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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_x 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^-. The $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in TSP at Yongxing Island ranged from −2.5 to +4.9‰, and +48.1 to +99.0‰, with annual weighted averages of +1.5‰ and +83.2‰, respectively. Both $\delta^{15}N$ and $\delta^{18}O$ had higher values in cool months, indicating that NO_x 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.

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_y, and organic

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nitrogen) (Kim et al., 2014). In most parts of the open ocean, concentrations of bio-available nitrogen limit primary production, which largely controls the efficiency of the 'biological pump' (Falkowski et al., 1998). One of major input pathways of new reactive nitrogen to the ocean is through atmospheric deposition, accounting for about 30% of new reactive nitrogen input (Duce et al., 2008). Global atmospheric nitrogen deposition has increased markedly over the last 100 years, and about 67 Tg of atmospheric-derived reactive nitrogen inputs into the global ocean every year, mainly owing to human activities (Duce et al., 2008; Hastings et al., 2009). Thus, about 50% of anthropogenic reactive nitrogen in the atmosphere is deposited to the ocean (Duce et al., 2008; Kim et al., 2014).

NO_x (NO and NO_2) is a major component of atmospheric reactive nitrogen and is a precursor of NO_3^- (Altieri et al., 2013; Galloway et al., 2008; Olivier et al., 1998; Yang et al., 2014). NO_x is mainly from combustion of fossil fuel, lightning, biomass burning and soil processes (Davidson and Kingerlee, 1997; Hsu et al., 2014; Finlayson-Pitts and Pitts Jr, 1999; Morin et al., 2009; Schumann and Huntrieser, 2007). Nitrate (NO_3^-), as the main nitrogen species involved in atmospheric deposition, is formed from oxidation of NO_x through several chemical pathways (Altieri et al., 2013; Chameides, 1984; Finlayson-Pitts and Pitts Jr, 1999; Morin et al., 2009; Seinfeld and Pandis, 2012). In general, NO is in photochemical equilibrium with NO_2 (R1 and R2), then NO_2 is oxidized to HNO_3 by the hydroxyl (OH) radical during the day (R3), and by ozone (O_3) to form the NO_3 radical (R4), which subsequently combines with NO_2 to form N_2O_5 (R5), and then undergoes hydrolysis to form HNO_3 (R7) over night (Altieri et al., 2013; Fang et al., 2011). In reaction R5, NO_2 and NO_3 have a thermal equilibrium reaction with N_2O_5. NO_3 also reacts with volatile organic compounds, including dimethyl sulfide (DMS) (R6) (Altieri et al., 2013; Gobel et al., 2013). OH pathways are more prevalent in the summer than in the winter, but N_2O_5 pathways are more important than OH pathways in winter (Altieri et al., 2013; Calvert et al., 1985). These major oxidation pathways are shown in Supplementary Text S1.

Nitrogen and oxygen isotopic compositions ($\delta^{15}N$ and $\delta^{18}O$) are usually used to distinguish nitrate sources and the chemical formation processes in the atmosphere (Altieri et al., 2013; Elliott et al., 2009; Gobel et al., 2013; Hastings et al., 2003; Morin et al., 2009; Yang et al., 2014). Values of $\delta^{15}N$ of atmospheric NO_3^- are often used to identify NO_x sources, because most NO_x is converted to NO_3^- through atmospheric reactions (Elliott et al., 2009; Heaton, 1987; Moore, 1977; Xiao and Liu, 2002; Xiao et al., 2012). Different NO_x sources have different nitrogen isotopic composition, including vehicle fuel combustion, coal combustion, diesel combustion, natural gas combustion, lightning, livestock and biogenic soil emissions, shown as in Fig. S1 (Ammann et al., 1999; Felix et al., 2012; Felix and Elliott, 2014; Fibiger et al., 2014; Hastings et al., 2009; Heaton, 1990; Hoering, 1957; Kiga et al., 2000; Li and Wang, 2008; Moore, 1977). Direct measurements values of $\delta^{15}N$ of NO_x from biomass burning are not reported, but previous studies of NO_3^- in pre-industrial ice suggest that natural sources of NO_x have positive $\delta^{15}N$ source signatures (Freyer, 1996; Hastings et al., 2009). In contrast, $\delta^{18}O$ values change very much during conversion of NO_x to NO_3^- because oxygen atoms in NO_x are exchanged rapidly with O_3 (R1 and R2). Then, NO_3^- is formed through multiple pathways, including but not limited to N_2O_5 and OH pathways. These pathways are influenced by many factors, e.g., weather conditions, and the availability of reactive aerosol surfaces (Wankel et al., 2010). Typically, $\delta^{18}O{-}O_3$ ranges from +90 to +122‰, while the $\delta^{18}O{-}OH$ radical ranges from −15 to 0‰ over Asia (Fang et al., 2011; Johnston and Thiemens, 1997; Krankowsky et al., 1995).

In this study, nitrate concentrations, and $\delta^{15}N$ and $\delta^{18}O$ of nitrate 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 NO_x to NO_3^- 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 "Shiyan 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 m^3/min) KC-1000 sampler (see supplementary text S2).

The concentrations of NO_2^- and NO_3^- in TSP samples were determined using the Dionex ICS-90 Ion Chromatography System (Dionex Corporation, California, USA). The $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- were measured using the Cd-reduction method (see supplementary text S2; McIlvin 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/m^3, with an average concentration of 58.1 ± 20.6 μg/m^3 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. NO_3^- concentrations ranged from 4.9 to 103.8 nmol/m^3, with an average concentration of 34.9 ± 12.1 nmol/m^3. In the warm months (May to Aug.), average NO_3^- concentration was 27.3 nmol/m^3, much lower than that for cooler months (45.1 nmol/m^3, Mar. 2013, Oct. 2013 to Jan. 2014). However, there were no significant correlations between NO_3^- concentration and month ($P > 0.05$).

Table 1
Concentrations of TSP, NO_3^-, $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in TSP at Yongxing Island and on two cruises in Northern South China Sea.

Location	Month	TSP (μg/m^3)	NO_3^- (nmol/m^3)	$\delta^{15}N$ (‰)[a]	$\delta^{18}O$ (‰)[a]
Yongxing Island	2013.03	30.4 ± 17.5	35.9 ± 9.5	+(2.4 ± 0.9)	+(83.1 ± 7.8)
	2013.04	37.5 ± 15.8	34.7 ± 11.5	+(2.4 ± 1.0)	+(86.1 ± 7.7)
	2013.05	46.2 ± 27.8	32.2 ± 8.2	-(0.6 ± 1.5)	+(72.6 ± 1.3)
	2013.06	42.0 ± 32.5	24.5 ± 13.7	-(0.1 ± 0.9)	+(75.1 ± 4.1)
	2013.07	43.5 ± 27.2	19.9 ± 10.6	(0 ± 1.6)	+(67.1 ± 7.6)
	2013.08	68.4	32.5	+(0.9 ± 0.6)	+(58.9 ± 4.9)
	2013.09	45.7 ± 35.8	21.6 ± 15.2	+(1.4 ± 0.8)	+(72.4 ± 3.8)
	2013.10	82.7 ± 28.5	52.8 ± 33.7	+(2.4 ± 1.4)	+(87.8 ± 4.4)
	2013.11	79.5 ± 31.4	37.5 ± 21.8	+(1.8 ± 0.9)	+(88.6 ± 6.4)
	2013.12	78.0 ± 3.9	59.2 ± 15.5	+(2.0 ± 0.6)	+(92.8 ± 1.9)
	2014.01	85.1 ± 5.0	40.2 ± 8.8	+(0.3 ± 0.4)	+(94.2 ± 2.4)
	Average	58.1 ± 20.6	34.9 ± 12.1	+(1.5 ± 1.6)	+(83.2 ± 10.6)
Northern[b] South China Sea	2012.08	101.8 ± 47.3	113.5 ± 84.9	+(4.9 ± 6.4)	+(65.6 ± 12.1)
	2013.11	104.3 ± 24.7	130.6 ± 54.7	+(5.4 ± 0.9)	+(71.8 ± 9.2)

[a] Weighted average by the amount of nitrate with standard deviation.
[b] See the Table S1 for more information about data.