Response to Referee #2

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

RC1: This paper estimated the relative contributions of main sources to ammonium and nitrate aerosols in a subtropical megacity of South China using stable N isotope analysis. They found that anthropogenic activities (e.g., coal combustion, biomass burning and vehicle exhaust) are important sources and should be considered seriously in future for the improvement of air quality. In my opinion, few studies simultaneously reported 15N signatures for both NH_4^+ and NO_3^- and I think this one-year dataset is valuable and probably will improve our knowledge on the sources of air pollution. I support its publication after some minor revisions.

AC1: Thanks for your recognition of our work and for providing professional comments and valuable suggestions. These comments and suggestions are valuable and helpful for improving our manuscript. We have made revisions based on these comments (The detailed corrections are marked in the revised manuscript). If you have any further comments and suggestions, we will try our best to improve our manuscript.

RC2: Line 66-68: The dominant source of atmospheric NH_3 highly depends on the scale of study area. For example, the dominant emitter of NH_3 in the whole China should be the agricultural source; while the dominant emitter may be the vehicular emission for a city site. Therefore, cautions need to be taken when you describe this sentence.

AC2: Thanks for your professional comments. We agree with you that the dominant emitter of NH_3 in the whole China should be the agricultural source; while the dominant emitter may be the vehicular emission for a city site. In addition, there is a potential impact of biomass burning in suburban areas on urban NH_3. In general, biomass burning activity increases during autumn in Central China. Xiao et al. found that biomass burning contributed 34.5 ± 20.4%, 46.4 ± 21.4%, and 40.4 ± 17.4% to NH_4^+ for three urban sites Nanchang, Wuhan, and Changsha, respectively, during autumn(Xiao et al., 2020). The combustion sources in Lines 66-68 represent coal combustion, vehicle emission, and biomass burning. Now, we have rewritten this sentence, as shown in the marked revised manuscript **lines 75-78**: Biomass burning in the suburbs also has a potential impact on urban NH_3(Xiao et al., 2020). As for urban NH_3, combustion sources (including coal combustion, vehicles emission, and biomass burning) were gradually becoming dominant sources in recent years verified by δ^{15}N-NHx (NH_3+NH_4^+)(Xiao et al., 2020; Pan et al., 2018).

RC3: Line 122-126: Many δ^{15}N-NH_3 endmembers of sources were collected by passive samplers. Did you correct these values when you conducted the source apportionment? Also, the endmembers and source numbers are important parameters for δ^{15}N-derived source apportionment model and I suggest you add these in the main manuscript.

AC3: Thanks for your kind suggestion. We considered and corrected the difference of δ^{15}N-NH_3 values resulting by passive samplers. The δ^{15}N-NH_3 values collected by passive samplers were significantly lower than that of the active sampler, with a difference of 15.4 ± 3.5‰(Pan et al., 2020). The δ^{15}N of NH_3 from fertilizer, livestock, and urban waste collected by passive sampler(Chang et al., 2016; Felix et al., 2013; Bhattarai et al., 2020) were corrected using 15.4 ± 3.5‰ (Bhattarai et al., 2021; Pan et al., 2020). In addition, we have added the parameters of δ^{15}N of NH_3 from different sources, as shown in **line 212** (**Table 1** in marked manuscript).

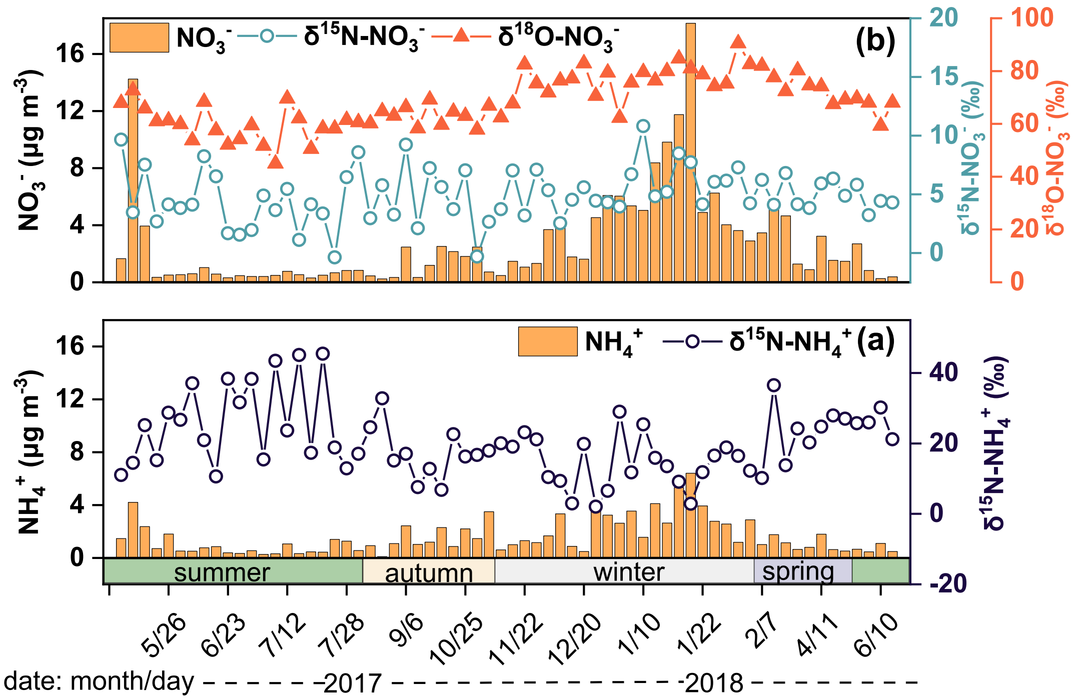
Referee#2_ Table 1 (**Table 1** in manuscript)**.** The estimation of δ^{15}N-NH_3 and δ^{15}N-NOx from various sources.

Source	δ^{15}N-NH_3(‰)	References
Biomass burning	17.5±7.8	(Kawashima and Kurahashi, 2011; Xiao et al., 2020)
Coal combustion	-2.5±6.4	(Felix et al., 2013; Pan et al., 2016)
Urban traffic	6.6±2.1	(Walters et al., 2020)
Fertilizer	-28.3±5.8	(Bhattarai et al., 2021; Chang et al., 2016; Felix et al., 2013; Bhattarai et al., 2020)
Livestock	-18.3±7.7	(Bhattarai et al., 2021; Chang et al., 2016; Felix et al., 2013; Bhattarai et al., 2020)
Urban waste	-22.8±3.6	(Bhattarai et al., 2021; Chang et al., 2016)
Source	**δ^{15}N-NOx(‰)**	**References**
Biomass burning	1.04±4.13	(Zong et al., 2017; Fibiger and Hastings, 2016; Zong et al., 2022)
Coal combustion	13.72±4.57	(Zong et al., 2017; Felix et al., 2015; Felix et al.,

		2012)
Mobile source	-7.25±7.80	(Zong et al., 2017; Walters et al., 2015)
Soil microbial process	-33.77±12.16	(Zong et al., 2017; Felix and Elliott, 2013)

RC4: Line 149: Fig 1. Can you please highlight/mark the seasonal periods in this figure? I think this will improve the readability because you mentioned the seasonal values.

AC4: Thanks for your kind suggestion. We have marked the season in **Figure 1**, as shown in the marked manuscript **line 236**.



Referee#2_Figure 1(Figure 1 in manuscript). The concentration and $\delta^{15}N$ of NH_4^+ (a) and concentration, $\delta^{15}N$, and $\delta^{18}O$ of NO_3^- (b).

RC5: Line 157: "average+"?

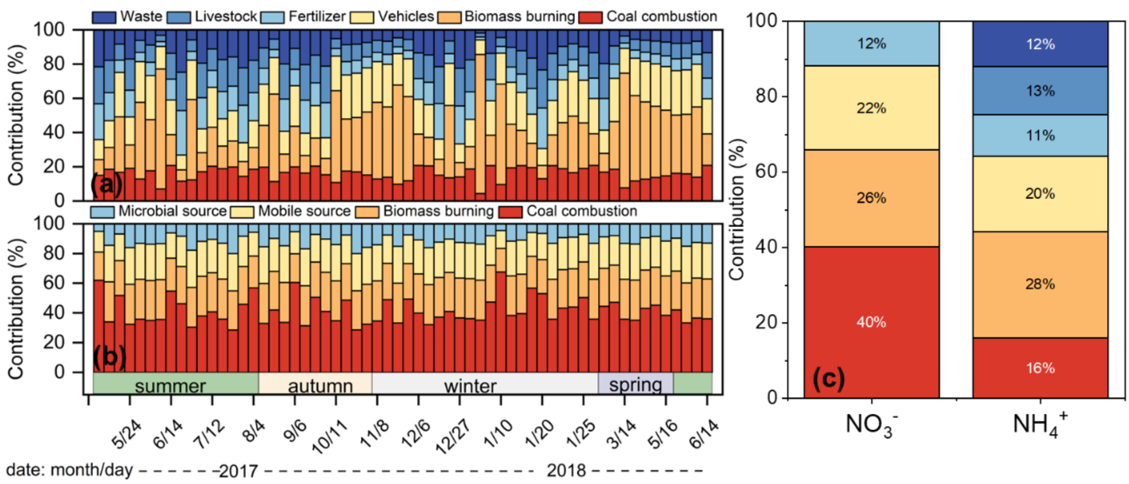
AC5: We apologize for the confusion caused by "average+". The plus symbol ("+") means positive number. Now we have deleted the + symbol, as shown in the marked manuscript **lines 245-246**.

RC6: Line 163: It would be better to provide the way you got the NH_3 concentration in the main manuscript.

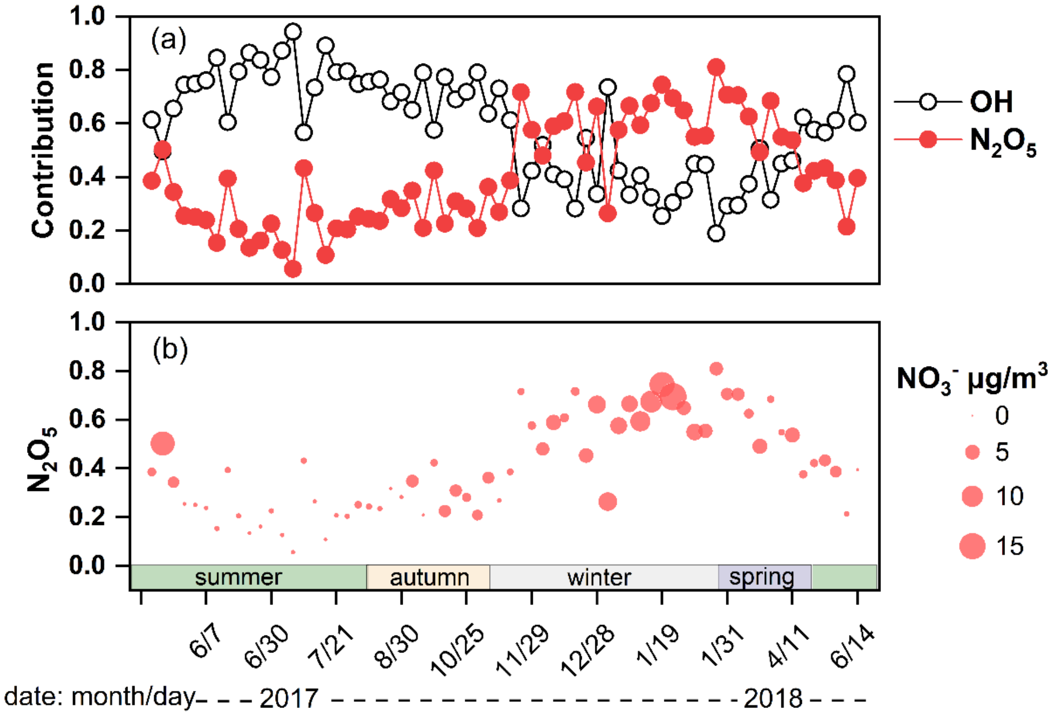
AC6: We are sorry for that we don't measure the NH_3 concentration. The proportion of the initial NH_3 converted to NH_4^+ (f, $NH_4^+/(NH_3+NH_4^+)$) for different months referenced from a previous study in Guangzhou(Liao et al., 2014).

RC7: Line 238/274 (Fig2, Fig3): again, please highlight/mark the seasonal periods (spring, summer, autumn, and winter).

AC7: Thanks for your kind suggestion. We have marked the season in Figure 2 and Figure 3, as shown in the marked manuscript **line 329** and **line 368**.



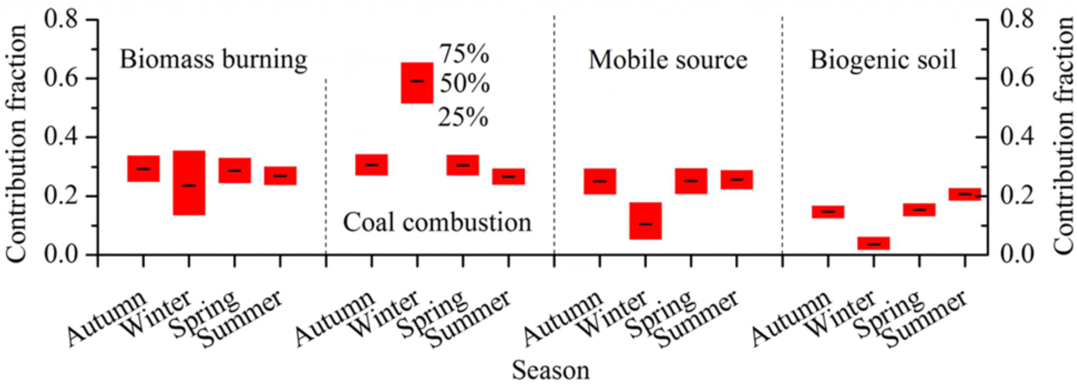
Referee#2_Figure 2 (Figure 2 in manuscript). The sources apportionment results of atmospheric NH_4^+ (a) and NO_3^- (b) in Guangzhou, and the comparison of sources results between NH_4^+ and NO_3^- (c).



Referee#2_Figure 3 (Figure 3 in manuscript). The contribution of the OH radical oxidation and N_2O_5 hydrolysis pathway to NO_3^- (a). The vertical position of the dots corresponded to the contribution of N_2O_5 pathway and the size of the dots corresponded to the concentration of NO_3^- (b).

RC8: Line 291-292: Why you defined BeiChengHuang Island and Heshan as the sites receiving strong anthropogenic impact? These two sites are not located in cities and should be impacted less anthropogenic activities than megacities such as Beijing and Guangzhou.

AC8: Firstly, we apologize for the wrong place name "BeiChengHuang Island". It should be BeiHuangCheng Island. We have revised it in the marked manuscript. Secondly, we doubtless agree with you that these two sites are not located in cities. However, in winter, 74% of the air mass in Beihuangcheng Island come directly from the heavily polluted Beijing-Tianjin-Hebei region(Zong, 2017). And about 26% of the air mass reached Beihuangcheng Island from the Beijing-Tianjin-Hebei region through the Shandong Peninsula(Zong, 2017). Zong et al. reported that coal combustion, mobile source, and biomass burning contributed 86.3% to NO_3^- in Beihuangcheng Island, as shown in the following figure (Zong et al., 2017). The Heshan Atmospheric Environment Monitoring Superstation is a rural station located 50 km southwest of Guangzhou (Xu et al., 2022). During the winter northeast-monsoon season, Heshan site well intercepts high anthropogenically dominated outflow airmass from Chinese continental(Xu et al., 2022). The anthropogenic sources (including fossil and biomass burning) accounted for 78% of total oxalic acid, tracers of aqueous secondary organic aerosol, in the continental outflow samples(Xu et al., 2022). Su et al. reported that coal combustion, mobile source, and biomass burning contributed 90.6% to NO_3^- in Heshan (Su et al., 2020). Therefore, NO_3^- was predominantly derived from anthropogenic sources in Beihuangcheng island and Heshan.



Referee#2_Figure 4. Contributions of coal combustion, mobile source, biomass burning, and biogenic soil emissions for NOx in different seasons on Beihuangcheng Island. (Zong et al., 2017)

RC9: Line 311-313. This explanation sounds reasonable. I suggest you add the references to support the facts you mentioned here (stricter vehicle emission standard, promotion of new electric vehicles etc.).

AC9: We appreciate your explicit suggestion. In order to continuously improve the Guangdong province's ambient air quality, the Guangdong Provincial Government formulated the Guangdong Air Pollution Prevention and Control Action Plan (2014-2017). The plan includes in-depth promotion of power plant pollution reduction, comprehensive promotion of boiler pollution remediation, raising the environmental standard of new vehicles, acceleration the improvement of gasoline and diesel quality, etc(Guangdongprovince, 2014). Especially in Guangzhou and Shenzhen, clean energy vehicles will account for more than 60% of annual new buses from 2014 (Guangdongprovince, 2014). In addition, China introduced an ultra-low emissions (ULE) standards policy for renovating coal-fired power-generating units in 2014. Tang et al., found that between 2014 and 2017 China's annual power emissions of NOx dropped by 60% since the implementation of ULE policy (Tang et al., 2019). Now, we have added the above references to the marked manuscript **line 408**.

RC10: Line 324-325: "The contribution of biomass burning and vehicle was stable through a year." The vehicular emission, in my opinion, is likely constant because people drive cars in all seasons. However, the biomass burning activity generally is highly related with seasons. Can you make some explanations on this?

AC10: Thanks for your insightful comment and kind suggestion. We totally agree with you that biomass burning is highly related to the seasons. Generally, high intensity biomass burning occurred in winter in Guangdong province (dry season, i.e., from November to March)(Xu et al., 2019). K^+ is a typical tracer of biomass burning. The concentration of K^+ enhanced in winter (0.4μg/m^3) was higher than that in summer(0.2μg/m^3) and autumn(0.2μg/m^3), respectively, indicating enhancement of biomass burning intensity. Also, NO_3^- concentration of biomass burning remarkably enhanced in winter (1.2μg/m^3) and was higher than that in summer (0.4μg/m^3) and autumn (0.3μg/m^3), respectively. However, coal combustion also enhanced in winter due to the demand for heating in North China. Our sampling site was influenced by the air mass with high coal combustion contribution from the North by long-range transportation, which may reduce the contribution of biomass burning relatively. Thus, the contribution of biomass burning showed stable compared with coal combustion. We have added the explanation in the marked manuscript, **lines 421-431**.

References:

Bhattarai, N., Wang, S., Pan, Y., Xu, Q., Zhang, Y., Chang, Y., and Fang, Y.: δ^{15}N-stable isotope analysis of NHx : An overview on analytical measurements, source sampling and its source apportionment, Front. Environ. Sci. Eng., 15, 126, https://doi.org/10.1007/s11783-021-1414-6, 2021.

Bhattarai, N., Wang, S., Xu, Q., Dong, Z., Chang, X., Jiang, Y., and Zheng, H.: Sources of gaseous NH_3 in urban Beijing from parallel sampling of NH_3 and NH_4^+, their nitrogen isotope measurement and modeling, Sci. Total Environ., 747, 141361, https://doi.org/10.1016/j.scitotenv.2020.141361, 2020.

Chang, Y., Liu, X., Deng, C., Dore, A. J., and Zhuang, G.: Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures, Atmos. Chem. Phys., 16, 11635-11647, https://doi.org/10.5194/acp-16-11635-2016, 2016.

Felix, J. D. and Elliott, E. M.: The agricultural history of human-nitrogen interactions as recorded in ice core δ^{15}N-NO_3^-, Geophys. Res. Lett., 40, 1642-1646, https://doi.org/10.1002/grl.50209, 2013.

Felix, J. D., Elliott, E. M., and Shaw, S. L.: Nitrogen isotopic composition of coal-fired power plant NOx: influence of emission controls and implications for global emission inventories, Environ. Sci. Technol., 46, 3528-3535, https://doi.org/10.1021/es203355v, 2012.

Felix, J. D., Elliott, E. M., Gish, T. J., McConnell, L. L., and Shaw, S. L.: Characterizing the isotopic composition of atmospheric ammonia emission sources using passive samplers and a combined oxidation-bacterial denitrifier approach, Rapid Commun. Mass Spectrom., 27, 2239-2246, https://doi.org/10.1002/rcm.6679, 2013.

Felix, J. D., Elliott, E. M., Avery, G. B., Kieber, R. J., Mead, R. N., Willey, J. D., and Mullaugh, K. M.: Isotopic composition of nitrate in sequential Hurricane Irene precipitation samples: Implications for changing NOx sources, Atmos. Environ., 106, 191-195, https://doi.org/10.1016/j.atmosenv.2015.01.075, 2015.

Fibiger, D. L. and Hastings, M. G.: First Measurements of the Nitrogen Isotopic Composition of NOx from Biomass Burning, Environ. Sci. Technol., 50, 11569-11574, https://doi.org/10.1021/acs.est.6b03510, 2016.

Action Plan for Air Pollution Control of Guangdong Province (2014-2017): http://www.gd.gov.cn/gkmlpt/content/0/142/mpost_142687.html, last access: February 14, 2014.

Kawashima, H. and Kurahashi, T.: Inorganic ion and nitrogen isotopic compositions of atmospheric aerosols at Yurihonjo, Japan: implications for nitrogen sources, Atmos. Environ., 45, 6309-6316, https://doi.org/10.1016/j.atmosenv.2011.08.057, 2011.

Liao, B., Wu, D., Chang, Y., Lin, Y., Wang, S., and Li, F.: Characteristics of particulate SO_4^{2-}, NO_3^-, NH_4^+, and related gaseous pollutants in Guangzhou (in Chinese), Acta Sci. Circumst., 34, 1551-1559, https://doi.org/10.13671/j.hjkxxb.2014.0218, 2014.

Pan, Y., Tian, S., Liu, D., Fang, Y., Zhu, X., Zhang, Q., Zheng, B., Michalski, G., and Wang, Y.: Fossil fuel combustion-related emissions dominate atmospheric ammonia sources during severe haze episodes: evidence from ^{15}N-stable isotope in size-resolved aerosol ammonium, Environ. Sci. Technol., 50, 8049-8056, https://doi.org/10.1021/acs.est.6b00634, 2016.

Pan, Y., Tian, S., Liu, D., Fang, Y., Zhu, X., Gao, M., Wentworth, G. R., Michalski, G., Huang, X., and Wang, Y.: Source Apportionment of Aerosol Ammonium in an Ammonia-Rich Atmosphere: An Isotopic Study of Summer Clean and Hazy Days in Urban Beijing, J. Geophys. Res.: Atmos., 123, 5681-5689, https://doi.org/10.1029/2017jd028095, 2018.

Pan, Y., Gu, M., Song, L., Tian, S., Wu, D., Walters, W. W., Yu, X., Lü, X., Ni, X., Wang, Y., Cao, J., Liu, X., Fang, Y., and Wang, Y.: Systematic low bias of passive samplers in characterizing nitrogen isotopic composition of atmospheric ammonia, Atmos. Res., 243, https://doi.org/10.1016/j.atmosres.2020.105018, 2020.

Su, T., Li, J., Tian, C., Zong, Z., Chen, D., and Zhang, G.: Source and formation of fine particulate nitrate in South China: Constrained by isotopic modeling and online trace gas analysis, Atmos. Environ., 231, https://doi.org/10.1016/j.atmosenv.2020.117563, 2020.

Tang, L., Qu, J., Mi, Z., Bo, X., Chang, X., Anadon, L. D., Wang, S., Xue, X., Li, S., Wang, X., and Zhao, X.: Substantial emission reductions from Chinese power plants after the introduction of ultra-low emissions standards, Nat. Energy, 4, 929-938, https://doi.org/10.1038/s41560-019-0468-1, 2019.

Walters, W. W., Tharp, B. D., Fang, H., Kozak, B. J., and Michalski, G.: Nitrogen Isotope Composition of Thermally Produced NOx from Various Fossil-Fuel Combustion Sources, Environ. Sci. Technol., 49, 11363-11371, https://doi.org/10.1021/acs.est.5b02769, 2015.

Walters, W. W., Song, L., Chai, J., Fang, Y., Colombi, N., and Hastings, M. G.: Characterizing the spatiotemporal nitrogen stable isotopic composition of ammonia in vehicle plumes, Atmos. Chem. Phys., 20, 11551-11567, https://doi.org/10.5194/acp-20-11551-2020, 2020.

Xiao, H. W., Wu, J. F., Luo, L., Liu, C., Xie, Y. J., and Xiao, H. Y.: Enhanced biomass burning as a source of aerosol ammonium over cities in central China in autumn, Environ. Pollut., 266, 115278, https://doi.org/10.1016/j.envpol.2020.115278, 2020.

Xu, B., Zhang, G., Gustafsson, O., Kawamura, K., Li, J., Andersson, A., Bikkina, S., Kunwar, B., Pokhrel, A., Zhong, G., Zhao, S., Li, J., Huang, C., Cheng, Z., Zhu, S., Peng, P., and Sheng, G.: Large contribution of fossil-derived components to aqueous secondary organic aerosols in China, Nat. Commun., 13, 5115, https://doi.org/10.1038/s41467-022-32863-3, 2022.

Xu, Y., Huang, Z., Jia, G., Fan, M., Cheng, L., Chen, L., Shao, M., and Zheng, J.: Regional discrepancies in spatiotemporal variations and driving forces of open crop residue burning emissions in China, Sci. Total Environ., 671, 536-547, https://doi.org/10.1016/j.scitotenv.2019.03.199, 2019.

Zong, Z.: Composition and source apportionment of $PM_{2.5}$ at the background area in North China, Doctor, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, 2017.

Zong, Z., Shi, X., Sun, Z., Tian, C., Li, J., Fang, Y., Gao, H., and Zhang, G.: Nitrogen isotopic composition of NOx from residential biomass burning and coal combustion in North China, Environ. Pollut., 304, 119238, https://doi.org/10.1016/j.envpol.2022.119238, 2022.

Zong, Z., Wang, X., Tian, C., Chen, Y., Fang, Y., Zhang, F., Li, C., Sun, J., Li, J., and Zhang, G.: First assessment of NOx sources at a regional background site in North China using isotopic analysis linked with modeling, Environ. Sci. Technol., 51, 5923-5931, https://doi.org/10.1021/acs.est.6b06316, 2017.