

## Response to Referee #1

RC- Reviewer's Comments; AC – Authors' Response Comments

RC1: The manuscript by Li et al. simultaneously reported concentrations and stable nitrogen isotope and oxygen isotopes compositions of atmospheric  $\text{NO}_3^-$  and concentrations and nitrogen isotopes compositions of atmospheric  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  samples collected in Guangzhou from May 2017 to June 2018. Then, authors restrained nitrogen isotope fractionation values of the process of  $\text{NH}_3$  to formed  $\text{NH}_4^+$  and  $\text{NO}_x$  to formed  $\text{NO}_3^-$ . Finally, using the IsoSource model, authors quantified the relative contributions of major sources of  $\text{NH}_3$  and  $\text{NO}_x$  to atmospheric  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , respectively. Authors found the focus of  $\text{NH}_3$  reduction should be on anthropogenic combustion sources especially on biomass burning, which might be responsible for the lag of the decline in deposition of air pollutions behind the reduction in emission. Additionally, despite a series of measures to reduce emissions of  $\text{NO}_x$ , fossil fuels, as the main energy for production and living, will still inevitably emit a large amount of  $\text{NO}_x$ . Authors emphasized that the emission of atmospheric inorganic nitrogen is largely related to anthropogenic combustion sources. The development and promotion of clean energy and efficient use of biomass are conducive to the deep reduction of atmospheric nitrogen. I believe that this result is meaningful and would make a substantial contribution to the field. The manuscript is generally well-organized in structure. If the following comments are adequately addressed, I believe the manuscript could be accepted to Atmospheric Chemistry and Physics.

AC1: We appreciate your constructive comments and professional suggestions. These comments and suggestions are helpful for improving our manuscript. Based on your comments and suggestions, we have revised our manuscript. If you have any further comments and suggestions, we will do our best to improve our manuscript.

We would like to show the details as follows:

RC2: Lines 112-113: The author needs to provide the analytical accuracy of isotopes nitrogen and oxygen isotopes.

AC2: Thanks for your suggestion. We have added details on the accuracy of nitrogen and oxygen isotope analysis, as shown in the marked revised manuscript **lines 120-127**: To ensure the stability of the instrument, standard samples were tested for every ten samples. The standard deviation of replicates was generally less than 0.4‰, 0.8‰, and 0.5‰ for  $\delta^{15}\text{N-NO}_3^-$ ,  $\delta^{18}\text{O-NO}_3^-$ , and  $\delta^{15}\text{N-NH}_4^+$ , respectively. The instrumental values of  $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{18}\text{O-NO}_3^-$  were corrected by multi-point correction ( $\delta^{18}\text{O}$   $r^2=0.99$ ,  $\delta^{15}\text{N}$   $r^2=0.999$ ) based on international standards (IAEA-NO-3, USGS32, USGS34, and USGS35). The measured values of  $\delta^{15}\text{N-NH}_4^+$  were also corrected by multi-point correction ( $r^2=0.999$ ) based on international standards (IAEA-N1, USGS25, and USGS26).

RC3: Nitrogen isotope fractionation values of the process of  $\text{NH}_3$  to formed  $\text{NH}_4^+$  and  $\text{NO}_x$  to formed  $\text{NO}_3^-$  are key parameters for quantifying the relative contributions of major sources of  $\text{NH}_3$  and  $\text{NO}_x$  to atmospheric  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . The calculation methods for the two parameters should be include in the text of manuscript. In addition, it is necessary to give readers detailed data of each parameter, especially the fractionation value.

AC3: Thanks for your professional comment and kind suggestion.

**a. Nitrogen isotope fractionation values of the process of  $\text{NH}_3$  to form  $\text{NH}_4^+$ .**

Atmospheric initial  $\delta^{15}\text{N-NH}_3$  was calculated by following equation 1.

$$\delta^{15}\text{N-NH}_{3\text{-initial}} = \delta^{15}\text{N-NH}_4^+ - \varepsilon(\text{NH}_4^+ - \text{NH}_3) \times (1 - f) \quad (1)$$

Where,  $\delta^{15}\text{N-NH}_4^+$  and  $\delta^{15}\text{N-NH}_{3\text{-initial}}$  represent the  $\delta^{15}\text{N}$  of particulate  $\text{NH}_4^+$  and atmospheric initial  $\text{NH}_3$ , respectively.  $\varepsilon(\text{NH}_4^+ - \text{NH}_3)$  represents the isotope fractionation factor in the gaseous  $\text{NH}_3$  conversion to particulate  $\text{NH}_4^+$  in the atmosphere. The  $f$  value represents the proportion of the initial  $\text{NH}_3$  converted to  $\text{NH}_4^+$ , referring to  $\text{NH}_3$  and  $\text{NH}_4^+$  observed in Guangzhou (Liao et al., 2014).

The  $\varepsilon(\text{NH}_4^+ - \text{NH}_3)$  value is temperature dependent(Huang et al., 2019), which can

be deduced from(Urey, 1947), as shown in equation 2. The atmospheric average temperature was 24.5°C in our sampling period, and the corresponding  $\epsilon(\text{NH}_4^+-\text{NH}_3)$  value was 34.2‰ calculated by equation 2. In addition, the  $\epsilon(\text{NH}_4^+-\text{NH}_3)$  in Guangzhou was estimated to be 32.4‰ according to equation 6. Equation 6 was deduced by equations 3-5. According to equation 6, a linear fitting equation was observed between  $f\text{NH}_4^+$  and  $\delta^{15}\text{N}-\text{NH}_4^+$  (**Referee#1\_Figure 1**), and the absolute value of the slope (32.4‰) was equal to  $\epsilon(\text{NH}_4^+-\text{NH}_3)$ . The  $\epsilon(\text{NH}_4^+-\text{NH}_3)$  average of the two methods (34.2‰ and 32.4‰) was 33.3‰ and approximated to the experimental isotope enrichment factor (33‰)(Heaton et al., 1997). Therefore, +33‰ was used for deducing the  $\delta^{15}\text{N}$  of the initial  $\text{NH}_3$ . We have added the calculation process to manuscript. Please see **lines 137-162** in the marked revised manuscript.

$$\epsilon_{(\text{NH}_4^+-\text{NH}_3)} = 12.4678 * \frac{1000}{T+273.15} - 7.6694 \quad (2)$$

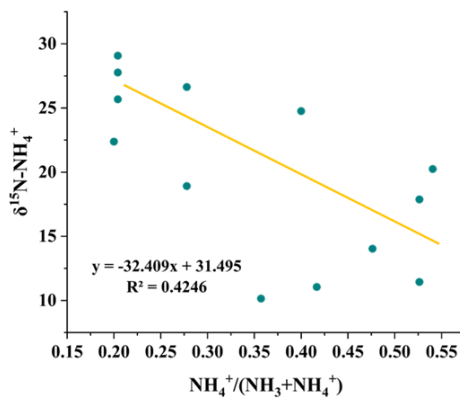
$$\delta^{15}\text{N}-\text{NH}_4^+ - \delta^{15}\text{N}-\text{NH}_3 = \epsilon_{(\text{NH}_4^+-\text{NH}_3)} \quad (3)$$

$$f\text{NH}_4^+ + f\text{NH}_3 = 1 \quad (4)$$

$$\delta^{15}\text{N}-\text{NH}_4^+ * f\text{NH}_4^+ + (\delta^{15}\text{N}-\text{NH}_4^+ - \epsilon_{(\text{NH}_4^+-\text{NH}_3)}) * (1 - f\text{NH}_4^+) = \delta^{15}\text{N} \quad (5)$$

$$\delta^{15}\text{N}-\text{NH}_4^+ = -\epsilon_{(\text{NH}_4^+-\text{NH}_3)} * f\text{NH}_4^+ + (\delta^{15}\text{N} + \epsilon_{(\text{NH}_4^+-\text{NH}_3)}) \quad (6)$$

Where, T represents the atmospheric temperature (°C).  $\delta^{15}\text{N}-\text{NH}_4^+$  and  $\delta^{15}\text{N}-\text{NH}_3$  represent the  $\delta^{15}\text{N}$  of particulate  $\text{NH}_4^+$  and atmospheric  $\text{NH}_3$ , respectively.  $\delta^{15}\text{N}$  represents the sum of  $\delta^{15}\text{N}-\text{NH}_4^+$  and  $\delta^{15}\text{N}-\text{NH}_3$ .  $f\text{NH}_3$  and  $f\text{NH}_4^+$  represent the proportion of atmospheric  $\text{NH}_3$  and particulate  $\text{NH}_4^+$ , respectively.

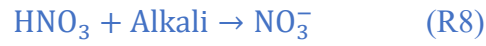
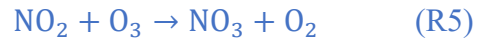


**Referee#1\_Figure 1 (Figure S1 in SI).** Linear fitting of  $\text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$  with  $\delta^{15}\text{N}-$

NH<sub>4</sub><sup>+</sup>.

## b. Nitrogen isotope fractionation values of the process of NO<sub>x</sub> to form NO<sub>3</sub><sup>-</sup>

In Central Pearl River Delta, NO<sub>3</sub><sup>-</sup> formed through ·OH and N<sub>2</sub>O<sub>5</sub> pathways contributed to 94% simulated by CAMQ model (Qu et al., 2021). In this study, only ·OH (R4) and N<sub>2</sub>O<sub>5</sub> (R5-R7) formation pathways were considered. The reasons why we only consider the ·OH oxidation and N<sub>2</sub>O<sub>5</sub> hydrolysis pathway to form NO<sub>3</sub><sup>-</sup> were explained in detail in the AC7.



The specific details of the Bayesian mixing model were reported by our previous studies (Zong et al., 2017; Zong et al., 2020). The principle and process of Bayesian mixing model was shown in **Referee#1\_Figure 2** adapted from Zong et al., (Zong et al., 2017). The atmospheric δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> can be expressed by equation 7. The [δ<sup>18</sup>O-HNO<sub>3</sub>]<sub>OH</sub> can be further expressed by equation 8 assuming no kinetic isotope fractionation (Walters and Michalski, 2016). And [δ<sup>18</sup>O-HNO<sub>3</sub>]<sub>H<sub>2</sub>O</sub> can be estimated by equation 9 (Walters and Michalski, 2016). The δ<sup>18</sup>O values in tropospheric H<sub>2</sub>O, NO<sub>x</sub>, O<sub>3</sub>, and OH were within a certain range. The tropospheric δ<sup>18</sup>O-H<sub>2</sub>O, δ<sup>18</sup>O-NO<sub>x</sub>, δ<sup>18</sup>O-O<sub>3</sub>, and δ<sup>18</sup>O-OH ranged from -25‰ to 0‰(Baskaran et al., 2011; Walters and Michalski, 2016), 112‰ to 122‰ (Michalski et al., 2014; Walters and Michalski, 2016), 90‰ to 122‰, and -15‰ to 0‰, respectively(Fang et al., 2011; Johnston and Thiemens, 1997). Therefore, the γ (the contribution of ·OH formation pathway) can be estimated by *f*NO<sub>2</sub> and oxygen isotope fractionation i.e., αNO<sub>2</sub>/NO, αOH/H<sub>2</sub>O, and αN<sub>2</sub>O<sub>5</sub>/NO<sub>2</sub>. The oxygen isotope fractionations are temperature dependent and can be estimated by equation 11. The *f*NO<sub>2</sub> varied from 0.20 to 0.95(Zong et al., 2017; Walters et al., 2016).

Based on  $\delta^{18}\text{O-NO}_3^-$ ,  $\delta^{18}\text{O-H}_2\text{O}$ ,  $\delta^{18}\text{O-NO}_x$ ,  $\delta^{18}\text{O-O}_3$ , and temperature (equations 7-11, **Referee#1\_Table 1**),  $\gamma$  (maximum  $\gamma$  and minimum  $\gamma$ ) was estimated by Monte Carlo simulation nested in Bayesian mixing model (Zong et al., 2017). Assuming no kinetic isotope fractionation, the nitrogen isotope fractionation value in the formation process of  $\text{NO}_3^-$  ( $\epsilon\text{N}$ ) was calculated by equations 11-14 combined with  $\gamma$  and temperature (Zong et al., 2017; Walters and Michalski, 2016; Walters et al., 2016). The  $\epsilon\text{N}$  value in our sampling period was  $5.1\pm 2.5\%$ , which was comparable to that in Beijing (average  $6.5\%$ ) (Fan et al., 2020). The contributions of different sources to atmospheric  $\text{NO}_x$  were quantified by Bayesian mixing model coupled with  $\epsilon\text{N}$ ,  $\delta^{15}\text{N-atmospheric-NO}_3^-$ , and  $\delta^{15}\text{N-NO}_x$  endmembers. We have added the methods in the marked revised manuscript, **lines 169-211**.

$$\delta^{18}\text{O-NO}_3^- = \gamma \times [\delta^{18}\text{O-NO}_3^-]_{\text{OH}} + (1 - \gamma) \times [\delta^{18}\text{O-NO}_3^-]_{\text{H}_2\text{O}} = \gamma \times [\delta^{18}\text{O-HNO}_3]_{\text{OH}} + (1 - \gamma) \times [\delta^{18}\text{O-HNO}_3]_{\text{H}_2\text{O}} \quad (7)$$

$$[\delta^{18}\text{O-HNO}_3]_{\text{OH}} = \frac{2}{3} [(\delta^{18}\text{O-NO}_2)]_{\text{OH}} + \frac{1}{3} [\delta^{18}\text{O-OH}]_{\text{OH}} = \frac{2}{3} \left[ \frac{1000 \times ({}^{18}\alpha_{\text{NO}_2/\text{NO}} - 1)(1 - f_{\text{NO}_2})}{(1 - f_{\text{NO}_2}) + ({}^{18}\alpha_{\text{NO}_2/\text{NO}} \times f_{\text{NO}_2})} + [\delta^{18}\text{O-NO}_x] \right] + \frac{1}{3} [(\delta^{18}\text{O-H}_2\text{O}) + 1000 \times ({}^{18}\alpha_{\text{OH}/\text{H}_2\text{O}} - 1)] \quad (8)$$

$$[\delta^{18}\text{O-HNO}_3]_{\text{H}_2\text{O}} = \frac{5}{6} (\delta^{18}\text{O-N}_2\text{O}_5) + \frac{1}{6} (\delta^{18}\text{O-H}_2\text{O}) \quad (9)$$

$$\delta^{18}\text{O-N}_2\text{O}_5 = \delta^{18}\text{O-NO}_2 + 1000 \times ({}^{18}\alpha_{\text{N}_2\text{O}_5/\text{NO}_2} - 1) \quad (10)$$

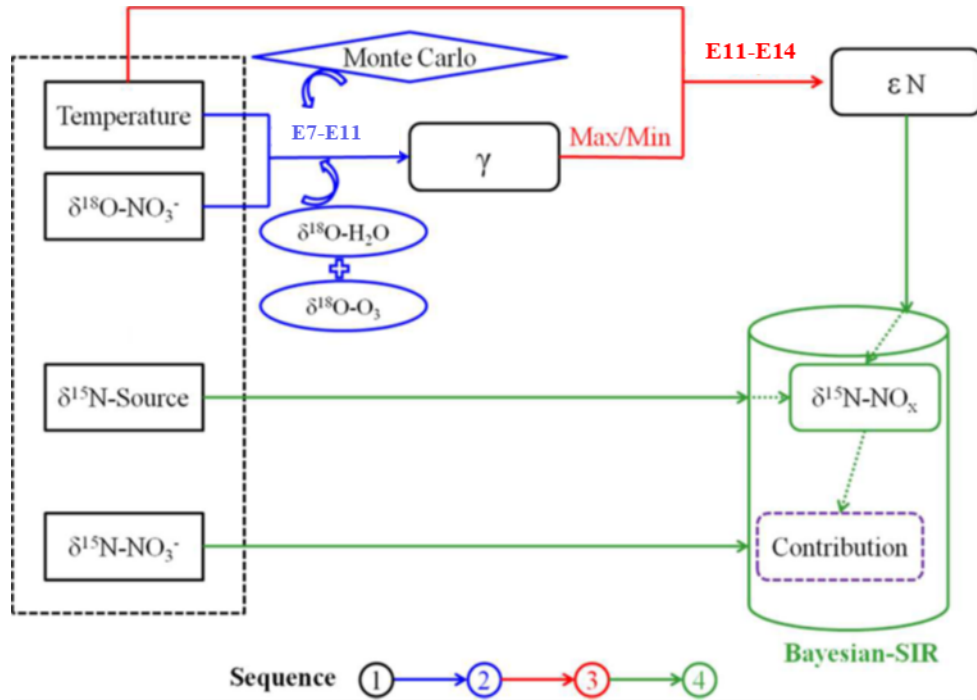
$$1000({}^m\alpha_{X/Y} - 1) = \frac{A}{T^4} \times 10^{10} + \frac{B}{T^3} \times 10^8 + \frac{C}{T^2} \times 10^6 + \frac{D}{T} \times 10^4 \quad (11)$$

$$\begin{aligned} \epsilon\text{N} &= \gamma \times \epsilon(\delta^{15}\text{N-NO}_3^-)_{\text{OH}} + (1 - \gamma) \times \epsilon(\delta^{15}\text{N-NO}_3^-)_{\text{H}_2\text{O}} \\ &= \gamma \times \epsilon(\delta^{15}\text{N-HNO}_3)_{\text{OH}} + (1 - \gamma) \times \epsilon(\delta^{15}\text{N-HNO}_3)_{\text{H}_2\text{O}} \end{aligned} \quad (12)$$

$$\epsilon(\delta^{15}\text{N-HNO}_3)_{\text{OH}} = \epsilon(\delta^{15}\text{N-NO}_2)_{\text{OH}} = 1000 \times \left[ \frac{({}^{15}\alpha_{\text{NO}_2/\text{NO}} - 1)(1 - f_{\text{NO}_2})}{(1 - f_{\text{NO}_2}) + ({}^{15}\alpha_{\text{NO}_2/\text{NO}} \times f_{\text{NO}_2})} \right] \quad (13)$$

$$\epsilon(\delta^{15}\text{N-HNO}_3)_{\text{H}_2\text{O}} = \epsilon(\delta^{15}\text{N-N}_2\text{O}_5)_{\text{H}_2\text{O}} = 1000 \times ({}^{15}\alpha_{\text{N}_2\text{O}_5/\text{NO}_2} - 1) \quad (14)$$

Where,  $\gamma$  is the contribution of  $\cdot\text{OH}$  formation pathway to  $\text{NO}_3^-$ ,  $\epsilon\text{N}$  is the nitrogen isotope fractionation value.  $f\text{NO}_2$  is the fraction of  $\text{NO}_2$  in the total  $\text{NO}_x$ .  $^{18}\alpha\text{NO}_2/\text{NO}$ ,  $^{18}\alpha\text{OH}/\text{H}_2\text{O}$ ,  $^{18}\alpha\text{N}_2\text{O}_5/\text{NO}_2$  are the oxygen isotope equilibrium fractionation factors between  $\text{NO}_2$  and  $\text{NO}$ ,  $\cdot\text{OH}$  and  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}_5$  and  $\text{NO}_2$ , respectively.  $^{15}\alpha\text{NO}_2/\text{NO}$  and  $^{15}\alpha\text{N}_2\text{O}_5/\text{NO}_2$  are the nitrogen isotope equilibrium fractionation factor between  $\text{NO}_2$  and  $\text{NO}$ ,  $\text{N}_2\text{O}_5$  and  $\text{NO}_2$ , respectively.



**Referee#1\_Figure 2.** Principle and process of Bayesian mixing model in this study, the “E” represents equation in the following section, “ $\epsilon\text{N}$ ” refers to N fractionation, and “SIR” is “sampling-importance-resampling”(Zong et al., 2017).

**Referee#1\_Table 1 (Table S1 in SI).** Test constants of A, B, C, and D over the settled temperature range of 150–450K(Zong et al., 2017; Walters and Michalski, 2016; Walters and Michalski, 2015; Walters et al., 2016).

$^{m}\alpha_{X/Y}$	A	B	C	D
$^{15}\text{NO}_2/\text{NO}$	3.8834	-7.7299	6.0101	-0.17928
$^{15}\text{N}_2\text{O}_5/\text{NO}_2$	0.69398	-1.9859	2.3876	0.16308
$^{18}\text{NO}/\text{NO}_2$	-0.04129	1.1605	-1.8829	0.74723
$^{18}\text{H}_2\text{O}/\text{OH}$	2.1137	-3.8026	2.5653	0.59410

RC4: Authors should explain why these four sources are selected as main sources of atmospheric  $\text{NO}_3^-$  and these six sources are selected as main sources of atmospheric  $\text{NH}_4^+$ ?

AC4: Thanks for your comment. The following was the explanation for our selection of sources of atmospheric  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . We have also added the explanations in **SI Text S2**.

a. We considered coal combustion, mobile traffic sources, biomass burning, and soil microbial activity as dominant atmospheric NOx sources. Based on bottom-up emission inventory, power plant, industry, residential use, and transportation were the traditional NOx emission sources in cities in China, including Guangzhou (Liu et al., 2017). According to the type of fuel combustion, traditional sources of NOx could be roughly divided into coal combustion (power plant, industry, and residential use) and mobile sources (transportation including vehicle exhaust and ship emission). Furthermore, recent studies show that biomass burning is an essential source of NOx based on emission factor study (Mehmood et al., 2017) and isotopic evidence (Zong et al., 2020). Microbial process emission is another important source of NOx, in which nitrification or denitrification microbial bacteria widely distributed in soils consume accumulated nitrogen and release NO as a byproduct (Hall and Matson, 1996; Jaeglé et al., 2004). The cultivated land with extensive use of nitrogen fertilizer in the suburbs around Guangzhou is also an important source of NOx, which is named as microbial process in this study.  $\delta^{15}\text{N}$ -NOx values differed significantly among these four sources, which allows us to differentiate their relative contributions to the mixture of atmospheric. We did not consider  $\text{NO}_3^-$  from lightning because it accounts for less than 5% of global terrestrial NOx emissions (Song et al., 2021; Qu et al., 2020; Pickering et al., 2016).

b. There are two major groups of atmospheric  $\text{NH}_3$  emission sources (Chen et al., 2022). One is  $\text{NH}_3$  volatilization from  $\text{NH}_4^+$ -containing substrates (mainly fertilized and natural soils, livestock, human wastes, and natural and N-polluted water). Although Guangzhou is an urban site, the emission inventory results showed a high contribution of nitrogen fertilizers application and livestock to atmospheric  $\text{NH}_3$  (Zheng et al., 2012),

which may be influenced by agricultural activities around Guangzhou. Human waste is also an important contributor to  $\text{NH}_3$  in cities, as suggested by a study in Shanghai (Chang et al., 2015). Guangzhou is one of China's megacities with a dense population, so the contribution of human waste to atmospheric  $\text{NH}_3$  in Guangzhou cannot be ignored. Therefore, nitrogen fertilizers application, livestock, and human waste were considered as sources of volatilization  $\text{NH}_3$  in this study. In addition, the other group is  $\text{NH}_3$  associated with combustion sources (such as coal burning, vehicles, and biomass burning). The contribution of biomass burning and coal combustion to  $\text{NH}_3$  was very high (about 76.3%) in developing countries, suggested by the global high-resolution emissions inventory (Meng et al., 2017).  $\text{NH}_3$  in Chinese cities was indeed influenced by coal and biomass combustion evidenced by isotopes (Xiao et al., 2020; Liu et al., 2018; Pan et al., 2018). Selective catalytic reduction technology equipped with vehicles and industrial boiler is also an important source of  $\text{NH}_3$  (Meng et al., 2017). With the rapid increase in vehicle ownership, vehicle emission has a significant impact on urban  $\text{NH}_3$ , which was confirmed by tunnel tests in Guangzhou (Liu et al., 2014). Therefore, biomass burning, coal combustion, and vehicles were considered as sources of combustion  $\text{NH}_3$  in this study.

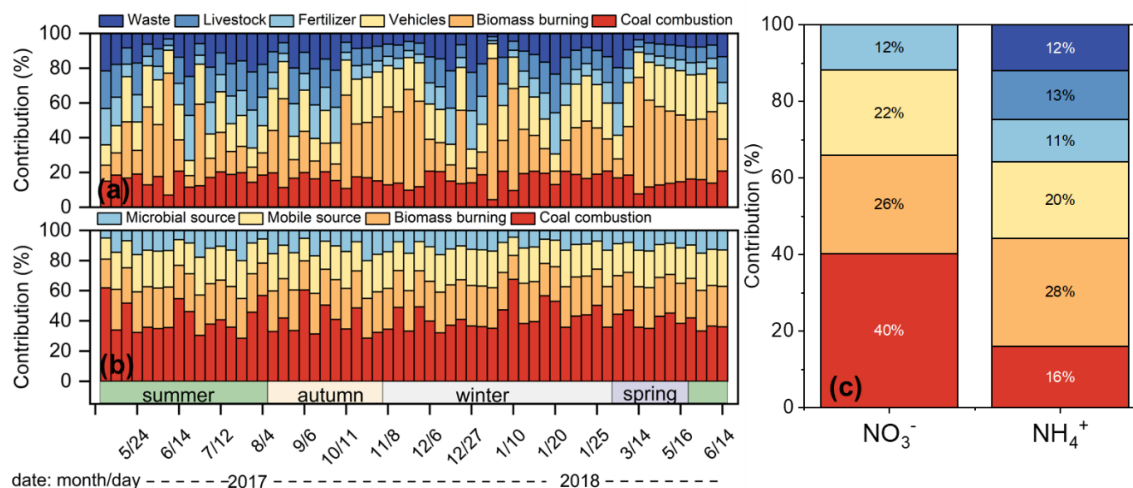
RC5: Lines 176-178: Does the combustion of sugarcane leaf emit  $\text{NH}_4^+$  directly or emit  $\text{NH}_3$  and then formed  $\text{NH}_4^+$ ?

AC5: We have no field measurements of smoke and particulate matter released by sugarcane burning. Gases such as  $\text{NH}_3$ ,  $\text{NO}_x$ , and HCN can be released during biomass burning (Zhou et al., 2006; Stubenberger et al., 2008). Therefore, we speculate that  $\text{NH}_3$  was released directly from the burning of sugarcane leaves, and then converted into  $\text{NH}_4^+$  by atmospheric aging. Now, we have rewritten lines 176-178. The new sentence was shown in the marked manuscript **lines 267-269**: The  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  formed from  $\text{NH}_3$  released by sugarcane leaves burning was 44.1‰ (SI Text S3), which was consistent with the highest  $\delta^{15}\text{N-NH}_4^+$  values (45.5‰ and 45.1‰) in July.



RC6: Lines 236-237: The sources apportionment results of atmospheric  $\text{NO}_3^-$  in Figure c does not correspond to that in Figure b.

AC6: We are sorry for making this mistake. Thanks for your reminding. The colors in Figure 2a and 2b do not match the previous colors in Figure 2c. Now, we have corrected this error as shown below and in the marked manuscript, **line 329**.



**Referee#1\_Figure 3 (Figure 2 in manuscript).** The sources apportionment results of atmospheric  $\text{NH}_4^+$  (a) and  $\text{NO}_3^-$  (b) in Guangzhou, and the comparison of sources results between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (c).

RC7: Lines 272-273: Why does the author only consider the OH radical oxidation and  $\text{N}_2\text{O}_5$  hydrolysis pathway to  $\text{NO}_3^-$ , and not consider other pathways? The author needs to explain.

AC7: Thanks for your comment and suggestion.

There are several major formation pathways of  $\text{NO}_3^-$ .

P1 ( $\text{NO}_2 + \cdot\text{OH}$ ),  $\text{NO}_2$  is oxidized by  $\cdot\text{OH}$  to form  $\text{HNO}_3$ , then reacts with alkaline substances (such as  $\text{NH}_3$ ) to form  $\text{NO}_3^-$ .

P2 ( $\text{N}_2\text{O}_5$ ),  $\text{NO}_2$  is oxidized by  $\text{O}_3$  to form  $\cdot\text{NO}_3$ ,  $\cdot\text{NO}_3$  reacts with  $\text{NO}_2$  to form  $\text{N}_2\text{O}_5$ , then the hydrolysis of  $\text{N}_2\text{O}_5$  on aerosol surfaces produces  $\text{NO}_3^-$ .

P3 ( $\cdot\text{NO}_3 + \text{org}$ ), the  $\text{NO}_2$  is oxidized by  $\text{O}_3$  to form  $\cdot\text{NO}_3$ , then the  $\cdot\text{NO}_3$  reacts with organic, such as dimethyl sulfide (DMS) or hydrocarbons (HC) to form  $\text{HNO}_3$ , and then  $\text{NO}_3^-$ .

P4( $\cdot\text{NO}_3+\cdot\text{HO}_2$ ),  $\text{NO}_2$  is oxidized by  $\text{O}_3$  to form  $\cdot\text{NO}_3$ ,  $\cdot\text{NO}_3$  reacts with  $\cdot\text{HO}_2$  to form  $\text{HNO}_3$ .

The P1 ( $\cdot\text{OH}$ ) and P2 ( $\text{N}_2\text{O}_5$ ) pathways are dominant formation pathways. Song reported that  $\cdot\text{OH}$  and  $\text{N}_2\text{O}_5$  pathways contributed 43% and 32% to  $\text{NO}_3^-$ , respectively, by isotope tracing (Song et al., 2021). Based on isotopic estimates, the contribution of  $\cdot\text{NO}_3+\text{org}$  to  $\text{NO}_3^-$  was relatively high, e.g., about 16% in Beijing (Song et al., 2021). However, the proportion of  $\cdot\text{NO}_3+\text{org}$  estimated by the Community Multiscale Air Quality (CAMQ) model was very low in the YRD (Sun et al., 2022) and PRD (Qu et al., 2021), especially in Guangzhou (central PRD) where it is only 4% (Qu et al., 2021). The  $\cdot\text{OH}$  and  $\text{N}_2\text{O}_5$  were the dominant pathways and contributed 94% to  $\text{NO}_3^-$  in Guangzhou (Qu et al., 2021). We speculate that the different contribution of  $\cdot\text{NO}_3+\text{org}$  pathway between Guangzhou and Beijing may be caused by the difference in atmospheric oxidation. The ozone pollution is serious in Guangzhou due to a unique synoptic system including the surface high-pressure system, hurricane movement, and sea-land breeze (Tan et al., 2019). And the atmospheric  $\cdot\text{OH}$  reactivity in Guangzhou was higher than in several cities, including Beijing (Tan et al., 2019). Take DMS as an example, the main oxidant of DMS is  $\cdot\text{OH}$  (Andreae and Crutzen, 1997). However, in the cold season or remote regions, the  $\cdot\text{NO}_3$  radical can also play an important role in reaction with DMS (addition reaction and hydrogen abstraction) (Andreae and Crutzen, 1997; Yin et al., 1990). The high reactivity of  $\cdot\text{OH}$  may reduce the contribution of  $\cdot\text{NO}_3$  to DMS in Guangzhou due to the competition between  $\cdot\text{OH}$  and  $\cdot\text{NO}_3$  to react with DMS. Therefore, the contribution of  $\cdot\text{NO}_3+\text{org}$  to  $\text{NO}_3^-$  was relatively low. In addition, the  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  formed by the  $\text{N}_2\text{O}_5$  and  $\cdot\text{NO}_3+\text{org}$  pathway is similar (Walters and Michalski, 2016). The introduction of the  $\cdot\text{NO}_3+\text{org}$  pathway would greatly increase the uncertainty of the contribution of  $\text{N}_2\text{O}_5$  pathways. While the  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  formed by the  $\cdot\text{OH}$  and  $\text{N}_2\text{O}_5$  pathway differ significantly, which allows to differentiate their relative contributions to  $\text{NO}_3^-$ . Therefore, we only considered the  $\cdot\text{OH}$  and  $\text{N}_2\text{O}_5$  pathways in this study. We have also added the explanation in **SI text S2**.

## References:

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