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 #1

Comment 1: The authors of this manuscript estimated the photolysis rate constants of particulate nitrate for HONO production ($J_{NO_3^- - HONO}$) through photolysis of $PM_{2.5}$ samples collected from five typical sites in China. They smartly revealed the "shadowing effect" of $PM_{2.5}$ filter samples on nitrate photolysis through investigating the difference of HONO production rates through photolysis of the $PM_{2.5}$ samples collected on a whole day and those sampled in both daytime and nighttime, finding that OC and EC played key roles in the "shadowing effect". Additionally, the authors further derived a parameterization equation of $J_{NO_3^- - HONO}$ for atmospheric $PM_{2.5}$ based on significantly positive correlation between $J_{NO_3^- - HONO}$ of $PM_{2.5}$ and OC/NO_3^- ratio, which will be useful for precisely estimating $J_{NO_3^- - HONO}$ in different areas with different aerosol chemical composition. In general, this manuscript is well organized, containing useful information about daytime HONO source from photolysis of atmospheric $PM_{2.5}$. This reviewer recommends the manuscript to be published in the journal.

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

Comment 2: The symbol used for indicating photolysis rate constant of particulate nitrate for HONO production is suggested to be $J_{NO_3^- - HONO}$, rather than J_{HONO} because J_{HONO} is prevailingly adopted to represent the photolysis rate constant of HONO.

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 J_{HONO} has been replaced by $J_{NO_3^- - HONO}$ in our revised manuscript to represent the photolysis rate constant of particulate nitrate for HONO production.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: The information of the five sampling sites are suggested to cite corresponding references.

Answer: The corresponding references of the five sampling sites have been added in the Supporting Information (S1.1 Sampling sites).

Comment 4: The derived $J_{NO_3^- - HONO}$ values strongly depended on the irradiation time, light intensity and RH according to Eq.(1)-(2) and Fig. 2, and thus it is better to mention about the key information for comparison of the J values with previous studies, e.g., the experiments with irradiation time of ~10 min for Ye et al. (2017), 15min for Bao et al. (2018), whereas 20 min for your experiments. Additionally, the J values derived by Ye et al. (2017) were based on production of the sum of HONO and NO_2.

Answer: Thank you for your valuable comments. According to your suggestions, we have added the information of the experimental conditions, such as irradiation time, temperature and RH, when comparing the derived $J_{NO_3^- - HONO}$ values with previous studies.(Page 12, line 261–264)

Comment 5: Did you measure the particulate nitrate concentration after the irradiation? How much did the formed HONO account for the consumed nitrate?

Answer: We had not measured the particulate nitrate concentration after the irradiation. Ye et al. (2017) has conducted an experiment to compare the amounts of particulate nitrate on two halves of a filter sample, one half undergone the light-exposure and the other half kept in freezer. The difference in the determined amounts of particulate nitrate between these two half filters was well predicted by HONO and NO_2 production in the light-exposure experiment, with an error less than 10%.

Comment 6: Lines 173-174, the description of "the consumption of reactive electron donors, such as acidic proton" is not correct because acidic proton is a proton donor, rather than a reactive electron donor.

Answer: The work by Bao et al. (2018) found that decrease in the HONO production was caused by consumption of reactive electron donors through Eq. (1). The mistake has been corrected in our revised manuscript:
" Previous works have revealed that the decay of HONO generation during light exposure period was not resulted from the evaporation loss of particulate nitrate (Ye et al., 2017), but mainly related to the inhomogeneity of particulate nitrate photochemical reactivity or the consumption of reactive electron donors." (Page 8, line 175)

$$HNO_3 + 2H^+ + 2e^- + hv \rightarrow HONO + H_2O \qquad (1)$$

Comment 7: Lines 190-192, "P_{HONO} does not increase" should be "P_{HONO} didn't increase".

Answer: "P_{HONO} does not increase"→"P_{HONO} did not increase".(Page 9, line 192)

Comment 8: Line 207, the meaning of the second item in Eq. (4) is not clear.

Answer: Thank you for valuable comments. $P^{HONO}_{observed}$ represented the observed production rate of HONO from particulate nitrate photolysis through photochemical experiment, and $P^{HONO}_{corrected}$ represented the corrected value of P_{HONO} after eliminating the shadowing effect. The above description has been added in our revised manuscript. (Page 10, line 210–212)

Comment 9: Lines 271-273, the values of various parameters for clean and polluted should present in a range, rather than fix values, or you have to mention the representatives of the values, e.g., the mean or average.

Answer: Thank you for valuable comments. The values of various parameters for clean and polluted conditions have been presented in a range (mean ± 1SD) in Table R1.

Table R1. The concentrations of $PM_{2.5}$, NO_3^-, and OC, OC/NO_3^-, corrected $J_{NO_3^- - HONO}$, and S_{HONO} in five representative cities in China under different air conditions during the sampling period.

Site	Air condition	$PM_{2.5}$ ($\mu g\ m^{-3}$)	NO_3^- ($\mu g\ m^{-3}$)	OC ($\mu g\ m^{-3}$)	OC/NO_3^-	Corrected $J_{NO_3^- - HONO}$ ($10^{-5}\ s^{-1}$) [a]	S_{HONO} (10^{-5} mol $h^{-1}\ m^{-2}$) [b]	S_{HONO} (ppbv h^{-1}) [c]
Beijing	Clean	19.71±8.65	3.15±2.34	3.89±2.13	2.25±3.03	2.01±2.44	0.15±0.07	0.03±0.02
	Polluted	72.56±23.78	19.71±10.72	12.62±2.18	0.87±0.62	0.61±0.30	0.38±0.11	0.09±0.02
	Whole-Min	4.32	0.08	1.07	0.32	0.21	0.04	0.01
	Whole-Max	102.64	32.90	15.95	12.82	11.06	0.57	0.13
	Whole-Mean	32.92	7.29	6.07	1.85	1.57	0.22	0.05
Changji	Clean	20.39±6.00	3.05±1.75	3.61±1.08	1.66±1.11	0.65±0.18	0.07±0.03	0.02±0.01
	Polluted	80.49±39.54	20.59±4.74	8.35±2.97	0.44±0.08	0.21±0.03	0.16±0.04	0.04±0.01
	Whole-Min	14.45	0.88	2.69	0.28	0.16	0.03[d]	0.01[d]
	Whole-Max	169.35	28.28	14.34	3.65	0.91	0.22	0.05
	Whole-Mean	57.37	13.84	6.53	0.91	0.39	0.13	0.03
Guangzhou	Clean	25.62±6.08	3.29±1.68	6.89±2.21	2.72±1.79	3.25±1.28	0.36±0.15	0.08±0.03
	Polluted	40.32±2.23	4.38±1.30	13.82±1.34	3.35±0.86	3.53±0.61	0.59±0.15	0.13±0.03
	Whole-Min	14.77	0.85	3.67	0.82	1.37	0.17	0.04
	Whole-Max	42.74	6.63	15.62	8.05	5.83	0.75	0.17
	Whole-Mean	29.12	3.55	8.54	2.87	3.31	0.41	0.09
Wangdu	Clean	22.16±7.66	3.29±2.59	5.36±2.38	4.79±6.46	3.80±5.10	0.20±0.09	0.04±0.02
	Polluted	83.53±30.47	18.06±12.48	23.23±9.62	1.88±1.67	1.09±0.87	0.50±0.15	0.11±0.03
	Whole-Min	10.67	0.24	2.72	0.22	0.23	0.06	0.01
	Whole-Max	173.45	60.28	63.07	22.06	19.60	0.88[e]	0.20[e]
	Whole-Mean	68.38	14.41	18.82	2.60	1.75	0.42	0.10

	Clean	23.53±5.45	4.35±1.41	5.69±2.46	1.37±0.61	1.28±0.49	0.21±0.07	0.05±0.02
	Polluted	68.98±33.43	24.87±21.5	14.63±4.41	0.87±0.45	0.62±0.35	0.40±0.12	0.09±0.03
Xinxiang	Whole-Min	18.32	2.37	2.33	0.30	0.19	0.09	0.02
	Whole-Max	143.10	73.47	22.06	2.02	1.96	0.59	0.13
	Whole-Mean	57.62	19.74	12.40	0.99	0.78	0.35	0.08

[a] represented the photolysis rate constant of particulate nitrate leading to HONO production after considering the influence of the shadowing effect. [b, c] represented the noontime source strength of HONO through the photolysis of particulate nitrate with the units of 10^{-5} mol h^{-1} m^{-2} and ppbv h^{-1}, respectively.[d, e] represented the minimum and maximum values of S_{HONO} during the observation period.

References

Bao, F., Li, M., Zhang, Y., Chen, C., and Zhao, J.: Photochemical aging of Beijing urban $PM_{2.5}$: HONO production, Environ. Sci. Technol., 52, 6309-6316, 10.1021/acs.est.8b00538, 2018.

Ye, C., Zhang, N., Gao, H., and Zhou, X.: Photolysis of particulate nitrate as a source of HONO and NOx, Environ. Sci. Technol., 51, 6849-6856, 10.1021/acs.est.7b00387, 2017.