Use of isotopic compositions of nitrate in TSP to identify sources and chemistry in South China Sea

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Highlights

- $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ were observed in oligotrophic South China Sea.
- NO$_3^-$ is major from anthropogenic sources of southern China in cool months.
- Decrease in $\delta^{15}$N and increase in $\delta^{18}$O during transport from coast to remote marine.
- 47.9% of NO$_3^-$ is from NO$_x$ conversion in South China Sea during transport.

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Abstract

NO$_3^-$ concentration, nitrogen and oxygen isotopic compositions ($\delta^{15}$N and $\delta^{18}$O) of NO$_3^-$ were measured in total suspended particulates (TSP) at Yongxing Island in the South China Sea (SCS) between Feb. 2013 and Jan. 2014, as well as on two cruises in the northern South China Sea (NSCS). Measurements aimed to identify NO$_3^-$ sources, and possible chemical formation processes of NO$_3^-$ in TSP at Yongxing Island ranged from $-2.5$ to $4.9\%\circ$, and $+48.1$ to $+99.0\%\circ$, with annual weighted averages of $+1.5\%\circ$ and $+83.2\%\circ$, respectively. Both $\delta^{15}$N and $\delta^{18}$O had higher values in cool months, indicating that NO$_3^-$ sources and oxidants were different between seasons. In cool months, NO$_x$ was mainly from anthropogenic sources, particularly from coal combustion in South China, resulting in high nitrogen deposition that was oxidized by O$_3$ to NO$_3^-$. In warm months, natural emissions were an important source of NO$_x$. TSP samples in the NSCS had higher NO$_3^-$ concentrations, higher $\delta^{15}$N and lower $\delta^{18}$O values than samples from Yongxing Island over the same period. This suggests that atmospheric processes caused a decrease in NO$_3^-$ concentrations and $\delta^{15}$N but increase in $\delta^{18}$O from coast to remote marine. Assuming to oxygen atoms were derived from O$_3$ during transport in cool months, the mean ratio of NO$_3^-$ formed by NO$_x$ to total NO$_3^-$ was calculated to be 47.9%. This suggests the mean loss ratio of NO$_x$ was 89% while the loss ratio of NO$_3^-$ was 87% during transport between Chinese coastal areas and Yongxing Island in Nov., 2013.

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1. Introduction

Nitrogen is an essential element for growth and reproduction in both plants and animals in terrestrial and marine ecosystems. Most nitrogen is present as N$_2$, comprising about 80% of the atmosphere, which is available only to diazotrophs (Duce et al., 2008). Most life can only use reactive nitrogen species (NO$_x$, NH$_3$, and organic
in TSP at Yongxing Island and on two cruises in the NSCS were measured to investigate nitrate sources. We also use these data to provide insights into the chemical pathways involving conversion of NO₃ to NO₂ in this region.

2. Methods

Total suspended particulates (TSP) were sampled at Yongxing Island (16.83°N, 112.33°E) between Feb. 28, 2013 and Jan. 17, 2014 and on two cruises of the Research Vessel “Shiyian 3”, in the NSCS, over two periods from 6 to 16 Aug. 2012 and from 4 Nov. to 6 Dec. 2013, (Fig. S2 and Table S1). TSP samples were collected using a special high-flow rate (1.05 ± 0.03 m³/min) KC-1000 sampler (see supplementary text S2).

The concentrations of NO₂ and NO₃ in TSP samples were determined using the Dionex ICS-90 Ion Chromatography System (Dionex Corporation, California, USA). The δ¹⁵N and δ¹⁸O values of NO₃ were measured using the Cd-reduction method (see supplementary text S2; McLvin and Altabet, 2005; Ryabenko et al., 2009).

To determine the sources of TSP, air mass back trajectories and a concentration weighted trajectory (CWT) for nitrate were computed using TrajStat software (Wang et al., 2009; see supplementary text S3).

3. Results

3.1. Nitrate concentrations in TSP

Concentrations of TSP ranged from 11.8 to 117.4 µg/m³, with an average concentration of 58.1 ± 20.6 µg/m³ at Yongxing Island between Feb., 2013 and Jan., 2014 (Table 1). The TSP values show no significant correlations with temperature, relative humidity, or rainfall amount, but are correlated with wind speed (R = 0.65, P < 0.001). There is a strong sinusoidal relationship between TSP concentrations and month (R = 0.91, P = 0.0048), with higher values in winter and lower ones in summer. NO₃ concentrations ranged from 4.9 to 103.8 nmol/m³, with an average concentration of 34.9 ± 12.1 nmol/m³. In the warm months (May to Aug.), average NO₃ concentration was 27.3 nmol/m³, much lower than that for cooler months (45.1 nmol/m³, Mar. 2013, Oct. 2013 to Jan. 2014). However, there were no significant correlations between NO₃ concentration and month (P > 0.05).

<table>
<thead>
<tr>
<th>Location</th>
<th>Month</th>
<th>Concentration (µg/m³)</th>
<th>NO₂ (nmol/m³)</th>
<th>δ¹⁵N (‰)</th>
<th>δ¹⁸O (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yongxing Island</td>
<td>2013.03</td>
<td>30.4 ± 17.5</td>
<td>35.9 ± 9.5</td>
<td>+2.4 ± 0.9</td>
<td>+83.1 ± 7.8</td>
</tr>
<tr>
<td></td>
<td>2013.04</td>
<td>37.5 ± 15.8</td>
<td>34.7 ± 11.5</td>
<td>+2.4 ± 1.0</td>
<td>+86.1 ± 7.7</td>
</tr>
<tr>
<td></td>
<td>2013.05</td>
<td>46.2 ± 27.8</td>
<td>32.8 ± 8.2</td>
<td>+0.6 ± 1.5</td>
<td>+72.6 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>2013.06</td>
<td>42.0 ± 23.5</td>
<td>24.5 ± 13.7</td>
<td>-0.1 ± 0.9</td>
<td>+75.1 ± 4.1</td>
</tr>
<tr>
<td></td>
<td>2013.07</td>
<td>43.5 ± 27.2</td>
<td>19.9 ± 10.6</td>
<td>0 ± 1.6</td>
<td>+67.1 ± 7.6</td>
</tr>
<tr>
<td></td>
<td>2013.08</td>
<td>68.4</td>
<td>32.5</td>
<td>+0.9 ± 0.6</td>
<td>+58.9 ± 4.9</td>
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<tr>
<td></td>
<td>2013.09</td>
<td>45.7 ± 35.8</td>
<td>21.6 ± 15.2</td>
<td>+1.4 ± 0.8</td>
<td>+72.4 ± 3.8</td>
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<tr>
<td></td>
<td>2013.10</td>
<td>82.7 ± 28.5</td>
<td>52.8 ± 33.7</td>
<td>+2.4 ± 1.4</td>
<td>+87.8 ± 4.4</td>
</tr>
<tr>
<td></td>
<td>2013.11</td>
<td>79.5 ± 31.4</td>
<td>37.5 ± 21.8</td>
<td>+1.8 ± 0.9</td>
<td>+88.6 ± 6.4</td>
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<tr>
<td></td>
<td>2013.12</td>
<td>78.0 ± 3.9</td>
<td>59.2 ± 15.5</td>
<td>+2.0 ± 0.6</td>
<td>+92.8 ± 1.9</td>
</tr>
<tr>
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<td>2014.01</td>
<td>85.1 ± 5.0</td>
<td>40.2 ± 8.8</td>
<td>+0.3 ± 0.4</td>
<td>+94.2 ± 2.4</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>58.1 ± 20.6</td>
<td>34.9 ± 12.1</td>
<td>+1.5 ± 1.6</td>
<td>+83.2 ± 10.6</td>
</tr>
</tbody>
</table>

* Weighted average by the amount of nitrate with standard deviation.
* See the Table S1 for more information about data.

Additionally, concentrations of TSP, NO₂, δ¹⁵N and δ¹⁸O of NO₃ in TSP at Yongxing Island and on two cruises in Northern South China Sea.
In samples collected on the two cruises in the NSCS, average concentrations of TSP were 101.8 ± 47.3 μg/m³ in Aug. 2012 and 104.3 ± 24.7 μg/m³ in Nov. 2013 (Table 1), showing that there were no significant changes between warm (Aug. 2012) and cool (Nov. 2013) months in the NSCS. However, atmospheric aerosol concentrations in the remote ocean were much lower than that for coastal regions. Likewise, the average concentrations of NO₃⁻ in the NSCS were 113.5 ± 84.9 nmol/m³ in Aug. 2012 and 130.6 ± 54.7 nmol/m³ in Nov. 2013. Differences in NO₃⁻ concentrations between warm and cool months were also observed in the SCS on two cruises reported in Hsu et al. (2014).

3.2. δ¹⁵N–NO₃ in TSP

At Yongxing Island, δ¹⁵N–NO₃ in TSP varied between −2.5 and +4.9‰, with an annual weighted average (by NO₃⁻ concentrations) of +1.5‰ (Table 1). In warm months, δ¹⁵N–NO₃ in TSP ranged from −2.5‰ to +4.8‰, with a weighted average (by NO₃⁻ concentrations) of −0.3‰. While in cool months, it ranged from −0.1‰ to +4.9‰, with a weighted average (by NO₃⁻ concentrations) of +2.1‰. There were no significant correlations between δ¹⁵N and NO₃⁻ (P > 0.05). Values of δ¹⁵N exhibited sinusoidal variation with months (warmer seasons) and highest values during the northeast monsoon (cooler seasons). The average δ¹⁵N value also was lower in Aug. 2012 than in Nov. 2013 in the NSCS (Table 1). The differences in δ¹⁵N values between Yongxing Island and the NSCS for the same months were −4.0‰ in Aug. and −3.6‰ in Nov., indicating that the δ¹⁵N value decreased from the NSCS to Yongxing Island.

3.3. δ¹⁸O–NO₃ in TSP

The δ¹⁸O–NO₃ in TSP samples varied from +48.1‰ to +99.0‰, with a weighted average value (by NO₃⁻ concentrations) of +83.2‰ at Yongxing Island, consistent with previous data (Altieri et al., 2013; Fang et al., 2011; Hastings et al., 2003; Morin et al., 2009; Yang et al., 2014). There was a significant correlation between δ¹⁸O and NO₃⁻ (P < 0.0001, R = 0.57). Values of δ¹⁸O also exhibited sinusoidal variation with months (y = 77.5 + 13.2sin(2πx/8.7 + 6.3), R = 0.88, P = 0.01). During warm months, the average value was +71.2‰; while during cool months, it was −88.9‰. In the NSCS, the values of δ¹⁸O were +65.6‰ in Aug. 2012 and 71.8‰ in Nov. 2013, respectively. The differences in δ¹⁸O values between Yongxing Island and NSCS were +6.7‰ in Aug. and −16.8‰ in Nov., respectively.

4. Discussions

4.1. Backward trajectories and concentration weighted trajectory

Backward trajectories indicate that almost all air masses were originated from northeast of Yongxing Island during the cool months (from Oct. to Mar.), or from southwest of the island during the warm months (from May to Aug.), as shown in Fig. 5a. But during transition months (Apr. and Sep.), air masses originated from the regions of northeast and southwest of the island (Fig. 5b). Backward trajectories calculated for the summer cruise in the NSCS, showed air masses were from the southwest quadrant of the SCS; while during winter cruise, they were from northeastern quadrant. These results are consistent with the backward trajectories calculated for Yongxing Island.

The CWT method applied to NO₃⁻ in TSP samples clearly shows that high concentrations came from developed coastal regions of China, with large anthropogenic emissions (Fig. 1). For instance, the NO₃⁻ was 228.9 nmol/m³ at Shanghai (Wang et al., 2006), 96.8 nmol/m³ at Taichung (Fang et al., 2002) and 154.7 nmol/m³ at Guangzhou (Wang et al., 1992). Relatively lower concentrations were from Southeast Asia or locally in the SCS. These regions both have low emissions of NOₓ, with values such as 19.4 nmol/m³ at Phnom Penh, 17.6 nmol/m³ at Serpong, 17.9 nmol/m³ at Petaling Jaya, 2.84 nmol/m³ at Tanah Rata, 1.28 nmol/m³ at Danum Valley, 3.02 nmol/m³ at Mt. Sto. Tomas, respectively (EANET sites; http://www.eanet.asia/).

4.2. Temporal and spatial variation in δ¹⁵N

The δ¹⁵N of NO₃⁻ in TSP samples at Yongxing Island ranged from −2.5‰ to +4.9‰ from Feb. 2013 to Jan 2014, with a weighted average (by NO₃⁻ concentrations) of +1.5‰. The δ¹⁵N of NO₃⁻ in TSP samples from the two cruises varied between −7.7‰ and +10.9‰ in Aug., with a weighted average (by NO₃⁻ concentrations) of +4.9‰; while in Nov., they were between +3.7‰ and +6.7‰, with a weighted average (by NO₃⁻ concentrations) of +5.4‰. All of the δ¹⁵N values were within the previously reported ranges of δ¹⁵N from NO₃⁻ (Elliott et al., 2009; Fang et al., 2011; Hastings et al., 2003; Heaton et al., 2004; Kendall, 1998; Morin et al., 2009; Savarino et al., 2007; Yang et al., 2014). The δ¹⁵N average at Yongxing Island was lower than for both NSCS cruises. In addition, the δ¹⁵N average for precipitation in urban and rural sites of Guangdong Province, near to the NSCS, also were higher than for NO₃⁻ in TSP at Yongxing Island, but close to values for NSCS TSP samples (Fang et al., 2011). In contrast, much lower values were found in aerosols from weddell Sea (Antarctic), Ny-Alesund (Arctic) and over the Atlantic Ocean (Morin et al., 2009).

Seasonal variation in δ¹⁵N in the atmosphere has been reported in many previous studies (Altieri et al., 2013; Elliott et al., 2009; Fang et al., 2011; Morin et al., 2008; Wankel et al., 2010). However, the seasonal variation pattern observed in this study was different. The δ¹⁵N values exhibited a sinusoidal variation with months at Yongxing Island, with higher values in cool months and lower values in warm months (Fig. 2a and b). This is contrary to the seasonal pattern observed in other studies (Altieri et al., 2013; Hastings et al., 2003; Wankel et al., 2010), and may be explained by differences in TSP sources.

Samples with backward trajectories from northeast of Yongxing Island during cool months, had higher NO₃⁻ concentrations and δ¹⁵N values than samples with trajectories from southwest of Yongxing Island during warm months (Figs. 1 and 2). In the Pearl River Delta region, and east China, NOₓ emissions are high (Zhang et al., 2007; Zheng et al., 2009), with >70% of NOₓ emission from coal combustion (Tian et al., 2001). Thus, the higher NOₓ concentrations and δ¹⁵N values during cool months indicate an anthropogenic NOₓ source, mainly from coal combustion (Fang et al., 2011). In contrast, most air masses originate from south of Yongxing Island during warm months (Fig. 2b and S3a). The average δ¹⁵N value during warm months (−0.3‰) was close to that for the δ¹⁵N lightning NOₓ (Hoering, 1957), suggesting that the contribution of lightning NOₓ increased during warm months. A global distribution map of lightning NOₓ shows that maximum NOₓ was produced from lightning during warm seasons in the SCS (Price et al., 1997). However, the maximum δ¹⁵N value during the warm months (+4.6‰) suggests that NOₓ may also originate from biomass burning (Hsu et al., 2014), since these emissions have possibly positive values (Hastings et al., 2003) and highest fire frequencies in northeast India and Southeast Asia countries occur during warm seasons (Hsu et al., 2014; Streets et al., 2003; Vardav et al., 2014).
So, the contribution of lightning NO\textsubscript{3} is major with mix of other sources (biomass burning, livestock or biogenic soil emissions).

Interestingly, the concentrations and δ\textsuperscript{15}N values near the coast and on the Pearl River were much higher than those over open sea on the two NSCS cruises (Table S1); although we found that the differences in NO\textsubscript{3} concentrations and δ\textsuperscript{15}N between NSCS and Yongxing Island suggest that NO\textsubscript{3} or NO\textsubscript{x} may be lost during air masses transport from polluted to remote regions, and δ\textsuperscript{15}N was preferentially removed. A number of potential mechanisms could account for these changes.

One mechanism involves equilibrium fractionation between NO and NO\textsubscript{x}, which depends on the NO, or O\textsubscript{3} concentration in the atmosphere (R1 and R2) (Freyer et al., 1993). As nitrogen isotope exchange reactions take place, they result in 15N enriched NO\textsubscript{x}, when the ratio of NO\textsubscript{3} concentration to O\textsubscript{3} concentration is higher than 1 (Fang et al., 2011; Freyer et al., 1993). However, the δ\textsuperscript{15}N of NO\textsubscript{2} would be equivalent to NO\textsubscript{3} when the ratio of NO\textsubscript{3} concentration to O\textsubscript{3} concentration is lower than 1, because in this case most of the NO is oxidized to NO\textsubscript{2} (Altieri et al., 2013; Freyer et al., 1993). O\textsubscript{3} concentrations always exceeded NO\textsubscript{3} concentrations during cool months in the NSCS (Fig. S4), indicating that the δ\textsuperscript{15}N of NO\textsubscript{2} reflects δ\textsuperscript{15}N of sources. Although there are no data for NO\textsubscript{3} and O\textsubscript{3} concentrations at Yongxing Island, much data have shown that O\textsubscript{3} concentrations exceed NO\textsubscript{3} concentrations in remote marine atmospheres (Altieri et al., 2013; Ou-Yang et al., 2013). So, NO\textsubscript{3} is mainly in the form of NO\textsubscript{2}. This suggests that exchange reactions were not important in the source region and during the long-distance transmission to the Yongxing Island.

When atmospheric NO\textsubscript{3} or N\textsubscript{2}O\textsubscript{5} occur over the ocean, they probably react with halogens (R9, R10, R12, and R17 in supplementary text). Such heterogeneous processes cause nitrogen isotopic fractionation and 15N is preferentially incorporated into the more stable phase (Altieri et al., 2013). Overnight and in winter months, N\textsubscript{2}O\textsubscript{5} potentially reacts with halides to form CINO\textsubscript{2} and NO\textsubscript{x}, because this pathway is significant in coastal marine atmospheres (Davidson and Kingerlee, 1997; Finlayson-Pitts, 2003; Keene et al., 1990; Knipping and Dabdub, 2003; Pechtl and von Glasow, 2007; Thornton et al., 2010). In this case, 15N is preferentially incorporated into NO\textsubscript{3}, leaving 14N in gaseous CINO\textsubscript{2} (Altieri et al., 2013). CINO\textsubscript{2} reverts to NO\textsubscript{3} via photolysis at the day. Another possible mechanism involves the reaction of NO\textsubscript{2} and NaCl to form NaNO\textsubscript{3} and CINO (R16), in which case, 15N is also preferentially incorporated into NaNO\textsubscript{3}. The life time of NO\textsubscript{3} deposition is much shorter than NO\textsubscript{2}. Therefore, the downwind concentration and δ\textsuperscript{15}N of NO\textsubscript{3} is lower than for the source region. Since wind speed in cool seasons is higher than in warm seasons, more halides are likely released to the marine atmosphere in cool months (Lewandowska and Falkowski, 2013). In our study, the difference in δ\textsuperscript{15}N between the NSCS and Yongxing Island was +3.6‰ in Nov. 2013 (cool month).

4.3. Temporal and spatial variations in δ\textsuperscript{18}O

The weighted average (by NO\textsubscript{3} concentrations) δ\textsuperscript{18}O values for Aug. and Nov. from the NSCS (+65.6‰ and +71.8‰, respectively) are consistent with the δ\textsuperscript{18}O values in rainwater for summer and winter at Guangzhou (+63.5‰ in summer and +73.2‰ in winter; Fang et al., 2011), while the δ\textsuperscript{18}O values of NO\textsubscript{3} in particles appear to reflect regions. They ranged from +53.1‰ to +111.4‰, with an average of +80.2‰ near Antarctica (Morin et al., 2009; Savarino et al., 2007), whereas Morin et al. (2009) reported δ\textsuperscript{18}O of NO\textsubscript{3} in particles between +63.7‰ and +91.9‰, with an average of +74.6‰ above the Atlantic Ocean; these values are closest to our observed values. However, the average δ\textsuperscript{18}O values at Yongxing Island were much higher than at Dongsha Island (Yang et al., 2014) and our samples collected on two cruises in the NSCS. The weighted average (by NO\textsubscript{3} concentrations) δ\textsuperscript{18}O value in TSP at Yongxing Island (+83.2‰) was only slightly higher than the average δ\textsuperscript{18}O value in rainwater at Guangzhou (+66.0‰) and Bermuda (+71.1‰) (Altieri et al., 2013; Fang et al., 2011).

As elsewhere, the δ\textsuperscript{18}O values exhibit seasonal variation, with higher values in cool months (Fig. 3a) and lower values in warm months (Fig. 3b), reflecting different oxidation pathways of NO\textsubscript{3} to NO\textsubscript{2} (Altieri et al., 2013; Fang et al., 2011). The different pathways are controlled by temperature, and solar radiation, and other
meteorological conditions, in which N$_2$O$_5$ is thermally decomposed and OH is photolytically produced (Fang et al., 2011; Wankel et al., 2010). Generally, the oxygen atoms in NO$_3^-$ are derived from 5/6O$_3$ and 1/6H$_2$O in the N$_2$O$_5$ pathway (R5 and R7) and from 2/3O$_3$ and 1/3OH radical in the OH radical pathway (R3) (Hastings et al., 2003). The $\delta^{18}$O of O$_3$ has a relatively high value, within the range from $+90\%$ to $+122\%$; while the $\delta^{18}$O of OH is close to water vapour in the troposphere, ranging from $-15.0\%$ to $0\%$ in Asia (Dubey et al., 1998; Fang et al., 2011; Johnston and Thiemens, 1997). Using the minimum and maximum values of $\delta^{18}$O in O$_3$ and OH as estimates, then the $\delta^{18}$O of NO$_3^-$ should range from $+55\%$ to $+102\%$ (Fang et al., 2011). Most of our $\delta^{18}$O values fell within this range. The longer daylight hours would increase OH concentration in the troposphere during warm months, but decreased daylight hours in cold months would enhance N$_2$O$_5$ hydrolysis. Therefore, seasonal variation in $\delta^{18}$O values of NO$_3^-$ could reflect seasonal variation in the chemical conversion of NO$_3^-$ to NO$_2^-$. In our study, the weighted average (by NO$_3^-$ concentrations) of $\delta^{18}$O of NO$_3^-$ was $+71.2\%$ during warm months and $+88.9\%$ during cool months. Higher $\delta^{18}$O values were recorded from the northeast of SCS during cool months, while lower $\delta^{18}$O values were recorded from the southwest during warm months. Furthermore, both the O$_3$ and OH concentrations have pronounced latitudinal gradients and seasonal variation that would amplify this pattern (Fishman et al., 1990; Spivakovsky et al., 2000; Weller et al., 1996).

During cooler hours at night or during winter, N$_2$O$_5$ reacts not only with H$_2$O, but also with HCl and NaCl to form NO$_3^-$ in the marine atmosphere (R9 and R10). Given that the $\delta^{18}$O of NO$_3^-$ in the NSCS was much lower than at Yongxing Island (Table 1), we concluded that the $\delta^{18}$O of NO$_3^-$ increased because it was not diluted by oxygen atoms from water and/or OH. In addition to the OH and N$_2$O$_5$ oxidation pathways, halogen also provides a pathway (R15...
and R16), Cl is produced in the reactions R10 and R18, and allowing it to react with O3 to form ClO (R13). NO2 reacts with ClO (R15) to form CINO3, and then CINO3 reacts with NaCl (R16) to form NaNO3. The oxygen atom in ClO is obtained from O3, so the d18O of NaNO3 formed from CINO3 is high. The CNO3 concentration in R10, and ClNO concentration in R17 are highest, when sea salt concentration and O3 concentration are highest during cool seasons (Njegic et al., 2010; Osthoff et al., 2008). This suggests that there is an influence from heterogeneous halogen chemistry on the d18O of NO3 in the cool season (Altieri et al., 2013).

4.4. Relationship between δ15N and δ18O of NO3

Previous studies found a negative linear correlation between δ15N and δ18O values of NO3 in marine atmospheric environments, suggesting that atmospheric chemical processes and variations in nitrogen sources influence nitrogen and oxygen isotopic composition (Altieri et al., 2013; Hastings et al., 2003; Yang et al., 2014). Terrestrial studies suggested there was a positive linear correlation between them (Elliott et al., 2009). We found a positive linear relationship between δ15N and δ18O values of NO3 in all TSP samples (R = 0.26, P = 0.047) at Yongxing Island (Fig. 4). A positive linear relationship was also found in transition months (Apr. or Aug.) at Yongxing Island (R = 0.62, P = 0.03) and in the NSCS in Aug. (R = 0.79, P = 0.02; Fig. 4). In those months, the δ15N and δ18O values in NO3 were controlled by sources with different nitrogen isotope composition and different oxidation pathway. In cool months, high δ15N was associated with high δ18O at Yongxing Island because of the influx of high concentrations of NOx with high δ15N values from Chinese coastal cities, and the increased role of O3 with lower temperature and longer nights (Altieri et al., 2013). In warm months, the O3 signal was diluted by the increased participation of OH and H2O in the formation of nitrate, resulting in an overall lower δ18O. The increased contribution from lighting, and biogenic soil
contributed to lower $\delta^{15}N$ values. Although the negative linear relationship was found at Dongsha Island (Yang et al., 2014), this may reflect the unusually low $\delta^{18}O$ in summer. No relationship between $\delta^{15}N$ and $\delta^{18}O$ was found at Yongxing Island, the NSCS or at Dongsha Island (Yang et al., 2014) in cool months ($P > 0.05$), suggesting that complex sources of NO$_x$ and high concentrations of O$_3$ influence this relationship.

We found lower $\delta^{15}N$ and higher $\delta^{18}O$ in TSP at Yongxing Island compared with TSP and rainwater samples from South China coastal areas (Fig. 4). This suggests that $\delta^{15}N$ decreased and $\delta^{18}O$ increased during transport from coastal to remote sea setting. If the source of the NO$_3$ deposited in Yongxing Island during the cool months is the same as that deposited in the South China coastal areas, then the pool of NO$_x$ and its oxidation products must preferentially lose $^{15}N$ and have a high $\delta^{18}O$. If the NO$_3$ in the coarse mode derived all its oxygen atoms from O$_3$ (R12-R15) (Gobel et al., 2013), the $\delta^{18}O$ of NO$_3$ formed in the coastal areas should not be changed during transport to Yongxing Island. However, the $\delta^{18}O$ of NO$_3$ formed during transport did increase. To explore this, we assumed that during the cool months, the oxygen atoms in NO$_3$ formed by NO$_x$ are derived from O$_3$ and oxygen atoms of NO$_3$ from coastal NO$_3$ (formed before transport) did not change during transport or deposition from the coast to Yongxing Island. Thus,

$$\delta^{18}O - NO_3^{(TSP)} = \delta^{18}O - NO_3^{(NO_x)} \times Z + \delta^{18}O - NO_3^{(coast)} \times (1 - Z)$$

where $Z$ is the ratio of NO$_3$ formed by NO$_x$ to the total NO$_3$ of TSP.

Fig. 4. The relationship between $\delta^{15}N$ and $\delta^{18}O$ in TSP at Yongxiang Island, in TSP in Northern South China Sea, in rainwater at Guangzhou (Yang et al., 2011), in bulk deposition at Dongsha Island (Yang et al., 2014), in rainwater at Bermuda (Altieri et al., 2013) and in aerosol in Atlantic Ocean (Morin et al., 2009). For all samples at Yongxiang Island, $R = 0.26, P = 0.047$; for transition season at Yongxing Island, $R = 0.62, P = 0.03$. For samples in warm months in NSCS, $R = 0.79, P = 0.02$; for samples in cool months in NSCS, $R = 0.42, P > 0.05$.

Fig. 5. The ratios of NO$_3$ formed by NO$_x$ to total NO$_3$ of TSP at Yongxing Island in different cool months.
The $^{31}\text{O}$ of coastal NO$_3^-$ is $+73\%$, which is equivalent to the mean $^{18}\text{O}$ value of TSP from NSCS in Nov. (this study) and winter rainwater samples from Guangzhou (Fang et al., 2011). Thus, the ratio of NO$_3^-$ formed by NO to total NO$_3^-$ can be calculated for cool months at Yongxing Island (Fig. 5). Given the wide range of $^{18}\text{O}$ of NO$_3^-$ ($+90\%$ to $+122\%$), the minimum ($+90\%$), maximum ($+122\%$), and median ($+106\%$) values were used to calculate this ratio, yielding values of $82.5\%$, $32.2\%$ and $47.9\%$, respectively. In the open sea, the molar ratio of NO$_3^-$ to NO was relatively high ($>10$ at Hedo Island; http://www.epd.gov.hk). If we ignore the NO$_3^-$ concentration at Yongxing Island and use the synchronous observations in Nov. 2013 between Yongxing Island and the Chinese coast ($130.6 \text{nmol/m}^3$), NO$_3^-$ data from our observations, and $188.4 \text{nmol/m}^3$ NO$_3^-$ data from www.epd.gov.hk), then NO$_3^-$ from NO$_3$ is calculated to be $17.6 \text{nmol/m}^3$ and the coastal NO$_3^-$ was $19.9 \text{nmol/m}^3$ (formed before transport), using a median ratio for NO$_3^-$ formed by NO to total NO$_3^-$ of TSP of 46.5%. Hence, $87\%$ of NO$_3^-$ and $89\%$ of NO$_3^-$ were lost during the transport from coast to Yongxing Island; although inclusion of other chemical pathways involving conversion of NO to NO$_3^-$, dry and wet NO$_3^-$ deposition during transport must be evaluated to obtain exact loss ratios.

5. Conclusions

Average NO$_3^-$ concentrations, and $^{15}\text{N}$ and $^{18}\text{O}$ values for NO$_3^-$ in TSP at Yongxing Island over the yearlong study period were $34.9 \text{nmol/m}^3$, $+1.5\%$ and $+83.2\%$, respectively. Values of $^{15}\text{N}$ and $^{18}\text{O}$ in TSP showed spatial and seasonal variations, indicating that $^{15}\text{N}$ and $^{18}\text{O}$ values indicated that origins were from northeast of Yongxing Island, from anthropogenic sources in South China with high nitrogen deposition. In warm months, the contribution of natural emissions was more important. There was a decrease in $^{15}\text{N}$ and increase $^{18}\text{O}$ during transport from coast of South China to Yongxing Island during cool months, because $^{15}\text{N}$ is preferentially lost and oxygen atoms were mainly from O$_3$ during transport.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.03.006.

References

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