Traffic-related dustfall and NO_x, but not NH_3, seriously affect nitrogen isotopic compositions in soil and plant tissues near the roadside[☆]

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ABSTRACT

Ammonia (NH_3) emissions from traffic have received particular attention in recent years because of their important contributions to the growth of secondary aerosols and the negative effects on urban air quality. However, few studies have been performed on the impacts of traffic NH_3 emissions on adjacent soil and plants. Moreover, doubt remains over whether dry nitrogen (N) deposition still contributes a minor proportion of plant N nutrition compared with wet N deposition in urban road environments. This study investigated the $\delta^{15}N$ values of road dustfall, soil, moss, camphor leaf and camphor bark samples collected along a distance gradient from the road, suggesting that samples collected near the road have significantly more positive $\delta^{15}N$ values than those of remote sites. According to the SIAR model (Stable Isotope Analysis in R) applied to dustfall and moss samples from the roadside, it was found that NH_3 from traffic exhaust ($8.8 \pm 7.1\%$) contributed much less than traffic-derived NO_2 ($52.2 \pm 10.0\%$) and soil N ($39.0 \pm 13.8\%$) to dustfall bulk N; additionally, 68.6% and 31.4% of N in mosses near the roadside could be explained by dry N deposition (only $20.4 \pm 12.5\%$ for traffic-derived NH_3) and wet N deposition, respectively. A two-member mixing model was used to analyse the $\delta^{15}N$ in continuously collected mature camphor leaf and camphor bark samples, which revealed a similarity of the $\delta^{15}N$ values of plant-available deposited N to ^{15}N-enriched traffic-derived NO_x-N. We concluded that a relatively high proportion of N inputs in urban road environments was contributed by traffic-related dustfall and NO_x rather than NH_3. These information provide useful insights into reducing the impacts of traffic exhaust on adjacent ecosystems and can assist policy makers in determining the reconstruction of a monitoring network for N deposition that reaches the road level.

1. Introduction

Nitrogen oxides are key trace gases in the troposphere, and they can regulate the concentrations of ozone and hydroxyl radicals, as well as the formation of nitrate aerosols (Lawrence and Crutzen, 1999; Pinder et al., 2012; Miller et al., 2017). Similarly, low-molecular-weight NH_3 also plays a vital role in atmospheric chemistry by reacting with sulfuric and nitric acids to form fine particulate matter; moreover, molar-based aerosol chemical properties are more affected by atmospheric NH_x- N (NH_3 and NH_4^+) than the same mass of sulfate, nitrate, and organic pollutants (Sun et al., 2017). However, the growing levels of atmospheric NO_x (NO and NO_2) and NH_3 levels due to human activities not only degrade air quality for human health, but also impact the urban ecosystem structure and function (And et al., 2007; Elliott et al., 2007; Bobbink et al., 2010; Reche et al., 2015; Oluwoye et al., 2017).

Although pollutant emissions from industrial activities have been drastically reduced as a result of the enactment of legislation on atmospheric pollution control, high pollutant concentrations (e.g., particulates, NO, NO_2 and volatile organic compounds) induced by dense traffic in urban environments still cannot be avoided under the current social demand. Vehicles contribute approximately 32% of NO_x emissions in the United Kingdom (RoTAP, 2009); in the United States, approximately 58% of total

anthropogenic NO$_x$ emissions could be attributable to vehicle emissions as of 2010 (Mcdonald et al., 2012). A 344% increase in the total vehicle population was estimated in Guiyang City from 2005 to 2015, resulting in the NO$_x$ from vehicle emissions being responsible for approximately 56% of total NO$_x$ emissions in Guiyang in 2010 (He, 2013; Tian et al., 2013; Traffic Management Bureau of Guiyang, 2016). It has been known that the main NH$_3$ emission source is derived from agricultural activities at the regional to global scales (Liu et al., 2013; Paulot et al., 2014); however, recent studies have shown that vehicle emissions are another important NH$_3$ source following the increased utilization of the three-way catalyst (TWC) in gasoline-powered vehicles and the rapid development of the selective catalytic reduction (SCR) system in diesel-powered vehicles (Twigg, 2007; Bishop and Stedman, 2015; Stritzke et al., 2015). Therefore, vehicles are the crucial source of anthropogenic reactive N compounds. Additionally, high-density traffic also exacerbates the production and spread of road dust. Because dust is a main constituent and N source for PM$_{2.5}$ (Zhang, 2010; Huang et al., 2014), PM$_{2.5}$ pollution is further promoted by urban traffic. However, the impacts of the combined traffic-derived NO$_x$ and NH$_3$ emissions, as well as traffic-induced dust, on the surrounding plants and soils are still not well understood. Furthermore, the relative contributions of NO$_x$ and NH$_3$ from vehicle emissions to the N components in the road dust in busy traffic areas have not been investigated, although road dust is known to contain various N compounds from soil.

The deposition patterns of N compounds from vehicles differ from the patterns of pollutant transmission that start from regional pollution sources (e.g., smokestacks). This is because traffic-derived N pollutants can deposit locally, which may also lead to an underestimation of NO$_y$ (NO$_x$ and organic N) and total N deposition. Although plant N nutrition can be maintained by soil N via root uptake, it is generally accepted that atmospheric NO$_x$, NH$_3$ or even organic N compounds absorbed by the stomata can also directly contribute a great quantity of N to plants (Pérez-Soba et al., 1994; Lipson and Näsholm, 2001; Murphy et al., 2006; Lockwood et al., 2008; Padgett et al., 2009; Xu et al., 2017). Plants growing in roadside environments have experienced direct long-term exposure to high-concentration N pollutants (e.g., NO$_x$ and NH$_3$ with the character of local deposition) from vehicle exhaust. This exposure causes negative effects in plant growth rates, phenology, leaf senescence rates, and flower development (Bignal et al., 2007; Ashenden, 2009; Lee and Power, 2013). There is increasing evidence that the two primary N pollutant forms, the NH$_x$ and NO$_x$ forms, have distinct N isotopic compositions (Table 1 and Table S1), allowing for the identification of the input sources that contribute to plant, soil and atmosphere reactive N. Thus, with the help of isotopic analysis, it can be clearly observed that traffic-derived N pollutants significantly contribute to N nutrition of roadside plants (Table 2). This finding further confirms the above theory about the direct leaf uptake of atmospheric N compounds. Meanwhile, these previous studies (as shown in Table 2) only emphasized the variations in plant tissue N status following continuous exposure to vehicle NO$_x$, while the relative degree of the effect of traffic NO$_x$ sources on plant N nutrition remains unclear, and no investigation has been performed to analyse the environmental effects induced by vehicle NH$_3$ emission. Thus, it is necessary and valuable to identify the influence level of traffic-derived NO$_x$ and NH$_3$, as well as relevant wet NO$_3^-$ and NH$_4^+$ (precipitation) depositions on plants growing near road. In addition, dust produced by the movement of vehicles is the easiest to migrate to the roadside soil because of its fast deposition velocity. However, little is known about whether the traffic-induced dust impacts the N isotopic compositions of soil from roadside environments.

Here, the soil (divided into three layers), moss, camphor leaf (new, mature and old leaves), camphor bark and tunnel dustfall samples were collected from road environments in Guiyang (South China), and their N isotopic compositions were determined. Our research aim is to evaluate the effect of traffic-related dustfall and atmospheric N pollutants on the N isotopic compositions of soil and vegetation from roadside environments. In recent years, isotopic technology has been widely used in the field of environmental science, enabling quantification of the relative contributions of different N sources to road dust and plant N based on δ^{15}N analyses. Therefore, the fractional contribution of traffic-related atmospheric N pollutants to the bulk N of dustfall and mosses from the roadside was analysed by using a SIAR model (Stable Isotope Analysis in R), and the isotopic compositions of the deposited N originating from the vehicle exhaust was estimated based on the two-member mixing model, providing an indication of which traffic-related N pollutants severely disrupted the N isotopic signal of soil and vegetation from road environment. Altogether, the results will be integrated to assist in understanding how traffic-related dustfall and atmospheric N pollutants impact the δ^{15}N values of soils and plants from roadside environments. We expect that management measures toward reducing the adverse effects of traffic emissions can be formulated more reasonably and effectively in the future based on our study.

2. Materials and methods

2.1. Study sites and sample collection

The tunnel that was used to collect samples was located at North Second Ring Road (urban area) in Guiyang City (South China) (26°39′ 9″N, 106°42′ 50″E, 1351 m above sea level), corresponding to a traffic flow of more than 12,000 vehicles per day in 2015 (Xu and Xiao, 2017). All sampling sites are shown in Fig. S1. Sampling was continuously conducted from 2 May 2016 to 29 July 2016. During this period, the SSW and S wind directions were dominant, corresponding to a mean temperature and relative humidity of 22.0 °C and 78.5%, respectively (Fig. S2). The camphor tree (*Cinnamomum Camphora*), as the most important greening species, is widely distributed in Guiyang City. Thus, 3–5 g of new leaves (current-year verdant leaves at the shoot apex), mature leaves (current-year leaves) and old leaves (previous-year non-verdant leaves beneath the mature leaves) was sampled from the outer branches from approximately 5 m above the ground in the south, east, north, and west directions. Then, 2–4 g of approximately 2 mm thick bark was scraped off from the trunk at a height of 1.5 m above the ground using a drawknife. For each set of samples, the samples from four randomly chosen trees (approximately 6 m in height) were merged into 1–2 representatives. After harvesting the leaf and bark samples, soil samples was respectively removed from the root zone at the depths of 0–3 cm (topsoil), 3–15 cm and 15–25 cm. Considering that moss is an excellent bio-monitor of atmospheric pollution, moss samples (*Haplocladium microphyllum*) were also collected from the stone wall near the road (P1) or from bare rocks without coverage. At site P1 (less than 0.8 m from the edge of the road), only mature camphor leaf ($n = 61$) and bark ($n = 45$) samples were collected every two days; the number of representative new leaf, old leaf, moss, and each type of soil sample from six different samplings (2 May, 24 May, 6 June, 16 June, 10 July, and 29 July) were 12, 12, 24 (4 moss samples were collected at every turn) and 9, respectively. Because the plant samples were not available at site P2 (25 m from the edge of the road), only soil samples ($n = 4$ for each type of soil) were collected. Moreover, 9–12 representatives were collected for moss, each type of soil, bark, new leaf, mature leaf and old leaf samples at site P3 (800 m from the road), respectively. Along with the collection of plant and soil

Table 1
N isotopic compositions (mean ± SD or minimum value to maximum value) of potential N sources in the atmosphere.

Sources	N species	$\delta^{15}N$ (‰)	References
Vehicle exhausts	NO_2	+15.0 ± 1.6	Felix and Elliott (2014)
Vehicle exhausts	HNO_3	+5.7 ± 2.8	Felix and Elliott (2014)
Vehicle exhausts	NO_2	+5.7 ± 2.8	Ammann et al. (1999)
Vehicle exhausts	NO_2	+8.6 ± 1.2	Kim et al. (2014)
Vehicle exhausts (diesel engines)	NOx	+3.9 to +5.4	Widory (2007)
Vehicle exhausts	NO_2	+1 ± 3.5	Redling et al. (2013)
Vehicle exhausts	NO	+3.1 ± 5.4	Ammann et al. (1999)
Vehicle exhausts (warm engines)[a]	NO_x	+2.6 ± nd	Walters et al. (2015)
Coal combustion	NO_x	+6.0 to +13.0	Heaton (1990)
Coal combustion	NO_x	+19.8 ± 5.2	Felix et al. (2012)
Biomass burning	NO_x	+12.5 ± 3.1	Hastings et al. (2009); Felix et al. (2012)
Microbial N cycle	NO_2	−30.8 to −26.5	Felix and Elliott (2014)
Microbial N cycle	NO_x	−49 to −20	Li and Wang (2008)
Sewage and wastes	NH_x	−15 to −4	Freyer (1978), Heaton (1986, 1987)
Vehicle exhausts	NH_3	−3.4 ± 1.7	Felix et al. (2013)
Vehicle exhausts	NH_3	−5.0 to +0.4	Smirnoff et al. (2012)
Biomass burning	NH_3	+12.0 ± nd	Kawashima and Kurahashi (2011)
Coal combustion	NH_3	−8.9 ± 4.1	Freyer (1991); Felix et al. (2013)
Fertilizer use	NH_3	−26.8 ± 15.4	Felix et al. (2013, 2014)
Soil emissions	NH_3	−5.8 to −3.3	Freyer (1978)

nd: no data.
[a] Vehicles have run longer than 2 min prior to sampling.

Table 2
N isotopic compositions (mean ± SD or minimum value to maximum value) of plant leaves collected along a distance gradient from the roadside.

Plant species	Distance from the road (m)	Leaf $\delta^{15}N$ (‰)	References
Norway spruce needles (current year)	5	+1.3 ± 0.7	Ammann et al. (1999)
	980	−4.5 ± 0.3	Ammann et al. (1999)
Mixed moss species	10–20	+3.7 ± nd	Pearson et al. (2000)
	>100	−6.9 ± nd	Pearson et al. (2000)
Norway spruce needle (current year)	20	+1.3 ± 0.4	Saurer et al. (2004)
	1000	−4.4 ± 0.4	Saurer et al. (2004)
Norway spruce tree rings (1993–1995)	20	−0.4 ± 1.6	Saurer et al. (2004)
	1000	−3.2 ± 0.7	Saurer et al. (2004)
Picea abies needles (2-year-old)	50	−2.6 ± 0.8	Guerrieri et al. (2009)
	400	−5.3 ± 0.3	Guerrieri et al. (2009)
Picea abies tree rings (1997–2003)	50	−0.1 ± nd	Guerrieri et al. (2009)
	400	−4.1 ± nd	Guerrieri et al. (2009)
Mature camphor leaves (current year)	10	+0.1 ± 0.1	Xiao et al. (2011)
	160	−3.2 ± 0.1	Xiao et al. (2011)
Bentgrass (C-3 pathway)	30	+1.3 to +2.8	Redling et al. (2013)
	460	+0.1 to −0.7	Redling et al. (2013)
Switchgrass (C-4 pathway)	30	+0.8 to +2.2	Redling et al. (2013)
	460	+0.4 to −0.8	Redling et al. (2013)
Masson pine needles (current year)	4	+5.4 ± 0.3	Xu and Xiao (2017)
	800	−3.0 ± 0.2	Xu and Xiao (2017)
Mosses	4	+4.9 ± 0.4	Xu and Xiao (2017)
	800	−5.2 ± 0.4	Xu and Xiao (2017)

nd: no data.

samples, 4 sites were selected for dustfall sampling in nearby tunnels (Fig. S1). Nine different samplings were performed from 2 May 2016 to 29 July 2016 using containers with upper and side (road oriented) openings. Additionally, 8 dust samples were collected from near the road with a very small amount of traffic using a vacuum cleaner (8 different samplings from 2 May 2016 to 29 July 2016), which served as control samples. All sampling was conducted when there was no rain. A chilled box was used to preserve samples.

The samples were subsequently transported to the laboratory. After the samples were cleaned, they were immediately freeze-dried. Soil samples experienced the removal of litters and roots were dried for 24 h at 80 °C. These samples were finally pulverized to homogenize them using a grinding mill. The road dustfall samples were also freeze-dried and sieved through a 75 μm sieve to remove the large particles. All powder samples were preserved in a desiccator before analysis.

2.2. Analytical procedures of the samples

The N concentrations (%; dry weight) and $\delta^{15}N$ values of the samples were measured respectively using a Vario MACRO cube elemental analyser (Elementar, Frankfurt, Germany) and an element analysis-isotope ratio mass spectrometry (EA/IRMS) system (Thermo Scientific, Bremen, Germany), as in our previous study (Xu et al., 2018). The analytical precision was 0.02% (SD, n = 3) and 0.1‰ (SD, n = 3), respectively.

After determining the N concentrations and $\delta^{15}N$ values of the dustfall samples, every 4 samples (equal proportions) from the 4 sites of dustfall collection were combined into one sample for analysing water-soluble NO_3^- and NH_4^+ concentrations. Ultrasound extraction of the water-soluble ions in the dustfall samples was performed using ultrapure water (Milli-Q system) as the extractor. The extracts were then filtered through a 0.22 μm filter membrane. The water-soluble NO_3^- concentrations in the dustfall samples were

analysed by an ICS-90 ion chromatography system (Dionex, California, USA) with a relative standard deviation of 1.16% for NO_3^- standard samples. The detection limit of the NO_3^- concentration was $0.08\ mg\ L^{-1}$. In addition, NO_2^- concentrations in the dustfall samples were less than 2% of the NO_3^- concentrations; thus, the contribution of NO_2^- to NO_x^- was neglected. After treating the filtrate with Nessler's reagent, the NH_4^+ concentrations were determined using spectrophotometry with a detection limit of $0.1\ mg\ L^{-1}$. A relative standard deviation of less than 5.0% was determined for NH_4^+ standard samples. Each reported data in this study represents the average of at least two measurements of each sample.

2.3. Statistical analyses

The proportional contributions of the major N sources to dustfall and moss bulk N were estimated using a SIAR model. A detailed description of the methodology of the SIAR model is shown in the supporting information (SI). The Origin 9.0 software package (OriginLab Corporation, Massachusetts, USA) was used to perform regression analysis, so that the relationships between the response and the explanatory variables could be established; additionally, all graphs were plotted using this software. SPSS 19.0 program (SPSS Inc., Chicago, USA) was employed to statistically compare the differences in the N chemistry between the sample groups using both a two-tail Student's t-test and one-way ANOVA (with a Tukey-HSD test). A significant difference is accepted when the P value is less than 0.05.

3. Results and discussion

3.1. Dominant sources of N in the road dustfall from a tunnel

The $\delta^{15}N$ values of the dustfall samples ranged from +5.3‰ to +11.6‰, and the recorded average of +7.7 ± 1.5‰ (Fig. 1) was close to that of the dust samples (+6.8‰) from busy roads in London (Pearson et al., 2000). The average $\delta^{15}N$ value of the dust samples from the control site was +5.2 ± 1.0‰ (varied between +4.2‰ and +7.2‰), which was significantly lower than that of tunnel dustfall ($P < 0.05$). Because the road dustfall samples being collected in a tunnel, the dominant sources of the bulk N were relatively limited. A negligible contribution were assumed from NO_x or NH_3 emissions induced by the microbial N cycle, biomass burning, coal combustion, waste water, animal waste and fertilizer application to dustfall bulk N; moreover, we did not consider the impact of organic N on total dustfall N based on the limited organic N sources in the tunnel caused that organic N accounted for a relatively small proportion of total N in dustfall (an average of 3.4% was similar to the reports about organic N proportion in aerosol samples (only 3.0%) from Jeju Island in Korea (Kundu et al., 2010; Park et al., 2018)). In contrast, N from dust, NO_x from vehicle exhausts and NH_3 from vehicle exhausts can be assigned as the three main sources of dustfall bulk N. The $\delta^{15}N$ values of major gaseous N emissions from different sources are compiled in Table 1. Considering that surface soil is the most important component of dust, the $\delta^{15}N$ values of the soils in the Guiyang area (+4.2 ± 1.8‰ (Xu et al., 2018)) were regarded as the $\delta^{15}N$ values from dust N in this study, which is close to an average of +4.3‰ in northern China (Wang et al., 2014).

Many previous studies have reported the isotopic effect related to the formations of NH_4^+ and NO_2 in the aerosol, revealing that large ^{15}N enrichment in residual NH_4^+ and NO_2 would occur in the NH_3 (gas) $\leftrightarrow$ NH_4^+ (particulate) equilibrium and $NO–NO_2$ cycle, respectively (Freyer et al., 1993; Heaton et al., 1997). In fact, the isotopic effect between NO_x (gas) and NO_3^- (particulate) remains unclear. However, Walters et al. (2016) reported that the isotopic
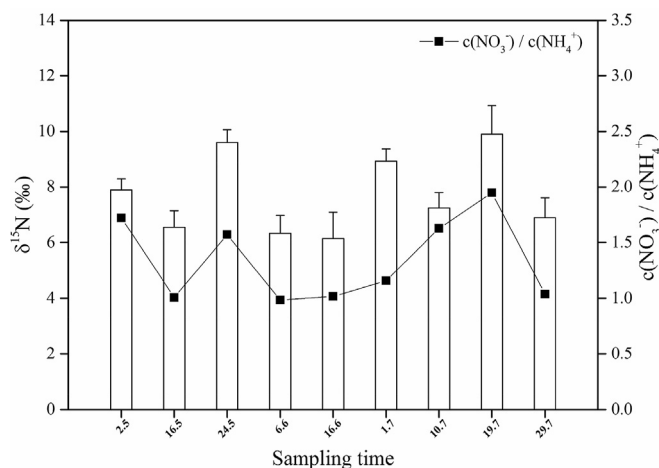

Fig. 1. The $\delta^{15}N$ values and mole ratios of NO_3^- to NH_4^+ in road dustfall collected from a tunnel. The vertical lines represent the standard deviations.

effect between NO and NO_2 was not significant when the atmospheric NO_x concentration was lower than the atmospheric O_3 concentration. In that case, $\delta^{15}N–NO_3^-$ may represent the $\delta^{15}N$ values of NO_x sources following the continuous formation of NO_2 from NO without being photolysed back to NO (Walters et al., 2016; Park et al., 2018). The mean atmospheric O_3 concentration (8 h) in the study area was significantly greater than the mean atmospheric NO_2 concentration (Table S2); moreover, a strong correlation ($P < 0.001$) between the concentrations of O_3 and NO_2 was found during this period (Fig. S3). Thus, the isotopic compositions of NO_x sources may directly reflect the $\delta^{15}N–NO_3^-$ patterns in dustfall. A similar inference has also been made for the amalgamation of atmospheric NO_x into $PM_{2.5}$ (Park et al., 2018). On the other hand, the average molar ratios of NO_3^- to NH_4^+ in the dustfall samples varied between 1.0 and 1.9 (mean = 1.3 ± 0.4) (Fig. 1), reflecting that inorganic N in dustfall was dominated by NO_3^-. The result suggested that a full fixation of NH_3 by acidic gases (e.g., NO_2 and SO_2) could occur to form relatively stable ammonium salts in dustfall. The fact that NH_4^+ in particulate had no significant ^{15}N enrichment when there was limited opportunity for NH_3 loss has been found, which indicated a similarity of particulate $\delta^{15}N–NH_4^+$ values to the $\delta^{15}N–NH_3$ values in emission sources (Kawashima and Kurahashi, 2011). Wang et al. (2017) also reported that a negligible difference in $\delta^{15}N$ values between NH_3 sources and $PM_{2.5}$ NH_4^+ can be expected following a relatively complete neutralization of NH_3 in $PM_{2.5}$ by acidic compounds (e.g., HNO_3 and H_2SO_4). The above explanations indicated that the mixture of N sources directly controlled the bulk $\delta^{15}N$ values in dustfall samples, but no obvious isotopic fractionations occurred. This assumption can also be proven from another perspective.

In our study, water-soluble inorganic N (NH_4^+ and NO_3^-) concentrations in the dust from the control site were only half of the tunnel dustfall water-soluble inorganic N concentrations (their inorganic N concentration ration averaged 0.5). Accordingly, if the remaining NH_4^+ and NO_3^- in the tunnel dustfall were originated from traffic-emitted N pollutants (NH_3 and NO_x) that have been experienced the transformation processes mentioned above, the expected dustfall $\delta^{15}N$ value would be at least more than +17‰ based on the least isotopic fractionation of +33‰ for NH_3 transformation processes and +34‰ for the $NO–NO_2$ cycle (Freyer et al., 1993; Heaton et al., 1997; Pan et al., 2016; Liu et al., 2017), as well as the $\delta^{15}N$ values of known N sources (Table 1). This result seems to be largely inconsistent with the actual dustfall $\delta^{15}N$ values of +7.7‰. The contribution of organic N to total dustfall N was

ignored because organic N only represented a relatively small percentage of total dustfall N, as mentioned above. Therefore, it was speculated that the difference in the $\delta^{15}N$ values between N emission sources and dustfall N that was contributed by them was relatively small. A recent analysis on the source appointment of precipitation NO_3^- and NH_4^+ by Liu et al. (2017) in the Guiyang area further revealed that the N isotopic effect could be deemed negligible in both the NH_3 (*gas*) ↔ NH_4^+ (*precipitation*) equilibrium and the NO_2 (*gas*)→NO_3^- (*precipitation*) process. Similarly, the assumption mentioned above was also presented by Baker et al. (2007), Elliott et al. (2009) and Morin et al. (2009). As is well known, although NO can be heavily emitted by combustion processes in vehicles, itself has a minor proportion of contributions to the N deposition based on its high chemical reactivity in the photochemical equilibrium with O_3. Meanwhile, much of the NO_2, as the precursor of NO_3^- in the atmosphere, is rapidly produced (Cape et al., 2004; Walters et al., 2016). The $\delta^{15}N-NO_3^-$ values in dustfall may thus exhibit the patterns of $\delta^{15}N-NO_2$ more than those of $\delta^{15}N-NO$, such that the $\delta^{15}N-NO_2$ values are assumed to represent the corresponding $\delta^{15}N$ values of NO_x emitted from pollutant sources. Based on the above discussion, it is possible to conclude that the isotopic compositions of dustfall bulk N in the study area were primarily controlled by the mixing of N sources (e.g., NO_2 and NH_3) with a relatively small isotopic fractionation in the processes of being adsorbed by particles.

The "IsoSources" isotopic mixing model has been applied to analyse the source attribution of NH_3 in aerosols (Pan et al., 2016). In contrast, since the $\delta^{15}N$ value and N concentration variations of N sources and samples (mean ± SD) can be incorporated into the SIAR model based on the Bayesian framework, this model provides a possibility of the relatively accurate estimation for proportional contributions of each source to the mixture (more details can be found in the SI). According to the isotopic compositions of dominant N sources (Table 1), the above model was used to calculate the contributions of traffic-derived NH_3 (−3.4 ± 1.7‰), traffic-derived NO_2 (+10.0 ± 4.7‰), and soil N (+4.2 ± 1.8‰) to dustfall bulk N. In particular, the $\delta^{15}N-NO_x$ data from Widory (2007), Redling et al. (2013) and Walters et al. (2015) were not used in considering the relatively higher dustfall $\delta^{15}N$ values and the dominance of gasoline-powered vehicles for urban traffic (Sun et al., 2017). The modelling results are shown in Fig. 2 and Fig. S4, revealing that NO_2 from traffic exhaust, NH_3 from traffic exhaust, and N from soil accounted for 52.2 ± 10.0%, 8.8 ± 7.1% and 39.0 ± 13.8% in dustfall bulk N, respectively. The contribution of NO_2 to dustfall N was much higher than that of NH_3, which appeared explainable by the following reasons: 1) vehicles are a more significant NO_2 source than NH_3 emissions, causing the atmospheric concentration of NH_3 to be significantly smaller than those of NO_2 and NO (Cape et al.,

2004), and 2) the rate of transfer from the atmosphere for NH_3 is quite fast because of its high chemical reactivity and low molecular weight, with a transfer rate of $1-10\ cm\ s^{-1}$; by comparison, the transfer rates for NO are $1-2\ mm\ s^{-1}$ and for NO_2 are $3-20\ mm\ s^{-1}$ (Hanson and Lindberg, 1991; Sutton et al., 1993; Harrison et al., 1996). The N from soil also showed a relatively high contribution to dustfall N (average of 39.0%). This estimate is in line with the fact that the N from water-soluble NH_4^+ and NO_3^- in dustfall was double the amount of N from water-soluble NH_4^+ and NO_3^- in dust from near the control site as mentioned above.

3.2. Characteristics of soil $\delta^{15}N$

To investigate the effects of traffic-related dustfall and N pollutants on the surrounding environment, the N isotopic compositions of different types of soil (topsoil, $3-15\ cm$ and $15-25\ cm$ layers) were analysed. The $\delta^{15}N$ values of these samples increased along soil depths, with values ranging from −0.3‰ to +4.8‰, +2.2‰ to +6.3‰, and +3.1‰ to +8.6‰, respectively. The average $\delta^{15}N$ values of the soil samples from different sites are presented in Fig. 3a. The soil $\delta^{15}N$ values changed substantially within and across sites. For the near site and mid-site samples, the soil $\delta^{15}N$ values showed a significant increase with soil depth ($P < 0.05$), whereas the increased trend of soil $\delta^{15}N$ values became insignificant from depths of $3-15\ cm$ to $15-25\ cm$ at the far site ($P > 0.05$). Comparing soil samples from the same layer, the soil $\delta^{15}N$ values at more near sites were notably higher than those at more remote sites, with one exception: the soil $\delta^{15}N$ values in the $3-15\ cm$ depth at the mid-site and far site were similar ($P > 0.05$). Across all the sampling sites, the $\delta^{15}N$ differences between the $15-25\ cm$ and $3-15\ cm$ depth layers were much smaller than those between the $3-15\ cm$ depth layers and the topmost layers.

The isotopic compositions of residual organic N are expected to increase following its degradation since mineralization discriminates against ^{15}N (Högberg, 1990; Gebauer et al., 1994), which exacerbates the higher $\delta^{15}N$ values in relatively deep soils (Ammann et al., 1999). This pattern was also confirmed by many other studies (Gebauer and Schulze, 1991; Guerrieri et al., 2009; Kuang et al., 2011). A similar mechanism may also be responsible for the presence of the increased $\delta^{15}N$ trend associated with increased soil depths in this study. The topsoil (mainly organic matter) in temperate forests usually had negative $\delta^{15}N$ values, ranging from −5% to −2% (Gebauer and Dietrich, 1993; Sutherland et al., 1993; Gebauer et al., 1994; Buchmann et al., 1995). It seems to be attributable to less N loss rates (nitrification and major N loss pathways, including denitrification, nitrate leaching and ammonia volatilization, can drive long-term ^{15}N enrichment in the remaining soil N) and low N_2-fixing capacity in forest soils (Högberg, 1990;
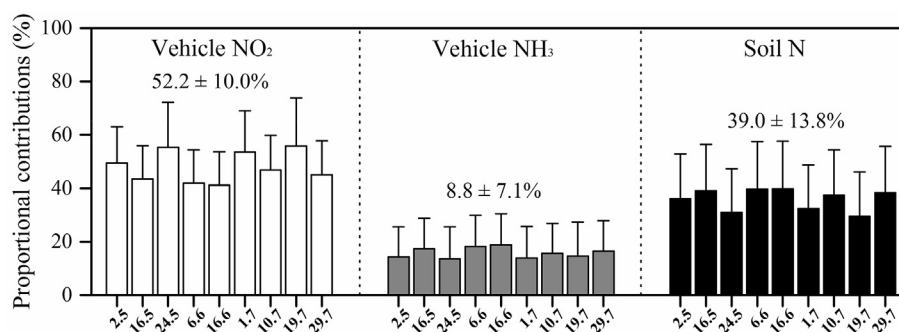

Fig. 2. Proportional contributions (%) of dominant N sources to bulk N in dustfall near the roadside from 2 May 2016 to 29 July 2016. The values above the bars represent the average results of the proportional contributions estimated by the SIAR model for nine different samplings. The vertical lines represent the standard deviations.
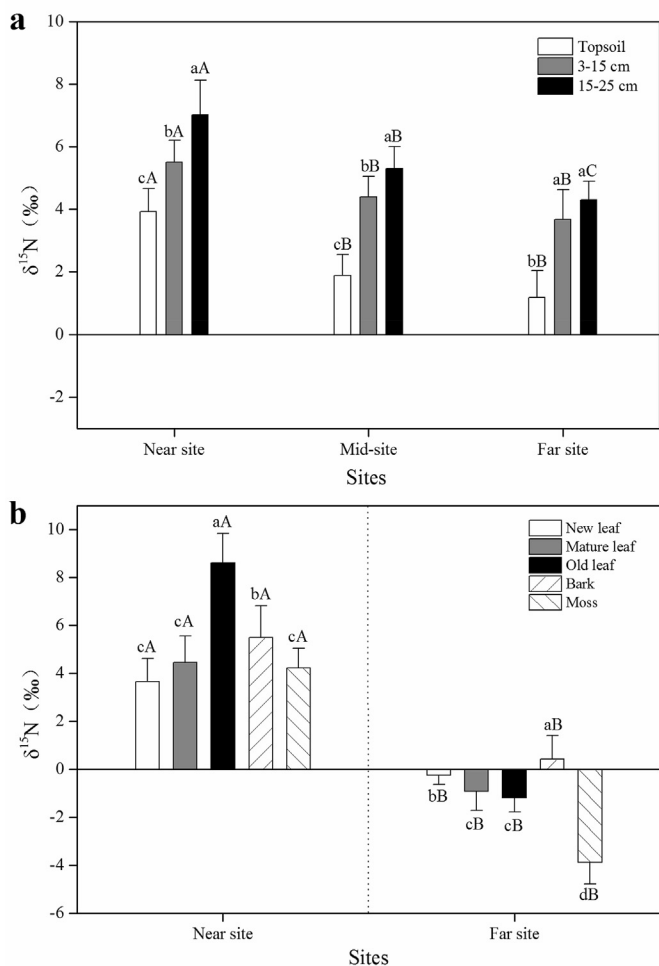
Fig. 3. Variations in $\delta^{15}N$ values of soil (a) and plant (b) samples from field sites with different distance from the roadside. Significant space differences in the same type of samples were marked with uppercase letters, while within the same site, the significant differences among different types of samples were marked with lowercase letters ($P < 0.05$). The vertical lines represent the standard deviations.

(Ammann et al., 1999), which may be attributed to a strong barrier function of the forest canopy (Saurer et al., 2004). Alternatively, decaying fallen leaves can provide the major supply of organic N into soils; however, the timely and continuous cleaning of fallen leaves in urban road environments (plants are directly adjacent to the road without canopy barrier) interrupted the above pathway. For sites relatively far from the roadside (mid-site and far site), the $\delta^{15}N$ values in the organic layer of soil was significantly lower than at the roadside; moreover, there were no significant differences in $\delta^{15}N$ in both the 0−3 cm depth soil (topsoil) and the 3−15 cm depth soil (Fig. 3a). Accordingly, inputs of traffic-related dustfall with a high ^{15}N abundance may be the only driving force for the strong $\delta^{15}N$ gradient observed in soil, although it is difficult to verify the direct correlation in soil $\delta^{15}N$ and atmospheric N inputs because of the lack of long-term historical observations on soil $\delta^{15}N$ values, as well as the dry and wet N deposition levels and their isotopic compositions.

3.3. Characteristics of plant tissue $\delta^{15}N$ and its relationship with the soil and atmosphere

The ranges of $\delta^{15}N$ values for mosses, new camphor leaves, mature camphor leaves, old camphor leaves, and camphor bark from the study area were from −5.6‰ to +5.7‰, −1.0‰ to +5.1‰, −2.0‰ to +6.7‰, −2.1‰ to +10.4‰, and −0.9‰ to +8.6‰, respectively. Plant tissue $\delta^{15}N$ patterns clearly exhibited site-specific differences along the distance gradient from the road, with more positive sample $\delta^{15}N$ values in the near site and relatively lower $\delta^{15}N$ values in samples from the far site (Fig. 3b). These findings are identical to many previous reports that showed decreases in plant tissue $\delta^{15}N$ in control sites compared with sites near roads (Table 2). Interestingly, camphor leaf $\delta^{15}N$ values substantially increased with increasing leaf age at the near site, while the age-related camphor leaf $\delta^{15}N$ pattern at the far site had exactly the opposite characteristics to those of the near site. Comparing the $\delta^{15}N$ in plant tissues and soils, the mean differences in plant tissue $\delta^{15}N$ between the near site and far site were much greater than those of the soils (especially for old camphor leaves and mosses) (Fig. S5). It is a pretty sure sign that plants closer to the road were subjected to the serious impacts of vehicle exhaust. Previous studies have revealed that the isotopic fractionation related to root absorption and assimilation of soil N is relatively small under an environment of N limitation, such that plant tissue $\delta^{15}N$ values reflect the isotopic compositions of available soil N (Nadelhoffer and Fry, 1994; Michelsen et al., 1998; Evans, 2001). Obviously, this mechanism is not applicable in this study because of the relatively high N supply in the urban environment. As discussed above, a strong ^{15}N abundance would be recorded in the remaining soil N after experiencing denitrification, nitrification, nitrate leaching and ammonia volatilization. Therefore, the main products (e.g., ammonium and nitrate) from these processes record lower $\delta^{15}N$ values than the original N sources. Under the condition of high N availability, when the abovementioned N products with lower $\delta^{15}N$ values were assimilated into plants by root uptake, the plant tissue $\delta^{15}N$ values were expected to be less than those of the original soil N. Our study showed that new and mature camphor leaves, as well as bark, from the near site record lower average $\delta^{15}N$ values compared to the mineral soil (at 3−25 cm depths) and that the $\delta^{15}N$ values of all plant samples at the far site were lower than those of the soils (Fig. 3). In both forest and urban ecosystems with sufficient N sources, plant tissues have also been found to record lower $\delta^{15}N$ values than soil N (Ammann et al., 1999; Kwak et al., 2009; Kuang et al., 2011). The result further supports the above interpretation, partly revealing that the isotopic effect during plant-soil processes tends to decrease the $\delta^{15}N$ values of original soil N sources.

Handley and Raven, 1992; Högberg et al., 1995). The $\delta^{15}N$ values of the topsoil in our study area were significantly more positive than those of temperate forests. The differences may be caused by multiple factors (e.g., the movement, transformation, and leaching of N, external N inputs, and microbial cycling of N) (Motavalli et al., 1995; Högberg, 1997; Bowden et al., 2004), but the degree of the impact derived from these factors should be the same in this study area, with the exception of the disturbance of traffic-related pollutants. Thus, the soil $\delta^{15}N$ pattern presented in the near site is clearly explainable by traffic-related N pollutants with strong ^{15}N enrichment (as mentioned in the previous section). However, we can first rule out the effect of precipitation N to soil $\delta^{15}N$ values, while traffic-derived NO_x and NH_3 become increasingly important contributors to precipitation N in the Guiyang area (Liu et al., 2017), particularly in road environments. This inference has also been demonstrated in a study by Ammann et al. (1999), where no detectable difference in soil $\delta^{15}N$ within and across sites was found when the potted trees originating from the same soil and seeds (grids were used to prevent leaves from falling into the pots) were exposed to a roadside environment (5 m, 130 m, and 980 m from the highway) for a long time. In a pot experiment, the direct contribution of dry NO_2 and dust deposition associated with traffic exhaust to forest soil $\delta^{15}N$ was also confirmed to be inappreciable

Differently, with one exception, old leaves collected from the near site have higher $\delta^{15}N$ values than the mineral soil layers. Since deposited N can also be an important plant N source via stomata uptake, leaf $\delta^{15}N$ values are growingly impacted by atmospheric N recorded the specific N isotopic compositions with increased exposure times (Gebauer et al., 1994; Xiao et al., 2011). While the original stored N in old leaves was partly transferred to the N demand tissues with their ageing process, the N isotopic effect associated with this process was not significant (Garten, 1993). If a certain proportion of the foliar N demand was continuously gained through the direct leaf uptake of ^{15}N-enriched atmospheric N, the $\delta^{15}N$ values in leaves should increase with increasing leaf age. On the contrary, when plants were exposed to ^{15}N-depleted atmospheric N, the age-related leaf $\delta^{15}N$ trend found at the far site was expected (Fig. 3b). Therefore, the higher $\delta^{15}N$ values in old leaves at the near site were typical of the effect of isotopically heavy N from traffic emissions.

Bark is an excellent passive adsorbent of pollutants from the atmosphere or throughfall, with porous and almost biologically inert surfaces. Such characteristics make it an outstanding bio-indicator (Schulz et al., 1999; Saarela et al., 2005; Suzuki, 2006). It has been documented that bark samples (*Pinus sylvestris* or mixed tree species) from polluted areas with high NH_3 emissions exhibited significantly lower $\delta^{15}N$ values than those from unpolluted areas (Schulz et al., 2001; Boltersdorf et al., 2014). Thus, the strongly decreased bark $\delta^{15}N$ along the increased distance from the road (Fig. 3b and Fig. S5) was clearly the result of spatially variable atmospheric N with different $\delta^{15}N$ values. Upon investigation, it was unexpectedly discovered that only bark samples collected from the far site recorded slightly positive $\delta^{15}N$ values (other plant samples from this site have negative $\delta^{15}N$ values, as shown in Fig. 3b). One

possible explanation for this difference is that the available deposited N for absorption in the underlayer of the canopy is isotopically heavier because the foliar retention of deposited N (mainly throughfall) discriminates against ^{15}N (Heaton et al., 1997).

The above discussion indicates that different N transformations can cause ^{15}N enrichment or depletion of key pathways, as illustrated in Fig. 4. Actually, these complex dynamics did not conclusively impact the responses of plant tissues to traffic-induced atmospheric pollution, which further reflected that the leaves or bark of vascular plants may be robust bio-monitors for atmospheric N pollution. However, doubts might arise when realizing the differences in N isotopic compositions of major pollution sources (Table 1 and Table S1), such as deciphering which source dominates plant tissue N and whether the relative contributions of different N sources to plant N can be quantified based on their $\delta^{15}N$ values. The use of the isotopic mixing model may provide an additional approach to respond to the above doubts.

3.4. Implication for traffic-induced N pollution based on the isotopic mixing model

The two-member mixing model ($\delta^{15}N_{tissues} = \delta^{15}N_a + N_b \times (\delta^{15}N_b - \delta^{15}N_a)/N_{tissues} = \delta^{15}N_a + constant/N_{tissues}$) proposed by Keeling (1958) and Saurer et al. (2004) showed that the N input to plant tissues can be assumed to originate from atmospheric N (N_a) and background N (N_b) (with corresponding $\delta^{15}N$ values of $\delta^{15}N_a$ and $\delta^{15}N_b$, respectively). Therefore, this model was applied to estimate the $\delta^{15}N$ value of deposited N that is available for leaf and bark uptake (although their *r* values are relatively low, the negative linear correlations between them still reveal that plant-available deposited N is ^{15}N-enriched in the current case, as shown in Fig. 5); the
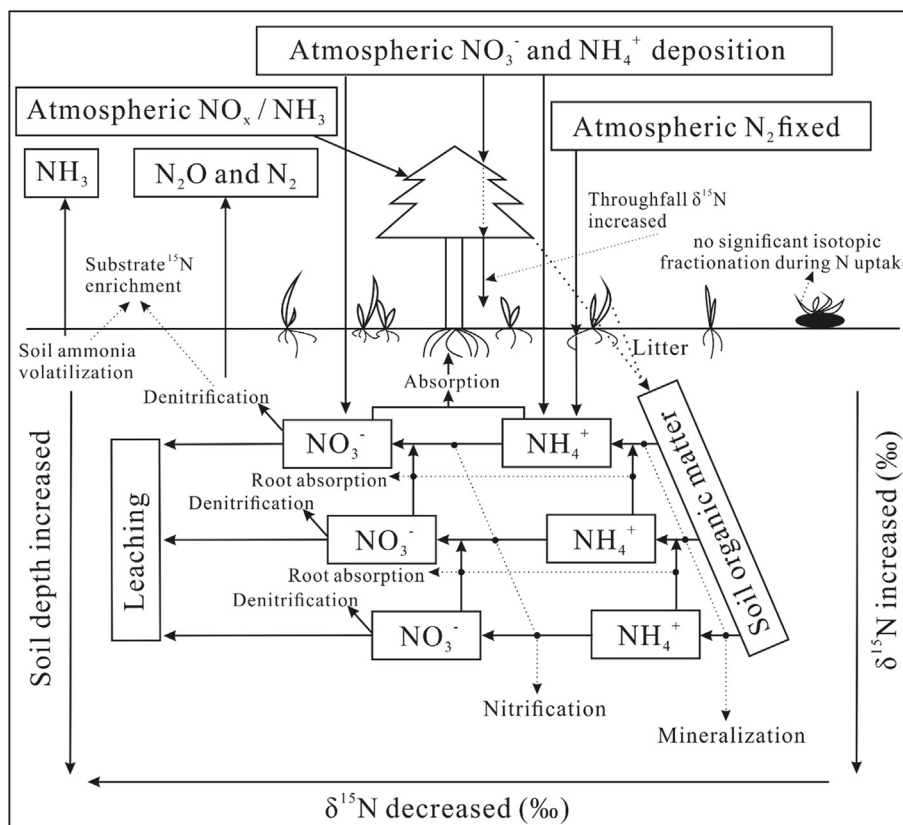

Fig. 4. The model of N isotope variations during atmosphere-plant-soil processes. The figure illustrates that different N transformations can cause ^{15}N enrichment or depletion based on the studies by Högberg (1990), Gebauer et al. (1994), Nadelhoffer and Fry (1994), Heaton et al. (1997) and Ammann et al. (1999).
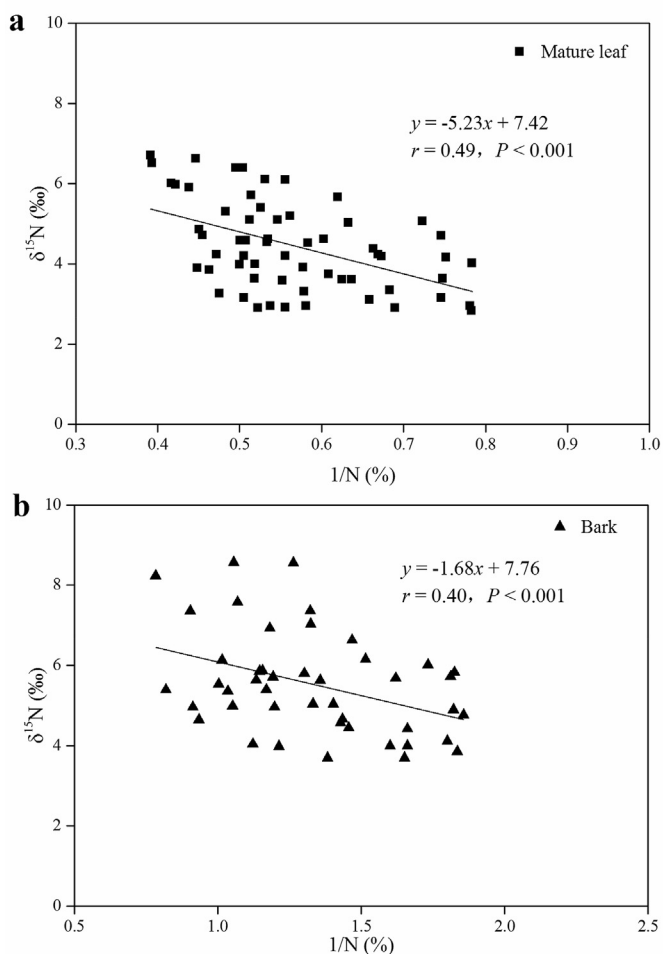
a

b

Fig. 5. The relationship between the inverse of the N concentrations in the mature leaves and bark of camphor and their corresponding $\delta^{15}N$ values for the data from samples collected near the roadside.

estimated $\delta^{15}N_a$ values were 7.4‰ and 7.8‰, respectively. The relatively lower emission proportion and fast deposition velocity of NH_3 in road environments (as discussed earlier) means that NH_3 may have a limited contribution to plant N status; besides, NO_2 with a high level of emission can be used as alternative plant N nutrition (NO, in contrast, is not readily absorbed because of its low water-solubility) (Ammann et al., 1999; Saurer et al., 2004). Accordingly, the calculated results from above model clearly indicated that ^{15}N-enriched dry deposition N (mainly NO_2; Table 1 and Table S1) may have made greater contributions to mature leaf and bark N status than wet deposition N in sites near the road. This finding also supports the theory that the net canopy exchange of N was largely controlled by the foliar uptake of dry deposition N although N provided by both dry and wet deposition can be incorporated into leaves (Lindberg et al., 1986; Garten et al., 1998). However, Saurer et al. (2004) also mentioned that the two-member mixing model could not efficiently explain the variability of data observed at unpolluted or slightly polluted sites, and the authors suggested that this could be caused by the variations in the relative importance of different N sources. Across the sites, it was observed that variation amplitudes of plant tissue $\delta^{15}N$ values between the near site (heavy pollution) and far site (relatively light pollution) were much greater than those of plant tissue N concentrations (data not shown). Similar phenomena were also found in many other studies (Kuang et al., 2011; Boltersdorf et al., 2014; Xu and Xiao, 2017; Xu et al., 2018). Thus, a

more specific explanation is that plant tissue $\delta^{15}N$ values are more sensitive to varying atmospheric N sources than tissue N concentrations, so that plant tissue $\delta^{15}N$ variations cannot be explained by their N concentration variations from polluted sites to lightly polluted sites.

Although mosses, depending on atmospheric inputs as their main N sources, have been widely used in the bio-monitoring of atmospheric N deposition (Xiao et al., 2010; Harmens et al., 2011; Boltersdorf et al., 2014), researchers have only emphasized the relationship between moss N concentrations and wet N deposition because the impact of dry N deposition on moss N may not be dominant in a large geographic region compared to that of wet N deposition. In contrast, in urban road environments, dry N deposition originating from vehicle exhaust has a significant contribution to the N status of the surrounding environments (Bell et al., 2011; Redling et al., 2013; Sun et al., 2017). However, little is known about the actual contribution of dry deposition to moss N. Additionally, during the whole growing period of mosses, their $\delta^{15}N$ values were primarily determined by the $\delta^{15}N$ values of the available N sources without a significant isotopic effect (Bragazza et al., 2005; Zechmeister et al., 2008; Felix et al., 2016; Dong et al., 2017). Thus, we used the SIAR model to evaluate the proportional contributions of different N sources to N in mosses near the roadside. In our case, the estimated mixtures mainly exhibited combinations of the $\delta^{15}N$ values in the four most potential contributors to the N of mosses in the road environments: traffic-derived NO_2, traffic-derived NH_3, precipitation NO_3^-, and precipitation NH_4^+, with average $\delta^{15}N$ values of $+10.0 \pm 4.7$‰, -3.4 ± 1.7‰, -1.9 ± 3‰ and -10.6 ± 7.7‰, respectively (based on the comprehensive inventory of N source $\delta^{15}N$ in Table 1 and Table S1). Water-soluble organic N was also not considered because it was mainly originated from biomass and coal combustions, agricultural activities, and the long-range transport of marine aerosols (Cornell et al., 1995; Neff et al., 2002; Cape et al., 2011). Clearly, these sources are not dominant in this particular study site. While vehicle exhausts are also the important primary sources of organic aerosols, they are primarily characterized by water insolubility (e.g., PAH without N atom) (Rogge et al., 1993; Khalili et al., 1995; Cape et al., 2011).

The results of the source attribution are showed in Fig. 6 and Fig. S6 after applying the SIAR model, which indicated that 68.6% and 31.4% of N in moss near the roadside can be attributed to dry N deposition and wet N deposition, respectively. For dry N deposition, traffic-derived NO_2 has the greatest contribution (48.2 ± 8.0%). Similar contributions were found between traffic-derived NH_3 (20.4 ± 12.5%) and precipitation NO_3^- (23.4 ± 13.6%). However, some researchers have suggested that mosses have a preference for NH_x-N utilization over NO_x-N uptake (Cape et al., 2009; Wiedermann et al., 2009; Fritz et al., 2014; Varela et al., 2016; Dong et al., 2017); moreover, they emphasized the dominance of wet N deposition in moss N. The main factors that caused the difference in this study may include that 1) NH_4^+ from wet deposition was the main N form of N deposition in their studies; 2) atmospheric NH_3 from vehicle exhausts has a fast transfer rate and relatively low emissions compared with NO_x (as discussed in section 3.1) and 3) a high relative humidity (average of 78.5%) in the study area favored the liquefaction of NH_3, promoting the rapid equilibration of NH_3 with particles (the NH_3 concentration then decreased) (Pan et al., 2016). Accordingly, it is concluded that a relatively high proportion of the N uptake of mosses was obtained from the gaseous N rather than from the wet deposition of N when the supply of ambient N compounds (mainly gas form) is high (e.g., in urban road environments). A similar deduction was also reported by Pearson et al. (2000).

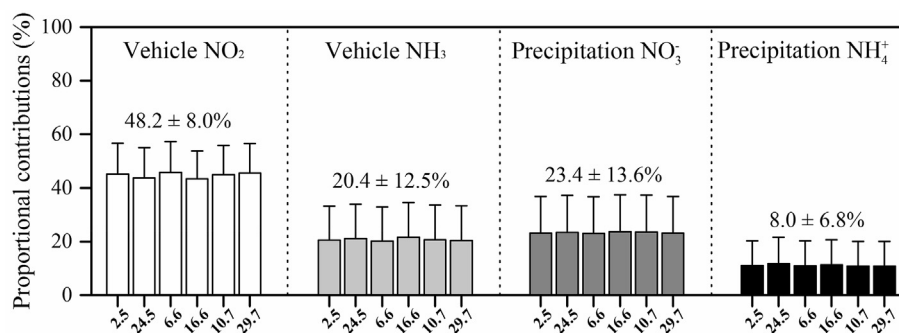The atmospheric diffusion of pollutants strongly reduced the

Fig. 6. Proportional contributions (%) of dominant N sources to bulk N in mosses near the roadside from 2 May 2016 to 29 July 2016. The values above the bars represent the average results of the proportional contributions estimated by the SIAR model for six different samplings. The vertical lines represent the standard deviations.

concentrations of atmospheric N pollutants, particularly in this study area where the forest canopy barrier always exists; under these conditions, more distant sites would be much less influenced by the ^{15}N-enriched NO_x-N, implying that tissue $\delta^{15}N$ values at these sites may reflect the integrated influence of isotopically heavy and light N depositions. Cape et al. (2004) also reported that the rate of decrease in traffic-derived N pollutant concentrations was fairly rapid, with NH_3 and NO_2 concentrations falling by 90% within 10 m and 15 m from the edges of the roads, respectively. According to the $\delta^{15}N$ patterns in plant samples collected from the far site (Fig. 3b) and the N isotopic compositions of potential N sources (Table 1 and Table S1), it can be inferred that ^{15}N-depleted NH_x-N from soil emissions or precipitation may significantly contribute to the N nutrition of plants at these sites.

4. Conclusions

Based on the isotopic mixing model applied to soil and plant samples collected from the roadside, it was found that traffic-related NO_x, but not NH_3, seriously affected N isotopic compositions in soils and plant tissues near the roadside, which indicated that traffic-derived NO_2 input is an important factor influencing the health of urban road ecosystems. However, N deposition fluxes near roads are still not captured or considered by the current monitoring networks of N deposition at regional or even national scales. These results highlighted the urgent demand for the exact evaluation of total atmospheric N deposition levels and for finding more accurate N budgets. The unambiguous characterization of N deposition reaching the road level should be achieved so that effective management strategies can be proposed to reduce the negative effects of traffic N emissions.

At the same time, more attention needs to be paid to the fact that source $\delta^{15}N$ related to the emission conditions may have temporal and spatial variations, although the analyses of dustfall and moss $\delta^{15}N$ with the help of the SIAR model and source $\delta^{15}N$ data offer a quantitative solution for source appointment of N in these samples. Furthermore, well limited parameters can be applied to correct the value of the target compound $\delta^{15}N$ that underwent isotopic fractionation. In order to minimize the uncertainty in the estimation of fractional contributions of different sources in the mixture, the end-member $\delta^{15}N$ patterns and *in situ* fractionation mechanisms must be further investigated in future field and laboratory studies.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.03.074.

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