Dear Reviewer,

We appreciate your careful consideration of our manuscript. We have carefully responded to all of your **point-by-point** comments and issues and have revised the manuscript accordingly. These revisions are described in detail below.

Reviewer #1

The authors have made commendable efforts to conduct a comprehensive field measurement in urban Beijing, spanning the unique transition period from the pre-pandemic COVID-19 era to the subsequent lockdown period. While the controversies outlined in the introduction section (lines 95-122) remain unresolved, this study observes a notable decrease in HONO concentration from the pre-pandemic eve to the lockdown phase. Furthermore, the study offers a reasonable explanation regarding the contributions of HONO sources. I find this work particularly valuable as it underscores the significance of vehicle emissions and highlights the rapid temporal shifts in the roles of HONO sources, which could be of great interest to readers of ACP. I recommend publication of the manuscript following minor revisions. Below are my specific comments.

Response: Thank you for your positive comments and good suggestions. We will respond to your comments point-by-point below.

1. The abstract requires improvement. Please remove lines 36-38 "which resulted in … to measure the HONO and related pollutants", and restructure the sentences for better clarity.

Response: Thank you for your suggestion. We have removed lines 36-38 "which resulted in the largest changes in air pollutant emissions in the history of modern atmospheric chemistry. A home-made Water-based Long-Path Absorption Photometer (LOPAP) along with other instruments were used to measure the HONO and related pollutants". In the revised manuscript, we reorganized them into "which resulted in a significant reduction in air pollutant emissions, providing a rare opportunity to understand the HONO budget in the atmosphere. We measured HONO and related pollutants" in lines 36-38.

2. Lines 67 and 80: The second and third paragraphs contain overlapping information. I recommend integrating the introduction about HONO concentrations into the first

paragraph. Subsequently, the second paragraph should focus solely on direct emissions, while the third paragraph should discuss secondary formation.

Response: Thank you for your good suggestion. We have integrated the introduction of HONO concentrations into the first paragraph, the original "Intensive studies have been carried out on HONO measurements and source analysis (Liu et al., 2020c; Liu et al., 2020d; Zheng et al., 2020; Zhang et al., 2020; Xue et al., 2020; Zhang et al., 2019a; Liu et al., 2019b). The concentrations of HONO in the atmosphere range from a few ppt in remote areas (Spataro et al., 2016) to several ppb, even several tens ppb in heavily polluted areas (Liu et al., 2019b; Liu et al., 2020c; Liu et al., 2020d; Zheng et al., 2020)." in lines 63-67 has been moved to lines 61-66 in the revised manuscript.

As you suggested, the second paragraph only focuses on direct emissions in lines 68-79 in the revised manuscript "Direct emissions include soils, biomass burning, vehicles, indoor air, and livestock farming. Soil emissions, which depend on soil types, microorganisms, water content, temperature, and pH (Kulmala and Petäjä, 2011; Weber et al., 2015; Kim and Or, 2019), are important sources of HONO. Biomass burning, often occurs in the summer and autumn when wheat/corn is harvested and wildfires are common (Zhang et al., 2019b; Sun et al., 2017; Sun et al., 2018; Peng et al., 2020). Vehicle emissions are considered an important source of HONO in traffic-intensive areas (Kramer et al., 2020; Li et al., 2021). This source is more important at nighttime compared with daytime (Zhang et al., 2016; Fu et al., 2019; Liu et al., 2020d). Recently, indoor emissions have also been proposed as a potential HONO source (Xue, 2022), which is related to the ventilation from high HONO concentrations in indoor air to low HONO concentrations in outdoor air (Zhang et al., 2019b). Livestock farming is a previously overlooked source of HONO, especially in agricultural areas."

The third paragraph discusses secondary formation in lines 80-88 in the revised manuscript "Secondary formation of HONO includes gas-phase reaction between NO and OH radicals, photolysis of particulate nitrate, and heterogeneous reaction of NO_2 on ground and particulate matter surfaces, including photochemical heterogeneous reaction of NO_2. Gas phase reaction between NO and OH, photolysis of nitrate particles, and light-enhanced conversion of NO_2 are the main daytime sources of HONO (Liu et al., 2019c; Liu et al., 2020d; Zhang et al., 2022b). Furthermore, acid replacement processes may be a non-negligible source of daytime HONO in locations affected by soil-borne mineral dust deposition (Vandenboer et al., 2014). The heterogeneous

reaction of NO_2 on various surfaces is widely regarded as an important source of HONO (Han et al., 2016; Liu et al., 2020b).".

3. Line 71: Here, "harvest season" may not be the most accurate term. Biomass burning encompasses a range of activities, including wildfires, which can be particularly significant under certain circumstances.

Response: Thank you for your good suggestion. We have modified it in the revised manuscript to "Biomass burning, often occurs in the summer and autumn when wheat/corn is harvested and wildfires are common (Zhang et al., 2019b; Sun et al., 2017; Sun et al., 2018; Peng et al., 2020)" in lines 71-73.

4. Line 85: The authors omitted the acid displacement (VandenBoer et al. 2015, Liu et al. 2019)?

Response: Thank you for your good suggestion. In lines 85-86 in the revised manuscript, we added a sentence "Furthermore, acid replacement processes may be a non-negligible source of daytime HONO in locations affected by soil-borne mineral dust deposition (Vandenboer et al., 2014)".

5. Line 79: Livestock HONO emission is negligible in urban Beijing. Similarly, the emission of HONO from soil, which may peak following fertilizer application, likely does not need to be considered.

Response: Thank you for your good suggestion. The HONO emissions from Livestock in urban Beijing can be ignored, while soil emissions are slightly more important than Livestock. In this study, the contribution of the soil is even comparable to that of heterogeneous conversion of NO_2 on the surfaces of aerosol. Therefore, we still include the soil emissions when performing the budget analysis.

6. Line 263: heterogeneous yield of HONO instead of NO_2?

Response: Thank you for your good suggestion. In the revised manuscript in line 263, we changed it to "heterogeneous yield of HONO".

7. Section 3.1 Please present the result following the order of Figure 1 (a) ~ (i).

Response: Thank you for your good suggestion. In Figure 1, we moved the

meteorological parameters to the end of this figure. And revised the description order of pollutants accordingly in lines 318-341 in the revised manuscript.

8. Line 406: How about the heterogenous conversion on ground?

Response: Thank you for your good comments. The description here is inaccurate, in the revised manuscript, we corrected the sentence "These results imply that HONO might be more influenced by vehicle emissions than by heterogeneous reactions on aerosol surfaces" in lines 405-407.

9. Line 236: Is $HONO_{corr}$ equivalent to $C_{HONO,corr,t}$ as indicated in Eq. (6)? Please maintain consistency in the use of abbreviations.

Response: Thank you for your good comments. In Section 2.2, to maintain the consistency of the formula, we use "$C_{HONO,corr,t}$", and in subsequent chapters, for the convenience of readers, we use "$HONO_{corr}$". In order not to mislead readers, in the revised manuscript, we use $HONO_{corr}$ to represent it uniformly.

10. Line 508: In fact, Song et al. (2023) proposed two HONO production pathways distinct from the homogeneous reaction between NO and OH.

Response: Thank you for your good suggestion. The quote here is inappropriate, in lines 508-512 in the revised manuscript, we have modified it to "This is consistent with previous studies in urban Beijing (Gu et al., 2021; Jia et al., 2020; Liu et al., 2021). Interestingly, a recent study proposed a new mechanism through smog chamber experiments, that is, NOx photooxidation (reaction of NO and adsorbed HNO_3) may be an important daytime HONO source (Song et al., 2023), although it has not yet been verified by field observations."

11. Line 534: "a change of 25% and 95% of HONO sources, respectively." What does this signify? It appears that the selection of the photolysis rate constant could have a significant influence.

Response: Thank you for your good comment. We agree with you that the selection of the photolysis rate constant has a significant influence on its contribution to the HONO source. The big difference in the estimated source here means both the upper and lower limits of the parameters might be improper. Thus, it requires a more restrictive method to evaluate the reasonability of the parameterization and assess the

overall uncertainty. In our study, we further compared the estimated hourly HONO concentrations with the observed values to evaluate the parameters finally chosen. In lines 605-608 in the revised manuscript, we added a short paragraph "It should be noted that each source is sensitive to the corresponding parameter as discussed above. Thus, a more restrictive criterion is required to evaluate the reasonability of the parameterization. We further estimated the HONO concentration according to Eq. (2) and the parameters described in Sect. 2.2 to verify these calculated sources and sinks of HONO". In addition, the overall uncertainty is 27.2% for the HONO budget evaluated based on Monte Carlo simulations. This has been pointed out in line 624 in the revised manuscript.

12. Lines 532-537: Move the results regarding soil emissions to the subsequent paragraph.

Response: Thank you for your good suggestion. We have moved the paragraph "The yield of soil emissions in the P2 stage is also higher than that in the P1 stage due to the temperature rise in the P2 stage because the temperature will affect the soil emission flux (Oswald et al., 2013), while the importance of this source is negligible in this study. In M15 and M16, we amplify and shrink the soil emission flux by 10 times, respectively, and the change of the simulated HONO sources was less than 5%." to the subsequent paragraph in lines 554-559 in the revised manuscript.

13. Line 564: The NO_2 concentration decreased significantly from 26.9 ppb to 17.2 ppb (-36%) from P1 to P2, indicating a substantial reduction rather than a slight decrease.

Response: Thank you for your good suggestion. In lines 563-565 in the revised manuscript, we revised it as "It is worth noting that the HONO formation rate from the heterogeneous conversion of NO_2 on the surface of aerosol does not decrease, which is caused by the increase in $PM_{2.5}$ concentration along with a decrease in NO_2 concentration during the P2 period".

14. Lines 570-573: It's noteworthy that HONO exhibits minimal sensitivity to both the uptake coefficient (γ) and surface area concentration (As). However, the authors should provide an explanation for this phenomenon.

Response: Thank you for your good comments. According to eq(7), the contribution of the heterogeneous reaction of NO_2 on aerosol surfaces to the HONO

source should be sensitive to both the uptake coefficient (γ) and surface area concentration (A_s). Although the absolute values change prominently as expected when the A_s or γ is increased or reduced, its relative contribution does not change obviously due to the small absolute value compared with other sources.

In lines 575-579 in the revised manuscript, we have revised the paragraph "It should be noted that HONO is sensitive to the uptake coefficient and surface area concentration. When the uptake coefficient is expanded by 5 times or reduced by 10 times, the absolute HONO flux attributed to heterogeneous reactions increases 5 times or decreases 10 times, while the relative contribution is very low due to the small absolute value of heterogeneous reactions compared with other sources."

15. Line 593: These variations (-9% to +40%) are significant and warrant attention.

Response: Thank you for your good comments. As mentioned in the previous reply, this sensitivity is closely related to the contribution of heterogeneous transformation of NO_2 at the ground surface to HONO. When the uptake coefficient is expanded by 5 times or reduced to 0.1, HONO changes by 40% and 9% respectively, indicating that HONO is sensitive to the NO_2 uptake coefficient on the ground surface, implying the importance of this source. In the revised manuscript, we added the sentence "Indicating that HONO is sensitive to the NO_2 uptake coefficient on the ground surface." in lines 592-593.

16. Lines 622: The method utilized to estimate the overall uncertainty of the parameterization should be presented in the Experimental section.

Response: Thank you for your good suggestion. In lines 296-298 in the revised manuscript, we added a sentence "Oracle Crystal Ball (version 11.1.2.4, Oracle's software for modeling, prediction, simulation, and optimization) (Rahmani et al., 2023) to evaluate the overall uncertainty of the parameterization through Monte Carlo simulations. The details are shown in Text S2 in the SI". In the revised SI, we added an introduction to the Monte Carlo algorithm as follows:

Text S2 Monte Carlo algorithm

The Monte Carlo algorithm is a method of estimating numerical values through random sampling. It can be used to estimate the overall uncertainty of the numerical value. A large number of samples are generated by random sampling from a probability distribution and the required numerical indicators are calculated based on these samples.

Due to the limited number of samples, there is a certain error between the estimated value and the true value. We increase the number of sampling times to 10,000 to reduce statistical uncertainty.

When establishing the simulation model, the respective change ranges of the variables that affect HONO intensity are input, and the uncertainty of the modeling is evaluated by sampling from the probability distribution of the parameters to obtain the overall uncertainty. In addition, the uncertainty of the model parameters is propagated to the model output through Monte Carlo sampling, and the uncertainty distribution of the results can be obtained. The formula for overall uncertainty can be expressed as:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$

σ represents the standard deviation of the overall uncertainty; N is the number of samples; x_i is the value of the i^{th} sample, and $\bar{x}$ is the mean of the sample.

References:

Gu, R., Shen, H., Xue, L., Wang, T., Gao, J., Li, H., Liang, Y., Xia, M., Yu, C., Liu, Y., and Wang, W.: Investigating the sources of atmospheric nitrous acid (HONO) in the megacity of Beijing, China, Science of The Total Environment, 10.1016/j.scitotenv.2021.152270, 2021.

Liu, Y., Nie, W., Xu, Z., Wang, T., Wang, R., Li, Y., Wang, L., Chi, X., and Ding, A.: Semi-quantitative understanding of source contribution to nitrous acid (HONO) based on 1 year of continuous observation at the SORPES station in eastern China, Atmospheric Chemistry and Physics, 19, 13289-13308, 10.5194/acp-19-13289-2019, 2019a.

Liu, Y., Ni, S., Jiang, T., Xing, S., Zhang, Y., Bao, X., Feng, Z., Fan, X., Zhang, L., and Feng, H.: Influence of Chinese New Year overlapping COVID-19 lockdown on HONO sources in Shijiazhuang, Sci Total Environ, 745, 141025, 10.1016/j.scitotenv.2020.141025, 2020a.

Liu, Y., Lu, K., Li, X., Dong, H., Tan, Z., Wang, H., Zou, Q., Wu, Y., Zeng, L., Hu, M., Min, K. E., Kecorius, S., Wiedensohler, A., and Zhang, Y.: A Comprehensive Model Test of the HONO Sources Constrained to Field Measurements at Rural North China Plain, Environ Sci Technol, 53, 3517-3525, 10.1021/acs.est.8b06367, 2019b.

Liu, Y., Zhang, Y., Lian, C., Yan, C., Feng, Z., Zheng, F., Fan, X., Chen, Y., Wang, W., Chu, B., Wang, Y., Cai, J., Du, W., Daellenbach, K. R., Kangasluoma, J., Bianchi, F., Kujansuu, J., Petäjä, T., Wang, X., Hu, B., Wang, Y., Ge, M., He, H., and Kulmala, M.: The promotion effect of nitrous acid on aerosol formation in wintertime in Beijing: the possible contribution of traffic-related emissions, Atmospheric Chemistry and Physics, 20, 13023-13040, 10.5194/acp-20-13023-2020, 2020b.

Shi, X., Ge, Y., Zheng, J., Ma, Y., Ren, X., and Zhang, Y.: Budget of nitrous acid and its impacts on atmospheric oxidative capacity at an urban site in the central Yangtze River Delta region of China,

Atmospheric Environment, 238, 10.1016/j.atmosenv.2020.117725, 2020.

Song, Y., Zhang, Y., Xue, C., Liu, P., He, X., Li, X., and Mu, Y.: The seasonal variations and potential sources of nitrous acid (HONO) in the rural North China Plain, Environ Pollut, 311, 119967, 10.1016/j.envpol.2022.119967, 2022.

Zhang, J., An, J., Qu, Y., Liu, X., and Chen, Y.: Impacts of potential HONO sources on the concentrations of oxidants and secondary organic aerosols in the Beijing-Tianjin-Hebei region of China, Sci Total Environ, 647, 836-852, 10.1016/j.scitotenv.2018.08.030, 2019a.

Zhang, J., Chen, J., Xue, C., Chen, H., Zhang, Q., Liu, X., Mu, Y., Guo, Y., Wang, D., Chen, Y., Li, J., Qu, Y., and An, J.: Impacts of six potential HONO sources on HOx budgets and SOA formation during a wintertime heavy haze period in the North China Plain, Sci Total Environ, 681, 110-123, 10.1016/j.scitotenv.2019.05.100, 2019b.

Breiman, L.: Random Forests, Machine Learning, 45, 5-32, https://doi.org/10.1023/A:1010933404324, 2001.

Grange, S. K. and Carslaw, D. C.: Using meteorological normalisation to detect interventions in air quality time series, Sci Total Environ, 653, 578-588, 10.1016/j.scitotenv.2018.10.344, 2019.

Grange, S. K., Carslaw, D. C., Lewis, A. C., Boleti, E., and Hueglin, C.: Random forest meteorological normalisation models for Swiss PM_{10} trend analysis, Atmospheric Chemistry and Physics, 18, 6223-6239, 10.5194/acp-18-6223-2018, 2018.