS) is one of the largest marginal seas of the world with widely oligotrophic deep basin, located in tropical-subtropical western North Pacific, which is largely surrounded by landmasses with the most dense population and vibrant economics (Fig. 1). The SCS is under the influence of East Asian monsoon system, showing that stronger northeasterly winds prevailing in winter and relatively weak southwesterly winds in summer. Many studies suggested that Asian outflow dusts and aerosols and air pollutants from northern China could be detected in the SCS and its coastal regions during winter monsoon (Hsu et al., 2007; Lin et al., 2007; Wang et al., 2005); while under summer monsoon biomass burning in southeast Asia could act as another provider (e.g. Ma et al., 2003). Several model results reported that  $\text{N}_r$  deposition to the SCS was higher than  $500 \text{ mg N m}^{-2} \text{ yr}^{-1}$  in last decade and highly likely

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the number will increase continuously in future (An et al., 2002; Dentener et al., 2006; Duce et al., 2008). Obviously, the SCS is a receptacle accepting anthropogenic nitrogen deposition to alter its oligotrophic ecosystem. Apart from monsoons, the episodic tropical cyclone (typhoon) may also generate  $\text{NO}_x$  through lightning. These typhoon events, average of 14 typhoons traversing the SCS each year (Lin et al., 2003), may bring significant precipitation into the SCS. However, the seasonal variation of  $\text{N}_r$  deposition to the SCS basin and its relative contributions from different sources (e.g. natural and anthropogenic) remains unclear.

Furthermore, the SCS as well as its adjacent areas is thought to be preferable for  $\text{N}_2$  fixation (Capone et al., 1997; Wong et al., 2002) with relatively higher  $\text{N}_2$  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 annual N-fixation flux to be  $\sim 20 \pm 26 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ , which was similar to that reported in BATS Station (e.g. Orcutt et al., 2001) and ALOHA Station (e.g. Karl et al., 1997). However, the isotope-derived estimation of  $\text{N}_2$  fixation could be biased by N supply from atmospheric dry and wet deposition (Kao et al., 2012; Knapp et al., 2010; Wankel et al., 2010). To clarify the relative contribution of the two external inputs from the atmosphere, atmospheric  $\text{N}_r$  and  $\text{N}_2$  fixation, it is also necessary to quantify the magnitude and characterize the isotopic imprints of nitrate from various atmospheric inputs onto the SCS.

Here we report the first hand data on the fluxes of water-soluble nitrate and ammonium and the dual isotopic compositions of nitrate ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) in bulk atmospheric deposition at a remote island (Dongsha) in the northern SCS. Under assumptions, we estimate the fluxes and examine the potential sources of deposited nitrate in varying seasons and also discuss the possible impacts of atmospheric nitrogen deposition on nitrogen cycling in the SCS, particularly in terms of the  $\text{N}_r$  supply to the upper ocean. In addition, we proposed atmospheric N inputs induced by typhoon could be important and evaluate its potential significance of  $\text{N}_r$  supply to the SCS.

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## 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, which is  $\sim 2.8$  km and  $\sim 0.9$  wide. The water depth around this island is  $\sim 1000$  m, and the biogeochemical characteristics (e.g. nutrients and chlorophyll *a*) in the vicinity of Dongsha are generally in the similar condition compared with the wide slope and basin of the northern SCS (Liu et al., 2007; M. H. Dai, unpublished data).

Four field experimental campaigns were conducted on Dongsha Island in each of the four months: July, September and December in 2010 as well as February 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 from November to April. Note that during collection in September, Typhoon Fanapi passed by the northern SCS and its influence can be seen in our chemistry and isotopic data. We deployed a surrogate surface water glass dish (19 cm in diameter and 8.5 cm in depth; SCHOTT DURAN) for collecting the dry deposition following the method employed by Hsu et al. (2013a), which was principally similar to those used previously (Azimi et al., 2003; Inomata et al., 2009). The pre-cleaned container was infused into 100 mL of Milli-Q water prior to deployment; once approximately half ( $\sim 50$  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, while 24 h for the first campaign (July 2010). The recovered water was filtrated through polycarbonate membrane (0.45  $\mu\text{m}$  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 PP bottles. Then the deposition samples were subjected to in-situ storage in refrigerator and to post-weighing, when returning back in land-based lab, to gravimetrically determine the recovered water volume. During the four field campaigns, a few samples were contaminated by rainfall, and therefore we

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treated these samples as bulk deposition samples in the present study. All samples were stored in  $-20^{\circ}\text{C}$  before isotopic analysis.

## 2.2 Chemical and isotopic analysis

Major ionic species ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{NH}_4^+$ ) in the deposition samples were analyzed by 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 ICS-900). Separator columns (AS11-HC for anions, and CS12A for cations) and guard columns (AG11-HC for anions and CG12A for cations) were used in analyses. The eluents used were 22–25 mM KOH for anions and 20 mM methansul-fonic acid (MSA) for cations. In general, detection limits were below  $0.01\text{ mg L}^{-1}$  for all ions except  $\text{Cl}^-$  and  $\text{NH}_4^+$  ( $\sim 0.015\text{ mg L}^{-1}$ ). The concentration of non-sea-salt  $\text{SO}_4^{2-}$  ( $_{\text{nss}}\text{SO}_4^{2-}$ ) sulfate was calculated by subtracting sea salt  $\text{SO}_4^{2-}$  ( $_{\text{ss}}\text{SO}_4^{2-}$ ) from total  $\text{SO}_4^{2-}$ , of which  $_{\text{ss}}\text{SO}_4^{2-}$  was estimated by multiplying  $\text{Na}^+$  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  $\text{Ca}^{2+}$  ( $_{\text{nss}}\text{Ca}^{2+}$ ) 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 as nitrate) was measured by the “denitrifier method” (Casciotti et al., 2002; Sigman et al., 2001). In brief, cultured denitrifying bacteria that lack  $\text{N}_2\text{O}$  reductase enzyme were used to quantitatively convert sample nitrate into  $\text{N}_2\text{O}$  ( $\sim 10\text{ nmol}$ ). Then, the dual isotopes of  $\text{N}_2\text{O}$  gas were determined online using Gas-Bench II coupled to a continuous flow isotope ratio mass spectrometer (IRMS, Thermo Finnigan DELTA<sup>plus</sup>). The N and O isotope ratios were corrected for drift, O isotopic exchange and blank by international nitrate standards USGS 34, USGS 35, USGS32 and IAEA-N3 (Böhlke et al., 2003) as well as lab working nitrate standard. Values are reported as the  $\delta$  notation ( $\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$ , where  $R$  denotes the

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ratios of heavy isotope to light isotope for N and O, unit in 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  $\pm 0.2\ \text{‰}$  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 yr.

Previous studies showed a large mass-independent contribution of  $^{17}\text{O}$  to the  $m/z$  45 signal of  $\text{N}_2\text{O}$  ( $^{14}\text{N}$ - $^{14}\text{N}$ - $^{17}\text{O}$ ) for  $\text{atmNO}_3^-$  samples could bias the results of  $\delta^{15}\text{N}$  measurements by the “denitrified method” (e.g. Hastings et al., 2003; Wankel et al., 2010). Due to the limited sample for quantifying the effects of  $^{17}\text{O}$ , 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 and discussion

#### 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 in order to evaluate the charge balance and further to identify the likely chemical forms of nitrate and ammonium that might be associated with deposited particles, as illustrated in Fig. 2. Obviously, total anions and total cations follow a nearly 1 : 1 good correlation (Fig. 2a), revealing good charge balance in deposition samples. Besides, both  $\text{Cl}^-$  and  $\text{Na}^+$  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 (1.17) of average seawater composition. Also, both  $\text{Na}^+$  and  $\text{Mg}^{2+}$  are well correlated ( $R^2 = 0.99$ ), with a slope of 0.24 for the linear regression line (Fig. 2c), which is similarly consistent with that (0.23) of average seawater composition. This clearly demonstrates that the origin of  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  is originated

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almost exclusively from sea salt aerosols which would thus serve as a vital component of deposition samples collected on Dongsha Island. On average, both sea salt derived  $\text{Cl}^-$  and the sum of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  accounted for 80 % or higher of each of the total anions and cations, respectively, on the basis of equivalent amounts. Accordingly, when further looking at the correlation between ammonium and sulfate, we only considered non-sea-salt  $\text{SO}_4^{2-}$  ( $_{\text{nss}}\text{SO}_4^{2-}$ ) (Fig. 2d), instead of the total  $\text{SO}_4^{2-}$ . According to the correlations of  $\text{NH}_4^+$  versus  $_{\text{nss}}\text{SO}_4^{2-}$  (Fig. 2d),  $\text{NH}_4^+$  versus  $\text{NO}_3^-$  (Fig. 2e), and  $\text{NH}_4^+$  versus ( $_{\text{nss}}\text{SO}_4^{2-} + \text{NO}_3^-$ ) (Fig. 2f),  $\text{NH}_4^+$  appeared to be relatively insufficient to neutralize acid species such as anthropogenic sulfate and nitrate as most of samples have much lower  $\text{NH}_4^+ / _{\text{nss}}\text{SO}_4^{2-}$  and  $\text{NH}_4^+ / \text{NO}_3^-$  equivalent ratios than unity. Hsu et al. (2007) have 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  $\text{NH}_4^+ / (_{\text{nss}}\text{SO}_4^{2-} + \text{NO}_3^-)$  equivalent ratio was only around 0.3–0.5 (Zheng et al., 2012) although no literature data on bulk deposition composition from adjacent areas for comparison.

### 3.2 Fluxes of atmospheric nitrate and ammonium deposition

The time series atmospheric nitrate and ammonium depositions for four collection periods are shown in Fig. 3 and statistically average values for relevant parameters are summarized in Table 1. Nitrate deposition (ranged from 2.6 to  $628 \mu\text{mol N m}^{-2} \text{ day}^{-1}$ ) is in general higher than ammonium deposition (from 0.4 to  $598 \mu\text{mol N m}^{-2} \text{ day}^{-1}$ ) except a few dates in mid-July and late September. In entire monitoring period, eight rainy events were observed. In non-rainy days, no parallel changes can be seen in ammonium and nitrate deposition; however, in rainy days both ammonium and nitrate

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depositions increased concomitantly and ammonium may reach even to the same level of nitrate deposition. During 16–20 September, Typhoon Fanapi passed by the northern SCS. The peripheral circumfluence deposited more nitrate than ammonium during 16 to 19 September (typhoon phase 1), yet, a similarly high level of nitrate and ammonium in 20 September with precipitation (typhoon phase 2).

Although arithmetic averages of  $_{\text{atm}}\text{NO}_3^-$  deposition were higher during sampling periods of September and November to December (Table 1) due to peak fluxes in rainy days, bulk depositional fluxes of nitrate showed no clear temporal trend over the four sampling periods and the averages among periods were not statistically different. The average of total nitrate deposition over collection periods was  $56.8 \pm 80.3 \mu\text{mol N m}^{-2} \text{ day}^{-1}$  (Table 1). By assuming this number to be representative throughout a year, we obtained the annual bulk nitrate deposition to be  $21 \pm 29 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ . Hsu et al. (2007) recently reported average aerosol concentration of  $1.1 \pm 0.6 \mu\text{g m}^{-3}$  for nitrate collected on board during wintertime of 2004 in the northern SCS around Dongsha. If the similar deposition velocity for  $\text{NO}_3^-$  of  $1.15 \text{ cm s}^{-1}$  used in the eastern China seas (Zhang et al., 2011, and references therein), the calculated dry nitrate deposition was  $18 \pm 10 \mu\text{mol N m}^{-2} \text{ day}^{-1}$ . These values derived from short investigated period are slightly lower than our data in wintertime mainly due to only considering dry deposition. 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. Similar to nitrate, bulk deposition of ammonium also showed no clear temporal trend over sampling periods (Table 1). Similarly, the arithmetic averages of bulk ammonium deposition were higher during September and November to December due to the sharp peaks in rainy days. The daily average of bulk ammonium deposition was  $33.1 \pm 71.5 \mu\text{mol N m}^{-2} \text{ day}^{-1}$  (Table 1), which was then converted into annual bulk ammonium deposition of  $12 \pm 26 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ .

When compared with the observed results from adjacent oceanic regions (e.g. Chen et al., 2011; Nakamura et al., 2005; Zhang et al., 2011, and references therein), we

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found nitrate fluxes through wet and dry deposition 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 quite lower than coasts of eastern China seas ( $80\text{--}90\text{ mmol N m}^{-2}\text{ yr}^{-1}$ ); ammonium depositions to the northern SCS were slightly lower than those measured over the YS, ECS and WNP ( $15\text{--}30\text{ mmol N m}^{-2}\text{ yr}^{-1}$ ), but considerably lower than in coastal areas of China (up to  $100\text{ mmol N m}^{-2}\text{ yr}^{-1}$ ). Similarly, the observed  $\text{NO}_3^-$  and  $\text{NH}_4^+$  fluxes from atmospheric deposition in the northern SCS were relatively lower than those in coastal urban stations in southern China ( $35\text{--}45\text{ mmol N m}^{-2}\text{ yr}^{-1}$  for nitrate and  $36\text{--}144\text{ mmol N m}^{-2}\text{ yr}^{-1}$  for ammonium, e.g. Jia and Chen, 2010; Wai et al., 2010). Such a spatial pattern with an offshore decreasing tendency implies that  $\text{N}_r$  (including nitrate and ammonium) was likely transported from the continent via the northeasterly wind during winter monsoon and dust storm outbreak in spring.

The  $\text{NO}_3^-/\text{NH}_4^+$  ratios in bulk deposition over entire period ranged widely from 0.2 up to 94 (Table 1). The range of mean  $\text{NO}_3^-/\text{NH}_4^+$  ratios for warm periods July and September (1.7 to 2.0) is significantly lower than that of cold period in November through March (3.7–8.4). A similar seasonal pattern was observed by Jia and Chen (2010) in a coastal city of south China. The high arithmetic mean of daily  $\text{NO}_3^-/\text{NH}_4^+$  ratio (4.4) of entire dataset (Table 1) indicates that nitrate is the major N component in atmospheric deposition year round. However, the annual  $\text{NO}_3^-/\text{NH}_4^+$  ratio is  $\sim 1.7$  ( $56.8$  divided by  $33.1\text{ }\mu\text{mol N m}^{-2}\text{ day}^{-1}$ ) revealing that  $\text{NH}_4^+$  occupied  $\sim 40\%$  in bulk inorganic nitrogen deposition and cannot be overlooked. Though we know atmospheric  $\text{NH}_4^+$  is important and mainly derived from volatilized  $\text{NH}_3$  (from waste, fertilizer and soil), and thermogenic  $\text{NH}_3$  (from biomass burning and fossil combustion) (Dentener and Crutzen, 1994; Jia and Chen, 2010), its isotope measurement is not available in our laboratory yet. Below, we will focus on nitrate isotopes to identify the potential sources of atmospheric nitrate.

### 3.3 Dual isotopic compositions and potential sources of nitrate in bulk deposition

Nitrate  $\delta^{15}\text{N}$  values in bulk deposition had a wide span, varying between  $-7.5\text{‰}$  and  $+3.9\text{‰}$  with a flux-weighted average value of  $-2.7 \pm 2.3\text{‰}$  (Fig. 3 and Table 1). All data fall within the wide range of previously reported  $\delta^{15}\text{N}$  values for  $\text{atmNO}_3^-$  in coastal and oceanic regions (e.g. Baker et al., 2007; Carrillo et al., 2002; Hastings et al., 2003; Russell et al., 1998; Savarino et al., 2007; Wankel et al., 2010; Yeatman et al., 2001). Unlike the bulk depositional flux of nitrate, the  $\delta^{15}\text{N}$  values exhibit a clear temporal trend. The flux-weighted average  $\delta^{15}\text{N}$  values decreased gradually from  $+0.7\text{‰}$  in July to  $-5.3\text{‰}$  in February. Similar seasonal trend in  $\delta^{15}\text{N}$  values of  $\text{atmNO}_3^-$  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 (Elliott et al., 2009; Yeatman et al., 2001). Different trends are likely attributed to the sources of  $\text{atmNO}_3^-$  and their respective nitrogen imprints varying temporally from site to site.

Nitrate  $\delta^{18}\text{O}$  values in bulk atmospheric deposition ranged from  $+16.8\text{‰}$  to  $+88.3\text{‰}$  with a flux-weighted average value of  $+65.6 \pm 21.4\text{‰}$ . The  $\delta^{18}\text{O}$  values were significantly higher during cold periods than those in warm season except those in rainy days (Fig. 3 and Table 1). The overall seasonal pattern with higher  $\delta^{18}\text{O}$  in winter is consistent with that from prior studies (e.g. Fang et al., 2011; Hastings et al., 2003; Wankel et al., 2010). However, the lower bound generally observed in the summer is far lower than the typical range reported in previous studies (e.g. Böhlke et al., 2003; Hastings et al., 2003; Savarino et al., 2007), deserving further discussion (see below).

An overall negative correlation ( $R^2 = 0.52$ ,  $n = 72$ ) was observed between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate (Fig. 4). The negative relationship (Fig. 4) was also reported for precipitation nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  at Bermuda (Hastings et al., 2003). They suggested that source changes in nitrate by air transport determined the seasonal variations in  $\delta^{15}\text{N}$  (source-driven signals) and  $\delta^{18}\text{O}$  (chemistry-driven signals) values and produced the

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correlation. However, the slope of the regression line is steeper, mainly due to quite low  $\delta^{18}\text{O}$  values we observed.

Such low  $\delta^{18}\text{O}$  values (down to  $\sim +17\text{‰}$ ) are unusual for  $\text{atmNO}_3^-$ . The  $\delta^{18}\text{O}$  values are thought to be mainly controlled by the relative proportion of oxidation reactions between ozone ( $+90\text{‰}$  to  $+122\text{‰}$ , Johnson and Thiemens, 1997) and OH radical (typically from  $-10\text{‰}$  to  $-6\text{‰}$  around the SCS from the Global Network of Isotopes in Precipitation (GNIP), International Atomic Energy Agency, available from <http://isohis.iaea.org>). Higher  $\delta^{18}\text{O}$  values in nitrate observed in winter are mainly due to the greater contribution of oxidation by  $\text{O}_3$ , while the lower  $\delta^{18}\text{O}$  values could be attributed to the dilution by the reaction of  $\text{NO}_2$  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  $\text{O}_3$  and OH, we calculate the expected  $\delta^{18}\text{O}$  values of nitrate would fall with the lower end value of  $\sim +56\text{‰}$  (assuming two oxygen molecules from  $\text{O}_3$  and one from OH) and the upper end of  $\sim +100\text{‰}$  (assuming 5/6 oxygen atoms from  $\text{O}_3$  and 1/6 from OH) based on chemical reactions (see Hastings et al., 2003; Fang et al., 2009). However, some of our  $\delta^{18}\text{O}$  data from summertime samples were out of range. One possible explanation for those is that NO oxidation to  $\text{NO}_2$  by peroxy radicals that could compete with  $\text{O}_3$  in some environments. The oxygen molecules of peroxy radicals are considered to derive from atmospheric  $\text{O}_2$  (see Salisbury et al., 2001, and references therein), which typically occupies lower  $\delta^{18}\text{O}$  value ( $\sim +23\text{‰}$ ), that could result in low  $\delta^{18}\text{O}$  values in atmospheric  $\text{NO}_3^-$ . The expected  $\delta^{18}\text{O}$  values could be down to  $+11\text{‰}$  followed by the reaction with peroxy radicals (Fang et al., 2011). However, the formation of peroxy radicals, which is the intermediates between OH radicals and  $\text{O}_3$  formation or destruction, is more prevalent in polluted cities (Salisbury et al., 2001). The importance of this process remains to be explored under relatively clean conditions.

Combined with the dual isotopes of nitrate and major ions in bulk deposition, we try to provide the basic and plausible interpretation for the potential sources of  $\text{atmNO}_3^-$ . Considering that relatively long sampling time for individual campaign (1–2 weeks) on a remote island, it is reasonable to assume that  $\text{atmNO}_3^- \delta^{15}\text{N}$  values could be represen-

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tative on a regional scale. In our study area, seasonal variation in  $\text{atmNO}_3^- \delta^{15}\text{N}$  might reflect the changes in likely sources, which is essentially driven jointly by monsoon system and tropical cyclone. During winter when the northeasterly wind is prevailing,  $\text{atmNO}_3^-$  deposition collected in the northern SCS, with  $\delta^{15}\text{N}$  ranging from  $-7.5\text{‰}$  to  $-1.5\text{‰}$ , could be presumably predominantly derived from anthropogenic emissions originated from mainland China and Central Asia via winter monsoon. Recent studies showed that aside from natural sources such as soil emission, lightning, and biomass burning, all the main sources of anthropogenic  $\text{NO}_x$  emissions including industry, power plants, residential, and transportation in China are relevant to fossil fuel combustion (Lin et al., 2010; Liu et al., 2013, references therein). Among which, coal is one of the primary fossil fuel (more than 70 %; Tian et al., 2001); different types of Chinese coals exhibit the  $\delta^{15}\text{N}$  values ranging from  $-6\text{‰}$  to  $+4\text{‰}$  with an average of  $\sim -1.5\text{‰}$  (Xiao and Liu, 2011). Thermal  $\text{NO}_x$  is generally characterized by negative  $\delta^{15}\text{N}$  values (e.g. Heaton, 1990), although some studies showed positive  $\delta^{15}\text{N}$  values (e.g. Fang et al., 2011, and references therein). Chen et al. (2011) found that rain nitrate had low  $\delta^{15}\text{N}$  values ( $-7.5\text{‰}$  to  $-3.1\text{‰}$ ) in southeast China coastal area, which was ascribed mostly to vehicle exhausts. Moreover, a strong correlation is found between  $\text{NO}_3^-$  and  $\text{nssSO}_4^{2-}$  in bulk atmospheric deposition ( $R^2 = 0.82$ ,  $P < 0.0001$ , not shown), suggesting that the transport and/or sources of  $\text{atmNO}_3^-$  might be associated with  $\text{SO}_4^{2-}$  that is dominated by S-enriched coal combustion in China. A similar positive correlation between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in precipitation also observed in south China, suggesting a simultaneous production through S-containing coal combustion (Fang et al., 2011). Accordingly, our data might indicate the dominance of anthropogenic sources for  $\text{atmNO}_3^-$  deposited to the northern SCS, of which coal combustion is of particular importance.

In order to further identify the likely sources of  $\text{atmNO}_3^-$ , we examine the correlations of  $\text{NO}_3^-$ ,  $\text{nssSO}_4^{2-}$ , and  $\text{nssCa}^{2+}$  deposition fluxes against dual isotopic compositions of  $\text{atmNO}_3^-$  (Fig. 5). Higher fluxes were almost associated with intermediate  $\delta^{15}\text{N}$  ( $-4\text{‰}$  to  $0\text{‰}$ ) but with higher  $\delta^{18}\text{O}$  ( $+60\text{‰}$  to  $+90\text{‰}$ ). Accordingly, this perhaps indicates that

these larger deposition might be contributed by the deposition of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CaSO}_4$  particles that are formed through heterogeneous reactions between  $\text{CaCO}_3$  dust and acid gases including  $\text{H}_2\text{SO}_4$  ( $\text{SO}_2$ ) and  $\text{HNO}_3$  ( $\text{NO}_x$  and  $\text{N}_2\text{O}_5$ ) (Sullivan et al., 2007). Such phenomenon of heterogeneous reaction between Asian dust bearing carbonate and anthropogenic acid gases has often been observed over the study ocean (Hsu et al., 2013b). These deliquescent  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CaSO}_4$  particles would be readily dissolved in the solution (Milli-Q water) used in collection once they were deposited.

As discussed, we have more clear idea about the sources of high  $\text{atmNO}_3^-$  deposition events from polluted sources in winter. However, in July small amounts of  $\text{atmNO}_3^-$  could be carried by relatively weak southwesterly wind mainly from south/southeast Asia and pelagic regions, together with considerably low level of continentally derived air pollutants and dust ( $\text{nssSO}_4^{2-}$  and  $\text{nssCa}^{2+}$ , see Fig. 5a–c), possibly suggesting the dominant of natural sources, rather than anthropogenic sources. This weak nitrate source in July was unknown and difficult to conjecture. Here we draw a tropical cyclone case, Typhoon Fanapi, to shed light on this notion. During 16–19 September (typhoon phase 1), the  $\text{atmNO}_3^-$  deposition was higher but  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  remained at constant levels around  $-0.5\text{‰}$  and  $+19\text{‰}$  (Figs. 3 and 4), respectively. The uniform dual isotopic compositions of nitrate did accompany with little substances via the continental outflows such as  $\text{nssSO}_4^{2-}$  and  $\text{nssCa}^{2+}$  (Fig. 5). The  $\text{atmNO}_3^- \delta^{15}\text{N}$  values are identical to the  $\delta^{15}\text{N}$  ( $-0.5\text{‰}$  to  $+1.4\text{‰}$ ) produced by lightning (Hoering, 1957). Many studies found similar N isotope signals (near  $0\text{‰}$ ) of  $\text{atmNO}_3^-$  in warm season, which were mainly attributed to lightning-derived (e.g. Elliott et al., 2009; Hastings et al., 2003; Morin et al., 2009). Yet the  $\delta^{18}\text{O}$  value derived from lightning was not well defined to date. Considering that high-temperature synthetic of  $\text{N}_2$  and  $\text{O}_2$  by lightning, isotopic fractionation should be generally little as we have seen for the  $\delta^{15}\text{N}$  of lightning-derived  $\text{NO}_x$  that approaches atmospheric  $\text{N}_2$ . We infer that the  $\delta^{18}\text{O}$  value of  $\text{NO}_x$  from lightning would be similar to that of  $\text{O}_2$  in the air ( $\sim +23.5\text{‰}$ ), similar to  $\text{atmNO}_3^- \delta^{18}\text{O}$  values during typhoon phase 1. The higher level of nitrate deposition and lightning-derived isotopic feature suggested that nitrate supply induced by tropical cy-

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clone is a potentially important nitrogen source to the SCS. Indeed, previous studies suggested that lightning-derived  $\text{NO}_x$  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. Levy et al. (1996) predicted that 60–80% of tropospheric  $\text{NO}_x$  was sourced from lightning source over west Pacific. Afterwards, Fanapi made the landfall in China on 20 September (typhoon phase 2). The storm swept southern China bringing high deposition of pollutants such as ammonium and nitrate (see counterclockwise circulation of Fanapi in Fig. 1) into the study ocean. During this rainfall peak, the  $\delta^{15}\text{N}_{\text{NO}_3}$  value decreased and  $\delta^{18}\text{O}_{\text{NO}_3}$  value increased approaching the pollution nitrate endmember of inland China, thus, again cyclone carried  $\text{N}_r$  from pollution source towards the northern SCS (Fig. 5), demonstrating that the storm tracks and air mass characteristics could be important factors governing the nitrate deposition and isotope signature (Buda and DeWalle, 2009). Then we attempt to roughly estimate the relative contribution from tropical cyclone to annual nitrate deposition to the SCS. The mean  $\text{NO}_3^-$  flux during the period affected by typhoon (16–20 September) was  $122 \pm 71 \mu\text{mol N m}^{-2} \text{day}^{-1}$ . Given an average of 14 typhoons passing over the SCS annually (Lin et al., 2003) with similar influenced period and magnitude of nitrate flux, we suggest that typhoon-induced contribution may be as much as  $\sim 40\%$  on an annual basis. This amount will be dependent on the pathway and intensity of typhoon. Nevertheless, this provides an insight into the importance of newly N supply to the SCS, although it is tentative under various assumptions. More studies are required to quantify its relative importance and explore such nitrate generation processes in future work.

### 3.4 Potential implications for atmospheric $\text{N}_r$ deposition to the South China Sea

As compared to previously simulated results for the northern SCS ( $500 \sim 1000 \text{ mg N m}^{-2} \text{yr}^{-1}$ , Dentener et al., 2006; Duce et al., 2008), our  $\text{N}_r$  deposition data ( $\sim 33 \pm 39 \text{ mmol N m}^{-2} \text{yr}^{-1}$  or  $462 \pm 546 \text{ mg N m}^{-2} \text{yr}^{-1}$ ) are slightly lower but fall within a rea-

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sonable range. The most likely reason why the observed  $N_r$  deposition fluxes are relatively lower is the lacking of dissolved organic nitrogen (DON) measurement. Recent studies suggests that organic  $N_r$  could account for 20–40 % of total  $N_r$  deposition to the adjacent marginal seas (Zhang et al., 2011) and open ocean (e.g. Cornell et al., 2001).

5 If we consider this fractional contribution from DON, total  $N_r$  deposition onto the northern SCS would increase to  $\sim 40\text{--}50 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ . On the other hand, we missed sampling in March, which is the prevailing time of Asian dust outflows that often bring more pollutants for long-range transport. Those dust events in March brought 2–5 $\times$  higher  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations in atmospheric loads to the eastern China seas and Northwest Pacific (Zhang et al., 2011), although the major pathway for dust outflow is toward the east, there are a few cases per year (Hsu et al., 2013a) that might still contribute certain amounts of  $N_r$  to the northern SCS. If we take  $50 \text{ mmol N m}^{-2} \text{ yr}^{-1}$  as total  $N_r$  deposition, this amount of  $N_r$  may stimulate  $\sim 330 \text{ mmol C m}^{-2} \text{ yr}^{-1}$  if Red-field ratio is applied. This amount is comparable to the annual  $\text{CO}_2$  emission in outer shelf and slope of the northern SCS ( $\sim 460 \pm 430 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ; Zhai et al., 2005, 2013). Due to its unique feature of thermocline circulation the SCS has been taken as an upwelling basin, thus, a source of  $\text{CO}_2$  (Dai et al., 2013). Since we know there has been no pristine marine environment due to significant anthropogenic alteration since industrial revolution, accordingly, the primitive northern SCS might release 2 $\times$  higher  $\text{CO}_2$  than present day if without this fertilization from atmospheric  $N_r$  input.

Relative to the nutricline depth (150 to 200 m) in the western Philippine Sea (WPS), the seasonal variations of nutricline and mixed layer depth in the SCS (40 to 90 m) are much shallower (e.g. Gong et al., 1992). The deeper nutricline depth implies less efficient  $N_r$  supply from the subsurface, thus, the impact of the atmospheric  $N_r$  deposition will be more significant in the WPS. Based on the coupled  $^{228}\text{Ra}$ -nitrate method, previous studies in November 1997 reported the upward nitrate flux was  $\sim 240 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ , mainly nitrate, from the bottom up to the euphotic zone to fuel  $\sim 1600 \text{ mmol C m}^{-2} \text{ yr}^{-1}$  of new production (Cai et al., 2002). Other independent methods, such as the new production derived from  $^{15}\text{NO}_3^-$ -labelled incubation ex-

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periment ( $\sim 3100 \pm 3200 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ; Chen, 2005), the export production derived from  $^{234}\text{Th}$ - $^{238}\text{U}$  disequilibrium method ( $\sim 3100 \pm 700 \text{ mmol C m}^{-2} \text{ yr}^{-1}$  from summer to late autumn with one exceptionally high value of  $9100 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ; Chen et al., 2008b) and export production measured by sediment trap below the euphotic zone ( $\sim 1400 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ ; Kao et al., 2012), together gave a quite wide range for upper ocean carbon sequestration. The higher values reported by using  $^{234}\text{Th}$ - $^{238}\text{U}$  disequilibrium were collected from shallower region near shelf break. And the comparably higher estimates of new production based on the  $^{15}\text{NO}_3^-$ -labelled incubation experiment is likely due to under-sampling with only a few extremely high values from winter. Though the overall range is wide and the uncertainty is high, the reasonable value for export production in the basin seems to be  $\sim 2000 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ . If this is the case, the atmospheric  $\text{N}_r$  contribution will be  $\sim 15\%$ , which is obviously not a small portion for such an upwelling basin; not mentioning the potential impact on the WPS where nutrients supplied vertically from the subsurface are much less than those in the SCS.

Meanwhile, nitrogen fixation shall also be considered as new production, thus, contributing to the export POC flux in N-limiting system as western Pacific (e.g. Shiozaki et al., 2010). So far, only three papers documented N-fixation rates for the oligotrophic SCS. The first one was based on nitrate anomaly ( $\text{N}^* = [\text{NO}_3^-] - 16 \times [\text{PO}_4^{3-}] + 2.9$ ; Deutsch et al., 2001), which provided an amount of  $40\text{--}240 \text{ mmol N m}^{-2} \text{ yr}^{-1}$  (Wong et al., 2007). The second one was that using  $^{15}\text{N}_2$ -labelled incubation obtained *Trichodesmium*-derived N-fixation rates of only  $2.4 \pm 1.7 \text{ mmol N m}^{-2} \text{ yr}^{-1}$  (Chen et al., 2008a). The third one was based on isotope balance for sinking particles collected by sediment trap, in which nitrogen fixation rate was estimated to be  $\sim 20 \pm 26 \text{ mmol N m}^{-2} \text{ yr}^{-1}$  (Kao et al., 2012). The values given by above studies are very inconsistent. Each of them inherited weakness. The calculation derived from  $\text{N}^*$  could be overestimated. One possibility is that they assumed N supply was only derived from  $\text{N}_2$  fixation, and neglect the effects of atmospheric deposition having substantial amounts of N and high N:P ratios (e.g. Baker et al., 2003). On the other hand, the lateral intrusion of Kuroshio Current, which holds high N-fixation rates (Chen et al.,

2008b), was not considered and this may result in overestimate of N-fixation by N\* method. The  $^{15}\text{N}_2$ -labelled method had been proved to underestimate  $\text{N}_2$  fixation rate (Mohr et al., 2010). As for the sediment trap method, since the trap was deployed at  $\sim 400$  m, which is deeper than what we oft-used depth for export production; thus the isotope balance at  $\sim 400$  m might underestimate N-fixation rates since Kao et al. (2012) indicated that diazotrophs may get remineralized rapidly and accumulated in the upper water column. One more problem in their isotope balance model is that both N-fixation and atmospheric  $\text{N}_r$  deposition provide low  $\delta^{15}\text{N}$ , which prohibit well separation of the two sources unless we have accurate isotopic signatures for various nitrogen species.

Note that atmospheric nitrate supplied into surface ocean is instantaneously re-worked through the assimilation-remineralization cycle that could erase the typically high  $\delta^{18}\text{O}$  signature and make little change in original low  $\delta^{15}\text{N}$  values. Below, we unravel the relative contributions of atmospheric  $\text{N}_r$  input and  $\text{N}_2$  fixation to the subsurface  $^{15}\text{N}$  depletion of nitrate in the water column, which may subsequently contribute to N dynamics in the upper ocean.

According to our direct observation on Dongsha the flux-weighted average  $\delta^{15}\text{N}$  of nitrate was  $-2.7\text{‰}$ , which is very similar to that by N-fixation ( $-2\text{‰}$  to  $0\text{‰}$ ). On the other hand, earlier documents near cities at coast China, the N isotopic compositions for  $\text{NH}_4^+$  range from  $-12.4\text{‰}$  to  $-0.6\text{‰}$  with an annual volume-weighted mean of  $-7.3\text{‰}$  (Jia and Chen, 2010), which is even lower than the flux-weighted mean of  $_{\text{atm}}\text{NO}_3^- \delta^{15}\text{N}$  for the northern SCS. As for the isotopic composition of dissolved organic nitrogen, little data were documented. The few reports gave a range of relatively wide  $\delta^{15}\text{N}$  for DON from  $-7\text{‰}$  to  $+10\text{‰}$  and it seems to be site-dependent (Cornell et al., 1995; Russell et al., 1998). Thus in this calculation we assume  $\delta^{15}\text{N}$  for DON is similar to the  $_{\text{atm}}\text{NO}_3^- \delta^{15}\text{N}$ . Collectively, as a result, atmospheric  $\text{N}_r$  deposition serves as a substantial contributor alternatively to further lower down the  $\delta^{15}\text{N}$  values of upwelled nitrate at subsurface layer below the euphotic zone.

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  $\text{N}_r$

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deposition ( $f_{\text{AND}}$ ) which are formulated as:

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

where  $F_a$  and  $F_f$  represent the fluxes of AND ( $\sim 50 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ , this study plus assumptions, see Sect. 3.2) and nitrogen fixation (here we used  $40 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ ), respectively; subscripts bt, a and f stand for nitrate below thermocline, atmospheric total  $\text{N}_r$  and  $\text{N}_2$  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  $-2.7 \text{ ‰}$ , same as  $\text{atm NO}_3^-$ );  $\Delta\delta^{15}\text{N}_{\text{bt-f}}$  stands for the discrepancy between  $\delta^{15}\text{N}_{\text{bt}}$  and  $\delta^{15}\text{N}_f$  ( $-1 \text{ ‰}$ ; Karl et al., 1997). Thus,  $f_{\text{AND}}$  is estimated as  $\sim 0.6$ , indicating that AND could account for  $\sim 60 \%$  of depression in nitrate  $\delta^{15}\text{N}$  of the SCS thermocline. Three numbers may result in uncertainty of this percentile, the N-fixation rate, total  $\text{N}_r$  deposition and the assumption of  $\delta^{15}\text{N}_a$  of  $-2.7 \text{ ‰}$ , among which more efforts should be paid for DON deposition and isotopic composition. As for the incubation estimates of the N-fixation rate, Mohr et al. (2010) suggested saturated  $^{15}\text{N}_2$ -labelled gas should be made since previously reported N-fixation rates derived by either unsaturated  $^{15}\text{N}_2$ -labelled method (e.g. Chen et al., 2008a; Montoya et al., 1996) or acetylene reduction method (Hardy et al., 1968) would underestimated and/or incorrect. From our result, we knew the observed nitrate  $\delta^{15}\text{N}$  value resembles that derived from  $\text{N}_2$  fixation. To better constrain the atmospheric impact on the nitrogen cycle in the SCS, more spatio-temporal data about  $\text{N}_r$  speciation and their relative contributions are required in isotopic balance model.

On the other hand, 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 enhance atmospheric  $\text{N}_r$  input may relax N-limitation to suppress  $\text{N}_2$  fixation. Thus, the relative importance of  $\text{N}_r$  deposition and  $\text{N}_2$  fixation may change over time as the continuously increasing atmospheric  $\text{N}_r$  inputs.

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## 4 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 major atmospheric  $N_r$  deposition was sourced from mainland China driven by the prevailing monsoon winds and occasionally by tropical cyclones. Specifically, tropical cyclone may carry with new  $N_r$  sourced from lightning. Coupled observation and some assumptions we suggest that atmospheric  $N_r$  deposition ( $\sim 50 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ ) may stimulate a new production of  $\sim 330 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ , which mitigate  $\sim 50\%$  of the  $\text{CO}_2$  release from the northern SCS. If the atmospheric  $N_r$  emission from China continuously increases as model predicted, the SCS might turn from a source into a sink in terms of  $\text{CO}_2$  sequestration. In our monitoring, overall mean nitrate/ammonium ratio in deposition was  $\sim 4.4$ , however, the ratio can be up to  $\sim 1$  during high wet deposition events suggesting that ammonium plays an important role on contributing to the N cycling of oligotrophic SCS. Unfortunately, the documented N-fixation rates by different methods varied over  $\sim 2$  orders of magnitude, revealing that researchers' appreciation of N-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 isotope model onto the euphotic zone. More comprehensive studies on isotopic compositions of nitrogen speciation in deposition on varying spatio-temporal scale and their relative importance versus potential impacts on N cycling in the SCS are urgently needed.

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**Table 1.** Summary of average fluxes of nitrate and ammonium in bulk atmospheric depositions and flux-weighted isotopic compositions of nitrate for four sampling periods.

Sampling period	Average fluxes (1 SD) ( $\mu\text{mol N m}^{-2} \text{ day}^{-1}$ )		$\text{NO}_3^-/\text{NH}_4^+$		$\delta^{15}\text{N}_{\text{NO}_3}$ (‰ vs. air)	$\delta^{18}\text{O}_{\text{NO}_3}$ (‰ vs. VSMOW)
	$\text{NO}_3^-$	$\text{NH}_4^+$	Range	Arith. mean		
9–19 Jul 2010	$29.1 \pm 18.5$	$21.5 \pm 13.4$	0.3–6.9	2.0	$+0.7 \pm 2.4$	$+44.3 \pm 21.5$
15–23 Sep 2010	$78.8 \pm 73.4$	$53.7 \pm 52.0$	0.2–6.6	1.7	$-1.1 \pm 1.0$	$+35.4 \pm 18.4$
27 Nov–13 Dec 2010	$72.3 \pm 118.3$	$42.9 \pm 111.9$	0.3–14.6	3.7	$-3.4 \pm 1.1$	$+80.8 \pm 10.7$
18 Feb 2010– 2 Mar 2011	$40.2 \pm 21.1$	$14.5 \pm 13.4$	0.3–94.1	8.4	$-5.3 \pm 1.4$	$+78.8 \pm 6.7$
Average	$56.8 \pm 80.3$	$33.1 \pm 71.5$	0.2–94.1	4.4	$-2.7 \pm 2.3$	$+65.6 \pm 21.4$

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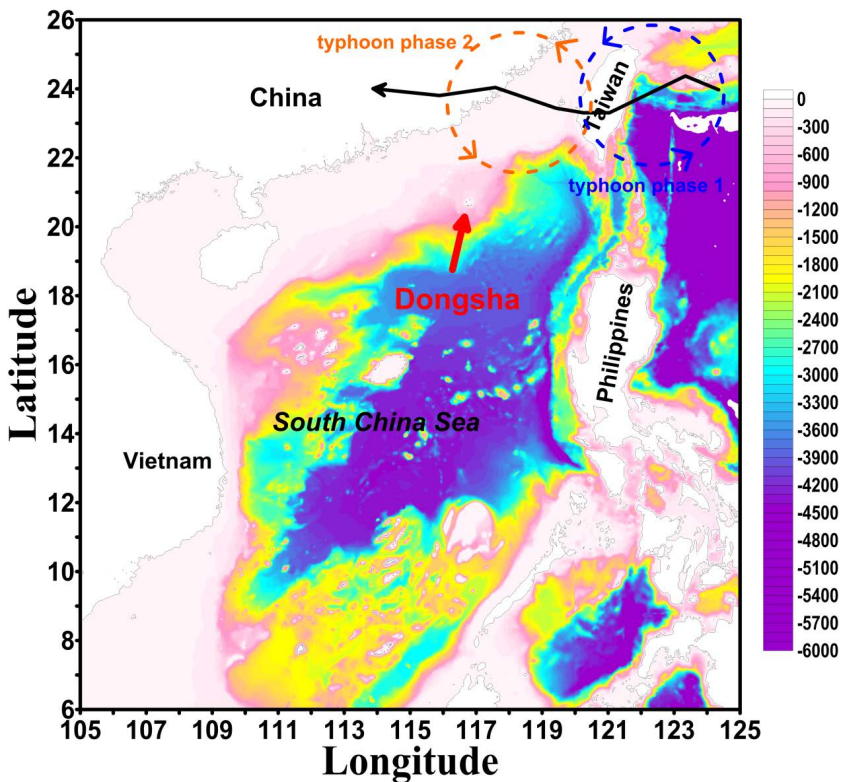
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**Fig. 1.** Map of the South China Sea and location of the Dongsha Island. The solid-arrow curve denotes the pathway of Typhoon Fanapi (from 16–20 September 2010). The blue and orange dashed circles represent influence areas (radius equals to 200 km and wind speed is more than  $15 \text{ m s}^{-1}$ ) for typhoon phase 1 (16–19 September) and phase 2 (20 September), respectively (see text). The counterclockwise circulation of Fanapi is also shown on circles.

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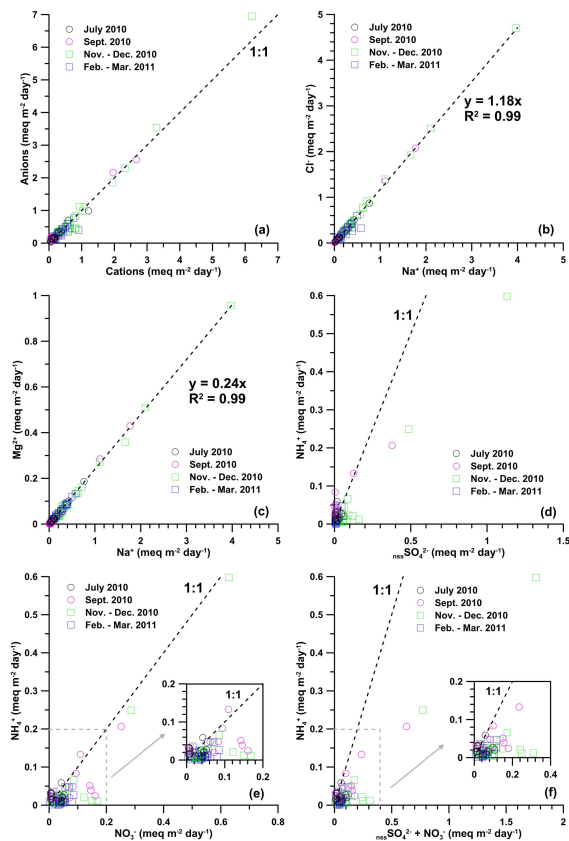
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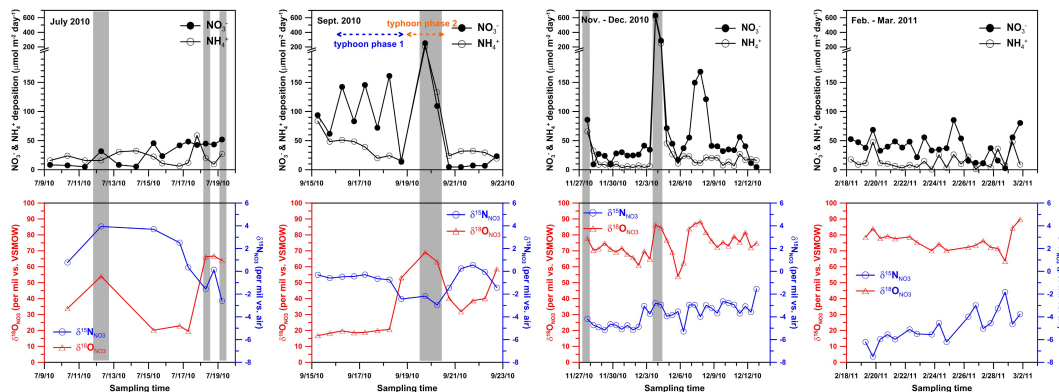


**Fig. 2.** Relationships for equivalent fluxes of **(a)** the total cations versus total anions, **(b)**  $\text{Cl}^-$  versus  $\text{Na}^+$ , **(c)**  $\text{Mg}^{2+}$  versus  $\text{Na}^+$ , **(d)**  $\text{NH}_4^+$  versus non-sea-salt  $\text{SO}_4^{2-}$  ( $_{\text{nss}}\text{SO}_4^{2-}$ ), **(e)**  $\text{NH}_4^+$  versus  $\text{NO}_3^-$ , **(f)**  $\text{NH}_4^+$  versus  $\text{NO}_3^-$  plus  $_{\text{nss}}\text{SO}_4^{2-}$  in bulk atmospheric deposition during collection periods.



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**Fig. 3.** Fluxes of atmospheric nitrate and ammonium deposition and dual isotopic composition of nitrate in bulk deposition during four collection periods. The shaded areas indicate rainy events.

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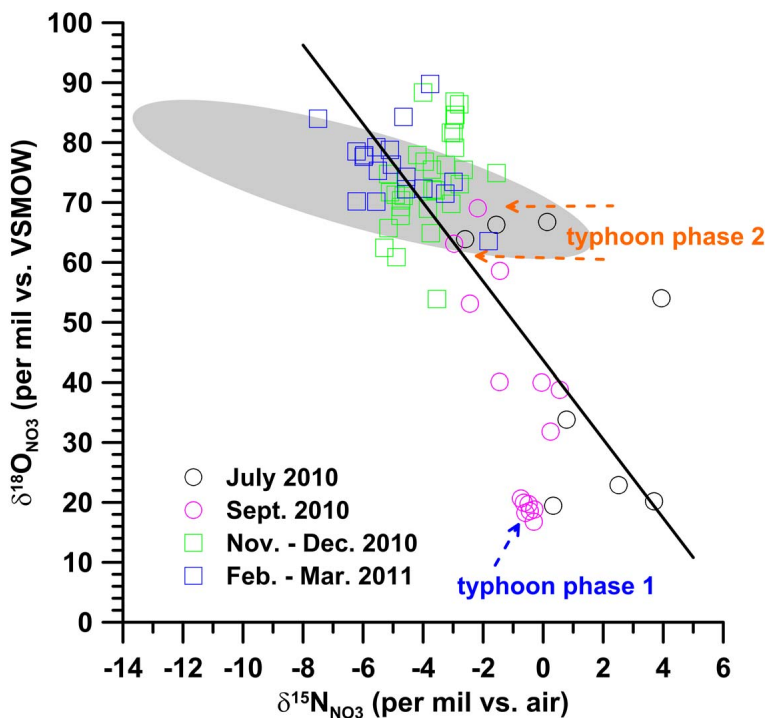
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**Fig. 4.** Correlation between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate in bulk deposition. The solid line indicates the regression line for the entire dataset. The shaded area covers the distribution of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of precipitation nitrate observed at Bermuda ( $32.27^\circ\text{N}$ ,  $64.87^\circ\text{W}$ ; Hastings et al., 2003).

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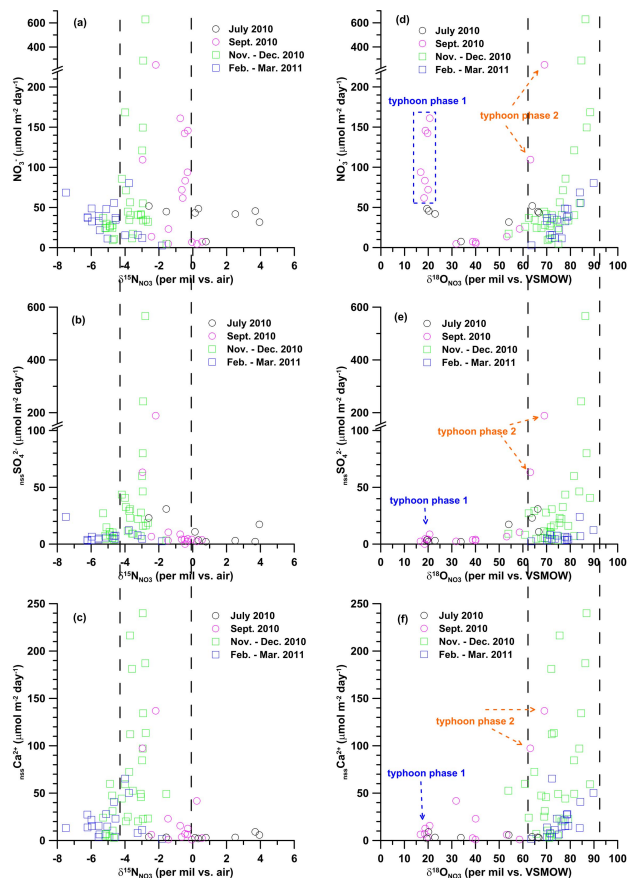
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**Fig. 5.** Scatter plots of  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  against bulk deposition fluxes of  $\text{NO}_3^-$  (**a, d**),  $\text{nssSO}_4^{2-}$  (**b, e**) and  $\text{nssCa}^{2+}$  (**c, f**), respectively. The dashed lines cover the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  ranges corresponding to higher deposition fluxes of  $\text{NO}_3^-$ ,  $\text{nssSO}_4^{2-}$  and  $\text{nssCa}^{2+}$ , respectively.