Monthly Variations of the Nitrogen Isotope of Ammonium in Wet Deposition in a Tropical City of South China

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ABSTRACT

Nitrogen isotope of ammonium (δ^{15}N-NH$_4^+$) in the wet deposition in Zhanjiang, a typical tropical city in the southernmost region of mainland China, were analyzed from October 2015 to November 2018 in order to examine the monthly variations and identify the sources of ammonia. The NH$_4^+$ exhibited higher concentrations during the dry season than the wet one, whereas the δ^{15}N-NH$_4^+$ displayed the opposite trend of higher values during the wet season. Comparing the δ^{15}N-NH$_4^+$ and the weather parameters (e.g., rainfall, temperature and duration of sunshine), we found the change in the duration of sunshine to be primarily responsible for the observed temporal isotopic variation. During the wet season, a significantly longer duration increased the opportunities for photooxidation and enhanced the formation of free radicals, which resulted in larger amounts of sulfur dioxide (SO$_2$) and nitrogen oxide (NO$_x$) being transformed into sulfuric acid (H$_2$SO$_4$) and HNO$_3$. This process accelerated the unidirectional conversion of NH$_3$ into (NH$_4$)$_2$SO$_4$- and NH$_4$NO$_3$-enriched ^{14}N particles, which can be deposited by aerosols, and led to ^{15}N-enriched residual NH$_3$ being present in the atmosphere; this NH$_3$ was then scavenged by precipitation and released as NH$_4^+$ during rainfall. By contrast, less isotopic fractionation occurred during the shorter sunshine duration of the dry season, suggesting that δ^{15}N-NH$_4^+$ in the precipitation should be similar to those of NH$_3$ in the atmosphere and can therefore be applied in source apportionment. A Bayesian isotope mixing model demonstrated that volatilization contributed less (18 ± 21% and 19 ± 20% from animal waste and fertilizer, respectively) than combustion (28 ± 26%, 24 ± 26% and 11 ± 5% from coal combustion, vehicle exhaust and biomass burning) to the concentration of NH$_4^+$ in Zhanjiang's precipitation.

Keywords: Ammonium; δ^{15}N; Wet deposition; Bayesian isotope mixing model; Tropical area.

INTRODUCTION

Nitrogen (N) is an important element in the ecosystem (Galloway *et al.*, 2008; Xiao *et al.*, 2012). Recently, excessive anthropogenic N emissions have greatly increased N deposition, particularly from the 1980s through the early 21st century (Galloway *et al.*, 2004; Fang *et al.*, 2010; Xu *et al.*, 2017; Biswas *et al.*, 2019). Increasing N deposition has induced harmful effects on the ecosystem and atmospheric environment (Galloway *et al.*, 2004; Fang *et al.*, 2010; Jiang *et al.*, 2019). Ammonium (NH$_4^+$) is an important form of N

deposition (Galloway *et al.*, 2008; Liu *et al.*, 2013) and mainly originates from fossil fuel consumption, volatilized sources (e.g., animal wastes and fertilizer) and biomass burning (Huang *et al.*, 2012; Kang *et al.*, 2016; Zheng *et al.*, 2018; Peng *et al.*, 2019). Previous studies indicate that the increase in ammonia (NH$_3$) emissions from 1980s to first few years of the 21st century in China was mostly from livestock waste (49%) and synthetic fertilizer applications (37%), and remain stable or slightly decreased over the past few years (Kang *et al.*, 2016). However, the ammonia concentration in atmosphere is still high, and has caused serious environmental pollution (Xiao *et al.*, 2012; Liu *et al.*, 2013; Liu *et al.*, 2017; Zheng *et al.*, 2018).

Nitrogen isotope in ammonium (δ^{15}N-NH$_4^+$) in precipitation provide a valuable geochemical tracing technique called *fingerprint identification* (Xie *et al.*, 2008; Jia and Chen, 2010; Xiao *et al.*, 2012; Altieri *et al.*, 2015; Liu *et al.*, 2017),

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which is powerful to trace the sources of NH_4^+ and the reaction process of deposited NH_4^+ in ecosystems (Jia and Chen, 2010; Altieri *et al.*, 2016; Liu *et al.*, 2017). For example, $\delta^{15}N$ in wet deposition has been used successfully to identify NH_4^+ sources in Guangzhou (Jia and Chen, 2010); Guiyang (Xiao *et al.*, 2012; Liu *et al.*, 2017; Zheng *et al.*, 2018); the Yangtze River Delta region (Zhao *et al.*, 2009); Chengdu (Li *et al.*, 2007); Pretoria, South Africa (Heaton, 1987); and Niigata Platin, Japan (Fukuzaki and Hayasaka, 2009). In addition, based on the stable isotope mixing model, Liu *et al.* (2017) found that volatilization sources (animal waste [22%] and fertilizer [22%]) contributed less pollution than ammonia derived from combustion sources (vehicle exhaust [19%], coal combustions [19%] and biomass burning [17%]) in Guiyang, China. Moreover, $\delta^{15}N\text{-}NH_4^+$ in wet deposition can be modified by weather conditions (Jia and Chen, 2010; Xiao *et al.*, 2012). For example, washout processes preferentially incorporate heavy isotopes (^{15}N), which leads to heavier $\delta^{15}N\text{-}NH_4^+$ in precipitation (Xiao *et al.*, 2012). Sunshine duration also influences $\delta^{15}N\text{-}NH_4^+$ in precipitation because free radicals and photooxidation can produce sulfur dioxide (SO_2) and nitrogen oxide (NO_x) to acidic matter (H_2SO_4 and HNO_3) in the atmosphere, which accelerates the transition of NH_3 (gas phase) into $(NH_4)_2SO_4$ and NH_4NO_3 (particulate phase) by unidirectional reactions for isotopically enriched ^{14}N (Xiao *et al.*, 2012). This process results in ^{15}N-enriched residual NH_3 (NH_4^+) in wet deposition. However, these studies mainly focus on the middle and high latitudes. In contrast, little is known about ammonium sources and the composition of nitrogen isotopes in precipitation in low latitude areas, which exhibit significantly different weather conditions relative to the middle and high latitude areas.

In this study, a time series investigation of NH_4^+ concentrations and $\delta^{15}N\text{-}NH_4^+$ in wet deposition was conducted from October 2015 to November 2018 in Zhanjiang, a typical tropical area in the southernmost region of mainland China. We strived to identify the main factors that control seasonal variations of $\delta^{15}N\text{-}NH_4^+$ and to elucidate the different sources of NH_4^+ in wet deposition in such tropical areas.

MATERIALS AND METHODS

Sampling Station and Sample Collection

Rainwater samples were collected in Zhanjiang (20.00–21.58°N, 109.52–110.92°E), which is located in western Guangdong Province in South China near the northern extent of the South China Sea (Fig. 1). As a tropical city, Zhanjiang has a tropical monsoon climate with relatively high annual mean temperatures (23.0°C) and high annual mean rainfall (1689 mm; China Meteorological Data Service Center, http://data.cma.cn/). The annual duration of sunshine in Zhanjiang is very long (~2000 hours) due to its low latitude (China Meteorological Data Service Center, http://data.cma.cn/n). The transitional months from the winter monsoon to the summer monsoon usually occur in spring, with rainfall sharply increasing in May, and subsequently decreasing after October (Fig. 2(e)). Thus, the wet season is defined as taking place from May to October, and the dry season is defined as taking place from November to April.

From October 2015 to November 2018, rainwater samples were collected for each precipitation event on the roof of a building at Guangdong Ocean University in Zhanjiang. A dry polyethylene bucket (80 cm in diameter) cleaned with acid was used to collect rainwater. Rain events with rainfall less than 0.5 mm were considered invalid and not collected. After collection, the rainwater samples were filtered through glass fiber filters (GF/Fs; 47 mm in diameter; Whatman) and into polyethylene bottles, which were previously soaked with 30% (v/v) HCl for 24 h and cleaned with ultrapure water and dried in the laboratory. Samples were stored frozen at –20°C, and they were analyzed soon after being melted. Similar procedures have been conducted in numerous studies (e.g., Jia and Chen, 2010; Liu *et al.*, 2017; Xiao *et al.*, 2012; Zheng *et al.*, 2018). During the period from October 2015 to November 2018, 315 rainwater samples were collected. The rainwater samples collected each month were proportionally mixed into a large sample according to the rainfall amount that month, thus composing a representative sample of wet deposition for the entire month. The results of the analysis of NH_4^+ concentrations in the mixed samples are monthly weighted averages.
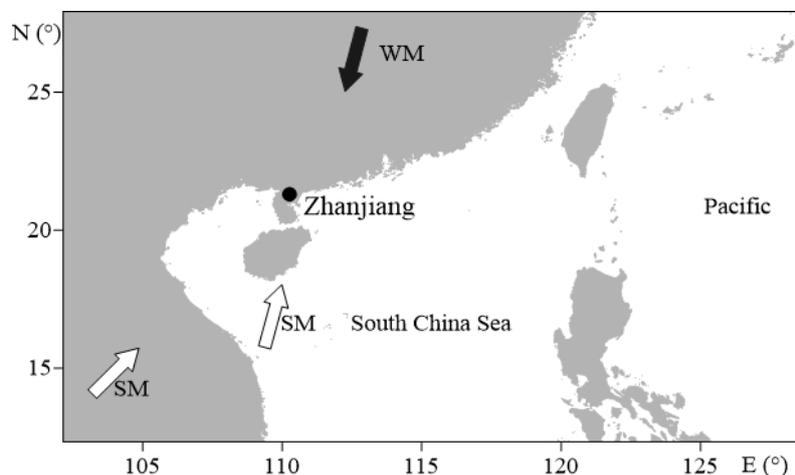

Fig. 1. The sampling site in Zhanjiang, South China (black dot). WM: winter monsoon; SM: summer monsoon.

Sample Analysis

NH_4^+ concentrations were determined by spectrophotometry after treatment with Nessler's reagent, and the detection limit was lower than 0.1 mg L^{-1}. For the isotopic analysis, NH_4^+ was first quantitatively oxidized to NO_2^- by hypobromite (BrO^-) at a pH of 12. Excess BrO^- was consumed by sodium arsenite. NO_2^- was further reduced to N_2O with 1:1 sodium azide in an acetic acid buffer (Lin *et al.*, 2007). Subsequently, N_2O was separated, purified and analyzed for $\delta^{15}N$ with a GasBench II-MAT 253. The international standards, IAEA-N1, USGS 25 and USGS 26, were used for $\delta^{15}N$ calibration. The analysis deviation for the standard was < 0.2‰ for $\delta^{15}N$. The reproducibility of duplicate analyses was < 0.3‰ for $\delta^{15}N$ (average ± 0.1‰).

Data Sources and Calculations

Monthly atmospheric SO_2 data was from historical air quality data in Zhanjiang (China air quality online monitoring and analysis platform, https://www.aqistudy.cn/). The sunshine duration, temperature, humidity, wind direction and wind speed were obtained from the China Meteorological Data Sharing Service System (China Meteorological Data Service Center, http://data.cma.cn/).

Backward Trajectories

To reveal possible sources of pollutants, the web version of the model Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) was used to calculate three days (72 h) of back trajectories (BTs; https://ready.arl.noaa.gov/HYSPLIT_traj.php). The BTs were generated from the sampling location at a height of 500 m above sea level. A trajectory time of three days (72 h) was chosen due to the short residence time of NH_4^+ in the atmosphere (less than three days) (Xiao and Liu, 2002).

Stable Isotope Analysis in R (SIAR) Mixing Model

To calculate the proportional contribution of potential NH_4^+ sources in Zhanjiang, a Bayesian stable isotope mixing model was conducted using the SIAR package. In this model, a Bayesian framework was used to calculate the probability distribution for the proportion of each source to the mixture. The following equation was used:

$$X_{ij} = \sum_{k=1}^{k} P_k \left(S_{jk} + c_{jk} \right) + \varepsilon_{ij} \tag{1}$$

$$S_{jk} \sim N \left(\mu_{jk}, \omega^2_{jk} \right) \tag{2}$$

$$c_{jk} \sim N \left(\lambda_{jk}, \tau^2_{jk} \right) \tag{3}$$

$$\varepsilon_{jk} \sim N \left(0, \sigma^2_j \right) \tag{4}$$

where X_{ij} denotes the isotopic values ($j = 1$, $\delta^{15}N-NH_4^+$) of the sample i ($i = 1, 2, 3, …, N$); S_{jk} denotes the isotopic value j of the source k ($k = 1, 2, 3, …, K$), which is normally distributed with the average μ_{jk} and the standard deviation ω_{jk}; P_k denotes the contribution of source k, which is determined by the SIAR model; c_{jk} denotes the fractionation factor for j in source k, where c_{jk} is normally distributed with the average λ_{jk} and the standard deviation τ_{jk}; and ε_{jk} denotes the residual error of the additional unquantified variation between individual samples, which are normally distributed with average 0 and standard deviation σ_j. This model was used by previous studies, therefore a more detailed model description can be found in Moore and Semmens (2010), Xue *et al.* (2012) and Zhang *et al.* (2018).

RESULTS

Monthly rainfall, NH_4^+ concentration, $\delta^{15}N-NH_4^+$ values, SO_2 and NO_2 concentration, sunshine duration and temperature, recorded from October 2015 to November 2018, are summarized in Fig. 2. The lack of NH_4^+ concentrations and $\delta^{15}N-NH_4^+$ during February 16, December 16, January 17 and December 17 is because very little (< 0.5 mm) or no rainfall occurred during these periods. The average NH_4^+ concentration ranged from 0.43 to 3.11 mg L^{-1} during the sampling period, with an average of 0.82 mg L^{-1}. Considering only the annual averages, we find that there is no significant trend in the variation of NH_4^+ concentration. The annual mean NH_4^+ concentration are 1.04 mg L^{-1}, 0.65 mg L^{-1} and 0.78 mg L^{-1} in 2016, 2017 and 2018, respectively, suggesting that the concentrations of NH_4^+ slightly decreased after 2016. Compared with the wet seasons, higher concentrations of NH_4^+ were found during the dry seasons (Fig. 2(e)). According to the precipitation and annual mean NH_4^+ concentration during the three study years, wet NH_4^+-N deposition in 2016, 2017 and 2018 in Zhanjiang was 22.7 kg N ha^{-2}, 13.3 kg N ha^{-2} and 19.0 kg N ha^{-2}, respectively. The $\delta^{15}N-NH_4^+$ ranged from –18.0 to –3.9‰, with an average of –9.6‰. The $\delta^{15}N-NH_4^+$ showed higher values during the wet seasons relative to lower values during the dry seasons, which is consistent with variations in rainfall, sunshine duration and temperature, but contradictory to variations in SO_2 and NH_4^+ concentrations (Fig. 2). This pattern in variation of $\delta^{15}N-NH_4^+$ in Zhanjiang is different from other areas, such as Guizhou in western China (Xiao *et al.*, 2012), which exhibited higher values in winter and lower values in summer.

DISCUSSION

Concentration of NH4+ in Precipitation

In this study, the NH_4^+ concentration in rainwater in Zhanjiang is lower than in Guangzhou (1.10 mg L^{-1}; Jia and Chen, 2010), Guiyang (1.98 mg L^{-1}; Xiao *et al.*, 2012) and in the Yangtze River Delta region (1.20 mg L^{-1}; Zhao *et al.*, 2009), but higher than the subtropical forest ecosystems in remote areas of South China (ranged from 0.02 to 0.05 mg L^{-1}; Chen and Mulder, 2007). The wet deposition fluxes in Zhanjiang (18.3 kg N ha^{-2} in three year average) are slightly lower than that reported values observed in Guangzhou (27.4 kg N ha^{-2}; Jia and Chen, 2010) and Guiyang (23.2 kg N ha^{-2}; Xiao *et al.*, 2012), and higher than that in the Yangtze River Delta region (14.9 kg N ha^{-2}; Zhao *et al.*, 2009), indicating significant N pollution in the city. In areas with intensive human activities, anthropogenic sources (such as industrial activities and agricultural productivity)
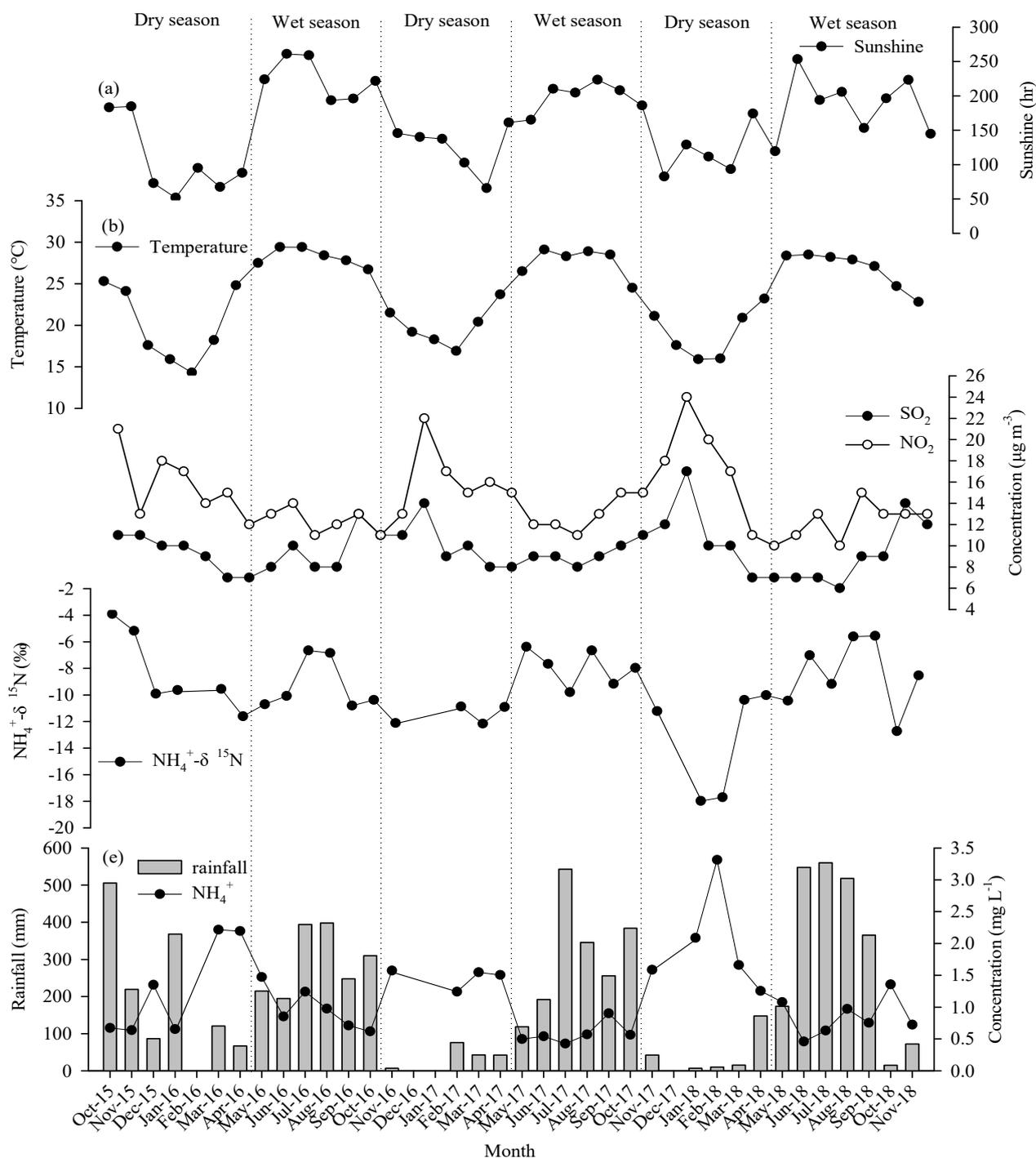
Fig. 2. Comparisons of $\delta^{15}N$-NH_4^+ with NH_4^+ concentration and atmospheric parameters in Zhanjiang. Monthly (a) sunshine duration, (b) temperature, (c) SO_2 and NO_2 concentration, (d) $\delta^{15}N$-NH_4^+ and (e) rainfall and NH_4^+ concentration. The lack of NH_4^+ concentrations and $\delta^{15}N$-NH_4^+ in Feb 16, Dec 16, Jan 17 and Dec 17 is because very little (< 0.5 mm) or no rainfall occurred during these periods.

may provide the most important contribution to NH_4^+ in wet deposition. In addition, sources of NH_4^+ include natural sources, such as human and animal excrement and fertilizer, which are closely associated with agricultural activities (Jia and Chen, 2010; Peng *et al.*, 2019; Zhao *et al.*, 2009). The annual averages of NH_4^+ concentration are 1.04 mg L^{-1}, 0.65 mg L^{-1} and 0.78 mg L^{-1} in 2016, 2017 and 2018,

respectively, suggesting that the NH_4^+ pollution is in an unstable level. This interannual variation might be related with the weather parameters, which will be monitored in the future to clarify this issue. Due to the seasonal distribution pattern, higher NH_4^+ concentrations occur in the dry seasons (November–April) and lower concentrations occur in the wet seasons (May–October); this pattern may be attributed

to the dilution of rainfall (Fig. 2(e)) and/or the origin of air masses (Fig. 3). The dominant air mass over the continent of China in the dry season could bring highly polluted continental air to Zhanjiang, whereas the dominant air mass from the southerly ocean could bring clean air to the city (Fig. 3). In addition, temporal changes in the relative contributions of different sources could affect nitrogen isotopes, as discussed later.

Influencing Factors of $\delta^{15}N$-NH_4^+ in Precipitation

The $\delta^{15}N$-NH_4^+ in Zhanjiang was similar to those reported in Guiyang (Xiao *et al.*, 2012) and Guangzhou (Jia and Chen, 2010), but the seasonal distribution pattern is the opposite, exhibiting higher values in the wet seasons and lower values in the dry seasons. This seasonal distribution pattern may be controlled by washout, temperature and sunshine duration (Xiao *et al.*, 2012). If rainfall was the key factor influencing the seasonal patterns, low precipitation during the dry seasons would preferentially wash out heavy ^{15}N-NH_3, then higher $\delta^{15}N$-NH_4^+ occurred in wet deposition. In contrast, complete NH_3 removal would result in relatively lower $\delta^{15}N$-NH_4^+ in wet deposition during the wet season than the dry one. In fact, a positive correlation between $\delta^{15}N$-NH_4^+ and rainfall was observed in Zhanjiang, and generally high $\delta^{15}N$-NH_4^+ were found during the rainy seasons (Fig. 2). This suggests that the isotopic effect of washout may be less important for $\delta^{15}N$-NH_4^+ in Zhanjiang. Significantly high temperatures were observed during the wet seasons in Zhanjiang. With increasing temperatures, microbial activity will increase and facilitate more ^{14}N-organic matter in the atmosphere to decompose into NH_4^+, resulting in negative values of $\delta^{15}N$-NH_4^+ (Xie *et al.*, 2008; Xiao *et al.*, 2012). In addition, temperature can increase the volatility of NH_3 from sources, leading to lighter NH_3 molecules being released into the atmosphere (Sommer *et al.*, 1991; Xiao *et al.*, 2012).

However, higher $\delta^{15}N$-NH_4^+ were found during the wet seasons (higher temperature) in Zhanjiang (Fig. 2). This suggests that temperature was not an important factor controlling seasonal variations of $\delta^{15}N$-NH_4^+ in Zhanjiang. Therefore, sunshine duration is the most likely factor controlling the variations of $\delta^{15}N$-NH_4^+ in precipitation discussed below.

NH_3 in the atmosphere is easily absorbed by acidic matter (e.g., H_2SO_4 and HNO_3; Xiao *et al.*, 2012). A significantly longer sunshine duration provided more photooxidation opportunities and free radicals that produce more sulfur dioxide (SO_2) and nitrogen oxide (NO_x) to acidic matter (H_2SO_4 and HNO_3), thereby accelerating the unidirectional conversion of light ^{14}N-NH_3 to $(NH_4)_2SO_4$ and NH_4NO_3 (Freyer, 2010; Ottley and Harrison, 1992; Pavuluri *et al.*, 2010). In addition, rain flushing is another way to consume SO_2 and NO_x. Thus, these reaction processes and heavy rainfall resulted in lower SO_2 and NO_x concentrations during the wet seasons. However, rain flushing only occurred in precipitation event, while the reaction processes that produced SO_2 and NO_x to acidic matter (H_2SO_4 and HNO_3) occurred at all time. Thus, the reaction process may be the most important way to consume SO_2 and NO_x. These products by reaction processes are solids, which can be adsorbed and deposited by aerosols. This process results in ^{15}N-enriched residual NH_3 in atmosphere. When it rains, rain mainly capture ^{15}N-enriched residual NH_3 to produce NH_4^+ (Xiao *et al.*, 2012). We realize that rain can also capture NH_4^+ from $(NH_4)_2SO_4$ and NH_4NO_3 in aerosol. However, $(NH_4)_2SO_4$ and NH_4NO_3 in aerosol were deposited all the time, thus NH_4^+ in rain sourced from aerosol seems to be less important (Xiao *et al.*, 2012). In addition to the sunshine (photooxidation and free radicals) pathway for the formation of acidic matter, SO_2 can be also oxidized by natural transition metal ions to form H_2SO_4 (Harris *et al.*, 2013). However, this oxidation pathway by metal ions primarily
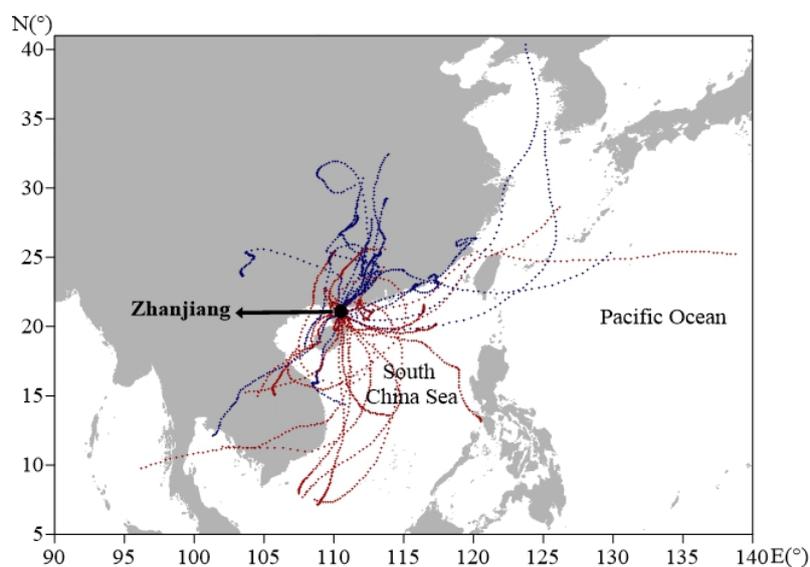

Fig. 3. Backward air mass trajectories in precipitation events in Zhanjiang, based on NOAA HYSPLIT model back trajectories; the red lines denote air mass trajectories occurring in the wet season and the blue lines denote trajectories in the cool dry seasons. (For interpretation of the references to the color in this figure, the reader is referred to the Web version of this article.)

occur on coarse mineral dust, and the sulfate produced has a short lifetime and little direct or indirect climatic effect (Harris *et al.*, 2013). Thus, this oxidation pathway by metal ions can be less important for the formation of acidic matter. As shown in Fig. 2, there is a significant correlation between sunshine hours and $\delta^{15}N$-NH_4^+ in Zhanjiang, indicating that sunshine duration was indeed the most important factor affecting seasonal variations of $\delta^{15}N$-NH_4^+. SO_4^{2-} and NO_3^- are the most abundant chemical component anion in precipitation (Xiao *et al.*, 2012) and total suspended particulate (TSP; Xiao and Liu, 2004). Thus, the predominant SO_2 and NO_x oxidation pathways may be considered as a driver for the trends of $\delta^{15}N$-NH_4^+. The photooxidation and reaction with free radicals are the main oxidation pathways of SO_2 and NO_x in the atmosphere. The rate of photooxidation is about 1% SO_2 h^{-1}, thus the longer sunshine time would produce more oxidation products. In addition, since the formation of free radicals need sunshine, the high free radicals generally occur in summer and low free radicals occur in winter (Xiao *et al.*, 2012). Due to its low latitude, the sunshine duration of Zhanjiang is relatively longer in the wet season and shorter in the dry season (Fig. 2(a)). In Zhanjiang, due to longer sunshine time in this tropical area, NO_x oxidation via free radical was the predominant pathway (accounting for 87% in winter and 94% in summer; Chen *et al.*, 2019). Further SO_2 and NO_x oxidized by photooxidation and free radicals in the atmosphere produces more H_2SO_4 and HNO_3 (Fig. 2(c)). The more H_2SO_4 and HNO_3 is produced, the more ammonia is absorbed onto $(NH_4)_2SO_4$ and NH_4NO_3, which can be deposited by aerosols. The reaction of ammonia with H_2SO_4 and HNO_3 is a kinetic process (unidirectional reactions) that favors the light isotope of nitrogen in the product, and leads to ^{15}N-enriched residual NH_4^+ in wet deposition (Xiao *et al.*, 2012). Thus, the significantly longer sunshine duration in the wet season and shorter sunshine duration in the dry season may be responsible for the seasonal variations of $\delta^{15}N$-NH_4^+ in Zhanjiang. The pattern of seasonal variation of $\delta^{15}N$-NH_4^+ in Zhanjiang is opposite to the patterns in Guiyang (Xiao *et al.*, 2012) and Guangzhou (Jia and Chen, 2010), where higher $\delta^{15}N$-NH_4^+ occurred in winter and lower values occurred in summer. In contrast to this study, the authors considered temperature to be the most important factor controlling seasonal variations of $\delta^{15}N$-NH_4^+ in Guiyang (Xiao *et al.*, 2012) and Guangzhou (Jia and Chen, 2010). This is likely due to shorter sunshine durations in those areas, particularly in Guiyang, which averages only 78 h $month^{-1}$ (ranging from 42 to 159 h $month^{-1}$) of sunshine (Xiao *et al.*, 2012). In contrast, the amount of sunshine in Zhanjiang is significantly greater (average of 150 h $month^{-1}$ in 2016 and 154 h $month^{-1}$ in 2017). Therefore, we hypothesize

that sunshine duration is the most important factor controlling seasonal variations of $\delta^{15}N$-NH_4^+ in precipitation in Zhanjiang, a typical tropical area.

Sources of NH_4^+ in Precipitation

The $\delta^{15}N$ of dominant NH_3 emissions are distinct and well characterized as shown in Table 1. The $\delta^{15}N$ in fertilizer and animal waste is relatively low, while $\delta^{15}N$ from biomass burning and fossil fuel-derived NH_3 are higher (Table 1). As discussed above, isotopic fractionation occurred significantly in the wet seasons due to a longer sunshine duration, suggesting that the $\delta^{15}N$-NH_4^+ values in wet seasons were not suitable to be used in the model to quantify the proportional contribution of the sources. On contrast, isotopic fractionation would be less in the dry seasons due to a shorter sunshine duration. Thus, it is more representative to apply $\delta^{15}N$-NH_4^+ from the dry seasons to identify ammonia sources in Zhanjiang. Here, relative contributions of the sources listed above were estimated in wet deposition using a Bayesian model. Outputs from the SIAR mixing model show that precipitated NH_4^+ in Zhanjiang originated more from fossil fuel-derived ammonia emissions ($24 \pm 26\%$ from vehicle exhaust, $28 \pm 26\%$ from coal combustion) than from volatilized ammonia emissions ($18 \pm 21\%$ from animal waste, $19 \pm 20\%$ from fertilizers) and biomass burning ($11 \pm 5\%$) (Fig. 4). Summarily, the result of our estimation showed that fossil fuel-derived ammonia emissions dominated Zhanjiang (52%), which was similar to estimates in Guiyang (38%; Liu *et al.*, 2017). In Guiyang, the depletion of $\delta^{15}N$-NH_4^+ in precipitation for the past decades was attributed to ammonia emissions from domestic waste and sewage (Xiao and Liu, 2002). However, the latest research showed that the ammonia in precipitation in Guiyang was originated from fossil fuel-derived ammonia emission and biomass burning than from domestic waste and sewage and fertilizer (Liu *et al.*, 2017). This is mainly influenced by the increasing human activities. In Zhanjiang, coal is commonly used to generate electricity (Chen *et al.*, 2019). In addition, the dominant air mass over the continent of China during the dry seasons could bring highly polluted continental air to Zhanjiang (Fig. 3). Combustion ammonia sources particularly that from fossil fuels substantially contributed to the observed $\delta^{15}N$-NH_4^+ in precipitation in this tropical city, which should be emphasized in source of anthropogenic ammonia deposition. This suggestion agrees with the bottom-up inventory, which reveals that most N emissions are derived from coal combustion in China (Fang *et al.*, 2010). Therefore, our results indicate that $\delta^{15}N$-NH_4^+ in precipitation is more applicable for source identification in dry seasons than in wet seasons in Zhanjiang due to minimal isotope fractionation.

Table 1. The $\delta^{15}N$ of NH_3 from different sources.

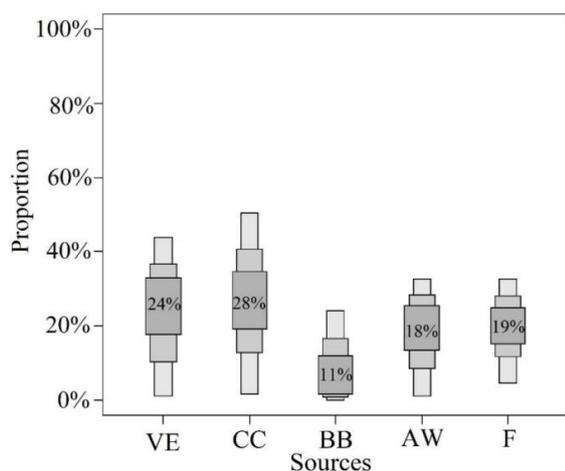| Sources	$\delta^{15}N$-NH_3 (‰)	References
Coal combustion	-8.9 ± 4.1	(Freyer, 1991; Felix *et al.*, 2013)
Vehicle exhaust	-3.4 ± 1.7	(Felix *et al.*, 2013)
Biomass burning	$+12.0$ (an average)	(Kawashima and Kurahashi, 2011)
Animal waste	-19.0 ± 14.1	(Freyer, 1978; Heaton, 1987; Felix *et al.*, 2013, 2014)
Fertilizers	-26.8 ± 15.4	(Felix *et al.*, 2013, 2014)

Fig. 4. Percentage contribution of five potential NH_4^+ sources (VE: vehicle emissions; CC: coal combustion; BB: biomass burning; AW: animal waste; F: fertilizer) for dry season deposition estimates by SIAR.

CONCLUSIONS

The NH_4^+ and $\delta^{15}N\text{-}NH_4^+$ in the wet deposition in Zhanjiang averaged 0.82 mg L^{-1} and –9.6‰, respectively. The NH_4^+ exhibited higher concentrations during the dry season than the wet one. Comparing the $\delta^{15}N\text{-}NH_4^+$ with seasonal patterns of different weather parameters, we found the observed temporal isotopic variation to be primarily caused by the change in sunshine duration. During the wet season, a significantly longer duration increased the opportunities for photooxidation and enhanced the formation of free radicals that produced H_2SO_4. This process accelerated the unidirectional conversion of NH_3 into $(NH_4)_2SO_4$- and NH_4NO_3-enriched ^{14}N particles, which can be deposited by aerosols, and resulted in lower atmospheric concentrations of SO_2 and NO_2 and higher levels of ^{15}N-enriched residual NH_4^+. By contrast, less isotopic fractionation occurred during the shorter sunshine duration of the dry season, suggesting that $\delta^{15}N\text{-}NH_4^+$ in the precipitation should be similar to those of NH_3 in the atmosphere and can be applied in source apportionment. A Bayesian model demonstrated that a higher proportion of the concentration of NH_4^+ in Zhanjiang's precipitation was contributed by fossil fuel-derived sources (including vehicle exhaust and coal combustion) than ammonia volatilization and biomass burning.

ACKNOWLEDGEMENTS

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