A point-by-point response to the reviews

Thank you for your valuable comments. The followings are our responses to your comments.

Response to Reviewer #2

Comment 1: This work studied HONO production from particulate nitrate photolysis in $PM_{2.5}$ at five Chinese cities. The method is well-designed and the shadowing effect of the artificial filter samples is corrected to some degree. This work provided good evidence to show the important role of OC/NO_3^- in determining the JNO_3^-. The parameterization of corrected JNO_3^- using the OC/NO_3^- could improve the atmospheric relevance of laboratory studies conducted with aerosol filter samples and better quantify of HONO production from the photochemical reduction of nitrate. In general, this work is of high quality and significant importance to atmospheric chemistry and physics. I recommend the manuscript be accepted for publication after minor revisions.

Answer: Thank you for your approval. According to your valuable comments, we have made corresponding revisions in our revised manuscript.

Comment 2: J_{HONO} can be confused with the photolysis of HONO. I suggest using "$J_{NO_3^- - HONO}$" instead.

Answer: Thank you for your valuable comments. J_{HONO} has been replaced by $J_{NO_3^- - HONO}$ in our revised manuscript to represent the photolysis rate constant of particulate nitrate for HONO production.

Comment 3: I suggest NO_3^- be considered and normalized while studying pH influence.

Answer: Thank you for your valuable comments. According to your suggestions, we considered NO_3^- when studying the influence of pH on $J_{NO_3^- - HONO}$. As shown in Figure S1, the correlation between $J_{NO_3^- - HONO}$ and pH/NO_3^- has enhanced comparing with that between $J_{NO_3^- - HONO}$ and pH, however this relationship was still weak (R^2=0.15), which indicated that pH was an important factor, but not the key one driving the spatial differences of $J_{NO_3^- - HONO}$ in this work. This conclusion was the same as before.

In general, there was no significant relationship between pH and NO_3^- for $PM_{2.5}$ samples, thus there is no need to eliminate the influence of NO_3^-. Besides, previous works generally considered pH instead of pH/NO_3^- when studying the influence of pH (Scharko et al., 2014). Thus, for better comparison with previous studies, we recommended to use a uniform expression and use pH instead of pH/NO_3^- in this work when exploring the influence of pH on $J_{NO_3^- - HONO}$.

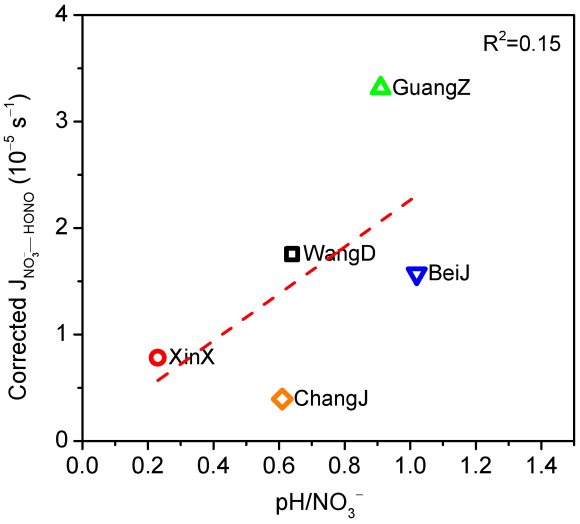

Figure S1. Relationships between the average corrected $J_{NO_3^- - HONO}$ and pH/NO_3^- under different sampling locations.

Comment 4: Line 17, the light screening coefficient needs to be determined before use.

Answer: Thank you for your suggestions. The content in abstract has been reorganized and revised in our manuscript (Page 1, line 16–19):
"We developed a method to correct and quantify the 'shadowing effect'— potential light extinction within aerosol layers at heavy $PM_{2.5}$ loadings on the filters—for $J_{NO_3^- - HONO}$ measurements, which showing that elemental carbon (EC), the dominant light-absorbing component in $PM_{2.5}$, played a dominant role in it."

Comment 5: Line 17, EC may be determined before use.

Answer: The content in abstract has been reorganized and revised in our manuscript (Page 1, line 16–19):
"We developed a method to correct and quantify the 'shadowing effect'— potential light extinction within aerosol layers at heavy $PM_{2.5}$ loadings on the filters—for $J_{NO_3^- - HONO}$ measurements, which showing that elemental carbon (EC), the dominant light-absorbing component in $PM_{2.5}$, played a dominant role in it."

Comment 6: Line 18, what is "corrected" J_{HONO}?

Answer: "Corrected $J_{NO_3^- - HONO}$" represented the corrected value of $J_{NO_3^- - HONO}$ after considering the influence of the "shadowing effect".

Comment 7: Line 25-28, I am confused by the sentence, is the contribution of photolysis of nitrate potentially important or limited? and why?

Answer: In this work, the calculated noontime source strength of HONO (S_{HONO}) through the photolysis of particulate nitrate ranged from 0.03×10^{-5} mol h^{-1} m^{-2} to 0.88×10^{-5} mol h^{-1} m^{-2} (0.01 ppbv h^{-1}–0.2 ppbv h^{-1}), with the mean value of 0.36×10^{-5} mol $h^{-1}m^{-2}$ (0.08 ppbv h^{-1}), which was comparable or higher than other HONO sources (Bhattarai et al., 2019; Wang et al., 2023; Ye et al., 2017). For example, the soil HONO emission flux was measured in the range of 1.81×10^{-6} mol h^{-1} m^{-2}–4.55×10^{-6} mol h^{-1} m^{-2} in the soil without suffering nitrogen fertilizer (Bhattarai et al., 2019). However, it should be noted that the photolysis of particulate nitrate contributed only a small fraction to the reported daytime HONO unknown source in these regions, such as 1.26–3. 82 ppbv h^{-1} in the cities in the North China Plain (Hou et al., 2016; Wang et al., 2017; Lian et al., 2022; Li et al., 2018), 0.75 ppbv h^{-1} in the Western China (Huang et al., 2017), and 0.77–4.90 ppbv h^{-1} in Southern China (Li et al., 2012; Su et al., 2008). Therefore, the contribution of the photolysis of particulate nitrate to daytime HONO unknown source was still limited, and other sources were still needed to account for the daytime unknown HONO source in these regions. To avoid misunderstandings, this sentence has been revised in our manuscript (Page 1, line 26–28):
"This study confirms that the photolysis of particulate nitrate can be a potential HONO daytime source in rural or southern urban sites, which are characterized by high proportion of organic matter in $PM_{2.5}$."

Comment 8: Line 67-69, How do mechanisms and dominant factors contribute to accurately estimating contributions?

Answer: The rate constant of nitrate photolysis ($J_{NO_3^- - HONO}$) showed large variability in different environments. In New York, Ye et al. (2017) reported that the photolysis rates of particulate nitrate in clean areas were two orders of magnitude higher than that in polluted areas, ranging from 6.2×10^{-6} to 5.0×10^{-4} s^{-1}. The large discrepancies may undoubtedly impacted the estimation of HONO production rates from nitrate photolysis. This highly-varied value of $J_{NO_3^- - HONO}$ was closely associated with environmental conditions and the aerosol chemical or physical characteristics, such as relative humidity (RH), aerosol acidity, light intensity, and coexisting components

(organic components, halogen, etc.). Thus, elucidating the mechanism and dominant factors controlling the photolysis of particulate nitrate can reduce the uncertainty in $J_{NO_3^- - HONO}$ predictions and improve estimations of the source strength of HONO production from this process. This sentence has been revised in our manuscript (Page 4, line 68–70):
"Elucidating the mechanism and dominant factors controlling the photolysis of particulate nitrate is important to accurately estimate the HONO production rates from nitrate photolysis, thus improving estimations of HONO budgets."

Comment 9: Line 74, why is the shadowing effect significant only under haze conditions? Are the authors assuming that all samples were collected within 24 hours? is this true?

Answer: Yes. Generally, we assumed that the sampling time of all the aerosol samples were the same. The $PM_{2.5}$ loading on the filters collected under haze conditions was much higher than that under clean conditions, thus showing much significant shadowing effect.

Comment 10: Line 80, NO_3^- changed over time or location?

Answer: NO_3^- change over locations. This sentence has been revised in our manuscript (Page 4, line 80–81):
"According to previous field observations, the $PM_{2.5}$ chemical composition, especially particulate nitrate (NO_3^-), showed obvious spatial differences across China."

Comment 11: Line 190, I understand that the shadowing effect causes a lower j at higher nitrate loading. How could it lead to a lower P at higher nitrate loading?

Answer: Thank you for your valuable comments. It is noted that this phenomenon—lower P at higher nitrate loading—has also been observed in other works (Ye et al., 2017; Bao et al., 2018).We assumed that more than single layer of $PM_{2.5}$ particles were collected on the filter samples at higher $PM_{2.5}$ loading. Light absorption components in $PM_{2.5}$, such as EC, may prevent the UV light transmitting efficiently through the upper layers. The particulate nitrate underneath the aerosol filters may receive less UV light, thus inhibiting the photolysis of particulate nitrate. Thus, the increase of light absorption components in $PM_{2.5}$ at very high NO_3^- loading condition may hinder the light absorption of nitrate inside and underside of the particle, which may not only lead to the decrease of the upward trend of P_{HONO} but also a lower value at higher nitrate loading.

Comment 12: Line 195: should the underestimation of the p or J value primarily depend on the loading time or the amount of light-absorbing species? Is it not necessarily related to whether the environment is polluted or not?

Answer: The underestimation of the P_{HONO} or $J_{NO_3^- - HONO}$ value primarily depended on the amount of light-absorbing species on the filters. But the the amount of light-absorbing species was related to the sampling time and air conditions. Generally, we assumed that the sampling time of all the aerosol filter samples were the same. Thus, the $PM_{2.5}$ loading on the filters collected under polluted conditions was much higher than that under clean conditions, thus showing much significant shadowing effect.

Comment 13: Line 337, I can hardly see a clear dependence of OC/NO_3^- on $PM_{2.5}$ levels.

Answer: As can be seen in Figure 7c, high OC/NO_3^- ratios generally happened in clean areas, such as Guangzhou, where the averaged $PM_{2.5}$ level was the lowest among these cites. Cities with high $PM_{2.5}$ levels generally have low ratios of OC/NO_3^-, such as Changji and Xinxiang, however, there was an exception—Wangdu, a rural site in the North China Plain, where the $PM_{2.5}$ was high but dominated by OM mainly due to local residential coal combustion. The expression has been revised in our manuscript (Page 17, line 345–348):
"Generally, cities with higher $PM_{2.5}$ levels have lower OC/NO_3^- ratios, such as Changji and Xinxiang, however, there was an exception—Wangdu, a rural site in the North China Plain, where the $PM_{2.5}$ was high but dominated by OM mainly due to local residential coal combustion."

Comment 14: More details should be added to the caption of Fig. 9, such as an explanation of how these values were obtained.

Answer: The explanation of how these values were obtained has bee added in our revised manuscript (Page 22, line 433–435):
" The daily average concentrations of NO_3^- and OC were extracted from the Chinese high resolution $PM_{2.5}$ Component simulation concentration dataset (Kong, et al., 2024). "

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