

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,

Pro. Xiaodong Li

E-mail: xiaodong.li@tju.edu.cn

Institute of Surface-Earth System Science, School of Earth System Science

Tianjin University, Tianjin, P. R. China, 300072

Reviewer #2:

This work reports the measurement of the nitrogen isotopes ($\delta^{15}\text{N}$) from major domestic NO_x sources such as vehicle exhaust, industrial emissions, and natural gas combustion in Tianjin, China. The authors directly collected $\delta^{15}\text{N}$ samples from many NO_x sources using active sampling methods and compared their values with previous studies. Different $\delta^{15}\text{N}(\text{NO}_x)$ values from the previous studies were obtained in this area due to the local characteristics of NO_x sources. They also measured inorganic ions of $\text{PM}_{2.5}$ over three different heating periods to understand the contribution of NO_x to nitrate formation in Tianjin. Coal combustion is reported as the main source of NO_3^- during heating periods in this area. In addition, the contributions from different NO_x sources to NO_3^- in $\text{PM}_{2.5}$ were quantified using a stable isotope mixing model depending on many different scenarios. In general, the study primarily focuses on refining the $\delta^{15}\text{N}(\text{NO}_x)$ values from various NO_x sources in Tianjin, China, suggesting that these values reflect the local characteristics. While I appreciate the effort to collect and determine $\delta^{15}\text{N}(\text{NO}_x)$ values from various NO_x sources and quantify NO_3^- formation in China, I believe several issues should be addressed and further discussion should be added when considering this study for publication in the ACP.

First, the manuscript type of technical notes in the ACP is meant to be peer-reviewed publications that report new developments, significant advances, or novel aspects of experimental and theoretical methods and techniques -- I feel like this study doesn't meet the standard of ACP publication as a technical note. Rather, it looks closer to a measurement report since they mainly reported the measured $\delta^{15}\text{N}(\text{NO}_x)$ values depending on the NO_x sources and inorganic ions of $\text{PM}_{2.5}$. Additionally, their major discussion focuses on the isotope mixing model to estimate the contribution of NO_x sources, but their outputs are not validated. The isotope mixing model is commonly used in the isotope field to identify and quantify the contributions of multiple sources using potential source end-members. However, this statistical approach has limitations in accurately quantifying source portions. In this study, the measurement values used as inputs show high standard deviations and wide ranges. Given the isotope mixing model is sensitive to input parameters, large variabilities can lead to significant uncertainties in the output. Further, there are known large fractionations of nitrogen isotope between NO_x to NO_3^- conversion (Li et al., 2020; Bekker et al., 2023), but these isotope effects are not considered in this study. It is also unclear which values are used for the mixing model. The model output should be validated to ensure its reliability through NO_x emission inventory data or other types of observations from the Tianjin area. Lastly, the authors mentioned that a systematic study of $\delta^{15}\text{N}(\text{NO}_x)$ values from domestic NO_x sources is crucial for accurately identifying nitrate sources (Lines 15-16). The distinct values obtained in this study reflect the local characteristics of NO_x emissions, indicating that these $\delta^{15}\text{N}(\text{NO}_x)$ values might have limitations when applied to other regions. Therefore, it would be helpful if the author provided recommendations on how to best use these values and clarified their scientific relevance to other regions.

Response: We thank the reviewers for investing the time to thoroughly evaluate our initial manuscript and for the constructive comments.

First, the reviewers suggested that our study resembles a measurement report. Initially, our

manuscript was indeed submitted to "Measurement Report." However, since the focus is on an enhanced framework for identifying aerosol nitrate sources through stable nitrogen isotopic analysis of local sources, the editor recommended that the paper be considered a "Technical Note." We are open to publishing the manuscript as a "Measurement Report" if feasible.

Second, reviewers were concerned about the results of our model quantification. 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 (Parnell et al., 2013; 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. Although some of them propose to the results may be inaccurate when utilizing one variable ($\delta^{15}\text{N}$) to mix between several parameters (4 or 5 sources). Generally, prior beliefs about proportional source contributions (f_q) are defined using the Dirichlet distribution, with an interval of [0, 1], and the sum of the contributions of the sources of all input models defaults to 1. For example, if only 3 sources are input to the model, the model will evaluate the source contributions based on the sum of their contributions being 1. However, if the sum of the contributions from these three sources is much less than 1 in a mixed environment, then data from more sources will need to be entered to more accurately estimate the corresponding contribution from each source. In other words, the absence of the number of source input models may lead to increased uncertainty in the quantitative results of the model. More important, a growing number of recent studies have suggested the need to increase the number of sources in the model to eliminate the interactions between the various sources (Lin et al., 2024; Lin et al., 2021; Zhang et al., 2024). In the SIAR model, the Monte Carlo approach was used to quantify the emission sources of nitrate aerosols (Zong et al., 2017), it is also widely used in similar studies (Wu et al., 2024; Cheng et al., 2022; Chen et al., 2022; Song et al., 2021). 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). Finally, 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. Overall, we believe that the results quantified by the model in this study are acceptable.

Third, the effect of the fractionations of nitrogen isotope between NO_x to NO₃⁻ conversion has been added in the revised version. In this study, the $\delta^{18}\text{O}$ -NO₃⁻ values helped constrain the fractionation factor from NO_x to NO₃⁻ (Xiao et al., 2020), but only two primary pathways, hydroxyl radical oxidation and nitrogen pentoxide hydrolysis, were taken into account. Previous research supports the view that these pathways account for up to 95% of NO₃⁻ production (Lin et al., 2021; Xiao et al., 2020), implying that alternative pathways might exert a relatively minor impact on ϵN calculations. Nonetheless, future measurements of $\Delta^{17}\text{O}$ -NO₃⁻ are essential to elucidate the isotopic fractionation coefficients comprehensively during the formation of NO₃⁻.

Finally, we acknowledge the limitations of our study and offer recommendations for future research. We analyzed only six samples from typical NO_x sources in Tianjin, without examining all NO_x sources in China. Variations in $\delta^{15}\text{N}$ background values, combustion processes, and NO_x emission standards affect the $\delta^{15}\text{N}$ signal of NO_x emissions from different sources. Given the

uniformity of industrial standards across Chinese cities, these values could also help determine the source of NO_3^- in other locations. Our study emphasizes the need for a comprehensive determination of $\delta^{15}\text{N}$ values for typical NO_x sources. Refining NO_x source types and improving $\delta^{15}\text{N}$ values for other NO_x sources would enhance NO_3^- source apportionment in future research. 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. Relevant content can be found in section 3.5 of the revised manuscript.

We have carefully modified and proofread the manuscript. Below, we will provide detailed one-on-one revisions and responses to deficiencies in the original manuscript. All changes are marked by the red font in the revised manuscript.

Major Comments:

***Question 1:** This manuscript aims to explore NO_x emission sources in the Tianjin area using isotope analysis. The author mentioned in the introduction that this area predominantly has high NO_x emissions from coal combustion for heating during the heating period (Lines 93-94). However, there is no mention of other periods, such as preheating and late heating, or other potential emission sources, even though the highest NO_3^- and $\text{PM}_{2.5}$ concentrations were observed during the preheating period. What would be the potential sources of NO_3^- and $\text{PM}_{2.5}$ during these three different periods? It would be helpful if this argument could be supported or compared with NO_x emission inventory data or another type of observation from the Tianjin area.*

Response 1: Thanks for the comment. Apologies for our unclear presentation. We have cited previous studies to confirm the significant contribution of coal combustion during heating in Tianjin. However, it is important to note that coal combustion only contributes a higher proportion during the heating period, rather than a change in the overall source structure. In other words, only the proportion of the source contribution changed during the three sampling periods, not the source structure.

L97-99: For instance, previous studies have demonstrated that NO_2 emissions in the Beijing-Tianjin-Hebei region exhibit a marked increase during the heating season, reaching an annual peak in winter (Meng et al., 2018).

***Question 2:** In this study, $\text{PM}_{2.5}$ samples were collected for the day and night time from Oct to Apr, but the diurnal or seasonal pattern of NO_x and NO_3^- are not considered at all in this study. Meteorological factors, especially temperature, have a significant effect on nitrogen isotope fractionation and nitrate formation. Further, the major sources of NO_x emission could be variable depending on meteorological conditions. How do the meteorological factors affect the NO_x and NO_3^- in this study?*

Response 2: Thanks for the comment. The change pattern of NO_x and NO_3^- are considered in this study. In addition, we have added a discussion of the effects of meteorological parameters on NO_3^- concentrations. In conclusion, the combination of NO_2 emissions and variations in meteorological parameters, including wind speed and relative humidity, contributed to the observed differences in nitrate concentrations between sampling periods in this study. It is

important to note that the main purpose of this study is to discuss the importance in refined isotopic fingerprint of NO_x source in a region-specific context. Consequently, the seasonal pattern of NO_x and NO_3^- , along with the influence of meteorological factors, was only superficially examined.

L358-384: The variation pattern of NO_3^- concentration during different sampling periods aligned with that of $\text{PM}_{2.5}$ (Figure 2). The highest concentration of NO_3^- was observed during pre-heating ($16.0 \pm 12.4 \mu\text{g m}^{-3}$), and the lowest concentration was observed during late-heating ($9.7 \pm 8.7 \mu\text{g m}^{-3}$) (Table 2). This pattern of change is associated with the discrepancy in wind speed (Table S1), as higher wind speeds may not be conducive to NO_3^- accumulation. That is, the mean wind speed is lowest during pre-heating periods, resulting in greater NO_3^- accumulation in the atmosphere. Notably, NO_2 , as the precursor of NO_3^- , did not follow the observed pattern of change in NO_3^- concentration. The highest concentration of NO_2 was observed during mid-heating (Table S1 and Figure S7), potentially influenced by increased coal combustion for heating (Luo et al., 2019). Generally, NO_2 concentration and its secondary conversion efficiency were the key factors affecting the concentration of NO_3^- . Therefore, the difference could be attributed to biases in the secondary conversion efficiency of NO_2 (Xiao et al., 2023). This is also corroborated by the considerable discrepancy between the sampling periods in the key meteorological factors influencing nitrate formation, such as relative humidity. Compared to NO_3^- , the SO_4^{2-} concentration was highest during mid-heating. In addition, SO_2 , mainly originating from coal combustion, exhibited a similar variation pattern to SO_4^{2-} , potentially attributed to increased coal combustion for heating (Figure S9) (Feng et al., 2020). Markers primarily originating from coal combustion, including CO and Cl^- (Figure S9), also showed higher concentration during mid-heating, supporting our speculation (Luo et al., 2019; Xiao et al., 2022). While the increase in NO_2 could be attributed to enhanced biomass burning during mid-heating, the concentration of K^+ , primarily a biomass burning marker (Xiao et al., 2024), exhibited slight variation during the three periods and was significantly lower than Cl^- (Table 2). Thus, the impact of coal combustion heating on NO_3^- sources was evident, despite mid-heating periods being unfavorable for NO_3^- generation.

Question 3: Lines 381-382: As previously mentioned, given that the Coal Replacement Project has led to more natural gas usage in the recent year (Lines 356-357), I suspect natural gas combustion might be an important NO_x source in your area too. Also, in a previous study, it was reported that NO_x emissions driven by natural gas (i.e., liquid-fuel) combustion are one of the important NO_x sources in urban areas, accounting for a larger portion than soil and biomass burning (e.g., Bekker et al., 2023). Please clarify why four sources except for natural gas specifically are chosen for the mixing model run (Line 381-382).

Response 3: Thanks for the comment. We extend our sincerest apologies for any confusion caused by our lack of clarity, which has resulted in a misunderstanding on your part. Only four sources are considered here, mainly for comparison with previous studies and thus to emphasize the importance of isotopic fingerprint of NO_x sources in a region-specific context. Indeed, our findings substantiate our hypothesis that there are discrepancies in the outcomes of model resolution utilizing the $\delta^{15}\text{N}-\text{NO}_x$ values of disparate sources reported abroad in comparison to those established locally (Figure 3). In addition, we also assess the contribution of natural gas

sources in the following. It was found that neglecting the contribution of natural gas sources may lead to a lack of clarity in our understanding of the sources of nitrate in Tianjin.

L442-451: Previous studies have employed the MixSIAR model to estimate the contribution of NO_x sources, utilizing the known $\delta^{15}\text{N}$ values of NO_x in diverse sources, primarily sourced from overseas research (Zong et al., 2017; Zong et al., 2020b; Zhao et al., 2020; Zhang et al., 2020). Additionally, these studies have focused on four primary sources of NO_x, namely coal combustion, biomass combustion, vehicle exhaust, and soil sources. Therefore, in order to compare with previous studies, this study have focused on above four sources of NO_x: coal combustion, biomass combustion, vehicle exhaust, and soil sources. That is, the $\delta^{15}\text{N}$ data of above four sources from previous studies (Scenario 1) and this study (Scenario 2) were input into the MixSIAR model to quantify the sources of NO₃⁻, respectively (Table 1).

Question 4: Lines 386-389: The author argued that if the mixing model is run for the entire sampling period, the results for scenarios 1 and 2 are insignificantly different. However, the results for scenario 1 are slightly lower than those for scenario 2 during the pre-heating periods. This part is confusing and there is no reported statistical analysis. Considering the larger uncertainties, especially for scenario 2, it is likely that the difference is not significant, but this should be more thoroughly addressed. In addition, what does it mean if the scenarios do not produce different results? How can you state that scenario 2 leads to fewer inaccuracies (Lines 398-399) through the mixing model results?

Response 4: Thanks for the comment. We apologies for any confusion caused by our lack of clarity. We have reorganized the logic of this section in the revised manuscript. Note that we did not perform statistical analyses as the model outputs were averaged. Therefore, we have corrected some inappropriate expressions in the revised manuscript. Nevertheless, the 4.9% overestimation of the contribution of Case 1 to vehicle emissions in comparison to Case 2 during the pre-heating period is evident. Considering that most of the source data of Scenario 1 originated from foreign studies (Table 1), the Tianjin source data of Scenario 2 is more representative of its localized characteristics. Therefore, we conclusion that the calculation of the contributions of various sources to NO₃⁻ using $\delta^{15}\text{N}$ data in NO_x sources from previous studies may result in inaccuracies. In addition, we have also added a discussion of the uncertainty of the results of the two scenarios in the subsequent discussion. It was found that the contributions of certain sources in Scenario 2 remained relatively stable, suggests that the results of Scenario 2 are more reliable than those of Scenario 1. However, 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 (Lin et al., 2024). Therefore, we added the effect of natural gas combustion sources in the subsequent discussion. In addition, the reviewers questioned the lack of difference in mean results between the two Scenario throughout the sampling period. This is mainly influenced by the offset between the differences in the results of the two Scenario for the different sampling periods. For instance, the contributions of biomass burning in Scenario 1 are underestimated by 1.5% and overestimated by 1.6% during pre-heating periods and mid-heating periods, respectively, in comparison to Scenario 2 (Figure 3a and 3b).

L452-467: Throughout the entire sampling duration, the average contributions estimated by the MixSIAR model exhibited no substantial disparities between Scenarios 1 and 2 (Figure 3a and 3b),

suggesting that localized $\delta^{15}\text{N}$ data acquisition for NO_x sources might be superfluous. However, the contributions of individual NO_x sources to NO_3^- in $\text{PM}_{2.5}$ were found to be large different in **Scenario 1 and Scenario 2** during a certain sampling period. For instance, the contributions of vehicle exhaust **during the pre-heating periods** exhibited a notable discrepancy, i.e., **Scenario 1** ($35.1 \pm 22.8\%$) is overestimated by 4.9% compared to the **Scenario 2** ($30.2 \pm 21.1\%$). Similar difference also can be found in other sampling periods. Specifically, the contributions of vehicle exhaust in **Scenario 1** are overestimated by 1.3% and underestimated by 3.8% during late heating periods and mid-heating periods, respectively, in comparison to **Scenario 2** (Figure 3a and 3b). Considering that most of the source data of **Scenario 1** originated from foreign studies (Table 1), the **Tianjin source data of Scenario 2** is more representative of its localized characteristics. Therefore, the calculation of the contributions of various sources to NO_3^- using $\delta^{15}\text{N}$ data in NO_x sources from previous studies may result in inaccuracies.

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).

***Question 5:** Lines 420-430: Again, it was mentioned that natural gas combustion could not be negligible in this area and the measured $\delta^{15}\text{N}(\text{NO}_x)$ values from natural gas combustion were compared with the previous study. It would be helpful if you added more explanation about why your area shows more negative values compared to the previous study. Also, please add the referred values or table 1 reference in the main text.*

Response 5: Thanks for the comment. First, we added to the revised manuscript why natural gas combustion sources were considered. In addition, we further elaborate on why the $\delta^{15}\text{N}\text{-NO}_x$ values of natural gas combustion emissions measured in this study was compared to the results of previous studies. Also, we explained the reason why the $\delta^{15}\text{N}\text{-NO}_x$ values of natural gas combustion emissions in Tianjin were negative compared to the results of previous studies. Finally, we also added reference values of the $\delta^{15}\text{N}\text{-NO}_x$ values for natural gas combustion in the revised manuscript.

L488-509: Since the initiation of the Coal Replacement Project in 2017, the contribution of natural

gas combustion to NO_3^- may not be negligible in recent years in Tianjin (Meng et al., 2022; Wang et al., 2022). For instance, Multi-resolution emission inventory for China shown that annual NO_x emissions from natural gas combustion increased from 0.6×10^5 t in 2013 to 0.7×10^5 t in 2020 (Lin et al., 2024). However, previous studies have seldom examined the role of natural gas combustion in contributing to NO_3^- in $\text{PM}_{2.5}$, due to limited availability of reported $\delta^{15}\text{N}$ values of NO_x resulting from natural gas combustion (Zong et al., 2022b; Walters et al., 2015b). Previous study has found that when only four sources are considered in the MixSIAR model, there is more misclassification between the contributions of any two sources (Lin et al., 2024). Furthermore, these studies demonstrate that natural gas combustion may represent a potential source of NO_3^- in $\text{PM}_{2.5}$. However, as mentioned in Section 3.1 in this study, the $\delta^{15}\text{N}$ - NO_x values (Table 1) emitted from the combustion of natural gas in Tianjin ($-24.8 \pm 5.6\%$) are more negative than previous reported in foreign countries ($-16.5 \pm 1.7\%$) due to the effects of combustion efficiency and differences in combustion temperatures, among others. Therefore, in order to clarify the necessary for identify isotopic fingerprint in a region-specific context, the following comparative analyses have been conducted. That is, we refer to the $\delta^{15}\text{N}$ - NO_x end-member values from natural gas combustion obtained from previous studies (Scenario 3) and locally acquired in Tianjin (Scenario 4) to calculate the relative contribution fractions of the five NO_x sources using the MixSIAR model (Figure 3c and 3d).

Question 6: *The Figure 3 is missing in the manuscript. Also, please clarify the x-axis of the graphs.*

Response 6: Thanks for the comment. The mistake has been rectified, and the x-axis of the graphs has been clarified.

L52-455: Throughout the entire sampling duration, the average contributions estimated by the MixSIAR model exhibited no substantial disparities between Scenarios 1 and 2 (Figure 3a and 3b), suggesting that localized $\delta^{15}\text{N}$ data acquisition for NO_x sources might be superfluous.

L503-509: Therefore, in order to clarify the necessary for identify isotopic fingerprint in a region-specific context, the following comparative analyses have been conducted. That is, we refer to the $\delta^{15}\text{N}$ - NO_x end-member values from natural gas combustion obtained from previous studies (Scenario 3) and locally acquired in Tianjin (Scenario 4) to calculate the relative contribution fractions of the five NO_x sources using the MixSIAR model (Figure 3c and 3d).

L510-511: In contrast to the findings of the four sources (Scenario 1 and Scenario 2), large discrepancies exist between Scenario 3 (Figure 3c) and Scenario 4 (Figure 3d).

L529-530: In both scenarios, the contribution of natural gas combustion to NO_3^- was close to or even exceeds that of soil sources (Figure 3).

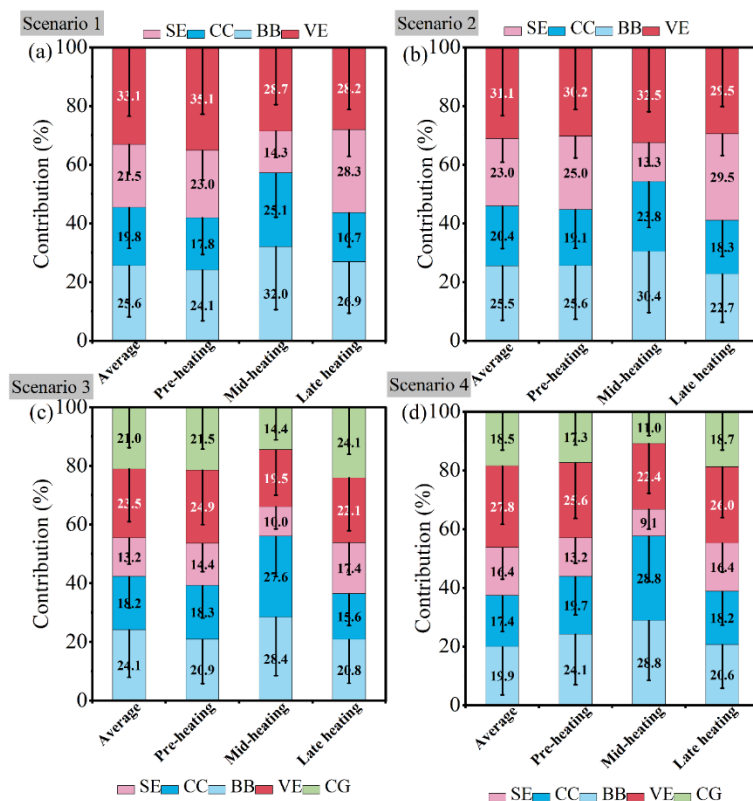


Figure 3 Comparison of fractional contributions of NO_3^- sources in $\text{PM}_{2.5}$ in Tianjin estimated by different $\delta^{15}\text{N}$ values of NO_x sources. The results of Scenario 1 and Scenario 3 were estimated using the $\delta^{15}\text{N}$ values of four and five NO_x sources obtained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

Question 7: Lines 444-454: The mixing model was run for different scenarios, with scenarios 3 and 4 using different $\delta^{15}\text{N}(\text{NO}_x)$ values of natural gas combustion (i.e., scenario 3 is the previous values from other study and 4 is the measured value in this study). After that, the author compared scenario 3 and 4 results from the mixing model (Line 431-448) and made a conclusion that natural gas combustion is important for NO_3^- formation in this area. This part lacks an explanation in drawing the conclusion. Please clarify why natural gas is important from the two scenario results even though they account for a smaller portion than the other sources.

Response 7: Thanks for the comment. We have further justified why it is important to consider natural gas combustion in the revised manuscript. On the one hand, the exclusion of natural gas combustion may directly result in the contribution fraction of other sources being overestimated by the model by more than 16%. On the other hand, the contribution of various NO_x sources was becoming more stable, and the inter-influence between various sources reduced when the natural gas combustion input was introduced into the MixSIAR model.

L510-545: In contrast to the findings of the four sources (Scenario 1 and Scenario 2), large discrepancies exist between Scenario 3 (Figure 3c) and Scenario 4 (Figure 3d). Especially the contribution fractions of natural gas combustion (Scenario 3: $21.0 \pm 13.8\%$, Scenario 4: $16.5 \pm$

11.5%) and coal combustion (Scenario 3: $18.2 \pm 10.7\%$, Scenario 4: $22.0 \pm 12.7\%$), the results estimated in Scenario 4 significantly differ from those in Scenario 3. These disparities are also present across different sampling periods. During pre-heating periods, contributions of vehicle exhaust (Scenario 3: $24.9 \pm 18.5\%$, Scenario 4: $25.6 \pm 19.0\%$) and biomass burning (Scenario 3: $20.9 \pm 15.1\%$, Scenario 4: $24.1 \pm 17.2\%$) were lower in Scenario 4 compared to Scenario 3. Conversely, natural gas combustion (Scenario 3: $21.5 \pm 14.3\%$, Scenario 4: $17.3 \pm 11.3\%$) and soil sources (Scenario 3: $14.4 \pm 9.7\%$, Scenario 4: $13.2 \pm 8.7\%$) estimates in Scenario 3 were higher than those in Scenario 4. Similar differences were observed during the mid-heating periods. However, in the late-heating periods, contributions of vehicle exhaust (Scenario 3: $22.1 \pm 18.0\%$, Scenario 4: $26.0 \pm 17.3\%$) and coal combustion (Scenario 3: $15.6 \pm 10.8\%$, Scenario 4: $18.2 \pm 11.6\%$) calculated in Scenario 4 was higher than those in Scenario 3. In addition, biomass burning (Scenario 3: $20.8 \pm 14.9\%$, Scenario 4: $20.6 \pm 14.9\%$), natural gas combustion (Scenario 3: $24.1 \pm 16.1\%$, Scenario 4: $18.7 \pm 13\%$) and soil sources (Scenario 3: $17.4 \pm 10.8\%$, Scenario 4: $16.4 \pm 9.9\%$) in Scenario 4 were lower than those in Scenario 3. In both scenarios, the contribution of natural gas combustion to NO_3^- was close to or even exceeds that of soil sources (Figure 3). This implies that the exclusion of natural gas combustion may directly result in the contribution fraction of other sources being overestimated by the model by more than 16%. 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. This underscores the need to consider natural gas combustion when assessing NO_3^- sources in $\text{PM}_{2.5}$, particularly in urban areas impacted by the Coal Replacement Project (Zhang et al., 2024; Lin et al., 2024). Consequently, our result further highlights that the natural gas combustion as a source input the model could improve the validity of the calculations to a certain extent. Additionally, measuring the $\delta^{15}\text{N}$ values of the local NO_x source is necessary to accurately identify the source of NO_3^- in $\text{PM}_{2.5}$.

Question 8: Lines 462-465: how is the $\delta^{15}\text{N}(\text{NO}_x)$ value from the iron and steel industry distinct from other sources? And why? In Figure 1, $\delta^{15}\text{N}(\text{NO}_x)$ from the industrial emission shows the largest range, encompassing all the values. Please clarify how you can differentiate this value from others.

Response 8: Thanks for the comment. Based on the LSD test, there was a significant difference between the various sources of $\delta^{15}\text{N}\text{-NO}_x$ signature (Figure S5). Generally, the combustion sources can produce both thermal and fuel NO_x . Thermal NO_x is generated at high temperatures exceeding 1500°C and is influenced by factors such as the molar concentrations of O_2 and N_2 and combustion temperature (Walters et al., 2015b). In contrast, fuel NO_x is primarily related to the nitrogen content of the fuel (Walters et al., 2015b). It should be noted that the raw materials of steel industry used for sintering were iron ore fines and coke powder, which differed from those used in coal combustion in power plants. Consequently, the $\delta^{15}\text{N}$ values of NO_x released cannot be considered to be the same source isotopic fingerprint, as they are influenced by differences in ^{15}N

abundance and combustion temperature (Heaton, 1990). There is an area of overlap between the $\delta^{15}\text{N-NO}_x$ data from industrial emissions and that from natural gas combustion (Figure). This is primarily attributable to the intricate and multifaceted mechanisms through which NO_x is produced by steel smelting apparatus or procedures. Overall, however, the mean $\delta^{15}\text{N-NO}_x$ value of industrial emissions was much higher than in natural gas combustion. This suggest that they are two independently existing source signal features. Of course, more work needs to be done in the future to explore in depth and refine the $\delta^{15}\text{N-NO}_x$ values from these sources.

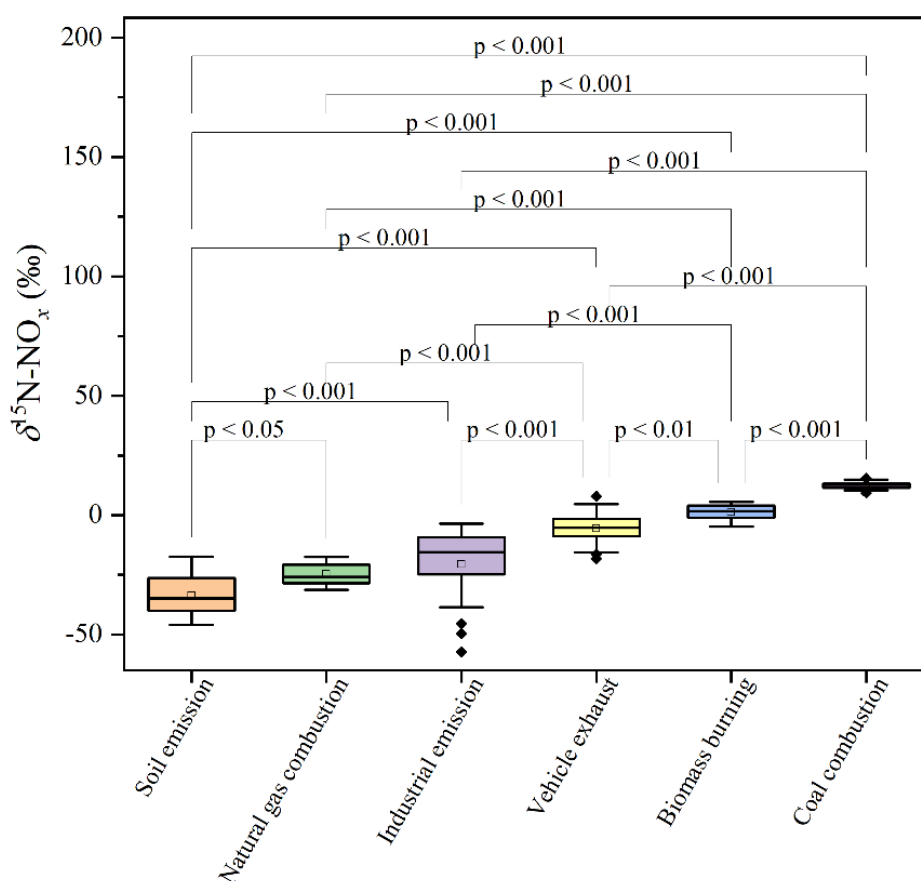


Figure S5 Comparison of the significance of differences between various sources of $\delta^{15}\text{N-NO}_x$ values. The p-values at the top of the rectangular boxes indicate significant differences between different data based on Fisher's least significant difference (LSD) test.

L283-306: NO_x emissions from industrial sources, such as the iron and steel industry, arise from various processes including sintering, pelletizing, and hot blast furnaces (Wang et al., 2019; Zhao et al., 2017). Generally, the $\delta^{15}\text{N-NO}_x$ value from industrial emission sources differs significantly from those of emissions from fossil fuel combustion (Figure S5), as indicated by the LSD test. This emphasizes the representativeness of the isotopic fingerprint in industrial emission sources. It should be noted, however, that there is an area of overlap between the $\delta^{15}\text{N-NO}_x$ data from industrial emissions and that from natural gas combustion (Figure S5). This is primarily attributable to the intricate and multifaceted mechanisms through which NO_x is produced by steel smelting apparatus or procedures. For instance, the $\delta^{15}\text{N}$ values of NO_x emitted from the hot blast furnace were -43.1 ± 12.3 ‰, in contrast to the more positive value observed for the sintering

process ($-14.5 \pm 3.2\%$) and the pelletizing process ($-6.4 \pm 2.5\%$) (Figure S6). The maximum temperature in the central area of the hot air stove can exceed 2000 °C, with the majority of emitted NO_x being thermal NO_x (Toof, 1986). Due to the continuous $^{14}\text{N}^{14}\text{N}$ supplementation, generated NO_x exhibits a negative $\delta^{15}\text{N}$. In contrast, the temperatures of sintering and pelletizing processes are relatively low (1200 ~ 1400 °C), with the majority of emitted NO_x being fuel-type NO_x (Toof, 1986). Specifically, functional groups such as pyrrole and pyridine in coke powder decompose at high temperatures and react with O_2 to produce NO_x , resulting in a positive value of $\delta^{15}\text{N-NO}_x$ (Hayhurst and Vince, 1980). It should be noted that the raw materials used for sintering were iron ore fines and coke powder, which differed from those used in coal combustion in power plants. Consequently, the $\delta^{15}\text{N}$ values of NO_x released cannot be considered to be the same source isotopic fingerprint, as they are influenced by differences in ^{15}N abundance (Heaton, 1990).

L553-559: Our investigation has revealed that the $\delta^{15}\text{N-NO}_x$ signature from the iron and steel industry is distinct from that of other sources, such as vehicle exhaust, coal combustion, and biomass burning (Figure S5). The discrepancy was primarily attributed to variations in the ^{15}N abundance of the fuel and the combustion technology employed, among other factors, as discussion can be found in section 3.1 in this study. Consequently, it is necessary to treat this source as a unique end-member in the apportionment of NO_3^- .

Question 9: Line 198: it was mentioned that the nitrogen isotope fractionation coefficient during NO_x to NO_3^- conversion is calculated in Text S2, but it is unclear how these calculations and final values are applied to the $\delta^{15}\text{N}$ values for the mixing model input.

Response 9: Thanks for the comment. we have added a discussion of isotope fractionation to the revised manuscript.

L410-438: As shown in Figure 2c, the $\delta^{18}\text{O-NO}_3^-$ 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 $\delta^{15}\text{N-NO}_3^-$ values, the most positive $\delta^{18}\text{O-NO}_3^-$ 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 $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$, 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 $\delta^{15}\text{N-NO}_3^-$ values in $\text{PM}_{2.5}$ does not fully reflect the initial $\delta^{15}\text{N-NO}_x$ due to the fractionation process between NO_x and NO_3^- (Fan et al., 2020; Song et al., 2019). Therefore, we calculated the initial $\delta^{15}\text{N-NO}_x$ 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 $\delta^{18}\text{O-NO}_3^-$ values of $\text{PM}_{2.5}$. Second, the corresponding ϵ_{N} 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 ϵ_{N} 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 ϵ_N 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 ϵ_N 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.

Minor comments:

Question 1: Line 2: Please make the subscript x for NO_x in the entire manuscript and supplementary.

Response 1: Thanks for the comment. The x for NO_x is all revised to subscripts in the entire manuscript and supplementary.

Question 2: Lines 42-44: Please check the sentence.

Response 2: Thanks for the comment. The sentence has been rewrite.

L41-44: A series of scientific and effective measures to control air pollutant emissions has resulted in a notable reduction in the concentration of SO_4^{2-} in $\text{PM}_{2.5}$ in urban areas of China (Wang et al., 2022).

Question 3: Lines 58-62: Please make clear these lines since however are repeated in every sentence.

Response 3: Thanks for the comment. These sentences have been rewrite.

L55-64: The reliable identification of the sources of NO_x in the atmosphere was achieved using the stable nitrogen isotopes composition ($\delta^{15}\text{N}$) (Zong et al., 2017; Song et al., 2021). Furthermore, to accurate identification of NO_3^- sources, it is essential to accurately identify the $\delta^{15}\text{N}$ values of the atmospheric NO_x source (Zhang et al., 2024; Lin et al., 2021). 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). However, these $\delta^{15}\text{N}$ values of NO_x in different sources mainly from foreign countries, and the collection methods have not been unified (Elliott et al., 2019; Walters et al., 2015a; Walters et al., 2015b), resulting in some variation in $\delta^{15}\text{N}$ values of NO_x from the same source.

Question 4: Lines 123-124: I would suggest adding a detailed site description in this part, including information on the population of Tianjin and its size, to provide a better understanding of the area.

Response 4: Thanks for the comment. We have added a detailed site description in this part in the revised manuscript.

L128-134: Tianjin is a representative megacity situated in the eastern portion of the North China Plain (Xiao et al., 2024). As of the end of 2018, the permanent population of Tianjin had reached

16 million, representing a growth rate of 27,300 compared to the previous year (National Bureau of Statistics of China, 2018). The city occupies an area of approximately 11,919.7 square kilometers, with agricultural land accounting for 6,921.4 of those square kilometers and arable land representing 4,367.6 square kilometers (National Bureau of Statistics of China, 2018).

Question 5: Lines 132-135: It would be helpful to mark the monitoring stations on the map.

Response 5: Thanks for the comment. We have added it. See in particular the lower right-hand panel in figure S1.

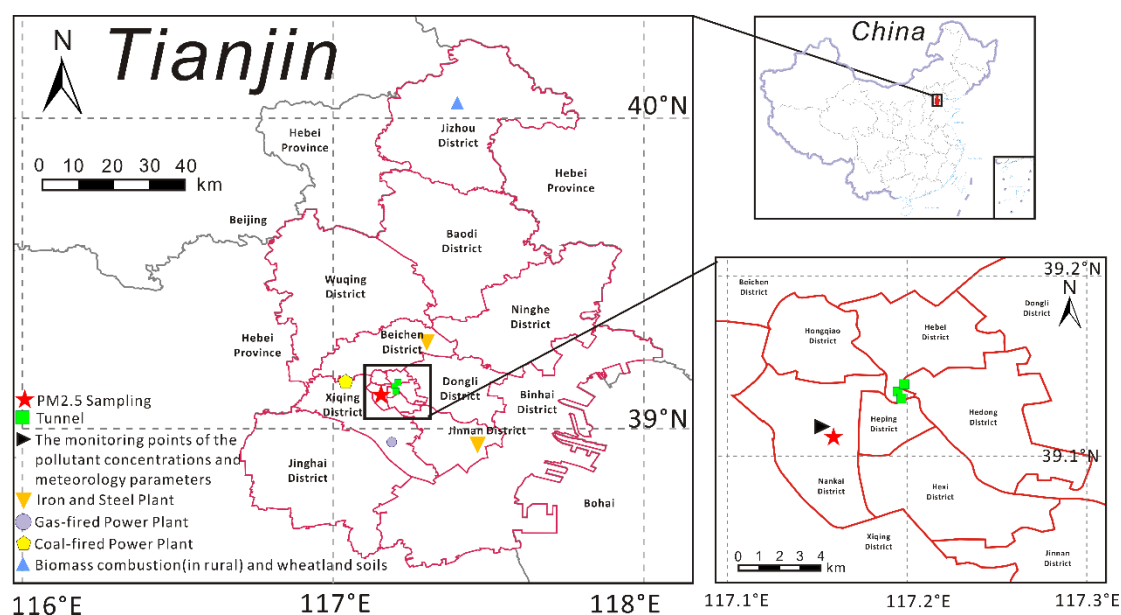


Figure S1 Map of PM_{2.5} and NO_x source sampling locations

Question 6: Line 430: Can you check if the figure number is correct? Can't find (d) in Figure 4.

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

Therefore, we refer to the $\delta^{15}\text{N-NO}_x$ end-member values from natural gas combustion obtained from previous studies (Scenario 3) and locally acquired in Tianjin (Scenario 4) to calculate the relative contribution fractions of the five NO_x sources using the MixSIAR model (Figure 3c and 3d).

Question 7: Lines 431-446: It is quite hard to compare which fraction values represent scenarios 3 and 4 in parentheses. Please clarify these values.

Response 7: Thanks for the comment. We apologize for the confusion caused by our oversight. We have improved this section in the revised manuscript.

L510-530: In contrast to the findings of the four sources (Scenario 1 and Scenario 2), large discrepancies exist between Scenario 3 (Figure 3c) and Scenario 4 (Figure 3d). Especially the contribution fractions of natural gas combustion (Scenario 3: $21.0 \pm 13.8\%$, Scenario 4: $16.5 \pm 11.5\%$) and coal combustion (Scenario 3: $18.2 \pm 10.7\%$, Scenario 4: $22.0 \pm 12.7\%$), the results

estimated in Scenario 4 significantly differ from those in Scenario 3. These disparities are also present across different sampling periods. During pre-heating periods, contributions of vehicle exhaust (Scenario 3: $24.9 \pm 18.5\%$, Scenario 4: $25.6 \pm 19.0\%$) and biomass burning (Scenario 3: $20.9 \pm 15.1\%$, Scenario 4: $24.1 \pm 17.2\%$) were lower in Scenario 4 compared to Scenario 3. Conversely, natural gas combustion (Scenario 3: $21.5 \pm 14.3\%$, Scenario 4: $17.3 \pm 11.3\%$) and soil sources (Scenario 3: $14.4 \pm 9.7\%$, Scenario 4: $13.2 \pm 8.7\%$) estimates in Scenario 3 were higher than those in Scenario 4. Similar differences were observed during the mid-heating periods. However, in the late-heating periods, contributions of vehicle exhaust (Scenario 3: $22.1 \pm 18.0\%$, Scenario 4: $26.0 \pm 17.3\%$) and coal combustion (Scenario 3: $15.6 \pm 10.8\%$, Scenario 4: $18.2 \pm 11.6\%$) calculated in Scenario 4 was higher than those in Scenario 3. In addition, biomass burning (Scenario 3: $20.8 \pm 14.9\%$, Scenario 4: $20.6 \pm 14.9\%$), natural gas combustion (Scenario 3: $24.1 \pm 16.1\%$, Scenario 4: $18.7 \pm 13\%$) and soil sources (Scenario 3: $17.4 \pm 10.8\%$, Scenario 4: $16.4 \pm 9.9\%$) in Scenario 4 were lower than those in Scenario 3. In both scenarios, the contribution of natural gas combustion to NO_3^- was close to or even exceeds that of soil sources (Figure 3).

Question 8: Line 524: What does mean “these two sources”? Please clarify this.

Response 8: Thanks for the comment. These two sources are coal combustion and biomass combustion, which we have clarified in the revised manuscript.

L617-619: Additionally, the contributions of **coal combustion and biomass burning** were higher during pre-heating compared to late-heating periods, when six sources were considered in the MixSIAR model.

Question 9: Lines 902-905: the description of IE is missing in the caption.

Response 9: Thanks for the comment. The description of IE is industrial emissions, the description has been added in the revised manuscript.

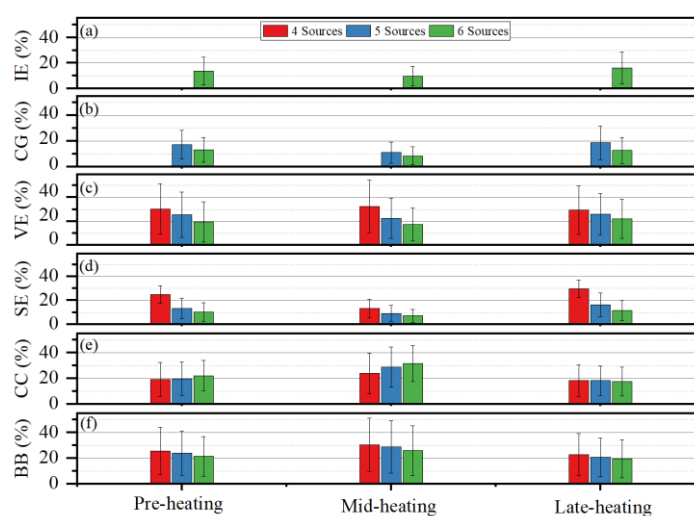


Figure 5 The contribution fraction of the four, five, and six sources in different periods estimated by the isotopic fingerprint in NO_x sources obtained from this study. Also, **IE = Industrial emissions**, SE = soil emission, CC = coal combustion, BB = biomass burning, VE = vehicle

emission, and CG = combustion of natural gas.

Question 10: *Figure 6: (a) and (b) appear to be repetitive of Fig 5. Please revise to avoid redundancy.*

Response 10: Thanks for the comment. Although some of the results in Figures 6a and 6b have been shown in Figure 5. However, the results in Figs. 6a and 6b are meant to be compared with the concentrations of K^+ and Cl^- to further illustrate the reliability of our results. Therefore, we did not remove Figures 6a and 6b.

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