**Nitrate sources and formation of rainwater constrained by nitrate isotopes in Southeast Asia: Example from Singapore**

Cai Li a,b, Si-Liang Li a\*, Fu-Jun Yue c, Shao-Neng He d\*, Zong-Bo Shi a,e, Chong-Li Di a, Cong-Qiang Liu a

a Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

b School of Urban and Environmental Science, Huaiyin Normal University, Huai’an 223300, China

c School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, United Kingdom

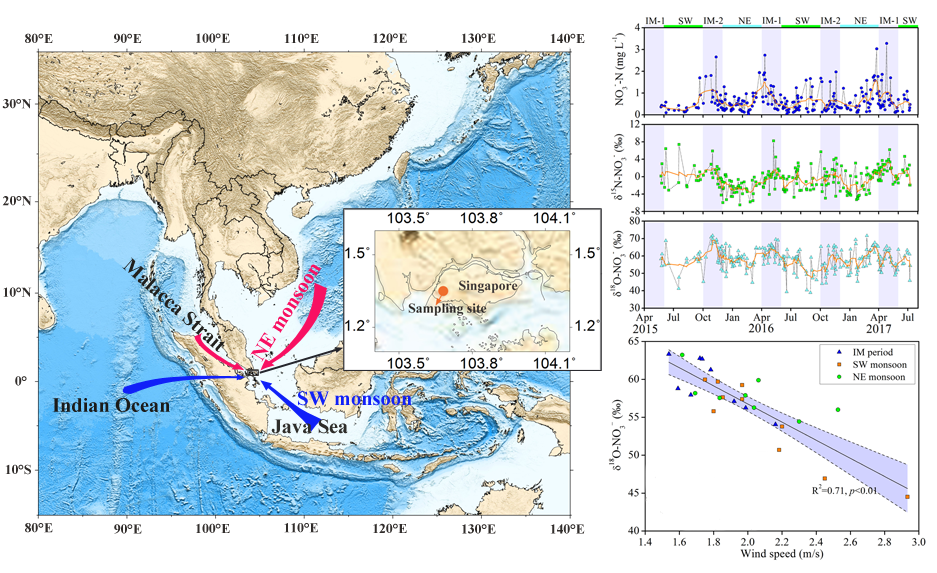
d Earth Observatory of Singapore, Nanyang Technological University, Singapore, 639798, Singapore

e School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, United Kingdom

Corresponding author: Dr. S-L LI, siliang.li@tju.edu.cn; Fax, +86 22 27405053 and Dr. S-N HE, snhe@ntu.edu.sg

**Highlights:**

* δ15N-NO3− and δ18O-NO3− of rainwater varied seasonally in Singapore.
* Traffic emission contributed the most to atmospheric NO3− in NE monsoon.
* Nitrate formation process is strongly influenced by meteorological conditions.
* Nitrate source apportionments were impacted by the secondary processes.



**Abstract** Emission of reactive nitrogen species has a major impact on atmospheric chemistry, ecosystem and human health. The origin and formation mechanisms of wet-deposited nitrate are not well understood in Southeast Asia (SEA). In this study, we measured stable isotopes of nitrate (δ15N and δ18O) and chemical compositions of daily rainwater from May 2015 to July 2017 in Singapore. Our results showed that δ15N-NO3− and δ18O-NO3− varied seasonally with higher values during the Inter-monsoon period (April−May and October−November) than during Northeast (December−March) and Southwest monsoon (June−September). Bayesian mixing modeling, which took account of the isotope fractionation, indicated that traffic emission (47±32%) and lightning (19±20%) contributed the most to NO3− with increased traffic contribution (55±37%) in the Northeast monsoon and lightning (24±23%) during the Inter-monsoon period. Biomass burning and coal combustion, likely from transboundary transport, contributed ~25% of nitrate in the rainwater. Monte Carlo simulation of δ18O-NO3− indicated that oxidation process by hydroxyl radical contributed 65±14% of NO3−, with the rest from hydrolysis of N2O5. Wind speed had large effect on δ18O-NO3− variations in the atmosphere with more involvement of hydroxyl radical reactions when wind speed increased. Our study highlights the key role of isotopic fractionation in nitrate source apportionment, and the influence of meteorological conditions on nitrate formation processes in SEA.

**Keywords**: Stable isotopes, Nitrate formation, Source apportionment, Meteorological condition, Southeast Asia

**1. Introduction**

Global production of reactive nitrogen increased eleven folds from 1860 to 2000 due to extensive anthropogenic activities (Galloway et al., 2008). Excessive nitrogen deposition leads to eutrophication, soil acidification, nitrogen saturation, loss of biodiversity and human health risk (Clark and Tilman, 2008; Liu et al., 2013). Nitrate is an important species in the atmosphere, which can be transported and deposited hundreds of kilometers away from the source emissions due to the relatively long lifetime (~5 days) compared with nitrogen oxides (NOx=NO+NO2) (<48 h) (Neuman et al., 2006). As the main precursor of nitrate, NOx origins include anthropogenic activities such as coal-fired power plants and road traffic, as well as natural inputs such as lightning and soil emission(Elliott et al., 2007; Hastings et al., 2003). Identification of nitrogen sources is the first step for mitigating impacts of nitrogen deposition on ecosystem and human health.

Atmospheric chemistry alone is unable to accurately trace the nitrate sources due to the complicated formation mechanism of nitrate (Elliott et al., 2007). Coupled nitrogen and oxygen isotopes of nitrate have been widely used to investigate nitrate origins and formation pathways (Beyn et al., 2014; Chen et al., 2019; Elliott et al., 2007; Kawashima and Kurahashi, 2011). Atmospheric nitrates from different NOx emissions generally have distinct ranges of δ15N-NOx. For example, coal-fired power plants are characterized by higher δ15N-NOx values ranging from +6‰ to +13‰, while vehicle fuel combustion has relatively 15N-depleted nitrogen isotope values with a range of −13‰ to +6‰ (Heaton, 1990). δ15N-NOx values of natural source are more depleted with δ15N values from lightning around 0‰ (Hoering, 1957) and biogenic soil emissions around −49‰ to −20‰ (Li and Wang, 2008). In contrast, δ18O-NO3− reflects the formation mechanism of NO3− since the oxygen atoms of atmospheric NOx are rapidly exchanged with O3 in the NO-NO2 cycle (Hastings et al., 2003). In summer (or during the day), more involvement of hydroxyl radical (close to δ18O-H2O(g)=−25‰ to 0‰, Eqs R1−R3 in Text S1) will cause lower δ18O-NO3− (Zong et al., 2017), whereas in winter (or at night) δ18O-NO3− is expected to be higher due to more incorporation of O3 (δ18O-O3=+90‰ to +122‰, Eqs R4−R6 in Text S1) (Johnston and Thiemens, 1997). Some recent studies use Monte Carlo simulation to apportion these two oxidation pathways (Zong et al., 2017; Chang et al., 2018).

Source apportionment of atmospheric nitrate via isotopic approach is however complicated by kinetic and equilibrium isotope effects involved in different oxidation pathways and during nitrate transport (Elliott et al., 2019; Geng et al., 2014; Xiao et al., 2015). Advance in Bayesian model has improved our ability to incorporate the equilibrium isotope fractionation when apportioning the source of particulate nitrate (Chang et al., 2018; Zong et al., 2017).

Southeast Asia (SEA) makes a substantial contribution (~10%) to reactive nitrogen in terms of global biomass burning emissions (Kondo et al., 2004; Nations, 2014). Singapore is located in SEA and has suffered from recurring haze events since the late 1990s due to uncontrolled biomass burning with association of forest fires, peatland combustion and agricultural waste burning from neighboring countries (Balasubramanian et al., 1999; Hansen et al., 2018; See et al., 2007; Sharma and Balasubramanian, 2017). However, the origins and formation pathways of rainwater NO3− is poorly understood in SEA, which is influenced by complex weather conditions including EI Niño-Southern Oscillation.

We determined the nitrogen and oxygen isotopes of nitrate in rainwater collected on a daily basis for more than two years in Singapore with the expectation that nitrate isotopes of rainwater might show seasonal patterns due to the variations in nitrate sources and formation pathways during alternating monsoons characterized by different origins of air masses in SEA. The objective is to provide insight into origins and formation pathways of nitrate under complex tropical convection using Monte Carlo simulation and Bayesian isotope mixing model. The quantitative estimation of nitrate sources will make a comprehensive evaluation of nitrate sources from the perspective of natural and human activities in tropical regions under complex weather conditions. Our results will help policy makers make nitrogen management strategies to mitigate air contamination in SEA.

**2. Materials and Methods**

2.1 Study area

Southeast Asia covers a total area of 4,470,000 km2, with forest, cropland and urban as the dominant land uses (Reid et al., 2013). The transboundary haze pollution poses serious problems in this region due to the biomass burning and industrialization and urbanization, with the estimated urban population surpassing 500 million by 2025 (Nations, 2014). Singapore has an urbanization rate of 100%, which differs from other countries in SEA. Singapore is located between 103°36′E−104°25′E and 1°09′N −1°29′N, with a dense population of about 5.6 million (Singapore Department of Statistics, 2017). The climate of Singapore belongs to tropical rainforest system with a mean annual precipitation of 2,430 mm. The rainfall events are characterized by high frequency and short duration with most rainfall events lasting less than 1 h. The mean annual temperature ranges from 26°C to 27.5°C (Li et al., 2016). The regional climate is shaped by two alternating monsoons, Northeast (NE) monsoon (November−March) and Southwest (SW) monsoon (June−September). There are two Inter-monsoon (IM) periods between these two monsoons, the first Inter-monsoon period (IM-1) from late March to May and the second Inter-monsoon period (IM-2) from October to November. In contrast to the SW monsoon, the NE monsoon is accompanied by relatively more rainfall and stronger wind strength (Fong, 2012). In the SW monsoon, smoke haze is often observed due to the localized sources near Singapore such as biomass burning and industrial emission (Fong, 2012).

2.2 Sampling and Analyses

The sampling site (1.35°N, 103.68°E, Fig. S1) was situated at the building that hosts the Asian School of the Environment at Nanyang Technological University (NTU), Singapore. The rain collector was installed at approximately 1.5 m above the roof to reduce the impact of local turbulence and input of particles into the samples. Rainfall, ambient temperature, relatively humidity (RH) and wind speed (WS) were recorded every minute by a HOBO Data Logging Rain Gauge (www.onsetcomp.com) (He et al., 2018). Daily rain water samples were collected from May 2015 to July 2017 using a collection funnel connected with a 1-L Polyethylene bottle (He et al., 2018). The samples were stored in 30 ml Polyethylene bottles and frozen in the refrigerator before they were delivered to the State Key Laboratory of Environment Geochemistry (Institute of Geochemistry, Chinese Academy of Science) for chemical and isotopic analyses.

All the samples were filtered through 0.45-μm microporous membranes prior to analyses. Concentrations of Cl− and SO42− were analyzed by ion chromatography (Dionex 90) with a precision of ≤5%. Concentrations of NO3−-N and NH4+-N were determined by automatic flow analyzer (SKALAR Sans Plus Systems). The nitrogen detection limit was 10 μg L−1 for NO3−-N and NH4+-N. Nitrogen and oxygen isotopes of nitrate were measured by analyzing isotopes of N2O, which was produced by denitrifying bacteria. N2O was purified by a Trace Gas Pre-concentrator unit before isotopic analyses using an isotope ratio mass spectrometer (Yue et al., 2015). δ15N-NO3− and δ18O-NO3− was corrected for blank and oxygen isotopic exchange using the international reference materials of USGS-34 and USGS-35 as well as three mixtures of USGS-35 and USGS-34 (1:3, 1:1, and 3:1) (Costa et al., 2011). The δ15N and δ18O-NO3− measurements of standards had precisions of 0.3‰ and 0.5‰, respectively. The stable isotope ratios are expressed in delta (δ) and a permil (‰) notation as follows:

(1)

where Rsample and Rstandard are sample and standardfor 15N/14N or 18O/16O, respectively. δ15N Values are reported relative to N2 in the atmospheric, and δ18O values to Vienna Standard Mean Ocean Water (VSMOW).

2.3 Bayesian isotope mixing model

Proportional contributions of nitrate sources were estimated using a Bayesian isotope mixing model “MixSIAR”, which has been implemented in an open source R package MixSIAR (Stock and Semmens, 2013). MixSIAR represents a collaborative coding project between the investigators behind MixSIR and SIAR. MixSIAR was run with the residual error and process error term as well as uninformative priors. Residual error accounts for unknown sources of variability in the mixture/sediment. The Markov chain Monte Carlo parameters were set as follows: number of chains = 3; chain length = 300,000; burn-in = 200,000; thin = 100. Convergence of both mixing models was evaluated using the Gelman–Rubin diagnostic, not allowing any variables above 1.05 (Stock and Semmens, 2016). MixSIAR provides the posterior probability distribution of the proportional contribution of the sources and reports overview statistics including median, mean, standard deviation, and credible interval (50% and 95%). In our study, lightning, mobile source, biomass burning, coal combustion and biogenic soil emission were considered to be major NOx sources. The mean values of δ15N-NO3− (± SD) of each end-member were listed in Table S1. The effect of equilibrium isotopic fractionation on δ15N-NO3− was estimated using the approach by Walters and Michalski (Walters and Michalski, 2016) and Zong et al. (2017), which was then taken into account into the MixSIAR model. More details can be found in the supplementary information.

**3. Results and Discussion**

3.1 Temporal variations in nitrate concentration and influencing factors

NO3−-N concentrations ranged from 0.05 to 3.28 mg L−1, with an average of 0.64±0.54 mg L−1 (Table S2). NO3− concentrations showed significant seasonal variation (*p*<0.05) with a higher concentration observed during IM periods relative to NE and SW monsoons (Fig. 1). This seasonality of NO3− concentrations might be ascribed to varied meteorological conditions and nitrate sources during different periods. No significant correlation was observed between NO3− concentrations and various meteorological factors (Tables S3 and S4) except for rainfall. Rainfall was negatively correlated with NO3− concentration (*p*<0.05), which might be ascribed to the dilution effect. However, this cannot explain the seasonality of NO3− concentrations since rainfall did not show a significant seasonal variation (*p*>0.05). Thus, the origins of nitrate were the main control of seasonality of NO3− concentrations. In this study, the wet deposition flux of NO3− and NH4+ was 12.2 kg N ha−1 yr−1 and 12.8 kg N ha−1 yr−1, respectively. Hence, the total wet inorganic N flux was 25.0 kg N ha−1 yr−1. This was higher than the rural area in Indo-Gangetic Plain region (4.8 kg N ha−1 yr−1, Singh et al., 2017) and coastal areas in Germany (7.7 kg N ha−1 yr−1, Beyn et al., 2014) as well as Japan (21.1 kg N ha−1 yr−1, Ham and Tamiya, 2007), reflecting the mixed influence of marine and terrestrial emissions associated with human activities (Fang et al., 2011).

During the IM period, air masses were characterized by multiple directions or a loop trajectory with a short pathway (He et al., 2018), which contained more nitrogen-containing pollutants from terrestrial sources. This resulted in the higher NO3− concentrations during the IM period. In contrast, during the SW monsoon, the air masses were mainly from the Indian Ocean and Java Sea (He et al., 2018), leading to the lower NO3− concentration in SW monsoon.

On the long-term scale, the NO3−-N concentrations observed in this study fell into the range of previous observations in Singapore (Balasubramanian et al., 2001; He and Balasubramanian, 2008; He et al., 2011; Hu et al., 2003). As shown by Fig. 2, the mean NO3−-N concentration showed an increasing trend from 1997 to 2017. Accordingly, a decreasing trend in SO42−/NO3− was observed in the last 20 years in Singapore, reflecting the increasing influence of NO3− relative to SO42−. This result is consistent with the decreasing trend in SO2 emission in its neighboring countries in SEA over the past 17 years (Fig. S2).

3.2 Formation pathways and associated isotopic fractionation of nitrate

The values of δ15N-NO3− and δ18O-NO3− ranged from −6.5‰ to +8.2‰ and from +38.9‰ to +71.7‰, respectively (Table S2), with a significant seasonal variation (*p*<0.05). The seasonality of δ15N-NO3− reflects the variations in emission sources of NOx and/or the isotopic fractionation during NOx oxidation as well as during nitrate transport (e.g. washout, gas-particle partition) (Elliott et al., 2007; Freyer et al., 1993; Hastings et al., 2003). On the other hand, δ18O-NO3− is controlled by the NO3− formation pathways and associated isotopic fractionation instead of NOx sources (Hastings et al., 2003). Here we will firstly explore NO3− formation pathways and the associated isotopic fractionation effects based on δ18O-NO3− values.

3.2.1 Nitrate formation pathways constrained by δ18O-NO3−

In order to examine the isotope fractionation effects on the seasonality of stable isotopes of nitrate, we calculated the difference of equilibrium isotope fractionation of oxygen (ΔεO) and nitrogen (ΔεN) in rainwater nitrate between seasons (Table 1). Table 1 shows that the seasonal differences in equilibrium isotope fractionation of oxygen (ΔεO, −0.4, 0.7, 0.3) were much lower than the magnitude of seasonal variability in δ18O-NO3− (Δ18O, −2.7, 3.7, 1.0), indicating that isotope fractionation cannot explain the seasonality of δ18O-NO3−. Thus, the seasonality of δ18O-NO3− was primarily determined by the relative proportion of NO3− formation pathways.

Different NO3− formation pathways will generate distinct δ18O-NO3− signatures (Freyer et al., 1993; Walters and Michalski, 2016). δ18O-NO3− of rainwater typically ranges from +52‰ (assuming 2/3 of oxygen atoms of NO3− from O3 and 1/3 from OH radical, see Eqs R1−R3 in Text S1) to +102‰ (5/6 of oxygen atoms originate from O3 and 1/6 from OH, see Eqs R4−R6 in Text S1) (Fang et al., 2011; Hastings et al., 2003). In our study, 83% of the samples had δ18O-NO3− falling in the theoretical range derived from OH radical and N2O5 pathway. Assuming that OH oxidation and N2O5 hydrolysis were the dominant nitrate formation pathways, we estimated the fractional contribution of these two pathways using a Monte Carlo simulation (Text S3 in supplementary information) based on the approach by Zong et al. (2017). The results showed that contributions of OH pathway spanned a wide range (27−100%, Fig. S3). However, the average contribution of OH pathway exhibited a seasonal pattern with a higher contribution (68±12%) during SW monsoon in comparison to the NE monsoon (65±14%) and IM period (64±14%). This estimate was higher than the results of previous models in SEA (30−50%, Dentener and Crutzen, 1993) but lower than that of tropical region (up to 87%, Alexander et al., 2009). This pattern may reflect the combined effects of higher photolysis-produced OH concentrations in tropical region and high aerosol concentrations in SEA. This interpretation can be further supported by the opposite trend between δ18O-NO3− and sunshine duration or radiation in the second half year of 2015 and 2016 (Fig. 3) as well as the highest monthly δ18O-NO3− during the 2015 haze episode (September−October).

About 17% of rainwater samples had δ18O-NO3− lower than +52‰, suggesting that other reaction pathways or isotopic exchange produced 18O-depleted nitrate. Isotopic exchange of oxygen atoms between OH radical and H2O vapor may lead to low δ18O-NO3− values (Walters and Michalski, 2016). However, this possibility can be excluded because the low δ18O-NO3− values (July 2015 and August 2016) did not have correspondingly low δ18O-H2O (Fig. 3). The involvement of peroxy radicals (HO2 or RO2) during nitrate formation can lead to δ18O-NO3− as low as 11‰ because the oxygen atoms in peroxy radicals come from atmospheric O2 with low δ18O values (Fang et al., 2011), which was observed in other tropical cities (Chen et al., 2019; Fang et al., 2011). Unfortunately, it is not possible to estimate the relative contribution of NOx oxidation by peroxy radicals as the related isotope fractionation is not known. In addition, primary NO2 emission from traffic may also lead to lower δ18O values (Felix et al., 2014), but the relative contribution of directly emitted NO2 versus that involved in the nitrate formation is still unknown. These processes should be taken into account in the future study.

A significant negative correlation was observed between monthly δ18O-NO3− and wind speed (Fig. 4). The variation in δ18O-NO3− is primarily controlled by the formation mechanism of NO3− (Hastings et al., 2003), thus this negative correlation is likely related to mechanisms associated with nitrate formation. One potential mechanism was the preferential deposition of 18O-enriched particles during the long-distance transport of nitrogen-containing particles under high wind conditions, leading to the remaining nitrate with low δ18O-NO3− values. Another potential mechanism was related to the different reaction time of two main nitrate formation pathways, with a relatively low reaction rate constant for N2O5 hydrolysis compared with the oxidation of NO2 by OH radicals (Sander et al., 2006). The lower wind speed provided longer reaction time for N2O5 pathway and consequently produced 18O-enriched nitrate, leading to an increase in δ18O-NO3− values with decreasing wind speed.

3.2.2 Nitrogen isotope fractionation during nitrate formation

Combined with the contribution of OH pathway and hydrolysis of N2O5 pathway during NO3− formation, the equilibrium isotope fractionation factor of nitrogen (εN) was estimated since nitrogen exchange between nitrogen species mainly occurred during the OH pathway and hydrolysis of N2O5 pathway (Text S3 in Supplementary information). The average values of N equilibrium isotope fractionation during IM period, SW and NE monsoons were calculated to be 18‰, 17‰ and 18‰, respectively, implying the important influence of isotope fractionation on variations in δ15N-NO3−. However, the seasonal difference of equilibrium isotope fractionation of nitrogen (ΔεN) between NE monsoon and SW (Δ(SW−NE)) or IM period (Δ(IM−NE)) were much lower than the corresponding seasonal difference of δ15N-NO3−, suggesting that NOx emission rather than isotopic fractionation was the main control on seasonal difference of δ15N-NO3− between NE monsoon and SW (Δ(SW−NE)) or IM period (Δ(IM−NE)). As for the difference of εN between IM period and SW monsoon, ΔεN was large enough to mask the isotopic signal of NOx emission. Thus, the isotope fractionation should be considered before the estimation of source contribution in this study.

The isotopic fractionation of nitrogen can also occur during transport of nitrate, in which 15N is preferentially incorporated into condensed phase and then preferentially washed out (Chen et al., 2019; Gobel et al., 2013). Thus, we expect lower δ15N-NO3− in rainwater during the successive precipitation. However, the correlation of dual isotopes of nitrate and rainfall was rather weak (Tables S3 and S4), implying an insignificant influence of rainfall on dual isotopes of nitrate in Singapore on a seasonal timescale. Thus, the isotope fractionation associated with washout and phase partitioning was not considered during the seasonal variations in δ15N-NO3− and δ18O-NO3−. In summary, the isotopic fractionation associated with oxidation process and transport was insufficient to explain the observed seasonal pattern of δ15N-NO3−, and additional changes in source emissions were needed.

3.3 Nitrate sources constrained by chemical compositions and δ15N-NO3−

In Singapore, shipping emission is a potentially important NOx source since it is close to two very active shipping lanes, i.e., the Malacca Strait in the west and South China Sea (SCS) in the northeast. Transport-sourced NOx had negative δ15N-NOx, which might explain the lower δ15N-NO3− in NE monsoon when most of air masses travelled over the SCS and Malacca Strait (He et al., 2018). Previous studies also highlighted the importance of shipping emission at coastal sites (Beyn et al., 2014; Zong et al., 2017). In addition, vehicles can also be a source since the number of vehicles increased by 41% in the past 20 years in Singapore (Yearbook of statistic Singapore). Some samples had δ15N-NO3− values falling into the range of coal combustion, suggesting a potential influence of coal combustion. Although only 1% of Singapore’s electricity was generated from coal combustion (2017 Singapore energy statistics), coal combustion from neighboring countries (BP statistical review of world energy) might affect Singapore. The significant correlations among NO3−, SO42− and δ15N-NO3− during the NE monsoon (Table S3) provided additional evidence of coal combustion (Elliott et al., 2007). Transboundary transport of biomass burning pollutants from Indonesia was reported as a primary source of smog haze in Singapore (Balasubramanian et al., 1999; Hansen et al., 2018). In our study, the average NO3− concentration during the 2015 haze episode was 3.7 times higher than that during pre-haze period. The much higher NH4+/NO3− ratios (~4.0) during haze period (Fig. 5) further suggested the contribution of biomass burning, which generally had high NH4+/NO3− ratio in contrast to the low NH4+/NO3− ratios (<1.0) from industrial emission (Beyn et al., 2014; Pan et al., 2012). Lightning was a potentially important source of NOx in tropical areas with frequent lightning (Price et al., 1997). Lightning was recorded 676,680 times during our study periods (http://www.weather.gov.sg/lightning) with more lightning during IM period in Singapore (Fig. 5). A significant positive correlation between monthly lightning frequency and δ15N-NO3− (R2=0.53, *p*<0.01) from January 2016 to July 2017 also suggested the influence of lightning. Another possible natural source of NOx was biogenic soil emissionconsidering that forest was the main land use in SEA with crop and peatland widely distributed in Malaysia and Indonesia (Reid et al., 2013). The abundant precipitation and higher temperature was favorable for biogenic soil emission (Zong et al., 2017).

3.4 Source apportionment of atmospheric NO3−

A Bayesian mixing model (MixSIAR) was applied to apportion the sources of atmospheric NO3− in Singapore, including mobile source (vehicles and ships), lightning, biomass burning, coal combustion and soil emission (Fig. 6). When incorporating the N equilibrium isotope fractionation (~18‰) in the MixSIAR model, the calculated soil emission was as high as 51±5%, which was much higher than the global estimation (Miyazaki, et al., 2017). This overestimation of soil contribution may be related to the negligence of kinetic isotope fractionation, which could produce 15N-depeleted nitrate relative to NOx. To examine the influence of kinetic isotope fractionation on the source apportionment, we calculated the proportional contribution of nitrate sources under different kinetic isotope fractionation factors (i.e., −3‰, −8‰, −13‰ and −18‰), which led a final isotopic fractionation factor (ε) to be 0‰, 5‰, 10‰ and 15‰, respectively. The results showed that the contribution of mobile and soil emission varied greatly under different ε scenarios, with a much higher contribution of soil than that of global estimation when ε was 10‰ and 15‰. The result from a net isotopic fractionation of 0‰ was also excluded since the multi processes would change isotopic compositions of nitrate in the atmosphere (Elliott et al., 2007; Hastings et al., 2013). Meanwhile, the calculated result based on no isotopic fractionation was contrary to the inventory of NOx emission in SEA (75% of NOx from anthropogenic activities) via an assimilation of multiple satellite data sets (Miyazaki et al., 2017). In addition, the result from NO3− deposition further verified the dominant source from human activities when considering that rainwater NO3− in remote regions was of natural source (0.15 mg L−1), then about 65% of atmospheric NO3−-N was derived from anthropogenic source (Table S5). Thus, we considered the lowest ε (5‰) as a more likely estimate. In this case, traffic sources contributed the most (47%) to atmospheric nitrate, followed by lightning (19%) and biomass burning (14%), with coal combustion (9%) and soil emission (11%) contributed the least. Overall, natural source (lightning and soil) contribute ~30% to NO3−, and anthropogenic source contributed ~70% in this study.

The traffic source might be overestimated because δ15N-NOx of natural gas combustion overlapped with that of traffic source (Walters et al., 2015). Even so, our estimate of mobile source was comparable with transportation-sourced NOx (42%) in the MIX Asian anthropogenic emission inventory for Singapore in 2010 (Li et al., 2017). Although coal only accounted for only 1% of energy structure (2017 Singapore energy statistics), coal combustion contributed about 10% of NO3−, reflecting the transboundary pollution from nearby countries (BP statistical review of world energy). Indeed, rainwater in Singapore had high NO3− and SO42− concentration similar to some cities in Malay Peninsula and Indonesia (Fig. S2). The transboundary pollution from Peninsular Malaysia and Indonesia has been identified by previous studies (Balasubramanian et al., 1999; Hansen et al., 2018; Sharma and Balasubramanian, 2017).

Seasonally, traffic source was higher in NE monsoon than other seasons, when air masses moved towards Singapore across the SCS and Malacca Strait (Fig. S2). The contribution of lightning was higher during IM period than other periods, which was in agreement with the more intense lightning frequency during the IM period (Fig. 5). Biomass burning was detectable throughout the seasons although the peak biomass burning is during the period of August−October in Indonesia (Hansen et al., 2018; Reid et al., 2013). Peatland fires could last for months and smolder deep underground indefinitely, and flare up again during the next dry period (See et al., 2007), which might contribute NOx in other periods.

In summary, the source apportionment results were very sensitive to isotope fractionation factors in the Bayesian model. Our results suggest that ~5‰ of nitrogen isotope fractionation, i.e., when the kinetic isotope fractionation factor was −13‰ and equilibrium isotope fractionation factor was +18‰, was a reasonable scenario to estimate the atmospheric nitrate in Singapore. Additionally, some uncertainties are due to the overlap values of δ15N-NOx and its spatio-temporal variability among each emission sources of NOx even though they have been well used in other studies (Chen et al., 2019; Chang et al., 2018; Zong et al., 2017). However, the uncertainties will not affect the conclusion that traffic source is the main NOx emission source in this study. In order to decrease uncertainty, kinetic isotope fractionation should be considered in the model calculation, and stable isotope signatures of local NOx emission are also helpful for more accurate identification of atmospheric NOx.

**4. Conclusions**

This study investigated the sources and formation mechanisms of rainwater nitrate based on a two-year observation of chemical compositions and isotopes of nitrate in rainwater from Singapore. The nitrogen and oxygen isotopes of nitrate varied seasonally with both slightly higher during the IM period in comparison with NE and SW monsoon. The isotopic fractionation had influence on the seasonal pattern of δ15N-NO3− in rainwater, which should be taken into account when apportioning sources of nitrate in rainwater on a seasonal scale. Based on a conservative estimation from MixSIAR, traffic emission was the main source of nitrate in Singapore in NE monsoon and more lightning contribution for nitrate was found during the IM period compared with that in the NE monsoon. The Monte Carlo simulation suggested that the contribution of NO2 oxidation by OH radical was lower than expected in tropical regions, reflecting the influence of high aerosol concentrations in SEA on the formation of nitrate. The significant correlation of δ18O-NO3− and wind speed reflected the effect of meteorological conditions on secondary formation of nitrate in the tropical region. The study suggested that isotopic fractionation and secondary processes could be taken into account for nitrate source apportionments in the atmosphere.

**Notes**: The authors declare no competing financial interests.

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**Table Captions**

Table 1 Seasonal difference of parameters including stable isotopes of nitrate, temperature (T), NO2/NOx ratios, equilibrium isotope fractionation of oxygen (εO) and nitrogen (εN)

**Figure Captions**

**Fig. 1**. Time series of rainfall and temperature (a), NO3−-N concentration (b), δ15N-NO3− value (c) and δ18O-NO3− values (d). Red curves represent weekly running mean value. Shaded areas represent the IM periods.

**Fig. 2**. A comparison of NO3− concentration, ratios of NH4+/NO3− and SO42−/NO3− in rainwater observed in this study (2015.5−2017.7) with previous studies (Balasubramanian et al., 2001; He and Balasubramanian, 2008; Hu et al., 2003) in Singapore.

**Fig. 3**. Average monthly δ18O-NO3− (a), solar radiation (b), daily bright sunshine duration (c) and δ18O-H2O of rainwater in Singapore (d).

**Fig. 4**. Relationship between δ18O-NO3− and wind speed in Singapore. The dashed lines represent 95% confidence interval.

**Fig. 5**. Average monthly NH4+/NO3− molar ratios (a), SO42− concentration (b), lighting frequency (c) and δ15N-NO3− in Singapore (d).

**Fig. 6**. Contribution of rainwater NO3− in Singapore under different isotopic fractionation.



Fig.1



Fig.2



Fig.3



Fig.4



Fig.5



Fig.6

Table 1 Seasonal difference of parameters including stable isotopes of nitrate, temperature (T), NO2/NOx ratios, equilibrium isotope fractionation of oxygen (εO) and nitrogen (εN)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Δa | Δ18O(‰) | Δ15N(‰) | ΔT(°C) | Δ(NO2/NOx)b | ΔεO(‰) | ΔεN(‰) |
| Δ(SW−NE) | −2.7\* | 1.5\* | 0.3 | −0.09 | −0.4 | −1.5 |
| Δ(IM−SW) | 3.7\* | 1.1\* | 0.3 | 0.08 | 0.7 | 1.6 |
| Δ(IM−NE) | 1.0 | 2.6\* | 0.6\* | −0.01 | 0.3 | 0.1 |

\* Seasonal difference is significant for the daily-based data (*p* < 0.05).

a Δ(c−d) represents the difference between c and d.

b NO2/NOx ratios in atmosphere were obtained from cities in SEA (<http://www.eanet.asia/>).