

Detailed response to the reviewers' comments

Atmospheric Chemistry and Physics (Paper egusphere-2024-1621)

Title: "Technical note: Refining $\delta^{15}\text{N}$ isotopic fingerprints of local NO_x for accurate source identification of nitrate in $\text{PM}_{2.5}$ "

Dear Editor(s) and reviewers,

We would like to express our gratitude for your valuable comments and suggestions. The manuscript has been carefully revised according to the comments.

Response to the editor(s)' comments and detailed point-by-point responses to the reviewers' comments are provided in the following pages. Please note that the comments are presented in *italics font*, and our responses are in Roman font and marked in blue. In addition, all the line numbers in the responses refer to the revised manuscript. All changes made to the manuscript are marked in red.

Please let us know if you have any further questions regarding our manuscript.

We are looking forward to your reply.

Sincerely,

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Reviewer #1:

The authors present a manuscript detailing various stable nitrogen isotope ratio measurements of major nitrogen oxide (NO_x) sources and use these values for particulate nitrate source apportionment during a typically heavily polluted period in Tianjin, China. This manuscript provides an impressive wealth of new $\delta^{15}N(NO_x)$ emission source measurements. Specifically, they have quantified $\delta^{15}N(NO_x)$ values for previously unmeasured NO_x sources, such as industrial emissions, and have made measurements representative of emissions in China, contrasting with most literature values which are predominantly for the US, potentially influencing the results due to different combustion and emission control technologies. They have also employed appropriate measurement techniques (Fibiger et al., 2014), crucial since some previous $\delta^{15}N(NO_x)$ measurements utilized a wide range of NO_x collection techniques that may not all be suitable for $\delta^{15}N(NO_x)$ source characterization. I strongly support their initiative to enhance the $\delta^{15}N$ values of NO_x sources.

However, I have major reservations about this work, including its presentation and application for particulate nitrate source apportionment. There appears to be significant confusion in their literature review and citations, which require substantial editing. I have tried to point out some areas that need to be refined, though I suspect that there might be others as well. While the authors are commended for attempting to correct for isotope fractionation, I believe there are issues with their approach. They should have reported the $\delta^{18}O(NO_3^-)$ data and calculated fractionations necessary for accurate source apportionment. This approach to isotope fractionation correction is described in the supplement, but the actual $\delta^{18}O(NO_3^-)$ data is not included, shown, or discussed in the present work. Additionally, it is unclear whether the mixing model results are valid or contribute any meaningful insight into NO_x emission source apportionment. The model is significantly under-constrained (4-5 parameters for one variable), making the output nonsensical. In conclusion, I believe this paper has the potential to be publishable after significant revisions and would recommend resubmission.

Response: We would like to express our sincerest gratitude for your invaluable feedback, which has been instrumental in enhancing the quality of our manuscript. We have endeavored to optimize the manuscript and have incorporated the requisite changes, highlighted in red in the revised paper, which will not impact the content or framework of the paper. We hope that these amendments will meet with your approval. Firstly, we have revised both the literature review and inappropriate citations, including but not limited to errors noted by the reviewers. Second, we have added a discussion of the data on $\delta^{18}O-NO_3^-$ to the revised manuscript. In addition, we refer to previous studies and add a description of the isotopic fractionation calculation process, which have been widely used in similar studies. Finally, we also refine the discussions in validity of the quantitative results of the model as well and add additional evidence. It is acknowledged that the present study is not without shortcomings, including the fractionation calculations of isotopes and the constraints of the model. However, every effort has been made to improve these aspects in the revised manuscript. Furthermore, more in-depth studies will be conducted in the future to address these shortcomings. We also summaries these deficiencies in section 3.5 Limitations and outlook

of the manuscript. We would like to reiterate our appreciation for your comments and suggestions. Below, we will provide detailed one-on-one revisions and responses to deficiencies in the original manuscript.

Major Comments:

Question 1: Lines 64-67: Double-check these references. Felix and Elliott, 2014 used a passive sampler and collected NO_2 only (not total NO_x). Walters et al., 2018 report ambient $\delta^{15}\text{N}$ measurements of NO_2 and are not direct source emission measurements.

Response 1: Thanks for the comment. This error has been corrected.

Lines 64-70: For instance, Zong et al. (2020a) reported $\delta^{15}\text{N}\text{-NO}_x$ values from vehicle exhaust to be $-8.7 \pm 5.3\%$, using an active sampler with an absorption solution (100 mL, $0.25 \text{ mol L}^{-1} \text{KMnO}_4 + 0.50 \text{ mol L}^{-1} \text{NaOH}$). However, more negative $\delta^{15}\text{N}\text{-NO}_x$ values ($-11.2 \pm 6.8\%$) were observed for vehicle exhaust collected using a sealed static absorption method, in which 2.8 ml of concentrated sulphury acid (H_2SO_4) was mixed with 0.6 ml of 30% hydrogen peroxide (H_2O_2) to capture NO_x (Walters et al., 2015a).

Question 2: Lines 73-76: You might also consider citing, (Fibiger and Hastings, 2016) here.

Response 2: Thanks for the comment. We have added it.

Lines 75-78: However, biomass burns at low temperatures (250 to 1200 °C), and the process produces mainly fuel NO_x , with $\delta^{15}\text{N}$ depending on the relative abundance of nitrogenous organic matter ^{15}N in the biomass itself (Zong et al., 2022a;Fibiger and Hastings, 2016;Jin et al., 2024).

Question 3: Lines 95-96: Please define “dual isotopic compositions”. Do you mean the ^{15}N and ^{14}N (as dual isotopes of nitrogen), or are you referring to dual isotope deltas of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$? If you refer to $\delta^{18}\text{O}$, more discussion/explanation is needed here. The $\delta^{18}\text{O}$ values are known to derive from the oxidants involved in NO_x chemistry and do not reflect NO_x sources, which is currently implied by the wording of this sentence.

Response 3: Thanks for the comment. This error has been corrected.

Lines 99-101: Recent research efforts in Tianjin have focused on identifying the sources of NO_3^- through its $\delta^{15}\text{N}$ values (Zhang et al., 2019;Xiao et al., 2023).

Question 4: Lines 132-134: Please indicate the location of the auxiliary pollutant concentrations and meteorology parameters in Fig. S1.

Response 4: Thanks for the comment. We have added it. See in particular the lower right-hand panel in figure S1.

Lines 193-196: The study employed three isotopic international standards: USGS32, USGS34 and IAEA-N3, and the analytical accuracies for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ were $\pm 0.2\%$ and $\pm 0.3\%$, respectively (Böhlke et al., 2003; Sigman et al., 2001).

Question 8: Lines 202: How is the mixing model output utilized? Most of the mixing model development papers indicate that the average and standard deviation may not be the best metrics for these mixing models, particularly when utilizing one variable ($\delta^{15}\text{N}$) to mix between several parameters (4 or 5 sources). Please justify the use of this type of under-constrained model for source apportionment application. For example, if you apply your mixing model to the tunnel measurements (as a test case), would your mixing model results show that vehicles were the dominant source? Or would it suggest many other sources?

Response 8: Thanks for the comment. The Bayesian mixing model is capable of utilizing stable isotope analysis to ascertain the probability distribution of source contributions to an analyzed mixture, while explicitly accounting for the uncertainty associated with the presence of multiple sources, fractionation effects, and isotopic signatures (Moore and Semmens, 2008; Parnell et al., 2010; Parnell et al., 2013). One of the benefits to conducting mixture models in a Bayesian framework is that information from other data sources can be included via informative prior distributions (Moore and Semmens, 2008). Once an informative prior for the proportional contribution of sources is established, MixSIAR can accept the prior as an input during the model specification process.

$$p(f_q | data) = \theta(data | f_q) \times p(f_q) / \sum \theta(data | f_q) \times p(f_q)$$

where $\theta(data|f_q)$ and $p(f_q)$ are the likelihood of the given mixed data and the prior probability of the given state of nature being true based on prior information, respectively. Prior beliefs about proportional source contributions (f_q) are defined using the Dirichlet distribution, with an interval of [0, 1] (Zong et al., 2017). Of course, we agree that the average and standard deviation may not be the best metrics for these mixing models, particularly when utilizing one variable ($\delta^{15}\text{N}$) to mix between several parameters (4 or 5 sources). However, the average provides a central tendency estimate, giving a clear picture of the most likely contribution from each source, while the standard deviation offers insight into the variability and uncertainty in these estimates. These metrics are widely understood and allow for straightforward comparison between different studies or models (Zong et al., 2022b; Zong et al., 2020b; Walters et al., 2022). Although the model might be under-constrained (given the number of sources relative to the number of isotopic markers), the average and standard deviation help in summarizing the outcomes of the model in a way that is interpretable and useful for decision-making. Furthermore, to enhance the reliability of the study results, the model generated 10,000 potential scenarios for each evaluated potential source (Song et al., 2019; Fan et al., 2020). The more iterations, the more likely that the model output will reflect the true posteriors of the source contributions (Stock et al., 2018). The specific number of iterations required to generate sufficient posterior draws depends on the data, the variances in source isotope signatures and fractionations, and the extent to which the isotope mixture precludes the contribution of specified sources (Moore and Semmens, 2008). A large number of iterations are also important in order to establish an appropriate threshold (T), as the more iterations the model uses to develop a T value, the closer this value will be to the true maximum likelihood of the posterior. If too few iterations are used, the threshold establishment phase of the model run

may yield an inappropriately small T, and this in turn may cause the SIR algorithm to resample a single fq with high likelihood tens or even thousands of times. On the other hand, a strong negative correlation of probability density functions (PDFs) between two different sources indicated that the model was unable to completely differentiate one source from another. The study revealed a significant negative correlation between the PDFs of vehicle emissions and coal combustion and soil sources both in both Scenario 1 and Scenario 2 (Table S2), indicating that these sources cannot be completely differentiated. Therefore, the inclusion of additional sources is recommended to enhance the accuracy of estimates provided by the MixSIAR model (Lin et al., 2021). Moreover, a low UI_{90} value indicates a low degree of uncertainty, which suggests that the results of the source contribution were stable (Shang et al., 2020). In this study, as the number of sources input to the model increased, the contribution of various NO_x sources was becoming more stable (Figure 4c). Taken together, we consider the results of this study to be feasible. Of course, the absence of constraints in the model may introduce some uncertainty into the results of this study. Consequently, further refinement may be necessary in the future to address this issue. It was worth noting that modelling is mainly applied to resolve the ratio of possible contributions from different sources in a mixed and complex environment. The tunnel, as an approximately confined space, has a relatively homogeneous source structure. Therefore, it is not possible to use the change model for source resolution.

Lines 208-222: Briefly, the model initiates with establishing a logistic prior distribution, followed by determining the probability contribution distribution of each source to the mixture. Further details are available in our previous study (Xiao et al., 2023; Li et al., 2021). It was noteworthy that an obvious isotopic fractionation process occurs during the conversion of NO_x to NO_3^- . Therefore, the nitrogen isotope fractionation coefficient (ϵ_N) resulting from NO_x to NO_3^- conversion should be calculated prior to determining the relative contribution of NO_x sources using MixSIAR model (Text S2). To enhance the reliability of the study results, the model generated 10,000 potential scenarios for each evaluated potential source (Song et al., 2019; Fan et al., 2020). It was worth noting that the probability density functions (PDFs) of each emission source to NO_3^- should be considered to determine the separation between individual sources (Fan et al., 2020; Lin et al., 2024). Finally, we also have to assess the MixSIAR model calculation result uncertainty based on the uncertainty index (UI_{90}) (as detailed in Text S3) of the posterior distribution data (Zhang et al., 2024).

L468-487: The uncertainty index (UI_{90}), derived from posterior distribution data, serves as a metric to evaluate the uncertainty in the results calculated by the MixSIAR model (Zhang et al., 2024). A low UI_{90} value indicates a low degree of uncertainty, which suggests that the results of the source contribution were stable (Shang et al., 2020). As shown in Figure 4, the UI_{90} values of coal combustion and biomass combustion were lower in Scenario 1 than in Scenario 2, indicating that the results in Scenario 1 were relatively stable. However, the contributions of vehicle exhaust and soil sources in Scenario 2 were relatively stable, as their UI_{90} values were lower in Scenario 2 than in Scenario 1. It can therefore be observed that the uncertainty in contributions from different sources exhibited a variety of degrees of variability that were influenced by the differing end-member values inputted into the model. Generally, the correlation of PDFs between different sources may provide insight into the validity of model calculations (Parnell et al., 2010). For instance, if the two sources cannot be completely differentiated by the model, their correlation in PDFs will exhibit a strong negative correlation (Lin et al., 2021). The study revealed a significant

negative correlation between the PDFs of vehicle emissions and coal combustion and soil sources both in both Scenario 1 and Scenario 2 (Table S2), indicating that these sources cannot be completely differentiated. Therefore, the inclusion of additional sources is recommended to enhance the accuracy of estimates provided by the MixSIAR model (Lin et al., 2021).

L532-539: Moreover, the correlation of PDFs between any two sources decreased in Scenario 4 than in other Scenario (Table S2). It can be inferred that the inter-influence between these sources diminished in Scenario 4 (Lin et al., 2024). On the other hand, the observed decline in UI_{90} values of all sources when the natural gas combustion input was introduced into the MixSIAR model indicates that the result is a relatively stable calculated outcome (Figure 4) (Zhang et al., 2024). Overall, the performance of the SIAR model for Scenario 4 was much better than other Scenarios.

L593-605: Furthermore, the correlations of PDFs between coal combustion and biomass burning remained unchanged, while those between the other sources decreased further when the number of sources input into the model increased from four to six (Table S2). This indicated that the inter-influence between these sources was further reduced, and the model was able to distinguish between them (Lin et al., 2021). Moreover, the contributions of all sources demonstrated more relatively stable results, with UI_{90} values exhibiting the lowest values compared to the results estimated by the four or five sources (Figure 4c) (Zhang et al., 2024). This is because after setting the total contribution of all sources in the model to 1, the lack of input sources in the model may lead to an increase in the fluctuation of the calculated results (Lin et al., 2021; Zhang et al., 2024; Feng et al., 2023). Therefore, it was concluded that incorporating industrial sources in MixSIAR model could decrease uncertainty in calculating the contribution of NO_x sources.

L664-674: Besides, the absence of constraints in the model may introduce some uncertainty into the results of this study. Consequently, further refinement may be necessary in the future to address this issue. Nevertheless, it can be determined that in the calculation results of the MixSIAR model, the role of local $\delta^{15}N$ - NO_x source values is critical and should not be overlooked. And as we introduced more sources into the model, the estimates of the contribution of each NO_x source grew steadier, and the mutual influence among these sources diminished significantly. This also highlights the importance of comprehensively determining the $\delta^{15}N$ values of typical NO_x sources. Therefore, it would be beneficial for NO_3^- source apportionment to further refine the NO_x source types and improve the $\delta^{15}N$ values of other NO_x sources in the future.

Question 9: Text S2: This is really important information, and it is somewhat of a shame that it has been moved to the supplement since it is quite important for the source apportionment calculations. One thing to note is that for the nitrogen isotope fractionation for $NO_2 + OH$ reaction, the authors only consider the isotope exchange between NO/NO_2 . However, ambient measurements and models have indicated that this isotope effect is generally quite small and often counterbalanced by $NO + O_3$ reactions (Bekker et al., 2023; Li et al., 2020; Walters et al., 2018), under conditions of high NO_2 to NO_x molar ratios. The authors need to justify or revisit the use of this fractionation. Further, what about the isotope effect associated with $NO_2 + OH$. Recent modeling work has suggested that this reaction could be important in setting the $\delta^{15}N$ of nitrate (Fang et al., 2021). Once the ϵ value has been determined (which, again, I have some reservations about), how is it applied to back out the $\delta^{15}N(NO_x)$ data? The authors should have shown the calculated ϵ values and the backed-out $\delta^{15}N(NO_x)$ results in the main text (note: it is not included

in the supplement either). Further, the authors utilize $\delta^{18}\text{O}$ data to estimate the nitrate formation pathways. The $\delta^{18}\text{O}$ data should be included in the manuscript, as well as the estimated nitrate formation pathways since all of this data is critical in the author's approach for NO_x source apportionment using $\delta^{15}\text{N}$.

Response 9: Thanks for the comment. The calculation process for ϵN value of NO_x to NO_3^- has been added in the revised manuscript. Our calculation for the ϵN value of NO_x to NO_3^- has also been widely used in similar studies by previous (Zong et al., 2022b; Zong et al., 2020b; Zong et al., 2017; Fan et al., 2020; Song et al., 2019; Luo et al., 2019; Zhao et al., 2021; Zhao et al., 2020; Li et al., 2023; Li et al., 2022). In this study, only two fractionation processes (ϵ_{OH} and $\epsilon_{\text{N}_2\text{O}_5}$) are considered. We strongly agree with the reviewer's suggestion that the isotope effect associated with $\text{NO}_2 + \text{OH}$ could be important in setting the $\delta^{15}\text{N}$ of NO_3^- , especially in under conditions of high NO_2 to NO_x molar ratios (Fang et al., 2021; Li et al., 2020). However, we have limited monitoring data to achieve such a precise calculation of the ϵN value of NO_x to NO_3^- . Therefore, we quantified the different formation pathway of NO_3^- based on its oxygen isotopes ($\delta^{18}\text{O}$) and derived the ϵN value of NO_x to NO_3^- . Although previous studies have similarly pointed out that the HC pathway may need to be considered when using $\delta^{18}\text{O}\text{-NO}_3^-$ to calculate NO_3^- formation pathways. However, there is a clear positive linear correlation between $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ values ($r = 0.7$, $p < 0.01$), suggesting that NO_3^- is primarily formed through the $\bullet\text{OH}$ and N_2O_5 pathways (Xiao et al., 2020). Consequently, other pathways of NO_3^- formation, such as $\text{NO}_3 + \text{HC}$ oxidation pathway, can be disregarded (Walters and Michalski, 2015). More importantly, our study focuses on the importance of local $\delta^{15}\text{N}\text{-NO}_x$ source establishment for NO_3^- source resolution. Therefore, we trace the computational methods of our predecessors, both to compare our results with those of our predecessors and to determine the refined isotopic fingerprint in a region-specific context could more effectively distinguish source of NO_3^- .

L410-438: As shown in Figure 2c, the $\delta^{18}\text{O}\text{-NO}_3^-$ values in this study ranged from 48.3‰ to 102.9‰, with a mean $\delta^{18}\text{O}$ value of $81.1 \pm 11.5\%$ (Table 2). Similar to $\delta^{15}\text{N}\text{-NO}_3^-$ values, the most positive $\delta^{18}\text{O}\text{-NO}_3^-$ value was observed during mid-heating ($89.8 \pm 9.9\%$), followed by pre-heating ($84.5 \pm 8.4\%$) and late-heating ($73.0 \pm 9.8\%$) (Table 2). Furthermore, a significant positive linear correlation ($r = 0.7$, $p < 0.01$) was identified between $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$, indicating that only two predominant oxidation pathways ($\bullet\text{OH}$ and N_2O_5 hydrolysis) govern NO_3^- formation in this study (Xiao et al., 2020; Walters and Michalski, 2016). Previous studies have shown that the $\delta^{15}\text{N}\text{-NO}_3^-$ values in $\text{PM}_{2.5}$ does not fully reflect the initial $\delta^{15}\text{N}\text{-NO}_x$ due to the fractionation process between NO_x and NO_3^- (Fan et al., 2020; Song et al., 2019). Therefore, we calculated the initial $\delta^{15}\text{N}\text{-NO}_x$ values based on the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- as follows (Zong et al., 2017). First, the relative contributions of the $\bullet\text{OH}$ and N_2O_5 pathway were calculated separately using the $\delta^{18}\text{O}\text{-NO}_3^-$ values of $\text{PM}_{2.5}$. Second, the corresponding ϵN values (ϵ_{OH} and $\epsilon_{\text{N}_2\text{O}_5}$) for the $\bullet\text{OH}$ and N_2O_5 pathways were estimated by considering the equilibrium isotopic fractionation between NO_2 and NO , and between N_2O_5 and NO_2 , respectively. Finally, the ϵN value of NO_x to NO_3^- in $\text{PM}_{2.5}$ was calculated using the contributions of the two pathways and their corresponding ϵ_{OH} and $\epsilon_{\text{N}_2\text{O}_5}$ values. The detailed procedures for all calculations can be found in the Supporting Information (Text 2). As shown in Figure S11, the contributions of $\bullet\text{OH}$ and N_2O_5 pathways were $35.4 \pm 19.8\%$ and $64.6 \pm 19.8\%$, respectively, suggesting that N_2O_5 pathways dominates NO_3^- formation. However, the contributions varied across different sampling

periods, indicating that the pathway for NO_3^- formation also varied. This finding aligns with the results presented in section 3.2.1. The calculated ϵN value of NO_x to NO_3^- were $7.5 \pm 3.4\%$ (Figure S12), close to the results of the previous studies in Beijing (Fan et al., 2020; Song et al., 2019), a large municipality near Tianjin. Furthermore, a slight difference in the ϵN value was found during different sampling periods (Figure S12), further indicating that isotopic fractionation similarly affects the feedback of $\delta^{15}\text{N}\text{-NO}_3^-$ to the NO_x source.

Question 10: Lines 210-214: What about fuel types? There is evidence that gasoline vs diesel-powered vehicles have different $\delta^{15}\text{N}(\text{NO}_x)$ values (Fibiger et al., 2014; Miller et al., 2017; Walters et al., 2015a, b). Could this have impacted the results if the vehicle-fleet distributions varied between these locations?

Response 10: Thanks for the comment. Fuel types include light petrol National IV, heavy petrol National III and diesel National IV, all of which are commonly used by motor vehicles in the Tianjin area. In addition, NO_x samples were collected at heavily trafficked intersections and tunnels to more accurately characterize the $\delta^{15}\text{N}$ signals of NO_x emitted from local vehicle exhausts in Tianjin. Results shown that slight differences were observed between the $\delta^{15}\text{N}$ values in vehicle exhaust at different sampling sites (Figure S3). This suggests that our sampling results are representative.

Support Information Text S1: A vehicle exhaust test station in Tianjin was chosen for bench testing (Figure S2b). Fuel types include light petrol National IV, heavy petrol National III and diesel National IV, all of which are commonly used by motor vehicles in the Tianjin area. NO_x emissions from vehicles ($n = 19$) were collected at the tailpipe outlets, meeting the standard with measured NO_x concentrations ranging from 0.1 to 3.6 ppm. Considering the significant range of NO_x emission concentrations, a flow rate of 1 L min^{-1} and a sampling duration of 20 min were established in this study to ensure sufficient NO_3^- for concentration determination and $\delta^{15}\text{N}$ analysis. Additionally, NO_x was collected from two specific atmospheric environments: an urban intersection ($n = 18$) (Figure S2b) and a tunnel ($n = 28$) (Figure S2b). The intersection was situated at the junction of Tianjin, with the instrument placed approximately 20 m from the center of the crossroads and at a height of 1.5 m above the ground (Figure S1). Sampling instruments were positioned 30 m from the tunnel entrance ($n = 10$) and at a midpoint 550 m from the exit ($n = 18$), with the extraction ports at a height of approximately 1.5 m above ground level. The intersection was determined to be relatively open and illuminated, with NO_x concentrations ranging from 0.04 to 0.2 ppm during sampling periods. The sampling flow rate was set to 1.5 L min^{-1} , requiring approximately 120 min to obtain sufficient nitrogen for isotope measurements. The tunnel space is more confined, with weaker lighting, especially at the midpoint. Wind speed mainly depends on the traveling speed of oncoming vehicles. Monitoring data indicated NO_x concentrations at the entrance and midpoint of the tunnel ranged from 0.006 to 0.08 ppm and 0.03 to 0.1 ppm, respectively. Consequently, the air extraction flow rate was set to 2 to 3 L min^{-1} for approximately 60 minutes.

Question 11: Lines 214-215: Generally, gasoline has very low nitrogen content, such that “fuel NO_x ” should be low. Is there evidence that the fuel content utilized in the study location had significant amounts of nitrogen?

Response 11: Thanks for the comment. Gasoline typically has very low nitrogen content, usually below 0.1%. Therefore, the contribution of "fuel NO_x" should indeed be minimal in most cases. We have also revised this section.

L242-253: Walters et al. (2015a) observed that fuel NO_x exhibited more positive δ¹⁵N values than thermal NO_x, and catalytic treatment could also yield positive δ¹⁵N values. However, the nitrogen content of gasoline is low, typically below 0.1% (Tang et al., 2015), and the contribution of fuel NO_x from vehicle exhaust is generally minimal in most cases. When compared with previous studies (Figure S4a and Table 1), our results align with domestic reports but significantly differ from foreign studies (Fisher's least significant difference (LSD) test, the same as below; $p < 0.05$). The differences in δ¹⁵N values of oils, influenced by their generation and depositional settings (Williams et al., 1995), lead to varying δ¹⁵N values of fuels NO_x. More importantly, the differing emission standards for vehicle exhaust across countries, result in local characteristics of δ¹⁵N values of NO_x in vehicle exhaust (Zong et al., 2020a).

Question 12: Lines 222-225: This could only be true if the oil/gas had significant amounts of nitrogen. If the N content is low and NO_x is primarily derived from thermal NO_x, then the differences between regions would potentially reflect vehicle fleet differences, combustion differences, and/or combustion technology differences, which would have a direct impact on δ¹⁵N(NO_x). It is also important to note here that according to Fig. 1, there is a wide range in emitted NO_x concentration for vehicles (similar to Walters et al., 2015b). In this case, it might be better to utilize a mass-weighted δ¹⁵N(NO_x) rather than an unweighted option since the NO_x emission will be weighted towards the heavier NO_x emitters.

Response 12: Thanks for your comment. It is true that petrol is very low in nitrogen and a large amount of motor vehicle exhaust NO_x is mainly of the thermal type. Therefore, the differences between regions would potentially reflect vehicle fleet differences, combustion differences, and/or combustion technology differences, which would have a direct impact on δ¹⁵N-NO_x. For instance, Zong et al. (2020a) has reported that the highest δ¹⁵N-NO_x values displayed a rising trend as emissions standards were continuously updated. Therefore, we have re-analyzed the reasons for the regional differences in δ¹⁵N-NO_x values in vehicle exhaust in the revised manuscript. In addition, since the NO_x concentrations of the vehicle exhaust samples showed great fluctuations, the reviewers suggested that we use a weighted average to express the δ¹⁵N-NO_x values of vehicle exhaust. We are sorry that we didn't go into explaining the reasons for the large fluctuations in NO_x concentrations in vehicle exhaust in our manuscript, which led to your misunderstanding. As a matter of fact, sampling of vehicle exhaust includes various kinds of sampling, i.e. direct sampling from the exhaust pipe, sampling at intersections where the road is congested, and sampling in tunnels where the traffic flow is high. Therefore, if it is expressed as a weighted average, it may instead introduce greater uncertainty.

L230-233: This considerable fluctuation is primarily due to the fact that the NO_x samples from tunnels and intersections are the consequence of atmospheric dilution, which results in markedly lower concentrations than those obtained directly from vehicle exhausts (Text S1).

L244-246: However, the nitrogen content of gasoline is low, typically below 0.1% (Tang et al.,

2015), and the contribution of fuel NO_x from vehicle exhaust is generally minimal in most cases.

L248-253: The differences in $\delta^{15}\text{N}$ values of oils, influenced by their generation and depositional settings (Williams et al., 1995), lead to varying $\delta^{15}\text{N}$ values of fuels NO_x. More importantly, the differing emission standards for vehicle exhaust across countries, result in local characteristics of $\delta^{15}\text{N}$ values of NO_x in vehicle exhaust (Zong et al., 2020a).

Question 13: Lines 228-229: Again, how is “significant” defined? Also, in the mentioned Figure S4b, it appears to have an error. Felix et al., 2012 report a $\delta^{15}\text{N}(\text{NO}_x)$ from coal combustion up to 21.0 ‰ but this graph shows it only goes up to ~12‰. Please double-check this figure.

Response 13: Thanks for the comment. Inappropriate statements have been corrected in the revised version. In addition, the values in Figure S4b are means and standard deviations, not all ranges.

L256-257: Our results were differing from previous reported $\delta^{15}\text{N}\text{-NO}_x$ values from coal combustion (Figure S4b).

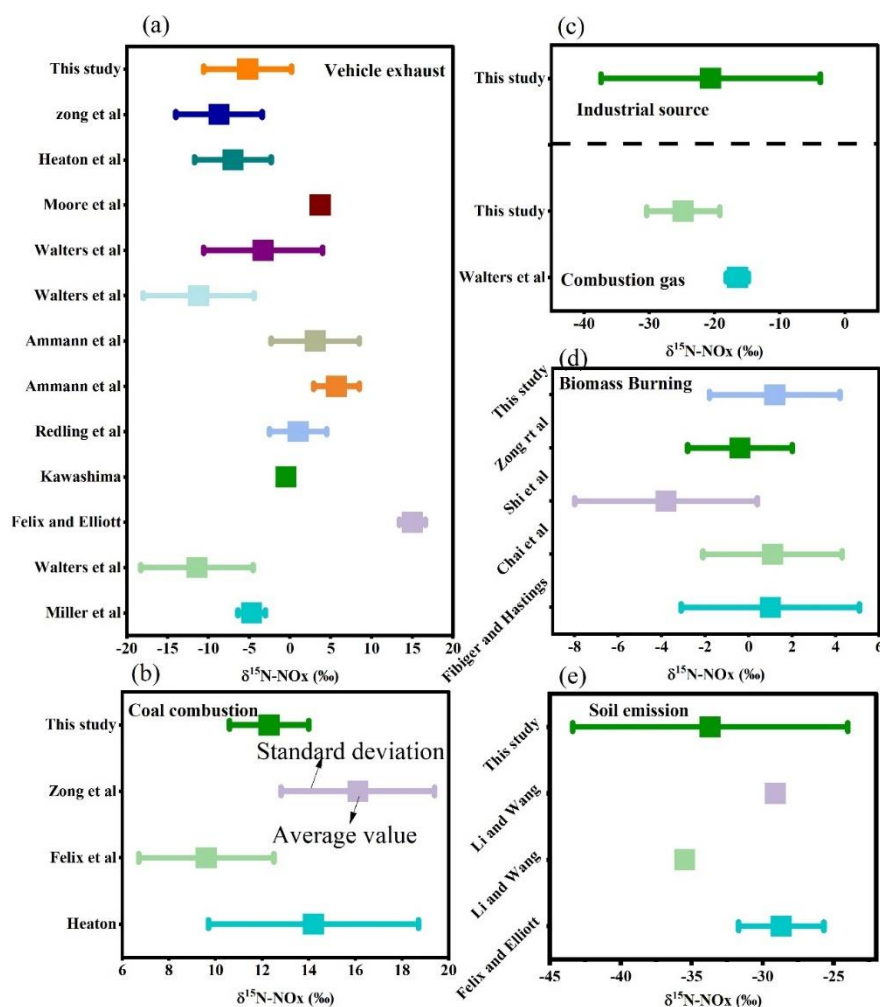


Fig S4 Comparison of $\delta^{15}\text{N}$ values in NO_x sources between this study and previous studies (Average \pm standard deviation) (Fibiger and Hastings, 2016; Felix and Elliott, 2013, 2014; Felix et al., 2015; Felix et al., 2012; Li and Wang, 2008; Walters et al., 2015a; Walters et al., 2015b; Heaton, 1990; Miller et al., 2017; Zong et al., 2020a; Moore, 1977; Ammann et al., 1999; Redling et al.,

2013; Kawashima, 2019). Solid boxes indicate the mean value, and the left and right solid lines indicate the standard deviation.

Question 14: Lines 247-249: In Walters et al., 2015a, both a residential furnace and a natural gas power plant were measured.

Response 14: Thanks for the comment. Inappropriate statements have been corrected in the revised version.

L275-278: However, our results were more negative than those reported by Walters et al. (2015b) for NO_x emitted from residential gas furnaces and natural gas power plant in Indiana, USA (ranging from -19.7 ‰ to -13.9 ‰ and -16.5 ± 1.7 ‰).

Question 15: Lines 323-326: Nitrate is noted to be positively correlated with PM_{2.5}. Please provide the correlation statistics.

Response 15: Thanks for the comment. The correlation statistics were added in the revised version.

L354-357: The concentration of NO₃⁻ showed a significant positive linear correlation with PM_{2.5} (Figure 2) ($r=0.8$, $p < 0.01$), suggesting that the substantial increase in PM_{2.5} pollution is linked to an increase in NO₃⁻ concentration.

Question 16: Lines 335-337: Was there a noticeable change in nitrate production mechanisms elucidated from $\delta^{18}\text{O}(\text{NO}_3^-)$ data?

Response 16: Thanks for the comment. $\delta^{18}\text{O}-\text{NO}_3^-$ values similarly showed differences in NO₃⁻ production mechanisms across sampling periods (Figure 2C and Figure S10). We have added specific analyses in the revised manuscript.

L410-414: As shown in Figure 2c, the $\delta^{18}\text{O}-\text{NO}_3^-$ values in this study ranged from 48.3‰ to 102.9‰, with a mean $\delta^{18}\text{O}$ value of 81.1 ± 11.5 ‰ (Table 2). Similar to $\delta^{15}\text{N}-\text{NO}_3^-$ values, the most positive $\delta^{18}\text{O}-\text{NO}_3^-$ value was observed during mid-heating (89.8 ± 9.9 ‰), followed by pre-heating (84.5 ± 8.4 ‰) and late-heating (73.0 ± 9.8 ‰) (Table 2).

L428-433: As shown in Figure S11, the contributions of •OH and N₂O₅ pathways were 35.4 ± 19.8 % and 64.6 ± 19.8 %, respectively, suggesting that N₂O₅ pathways dominates NO₃⁻ formation. However, the contributions varied across different sampling periods, indicating that the pathway for NO₃⁻ formation also varied. This finding aligns with the results presented in section 3.2.1.

Question 17: Lines 366-369: The authors argue that the $\delta^{15}\text{N}(\text{NO}_3^-)$ differences between these three periods could be related to NO_x source differences. However, what about isotope fractionation? They previously mentioned that the NO_x oxidation efficiency changed as elucidated by NO₃⁻ and NO₂ concentration trends (in which NO₃⁻ concentrations didn't increase, but NO₂ did during the heating period). Including $\delta^{18}\text{O}(\text{NO}_3^-)$ data, as well as the fractionation corrected $\delta^{15}\text{N}(\text{NO}_x)$, would be important here to normalize the influence of potential chemical changes that might also impact $\delta^{15}\text{N}(\text{NO}_3^-)$.

Response 17: Thanks for the comment. This less appropriate sentence has been corrected in the revised manuscript. In addition, we have added a discussion of isotope fractionation to the revised manuscript.

L400-401: These results mainly attributed to the variations in the sources of NO_x during three sampling periods.

L410-438: As shown in Figure 2c, the $\delta^{18}\text{O}\text{-NO}_3^-$ values in this study ranged from 48.3‰ to 102.9‰, with a mean $\delta^{18}\text{O}$ value of $81.1 \pm 11.5\%$ (Table 2). Similar to $\delta^{15}\text{N}\text{-NO}_3^-$ values, the most positive $\delta^{18}\text{O}\text{-NO}_3^-$ value was observed during mid-heating ($89.8 \pm 9.9\%$), followed by pre-heating ($84.5 \pm 8.4\%$) and late-heating ($73.0 \pm 9.8\%$) (Table 2). Furthermore, a significant positive linear correlation ($r = 0.7$, $p < 0.01$) was identified between $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$, indicating that only two predominant oxidation pathways ($\bullet\text{OH}$ and N_2O_5 hydrolysis) govern NO_3^- formation in this study (Xiao et al., 2020; Walters and Michalski, 2016). Previous studies have shown that the $\delta^{15}\text{N}\text{-NO}_3^-$ values in $\text{PM}_{2.5}$ does not fully reflect the initial $\delta^{15}\text{N}\text{-NO}_x$ due to the fractionation process between NO_x and NO_3^- (Fan et al., 2020; Song et al., 2019). Therefore, we calculated the initial $\delta^{15}\text{N}\text{-NO}_x$ values based on the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- as follows (Zong et al., 2017). First, the relative contributions of the $\bullet\text{OH}$ and N_2O_5 pathway were calculated separately using the $\delta^{18}\text{O}\text{-NO}_3^-$ values of $\text{PM}_{2.5}$. Second, the corresponding ϵN values (ϵ_{OH} and $\epsilon_{\text{N}_2\text{O}_5}$) for the $\bullet\text{OH}$ and N_2O_5 pathways were estimated by considering the equilibrium isotopic fractionation between NO_2 and NO , and between N_2O_5 and NO_2 , respectively. Finally, the ϵN value of NO_x to NO_3^- in $\text{PM}_{2.5}$ was calculated using the contributions of the two pathways and their corresponding ϵ_{OH} and $\epsilon_{\text{N}_2\text{O}_5}$ values. The detailed procedures for all calculations can be found in the Supporting Information (Text 2). As shown in Figure S11, the contributions of $\bullet\text{OH}$ and N_2O_5 pathways were $35.4 \pm 19.8\%$ and $64.6 \pm 19.8\%$, respectively, suggesting that N_2O_5 pathways dominates NO_3^- formation. However, the contributions varied across different sampling periods, indicating that the pathway for NO_3^- formation also varied. This finding aligns with the results presented in section 3.2.1. The calculated ϵN value of NO_x to NO_3^- were $7.5 \pm 3.4\%$ (Figure S12), close to the results of the previous studies in Beijing (Fan et al., 2020; Song et al., 2019), a large municipality near Tianjin. Furthermore, a slight difference in the ϵN value was found during different sampling periods (Figure S12), further indicating that isotopic fractionation similarly affects the feedback of $\delta^{15}\text{N}\text{-NO}_3^-$ to the NO_x source.

Question 18: Lines 415-419: Adding more parameters to an under-constrained mixing model will make the results more under-constrained. All the mixing model results have large standard deviations/uncertainties, and I'm not sure if it is warranted to discuss the differences between various model simulations, as all of the source estimates appear to overlap. For example, soil emissions are estimated to be as important as some combustion-related NO_x emissions. This tends to invalidate the mixing model results, in my opinion, as these emissions should be rather low for a highly urbanized location during a cooler period.

Response 18: Thanks for the comment. One advantage of using mixture models within a Bayesian framework is the ability to incorporate information from other data sources via informative prior distributions (Moore and Semmens, 2008). Once an informative prior for the proportional contributions of sources is established, MixSIAR can use this prior during model specification.

Prior beliefs about source contributions (f_q) are defined using the Dirichlet distribution, with an interval of [0, 1], and the total contributions of all sources default to 1. For instance, if only three sources are input into the model, it will assess their contributions assuming their total equals 1. If the sum of these contributions is significantly less than 1 in a mixed environment, additional sources must be included to accurately estimate each source's contribution. Thus, omitting necessary source input models can increase uncertainty in the model's quantitative results. We recognize the reviewers' concerns about the uncertainty associated with multiple source contributions. In fact, Fan et al. (2020) demonstrated that adding irrelevant sources does not significantly affect the regularity of source resolution results. Specifically, during the cold winter months in Beijing, soil source inputs had little effect on the quantitative results of the model. In this study, the wide variation in the results resolved by the models in our multiple scenarios rather highlights the need for our study. Moreover, the posterior distributions and stability for the proportional contribution of each Scenarios were compared (Figure 4 and Table S2). In result, as the number of sources input to the model increased, the contribution of various NO_x sources was becoming more stable, and the inter-influence between various sources significantly reduced. This implied that is no significant interinfluence in terms of estimated source apportionments when the more emission sources were considered in SIAR model.

Additionally, the reviewers expressed skepticism regarding the contribution of soil sources in our results. While Tianjin is an urban environment, it is situated in the North China Plain and is surrounded by extensive agricultural land. Furthermore, the urban area includes a significant amount of green belt soil, which remains vegetated even in winter. It is important to note that temperatures were close to 10°C during both sampling periods, except for the mid-heating period, suggesting that microbial activity was still active. Under these conditions, more NO_x from biogenic soil emissions would be expected to enter the atmosphere due to the relatively high soil temperature (ambient temperature: $\sim 10^\circ\text{C}$) (Williams et al., 1992). Thus, it is not surprising that the mean contribution of soil sources was 10% during the sampling periods (Figure 5).

Question 19: Lines 585-589: Again, I think weighted averages might be better to report here than unweighted.

Response 19: Thanks for the comment. We have already responded to this question in **Question 12**. That is, sampling of vehicle exhaust includes various kinds of sampling, i.e. direct sampling from the exhaust pipe, sampling at intersections where the road is congested, and sampling in tunnels where the traffic flow is high. Therefore, if it is expressed as a weighted average, it may instead introduce greater uncertainty.

Question 20: Table 1. Walters et al., 2015b did not report coal combustion $\delta^{15}\text{N}(\text{NO}_x)$. For soil emissions, you may also consider adding (Yu and Elliott, 2017).

Response 20: Thanks for the comment. This error has been corrected.

Table 1 Comparison of the $\delta^{15}\text{N}$ characteristic spectra of NO_x sources reported in the previous and present study

NO_x sources	Previous studies	This study
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	av (%)	std (%)	n	Reference	av (%)	std (%)	n
Coal combustion	+13.7	4.6	47	(Felix et al., 2012;Heaton, 1990)	+12.3	1.7	13
Vehicle exhaust	-7.2	7.8	151	(Walters et al., 2015b;Walters et al., 2015a;Felix and Elliott, 2014;Heaton, 1990)	-5.2	5.4	62
Biomass burning	+1.0	4.1	24	(Fibiger and Hastings, 2016;Felix and Elliott, 2013)	+1.2	3.0	14
Soil emission	-33.8	12.2	6	(Felix and Elliott, 2014;Li and Wang, 2008;Yu and Elliott, 2017)	-33.7	9.7	12
Nature gas combustion	-16.5	1.7	23	(Walters et al., 2015b)	-24.8	5.6	5
Industrial source	N/A	N/A		N/A	-20.6	16.8	17

Note: N/A represents data unknown.

Question 21: Fig 3. It would be helpful if the stacked bar plots followed the legend order for easier visual interpretation. Furthermore, it appears that this is an error in the figure caption, as Scenarios 1 and 3 are defined twice, while Scenarios 2 and 4 are undefined.

Response 21: Thanks for the comment. This error has been corrected.

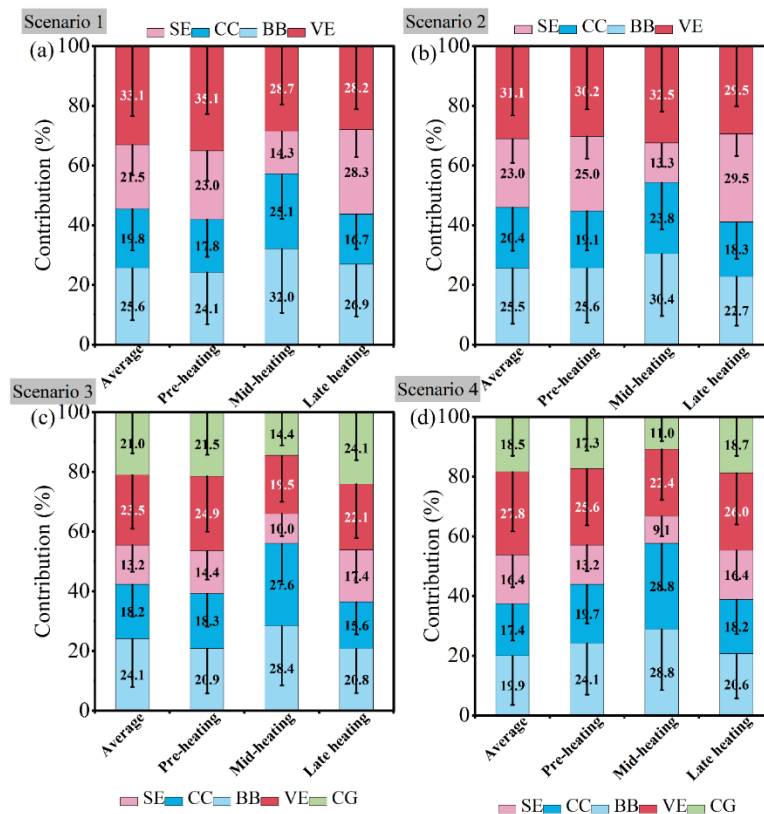


Figure 3 Comparison of fractional contributions of NO_3^- sources in $\text{PM}_{2.5}$ in Tianjin estimated by different $\delta^{15}\text{N}$ values of NO_x sources. The results of Scenario 1 and Scenario 3 were estimated

using the $\delta^{15}\text{N}$ values of four and five NO_x sources obtained from previous studies, while the results of **Scenario 2 and Scenario 4** were estimated using the $\delta^{15}\text{N}$ values of four and five NO_x sources obtained from this study. Also, SE = soil emission, CC = coal combustion, BB = biomass burning, VE = vehicle emission, and CG = combustion of natural gas.

Technical Corrections:

Technical Comment 1: Through the manuscript, please change NO_x to NO_x (with the “x” formatted as a subscript and in italics).

Response 1: Thanks for the comment. Similar problems have all been corrected in the revised manuscript.

Technical Comment 2: Please write all quantity symbols (including δ , n, etc) in italics.

Response 2: Thanks for the comment. Similar problems have all been corrected in the revised manuscript.

Technical Comment 3: Lines 59-61, this is an incomplete sentence.

Response 3: Thanks for the comment. We have rewritten the sentence.

L59-61: **It should be noted that the $\delta^{15}\text{N}$ values from various NO_x sources have been reported in previous studies (Zong et al., 2020a; Zong et al., 2022a).**

Technical Comment 4: Lines 138-141: You can delete the word “Initially” here.

Response 4: Thanks for the comment. The word “Initially” has been deleted.

L149-152: **Hydrophobic** Teflon membrane (TF-200, Pall, USA) and nylon membrane (BNRG810S, Pall, USA) were……

Technical Comment 5: Lines 156-157: Please change “cutted” to “cut”

Response 5: Thanks for the comment. This error has been corrected.

L167-168: ……a proportion of the particulate matter from the each $\text{PM}_{2.5}$ sample was **cut** and……

Technical Comment 6: Lines 166-170: Neutralized is used twice in this sentence. I would suggest deleting the “to neutralize…” part of the sentence.

Response 6: Thanks for the comment. This error has been corrected.

L177-180: ……**which was neutralized using electronic grade hydrochloric acid (HCl) at a mass concentration of approximately 38%.**

Technical Comment 7: Lines 170-171: You can delete “salt” from this sentence

Response 7: Thanks for the comment. “salt” has been deleted in this sentence.

L180-181: Finally, the supernatant was analyzed for NO_2^- and NO_3^- concentrations on a Skalar San++ continuous flow nutrient analyzer.

Technical Comment 8: Lines 179: “*Pseudomonas aureofaciens*” should be italicized.

Response 8: Thanks for the comment. We have corrected it.

L188-190: Briefly, extracted NO_3^- were quantitatively converted to N_2O through the action of denitrifying bacteria, namely *Pseudomonas aureofaciens*, ATCC 13985, which lacked N_2O reductase (Luo et al., 2020).

Technical Comment 9: Text S2: Nitrate-forming reactions aren’t typically expected to be “aqueous” reactions, such as in cloud reactions. Instead, I think the authors mean heterogeneous, and I would recommend switching these terms.

Response 9: Thanks for the comment. We have corrected it.

Text S2: The formation pathways of emitted NO_x ($\text{NO} + \text{NO}_2$) to NO_3^- in polluted cities are complex, which included heterogeneous and gas-phase reactions.

Technical Comment 10: Line 222: “Significantly” is used here and in other places in the manuscript. What significant test was utilized and what are the p-values to indicate significance?

Response 10: Thanks for the comment. Significance test methods and p-values have been added in the revised manuscript.

L246-248: …our results align with domestic reports but significantly differ from foreign studies (Fisher's least significant difference (LSD) test, the same as below; $p < 0.05$).

Technical Comment 11: Lines 363-366: Please provide p-values to indicate whether these differences are significant.

Response 11: Thanks for the comment. The p-values have been added in the revised manuscript.

L397-398: Significant differences were observed in $\delta^{15}\text{N}-\text{NO}_3^-$ values among the three sampling periods in this study ($p < 0.05$).

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